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# Cobalt(III), Copper(II), and Nickel(II) coordination compounds as cations in Polyborate Chemistry 

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## COBALT(III), COPPER(II), AND NICKEL(II) COORDINATION COMPOUNDS AS CATIONS IN POLYBORATE CHEMISTRY



A THESIS SUBMITTED
BY
MOHAMMED ABDULREDHA ALTAHAN
IN ACCORDANCE WITH THE REQUIREMENTS FOR THE DOCTOR OF PHILOSOPHY

SCHOOL OF CHEMISTRY<br>BANGOR UNIVERSITY

July 2017

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#### Abstract

This thesis describes the synthesis and characterization of a number of polyborate compounds containing transition metal complex cations; most of these compounds contain 6membered $\mathrm{B}_{3} \mathrm{O}_{3}$ boroxole rings within their structures.

A total of twenty-six transition metal complex polyborate salts are reported: one contains the triborate monoanion, $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$, three contain the tetraborate dianion $\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]^{2-}$, twelve contain the pentaborate anion, $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$, three contain the hexaborate dianion, $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ and five contain heptaborate anions (three of which are $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]^{2-}$, and two are $\left.\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}\right)$. Additionally, two compounds contain two isolated polyborate anion species (octaborate dianion $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ with pentaborate anion $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$, and triborate anion $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$with $\left.\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}\right)$. The crystal structures of fifteen salts containing these polyborate anions are reported: $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}(\mathbf{6}), \quad\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]_{3} \cdot 11 \mathrm{H}_{2} \mathrm{O}(9), s$ - $f a c-$ $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \cdot 9 \mathrm{H}_{2} \mathrm{O} \quad(11), \quad[\mathrm{Co}(\text { diNOsar })]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5} \cdot 4.75 \mathrm{H}_{2} \mathrm{O} \quad$ (12), $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O} \quad(\mathbf{2 0}), \quad\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O} \quad$ (22), $\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}(\mathbf{2 3}),\left[\mathrm{Cu}(\mathrm{dac})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Cu}(\mathrm{dac})_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}(\mathbf{2 4})$, $\left[\mathrm{Cu}(N, N-\mathrm{dmen})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ (27), $\left[\mathrm{Cu}(N, N-d m e n)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (28), $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O} \quad(37), \quad[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O} \quad(38), \quad\left[\mathrm{Ni}(\mathrm{dac})_{2}\left(\mathrm{H}_{2} \mathrm{O}-\right.\right.$ $\left.)_{2}\right]\left[\mathrm{Ni}(\mathrm{dac})_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O} \quad(39), \quad\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \quad(40), \quad$ and $\quad s$ - $f a c-$ $\left[\mathrm{Ni}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}(41)$. All the synthesized compounds reported were characterized using spectroscopic (IR, multi-element NMR) and analytical (melting point, elemental analysis, magnetic susceptibility, thermal analysis, powder X-ray diffraction) techniques.

The solid-state structures of transition metal complex polyborate salts all display multiple cation-anion H -bond interactions and these undoubtedly play a major role in the energetics of engineering these structures. For example, in compound $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B} 4 \mathrm{O} 5(\mathrm{OH})_{4}\right]_{3} \cdot 11 \mathrm{H}_{2} \mathrm{O}(9)$, fourteen of the 18 amino hydrogen atoms of the $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cation are involved in secondary coordination to anions via H -bonds.

Two unique polyborate anions, $\left.\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right)\right]^{2-}$ and $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ have been prepared and characterized in $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O} \quad$ (6) and $s$-fac$\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \cdot 9 \mathrm{H}_{2} \mathrm{O}(\mathbf{1 1})$, respectively.


The reaction of transition metal complex cations with boric acid in different ratios produced polyborate compounds with different polyborate anions e.g. reaction of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ with boric acid in 1:10 and 1:5 ratios produce polyborate compounds with pentaborate(1-) and tetraborate(2-) anions, respectively.

New polyborate anion structural architectures are identified in this thesis: (i) the pentaborate(1-) anion in $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}(22)$ acts as a monodentate ligand coordinated to the $\mathrm{Cu}(\mathrm{II})$ cation, (ii) the hexaborate(2-) anion in $\left[\mathrm{Cu}(\right.$ TMEDA $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O} \quad$ (23) and $\quad\left[\mathrm{Cu}(N, N-\mathrm{dmen})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O} \quad$ (28) coordinates as a tridentate ligand with the $\mathrm{Cu}(\mathrm{II})$ cations, and (iii) the hexaborate(2-) anion in $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}(37)$ coordinates as a bidentate ligand with the $\mathrm{Ni}(\mathrm{II})$ cation. This is the first time that such coordination mode (i) and (iii) have been observed.

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## The structures and abbreviations of ligands employed in this thesis

| Name | abbrevia |
| :--- | :---: | :---: | :---: | :---: | :---: |
| tion |  | en


| N,N,N',N'-tetramethyl ethylenediamine | TEDA |  |
| :---: | :---: | :---: |
| 1,2diaminocyclohexane | dach |  |
| $\mathrm{N}, \mathrm{N}$ - <br> dimethylethylenediam ine | $\begin{aligned} & N, N- \\ & \text { dmen } \end{aligned}$ |  |
| N-(2hydroxyethyl)ethylene diamine | hn |  |
| 2,4-dimethyl-1-(3-azapropyl)-1,5,8-triazaocta-2,4-dienato | AEN |  |

## Abbreviations

| Compound name | Formula | Abbreviation |
| :--- | :---: | :---: |
| Ethylenediamine | $\mathrm{C}_{2} \mathrm{H}_{8} \mathrm{~N}_{2}$ | en |
| Diethylenetriamine | $\mathrm{C}_{4} \mathrm{H}_{13} \mathrm{~N}_{3}$ | Dien |
| Triethylenetetramine | $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{~N}_{4}$ | trien |
| 1,2-Diaminopropane | $\mathrm{C}_{3} \mathrm{H}_{10} \mathrm{~N}_{2}$ | pn |
| 1,3-Diaminopropane | $\mathrm{C}_{3} \mathrm{H}_{10} \mathrm{~N}_{2}$ | tn |
| 1,8-Dinitro-3,6,10,13,16,19-hexaazabicyclo-(6.6.6)icosan | $\mathrm{C}_{14} \mathrm{H}_{30} \mathrm{~N}_{8} \mathrm{O}_{4}$ | diNOsar |
| N,N,N',N'-tetramethyl ethylenediamine | $\mathrm{C}_{6} \mathrm{H}_{16} \mathrm{~N}_{2}$ | TEDA |
| 1,2-diaminocyclohexane | $\mathrm{C}_{6} \mathrm{H}_{14} \mathrm{~N}_{2}$ | dach |
| $N, N$-dimethylethylenediamine | $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{~N}_{2}$ | $N, N$-dmen |
| N-(2-hydroxyethyl)ethylenediamine | $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{~N}_{2} \mathrm{O}$ | hn |
| 2,4-dimethyl-1-(3-azapropyl)-1,5,8-triazaocta-2,4-dienato | $\mathrm{C}_{9} \mathrm{H}_{2} \mathrm{~N}_{4}-$ | AEN |
| Protonated ethylenediamine | $\mathrm{C}_{2} \mathrm{H}_{10} \mathrm{~N}_{2}{ }^{2+}$ | H2en |
| Tris(2-aminoethyl)amine | $\mathrm{C}_{6} \mathrm{H}_{18} \mathrm{~N}_{4}$ | TREN |
| Piperazine | $\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{~N}_{2}$ | Pip |
| Acetate | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}-$ | OAc |
| $N, N, N, N$-Tetrakis-(2-aminoethyl)-1,2-ethandiamine | $\mathrm{C}_{10} \mathrm{H}_{28} \mathrm{~N}_{6}$ | - |
| 1,4,8,11-Tetraazacyclotetradecane | $\mathrm{C}_{10} \mathrm{H}_{24} \mathrm{~N}_{4}$ | Cyclam |
| 1,10-Phenanthroline | $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{~N}_{2}$ | PHEN |
| $N, N$-Dimethylacetamide | $\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{NO}^{2}$ | DMAc |
| $N$-Methyl-2-pyrolidine | $\mathrm{C}_{5} \mathrm{H}_{9} \mathrm{NO}_{3}$ | NMP |
| Pyridine | $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ | py |
| 1-Cyanopiperazinium | $\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{~N}_{3}{ }^{+}$ | - |
| Piprazinium | $\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{~N}_{2}{ }^{2+}$ | - |

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## Chapter One

## Introduction

### 1.1 Introduction

This introductory chapter reviews aspects of inorganic chemistry pertinent to this thesis. The introduction has been divided in to three main parts. Firstly, there is a review of the basic concepts of coordination compounds (i.e. complexes, coordination numbers and isomerism). Secondly, there is a review focused on boron oxygen compounds. Here, polyborate anion structures are discussed in more detail and a brief description of the anions present in known polyborate salts are included. Finally, there is a review of the experimental techniques used in this thesis to characterize the polyborate compounds and this includes a more detailed discussion of NMR spectroscopy.

### 1.2 Aim of study

Borates with alkali metals, alkaline earth metals, main group metals, rare earths, transition metals and non-metal cations have been widely studied and explored. ${ }^{1}$ It is well known that certain polyborate anions e.g. $\left[\mathrm{B} 9 \mathrm{O}_{12}(\mathrm{OH})_{6}\right]^{3-},\left[\mathrm{B}_{15} \mathrm{O}_{20}(\mathrm{OH})_{8}\right]^{3-}$ have only been observed partnered by specific cations. ${ }^{2,3} \mathrm{~B}(\mathrm{OH})_{3}$ in basic aqueous solution exists as a dynamic combinatorial library of a variety of polyborate anions and cations can self-assemble (crystal engineer) solid-state polyborate structures by crystallization from this aqueous solution. However, many of these polyborates contain the isolated pentaborate(1-) anion and this is believed to be for the reasons set out in the following two paragraphs.

Each pentaborate(1-) anion has four H -bond donor sites and ten H -bond acceptor sites and all 4 H -bond sites are always used as H -bond donor to other pentaborate anions and form supramolecular 3D frameworks. ${ }^{4}$ Structurally, pentaborates are best described as supramolecular networks of H-bonded anions, with cations occupying the 'cavities' within the network. However, with pentaborate(1-) anions, these lattice can expand (within limits) with cation size. A common structure motif in all pentaborate compounds is reciprocal $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$ bonds at $\alpha$ sites and this interaction is particulary strong. ${ }^{5}$ When 'innocent' cations are present these anion-anion H -bond interactions dominate the self-assembly energetics of the pentaborate salts.

Cation-anion H-bond interactions in the solid state can play a very important role in engineering structures of the polyborate compounds and may break up the dominance of anionanion interactions found in pentaborates, e.g. $\left[\mathrm{H}_{2} \mathrm{en}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]\left[\mathrm{B} 7 \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O}$, isolated heptaborate(2-) and tetraborate(2-) anions (rather than pentaborate(1-) anion) are observed with
non-metal cation $\left[\mathrm{H}_{2} \mathrm{en}\right]^{2+}$. Here all twelve amino H -atoms of the two $\left[\mathrm{H}_{2} \mathrm{en}\right]^{2+}$ cations are involved in H -bonds. ${ }^{6}$

The first main aim of the research covered within this thesis is to synthesize and structurally characterize new polyborate anions with sterically demanding and / or highly charged cations, i.e. transition metal coordination complex cations. Polyborate salts are formed by self-assembly reactions from boric acid templated by the cations. We have investigated whether the transition metal complex cation structure directly affects the structure of the polyborate anions and if so, how the transition metal complex influences that structure. This is to be achieved by examination of solid-state structures as determined by XRD studies.

The second aim is to investigate the physical properties of the new synthesized transition metal complex polyborate compounds. Magnetic properties and thermal properties are to be reported, along with spectroscopic (IR, NMR, and UV) data.

### 1.3 Coordination compounds

### 1.3.1 Coordination number and coordination geometry

The principle feature of the geometrical structures of complex compounds (coordination number) were first determined by the Swiss chemist Alfred Werner in 1893. ${ }^{7}$ The coordination number of the central metal atom is defined as the total number of atoms, ions, or molecules that are bonded to the central element or ion. The coordination number can vary from two to as many as fifteen, ${ }^{8}$ but four and six are by far the most commonly observed coordination numbers.

Two common structures are possible for 4-coordinate metal complexes, tetrahedral ( $T_{d}$ ) and square-planar ( $D_{4 h}$ ). The tetrahedral structure is mainly observed for most 4-coordinate non-transition metal complexes, also it is commonly found for 4-coordinate transition metal complexes. Square-planar geometry is commonly found for complexes of $2^{\text {nd }}$ and $3^{\text {rd }}$ transition metal series with $\mathrm{d}^{8}$ electronic configuration: $\mathrm{Rh}^{+}, \mathrm{Pd}^{2+}, \mathrm{Ir}^{+}, \mathrm{Pt}^{2+}$, and $\mathrm{Au}^{3+}$. The octahedral geometry is the most commonly observed shape for the 6 -coordinate transition metal complexes (Figure 1.1).

square planar (A)

tetrahedral (B)

octahedral (C)

Figure 1.1 The common shapes of 4-coordinate metal complexes (A and B) and 6-coordinate metal complexes $(\mathrm{C}), \mathrm{M}=$ metal, $\mathrm{L}=$ ligand.

In some octahedral cases distortions are observed due to unequal occupancy of degenerate orbitals in the idealized undistorted geometry. This distortion will lead to a system of lower energy and lower symmetry where the two axial bonds can be longer or shorter than those of the equatorial bonds. This geometry change is called the Jahn-Teller distortion (Figure 1.2). It is usually important when an odd number of electrons occupy the $E_{g}$ level, and mostly arises in complexes with the electronic configurations high spin $d^{4}$, low spin $d^{7}$, and d $d^{9}$. JahnTeller distortion also occurs when there is a degeneracy due to electrons in the $T_{2 g}$ level, such as configuration $\mathrm{d}^{1}$ and $\mathrm{d}^{2}$. In this case the effect is usually much less pronounced since the electrons occupies $T_{2 g}$ orbitals, which do not point directly at the ligands. ${ }^{9-12}$


Figure 1.2 Jahn-Teller distortion due to unequal occupancy of the degenerate orbitals.

### 1.3.2 Isomerism in transition metal complexes

The isomerism in coordination chemistry is classified into two main categories: structural isomers and stereoisomers. Stereoisomers are compounds which have the same chemical formula and the atoms are joined together in the same arrangement, but there is a different spatial arrangement of these atoms. Stereoisomers can be subdivided into geometric isomers and optical isomers.

Geometrical isomers are possible for both octahedral and square-planar geometries. For square-planar $\mathrm{MA}_{2} \mathrm{X}_{2}$ complexes ( A and X are monodentate ligands) there are two possible isomers: cis- and trans-. In the trans-isomer, the identical ligands are opposite to each other $\left(180^{\circ}\right.$ ), while in the cis- isomer these ligands are adjacent to each other ( $90^{\circ}$ ) (Figure 1.3). A similar situation applies to octahedral $\mathrm{MA}_{2} \mathrm{X}_{4}$ complexes.

cis-isomer

trans-isomer

Figure $\mathbf{1 . 3}$ cis- and trans-isomers of square-planar geometry.

For octahedral $\mathrm{MA}_{3} \mathrm{X}_{3}$ complexes two isomers are possible: facial ( $f a c$ ) and meridional (mer). The facial isomers have each set of three identical groups occupying one face of the eight octahedral faces, while the meridional isomer has each set of the three identical groups occupying a plane passing through the central metal atom (Figure 1.4).

facial isomer

meridional isomer

Figure 1.4 Facial and meridional isomers of octahedral $\mathrm{MA}_{3} \mathrm{X}_{3}$ complexes.

Complexes of $\left[\mathrm{MA}_{2}\right]$ formula (where A is a tridentate ligand) also can show geometrical isomerism, for example $\left[\operatorname{Co}(\operatorname{dien})_{2}\right]^{3+13}$ where is diethylentriamine (dien) shows three geometric isomers. These geometries can be designated as facial when three amino groups of the same diethylenetriamine ligands occupy one face or meridional when the three amino groups of the same diethylenetriamine occupy a plane passing through cobalt atom. In addition, there are two facial isomers which are conveniently labelled $s$ (symmetric) and $u$ (unsymmetric); these labels arise from whether or not the complex has a centre of symmetry, i (Figure 1.5). ${ }^{13-15}$

$s-f a c$

$u-f a c$

mer

Figure 1.5 The three geometrical isomers of $\left[\mathrm{Co}(\mathrm{dien})_{2}\right]^{3+}$.

Optical isomers are isomers that are non-superimposable mirror image of one another. The optical isomers are optically active compounds and they rotate plane-polarized light in opposite directions.

The absolute configuration of optical isomers has been denoted by various methods such as S or R , and $\Delta$ or $\Lambda$. Complexes with three bidentate ligands be designated by a symbol $\Lambda$, which is used as a prefix to describe a left-handed propeller twist, and $\Delta$ is used for a righthanded twist of the three bidentate ligands (Figure 1.6).

$\Lambda$ (lambda)
mirror

$\Delta$ (delta)

Figure 1.6 Left handed $\Lambda$ isomer and right handed $\Delta$ isomer.

In 1959 Corey and Bailar first applied the principle of conformation analysis to the stereochemistry of coordination complexes. ${ }^{16}$ They recognized that the chelation of ethylenediamine with a transition metal ion formed a ring with many possible stereochemical forms. In tris(ethylenediamine)cobalt(III) complex the coordination of three bidentate ligands to a cobalt(III) ion forms three twisting five membered chelate rings. The hydrogen atoms on adjacent atoms of the twisting rings are in a staggered conformation and these hydrogen atoms will be approximately equatorial or axial to the plane of the central transition metal ion and the two nitrogen atoms of the bidentate ligand. The conformation of the five-membered rings can be designated as $\delta$ or $\lambda$ (Figure 1.7).


Figure 1.7 The $\lambda$ and $\delta$ configurations in tris(ethylenediamine)cobalt(III).

### 1.4 Boron and boron-oxygen compounds

### 1.4.1 General background of boron ${ }^{17}$

The element boron can be defined as the chemical element with atomic number 5 and symbol B. Boron compounds have been known for thousands of years, while the element boron was believed to have been discovered independently in 1808 by Sir Humphry Davy (1778-1829 an English chemist), Louis Jaques Thenard (1777-1857 a French chemist) and Joseph Louis Gay Lussac (1778-1850 a French chemist and physicist). The isolation of boron was accomplished by the reaction of boric acid with potassium. Sir Humphrey Davy originally named this element boracium due to it being derived from boracic acid. The origin of the name boron is derived from a combination of the names boracium and carbon. Boron is a dark brown powder which is extremely hard but brittle. At room temperature, it is a poor electrical conductor, but at high temperature it is a good conductor. It is classified as a "metalloid" element because it has the properties of metallic and non-metallic elements. Boron occurs as boric acid $\mathrm{B}(\mathrm{OH})_{3}$ and in polyboric acid salts, and is never found free in nature. ${ }^{17}$

Boron is one of the most extensively studied elements. This is due to its diverse industrial applications, and its chemically unique behavior. ${ }^{18}$ Growing evidence from many experiments indicate that boron is an essential trace element for the human body. The many beneficial actions of boron include bone growth and maintenance, ${ }^{19}$ reduction of the risk for some cancers, inflammation and oxidative stress modulation, ${ }^{20}$ improved brain function, hormone facilitation, immune response, ${ }^{21}$ and a decrease in the risk of arthritis. Boron's bioactivity is primarily due to formation of borate esters with a ribose sugar moiety, such as oxidized nicotinamide adenine dinucleotide and $S$-adenosylmethionine. This has led to a proposal that $1 \mathrm{mg} /$ day human boron intake may help peoples to live better and longer. ${ }^{19}$

Boron is in the oxidation state of +3 in its most familiar compounds such as halides, nitrides, oxides, and sulphides. The main classes of boron compounds are boranes, borides, organoboron compounds and borates. The simplest borane has the chemical formula $\mathrm{B}_{2} \mathrm{H}_{6}$. Borides are compounds produced from a combination of boron with a more electropositive element such as titanium, e.g. titanium boride ( $\mathrm{TiB}_{2}$ ). Organoboron compounds are a large class of organic derivatives of borane $\mathrm{BH}_{3}$ e.g. trialkyl boranes. ${ }^{22}$ Borates represent a major division of boron compounds where boron is bonded to oxygen and is part of a borate ester or an oxyanion group.

### 1.4.2 Boron-Oxygen compounds

Boron-oxygen compounds (borates) represent a major class of boron compounds and these have attracted a great deal of attention. Many papers relating to borate minerals have been published and recently many synthetic novel borate compounds have greatly contributed to the diverse literature of solid-state borate chemistry. This steady interest is due to their intriguing variety of crystal architectures and their potential applications in many different fields e.g. in mineralogy, ${ }^{23-27}$ nonlinear optical behavior, ${ }^{28-31}$ photoluminescence, ${ }^{32,33}$ and industry applications such as agricultural micronutrients. ${ }^{34,35}$

A specially developed process in glass manufacture has led to the production of a glass (e.g. Pyrex) with very high heat and chemical attack resistances. ${ }^{36,37}$ Borate compounds are essential components in modern life with applications ${ }^{23-37}$ such as biocidal materials (wood preservatives), glass (display panels and insulation as fibre glass), cross linking (oil recovery chemical and adhesive), fire retardants (for wood and plastic), anticorrosion (water treatment and automotive fluids), cleaning agents (industrial detergent and consumer), metal processors (fluxes of steel and other metals), chemical source of boron (borohydride fuels), and nuclear and spectroscopic application (cooling water and control rods). The great variety of application of borate compounds result from the flexible coordination modes of the boron atom: four-fold coordination ( $\mathrm{BO}_{4}^{-}$, tetrahedral) or three-fold coordination $\left(\mathrm{BO}_{3}\right.$, triangular). The $\mathrm{BO}_{3}$ and $\mathrm{BO}_{4}^{-}$sub units can further link together via sharing common oxygen atoms to produce isolated rings and cages, or polymerize to produce infinite chains, sheets, and network leading to a rich structural chemistry. ${ }^{38,39}$

The most important species in aqueous solution of boric acid are $\mathrm{B}(\mathrm{OH})_{3}$ and $\mathrm{B}(\mathrm{OH})_{4}^{-}$ units:

$$
\begin{equation*}
\mathrm{B}(\mathrm{OH})_{3}+2 \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{~B}(\mathrm{OH})_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad K_{\mathrm{a}}=1.86 \times 10^{-10} \tag{Eq.1.1}
\end{equation*}
$$

According to the equilibrium constant, the main species in solution at low pH are $\mathrm{B}(\mathrm{OH})_{3}$ units and the dominant species at high pH are $\mathrm{B}(\mathrm{OH})_{4}{ }^{-}$units. However, in practice the speciation of borate ions in aqueous solution is more complex, particularly in the pH range 512 (Figure 1.8). The population of polyborate anion species in solution varying according to: pH , concentration, and temperature. The known isolated (as opposed polymeric) polyborate anions, prior to writing the thesis, are described in Table 1.1.


Figure 1.8 Variation in the distribution of boron species with solution pH at $25^{\circ} \mathrm{C}$. Total boron concentration is $0.4 \mathrm{M} .^{40}$

Table 1.1 Known isolated polyborate anion species.

| Polyborate anion | Formula | Structure |
| :---: | :---: | :---: |
| Triangular borate <br> unit | $\mathrm{B}(\mathrm{OH})_{3}$ |  |
|  |  | OH |
|  |  |  |


| Tetrahedral borate unit | $\mathrm{B}(\mathrm{OH})^{-}$ |  |
| :---: | :---: | :---: |
| Triborate(1-) anion | $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$ |  |
| Triborate(2-) anion | $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH}) 5\right]^{2-}$ |  |
| Tetraborate(2-) anion | $\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]^{2-}$ |  |


| Pentaborate(1-) anion | $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ |  |
| :---: | :---: | :---: |
| Hexaborate(2-) anion | $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ |  |
| Heptaborate(2-) anion | $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ |  |
| Heptaborate (2-) anion | $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ |  |


| Octaborate(2-) anion | $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ |  |
| :---: | :---: | :---: |
| Nonaborate(3-) | $\left[\mathrm{B}_{9} \mathrm{O}_{12}(\mathrm{OH})_{6}\right]^{3-}$ |  |
| Dodecaborate(4-) <br> anion | $\left[\mathrm{B}_{12} \mathrm{O}_{16}(\mathrm{OH})_{8}\right]^{4-}$ |  |



The structural units in Table $\mathbf{1 . 1}$ are referred to as hydrated borates due to the presence of B-OH groups and the absence of B-O groups. Many hydrated borates also contain interstitial water molecules and these compounds are referred to as hydroxy hydrated. The hydrated borate units can condense together into larger isolated clusters or infinite polyborate chains or networks. Boroxyl rings are common in polyborate structures and there are two primary modes connecting them. One mode involves the sharing of tetrahedral boron (Figure 1.9 A ), such as in $\mathrm{Na}_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{6}(\mathrm{OH})_{2}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O}$. The other mode of connection involves sharing exocyclic oxygen (Figure 1.9 B), such as $\mathrm{Ca}\left[\mathrm{B}_{3} \mathrm{O}_{4}(\mathrm{OH})_{3}\right] \cdot \mathrm{H}_{2} \mathrm{O}$.

(A)

(B)

Figure 1.9 Two common modes of polymerization for boroxyl rings in infinite chain borates.

The polyborate anions are partnered by cations to form salts. These different cations can be classified into three main kinds: metal, non-metal, and transition metal complexes.

Over recent decades, many hydrated borate compounds have been prepared with a variety of main group metals, alkali metals, alkaline earth metals. ${ }^{38,39,41-68}$

The metal cations are spherical and mostly accept electron density from oxygen atoms of hydrated borate units, with the metal cation acting as a Lewis acid. The acidity of the cationic metal unit should be very close to the basicity of the anionic hydrated borate unit to promote the formation of a stable metal borate compound. ${ }^{69}$ The polyborate anions with a higher fraction of $\mathrm{B}_{(4)}$ units are associated with higher average oxygen coordination numbers and higher average basicity (Table 1.2).

Table 1.2 The average $\mathrm{O}-\mathrm{CN}$ with fraction of $\mathrm{B}_{(4)}$ units of polyborate anions. ${ }^{70}$

| Isolated borate anion | Fraction <br> $B_{4}$ | Formula | Average <br> O-CN |
| :--- | :--- | :--- | :---: |
| $\left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}$ | 1.00 | $\mathrm{Ca}\left[\mathrm{B}(\mathrm{OH})_{4}\right]_{2}$ | 4.0 |
| $\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ | 0.50 | $\mathrm{Na}_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]\left(\mathrm{H}_{2} \mathrm{O}\right)_{8}$ | 3.8 |
| $\left[\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ | 0.20 | $\mathrm{~K}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left[\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]$ | 3.2 |
| $\left[\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ | 0.20 | $\mathrm{Na}_{2}\left[\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}$ | 3.0 |
| $\left[\mathrm{~B}_{15} \mathrm{O}_{30}(\mathrm{OH})_{8}\right]^{3-}$ | 0.20 | $\left(\mathrm{NH}_{4}\right)_{3}\left[\mathrm{~B}_{15} \mathrm{O}_{30}(\mathrm{OH})_{8}\right]\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$ | 2.8 |

In general, hydrated borate structural units with high Lewis basicity are commonly found in compounds partnered with metal cations of high Lewis acidity, while hydrated borate units with low Lewis basicity are often found with less Lewis acidic metal cation units or nonmetal cations.

The second kind of cation is a non-metal cation derived from an organic base. The nonmetal cation borate compounds have been studied far less than metal borate compounds. $\left[\mathrm{NH}_{4}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$, a mineral which is also synthetically available, was the first nonmetal pentaborate compound to be prepared. Related non-metal cation containing quaternary ammonium cations were first prepared in 1959 with a resurgence of interest in the 1990's. In recent years these compounds of non-metal cations have attracted a great deal of attention ${ }^{2-}$ $5,28,69,71-109$ due to their potential uses as non-linear optical (NLO) materials and their ability to act as a thermal precursors to new porous materials with many other applications. ${ }^{4,110}$

Non-metal cations may interact with the borate structural units through hydrogen bonds rather than by direct coordination with borate oxygen units as in metal borates. Non-metal cations are mainly found as protonated Bronsted bases (mostly nitrogen containing bases). Nonmetal cations exhibit a degree of Bronsted acidity and may be present as cations only over a given solution pH range. The variety of borate units with which a stable product can be produced are also dependent on the Bronsted acidity of non-metal cations. Hydrogen bonding is one of the most important factors that plays an important role in the stability and physical properties of non-metal borate materials.

More recently a new research area has been rapidly developing with the inclusion of transition metal complex cations in polyborate compounds. ${ }^{1}$ Due to their interesting coordination chemistry and attractive physical properties, a great variety of structural chemistry is possible. However, these transition metal complex cation polyborate compounds have been less explored than metal and non-metal borate compounds. Compounds templated by
cobalt(III), cobalt(II), zinc(II), nickel(II), manganese(II), cadmium(II), silver(I) and copper(II) transition metal complexes have been reported. ${ }^{1}$ At the time of writing this thesis the following list is exhaustive for isolated hydrated species: $\left[\mathrm{Co}_{2}(\operatorname{trien})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{4}$, $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}, \quad\left[\mathrm{~B}_{5} \mathrm{O}_{7} \mathrm{Co}(\mathrm{OH})_{3}(\right.$ TREN $\left.)\right],{ }^{111} \quad\left[\mathrm{Zn}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}$, $\left[\mathrm{B}_{5} \mathrm{O}_{7}(\mathrm{OH})_{3} \mathrm{Zn}(\right.$ TREN $\left.)\right],{ }^{112}$ $[\mathrm{Zn}(\mathrm{OAc}) \operatorname{trien}]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right],{ }^{113} \quad\left[\mathrm{Mn}\left(\mathrm{C}_{10} \mathrm{H}_{28} \mathrm{~N}_{6}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2},{ }^{114}$ $\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O} 6(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}, \quad\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right] \mathrm{Cl}_{3} \cdot 3 \mathrm{H}_{2} \mathrm{O},{ }^{115} \quad\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{13} \mathrm{H}_{3}\right],{ }^{116}$ $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O},{ }^{117} \quad \mathrm{Na}\left[\mathrm{V}_{12} \mathrm{~B}_{16} \mathrm{O} 50(\mathrm{OH})_{7}(\mathrm{en})\right]_{2}\left(\mathrm{enH}_{2}\right)_{6}(\mathrm{enH})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)_{19},{ }^{118}$ $\left[\mathrm{Zn}\left(\mathrm{B}_{4} \mathrm{O}_{8} \mathrm{H}_{2}\right)(\mathrm{pn})\right] \cdot \mathrm{H}_{2} \mathrm{O}, \quad\left[\mathrm{Zn}\left(\mathrm{B}_{5} \mathrm{O}_{10} \mathrm{H}_{3}\right)\left(\mathrm{C}_{10} \mathrm{H}_{2} \mathrm{~N}_{4}\right)\right] \cdot \mathrm{H}_{2} \mathrm{O}, \quad\left[\mathrm{Zn}\left(\mathrm{B}_{4} \mathrm{O}_{8} \mathrm{H}_{2}\right)(\mathrm{pn})\right]$, $\left[\mathrm{Zn}_{2}\left(\mathrm{~B}_{8} \mathrm{O}_{15} \mathrm{H}_{2}\right)(\mathrm{pn})_{2}\right],{ }^{119} \quad\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{2} \mathrm{P}_{3} \mathrm{O}_{11}(\mathrm{OH})_{2}\right],{ }^{120} \quad\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{H}_{2} \mathrm{O}$, $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{H}_{2} \mathrm{O},{ }^{121} \quad\left[\mathrm{Cu}(\mathrm{PHEN})_{2}(\mathrm{OAc})\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{C}_{4} \mathrm{H}_{9} \mathrm{NO},{ }^{122}$ $\left[\mathrm{Cu}(\mathrm{en})_{2}\left(\mathrm{C}_{5} \mathrm{H}_{9} \mathrm{NO}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{C}_{5} \mathrm{H}_{9} \mathrm{NO},{ }^{123} \quad[\mathrm{Cd}($ trien $)(\mathrm{OAc})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right],{ }^{124}$ $\left[\mathrm{Ag}(\mathrm{py})_{2}\right]_{2}\left[\mathrm{~B}_{10} \mathrm{O}_{14}(\mathrm{OH})_{4}\right]{ }^{125} \quad \mathrm{Co}\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{3}\left\{\mathrm{O}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{NH}_{2}\right\}_{3}\right]$, $\mathrm{Ni}\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{3}\left\{\mathrm{O}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{NH}_{2}\right\}_{3}\right],{ }^{126} \quad\left[\mathrm{Cd}(\mathrm{Dien})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}$,
$\left[\mathrm{Cd}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O},{ }^{127} \quad\left[\mathrm{Zn}(\mathrm{pn}) 0.5\left(\mathrm{pn}^{\prime}\right) 0.5\left\{\mathrm{~B}_{4} \mathrm{O}_{6}(\mathrm{OH})_{2}\right\}\right] \cdot \mathrm{H}_{2} \mathrm{O},{ }^{128}$
$\mathrm{K}_{7}\left\{\left(\mathrm{BO}_{3}\right) \mathrm{Zn}\left(\mathrm{B}_{12} \mathrm{O}_{18}(\mathrm{OH})_{6}\right\} \cdot \mathrm{H}_{2} \mathrm{O},{ }^{129} \quad\left[\mathrm{Zn}(\text { dien })_{2}\right]\left[\{\mathrm{Al}(\mathrm{OH})\}\left\{\mathrm{B}_{5} \mathrm{O} 9 \mathrm{~F}\right\}\right],{ }^{130}\right.$
$\left[\mathrm{Cu}(\mathrm{en})_{2} \mathrm{~B}(\mathrm{OH})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{5}(\mathrm{OH})_{7}\right],{ }^{131} \quad \mathrm{Li}_{2} \mathrm{~Pb}_{2} \mathrm{CuB}_{4} \mathrm{O}_{10},{ }^{132} \quad \mathrm{Zn} 8\left[\left(\mathrm{BO}_{3}\right)_{3} \mathrm{O}_{2}(\mathrm{OH})_{3}\right]^{133}$
$\mathrm{K}_{7}\left[\left(\mathrm{BO}_{3}\right) \mathrm{Mn}\left\{\mathrm{B}_{12} \mathrm{O}_{18}(\mathrm{OH})_{6}\right\}\right] \cdot \mathrm{H}_{2} \mathrm{O},{ }^{134}$
$\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right][\mathrm{OAc}]{ }^{136}$
$2\left\{\mathrm{Cu}(\mathrm{en})_{2} \mathrm{~B}(\mathrm{OH})_{3} \mathrm{H}_{2} \mathrm{O}\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]\right\} \cdot \mathrm{H}_{2} \mathrm{O}, \quad$ and $\quad\left\{\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left[\mathrm{~B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]_{2}\right\}\left(\mu-\mathrm{H}_{2} \mathrm{O}\right)$ $\left\{\mathrm{Ag}(\mathrm{en})_{2}\right\} \cdot\left(\mu-\mathrm{H}_{2} \mathrm{O}\right)\left\{\mathrm{Na}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right\} .{ }^{137}$

Hydrated borates templated by transition metal complex cations are also favourable candidates for the preparation of open network materials. A few transition metal complex cation pentaborate salts have previously been isolated with interstitial moieties such as $\mathrm{H}_{2} \mathrm{O},{ }^{117}$ $\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-},{ }^{136} \mathrm{H}_{3} \mathrm{BO}_{3},{ }^{137}$ and chloride, ${ }^{115}$ and a few transition metal complex cations with polyborate anion such as tetraborate, ${ }^{115,119,128,132}$ hexaborate, ${ }^{126}$ heptaborate, ${ }^{138,116}$ octaborate, ${ }^{139}$ decaborate ${ }^{125}$ and dodecaborate ${ }^{129,134}$ have been previously prepared.

Transition metal complex cations can possess a range of chemical sizes and structural shapes, they also possess unique spatial configurations, different charges and flexibilities, and the possibility of many hydrogen bonding interactions. These properties may stabilize and develop unusual polyborate system, producing good opportunities to explore polyborate structural units and determine structure stability relationship.

### 1.5 Experimental techniques used to study borate chemistry

The new polyborate species presented in this thesis have been characterized by several techniques. X-ray crystallography (EPSPC National Crystallography Service at the University of Southampton) is essential to this study but new compounds have also been characterized by a range of other techniques. These include p-XRD, spectroscopic analysis (FT-IR, NMR, UV/Vis), magnetic susceptibility and thermal analysis (TGA/DSC). NMR is a useful technique for the study of polyborate anions and this is discussed fully in Section 1.6.

Polyborate anions usually contain both tetrahedral and trigonal planar boron centres, with B-O stretches particularly strong in IR spectra. IR stretching frequencies have been assigned by Li and coworkers ${ }^{140}$ as follows: $1450-1300 \mathrm{~cm}^{-1}$-asymmetrical $\mathrm{B}_{(3)}-\mathrm{O}, 1150-1000$ $\mathrm{cm}^{-1}$ asymmetrical $\mathrm{B}_{(4)}-\mathrm{O}, 960-890 \mathrm{~cm}^{-1}$ symmetrical $\mathrm{B}_{(3)}-\mathrm{O}$, and $890-740 \mathrm{~cm}^{-1}$ symmetrical $\mathrm{B}(4)-\mathrm{O}$.

Another useful technique for the study of transition metal borate complexes is by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). This is a thermal analysis method that is used to detect changing physical and chemical properties of material as measured by weight loss and heat exchange as the sample is heated at a uniform rate. The thermogravimetric analysis of hydrated transition metal borate complexes generally shows three mass loss steps. ${ }^{124}$ The first mass loss step is observed between 50 and $190{ }^{\circ} \mathrm{C}$, which belongs to the loss of interstitial water molecules. The second mass loss step is observed between 200 and $290^{\circ} \mathrm{C}$ and this is attributed to the condensation of polyborate ions with removal of water from borate ions. The third mass loss step is observed between 300 and $800^{\circ} \mathrm{C}$, and they are related to oxygenolysis of ligands in the coordination sphere.

Elemental analysis also provides useful information on the stoichiometric composition of the transition metal complex borate compound. p-XRD can used to confirm the crystallinity and homogeneity of a solid sample. Transition metal complexes are amenable to further study by UV/Vis spectroscopy and by magnetic susceptibility measurements.

Generally, transition metal complexes show absorption bands in the ultraviolet-visible spectral region. These absorption bands are related to charge transfer transitions (CT), and d-d transitions. Charge transfer transitions may be attributed to MLCT or LMCT transitions and they are intense absorptions. The d-d transitions appear as weak absorptions in the ultraviolet region or visible region (Figure 1.10). UV/Vis spectra are characterized by absorption max $\left(\lambda_{\max }\right)$ and extinction coefficient $(\varepsilon) .{ }^{141}$


Figure 1.10 Possible electronic transition of the octahedral $\mathrm{d}^{3}$ transition metal complexes.

Magnetic susceptibility measurements of transition metal complexes can be used to characterize their magnetic properties. Magnetic susceptibility measurements offer a source of information about the number of unpaired electrons. All transition metal complexes can be classified in to one of three classes: those repelled by magnetic field (diamagnetic), those attracted to a magnetic field (paramagnetic), and the last class is ferromagnetic. The magnetic properties of paramagnetic and diamagnetic materials may only be observed in the presence of applied external magnetic field, while magnetic properties of ferromagnetic materials can be measured even after the external field is removed. The magnetic susceptibility can be defined as the ratio of the intensity of induced magnetism in a material to intensity of applied field.

The mass susceptibility, $\chi_{g}($ observed), as obtained using Johnson-Matthey balance, is calculated using Eq. 1.2. Where $\mathrm{C}=$ calibration constant of the balance, $\ell=$ length of the sample in $\mathrm{cm}, \mathrm{m}=$ mass of the sample in grams, $\mathrm{R}=$ reading value for tube with sample. Generally, if
the sample is paramagnetic R is a large positive value, if the sample is diamagnetic R is a small negative value, and $\mathrm{R}_{\circ}=$ value for tube and is generally small and negative. Mass susceptibility ( $\chi_{\mathrm{g} \text { (observed) })}$ ) is converted to molar susceptibility $\left(\chi_{\mathrm{m} \text { (observed })}\right)$ by multiplying by formula mass (Eq. 1.3).

$$
\begin{equation*}
\chi_{g(\text { observed })}=\frac{C \ell\left(R-R_{o}\right)}{10^{9} \mathrm{~m}} \tag{Eq.1.2}
\end{equation*}
$$

$$
\begin{equation*}
\chi_{m(\text { observed })}=\chi_{g(\text { observed })} \times \mathrm{MWt} \tag{Eq.1.3}
\end{equation*}
$$

In general, if $\chi_{\text {m(observed) }}$ value is positive and with a value of $c a .10^{-4} \mathrm{cgs}$ units the compound is paramagnetic and if the $\chi_{m \text { (observed) }}$ is negative the complex is diamagnetic. $\chi_{m \text { (observed) }}$ needs to be corrected for diamagnetism since this is observed in all matter and the molar susceptibility $\chi_{m \text { (para) }}$ is the sum of paramagnetic (caused by unpaired electrons) and diamagnetic terms (Eq. 1.4) (MWt is the molecular weight of the substance). From $\chi_{m(p a r a)}$ we can calculate the effective magnetic moment ( $\mu_{\text {eff }}$ ) (Eq. 1.6). We can then compare experimental value of $\mu_{\text {eff }}$ with the value obtained from 'spin-only' formula (Eq. 1.7) where n is the number of unpaired electrons. ${ }^{142}$

$$
\begin{equation*}
\chi_{m}(\text { para })=\chi_{m(o b s e r v e d)}-\chi_{m}(\text { dia }) \tag{Eq.1.4}
\end{equation*}
$$

$$
\begin{equation*}
\chi_{m(d i a)} \approx-\frac{M W t}{2} \cdot 10^{-6} \tag{Eq.1.5}
\end{equation*}
$$

$$
\begin{equation*}
\mu_{\mathrm{eff}}=2.828 \times\left(\chi_{m(p a r a)} \times \mathrm{T}\right)^{1 / 2} \tag{Eq.1.6}
\end{equation*}
$$

$$
\begin{equation*}
\mu_{\mathrm{eff}}=[\mathrm{n}(\mathrm{n}+2)]^{1 / 2} \tag{Eq.1.7}
\end{equation*}
$$

### 1.6 Nuclear magnetic resonance spectroscopy (NMR)

### 1.6.1 Introduction

The rapid progress in chemical analysis during the second half of the twentieth century has been mainly related to the development of nuclear magnetic resonance spectroscopy. NMR spectroscopy is one of the most powerful and theoretically complex analytical techniques. It is one of the few analytical techniques that does not require chemical processing and the chemical sample is neither destroyed nor consumed during the analysis. In 1946 Bloch et al. ${ }^{143}$ and Purcell et al. ${ }^{144}$ independently discovered NMR spectroscopy using liquid and solid samples, respectively. A brief overview of the some of the key concepts of nuclear magnetic resonance spectroscopy is now given with particular references to ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{11} \mathrm{~B}$ nuclei since these are the NMR spectra most commonly encountered in this thesis.

### 1.6.2 Nuclear spin $(\boldsymbol{I})^{145}$

Nuclei that have either an odd number of neutrons or protons (or both) possess a nuclear spin. $I$ is the nuclear spin quantum number, and its values can be $1 / 2,3 / 2 \ldots$ etc. Nuclei with nuclear spin quantum number values greater than zero are termed nuclear magnetic resonance active. Nuclei with an even number of both protons and neutrons have $I=0$, and they are termed as NMR silent.

The NMR spectroscopy active nucleus with a spin of $I$ possess $(2 I+1)$ possible orientations in a magnetic field (B). For example, a hydrogen nucleus of spin $I=1 / 2$ will have two possible orientations, $\mathrm{M}_{\mathrm{s}}= \pm 1 / 2$ (Figure 1.11).


Figure 1.11 Energy levels for a nucleus with spin quantum number, $S=1 / 2$.

In the absence of a magnetic field, all the spin states are of equal energy, however when an external magnetic field is applied then the spins states are no longer of equal energy. The lower energy level will contain slightly more nuclei than the higher energy level as described in the Boltzmann distribution law.

The NMR phenomenon occurs when nuclei aligned with the applied external magnetic field ( $\mathrm{B}_{0}$ ) are induced to absorb an identified amount of energy equal to the energy difference between the spin states involved and change their spin orientation $\left(\Delta m_{I}= \pm 1\right)$. The energy difference is a function of the applied magnetic field $\mathrm{B}_{0}$ (Figure 1.11), and it also depends on the particular nucleus involved. Each nucleus has a specific gyromagnetic ratio $(\gamma)$ which is constant for a particular nucleus and determines the energy dependence on the applied magnetic field (Eq. 1.8 and Eq. 1.9).

$$
\begin{equation*}
\Delta \mathrm{E} \propto \gamma \mathrm{~B}_{0} \tag{Eq.1.8}
\end{equation*}
$$

$$
\begin{equation*}
\Delta \mathrm{E}=\mathrm{h} / 2 \pi \gamma \mathrm{~B}_{0} \tag{Eq.1.9}
\end{equation*}
$$

### 1.6.3 Natural abundance

The vast majority of the elements have at least one nucleus that is NMR active. Taking carbon as an example, it has an average atomic mass of 12.01 and atomic number of six. With six neutrons and six protons the nucleus of carbon-12 would have $I=0$ and hence be NMR inactive. Carbon however also has the isotope carbon-13. The spin of carbon-13 is $1 / 2$ and hence is NMR active. The amount of carbon-13 in existence is referred to as its natural abundance. The natural abundance of an NMR active nuclei is a significant factor in the receptivity of the nucleus. The magnetic resonance properties of selected atomic nuclei are listed in Table 1.3.

Table 1.3 Magnetic resonance properties of selected atomic nuclei. ${ }^{145}$

| Nucleus | Spin | Natural <br> abundance <br> $(\%)$ | Magnetogyric <br> ratio $\gamma \times 10^{-8}(\mathrm{rad}$ <br> $\left.\mathrm{S}^{-1} \mathrm{~T}^{-1}\right)$ | Nucleus | Spin | Natural <br> abundance <br> $(\%)$ | Magnetogyric <br> ratio $\gamma \times 10^{-8}$ <br> $\left(\mathrm{rad} \mathrm{S}^{-1} \mathrm{~T}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{13} \mathrm{C}$ | $1 / 2$ | 1.108 | 0.6728 | ${ }^{14} \mathrm{~N}$ | 1 | 99.63 | 0.1933 |
| ${ }^{1} \mathrm{H}$ | $1 / 2$ | 99.99 | 2.6752 | ${ }^{15} \mathrm{~N}$ | $1 / 2$ | 0.365 | -0.2711 |
| ${ }^{2} \mathrm{H}$ | 1 | 0.015 | 0.4107 | ${ }^{19} \mathrm{~F}$ | $1 / 2$ | 100 | 2.516 |
| ${ }^{11} \mathrm{~B}$ | $3 / 2$ | 81.17 | 0.8583 | ${ }^{29} \mathrm{Si}$ | $1 / 2$ | 4.70 | -0.531 |
| ${ }^{10} \mathrm{~B}$ | 3 | 18.83 | 0.2875 | ${ }^{31} \mathrm{P}$ | $1 / 2$ | 100 | 1.082 |

${ }^{10} \mathrm{~B}$ and ${ }^{11} \mathrm{~B}$ are both NMR active with natural abundance 19.9 and $80.1 \%$ respectively. Both nuclei have overall spins of more than $1 / 2$ and they are termed quadrupolar. ${ }^{146}$ In general, ${ }^{11} \mathrm{~B}$ is preferred to ${ }^{10} \mathrm{~B}$ nuclei in NMR spectroscopy due to its higher natural abundance, sensitivity, and lower quadrupole moment. However, the rapid relaxation times and higher sensitivity of ${ }^{11} \mathrm{~B}$ nuclei generally leads to well defined, but broad, signals in NMR spectra.

### 1.6.4 The NMR experiment ${ }^{145}$

A short pulse of radiofrequency ( $c a .20 \mu \mathrm{~s}$ ) irradiates the chemical sample which causes an excitation and promotion of nuclei from a ground state to an excited state ( $\Delta m_{I}= \pm 1$ ). Some of the energy gain is re-emitted when the excited nuclei fall back down into the original energy level. This process is called the free induction decay (FID), which is recorded at times ranging from milliseconds to seconds, depending on the nuclei used and is called the acquisition time ( $\mathrm{taq}_{\mathrm{aq}}$. The whole process of $\mathrm{t}_{\mathrm{aq}}$ is repeated many times, so as to improve the signal to noise ratio in the spectrum and the resulting free induction decays are added together. When the FID undergoes Fourier transformation (FT), a spectrum is obtained.

### 1.6.5 Relaxation ${ }^{147}$

The excited nuclei in a NMR sample experiment may relax back to the thermal equilibrium by dispersion of their gained excited energy. There are two pathways to describe the mechanism of the nuclei relaxation in the NMR experiment.
(1) Spin-lattice relaxation mechanism: the spin lattice relaxation time, $\mathrm{T}_{1}$, corresponds to an exchange energy between nuclear spin system and neighbouring molecules (the lattice).
(2) Spin-spin relaxation mechanism: the spin-spin relaxation time, $\mathrm{T}_{2}$, which results from an exchange of energy between the individual spins in the system.

### 1.6.6 The chemical shift ( $\delta$ )

The chemical shift of a nucleus is the resonant frequency of a nucleus relative to a chemical standard in a magnetic field, therefore according to the local chemical environment, different nuclei in a molecule resonate at different frequencies. Tetramethylsilane (TMS) is used as an external standard reference for ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{29} \mathrm{Si}$ NMR spectroscopy, while boron trifluoride diethyl etherate, $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$, is used as an external reference for ${ }^{11} \mathrm{~B}-\mathrm{NMR}$. ${ }^{148}$

The chemical shift for a particular signal is given in part per million (ppm). The chemical shift of most ${ }^{1} \mathrm{H}$ NMR signals are observed between +0 and +10 ppm (normally between -20 and +30 ppm ), the chemical shift of ${ }^{13} \mathrm{C}$ NMR signals are observed between -20 and +200 ppm , while the total chemical shift range of ${ }^{11} \mathrm{~B}$ NMR also covers about +200 ppm .

There are many factors that affect the chemical shift of boron such as quadrupolar effects and the coordination number of boron. ${ }^{146}$ The coordination number of boron is an important factor that affects the chemical shift, so the chemical shift of a tetrahedral boron $\mathrm{sp}^{3}$ species are shifted more up field ( +20 to -128 ppm ) than a trigonal boron $\mathrm{sp}^{2}$ species ( +92 to 8 ppm ), this shifted can be attributed to increase the electron density around the tetrahedral boron centre, which causes an increase in the nuclear shielding, so there is an associated upfield shift compered to three-coordinate species.

### 1.7 NMR applied to polyborate species

One method for analysing and studying borate compounds is NMR spectroscopy of the ${ }^{11} \mathrm{~B}$ nucleus. The individual borate species may possess diagnostic chemical shifts which are easily identifiable.

The chemical shift regions of pure trigonal $\mathrm{B}(\mathrm{OH})_{3}$ and tetrahedral $\left[\mathrm{B}\left(\mathrm{OH}_{4}\right)\right]^{-}$units appear at +19.48 ppm and +2.48 ppm , respectively. ${ }^{149}$ The structural information on borate anions in solution is complicated due to the equilibria of borate anions in solutions. ${ }^{150,151}$ The ${ }^{11} \mathrm{~B}-\mathrm{NMR}$ spectrum of a concentration solution of hydrated potassium pentaborate, $\mathrm{K}\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$ shows three peaks at $+18,+13$, and +1 ppm which are attributed to $\mathrm{B}(\mathrm{OH})_{3}\left[\mathrm{~B}(\mathrm{OH})_{4}\right]^{-}, \quad\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$, and $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{\prime}$, respectively. These signals are concentration dependent. According to Salentine, ${ }^{149}$ approximately $90 \%$ of a solid pentaborate salt dissociates in solution by hydrolysis to give $\mathrm{B}(\mathrm{OH})_{3},\left[\mathrm{~B}(\mathrm{OH})_{4}\right]^{-}$, and $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$species. The resonance at +18 ppm is due to $\mathrm{B}(\mathrm{OH})_{3} /\left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}$ion. The signal at +13 ppm belongs to the triborate ion $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$. The resonance at +1 ppm arises from the $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ion. This
signal is assigned to the 4-coordinate $B$ centre and the 3 -coordinate $B$ centres are not observed due to exchange/relaxation effects.

In dilute NMR samples, where the polyborates are absent, only a single peak is observed due to $\mathrm{B}(\mathrm{OH})_{3} /\left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}$exchange. The chemical shift of this peak can be predicted by using Eq. 1.10, which can be derived from Salentine observations. Where $\delta_{\text {tet. }}$ is the chemical shift of tetrahedral $\left[\mathrm{B}(\mathrm{OH})_{4}\right]^{-}(+2.48 \mathrm{ppm})$, while $\delta_{\text {tri }}$ is the chemical shift of trigonal $\mathrm{B}(\mathrm{OH})_{3}(+19.48$ $\mathrm{ppm})$, and $\delta_{\text {obs. }}$ is the observed chemical shift of the borate sample. By rearrangement of Eq. 1.10, the boron:base ratio in dilute NMR sample can be calculated by using Eq. 1.11 and Eq. 1.12.

$$
\begin{align*}
& \delta_{\text {obs. }}=\delta_{\text {tet. }}+\left(\frac{\text { No.of B atoms }- \text { Charge of anion }}{\text { No.of B atoms }}\right) \cdot\left(\delta_{\text {tri. }}-\delta_{\text {tet. }}\right)  \tag{Eq.1.10}\\
& B: \text { base }=\frac{1}{1-\left(\frac{\left.\delta_{o b s .}-\delta_{\text {tet. }}\right)}{\delta_{\text {tri. }}-\delta_{\text {tet. }}}\right.} \tag{Eq.1.11}
\end{align*}
$$

$B:$ base $=\frac{17.00}{19.48-\delta_{o b s}}$

# Chapter Two <br> <br> Polyborate salts <br> <br> Polyborate salts <br> <br> containing cationic <br> <br> containing cationic <br> <br> cobalt(III) complexes 

 <br> <br> cobalt(III) complexes}

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### 2.1 Introduction

The chemistry of polyborate anions partnered with cobalt complexes shows great structural diversity. Salts containing isolated polyborate anions with cobalt complex cations are known in the literature: $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}{ }^{111,152} \quad\left[\mathrm{Co}_{2}(\operatorname{trien})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] 4,{ }^{111}$ $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right] \mathrm{Cl}^{2} \cdot 3 \mathrm{H}_{2} \mathrm{O},{ }^{115} \quad\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O},{ }^{117}$ $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{2} \mathrm{P}_{3} \mathrm{O}_{11}(\mathrm{OH})_{2}\right],{ }^{120}$ and $\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] 2 \cdot \mathrm{H}_{2} \mathrm{O} .{ }^{121}$ Complexes of cobalt are also known in which the polyborate anion is formally within the first coordination sphere of the metal centre. These is illustrated with the anionic complexes $\mathrm{Rb}_{2}\left[\mathrm{Co}\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}_{2}\right]{ }_{1}{ }^{153}$ $\left(\mathrm{C}_{4} \mathrm{H}_{12} \mathrm{~N}_{2}\right)\left[\mathrm{Co}\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}_{2}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}^{154}$ and $\left(\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{~N}_{3}\right)\left[\mathrm{Co}\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}_{2}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O},{ }^{135}$ all of which a coordinated tridentate $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ ligand. This coordination mode is also observed in the neutral complex, $\quad\left[\mathrm{Co}\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{3}\right\}\left\{\mathrm{O}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{NH}_{3}\right\}_{3}\right],{ }^{126}$ whilst the neutral complex $\left[\left\{\mathrm{B}_{5} \mathrm{O}_{7}(\mathrm{OH})_{3}\right\} \mathrm{Co}(\right.$ TREN $\left.)\right]$, (TREN $=\operatorname{tris}\left(2\right.$-aminoethyl)amine) ${ }^{111}$ has the $\left[\mathrm{B}_{5} \mathrm{O}_{7}(\mathrm{OH})_{3}\right]^{2-}$ ligand coordinated in a mono dentate manner via an anionic (deprotonated) oxygen centre of a pentaborate(2-) anion.

In this chapter, we report the synthesis and characterisation of nine new polyborate salts of cobalt(III) complex cations. These salts all contain isolated polyborate anions. Four of the salts have been characterized by single-crystal XRD studies and s-fac$\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{6}\right] \cdot 9 \mathrm{H}_{2} \mathrm{O}^{138}$ and $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}^{139}$ show previously unobserved heptaborate(3-) and octaborate(2-) anions, respectively.

### 2.2 Aims

The primary aim of this research area was to synthesize novel polyborate anions, using a strategy of templating such species using sterically demanding and/or highly charged cations. A set of cationic cobalt(III) coordination complexes of ethylenediamine (en), 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-(6.6.6)icosane (diNOsar), 1,2-diaminopropane (pn), $\mathrm{NH}_{3}$, and diethylenetriamine (dien) ligands were prepared to template polyborate salt formation. The cobalt(III) complex cations were chosen due to their high charge and their potential to form many donor H-bond interactions in their coordination sphere. Since these interactions play an important role in the formation of the three-dimensional supramolecular frameworks in polyborate salts.

The secondary aim is to evaluate the structure directing effects associated with the cobalt(III) complex cations seen in the solid-state supramolecular structures.

### 2.3 Result and discussion

### 2.3.1 Synthesis of cobalt(III) complex chlorides

The known cobalt(III) complexes $\left[\mathrm{Co}(\mathrm{en})_{3}\right] \mathrm{Cl}_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}(\mathbf{1}),{ }^{155}\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}(\mathbf{2}),{ }^{156}$ $\left[\mathrm{Co}(\text { dien })_{2}\right] \mathrm{Cl}_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O} \quad$ (3), ${ }^{13} \quad[\mathrm{Co}($ diNOsar $)] \mathrm{Cl}_{3} \quad$ (4), ${ }^{157} \quad$ and $\quad\left[\mathrm{Co}(\mathrm{pn})_{3}\right] \mathrm{Cl}_{3} \quad$ (5),,${ }^{158}$ of ethylenediamine (en), $\mathrm{NH}_{3}$, diethylenetriamine (dien), 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-(6.6.6)icosane (diNOsar), and 1,2-diaminopropane (pn) ligands were all prepared by standard literature methods. Physical properties of the prepared complexes were all in accord with literature data.

Compounds $\mathbf{1 - 5}$ were all prepared as their chloride salts and it was therefore necessary to convert these chloride salts to the corresponding hydroxide salts before reaction with boric acid. The hydroxide salts were prepared by ion exchange using Dowex $550 \mathrm{~A}\left(\mathrm{OH}^{-}\right.$form) from the chloride salts in aqueous solution. It was assumed that the hydroxide complex salts were formed in quantitative yields by the ion exchange reaction. The experiment details are explained in Chapter 6.

### 2.3.2 Preparation of cobalt(III) complex polyborate salts

A series of cobalt(III) complex polyborate salts 6-14 have been prepared as crystalline solids from cobalt(III) complex hydroxides. Boric acid was added in the ratios of 1:5, 1:7, 1:10, and $1: 15$ to the hydroxide solutions. The solutions were then stirred, concentrated using a rotary evaporator and cooled to yield polyborate salts as solid crude products ( $\mathbf{6 - 1 4}$ ). The crude products were isolated by filtration and dried.

Crystals suitable for single-crystal X-ray diffraction studies of the cobalt(III) complex polyborate salts were prepared by recrystallization of the crude products by dissolving them in distilled water. The recrystallized products were isolated by slow evaporation from aqueous solution or by vapour diffusion from aqueous solution using ethanol. The recrystallized yields of the cobalt(III) complex polyborate salts (6-14) and their formula are shown in Table 2.1.

Table 2.1 Yields of cobalt(III) complex polyborate salts.

| Compound | Formula | \% Yield |
| :---: | :---: | :---: |
| 6 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}$ | 41 |
| 7 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ | 57 |
| 8 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}$ | 45 |
| 9 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B} 4 \mathrm{O} 5(\mathrm{OH})_{4}\right]_{3} \cdot 11 \mathrm{H}_{2} \mathrm{O}$ | 41 |
| 10 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right] \mathrm{Cl} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ | 36 |
| 11 | $s$-fac- $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH}) 6\right] \cdot 9 \mathrm{H}_{2} \mathrm{O}$ | 35 |
| 12 | $\left[\mathrm{Co}(\text { diNOsar) }]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5} \cdot 4.75 \mathrm{H}_{2} \mathrm{O}\right.$ | 10 |
| 13 | [Co(diNOsar) $]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ | 54 |
| 14 | $\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ | 50 |

### 2.3.3 Characterisation of cobalt(III) complex polyborate salts

The magnetic properties of the cobalt(III) complex starting materials and their polyborate salts were measured at room temperature using a Johnson Matthey electronic balance with mercury tetrathiocyanatocobaltate(II) as a calibrant. The mass susceptibility and molar susceptibility of compounds $\mathbf{1 - 1 4}$ are shown in Table $\mathbf{2 . 2}$. The cobalt(III) complexes and their polyborate salts are all diamagnetic and there is no diagnostic change in magnetic properties between the starting cobalt(III) complex chlorides and their polyborate salts. The cobalt(III) complexes are all low-spin $\mathrm{d}^{6}$, and the magnetic susceptibility values are comparable to literature data on typical cobalt(III) complexes. ${ }^{159}$

Table 2.2 Mass and molar susceptibility of cobalt(III) complexes and their polyborate salts at $24^{\circ} \mathrm{C}$.

| Comp. | Mass <br> susceptibility <br> $\chi_{g}\left(\mathrm{~cm}^{3} \cdot \mathrm{~g}^{-1}\right)$ | Molar <br> susceptibility <br> $\chi_{\mathrm{m}}\left(\mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ | Comp. | Mass <br> susceptibility <br> $\chi_{g}\left(\mathrm{~cm}^{3} \cdot \mathrm{~g}^{-1}\right)$ | Molar <br> susceptibility <br> $\chi_{\mathrm{m}}\left(\mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | $-0.40 \times 10^{-6}$ | $-155 \times 10^{-6}$ | $\mathbf{8}$ | $-0.38 \times 10^{-6}$ | $-255 \times 10^{-6}$ |
| $\mathbf{2}$ | $-0.46 \times 10^{-6}$ | $-123 \times 10^{-6}$ | $\mathbf{9}$ | $-0.30 \times 10^{-6}$ | $-330 \times 10^{-6}$ |
| $\mathbf{3}$ | $-0.20 \times 10^{-6}$ | $-83 \times 10^{-6}$ | $\mathbf{1 0}$ | $-0.06 \times 10^{-6}$ | $-37 \times 10^{-6}$ |
| $\mathbf{4}$ | $-0.32 \times 10^{-6}$ | $-167 \times 10^{-6}$ | $\mathbf{1 1}$ | $-0.16 \times 10^{-6}$ | $-120 \times 10^{-6}$ |
| $\mathbf{5}$ | $-0.34 \times 10^{-6}$ | $-133 \times 10^{-6}$ | $\mathbf{1 2}$ | $-0.02 \times 10^{-6}$ | $-25 \times 10^{-6}$ |
| $\mathbf{6}$ | $-0.11 \times 10^{-6}$ | $-101 \times 10^{-6}$ | $\mathbf{1 3}$ | $-0.05 \times 10^{-6}$ | $-50 \times 10^{-6}$ |
| $\mathbf{7}$ | $-0.30 \times 10^{-6}$ | $-230 \times 10^{-6}$ | $\mathbf{1 4}$ | $-0.25 \times 10^{-6}$ | $-200 \times 10^{-6}$ |

Elemental analysis of the new cobalt(III) complex polyborate salts were consistent with their formulation. The elemental analysis data of the new polyborate salts (6-14) are shown in Table 2.3.

Table 2.3 CHN analysis of cobalt(III) complex polyborate salts.

| Compound | Calculated (\%) |  |  | Experimental (\%) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | C | H | N | C | H | N |
| $\mathbf{6}$ | 8.0 | 4.9 | 9.4 | 8.2 | 5.0 | 9.6 |
| $\mathbf{7}$ | 9.4 | 5.0 | 11.0 | 9.7 | 4.8 | 10.5 |
| $\mathbf{8}$ | 10.8 | 6.4 | 12.3 | 10.7 | 6.3 | 12.6 |
| $\mathbf{9}$ | - | 6.4 | 15.4 | - | 6.5 | 15.4 |
| $\mathbf{1 0}$ | - | 5.6 | 14.2 | - | 5.6 | 14.1 |
| $\mathbf{1 1}$ | 12.8 | 6.7 | 11.2 | 13.4 | 7.2 | 11.1 |
| $\mathbf{1 2}$ | 26.4 | 5.8 | 17.5 | 25.6 | 6.5 | 16.7 |
| $\mathbf{1 3}$ | 18.4 | 5.1 | 12.3 | 18.3 | 5.0 | 12.4 |
| $\mathbf{1 4}$ | 13.4 | 6.5 | 10.4 | 13.6 | 6.3 | 10.4 |

NMR $\left({ }^{1} \mathrm{H},{ }^{13} \mathrm{C},{ }^{11} \mathrm{~B}\right)$ data for compounds $\mathbf{6 - 1 4}$ are shown in Table 2.4. ${ }^{11} \mathrm{~B}$ NMR of the cobalt(III) complex polyborate salts showed that all the pentaborate salts 7, 13, and $\mathbf{1 4}$ contained the expected three signals associated with an equilibrium mixture at $\sim 18 \mathrm{ppm}$ (due to $\left.\left.\mathrm{B}(\mathrm{OH})_{3} / \mathrm{B}(\mathrm{OH})_{4}\right)^{-}\right), \sim 13 \mathrm{ppm}$ \{due to $\left.\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}\right\}$, and at $\sim 1.3 \mathrm{ppm}$ \{due to the 4-coordinate B centre of the $\left.\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}\right\}$or a single signal at $\sim+16.0 .{ }^{149-151}{ }^{11} \mathrm{~B}$ NMR spectra of the triborate (12), tetraborate (9), heptaborate ( $\mathbf{8}, \mathbf{1 0}$, and $\mathbf{1 1}$ ) salts are noticeably different from the spectra observed in the pentaborate salts with only one (averaged and exchanging) signal observed. The octaborate salt (6) shows two peaks at +16.5 and +13.4 ppm .
${ }^{1} \mathrm{H}$ NMR analysis of compounds $\mathbf{6 - 8}$ showed two signals at 2.7 ppm (due to protons of the en ligands) and at 4.8 ppm (due to exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons). These spectra are consistent with previously reported data. ${ }^{160}$ Compound $\mathbf{1 1}$ displayed two broad multiplets at 3.0 and 3.2 ppm (due to the methylene groups of the dien ligands) and an additional signal at 4.8 ppm (due to exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons). The relative intensities of peaks in the $\mathrm{CH}_{2}$ region were 1:3. The $s$-fac arrangement of the diethylenetriamine ligands gives rise to prochiral ethylene carbon centres and four inequivalent hydrogen atom sites and three of which overlap in the high field signal. The data we have found for $\mathbf{1 1}$ is in agreement with that reported for $s$ -fac- $\left[\mathrm{Co}(\text { dien })_{2}\right] \mathrm{Cl}_{2}(\mathrm{Bz}) \cdot \mathrm{H}_{2} \mathrm{O}^{161}$ and comparable with literature data. ${ }^{138,161}$ Compounds $\mathbf{1 2}$ and 13 showed two overlapping quartets, associated with the AB pattern of the en and cap methylene groups. In addition, they show one signal assigned to exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons. ${ }^{1} \mathrm{H}$ NMR data of $\mathbf{1 2}$ and $\mathbf{1 3}$ are all in accord with previously reported data of $\left[\mathrm{Co}\right.$ (diNOsar)]Cl3. ${ }_{3}{ }^{157,162}$ The resonances assigned to protons $\mathrm{H}_{1}$ and $\mathrm{H}_{2}$ of $\mathbf{1 4}$ occurring at 3.0 ppm and 2.9 ppm , respectively are distinguishable (Figure 2.1). The $\mathrm{H}_{1}$ resonance is a multiplet due to spin-coupling with $\mathrm{H}_{2}, \mathrm{H}_{3}$ and methyl group protons of each 1,2-diaminopropane ligand,
while $\mathrm{H}_{2}$ appears as a doublet of doublets arising from coupling with $\mathrm{H}_{1}$ and $\mathrm{H}_{3}$. The signal associated with $\mathrm{H}_{3}$ occurs at 2.5 ppm and consist of a doublet of doublets due to coupling with $\mathrm{H}_{1}$ and $\mathrm{H}_{2}$. Methyl group protons appear as a doublet at 1.3 ppm due to coupling with $\mathrm{H}_{1}$ and an additional resonance at 4.8 ppm attributed to exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons. The ${ }^{1} \mathrm{H}$ NMR data of compound $\mathbf{1 4}$ is compatible with that previously reported for $\left[\mathrm{Co}(\mathrm{pn})_{3}\right] \mathrm{Cl}_{3} .{ }^{160}$


Figure 2.1 Diagram showing the protons of propylene diamine ligand and the adopted numbering scheme in compound 14.
${ }^{13} \mathrm{C}$ NMR spectra of compounds $\mathbf{6 - 8}$ show only one peak for each complex in a range consistent with coordinated ethylenediamine ligand. ${ }^{160}$ Compound 11 displayed two signals for the dien ligand. These signals are consistent with literature data. ${ }^{138,161}$ Three signals are observed in $\mathbf{1 2}$ and $\mathbf{1 3}$ at $\sim 51 \mathrm{ppm}$ (due to methylene groups of the ethylenediamine ring residues), $\sim 55 \mathrm{ppm}$ (due to methylene groups of the capping units), and a signal at $\sim 87 \mathrm{ppm}$ (due to the tertiary carbon of the caps). These signals are in agreement with literature data. ${ }^{157,162}$ Compound $\mathbf{1 4}$ shows three signals at 16.5 ppm (due to carbon methyl $-\mathrm{CH}_{3}$ group), 49.9 ppm (belonging to the carbon methylene $-\mathrm{CH}_{2}$ group), and a signal at 53.9 ppm (due to carbon CH group). The ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{1 4}$ is consistent with literature data. ${ }^{160}$

Table 2.4 ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{11} \mathrm{~B}$ NMR data for compounds $\mathbf{6 - 1 4}$.

| Comp. | ${ }^{11} \mathrm{~B} / \mathrm{ppm}$ | ${ }^{1} \mathrm{H} / \mathrm{ppm}$ | ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}$ |
| :---: | :---: | :---: | :---: |
| 6 | $\begin{aligned} & 16.5(85 \%), \\ & 13.4(15 \%) \\ & \hline \end{aligned}$ | 2.7 (m, 12H, $\mathrm{CH}_{2}$ of en), $4.8(\mathrm{~s}, 32 \mathrm{H}$, exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons) | $44.5\left(\mathrm{CH}_{2}\right.$ groups of the en) |
| 7 | $\begin{gathered} \hline 17.4(59 \%), \\ 12.9(33 \%), \\ 1.2(8 \%) \end{gathered}$ | 2.7 (m, 12H, CH2 of en), 4.8 (s, 26 H , exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons) | $44.3\left(\mathrm{CH}_{2}\right.$ groups of the en) |
| 8 | 13.0 | 2.7 (m, 12H, $\mathrm{CH}_{2}$ of en), 4.8 (s, 30 H , exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons) | $44.2\left(\mathrm{CH}_{2}\right.$ groups of the en) |
| 9 | 10.4 | 4.8 (s, 70H, exchanging $\mathrm{BOH} / \mathrm{NH}_{3} / \mathrm{H}_{2} \mathrm{O}$ protons) | - |
| 10 | 13.4 | 4.8 ( $\mathrm{s}, 33 \mathrm{H}$, exchanging $\mathrm{BOH} / \mathrm{NH}_{3} / \mathrm{H}_{2} \mathrm{O}$ protons) | - |
| 11 | 12.3 | $\begin{aligned} & 3.0\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{CH}_{2}\right), 3.2\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), \\ & 4.8 \quad(\mathrm{~s}, \quad 34 \mathrm{H}, \quad \text { exchanging } \\ & \left.\mathrm{BOH} / \mathrm{NH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O} \text { protons }\right) \end{aligned}$ | $43.3\left(\mathrm{CH}_{2}\right.$ groups of the dien connect to $\mathrm{NH}_{2}$ ), $55.0\left(\mathrm{CH}_{2}\right.$ groups of the dien connect to NH ) |
| 12 | 16.2 | 3.3, 3.9 (AB doublet of doublet, 12H, J $=12 \mathrm{~Hz}, \mathrm{CH}_{2}$ Caps), 2.9, 3.5 (complex AA'BB' coupling pattern, $12 \mathrm{H}, \mathrm{CH}_{2}$ of en), 4.8 ( $\mathrm{s}, \quad 25.5 \mathrm{H}$, exchanging $\mathrm{BOH} / \mathrm{NH} / \mathrm{H}_{2} \mathrm{O}$ protons) | $51.4\left(\mathrm{CH}_{2}\right.$ groups of the en) , $55.1\left(\mathrm{CH}_{2}\right.$ groups of the capping units), 87.9 (tertiary C-NO ${ }_{2}$ of the caps) |
| 13 | 15.9 | 3.4, 3.9 (AB doublet of doublet, $12 \mathrm{H}, J$ $=12 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Caps}$ ), 3.0, 3.6 (complex $\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}$ coupling pattern, $12 \mathrm{H}, J=8$ $\mathrm{Hz}, \mathrm{CH}_{2}$ of en), 4.8 ( $\mathrm{s}, 16 \mathrm{H}$, exchanging $\mathrm{BOH} / \mathrm{NH} / \mathrm{H}_{2} \mathrm{O}$ protons) | $51.3\left(\mathrm{CH}_{2}\right.$ groups of the en), $55\left(\mathrm{CH}_{2}\right.$ groups of the capping units), 87.8 (tertiary C-NO2 of the caps) |
| 14 | $\begin{gathered} 16.6(56 \%), \\ 13.0(33 \%), \\ 1.3(11 \%) \end{gathered}$ | $1.3\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{CH}_{3}\right.$ of pn$), 2.5(\mathrm{t}, 3 \mathrm{H}, J=$ $13.2 \mathrm{~Hz}, J=26.4 \mathrm{~Hz}, \mathrm{C}_{\mathrm{b}}$ of $\mathrm{CH}_{2}$ of pn ), $2.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}_{\mathrm{a}}\right.$ of $\mathrm{CH}_{2}$ of pn$), 3.0(\mathrm{~m}$, $3 \mathrm{H}, \mathrm{CH}$ of pn), and 4.8 (s, 26 H , exchanging $\mathrm{BOH} / \mathrm{NH}_{2} / \mathrm{H}_{2} \mathrm{O}$ protons) | $16.5\left(\mathrm{CH}_{3}\right.$ of pn), 49.9 (CH of pn), $53.9\left(\mathrm{CH}_{2}\right.$ of pn) |

The FT-IR spectra and their tentative assignment for the new polyborate salts $\mathbf{6 - 1 4}$ are shown in Table 2.5. Infra-red spectroscopic investigation confirmed the formation of polyborate anions with in the cobalt(III) salts. The FT-IR data of compounds $\mathbf{6 - 1 4}$ have been assigned by comparison with assignment (data of Jun et al. $)^{140}$ for related polyborate anions.

Table 2.5 Selected frequencies of FT-IR spectra of the new polyborate salts 6-14.

| Comp. | $\begin{aligned} & \mathrm{v}(\mathrm{O}-\mathrm{H}), \\ & \mathrm{v}(\mathrm{~N}-\mathrm{H}) \\ & \hline \end{aligned}$ | $\begin{gathered} v \\ (\mathrm{C}-\mathrm{H}) \\ \hline \end{gathered}$ | $\begin{gathered} v_{\text {as }} \\ \left(\mathrm{B}_{(3)}-\mathrm{O}\right) \\ \hline \end{gathered}$ | $\begin{gathered} \delta \\ (\mathrm{B}-\mathrm{O}-\mathrm{H}) \end{gathered}$ | $\begin{gathered} v_{\mathrm{as}} \\ \left(\mathrm{~B}_{(4)}-\mathrm{O}\right) \\ \hline \end{gathered}$ | $\begin{gathered} v_{\mathrm{s}} \\ \left(\mathrm{~B}_{(3)}-\mathrm{O}\right) \end{gathered}$ | $\begin{gathered} v_{\mathrm{s}} \\ \left(\mathrm{~B}_{(4)}-\mathrm{O}\right) \end{gathered}$ | $\begin{gathered} \gamma \\ \left(\mathrm{B}_{(3)}-\mathrm{O}\right) \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 6 | 3461(s), 3265(s), 3149(s) | 2960(w) | $\begin{aligned} & \text { 1394(s), } \\ & 1324(\mathrm{~s}) \end{aligned}$ | 1170(s) | $\begin{aligned} & \text { 1059(s), } \\ & 1033(\mathrm{~m}) \end{aligned}$ | 939(s) | 779(m) | 710(w) |
| 7 | $\begin{aligned} & 3267(\mathrm{~s}), \\ & 3167(\mathrm{~s}) \\ & \hline \end{aligned}$ | 2945(w) | $\begin{aligned} & \text { 1409(s), } \\ & 1302(\mathrm{~s}) \\ & \hline \end{aligned}$ | 1154(m) | $\begin{aligned} & \text { 1057(m), } \\ & 1007(\mathrm{~m}) \end{aligned}$ | 916(m) | $\begin{aligned} & 895(\mathrm{~m}), \\ & 785(\mathrm{~m}) \end{aligned}$ | 709(m) |
| 8 | $\begin{aligned} & \hline 3413(\mathrm{~s}), \\ & 3253(\mathrm{~s}) \end{aligned}$ | $\begin{aligned} & \hline 2926(\mathrm{w}), \\ & 2855(\mathrm{w}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline 1385(\mathrm{~s}), \\ & 1322(\mathrm{~s}) \\ & \hline \end{aligned}$ | 1162(m) | $\begin{aligned} & \hline 1058(\mathrm{~s}), \\ & 1005(\mathrm{~s}) \\ & \hline \end{aligned}$ | 930(m) | $\begin{aligned} & \hline 825(\mathrm{w}), \\ & 757(\mathrm{w}) \\ & \hline \end{aligned}$ | 702(w) |
| 9 | $\begin{aligned} & 3400(\mathrm{~s}), \\ & 3308(\mathrm{~s}) \end{aligned}$ | - | $\begin{aligned} & \text { 1421(s), } \\ & \text { 1384(s) } \end{aligned}$ | 1190(s) | 1015(s) | $\begin{aligned} & \text { 995(s), } \\ & 943(\mathrm{~m}) \\ & \hline \end{aligned}$ | 809(m) | 704(w) |
| 10 | $\begin{aligned} & \hline 3477(\mathrm{~s}), \\ & 3407(\mathrm{~s}), \\ & 3320(\mathrm{~s} \end{aligned}$ | - | $\begin{aligned} & \text { 1440(s), } \\ & 1401(\mathrm{~m}) \end{aligned}$ | 1164(m) | $\begin{aligned} & \hline \text { 1114(s), } \\ & \text { 1037(s) } \end{aligned}$ | 954(m) | $\begin{aligned} & \hline 852(\mathrm{~m}), \\ & 800(\mathrm{~m}) \end{aligned}$ | 767(w) |
| 11 | $\begin{aligned} & 3432(\mathrm{~s}), \\ & 3201(\mathrm{~s}), \\ & 3095(\mathrm{~s}) \end{aligned}$ | 2950(m) | $\begin{aligned} & \text { 1415(s), } \\ & 1385(\mathrm{~s}) \end{aligned}$ | 1134(m) | $\begin{aligned} & \text { 1084(s), } \\ & \text { 1047(s) } \end{aligned}$ | 932(m) | $\begin{aligned} & 861(\mathrm{~m}), \\ & 750(\mathrm{w}) \end{aligned}$ | 656(w) |
| 12 | $\begin{aligned} & \hline 3552(\mathrm{~s}), \\ & 3475(\mathrm{~s}), \\ & 3413(\mathrm{~s}), \\ & 3236(\mathrm{~m}) \end{aligned}$ | 2866(m) | $\begin{aligned} & \hline \text { 1432(m), } \\ & \text { 1343(m) } \end{aligned}$ | 1134(w) | $\begin{gathered} \text { 1076(m), } \\ \text { 1018(w) } \end{gathered}$ | $\begin{aligned} & \hline 988(\mathrm{w}), \\ & 952(\mathrm{w}) \end{aligned}$ | $\begin{aligned} & 847(\mathrm{w}), \\ & 812(\mathrm{w}) \end{aligned}$ | 620(m) |
| 13 | $\begin{aligned} & 3437(\mathrm{~s}), \\ & 3025(\mathrm{~s}) \end{aligned}$ | 2859(s) | $\begin{aligned} & \text { 1447(s), } \\ & \text { 1348(s) } \\ & \hline \end{aligned}$ | 1100(m) | 1078(m) | 925(m) | 810(m) | 696(w) |
| 14 | $\begin{aligned} & 3437(\mathrm{~s}), \\ & 3249(\mathrm{~m}) \end{aligned}$ | 2925(m) | $\begin{aligned} & \text { 1435(s), } \\ & \text { 1352(s) } \end{aligned}$ | 1238(w) | $\begin{aligned} & \text { 1091(m), } \\ & \text { 1023(m) } \end{aligned}$ | 925(m) | 780(w) | 692(w) |

$\mathrm{s}=$ strong, $\mathrm{m}=$ middle, $\mathrm{w}=$ weak, $\mathrm{B}_{(3)}=$ three coordinate boron, $\mathrm{B}_{(4)}=$ four coordinate boron, $\mathrm{v}=$ stretching frequency, $\mathrm{v}_{\mathrm{s}}=$ symmetrical stretching frequency, $v_{\text {as }}=$ asymmetrical stretching frequency, $\delta=$ bending frequency.

### 2.3.4 Thermal properties of cobalt(III) complex polyborate salts

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were used to investigate the thermal properties of the new cobalt(III) complex polyborate salts. Samples were heated in an alumina $\left(\mathrm{Al}_{2} \mathrm{O}_{3}\right)$ crucible at a temperature ramp rate of $10{ }^{\circ} \mathrm{C} / \mathrm{min}$ between $25-800{ }^{\circ} \mathrm{C}$ under a flow air ( $100 \mathrm{~mL} / \mathrm{min}$.). The thermal decomposition stages of compounds 6-14 are detailed in Table 2.6. Hydrated transition metal complex polyborate salts undergo three mass-loss steps to form anhydrous transition metal borates. ${ }^{124}$ The first mass loss step is due to the loss of interstitial water molecules and the temperature at which this happens varies from compound to compound but is generally complete by $180{ }^{\circ} \mathrm{C}$. The release of these water molecules is associated with an endothermic peak in the DSC trace. The second mass loss step is due to dehydration of the isolated polyborate anions, by the formation of B-O-B bonds and polymeric polyborate anions (Figure 2.2). The temperature at with this step happens again varies from compound to compound but it is generally complete by $280^{\circ} \mathrm{C}$. The release of water molecules from polyborate anions is
also associated with an endothermic peak in the DSC trace. The last mass-loss step again varies from compound to compound and the reaction is generally complete by $800^{\circ} \mathrm{C}$. This reaction relates to the oxidation of the organic ligands around the transition metal of the cation along with elimination of any remaining water molecules. The oxidation of the cation is associated with a corresponding exothermic peak in the DSC trace.


Figure 2.2 An illustration of the second mass-loss process in thermal decomposition of polyborate anions.

Table 2.6 The mass loss steps of the new polyborate salts $\mathbf{6 - 1 4}$. ${ }^{*}$

| Comp. | $\begin{aligned} & \hline \hline \text { Step. } \\ & \text { No. } \end{aligned}$ | The thermal reactions | $\begin{gathered} \hline \text { Temp. } \\ \text { range }{ }^{\circ} \mathrm{C} \end{gathered}$ | $\begin{gathered} \hline \hline \text { Expt. } \\ (\%) \end{gathered}$ | Calc. (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 6 | 1 | $\begin{array}{lll} \hline \hline\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O} & \rightarrow & {\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]} \\ {\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]+5 \mathrm{H}_{2} \mathrm{O}} \end{array}$ | 100-150 | 9.7 | 10.1 |
|  | 2 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \rightarrow\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{13} \mathrm{O}_{21}\right]+5 \mathrm{H}_{2} \mathrm{O}$ | 150-250 | 20.5 | 20.1 |
|  | 3 | $\left[\mathrm{Co}(\text { en })_{3}\right]\left[\mathrm{B}_{13} \mathrm{O}_{21}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{13} \mathrm{O}_{21}+$ volatile oxidation products | 250-800 | 41.0 | 40.3 |
|  |  | Residue $\mathrm{CoBH}_{13} \mathrm{O}_{21}$ |  | 59.0 | 59.7 |
| 7 | 1 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}+3 \mathrm{H}_{2} \mathrm{O}$ | 100-180 | 7.8 | 7.1 |
|  | 2 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \rightarrow\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \mathrm{Cl}+4 \mathrm{H}_{2} \mathrm{O}$ | 180-280 | 17.7 | 16.5 |
|  | 3 | $\left[\mathrm{Co}(\text { en })_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \mathrm{Cl}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl}+$ volatile oxidation products | 280-800 | 40.0 | 40.1 |
|  |  | Residue $\mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl}$ |  | 60.0 | 59.9 |
| 8 | 1 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Co}(\text { en })_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]+6 \mathrm{H}_{2} \mathrm{O}$ | 70-180 | 15.0 | 16.1 |
|  | 2 | $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \rightarrow\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{12}\right]+3 \mathrm{H}_{2} \mathrm{O}$ | 180-280 | 23.2 | 24.1 |
|  | 3 | $\left[\mathrm{Co}(\text { en })_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{12}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{7} \mathrm{O}_{12}+$ volatile oxidation products | 280-800 | 49.8 | 51.2 |
|  |  | Residue $\mathrm{CoB}_{7} \mathrm{O}_{12}$ |  | 50.2 | 48.8 |
| 9 | 1 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]_{3} \cdot 11 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]_{3}+11 \mathrm{H}_{2} \mathrm{O}$ | 70-170 | 17.8 | 18.1 |
|  | 2 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]_{3}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{Co}_{2} \mathrm{~B}_{12} \mathrm{O}_{21}+$ volatile oxidation products | 170-350 | 46.5 | 46.7 |
|  |  | Residue $\mathrm{Co}_{2} \mathrm{~B}_{12} \mathrm{O}_{21}$ |  | 53.5 | 53.3 |
| 10 | 1 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \mathrm{Cl} \cdot 5 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right] \mathrm{Cl}+5 \mathrm{H}_{2} \mathrm{O}$ | 70-180 | 14.3 | 15.2 |
|  | 2 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{B} 7 \mathrm{O} 9(\mathrm{OH})_{5}\right] \mathrm{Cl}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{7} \mathrm{O}_{11.5 \mathrm{Cl}}+$ volatile oxidation products | 180-370 | 40.9 | 40.2 |
|  |  | Residue $\mathrm{CoB}_{7} \mathrm{O}_{11.5} \mathrm{Cl}$ |  | 59.1 | 59.8 |
| 11 | 1 | $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{6}\right] \cdot 9 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]+9 \mathrm{H}_{2} \mathrm{O}$ | 70-200 | 19.5 | 21.7 |
|  | 2 | $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \rightarrow\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{12}\right]+3 \mathrm{H}_{2} \mathrm{O}$ | 200-280 | 28.4 | 28.9 |
|  | 3 | $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{12}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{7} \mathrm{O}_{12}+$ volatile oxidation products | 280-800 | 56.9 | 56.6 |
|  |  | Residue $\mathrm{CoB}_{7} \mathrm{O}_{12}$ |  | 43.1 | 43.5 |
| 12 | 1 | $\begin{aligned} & \hline\left[\mathrm{Co}(\text { diNOsar }]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5} \cdot 4.75 \mathrm{H}_{2} \mathrm{O}\right. \\ & {[\mathrm{Co}(\text { diNOsar })]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5}+4.75 \mathrm{H}_{2} \mathrm{O}} \\ & \hline \end{aligned}$ | 70-150 | 7.8 | 6.7 |
|  | 2 | $[\mathrm{Co}(\text { diNOsar })]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5} \rightarrow[\mathrm{Co}(\text { diNOsar })]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{5}\right] \mathrm{Cl}_{5}+2 \mathrm{H}_{2} \mathrm{O}$ | 150-250 | 11.0 | 9.5 |


|  | 3 | $[\text { Co(diNOsar) }]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{5}\right] \mathrm{Cl}_{5}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{Co}_{2} \mathrm{~B}_{3} \mathrm{O}_{5} \mathrm{Cl}_{5}+$ volatile oxidation products | 250-800 | 68.8 | 68.1 |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Residue $\mathrm{Co}_{2} \mathrm{~B}_{3} \mathrm{O}_{5} \mathrm{Cl}_{5}$ |  | 31.3 | 31.9 |
| 13 | 1 | $\begin{aligned} & {[\mathrm{Co}(\mathrm{diNOsar})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O} \rightarrow[\mathrm{Co}(\text { diNOsar })]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}+} \\ & 3 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 70-150 | 7.9 | 7.9 |
|  | 2 | $\left[\mathrm{Co}(\text { diNOsar) }) \text { [ } \mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \rightarrow\left[\mathrm{Co}(\right.$ diNOsar) $]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \mathrm{Cl}+4 \mathrm{H}_{2} \mathrm{O}$ | 150-250 | 15.0 | 15.7 |
|  | 3 | $[\mathrm{Co}$ (diNOsar) $]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \mathrm{Cl}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl}+$ volatile oxidation products | 250-800 | 59.1 | 59.1 |
|  |  | Residue $\mathrm{CoBB}_{10} \mathrm{O}_{16} \mathrm{Cl}$ |  | 40.9 | 40.9 |
| 14 | 1 | $\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}+3 \mathrm{H}_{2} \mathrm{O}$ | 70-160 | 7.2 | 6.7 |
|  | 2 | $\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \rightarrow\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \mathrm{Cl}+4 \mathrm{H}_{2} \mathrm{O}$ | 160-250 | 16.0 | 15.6 |
|  | 3 | $\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \mathrm{Cl}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl}+$ volatile oxidation products | 250-800 | 44.8 | 43.2 |
|  |  | $\mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl}$ |  | 55.2 | 56.8 |

* Calculated values and experimental values are given as totals relative to $100 \%$, and include the process described and earlier mass loss process.

The new polyborate compounds 6-8, 11-14 followed the expected three step path of decomposition, with observed mass losses in agreement with calculated values. Compound 9 and $\mathbf{1 0}$ showed two mass-loss steps rather than three associated with the dehydration of the polyborate anions and the oxidation of the ammonia ligands occurring in one step rather than two (Figure 2.3 and Figure 2.4). The thermal behaviour of the cobalt(III) complex polyborate salts were in accord with published data describing thermal decomposition of transition metal complex cations containing polyborate anions. ${ }^{155,127}$


Figure 2.3 TGA diagram for the thermal decomposition of cobalt(III) complex polyborate salts 6-9.


Figure 2.4 TGA diagram for the thermal decomposition of cobalt(III) complex polyborate salts 10-14.

### 2.3.5 Structural characterisation of cobalt(III) complex polyborate salts

### 2.3.5.1 Structural characterisation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}$ (6)

Crystals of 6 are triclinic, $P-1$ and contain two $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]$. $5 \mathrm{H}_{2} \mathrm{O}$ formula units in the asymmetric unit cell. It is an ionic compound with one transition metal complex cation $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ partnered with one $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$and one $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anion and five interstitial water molecules (Figure 2.5). Crystallographic data are shown in Table 2.7. The ligands of tris(ethylenediamine)cobalt(III) moiety are disordered over two positions with s.o.f. in the ratio 0.87 and 0.13 .


Figure 2.5 Diagram showing the structure and numbering scheme for 6 . Colour code (used throughout this chapter): deep blue (Co), blue (N), red (O), pink (B), dark grey (C) and light grey (H).

Table 2.7 Crystal data and structure refinement of $\mathbf{6}$.

| Empirical formula | $\mathrm{C}_{6} \mathrm{H}_{44} \mathrm{~B}_{13} \mathrm{~N}_{6} \mathrm{O}_{31} \mathrm{Co}$ |
| :---: | :---: |
| Formula weight | 895.93 |
| Temperature | 100(2) K |
| Wavelength | 0.71075 £ |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $\begin{array}{ll} a=11.2993(8) \AA & \alpha=88.272(4)^{\circ} \\ b=11.5139(8) \AA & \beta=76.220(4)^{\circ} \\ c=13.7574(10) \AA & \gamma=88.984(4)^{\circ} \end{array}$ |
| Volume | 1737.4(2) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.713 \mathrm{mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.612 \mathrm{~mm}^{-1}$ |
| F(000) | 924 |
| Crystal | Cut Blade; Orange |
| Crystal size | $0.050 \times 0.050 \times 0.010 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $3.050-27.483^{\circ}$ |
| Index ranges | $-14 \leq h \leq 12,-14 \leq k \leq 14,-17 \leq l \leq 17$ |
| Reflections collected | 27217 |
| Independent reflections | $7900\left[R_{\text {int }}=0.0491\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.7\% |
| Absorption correction | Semi-empirical from equivalents |


| Max. and min. transmission | 1.000 and 0.785 |
| :--- | :--- |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | $7900 / 164 / 588$ |
| Goodness-of-fit on $F^{2}$ | 1.043 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0463, w R 2=0.1182$ |
| $R$ indices (all data) | $R 1=0.0645, w R 2=0.1280$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 1.281 and $-0.781 \mathrm{e} \AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha(0.71073 \AA)$ |

Special details: The $\operatorname{Co}(\mathrm{en})_{3}$ moiety was modelled as disordered over two positions with the lesser component left isotropic. Various geometrical restraints (SAME) were also employed.

The crystallographic data revealed that $\mathbf{6}$ was composed of two different isolated polyborate species: $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$and $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$. The pentaborate(1-) anion is well known but the $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anion present in this complex has never been previously observed. Their structures and their associated numbering schemes are shown in Figure 2.5. The $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ anion is frequently observed in polyborate chemistry with interstitial moieties such as $\mathrm{H}_{2} \mathrm{O},{ }^{115}$ pyridine, ${ }^{117} \mathrm{~B}(\mathrm{OH}) 3,{ }^{122}$ and chloride, ${ }^{131}$, but it has never been observed previously cocrystallized with another polyborate anion. The observation of two different polyborates in one compound is rare, with only one known example, $\left[\mathrm{H}_{2} \mathrm{en}_{2}\left[\mathrm{~B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right][\mathrm{B} 7 \mathrm{O} 9(\mathrm{OH}) 5] \cdot 3 \mathrm{H}_{2} \mathrm{O},{ }^{6}\right.$ which contains both the $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ and $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ anions. Cobalt(III) centred coordination complexes as cations with polyborate anions are very rare, with only one known compound: $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O} .{ }^{115}$

The isolated octaborate $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anion in 6 (Figure $2.6(\mathrm{~A})$ ) is an isomer of another isolated $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anion (Figure 2.6 (B)), which was reported in 2006. ${ }^{98}$ In 2007 a related polymeric $\left[\mathrm{B}_{8} \mathrm{O}_{11}(\mathrm{OH})_{4}\right]^{2-}$ anion, ${ }^{93}$ consisting of a chain of boroxole $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ rings connected by oxo bridges with pendant pentaborate moieties (Figure $\mathbf{2 . 6}$ (C)) was reported.

(A)

(B)

(C)

Figure 2.6 Structure of the octaborate(2-) anion present in the crystals of 6 (A) and isomeric $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anion $(\mathrm{B}),{ }^{98}$ and polymeric $\left[\mathrm{B}_{8} \mathrm{O}_{11}(\mathrm{OH})_{4}\right]^{2-}$ anion (C). ${ }^{93}$

The octaborate(2-) anion observed in $\mathbf{6}$ possesses several interesting structural features including a 3-coordinate formally positively charged oxygen (O11) centre. This O 11 is connected to three 4-coordinate boron centres (B11, B12, B13) and is the main fused connection point between three (six membered) boroxole rings. The octaborate(2-) anion in $\mathbf{6}$ consists of 4 rings. These four rings are non-planar. The octaborate(2-) anion offers many opportunities to partake in H -bond interactions. The OH groups provide six potential H -bond donor sites which are also capable of accepting H -bond interactions, and a further ten B-O-B units which are potential H -bond acceptor sites. The octaborate(2-) anion is comprised of three 4-coordinate $\mathrm{sp}^{3}$ boron centres, five 3 -coordinate $\mathrm{sp}^{2}$ boron centres, 10 bridging oxygen atoms, and six exoOH groups.

The B-O distances to the 4-coordinate tetrahedral B11 centre range from 1.439(4) to $1.554(3) \AA$ [av. $1.477 \AA$ ] with those to B12 and B13 ranging from 1.443(3) to 1.543(3) A [av. $1.481 \AA$ ], and $1.423(3)$ to $1.565(3) \AA$ [av. $1.479 \AA$ ], respectively. O11, with a formal positive charge, is bound to all three 4-coordinate boron centres and has the three longest $\mathrm{B}-\mathrm{O}$ bonds in the anion [av. $1.554 \AA$ ]. Coordination about O11 is pyramidal, and is situated $0.357 \AA$ above the plane containing B11, B12, and B13 and with the sum of its B-O-B angles $344.54^{\circ}$. This deviation from planarity is greater than that previously observed in $\left[\mathrm{H}_{3} \mathrm{~N}\left(\mathrm{CH}_{2}\right)_{7} \mathrm{NH}_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot \mathrm{H}_{2} \mathrm{O}, \quad\left[\text { cyclo }-\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NH}_{3}\right]_{2}\left[\mathrm{~B} 7 \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O} \cdot \mathrm{B}(\mathrm{OH})_{3}, \quad$ and $\left.\left[\text { cyclo }-\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NH}_{3}\right]_{2}\left[\mathrm{~B} 7 \mathrm{O}_{9}(\mathrm{OH})_{5}\right)\right] \cdot 2 \mathrm{H}_{2} \mathrm{O} \cdot 2 \mathrm{~B}(\mathrm{OH})_{3} \cdot{ }^{77,97} \mathrm{As}$ a consequence of the pyramidal O 11 , the octaborate(2-) anion in $\mathbf{6}$ is chiral, but the solid-state structure is racemic because the
octaborate(2-) anions are arranged as centrosymmetric (enantiomeric) pairs in the crystalline lattice. B-O bonds involving trigonal boron atoms range from 1.344(4) to 1.398(4) $\AA$ and terminal OH groups are at the shorter end of the range [av. $1.375 \AA$ ], whilst B-O bonds involving ring oxygen atoms are longer [av. $1.418 \AA$ A ]. Bond angles at the B11 range from $107.0(2)^{\circ}$ to $112.2(2)^{\circ}$, B12 range from $107.12(19)^{\circ}$ to $111.3(2)^{\circ}$, and B13 range from $105.34(19)^{\circ}$ to $112.3(2)^{\circ}$ consistent with $\mathrm{sp}^{3}$ hybridization. Angles at the trigonal boron centres range from $108.601(18)^{\circ}$ to $124.1(2)^{\circ}$ consistent with $\mathrm{sp}^{2}$ hybridization. The bond lengths and bond angles of $\mathbf{6}$ are listed in Appendix $\mathbf{I}$ (Table $\mathbf{1}$ and Table 2). The atomic numbering for the oxygen atoms in the octaborate(2-) anion is shown in Figure 2.7.


Figure 2.7 Diagram showing the H -bond acceptor sites and their numbers in the octaborate(2) anions.

The bond distances and bond angles for the pentaborate(1-) anion in $\mathbf{6}$ are within the ranges observed for previously reported structures involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ anions ${ }^{83,4,113}$. The B-O distances to the 4-coordinate B1 centre range from 1.459(4)-1.4919(4) $\AA$ [av. $1.471 \AA$ ] and are significantly longer than those involving the 3-coordinate B centres which range from 1.354(4)-1.391(4) A. B-O bonds involving 3-coordinate B centres and terminal OH groups are at the shorter end of the range [av. $1.362 \AA$ ] whilst $\mathrm{B}-\mathrm{O}$ bonds involving oxygen atoms distal $(\mathrm{O} 2, \mathrm{O} 5)$ to the 4 -coordinate B 1 centre are at the longer end of the range [av. $1.382 \AA$ ]. Bond angles at B1 range from $107.1(2)^{\circ}-112.4(2)^{\circ}$, and angles at the other ring
atoms range from $116.1(2)^{\circ}-122.6(2)^{\circ}$ for $B$ centres consistent with $\mathrm{sp}^{3}$ and $\mathrm{sp}^{2}$ hybridization, respectively, Appendix I (Table 1 and Table 2).

There are ten potential H -bond acceptor sites on the $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion, and all, with the exception of O 2 and O 4 , are acceptors. Each pentaborate(1-) anion has H -bonds to three cations, three $\mathrm{H}_{2} \mathrm{O}$ and two octaborate(2-) anions. The H-bonds data are shown Table 2.8.

Table 2.8 H-bond interactions in 6.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| N1-H1C...O17 | 2.939(3) | O8-H8..O15 | 2.686(3) |
| N1-H1D...O19 | 3.330(3) | O9-H9 ..O51 ${ }^{\text {vi }}$ | 2.670(4) |
| N1-H1D...O42 ${ }^{\text {i }}$ | 2.999(3) | O10-H10…O4 $1^{\text {vi }}$ | 2.733(3) |
| $\mathrm{N} 2-\mathrm{H} 2 \mathrm{C} \ldots \mathrm{O} 14{ }^{\text {ii }}$ | 3.088(3) | $\mathrm{O} 21-\mathrm{H} 21 \cdots \mathrm{O} 20^{\text {vii }}$ | 3.010(3) |
| N2-H2D...O10 ${ }^{\text {iii }}$ | 2.945(3) | $\mathrm{O} 22-\mathrm{H} 22 \cdots \mathrm{O} 1^{\mathrm{i}}$ | 2.813(3) |
| N6-H6D...O17 | 2.96 (2) | O23-H23..O3 | 2.830(3) |
| N11-H11C...O8 | 3.040(3) | O24-H24..O18 ${ }^{\text {viii }}$ | 2.738 (3) |
| N11-H11D...O43 ${ }^{\text {iii }}$ | 3.006(3) | O25-H25..O16 ${ }^{\text {viii }}$ | 2.705(3) |
| N12-H12C..O23ii | 2.982(3) | O26-H26..O11 ${ }^{\text {vii }}$ | 2.853(3) |
| N12-H12D...O9 ${ }^{\text {iv }}$ | 2.882(3) | O41-H41A $\cdots{ }^{\text {O }} 2^{\text {v }}$ | 3.095(4) |
| N16-H16D...O8 | 2.761(16) | O41-H41B...O44 ${ }^{\text {iii }}$ | 2.745(4) |
| N21-H21C...O8 | 3.082(3) | O42-H42A $\cdots$ O22 ${ }^{\text {ix }}$ | 2.753(3) |
| N21-H21C...O21 | 2.992(3) | O42-H42B $\cdots{ }^{\text {O }}$ O19 ${ }^{\text {v }}$ | 2.805(3) |
| N21-H21D $\ldots$ O4 ${ }^{\text {iv }}$ | 3.259(3) | O43-H43A $\cdots$ O6 | 2.959(3) |
| $\mathrm{N} 22-\mathrm{H} 22 \mathrm{C} \ldots \mathrm{O} 14{ }^{\text {ii }}$ | 2.972(3) | O43-H43B $\cdots$ O24 ${ }^{\text {iii }}$ | 2.856(3) |
| N22-H22D... ${ }^{\text {4 }}{ }^{\text {i }}$ | 2.956(3) | O44-H44A $\cdots$ O6 | 3.149(3) |
| N26-H26C...O19 | 3.304(17) | O44-H44B $\cdots$ O43 ${ }^{\text {iii }}$ | 2.935 (3) |
| N26-H26D $\cdots$ O21 | 2.761(17) | O51-H51A $\cdots$ O7 | 2.656(4) |
| O7-H7 $\ldots \mathrm{O} 12^{v}$ | 2.672(3) | O51-H51B $\cdots$ O41 | 3.124(5) |
| (i) $x, y, z-1$ (ii) $x+1, y, z$ <br> (vii) $-x+1,-y+1,-z$ (viii) $-x+1,-y,-z$ | (iii) $-x+1,-$ <br> (xi) $x+1, y, z$ | (iv) $-\mathrm{x}+1,-\mathrm{y}+1$ | z+1 (vi) |

Christ and Clark ${ }^{163}$ and Heller ${ }^{27}$ proposed a crystal chemical classification scheme. According to it, the shorthand notification of $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$and $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ are $[5: 4 \Delta+1 \mathrm{~T}]$ and $[8: 5 \Delta+3 T]$, respectively. In 1990 a nomenclature system was devised by Etter ${ }^{164}$ to describe H -bond connections between sets of molecules according to the nature of the donors and acceptors involved in the H -bond. This system indicates whether the motif is cyclic or linear, and finite or infinite. The designators R (ring), C (chain), and D (dimer) are used to denote intermolecular H-bonds, while S refers intramolecular H-bonds. These designators are followed by two numbers e.g. $\mathrm{R}_{2}{ }^{2}(8)$ and a further number is parenthesis. The subscript number
is the number of donor sites in the motif and the superscript is the number of acceptor sites in the motif, whilst the number in parenthesis signifies the number of atoms in the repeating motif.

All six donor sites on octaborate(2-) anion are involved in $\mathrm{R}_{2}{ }^{2}(8)$ interactions with neighbouring polyborates: two to pentaborates and four to octaborates. Details of the H bonding interactions are given in Table 2.8. These interactions are illustrated in Figure 2.8 and 2.9 .


Figure 2.8 Pentaborate(1-) anion $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond motif connections in 6. Dashed blue lines represent H-bonds.


Figure 2.9 Four octaborate(2-) anion - octaborate(2-) anion $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond motif connections in 6.

O11, the 3-coordinate O atom in the octaborate(2-) anions, effectively becomes 4coordinate in 6 because it accepts a H-bond from O26-H26. This interaction is approximately linear $\left(173.2^{\circ}\right)$, with $\mathrm{d}(\mathrm{D} \cdots \mathrm{A})$ and $\mathrm{d}(\mathrm{H} \cdots \mathrm{A})$ distances of $2.853(3)$ and $2.02 \AA$, respectively. The $\mathrm{R}_{2}{ }^{2}(8)$ interaction involving O 11 is unusual in that the heavy $(\mathrm{BO}) \mathrm{R}_{2}{ }^{2}(8)$ atoms are nonplanar (half-chair) with the 3-coordinate O centre ( O 11 ) out of the plane by $0.98 \AA$. As a further consequence of these H -bonding interactions, there is an intramolecular $\mathrm{O} 20 \cdots \mathrm{O} 21$ distance of $2.823 \AA$. These structural aspects have not been observed in polyborates before.


Figure 2.10 Diagram showing a 'plane' of polyborate anions (viewed along the $b$ direction of the unit cell) and water molecule with $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cations in 6 .

The $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cations, $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions, $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anions, and $\mathrm{H}_{2} \mathrm{O}$ molecules of crystallization of $\mathbf{6}$ are connected through a complex series of H-bond interactions, with the anion network templated by the cations. According to Figure $\mathbf{2 . 1 0}$ the supramolecular layered structure of 6 shows that the $[\mathrm{Co}(\mathrm{en}) 3]^{3+}$ cations connect the octaborate(2-) and pentaborate(1-) anion ribbons by H-bond interactions, forming a three dimensional network. The $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cations are situated in the cavities arising within the supramolecular $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-} /\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$framework.

Ten of the twelve amino hydrogen atoms of the $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cations are involved as $\mathrm{H}-$ bond donors to their neighbouring polyborate anions and water molecules. Each $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cation is H -bonded to three $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions, two $\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]^{2-}$ anions and two water molecules in the secondary coordination shell. Details of H -bond interactions are given in Table 2.8. The connections of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cation to $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions are $\mathrm{N} 2-\mathrm{H} 2 \mathrm{D} \cdots \mathrm{O}^{2} 0^{*}$, $\mathrm{N} 11-$ H11D $\cdots \mathrm{O} 8^{*}$, and N12-H12D $\cdots \mathrm{O}^{*}$ (where * represents a neighbouring molecule). The connections of cation to octaborate(2-) anions are N1-H1C $\cdots \mathrm{O}_{17}{ }^{*}$, $\mathrm{N} 21-\mathrm{H} 21 \cdots \mathrm{O} 21^{*}$, $\mathrm{N} 12-$ $\mathrm{H} 12 \mathrm{C} \cdots \mathrm{O} 23^{*}$, and $\mathrm{N} 22-\mathrm{H} 22 \mathrm{C} \cdots \mathrm{O} 14^{*}$. The connections of cation to water molecules are $\mathrm{N} 11-$ H11D $\cdots \mathrm{O} 43^{*}$, N1-H1D $\cdots \mathrm{O} 42^{*}$, and $\mathrm{N} 22-\mathrm{H} 22 \cdots \mathrm{O} 42^{*}$. Nine of the ten H-bond interactions are illustrated in Figure 2.11.


Figure 2.11 The connection of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ cation with pentaborate(1-) anions, water molecules, and octaborate(2-) anions in 6.

### 2.3.5.2 Structural characterisation of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]_{3} \cdot \mathbf{1 1 H}_{2} \mathrm{O}$ (9)

Crystallographic data of $\mathbf{9}$ are shown in Table 2.9. The crystals of $\mathbf{9}$ are monoclinic, $P 2_{1} / c$ and 9 is an ionic compound with two $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cations (A and B) partnered with three $\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]^{2-}$ anions (A, B, and C) and eleven interstitial water molecules (Figure 2.12). The structure unit of $\mathbf{9}$ in Figure $\mathbf{2 . 1 2}$ shows that there are three transition metal cations, but two of them are bisected by an internal plane of symmetry and there for equate to one cation in unit cell.


Figure 2.12 Diagram showing the structure and numbering scheme for 9 .

Table 2.9 Crystal data and structure refinement of 9 .

| Empirical formula | $\mathrm{B}_{12} \mathrm{H}_{70} \mathrm{~N}_{12} \mathrm{O}_{38} \mathrm{Co}_{2}$ |
| :---: | :---: |
| Formula weight | 1094.26 |
| Temperature | 100(2) K |
| Wavelength | 0.71075 A |
| Crystal system | Monoclinic |
| Space group | $P 2{ }_{1} / \mathrm{c}$ |
| Unit cell dimensions | $a=21.8873(15) \AA$ $\alpha=90^{\circ}$ <br> $b=8.8674(5) \AA$ $\beta=101.2910(10)^{\circ}$ <br> $c=21.6637(15) \AA$ $\gamma=90^{\circ}$ |
| Volume | $4123.2(5) \AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.763 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.933 \mathrm{~mm}^{-1}$ |
| F(000) | 2288 |
| Crystal | Plate; Light Orange |
| Crystal size | $0.210 \times 0.040 \times 0.020 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.951-27.483^{\circ}$ |
| Index ranges | $-28 \leq h \leq 28,-9 \leq k \leq 11,-28 \leq l \leq 28$ |
| Reflections collected | 53472 |
| Independent reflections | $9431\left[R_{\text {int }}=0.0492\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.8\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.752 |


| Refinement method | Full-matrix least-squares on $F^{2}$ |
| :--- | :--- |
| Data / restraints / parameters | $9431 / 36 / 670$ |
| Goodness-of-fit on $F^{2}$ | 1.034 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0296, w R 2=0.0756$ |
| $R$ indices (all data) | $R 1=0.0356, w R 2=0.0793$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.468 and $-0.593 \mathrm{e} \AA^{-3}$ |
| Radiation source (wavelength) | $\mathrm{Mo}-\mathrm{K} \alpha(0.71073 \AA)$ |

The transition metal in each $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cation is octahedrally coordinated by six nitrogen atoms from six monodentate (ammonia) ligands, with Co-N bond lengths in the range of $1.9625(14)-1.9820(14) \AA$. The bond length and bond angles in 9 are listed in Appendix I (Table 3 and Table 4).

The isolated $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ anion in 9 is well known. The shorthand designation, according to Christ and Clark ${ }^{163}$ and Heller ${ }^{27}$ schemes, for $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ anion is $4: 2 \Delta+2 \mathrm{~T}$. Bond lengths and bond angles of the tetraborate(2-) anion in 9 are in agreement with published data of transition metal complex cationic tetraborates, ${ }^{115}$ metal cationic tetraborates, ${ }^{165}$ and nonmetal cationic tetraborates. ${ }^{84,101,102,115}$ The structure of the isolated $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ anion consists of two 3-coordinate boron centres $\left\{\mathrm{BO}_{2}(\mathrm{OH})\right\}$ and two 4-coordinate boron centres $\left\{\mathrm{BO}_{3}(\mathrm{OH})\right\}$ linked by common oxygen atoms, forming a double six-membered ring with two boron and one oxygen atoms in common. Each tetraborate(2-) anion has four potential H -bond donor sites which are also capable of accepting H-bond interactions, and five additional potential H -bond acceptor sites. The four chemically non-equivalent oxygen sites are labelled $\alpha, \beta, \delta$, and $\varepsilon$ by using a similar nomenclature system to that previously described (Figure 2.13). ${ }^{98,77}$ The three tetraborate(2-) anions in $\mathbf{9}$ are all crystallographically independent and they here been labelled A-C. All 4 donor sites on tetraborate(2-) anions A, B, and C are involved in H -bond interactions with neighbouring polyborate anions and water molecules. The H -bond acceptor sites arising from donor H-bond sites of the three tetraborate(2-) anions A, B, and C are $\omega \alpha \omega \alpha, \varepsilon \delta \delta \omega$, and $\alpha \alpha \alpha \omega$, respectively, where $\alpha$ and $\delta$ are tetraborate acceptor sites, and $\omega$ is an water acceptor site.

The gross structures of tetraborate(2-) anions A, B, and C found in $\mathbf{9}$ are all very similar. B-O bond length and O-B-O and B-O-B angles are typical of those found in tetraborate(2-) and other polyborate systems ${ }^{115}$ and are illustrated in detail for anion A. The B-O distances to the 4-coordinate tetrahedral B1 and B3 centres of tetraborate(2-) anion (A) range from 1.4469(19) - 1.5104(19) A [av. $1.4778 \AA$ ] and these are significantly longer than those involving the 3coordinate boron centres, which range from $1.367(2)-1.378(2) \AA$ [av. $1.373 \AA$ ]. The B-O distances involving B-OH groups are dependent on whether the boron centre is tetrahedral
(1.4469(19), 1.452(2)) or trigonal (1.372(2), 1.378(2)). The O-B-O bond angles range from 105.61(12) - 113.76(13) ${ }^{\circ}$ for 4-coordinate centres (B1 and B3), while O-B-O bond angles for 3-coordinate centres (B2 and B4) range from 116.66(14)-122.91(14) ${ }^{\circ}$.


Figure 2.13 Diagram labelling the oxygen atom H-bond acceptor sites in the tetraborate(2-) anions.

The solid-state structure of $\mathbf{9}$ involves H -bonded giant supramolecular tetraborate(2-) anion structures with 'cavities' filled with the associated transition metal complex cations and water molecules. Table $\mathbf{2 . 1 0}$ shows H-bond interactions between tetraborate(2-) anions and the acceptor sites.

The tetraborate(2-) anion (A) has 19 acceptor H-bonds and 4 donor H-bonds with interactions to two cations, five $\mathrm{H}_{2} \mathrm{O}$ and three tetraborate(2-) anions. A view of the supramolecular layered structure of the tetraborate(2-) anions in 9 is shown in Figure 2.14. Details of H -bond interactions are given in Table 2.10. Here each tetraborate(2-) anion (A) is linked to three neighbouring tetraborate(2-) anions within the plane via two pairwise $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$ bond interactions $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 4^{*} / \mathrm{O} 9^{*}-\mathrm{H} 9^{*} \cdots \mathrm{O} 1$ and $\mathrm{O} 7^{*}-\mathrm{H} 7^{*} \cdots \mathrm{O} 4 / \mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O} 1^{*}$, and one H -bond interaction O16-H16 $\cdots{ }^{\circ} 8^{*}$.

The tetraborate(2-) anion (B) has twenty acceptor H-bonds and four donor H-bonds with interactions to four cations, five $\mathrm{H}_{2} \mathrm{O}$ and three tetraborate(2-) anions. A view of the H -bond interactions of the tetraborate(2-) anion (B) to another anions in 9 is shown in Figure 2.15. Here each tetraborate(2-) anion (B) is linked to three neighbouring tetraborate(2-) anions within the plane via one pairwise $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond interaction $\mathrm{O} 19^{*}-\mathrm{H} 19^{*} \cdots \mathrm{O} 25 / \mathrm{O} 28-\mathrm{H} 28 \cdots \mathrm{O} 13^{*}$ and two H -bond interactions $\mathrm{O} 16^{*}-\mathrm{H} 16^{*} \cdots \mathrm{O} 8$ and $\mathrm{O} 17^{*}-\mathrm{H} 17^{*} \cdots \mathrm{O} 28$.


Figure 2.14 H-bond interactions of tetraborate(2-) anion (A) to another anions in 9. Dashed blue lines represent H -bonds.


Figure 2.15 The H-bond interactions of the tetraborate(2-) anion (B) to another anions in 9.


Figure 2.16 The H-bond interactions of the tetraborate(2-) anion (C) to another anions in 9.

The tetraborate(2-) anion (C) has nineteen acceptor H-bonds and four donor H-bonds with interactions to $3\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cations, $4 \mathrm{H}_{2} \mathrm{O}$ and 4 tetraborate(2-) anions. A view of the H -bond interactions of the tetraborate(2-) anion (C) to another anions in 9 is shown in Figure 2.16. Here each tetraborate(2-) anion (C) is linked to four neighbouring tetraborate (2-) anions within the plane via three pairwise $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond interactions $\mathrm{O} 27^{*}-\mathrm{H} 27^{*} \cdots \mathrm{O} 24 / \mathrm{O} 29-$ $\mathrm{H} 29 \cdots \mathrm{O} 21^{*}, \mathrm{O} 27-\mathrm{H} 27 \cdots \mathrm{O} 24 * / \mathrm{O} 29^{*}-\mathrm{H} 29^{*} \cdots \mathrm{O} 21$, and $\mathrm{O} 19-\mathrm{H} 19 \cdots \mathrm{O} 25^{*} / \mathrm{O} 28^{*}-\mathrm{H} 28^{*} \cdots \mathrm{O} 13$ and one further H -bond interaction $\mathrm{O} 17-\mathrm{H} 17 \cdots \mathrm{O} 28^{*}$.

Table 2.10 H-bond interactions in 9.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdot \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| N1-H1A $\cdots$ O23 ${ }^{\text {iii }}$ | 2.9753(17) | O6-H6 $\cdots$ O42 | 3.0923(18) |
| N1-H1B...O16 ${ }^{\text {i }}$ | 2.9562(16) | O7-H7 $\ldots$ O4 $4^{\text {xi }}$ | $2.7485(16)$ |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{C} \cdots \mathrm{O} 2$ | 2.9791 (18) | O8-H8...O45 | 2.8547 (16) |
| N2-H2A $\cdots{ }^{\text {a }} 2^{\text {iv }}$ | $2.9665(18)$ | O9-H9...O1 ${ }^{\text {xii }}$ | 2.6793 (17) |
| N2-H2B $\cdots{ }^{\text {a }} 45^{\text {v }}$ | 3.0054(18) | O16-H16..O8 ${ }^{\text {i }}$ | $2.8588(16)$ |
| N2-H2C...O16 ${ }^{\text {i }}$ | 3.1682(18) | O17-H17...O28 ${ }^{\text {i }}$ | $2.6623(16)$ |


| N3-H3A $\cdots$ O12 ${ }^{\text {vi }}$ | 3.0282(17) | O18-H18...O51 ${ }^{\text {xiii }}$ | 2.7891(17) |
| :---: | :---: | :---: | :---: |
| N3-H3A $\cdots$ O13 ${ }^{\text {vi }}$ | 3.4351(17) | O19-H19 ..O25ix | 2.7127(16) |
| N3-H3B $\cdots$ O22 ${ }^{\text {iv }}$ | 3.3117(18) | O26-H26...O48 ${ }^{\text {ix }}$ | 2.8033(17) |
| N3-H3C $\cdots$ O29 ${ }^{\text {iii }}$ | 3.0984(18) | O27-H27...O24 ${ }^{\text {xiv }}$ | 2.6741(17) |
| $\mathrm{N} 4-\mathrm{H} 4 \mathrm{~A} \cdots \mathrm{O} 12^{\text {vi }}$ | 2.9027(17) | O28-H38…O13 ${ }^{\text {ix }}$ | 2.8640(15) |
| N4-H4B..O7 | 3.0027(18) | O29-H29...O21 ${ }^{\text {xv }}$ | 2.7320 (16) |
| N4-H4C...O41 ${ }^{\text {iv }}$ | $2.9773(19)$ | O41-H41A $\cdots$ O6 ${ }^{\text {viii }}$ | $3.2218(18)$ |
| N5-H5A ...O9 ${ }^{\text {v }}$ | $2.9558(19)$ | O41-H41A…O9 ${ }^{\text {x }}$ | 3.0760(17) |
| N5-H5B...O15 ${ }^{\text {i }}$ | 3.1928(16) | O41-H41A...O44 ${ }^{\text {viii }}$ | 3.2461(19) |
| N5-H5B $\cdots$ O16 ${ }^{\text {i }}$ | $3.2525(18)$ | O41-H41B $\ldots$ O50 ${ }^{\text {i }}$ | 2.8990(19) |
| N5-H5C...O3v | $3.1265(17)$ | O42-H42A $\cdots \mathrm{O} 41$ | 2.8505(19) |
| N5-H5C...O45 ${ }^{\text {v }}$ | $3.1750(18)$ | O42-H42B $\cdots$ O43 | 2.7612(18) |
| N6-H6A...017 ${ }^{\text {vi }}$ | 3.0189(17) | O43-H43A $\ldots$ O5 | 2.7988(16) |
| N6-H6B...O3v | 2.9152(17) | O43-H43B $\cdots$ O15 ${ }^{\text {i }}$ | 2.6911(17) |
| N6-H6C...O22 ${ }^{\text {iv }}$ | 3.0346(18) | O44-H44A $\cdots{ }^{\text {O }}{ }^{\text {xi }}$ | 3.2872(17) |
| N6-H6C...O47 ${ }^{\text {v }}$ | $3.325(2)$ | O44-H44A $\cdots{ }^{\text {a }}{ }^{\text {xi }}$ | 3.2883(16) |
| N11-H11A $\cdots$ O14 ${ }^{\text {i }}$ | 2.9759(18) | O44-H44B...O43 | 2.8477(18) |
| N11-H11B...O25 | $3.3539(17)$ | O45-H45A $\cdots$ O46 | 2.7471(18) |
| N11-H11B...O46 | $3.1938(19)$ | O45-H45B $\cdots$ O13 ${ }^{\text {ix }}$ | 3.1573(16) |
| N11-H11C...O49 ${ }^{\text {i }}$ | 2.9746 (19) | O45-H45B...O15 ${ }^{\text {ix }}$ | 2.8330(16) |
| N12-H12A $\cdots$ O14 | 3.1682(18) | O46-H46A $\cdots{ }^{\text {O }} 11^{\text {i }}$ | 2.8237(17) |
| N12-H12A $\cdots$ O16 | 3.2138(19) | O46-H46B $\cdots$ O25 | 2.8927(16) |
| N12-H12B...O49 ${ }^{\text {i }}$ | 3.1934(19) | O46-H46B...O28 | 3.1978(16) |
| N12-H12C...O26 | 3.0560(18) | O47-H47A…O22 ${ }^{\text {iii }}$ | 3.1089(18) |
| N13-H13A $\cdots{ }^{\text {O2 }}{ }^{\text {i }}$ | $2.8709(17)$ | O47-H47A $\cdots{ }^{\text {O }} 3^{\text {iii }}$ | 2.9462(17) |
| N13-H13B $\ldots$ O19 ${ }^{\text {i }}$ | $3.0535(19)$ | O47-H47B $\cdots$ O8 | 2.7520(18) |
| N13-H13C...O48 ${ }^{\text {i }}$ | 2.9930 (19) | O48-H48A $\cdots$ O47 | 2.7637(19) |
| $\mathrm{N} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O} 18^{\text {vii }}$ | 2.9976 (19) | O48-H48B...O45 | 3.1823(19) |
| $\mathrm{N} 21-\mathrm{H} 21 \mathrm{~B} \cdots \mathrm{O} 4^{\mathrm{ii}}$ | $3.1948(17)$ | O49-H49A $\cdots{ }^{\text {O }}$ 2 $1^{\text {iii }}$ | $3.3296(17)$ |
| $\mathrm{N} 21-\mathrm{H} 21 \mathrm{~B} \cdots \mathrm{O}^{\text {ii }}$ | 3.2251(18) | O49-H49A $\cdots{ }^{\text {O }}{ }^{\text {i }}$ | 3.2093(18) |
| $\mathrm{N} 21-\mathrm{H} 21 \mathrm{C} \cdots \mathrm{O} 44^{\text {viii }}$ | 2.9933 (19) | O49-H49B...O24 ${ }^{\text {ix }}$ | 3.1630(18) |
| $\mathrm{N} 22-\mathrm{H} 22 \mathrm{~A} \cdots \mathrm{O} 18^{\text {ix }}$ | 2.9444(18) | O49-H49B..O48 | 3.081(2) |
| N22-H22B $\cdots$ O7(x) | 3.1569(17) | O50-H50A $\cdots \mathrm{O}^{\text {vi }}$ | 2.9117(16) |
| $\mathrm{N} 22-\mathrm{H} 22 \mathrm{C} \ldots \mathrm{O}^{\text {ii }}$ | 3.0986(18) | O50-H50B $\cdots$ O28 ${ }^{\text {i }}$ | 3.0279(18) |
| N23-H23A $\cdots{ }^{\text {O }}{ }^{1}{ }^{\text {i }}$ | 3.0078(19) | O51-H51A…O5 ${ }^{\text {i }}$ | $2.6918(15)$ |
| N23-H23B $\cdots$ O42 ${ }^{\text {viii }}$ | 2.964(2) | O51-H51B $\cdots \mathrm{O} 17$ | 3.0070(17) |
| $\mathrm{N} 23-\mathrm{H} 23 \mathrm{C} \cdots \mathrm{O} 44^{\text {viii }}$ | 3.1008(18) |  |  |

(i) $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$
(ii) $-\mathrm{x},-\mathrm{y}+2,-\mathrm{z}+1$
(iii) $x,-y+3 / 2, z-1 / 2$ (iv) $x,-y+1 / 2, z-1 / 2$
(v) $x, y-1, z$
$-\mathrm{x}+1, \mathrm{y}-1 / 2,-\mathrm{z}+1 / 2$ (vii) $\mathrm{x}-1, \mathrm{y}, \mathrm{z}$
(viii) $-\mathrm{x},-\mathrm{y}+1,-\mathrm{z}+1 \quad$ (xi) $-\mathrm{x}+1,-\mathrm{y}+2,-\mathrm{z}+1$
(x) $x,-y+3 / 2, z+1 / 2$ (xi)
$-x, y-1 / 2,-z+1 / 2 \quad$ (xii) $-x, y+1 / 2,-z+1 / 2 \quad$ (xiii) $x, y+1, z \quad$ (xiv) $-x+1, y-1 / 2,-z+3 / 2$ (xv) $-x+1, y+1 / 2,-z+3 / 2$
(vi)

The tetraborate(2-) anions form a ribbon structure and these ribbons are interconnected to form a layer. A view of the ribbon / layered structure of the $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ anions of $\mathbf{9}$ is shown in Figure 2.17.


Figure 2.17 Tetraborate(2-) anions and water molecules layer structure (viewed along the $a$ direction of the unit cell) of 9 .

The two $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cations, and eleven $\mathrm{H}_{2} \mathrm{O}$ molecules of crystallization of $\mathbf{9}$ are connected through a complex series of H -bond interactions, with the tetraborate anion network templated by the cations. The connection of ribbon-layer shown in Figure 2.17 to the neighbouring planes is formed by further H -bond interactions, forming a three-dimensional network. Compound 9 possess two $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cations: A contains Co1 and B contains Co11 and Co 21 . These cations are involved in H -bonding to $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ anions as described below.

All eighteen of the amino hydrogen atoms of the $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}(\mathrm{A})$ and (B) cations are involved as H -bond donors to their neighbouring tetraborate(2-) anions and water molecules. Cation A has H-bonds to six $\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]^{2-}$ anions and three $\mathrm{H}_{2} \mathrm{O}$ molecules in its secondary coordination shell via twenty-two H -bond interactions. Fourteen of the twenty-two H -bond interactions are illustrated in Figure 2.18. Cation B acts as H-bond donors to eight $\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]^{2-}$ anions and six $\mathrm{H}_{2} \mathrm{O}$ molecules via twenty-one H -bond interactions. These are described in detail in Table 2.10.


Figure 2.18 The H-bond interactions of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ (A) cation with tetraborate(2-) anions and water molecules in 9 .

### 2.3.5.3 Structural characterisation of $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{\prime} \cdot 9 \mathrm{H}_{2} \mathrm{O}(11)$

Crystallographic data for compound $\mathbf{1 1}$ are shown in Table 2.11. The crystals of $\mathbf{1 1}$ are triclinic, $P 2_{1} / n$ and contain a discrete $s-f a c-\left[\operatorname{Co}(\operatorname{dien})_{2}\right]^{3+}$ cation partnered with a unique $\left[\mathrm{B} 7 \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ anion and nine water molecules of crystallization, held together by an extensive H -bond network (Figure 2.19). Two water molecules are disordered, each over two positions, however they were successfully modelled in to a predominant form O58 (s.o.f. 0.819(7)) and O59 (s.o.f. 0.600(11)).

Table 2.11 Crystal data and structure refinement of $\mathbf{1 1}$.

| Empirical formula | $\mathrm{C}_{8} \mathrm{H}_{50} \mathrm{~B}_{7} \mathrm{~N}_{6} \mathrm{O}_{24} \mathrm{Co}$ |  |
| :---: | :---: | :---: |
| Formula weight | 749.14 |  |
| Temperature | 100(2) K |  |
| Wavelength | 0.71075 § |  |
| Crystal system | Monoclinic |  |
| Space group | $P 2_{1} / n$ |  |
| Unit cell dimensions | $\begin{aligned} & a=11.7755(3) \AA \\ & b=15.3238(3) \AA \end{aligned}$ | $\begin{aligned} & \alpha=90^{\circ} \\ & \beta=96.515(3)^{\circ} \end{aligned}$ |


|  | $c=17.3965(7) \AA \quad$$\AA$ <br> Volume |
| :--- | :--- |
| $Z$ | $4118.85(16) \AA^{3}$ |
| Density (calculated) | $1.595 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.651 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 1576 |
| Crystal | Cut Blade; Orange |
| Crystal size | $0.150 \times 0.080 \times 0.010 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.357-27.680^{\circ}$ |
| Index ranges | $-15 \leq h \leq 15,-19 \leq k \leq 16,-22 \leq l \leq 19$ |
| Reflections collected | 29346 |
| Independent reflections | $7250\left[R_{\text {int }}=0.0491\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | $99.9 \%$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.797 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints $/$ parameters | $7250 / 0 / 414$ |
| Goodness-of-fit on $F^{2}$ | 1.008 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0483, w R 2=0.1159$ |
| $R$ indices (all data) | $R 1=0.0711, w R 2=0.1258$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 1.214 and $-0.801 \mathrm{e} \AA \AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha(0.71073 \AA)$ |

Special details: Two of the water molecules (labelled as O88 and O89) were modelled as disordered over two positions.


Figure 2.19 Diagram showing the structure and numbering scheme for $\mathbf{1 1}$.

Whilst salts containing the pentaborate(1-) anions are common, salts containing heptaborate anions are relatively rare, and are limited to two isomeric form of the heptaborate(2) anion ${ }^{6,77,97,166}$ (Figure 2.20, (A) and (B)). Compound 11 contains a novel heptaborate(3-) anion, $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ (Figure $2.20(\mathrm{C})$ ).

(A)

(B)

(C)

Figure 2.20 The two isomeric $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ anions $(\mathrm{A})$ and $(\mathrm{B})$ and the structure of the heptaborate(3-) anion (C) present in the crystals of $\mathbf{1 1}$.

The heptaborate(3-) anion in $\mathbf{1 1}$ has never been previously observed in minerals or in synthetic borates. According to Christ and Clark ${ }^{163}$ and Heller ${ }^{27}$ the shorthand notification for the $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ anion is $[7: 4 \Delta+3 \mathrm{~T}]$. The atomic numbering for the oxygen and boron atoms in the heptaborate(3-) anion is shown in Figure 2.21. The heptaborate(3-) anion is comprised of three almost planar (half-chair) boroxole $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ rings with B 2 , B 1 , and O 1 lying 0.044, 0.097 and $0.155 \AA$ out of best planes, respectively. These connect together by sharing two 4 coordinate boron centres (B1 and B2), in a similar way to that observed for one of the known isomers of $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ anion (Figure $\left.\mathbf{2 . 2 0}(\mathrm{A})\right) .{ }^{6}$ However, the $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ anion found in 11 (Figure 2.21) has an additional 4-coordinate boron centre (B7) formed by the addition of $\mathrm{OH}^{-}$to a 3-coordinate boron centre on a terminal boroxole ring in $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$. In addition, there are four 3-coordinate boron (B3, B4, B5, B6) centres, with each centre connected to two oxygen atoms and one hydroxyl group. The 'plane' of the middle ring is perpendicular to the 'best planes' of the outer two rings.

Bond lengths and bond angles for the heptaborate(3-) anion found in $\mathbf{1 1}$ are within the ranges observed for previously reported polyborate anions, and generally not significantly different to those found in the heptaborate(2-) anion with the exception of data associated with the outer boroxole ring containing the additional hydroxyl group. The B1, B2, and B7 atoms
are 4-coordinate centres with B-O distances ranging from 1.424(3)-1.507(3) $\AA, 1.444(3)$ $1.508(4) \AA$, and $1.448(3)-1.516(3) \AA$, respectively, and angles ranging from $105.42(19)^{\circ}$ $113.7(2)^{\circ}, 104.9(2)^{\circ}-111.7(2)^{\circ}$, and $104.40(19)-112.0(2)^{\circ}$, respectively. The B-O bond length and angle values of B1, B2, and B7 centres are appropriate for a distorted tetrahedral geometry. The B-O distances to the tetrahedral centres are significantly longer than those involving the 3coordinate (B3, B4, B5, and B6) centres which range from 1.356(3)-1.371(4) Å, 1.348(3)$1.400(3) \AA, 1.347(3)-1.385(3) \AA$, and $1.354(3)-1.366(3) \AA$, respectively with angles ranging from $117.5(2)^{\circ}-122.9(3)^{\circ}, 118.3(2)^{\circ}-121.2(2)^{\circ}, 116.0(2)^{\circ}-123.2(2)^{\circ}$, and $115 .(2)^{\circ}-124.3(2)^{\circ}$, respectively. The inclusion of the addition $\mathrm{OH}^{-}$group has little structural effects on other parameters within this boroxole ring, other than shortening B6-O8 [1.365(3) A $]$ relative to that observed in $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]^{2-}\left[1.393(7) \AA \AA^{6}{ }^{6}\right.$ These data are similar to that for $\left[\mathrm{B}_{3} \mathrm{O}_{4}(\mathrm{OH})_{4}\right]^{-},{ }^{39}$ and with adduct formation in boroxine ring systems since O8-B6 $\pi$-bonding increases in $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{6}\right]^{3-}$ as the 4 -coordinate B 7 can no longer partake in $\pi$-bonding. This outer boroxole ring in $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ has a similar bond length distribution to that found in $\mathrm{Ca}\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{5}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ (meyerhofferite) which contains a boroxole ring with two 4-coordinate boron centres. ${ }^{167}$ The bond lengths and angles of $\mathbf{1 1}$ are listed in Appendix I (Table $\mathbf{5}$ and Table 6).


Figure 2.21 Diagram showing atomic numbering for the heptaborate(3-) anions in $\mathbf{1 1}$.

Detailed inspection of Figure $\mathbf{2 . 2 2}$ shows that the ribbons of $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{6}\right]^{3-}$ anions are horizontally connected by $\mathrm{C}(10)$ chain motif interaction $\mathrm{O} 11-\mathrm{H} 11 \cdots \mathrm{O} 14$ *. The heptaborate anion ribbons are further linked to other heptaborate anion ribbons by two pairwise $\mathrm{R}_{2}{ }^{2}(8)$ connections O12-H12 $\cdots \mathrm{O} 8^{*} / \mathrm{O} 13^{*}-\mathrm{H} 13^{*} \cdots \mathrm{O} 6$ and $\mathrm{O} 12^{*}-\mathrm{H} 12^{*} \cdots \mathrm{O} 8 / \mathrm{O} 13-\mathrm{H} 13 \cdots \mathrm{O} 6^{*}$. Details of the H -bonding interactions are given in Table 2.12.

Table 2.12 H-bond interactions in $\mathbf{1 1}$.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| O10-H10..O57 | 2.787(2) | N33-H33D $\cdots$ O12 ${ }^{\text {iv }}$ | 2.915(3) |
| O11-H11...O14 | 2.645(2) | O51-H51A $\cdots$ O1 | 2.670(2) |
| $\mathrm{O} 12-\mathrm{H} 12 \cdots \mathrm{O} 8^{\mathrm{ii}}$ | 2.767(2) | O51-H51B...O59 | 2.870 |
| O13-H13..O66 ${ }^{\text {iii }}$ | 2.605(2) | O51-H51B $\cdots$ O89 | 2.767 |
| O14-H14..O58 ${ }^{\text {iii }}$ | 2.825(2) | O52-H52A $\cdots$ O53 | 2.828 |
| O14-H14..O888 ${ }^{\text {iii }}$ | 2.864(2) | O52-H52B $\cdots$ O51 | 2.775 |
| O15-H15..O52 | 2.787(2) | O53-H53A $\cdots{ }^{\text {O }}$ 57 ${ }^{\text {v }}$ | 2.841 |
| N21-H21C..O14 | 3.146(3) | O53-H53B $\cdots \mathrm{O}^{\text {v }}$ | 2.872(2) |
| N21-H21C...O15 | 2.887(3) | O53-H53B $\cdots{ }^{\text {O }}$ | 3.311(2) |
| N21-H21D..O5 ${ }^{\text {iv }}$ | 2.901(3) | O54-H54A ...O51 | 2.746 |
| $\mathrm{N} 22-\mathrm{H} 22 \cdots \mathrm{O} 4^{\mathrm{ii}}$ | 3.072(3) | O55-H55A $\cdots$ O10 ${ }^{\text {vi }}$ | $2.769(2)$ |
| $\mathrm{N} 22-\mathrm{H} 22 \cdots \mathrm{O} 11^{\text {ii }}$ | 3.008(3) | O55-H55B $\cdots$ O15 ${ }^{\text {i }}$ | 2.680(2) |
| $\mathrm{N} 23-\mathrm{H} 23 \mathrm{C} \cdots \mathrm{O} 13^{\mathrm{ii}}$ | 2.777(3) | O56-H56A $\cdots$ O55 ${ }^{\text {vii }}$ | $2.8333(19)$ |
| N23-H23D $\cdots$ O9 | 2.939(3) | O56-H56B $\cdots \mathrm{O}^{\text {iii }}$ | 3.0806(19) |
| N23-H23D $\cdots$ O15 | 3.358(3) | O56-H56B $\cdots \mathrm{O}^{\text {iii }}$ | 3.039(2) |
| N31-H31C...O7 ${ }^{\text {ii }}$ | 2.910 (3) | O57-H57A $\cdots$ O3 ${ }^{\text {viii }}$ | 2.949(2) |
| N31-H31C...O13ii | 3.260(3) | O57-H57A $\cdots$ O6 ${ }^{\text {viii }}$ | 3.014(2) |
| N31-H31D...O4 ${ }^{\text {ii }}$ | 3.104(3) | O57-H57B $\cdots$ O8 ${ }^{\text {ix }}$ | 3.048(2) |
| N31-H31D $\cdots$ O54 ${ }^{\text {ii }}$ | 3.063(3) | O58-H58A $\cdots$ O54 ${ }^{\text {vii }}$ | 2.934(3) |
| N32-H32...09 | 2.941(3) | O58-H58B $\cdots \mathrm{O}^{\text {iii }}$ | 2.781(2) |
| N32-H32 $\ldots$ O14 | 3.195(3) | O88-H88A $\cdots$ O54 ${ }^{\text {vii }}$ | 3.066(3) |
| N33-H33C..O11 ${ }^{\text {ii }}$ | 2.970(3) | O59-H59B $\cdots$ O56 | 2.748 |
| $\mathrm{N} 33-\mathrm{H} 33 \mathrm{C} \cdots \mathrm{O} 54{ }^{\text {ii }}$ | 3.337(3) | O89-H89A $\cdots$ O56 | 2.307 |

(i) $x-1, y, z$
(ii) $-\mathrm{x}+1 / 2, \mathrm{y}+1 / 2,-\mathrm{z}+1 / 2$
(iii) $-\mathrm{x}+1 / 2, \mathrm{y}-1 / 2,-\mathrm{z}+1 / 2$ (iv) $\mathrm{x}+1, \mathrm{y}, \mathrm{z}$ (v) $\mathrm{x}+1 / 2,-\mathrm{y}+1 / 2, \mathrm{z}+1 / 2$
(vi) $x-1 / 2,-y+1 / 2, z+1 / 2 \quad$ (vii) $-x,-y+1,-z+1$
(viii) $-\mathrm{x},-\mathrm{y}+1,-\mathrm{z}$ (xi) $\mathrm{x}-1 / 2,-\mathrm{y}+1 / 2, \mathrm{z}-1 / 2$


Figure 2.22 H-bond interactions between the heptaborate(3-) anions in 11. Dashed blue lines represent H -bonds.


Figure 2.23 Supramolecular structure involving heptaborate(3-) anions and $\left[\mathrm{Co}(\text { Dien })_{2}\right]^{3+}$ cations (viewed along the $c$ direction of the unit cell) in 11.

As shown in Figure $\mathbf{2 . 2 3}$ the supramolecular layered structure of $\mathbf{1 1}$ has the $[\operatorname{Co}(\operatorname{dien})]^{3+}$ cations connected to the heptaborate(3-) anion ribbons by additional H -bond interactions. The connection of plane shown in Figure $\mathbf{2 . 2 3}$ to the neighbouring planes is formed by further Hbond interactions, forming a three-dimensional network.


Figure 2.24 The H -bond connections of $\left[\mathrm{Co}(\mathrm{dien})_{2}\right]^{3+}$ with heptaborate(3-) anions and water molecule in 11.

All ten of the amino hydrogen atoms of the $\left[\mathrm{Co}(\text { dien })_{2}\right]^{3+}$ cations are involved as $\mathrm{H}-$ bond donors to three $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}$ anions and one water molecule in its secondary coordination shell. The ten H -bond interactions consist of nine H -bonds to three heptaborate(3) anions and one H -bond connection to a one $\mathrm{H}_{2} \mathrm{O}$ molecule (Figure 2.24). Details are in Table 2.12.

### 2.3.5.4 Structural characterisation of $[\mathrm{Co}(\mathrm{diNOsar})]_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5} \cdot 4.75 \mathrm{H}_{2} \mathrm{O}$ (12)

Crystallographic data for compound 12 are listed in Table 2.13. The crystals of compound $\mathbf{1 2}$ are monoclinic, $P-1$ consists of two $[\mathrm{Co}(\text { diNOsar })]^{3+}$ cations partnered with one isolated $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$polyborate anion, five $\mathrm{Cl}^{-}$anions, and 4.75 water molecules (Figure 2.25). There is one disordered water molecule that is positioned in either one of two positions, with an s.o.f. ratio of $0.75 / 0.25$.


Figure 2.25 Diagram showing the structure and numbering scheme for $\mathbf{1 2}$.

Table 2.13 Crystal data and structure refinement of $\mathbf{1 2}$.

| Empirical formula | $\mathrm{C}_{28} \mathrm{H}_{73.50} \mathrm{~B}_{3} \mathrm{Cl}_{5} \mathrm{~N}_{16} \mathrm{O}_{19.75} \mathrm{Co}_{2}$ |
| :---: | :---: |
| Formula weight | 1278.06 |
| Temperature | 100(2) K |
| Wavelength | 0.71075 A |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a=9.6900(4) \AA$ $\alpha=85.079(3)^{\circ}$ <br> $b=10.0170(6) \AA$ $\beta=88.439(3)^{\circ}$ <br> $c=29.1374(7) \AA$ $\gamma=62.137(5)^{\circ}$ |
| Volume | 2490.9(2) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.704 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.024 \mathrm{~mm}^{-1}$ |
| F(000) | 1331 |
| Crystal | Lath; Orange |
| Crystal size | $0.180 \times 0.030 \times 0.010 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.420-29.944^{\circ}$ |
| Index ranges | $-13 \leq h \leq 12,-13 \leq k \leq 13,-38 \leq l \leq 40$ |
| Reflections collected | 36914 |
| Independent reflections | $12826\left[R_{\text {int }}=0.0478\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.9\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.869 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 12826 / 0 / 668 |
| Goodness-of-fit on $F^{2}$ | 1.023 |
| Final $R$ indices [ $\left.F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0485, w R 2=0.0976$ |
| $R$ indices (all data) | $R 1=0.0740, w R 2=0.1072$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.881 and -0.662 e $\AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $(0.71073$ A) |

Special details: There was disordered water for which exists either one or two molecules. Hence the given fractional formula.

The triborate(1-) anion is structurally known but rare, and a triborate(1-) anion with transition metal complex cations has never been observed before. The shorthand notification for the $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$anion is $3: 2 \Delta+1 \mathrm{~T}$ according to Christ and Clark ${ }^{163}$ and Heller ${ }^{27}$ schemes. As shown in Figure $\mathbf{2 . 2 6}$ the $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$anion is a comprised of a planar boroxole $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ ring which contain one 4-coordinate boron centre (B1) and two 3-coordinate boron centres (B2, and B3). The B-O bonds to the 4-coordinate boron centre (B1) range from 1.466(4)-1.471(4) $\AA$ [av. $1.468 \AA$ ] and these bond lengths are significantly longer than those involving the 3coordinate boron centres (B2 and B3). The B-O distances to B2 and B3 centres range from $1.351(3)-1.380(4) \AA$ [av. $1.363 \AA$ ] and $1.347(4)-1.386(4) \AA$ [av. $1.363 \AA$ ], respectively. BOH bonds involving the 4-coordinate boron centre (B1) are $1.467(3) \AA$ and $1.468(3) \AA$, while B-OH bonds involving the 3-coordinate boron centres (B2 and B3) are 1.359(4) and 1.357(4)
$\AA$, respectively. B2-O1 (1.351(3) $\AA$ ) and B3-O3 (1.347(4) $\AA$ ) are significantly shorter than the other B-O bonds within the boroxole rings. The boroxole ring is planar with ring angles ranging from 112.3(2) - 122.4(2) ${ }^{\circ}$. The smallest ring angle (O1-B1-O3) involves the 4-coordinate boron centre, whereas ring angles at $\mathrm{O} 1, \mathrm{O} 2$, and O 3 average $121.1^{\circ}$ and those at the 3-coordinate boron centres ( B 2 and B 3 ) average $121.6^{\circ}$. This pattern of bond angles and bond lengths are in accord with previously reported data ${ }^{61,168-170}$ for this anion. The bond angles and lengths of $\mathbf{1 2}$ are listed in Appendix I (Table 7, and Table 8).

There are many H -bonding interactions to be found in the solid-state structure of $\mathbf{1 2}$. These include H -bonds from anion to anion, cation to anion, $\mathrm{H}_{2} \mathrm{O}$ to anion, and $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{H}_{2} \mathrm{O}$. The four chemically non-equivalent oxygen sites may be designated $\alpha, \alpha^{\prime}, \beta$, and $\gamma$ (Figure 2.26) by using a similar nomenclature system to that previously described. ${ }^{98,77}$ This labelling system may be used to classify the H -bond interactions between different neighbouring ions and to differentiate between the available sites


Figure 2.26 Diagram labelling the oxygen atom H-bond acceptor sites in the tetraborate(2-) anions.

The triborate(1-) anion in $\mathbf{1 2}$ displays four donor H -bond interactions involving three water molecules and one chloride anion acceptor sites. ${ }^{77,98}$ All the H -bond interactions are shown in Table 2.14 .

Table 2.14 H-bond interactions in $\mathbf{1 2}$.

| $\boldsymbol{D}-\mathbf{H} \cdots \boldsymbol{A}$ | $\boldsymbol{d}(\boldsymbol{D} \cdots \boldsymbol{A})$ | $\boldsymbol{D}-\mathbf{H} \cdots \boldsymbol{A}$ | $\boldsymbol{d}(\boldsymbol{D} \cdots \boldsymbol{A})$ |
| :--- | :--- | :--- | :---: |
| O4-H4 $\cdots \mathrm{O} 51$ | $2.783(2)$ | $\mathrm{N} 34-\mathrm{H} 34 \cdots \mathrm{Cl} 33^{\mathrm{ii}}$ | $3.182(2)$ |
| O5-H5 $\cdots \mathrm{O} 53$ | $2.804(2)$ | $\mathrm{N} 35-\mathrm{H} 35 \cdots \mathrm{O} 5$ | $2.898(3)$ |
| O6-H6 $\cdots \mathrm{Cl} 2$ | $3.082(2)$ | $\mathrm{N} 36-\mathrm{H} 36 \cdots \mathrm{Cl} 4$ | $3.087(2)$ |
| $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 55$ | $2.757(3)$ | $\mathrm{O} 51-\mathrm{H} 51 \mathrm{~A} \cdots \mathrm{Cl} 2$ | $3.2728(19)$ |


| O7-H7 ...O61 | 2.769(3) | O51-H51B $\cdots$ Cl5 | 3.056(2) |
| :---: | :---: | :---: | :---: |
| N11-H11..Cl1 | 3.148(2) | O52-H52A $\cdots$ Cl5 $5^{\text {iii }}$ | 3.121(3) |
| N12-H12...Cl5 ${ }^{\text {i }}$ | 3.136(2) | O52-H52B...Cl1 | 3.131(2) |
| N13-H13..O4 | 2.935(3) | O53-H53A $\cdots$ Cl2 ${ }^{\text {i }}$ | 3.1252(18) |
| N14-H14..Cl1 | 3.172(2) | O53-H53B $\cdots \mathrm{Cl} 3$ | 3.1404(14) |
| N15-H15..Cl5 ${ }^{\text {i }}$ | 3.080(2) | O54-H54A $\cdots$ O53 | 2.603 |
| N16-H16 $\cdots$ O4 | 2.731(3) | O54-H54B $\cdots{ }^{\text {O }}{ }^{\text {i }}$ | 2.934(2) |
| $\mathrm{N} 31-\mathrm{H} 31 \cdots \mathrm{Cl} 3^{\text {ii }}$ | 3.077(2) | O55-H55A $\cdots$ O54 | 2.656 |
| N32-H32 ..O5 | 2.810(3) | O55-H55B $\cdots$ O51 ${ }^{\text {iv }}$ | 2.858(2) |
| N33-H33 ...Cl4 | 3.091(2) | O61-H61B $\cdots$ O51 ${ }^{\text {iv }}$ | 3.165(2) |

(i) $x, y+1, z$
(ii) $\mathrm{x}+1, \mathrm{y}-1, \mathrm{z}$
$\begin{array}{ll}\text { (iii) }-x+1,-y+1,-z & \text { (iv) } x-1, y+1, z\end{array}$


Figure 2.27 The triborate(1-) anions and water molecules layer structure (viewed along the $c$ direction of the unit cell) of $\mathbf{1 2}$. Dashed blue lines represent H -bonds.

Polyborate anions usually display multiple anion to anion H -bond interactions and these are believed ${ }^{5}$ to be the driving force in the synthesis of non-metal cation pentaborate(1-) salts. Anion to anion interactions were found to be present in $\mathbf{6 , 9}$ and 11. However in 12, triboratetriborate H -bond interactions are absent and each $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$anion is isolated from others by $\mathrm{H}_{2} \mathrm{O}$ bridges, forming sheets (Figure 2.27). This isolation implies that the crystal structure of 12 is engineered by interactions with other components within the system. The triborate(1-) anion is able to form four donor H -bonds and has seven potential H -bond acceptor sites, and all, with the exception of $\alpha$ and $\gamma$-sites, are acceptors. The triborate(1-) anion accepts two Hbonds at $\alpha$-sites, and also at a $\beta$-site. The H -bonds directed at the $\alpha$-sites originate from amino
hydrogens of two $[\mathrm{Co}(\text { diNOsar })]^{3+}$ cations in a chelating mode, as shown in Figure 2.28. These H -bond interactions are likely to be responsible for templating this salt and assembling the triborate(1-) anion. Secondary amine hydrogens of $[\mathrm{Co}(\text { diNOsar })]^{3+}$ are known ${ }^{171}$ to form similar H-bond interactions e.g. $[\mathrm{Co}(\mathrm{diNOsar})]\left[\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{CH}_{2}\right)_{4}\right]_{3}$. Details of all the H -bonding interactions are given in Table 2.14.

The $[\mathrm{Co}(\text { diNOsar })]^{3+}$ cations, $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$anions, $\mathrm{Cl}^{-}$ions and $\mathrm{H}_{2} \mathrm{O}$ molecules of crystallisation of compound $\mathbf{1 2}$ are connected through a complex series of H-bond interactions, with the anion network templated by the cations. The connection of the plane shown in Figure 2.29 to its neighbouring planes is formed by further H-bond interactions, forming a threedimensional network


Figure 2.28 The H -bond connections of $[\mathrm{Co}(\mathrm{diNOsar})]^{3+}$ with triborate(1-) anions and chloride ions in $\mathbf{1 2}$.

The $[\mathrm{Co}(\text { diNOsar })]^{3+}$ cation comprises a central $\mathrm{Co}^{3+}$ ion surrounded by the six N donor atoms of the hexadentate neutral 1,8 -dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6.]icosan
(diNOsar) ligand in a distorted octahedral environment. Cis and trans $\mathrm{N}-\mathrm{Co}-\mathrm{N}$ angles range from 86.43(9)-92.58(9) ${ }^{\circ}$ [av. $\left.90.06^{\circ}\right]$ and $175.79(9)-178.12(10)^{\circ}$ [av. $\left.176.62^{\circ}\right]$, respectively. The Co-N bond lengths range from 1.963(2)-1.975(2) $\AA$, [av. $1.969 \AA$ ]. These data are not significantly different from previously reported data for this cation. ${ }^{171}$ According to Table $\mathbf{2 . 1 3}$ there are two $[\mathrm{Co}(\mathrm{diNOsar})]^{3+}$ cations (A and B) per unit cell. Each cation is involved in Hbonding to one $\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$anion and two chloride ions. Both cations interact at $\alpha^{\prime}$ sites with the triborate(1-) anions (Figure 2.29). Full details are given in Table 2.14.


Figure 2.29 Triborate(1-) anions are arranged in planes linked together by H-bonds (dashed blue lines) from $\mathrm{H}_{2} \mathrm{O}$ molecules. The $[\mathrm{Co}(\text { diNOsar })]^{3+}$ cations fill the cavities and link to the triborate(1-) anions by further H -bonds (viewed along the $c$ direction of the unit cell) in $\mathbf{1 2}$.

### 2.4 Conclusion and summary

The synthesis of cobalt(III) complex polyborate salts by the reaction of boric acid and cobalt(III) complex hydroxide salts in varying ratios yielded polyborate salts in good yields. Nine polyborate salts have been prepared containing different polyborate anions: triborate(1-) (12), tetraborate(2-) (9), pentaborate(1-) (6, 7, 13 and 14), heptaborate(2-) (10), heptaborate(3) (8 and 11), and octaborate(2-) (6) anions. Four of these salts have been characterized by singlecrystal XRD studies ( $\mathbf{6}, \mathbf{9}, \mathbf{1 1}$, and 12). Two compounds s-fac-[Co(dien) $\left.)_{2}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{6}\right] \cdot 9 \mathrm{H}_{2} \mathrm{O}$ $(11)^{138}$ and $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}(6)^{139}$ show previously unobserved heptaborate(3-) and octaborate(2-) anions, respectively.

Reaction of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ with boric acid in a 1:15 ratio produced compound $\mathbf{6}$ which contains two different polyborates anions, octaborate(2-) and pentaborate(1-), whereas the reaction in 1:10 ratio afforded two different polyborate compounds, $\mathbf{7}$ and 8, containing pentaborate(1-) and heptaborate(3-) anions, respectively. Tetraborate(2-) salt 9 was produced as a result of the reaction $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ with boric acid in a 1:10 ratio, whilst heptaborate(2-) salt $\mathbf{1 0}$ was produced from 1:7 ratio. Reaction of $[\mathrm{Co}(\mathrm{diNOsar})]^{3+}$ in a $1: 5$ or $1: 10$ ratio yielded the triborate(1-) salt $\mathbf{1 2}$ or pentaborate(1-) salt 13, respectively. The ratio of the boric acid and the complex cation reactions play a very important role in the identity of the polyborate salts formed.

The solid-state structures of $\mathbf{6}, \mathbf{9}, \mathbf{1 1}$, and $\mathbf{1 2}$, all display multiple cation-anion H-bond interactions and this undoubtably plays a major role in the energetics of engineering these structures. For example, in compound 9 , all eighteen of the amino hydrogen atoms of the $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cations are involved in secondary coordination to anions via H -bonds.

## Chapter Three

## Copper(II) complex

## polyborates

### 3.1 Introduction

Copper is capable of forming a wide range of coordination compounds with different ligands in both copper(I) or copper(II) oxidation states. Copper(I) (cuprous) complexes are dominated by four coordination, while copper(II) (cupric) complexes have varying coordination numbers. The most common coordination number for copper(II) is six, but complexes with a coordination numbers of four or five are also known. The octahedral geometry of six-coordinate copper(II) complexes is generally distorted due to unequal occupation of $e_{g}{ }^{*}$ orbitals $\left(\mathrm{d}_{\mathrm{x}}{ }^{2}-y^{2}\right.$ and $\mathrm{d}_{\mathrm{z}}{ }^{2}$ orbitals) when the copper(II) ion with $\mathrm{d}^{9}$ electronic configuration is subject to a Jahn-Teller effect (Section 1.3.2). The distortion (axial elongation) of copper(II) complexes has been described by the term tetragonality $(T) .{ }^{172}$ It is defined as the ratio of the mean in-plane bondlength $R_{S}^{n}$ and the mean out-of-plane bond-length $R_{L}^{n}, \mathrm{n}$ is the effective coordination number.

The chemistry of polyborate anions partnered with metal (e.g. sodium ion) or non-metal cations (e.g. ammonium ion) have been extensively studied. ${ }^{1}$ In contrast reports of transition metal complex cations with polyborate anions are rare. Only a few copper(II) amine complexes have successfully formed polyborate systems, e.g. $\left[\mathrm{Cu}\left(\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{~N}_{2}\right)_{2}(\mathrm{OAc})\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{C}_{4} \mathrm{H}_{9} \mathrm{NO},{ }^{122} \quad\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{13} \mathrm{H}_{3}\right]_{\mathrm{n}},{ }^{116}$ $\left[\mathrm{Cu}(\mathrm{en})_{2}\left(\mathrm{C}_{5} \mathrm{H}_{9} \mathrm{NO}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{C}_{5} \mathrm{H}_{9} \mathrm{NO},{ }^{123} \quad\left[\mathrm{Cu}(\mathrm{en})_{2} \mathrm{~B}(\mathrm{OH})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{5}(\mathrm{OH})_{7}\right],{ }^{131}$ $\left\{\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left[\mathrm{~B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right]_{2}\right\}\left(\mu \mathrm{H}_{2} \mathrm{O}\right)\left\{\mathrm{Ag}(\mathrm{en})_{2}\right\} \cdot\left(\mu \mathrm{H}_{2} \mathrm{O}\right)\left\{\mathrm{Na}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right\}\right.$, $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{~B}(\mathrm{OH})_{3}, \quad$ and $\quad\left[\mathrm{Cu}(\mathrm{en})_{2} \mathrm{~B}(\mathrm{OH})_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]\left[\mathrm{B}_{4} \mathrm{O} 5(\mathrm{OH})_{4}\right] \cdot 0.5 \mathrm{H}_{2} \mathrm{O} .{ }^{137}$ Polyborate anions associated with copper(II) complexes show considerable structural diversity. Copper(II) ions have also been found to coordinate with polyborate anions to produce anionic complex ions partnered with potassium or sodium cations. These form mixed-metal polyborate salts such as $\mathrm{K}_{5} \mathrm{H}\left\{\mathrm{Cu}_{4} \mathrm{O}\left[\mathrm{B}_{20} \mathrm{O}_{32}(\mathrm{OH})_{8}\right]\right\} \cdot 33 \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{Na}_{5} \mathrm{H}\left[\mathrm{Cu}_{4} \mathrm{O}\left[\mathrm{B}_{20} \mathrm{O}_{32}(\mathrm{OH})_{8}\right]\right\} \cdot 32 \mathrm{H}_{2} \mathrm{O} .{ }^{173}$

### 3.2 Aims

The main aim of this research was to synthesise and characterise some new copper(II) complex cation polyborate compounds. Several cationic copper(II) coordination complexes of ethylenediamine (en), $N, N, N^{\prime}, N^{\prime}$-tetramethyl ethylenediamine (TMEDA), 1,2-diaminopropane (pn), 1,2-diaminocyclohexane (dach), $N$-(2-hydroxyethyl)ethylenediamine (hn), and $N, N$ dimethylethylenediamine ( $\mathrm{N}, \mathrm{N}$-dmen) ligands have been prepared to template polyborate salt formation. Copper(II) complex cations have been chosen due to their potential to form many donor H-bond interactions with polyborate anions and their high steric bulk. These interactions
are believed to play an important role in the formation of the 3D supramolecular framework of the polyborate salts. In addition, the copper(II) polyborate compounds can be used to evaluate the structure directing effects in solid-state supramolecular structures associated with the copper(II) complex cations.

### 3.3 Result and discussion

### 3.3.1 Synthesis of copper(II) complexes

Previously reported copper(II) complexes; $\left[\mathrm{Cu}(\mathrm{en})_{2}\right] \mathrm{SO}_{4}(\mathbf{1 5}),{ }^{174}\left[\mathrm{Cu}(\mathrm{pn})_{2}\right] \mathrm{SO}_{4}(\mathbf{1 6}),{ }^{175}$ and $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{Cl}_{2}(\mathbf{1 7}){ }^{176}$ were all prepared by standard literature methods, while $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right] \mathrm{SO}_{4} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}(\mathbf{1 8})$ has been synthesised by method analogous to that described for $\left[\mathrm{Cu}(\mathrm{en})_{2}\right] \mathrm{SO}_{4} .\left[\mathrm{Cu}(N, N-\text { dmen })_{2}\right] \mathrm{Cl}_{2}(19)$ was prepared by a procedure modified from Cui et al. ${ }^{177}$ Physical properties of the prepared complexes were all in accordance with literature data. In general, a slight excess of ligand was added to the aqueous solutions of copper(II) sulphate or chloride salts. The solutions were stirred and then gently evaporated using a water bath. Finally, the concentrated solutions were cooled to yield the crude product. In the preparation of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right] \mathrm{SO}_{4}$ additional a large excess of ethylenediamine should be avoided due to formation $\left[\mathrm{Cu}(\mathrm{en})_{3}\right] \mathrm{SO}_{4}$ in addition to the desired $\left[\mathrm{Cu}(\mathrm{en})_{2}\right] \mathrm{SO}_{4} .{ }^{178,179}$

The synthesised copper(II) complexes were prepared as chloride (17 and 19) and sulphate $(\mathbf{1 5}, \mathbf{1 6}$, and $\mathbf{1 8})$ salts and it was therefore necessary to convert these salts to the corresponding hydroxide forms before reaction with boric acid (see Chapter 6 for experimental details). Copper(II) complex hydroxides were prepared using two different methods depending on the counter ion.
i- Copper(II) hydroxide complexes were synthesised from copper(II) chloride complexs by using Dowex monosphere 550A ion exchange resin as described in Section 2.3.2.
ii- Copper(II) chloride complexes were converted to the hydroxide salts using stoichiometric amount of silver(I) oxide. The solution was left to stir for 30 minutes at room temperature until a precipitate of AgCl had formed.
iii- Copper(II) sulphate complexes were converted to the hydroxide salts using stoichiometric amounts of barium hydroxide octahydrate. The mixture was rapidly stirred at room temperature for 10 minutes, then the white precipitate of barium sulphate was completely removed by filtration.

### 3.3.2 Preparation of copper(II) complex polyborate compounds

A series of copper(II) complex polyborate compounds 20-28 has been prepared as crystalline solids from the reaction of copper(II) complex cation hydroxides and boric acid in the ratios of 1:5 and 1:10. Seven copper(II) complex cations were used to react with boric acid. All nine compounds are new, except for 21, which has been previously reported. A crystal structure and IR data have been reported for 21. We now report additional data: ${ }^{11}$ B NMR, pXRD, magnetic properties, and thermal analyses. ${ }^{137}$ We re-synthesised this compound using a new method. Spectroscopic data for $\mathbf{2 1}$ is discussed in the next sections and are reported in the experimental chapter.

Crystals suitable for single-crystal X-ray diffraction studies of copper(II) complex polyborate compounds were prepared by recrystallization of crude products by dissolving them in distilled water. The recrystallized products were obtained as described in Section 2.3.2. The recrystallized yields of copper(II) complex polyborate compounds and their formula are shown in Table 3.1.

Table 3.1 Yields and formula of copper(II) complex polyborate compounds.

| Compound | Formula | \% Yield |
| :---: | :---: | :---: |
| 20 | $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | 52 |
| 21 | $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{~B}(\mathrm{OH})_{3}$ | 59 |
| 22 | $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ | 56 |
| 23 | $\left[\mathrm{Cu}\left(\right.\right.$ TMEDA) $\left.\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}$ | 53 |
| 24 | $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Cu}(\text { dach })_{2}\right]\left[\mathrm{B} 7 \mathrm{O} 9(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ | 52 |
| 25 | $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{~B}(\mathrm{OH})_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | 52 |
| 26 | $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \cdot \mathrm{B}(\mathrm{OH})_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ | 22 |
| 27 | $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N} \text {-dmen })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ | 53 |
| 28 | $\left[\mathrm{Cu}(N, N\right.$-dmen $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ | 41 |

### 3.3.3 Characterization of copper(II) complex polyborate compounds

The magnetic properties of the copper(II) complex starting materials and their polyborate derivatives were measured using Johnson Matthey balance. The mass susceptibility $\left(\chi_{\mathrm{g}}\right)$, molar susceptibility $\left(\chi_{\mathrm{m}}\right)$, diamagnetic susceptibility $\left(\chi_{\mathrm{d}}\right)$, paramagnetic susceptibility ( $\chi_{\mathrm{p}}$ ), and effective magnetic moment ( $\mu_{\text {eff }}$ ) of compounds 15-25, and 27-28 are shown in Table 3.2. The copper(II) complexes and their polyborate salts were all found to be paramagnetic and did
not show any diagnostic change in magnetic properties between starting copper(II) complexes and their polyborate salts. The experimental effective magnetic moment data are close to those calculated from spin-only formula. The $\mu_{\text {eff }}$ values of $\mathrm{Cu}(\mathrm{II})$ complexes and their polyborate compounds are in agreement with literature data for $\mathrm{Cu}(\mathrm{II})$ complexes. ${ }^{180}$

Table 3.2 Magnetic properties of copper(II) complexes and their polyborate compounds at 24 ${ }^{\circ} \mathrm{C}$.

| Compound | $\chi_{g}$ <br> $\left(\mathrm{~cm}^{3} \cdot \mathrm{~g}^{-1}\right)$ | $\chi_{\mathrm{m}}$ <br> $\left(\mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ | $\chi_{\mathrm{d}}$ | $\chi_{\mathrm{p}}$ | $\mu_{\text {eff }}$ <br> Bohr <br> magneton | N |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1 5}$ | $4.3 \times 10^{-6}$ | $1210 \times 10^{-6}$ | $-140 \times 10^{-6}$ | $1350 \times 10^{-6}$ | 1.79 | 1.05 |
| $\mathbf{1 6}$ | $4.5 \times 10^{-6}$ | $1380 \times 10^{-6}$ | $-150 \times 10^{-6}$ | $1530 \times 10^{-6}$ | 1.90 | 1.14 |
| $\mathbf{1 7}$ | $3.3 \times 10^{-6}$ | $1270 \times 10^{-6}$ | $-195 \times 10^{-6}$ | $1460 \times 10^{-6}$ | 1.86 | 1.11 |
| $\mathbf{1 8}$ | $3.7 \times 10^{-6}$ | $1170 \times 10^{-6}$ | $-158 \times 10^{-6}$ | $1180 \times 10^{-6}$ | 1.67 | 0.95 |
| $\mathbf{1 9}$ | $3.1 \times 10^{-6}$ | $960 \times 10^{-6}$ | $-160 \times 10^{-6}$ | $1110 \times 10^{-6}$ | 1.51 | 0.81 |
| $\mathbf{2 0}$ | $1.7 \times 10^{-6}$ | $1134 \times 10^{-6}$ | $-327 \times 10^{-6}$ | $1461 \times 10^{-6}$ | 1.86 | 1.11 |
| $\mathbf{2 1}$ | $2.0 \times 10^{-6}$ | $1007 \times 10^{-6}$ | $-249 \times 10^{-6}$ | $1256 \times 10^{-6}$ | 1.73 | 1.00 |
| $\mathbf{2 2}$ | $1.5 \times 10^{-6}$ | $1094 \times 10^{-6}$ | $-360 \times 10^{-6}$ | $1454 \times 10^{-6}$ | 1.85 | 1.10 |
| $\mathbf{2 3}$ | $2.3 \times 10^{-6}$ | $1320 \times 10^{-6}$ | $-283 \times 10^{-6}$ | $1603 \times 10^{-6}$ | 1.95 | 1.19 |
| $\mathbf{2 4}$ | $1.7 \times 10^{-6}$ | $1145 \times 10^{-6}$ | $-325 \times 10^{-6}$ | $1470 \times 10^{-6}$ | 1.86 | 1.12 |
| $\mathbf{2 5}$ | $1.8 \times 10^{-6}$ | $1365 \times 10^{-6}$ | $-369 \times 10^{-6}$ | $1734 \times 10^{-6}$ | 2.02 | 1.25 |
| $\mathbf{2 7}$ | $1.1 \times 10^{-6}$ | $820 \times 10^{-6}$ | $-370 \times 10^{-6}$ | $1200 \times 10^{-6}$ | 1.40 | 0.72 |
| $\mathbf{2 8}$ | $1.7 \times 10^{-6}$ | $880 \times 10^{-6}$ | $-250 \times 10^{-6}$ | $1140 \times 10^{-6}$ | 1.45 | 0.76 |

Elemental analysis of the copper(II) complex polyborate compounds were consistent with calculated values. The elemental analysis data of copper(II) complex polyborate compounds (20-28) are listed in Table 3.3.

Table 3.3 CHN analysis of copper(II) complex polyborate compounds.

| Compound | Calculated (\%) |  |  | Experimental (\%) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | C | H | N | C | H | N |
| $\mathbf{2 0}$ | 7.5 | 4.1 | 8.8 | 7.4 | 4.4 | 8.6 |
| $\mathbf{2 1}$ | 9.6 | 5.2 | 11.2 | 9.7 | 5.4 | 11.4 |
| $\mathbf{2 2}$ | 10.0 | 5.0 | 7.8 | 10.1 | 5.4 | 7.6 |
| $\mathbf{2 3}$ | 12.7 | 6.1 | 4.9 | 12.8 | 6.2 | 5.0 |
| $\mathbf{2 4}$ | 22.2 | 6.0 | 8.6 | 22.0 | 6.1 | 8.5 |
| $\mathbf{2 5}$ | 10.1 | 5.4 | 7.6 | 9.8 | 5.2 | 7.6 |
| $\mathbf{2 6}$ | 12.6 | 6.9 | 9.8 | 12.9 | 6.8 | 9.5 |
| $\mathbf{2 7}$ | 12.8 | 5.4 | 7.5 | 13.0 | 5.3 | 7.3 |
| $\mathbf{2 8}$ | 9.5 | 5.2 | 5.6 | 9.7 | 5.2 | 5.5 |

NMR $\left({ }^{11} \mathrm{~B}\right)$ data for compounds $\mathbf{2 0 - 2 8}$ are listed in Table 3.4. ${ }^{11}$ B-NMR spectroscopy of copper(II) complex polyborate salts showed that pentaborate salts 20, 22, and $\mathbf{2 7}$ contained the characteristic three peaks $\sim 18 \mathrm{ppm}$ (due to $\left.\mathrm{B}(\mathrm{OH})_{3} / \mathrm{B}(\mathrm{OH})_{4}-\right), \sim 13 \mathrm{ppm}\left\{\right.$ due to $\left.\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}\right\}$, and at $\sim 1.3 \mathrm{ppm}$ \{due to the 4 -coordinate boron centre of the $\left.\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}\right\}$or a single signal at $\sim+16.0 \mathrm{ppm} .{ }^{149-151}{ }^{11} \mathrm{~B}$ NMR spectra of the triborate(1-) (25), tetraborate(2-) (21 and 26), hexaborate(2-) (23 and 28), and heptaborate(2-) (24) salts are quantitatively different from the spectra observed in the pentaborate salts with generally only one (averaged and exchanging) signal observed.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were not obtained. This may be attributed to paramagnetic effects of the copper(II) ion broadening the signals associated with the organic ligands which are within the primary coordination sphere of the metal. However, ${ }^{11}$ B NMR spectra were obtainable since the polyborates in 20, 21, 24-27 are present as discrete anions, which are less influenced by the copper(II) ions. Compounds 22, 23, and $\mathbf{2 8}$ contain coordinated polyborates but the presence of ${ }^{11} \mathrm{~B}$ signals of these compounds would indicate that the borate ligands are labile, and undergo the expected equilibria reactions once ligand dissociation to the aqueous solution has taken place. ${ }^{149}$

Table 3.4 The chemical shift ( $\delta$ ) of ${ }^{11} \mathrm{~B}-\mathrm{NMR}$ spectra of copper(II) complex polyborate compounds (20-28).

| Compound | ${ }^{11} \mathrm{~B}$ NMR/ppm |
| :---: | :---: |
| $\mathbf{2 0}$ | $17.3(72 \%), 13.4(25 \%), 1.3(2 \%)$ |
| $\mathbf{2 1}$ | 13.9 |
| $\mathbf{2 2}$ | $16.9(74 \%), 13.2(24 \%), 1.5(2 \%)$ |
| $\mathbf{2 3}$ | 15.3 |
| $\mathbf{2 4}$ | 14.7 |
| $\mathbf{2 5}$ | 16.7 |
| $\mathbf{2 6}$ | 14.4 |
| $\mathbf{2 7}$ | 16.5 |
| $\mathbf{2 8}$ | 16.9 |

The FT-IR spectra assignment for the copper(II) complex polyborate compounds (2028) are illustrated in Table 3.5. Infra-red data for compounds 20-28 support the formation of new polyborate compounds with copper(II) complexes and are in agreement with the reported literature data for the various proposed polyborate anions. ${ }^{140}$

Table 3.5 Selected FT-IR spectroscopic data for the copper(II) complex polyborate compounds (20-28).
$\left.\begin{array}{|c|c|c|c|c|c|c|c|c|}\hline \text { Comp. } & \begin{array}{c}v(\mathrm{O}-\mathrm{H}), \\ \mathrm{v}(\mathrm{N}-\mathrm{H})\end{array} & \begin{array}{c}\mathrm{Y} \\ (\mathrm{C}-\mathrm{H})\end{array} & \begin{array}{c}\mathrm{v}_{\mathrm{as}} \\ \left(\mathrm{B}_{(3)}-\mathrm{O}\right)\end{array} & \begin{array}{c}\delta \\ (\mathrm{B}-\mathrm{O}-\mathrm{H})\end{array} & \begin{array}{c}\mathrm{v}_{\mathrm{as}} \\ \left(\mathrm{B}_{(4)}-\mathrm{O}\right)\end{array} & \begin{array}{c}\mathrm{v}_{\mathrm{s}} \\ \left(\mathrm{B}_{(3)}-\mathrm{O}\right)\end{array} & \begin{array}{c}\mathrm{v}_{\mathrm{s}} \\ \left(\mathrm{B}_{(4)}-\mathrm{O}\right)\end{array} & \begin{array}{c}\gamma \\ \left(\mathrm{B}_{(3)}-\mathrm{O}\right)\end{array} \\ \hline \mathbf{2 0} & \begin{array}{c}3459(\mathrm{bs}), \\ 3328(\mathrm{bs}), \\ 3282(\mathrm{bs})\end{array} & \begin{array}{c}2956(\mathrm{w}), \\ 2904(\mathrm{w})\end{array} & \begin{array}{c}1416(\mathrm{~s}), \\ 1314(\mathrm{~s})\end{array} & 1139(\mathrm{~s}) & 1094(\mathrm{~s}), \\ 1041(\mathrm{~s})\end{array}\right)$
$\mathrm{B}=$ broad, $\mathrm{m}=$ middle, $\mathrm{s}=$ strong, $\mathrm{w}=$ weak, $\mathrm{sh}=$ shoulder, $\mathrm{B}_{(3)}=$ three coordinate boron, $\mathrm{B}_{(4)}=$ four coordinate boron, $v=$ stretching frequency, $v_{s}=$ symmetrical stretching frequency, $v_{a s}=$ asymmetrical stretching frequency, $\delta$ $=$ bending frequency.

### 3.3.4 Thermal properties of copper(II) complex polyborate compounds

TGA and DSC analysis were used to investigate the thermal properties of copper(II) complex polyborate compounds. Samples were heated in an alumina $\left(\mathrm{Al}_{2} \mathrm{O}_{3}\right)$ crucible at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ between $25-800^{\circ} \mathrm{C}$ under a flow air ( $100 \mathrm{~mL} / \mathrm{min}$.). The thermal decomposition stages of compounds $\mathbf{2 0 - 2 8}$ are illustrated in Table $\mathbf{3 . 6}$ and shown in Figures 3.1, 3.2, and 3.3. Previous work on hydrated transition metal complex polyborate salts has shown that they thermally lose their lattice water molecules at temperature up to $180^{\circ} \mathrm{C}$ in air (via an endothermic process). At higher temperature (up to $280^{\circ} \mathrm{C}$ ), an endothermic process occurs due to dehydration of polyborate anion to afford anhydrous transition metal complex polyborate salts. Finally, at higher temperature (up to $850{ }^{\circ} \mathrm{C}$ ), exothermic processes occur which are consistent with oxidation of the copper(II) complex cation ligands.

All the copper(II) complex compounds 20, 22-28 followed the expected path of decomposition, with observed mass losses agreeing with calculated values. The thermal
behaviour of the copper(II) complex polyborate compounds agreed with published data describing thermal decomposition of transition metal complex cations containing polyborate anions. ${ }^{122,123,131}$ Compound 21 has only two mass loss steps rather than three due to the absence of lattice water (Table 3.6) in its formation.

Table 3.6 The mass loss steps of copper(II) polyborate compounds 20-28.*

| Comp. | $\begin{array}{\|l\|l} \hline \text { Step } \\ \text { No. } \end{array}$ | The thermal reactions | Temp. <br> Range ${ }^{\circ} \mathrm{C}$ | $\begin{gathered} \hline \text { Expt. } \\ (\%) \end{gathered}$ | Calc. (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 20 | 1 | $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}+2 \mathrm{H}_{2} \mathrm{O}$ | 70-180 | 6.0 | 5.5 |
|  | 2 | $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \rightarrow\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+4 \mathrm{H}_{2} \mathrm{O}$ | 180-280 | 16.0 | 16.5 |
|  | 3 | $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CuB}_{10} \mathrm{O}_{16}+$ volatile oxidation products | 280-600 | 32.9 | 34.9 |
|  |  | Residue $\mathrm{CuB}_{10} \mathrm{O}_{16}$ |  | 67.1 | 65.1 |
| 21 | 1 | $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{H}_{3} \mathrm{BO}_{3} \rightarrow\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{6} \mathrm{O}_{10}\right]+5 \mathrm{H}_{2} \mathrm{O}$ | 100-200 | 18.9 | 18.1 |
|  | 2 | $\begin{aligned} & {\left[\mathrm{Cu}(\text { en })_{2}\right]\left[\mathrm{B}_{6} \mathrm{O}_{10}\right]+\text { excess } \mathrm{O}_{2} \rightarrow \mathrm{CuB}_{6} \mathrm{O}_{10}+\text { Volatile oxidation }} \\ & \text { products } \end{aligned}$ | 200-550 | 41.2 | 42.2 |
|  |  | Residue $\mathrm{CuB}_{6} \mathrm{O}_{10}$ |  | 58.8 | 57.8 |
| 22 | 1 | $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B} 5 \mathrm{O}_{6}(\mathrm{OH})_{4} \cdot 4 \mathrm{H}_{2} \mathrm{O}\right.$ $\rightarrow$ $\left[\mathrm{Cu}(\mathrm{pn})_{2}\right.$ <br> $\left.\left\{\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]+4 \mathrm{H}_{2} \mathrm{O}$   | 70-180 | 9.1 | 10.0 |
|  | 2 | $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \rightarrow\left[\mathrm{Cu}(\mathrm{pn})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+4 \mathrm{H}_{2} \mathrm{O}$ | 180-250 | 18.2 | 20.0 |
|  | 3 | $\begin{aligned} & {\left[\mathrm{Cu}(\mathrm{pn})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+\text { excess } \mathrm{O}_{2} \rightarrow \mathrm{CuB}_{10} \mathrm{O}_{16}+\text { Volatile oxidation }} \\ & \text { products } \end{aligned}$ | 250-650 | 19.9 | 20.5 |
|  |  | Residue $\mathrm{CuB}_{10} \mathrm{O}_{16}$ |  | 61.9 | 59.4 |
| 23 | 1 | $\begin{aligned} & \hline\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \\ & +6 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 70-180 | 19.4 | 19.1 |
|  | 2 | $\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH}) 6\right\}\right] \rightarrow[\mathrm{Cu}($ TMEDA $)]\left[\mathrm{B}_{6} \mathrm{O}_{10}\right]+3 \mathrm{H}_{2} \mathrm{O}$ | 180-250 | 28.6 | 28.6 |
|  | 3 | $[\mathrm{Cu}($ TMEDA $)]\left[\mathrm{B}_{6} \mathrm{O}_{10}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CuB}_{6} \mathrm{O}_{10}+$ Volatile oxidation products | 250-650 | 48.1 | 49.2 |
|  |  | Residue $\mathrm{CuB}_{6} \mathrm{O}_{10}$ |  | 51.9 | 50.8 |
| 24 | 1 |  | 70-190 | 9.0 | 8.3 |
|  | 2 | $\left[\mathrm{Cu}(\text { dach })_{2}\right]_{2}\left[\mathrm{~B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \rightarrow\left[\mathrm{Cu}(\text { dach })_{2}\right]_{2}\left[\mathrm{~B}_{14} \mathrm{O}_{23}\right]+5 \mathrm{H}_{2} \mathrm{O}$ | 190-250 | 16.0 | 15.2 |
|  | 3 | $\begin{aligned} & {\left[\mathrm{Cu}(\text { dach })_{2}\right]_{2}\left[\mathrm{~B}_{14} \mathrm{O}_{23}\right]+\text { excess } \mathrm{O}_{2} \rightarrow \mathrm{Cu}_{2} \mathrm{~B}_{14} \mathrm{O}_{23}+\text { Volatile oxidation }} \\ & \text { products } \end{aligned}$ | 250-650 | 51.0 | 50.4 |
|  |  | Residue $\mathrm{Cu}_{2} \mathrm{~B}_{14} \mathrm{O}_{23}$ |  | 49.0 | 49.6 |
| 25 | 1 |  | 70-200 | 5.8 | 4.9 |
|  | 2 | $\begin{aligned} & {\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] 2 \mathrm{~B}(\mathrm{OH})_{3} \rightarrow\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+} \\ & 7 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 200-250 | 21.8 | 21.9 |
|  | 3 | $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CuB}_{10} \mathrm{O}_{16}+$ Volatile oxidation products | 250-850 | 42.5 | 42.1 |
|  |  | Residue $\mathrm{CuB}_{10} \mathrm{O}_{16}$ |  | 57.5 | 57.9 |
| 26 | 1 | $\begin{aligned} & \hline\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \mathrm{H}_{3} \mathrm{BO}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \mathrm{H}_{3} \mathrm{BO}_{3} \\ & +6 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 70-200 | 17.0 | 18.8 |
|  | 2 | $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \mathrm{H}_{3} \mathrm{BO}_{3} \rightarrow\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{8.5}\right]+3.5 \mathrm{H}_{2} \mathrm{O}$ | 200-300 | 27.1 | 29.8 |
|  | 3 | $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{8.5}\right]+\text { excess } \mathrm{O}_{2} \rightarrow \mathrm{CuB}_{5} \mathrm{O}_{8.5}+\text { volatile oxidation }$ products | 300-700 | 55.5 | 55.8 |
|  |  | Residue $\mathrm{CuB}_{5} \mathrm{O}_{8.5}$ |  | 44.5 | 44.2 |
| 27 | 1 | $\begin{aligned} & \hline\left[\mathrm{Cu}(\mathrm{~N}, \mathrm{~N}-\text { dmen })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]\left[\left(\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right)_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O} \rightarrow[\mathrm{Cu}(\mathrm{~N}, \mathrm{~N}-\right. \\ & \text { dmen } \left.)_{2}\right]\left[\left(\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right)\right]_{2}+4 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 30-90 | 9.8 | 9.6 |
|  | 2 | $\qquad$ $4 \mathrm{H}_{2} \mathrm{O}$ | 90-250 | 21.3 | 19.2 |
|  | 3 | $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\mathrm{dmen})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CuB}_{10} \mathrm{O}_{16}+$ volatile oxide product | 250-630 | 45.1 | 42.7 |


|  |  | Residue $\mathrm{CuB}_{10} \mathrm{O}_{16}$ |  | 54.9 | 57.3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 28 | 1 | $\begin{aligned} & \hline\left[\mathrm{Cu}(\mathrm{~N}, \mathrm{~N}-\mathrm{dmen})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O} \rightarrow[\mathrm{Cu}(\mathrm{~N}, \mathrm{~N}- \\ & \text { dmen } \left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]+4 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 30-120 | 14.2 | 14.3 |
|  | 2 | $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\mathrm{dmen})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \rightarrow\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\right.$ dmen $\left.) \mathrm{B}_{6} \mathrm{O}_{10}\right]+3 \mathrm{H}_{2} \mathrm{O}$ | 120-250 | 26.0 | 25.0 |
|  | 3 | $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\mathrm{dmen}) \mathrm{B}_{6} \mathrm{O}_{10}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{CuB}_{6} \mathrm{O}_{10}+$ volatile oxide product | 250-630 | 44.3 | 42.5 |
|  |  | Residue $\mathrm{CuB}_{6} \mathrm{O}_{10}$ |  | 55.7 | 57.5 |

* Calculated values and experimental values are given as totals relative to $100 \%$ and include the process described and the earlier mass loss process.


Figure 3.1 TGA diagram for the thermal decomposition of copper(II) complex polyborate compounds 20-23.


Figure 3.2 TGA diagram for the thermal decomposition of copper(II) complex polyborate compounds 24-26.


Figure 3.3 TGA diagram for the thermal decomposition of copper(II) complex polyborate compounds 27-28.

### 3.3.5 Structural characterisation of copper(II) complex polyborate

## compounds

### 3.3.5.1 Structural characterisation of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathbf{2 H}_{2} \mathrm{O}$ (20)

Crystallographic data for $\mathbf{2 0}$ are listed in Table 3.7. The crystals of $\mathbf{2 0}$ are triclinic, $P-1$ contains an ionic compound with one transition metal complex cation $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ partnered with two symmetry-related $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions and two symmetry-related water molecules as shown in Figure 3.4.



Figure 3.4 Diagram showing the complex cation $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$, pentaborate(1-) anion and water molecule in 20 and the adopted numbering scheme. Colour code (used throughout this chapter): brown $(\mathrm{Cu})$, blue $(\mathrm{N})$, red $(\mathrm{O})$, pink (B), dark grey $(\mathrm{C})$ and light grey $(\mathrm{H})$.

Table 3.7 Crystallographic data and structure refinement of $\mathbf{2 0}$.

| Empirical formula | $\mathrm{C}_{4} \mathrm{H}_{28} \mathrm{~B}_{10} \mathrm{~N}_{4} \mathrm{O}_{22} \mathrm{Cu}$ |  |
| :--- | :--- | :--- |
| Formula weight | 655.94 |  |
| Temperature | $100(2) \mathrm{K}$ |  |
| Wavelength | $0.71075 \AA$ |  |
| Crystal system | Triclinic |  |
| Space group | $P-1$ |  |
| Unit cell dimensions | $a=8.0286(5) \AA$ | $\alpha=92.867(5)^{\circ} \AA$ |
|  | $b=8.6193(5) \AA$ | $\beta=104.567(6)^{\circ} \AA$ |
|  | $c=9.6553(7) \AA$ | $\gamma=98.474(5)^{\circ}$ |
| Volume | $636.97(7) \AA \AA^{\circ}$ |  |


| $Z$ | 1 |
| :--- | :--- |
| Density (calculated) | $1.710 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.958 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 335 |
| Crystal | Blade; Purple |
| Crystal size | $0.180 \times 0.090 \times 0.030 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.968-27.477^{\circ}$ |
| Index ranges | $-10 \leq h \leq 10,-10 \leq k \leq 11,-12 \leq l \leq 11$ |
| Reflections collected | 9265 |
| Independent reflections | $2913\left[R_{\text {int }}=0.0341\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | $99.6 \%$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.808 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | $2913 / 0 / 194$ |
| Goodness-of-fit on $F^{2}$ | 1.076 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R l=0.0303, w R 2=0.0811$ |
| $R$ indices (all data) | $R l=0.0337, w R 2=0.0828$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.395 and $-0.330 \mathrm{e} \AA \AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $(0.71073 \AA)$ |
|  |  |

Compound 20 has $\mathrm{Cu}-\mathrm{N}$ distances ranging from to 2.0044(14)-2.0195(14) $\AA$ [av. 2.0120 $\AA$ ] and two pentaborate (1-) anions hydroxyl oxygen atoms (O7) at axial positions at $2.839 \AA$. The tetragonality ( $T^{n}$ ) approach of Hathaway and Hodgson, ${ }^{172}$ yields a $T$ value of 0.7 which is at the low end of the range for elongated tetragonal octahedral geometry and at the high end of the range for square planner geometry. However, the axial $\mathrm{Cu}-\mathrm{O}$ interactions are presumably weak, and we have formulated the $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ cation in $\mathbf{2 0}$ as distorted square-planar.

The pentaborate(1-) anions in 20 are structurally similar to, other transition metal complex cation pentaborate salts involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions. ${ }^{136,181}$ This also applies to non-metal cation pentaborate(1-) salts. ${ }^{1}$ The B-O distances to the 4 -coordinate B1 centre range from $1.455(2)-1.487(2) \AA$ [av. $1.469 \AA$ ] and are significantly longer than those involving the 3-coordinate boron centres which range from 1.356(2) - 1.393(2) A [av. $1.373 \AA$ ]. B-O bonds involving 3-coordinate boron centres and terminal OH groups are at the shorter end of the range [av. $1.3615 \AA$ ] whilst B-O bonds involving the oxygen atoms distal ( $\mathrm{O} 2, \mathrm{O} 5$ ) to the 4 -coordinate B1 centre are at the longer end of the range [av. $1.3855 \AA$ ]. Bond angles at the B1 centre range from $107.74(13)^{\circ}-111.51(13)^{\circ}$, and angles at the other ring atoms range from $115.96(15)^{\circ}-125.52(15)^{\circ}$ for $B$ centres consistent with $\mathrm{sp}^{3}$ and $\mathrm{sp}^{2}$ hybridization, respectively. The bond lengths and angles of 20 are listed in Appendix I (Table 9, and Table 10).

In general, each pentaborate(1-) anion has four potential H -bond donor sites ( $\mathrm{O} 7, \mathrm{O} 8$, O 9 , and O 10 ) which are also capable of accepting H -bond interactions, and six additional
potential H-bond acceptor sites with the B-O-B units. In 20 each pentaborate(1-) anion has twelve H -bond interactions ( 4 H -bond donors and 8 H -bond acceptors) but any H -bond interactions at O 2 are absent. According to Schubert ${ }^{98}$ the oxygen acceptor sites of pentaborate(1-) anion are labelled $\alpha, \beta$, or $\gamma$ (Figure 3.5). This labelling system have been used to classify the H -bond interactions between different neighbouring $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ions and to differentiate between the available sites.


Figure 3.5 Diagram showing the H -bond acceptor sites and their numbers in the pentaborate(1) anions.

In 20 the 4 H -bond donor sites of pentaborate(1-) anion are involved with H -bond acceptor oxygens of three different pentaborate(1-) anions (O8-H8 $\cdots{ }^{\circ} 3^{*}, \mathrm{O} 9-\mathrm{H} 9 \cdots 4^{*}$ and $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 3^{*}$ ) and one water molecule ( $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 21^{*}$ ). The H-bond acceptor sites arising from donor H-bond sites of the pentaborate(1-) anion can be designated as $\alpha \alpha \alpha \omega$, where $\omega$ is an water acceptor site. ${ }^{77,98}$ The direction of the four H atoms of the hydroxyl donor sites in the pentaborate(1-) anions of $\mathbf{2 0}$ are three "in" and one "out" (Figure 3.4). This is a very common structural motif. ${ }^{1}$ All the $\mathbf{H}$-bond data of $\mathbf{2 0}$ are given in Table 3.8.

Table 3.8 H-bonds [ $\AA$ and $^{\circ}$ ] in $\mathbf{2 0 .}$

| $D-H \cdots A$ |  | $d(D \cdots A)$ | $D-H \cdots A$ |  | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{C} \cdots \mathrm{O} 10^{\mathrm{ii}}$ |  | 3.1211(18) | O8-H8*O3 ${ }^{\text {vii }}$ |  | $2.7436(17)$ |
| N1-H1D...O1 ${ }^{\text {iii }}$ |  | 3.0289(17) | O9-H9...O4 $4^{\text {iv }}$ |  | $2.7595(16)$ |
| N1-H1D..O4 ${ }^{\text {iii }}$ |  | 3.4793(18) | O10-H10 ..O3 ${ }^{\text {viii }}$ |  | 2.9006(15) |
| N2-H2C..O5 ${ }^{\text {iv }}$ |  | 3.0157(18) | O21-H21A…O8 |  | 2.8108(18) |
| N2-H2D...O1 ${ }^{\text {v }}$ |  | 2.8998(18) | O21-H21B...O6 ${ }^{\text {v }}$ |  | 2.9334(17) |
| O7-H7...O21 ${ }^{\text {vi }}$ |  | 2.6936(18) | (iv) $-\mathrm{x}+1,-\mathrm{y},-\mathrm{z}$ |  |  |
| (i) $-x,-y,-z+1$ <br> (vi) $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$ | (ii) $\mathrm{x}-1, \mathrm{y}, \mathrm{z}+1$ <br> (iii) $-\mathrm{x}+1,-\mathrm{y},-\mathrm{z}+1$ <br> (iv) $-\mathrm{x}+1,-\mathrm{y},-\mathrm{z}$ <br> (vii) $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}$ <br> (viii) $-\mathrm{x}+2,-\mathrm{y}+1,-\mathrm{z}$ |  |  |  | (v) $x-1, y, z$ |



Figure 3.6 View of a plane of pentaborate(1-) anions (viewed along the $c$ direction of the unit cell) in 20. Dashed blue lines represent H -bonds.

A view of the layered structure of the $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions of $\mathbf{2 0}$ is shown in Figure 3.6. Detailed inspection of Figure 3.7 shows that ribbons of $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions are horizontally connected by two reciprocal interactions and these two interactions are composed of $\mathrm{R}_{2}{ }^{2}(8)$ and $\mathrm{R}_{2}{ }^{2}(12)$ motifs. The $\mathrm{R}_{2}{ }^{2}(8)$ reciprocal connection is formed between two pentaborate(1-) anions by one boroxyl $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ ring of each pentaborate(1-) anion O9-H9 $\cdots \mathrm{O}_{4} / \mathrm{O} 9^{*}-\mathrm{H} 9^{*} \cdots \mathrm{O} 4(\mathrm{O} \cdots \mathrm{O}$ distance is $2.75 \AA$ and a < OHO angle $171.74^{\circ}$ ), while the $\mathrm{R}_{2}{ }^{2}(12)$ reciprocal connection is formed by unprecedented participation of both boroxyl $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ rings of each pentaborate(1-) anion $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O}^{*} / \mathrm{O} 10^{*}-\mathrm{H} 10^{*} \cdots \mathrm{O} 3\left(\mathrm{O} \cdots \mathrm{O}\right.$ distance is $2.9 \AA$, and a <OHO angle $145.48^{\circ}$ ). The boroxyl $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ rings of the pentaborate(1-) anion ribbons are crosslinked to other pentaborate(1-) anion ribbons by a further $\mathrm{R}_{2}{ }^{2}(8)$ reciprocal $\beta \rightarrow \alpha$ interaction which O8$\mathrm{H} 8 \cdots \mathrm{O}^{*} / \mathrm{O}^{*}-\mathrm{H} 8^{*} \cdots \mathrm{O} 3\left(\mathrm{O} \cdots \mathrm{O}\right.$ distance is $2.74 \AA$ and a < OHO angle $167.02^{\circ}$ ). The final donor hydroxyl group of each $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion acts to crosslink the planes via a $\beta \rightarrow \omega$ interaction with a water molecule $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 21^{*}\left(\mathrm{O} \cdots \mathrm{O}\right.$ distance is $2.69 \AA$ and a $<\mathrm{OHO}$ angle $173.51^{\circ}$ ). Thus, each $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion participates in the supramolecular architecture by $3(\beta \rightarrow \alpha)$ and $1(\beta \rightarrow \omega)$ H-bond interactions.


Figure 3.7 The two $\mathrm{R}_{2}{ }^{2}(8)$ and $\mathrm{R}_{2}{ }^{2}(12) \mathrm{H}$-bond motif connections between pentaborate(1-) anions in 20.

The $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ cations, $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions, and $\mathrm{H}_{2} \mathrm{O}$ molecules of crystallization of 20 are connected through a complex series of H -bond interactions, with the anion network templated by the cations. Figure $\mathbf{3 . 8}$ shows that neighbouring planes connect via further H -bond interactions, forming a three-dimensional network. The $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ cation is included within the supramolecular framework structure, occupying the "cavities" present as shown in Figure 3.8. According to Table 3.7 there is one $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ cation per unit cell. This cation connects to $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ions by H -bonds. The $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ cation acts as a H -bond donor to two $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions via three H -bond interactions involving two bifurcated H -bonds to one of the pentaborate (1-) anion N1-H1D $\cdots 1^{*}$ and $\mathrm{N} 2-\mathrm{H} 2 \mathrm{D} \cdots \mathrm{O}^{*}$ ( $\mathrm{N} \cdots \mathrm{O}$ distances are 3.02 and 2.9 $\AA$, respectively and <NHO angles are 138.67 and $146.06^{\circ}$, respectively) and one H -bond to the other pentaborate(1-) anion $\mathrm{N} 2-\mathrm{H} 2 \mathrm{C} \cdots \mathrm{O}^{*}(\mathrm{~N} \cdots \mathrm{O}$ distance is $3.01 \AA$ and $<\mathrm{NHO}$ angle is $155.36^{\circ}$ ).


Figure 3.8 Diagram showing a 'plane' of polyborate anions (viewed along the $c$ direction of the unit cell) and water molecule with $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ cations in 20.

### 3.3.5.2 Structural characterisation of $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left[\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (22)

Crystallographic data of $\mathbf{2 2}$ compound are listed in Table 3.9. The crystals of $\mathbf{2 2}$ are triclinic, $P-1$ and 22 is an ionic compound with one transition metal complex cation $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]^{+}$partnered with a $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion and with four water molecules as shown in Figure 3.9.

Table 3.9 Crystal data and structure refinement details of $\mathbf{2 2}$.

| Empirical formula | $\mathrm{C}_{6} \mathrm{H}_{36} \mathrm{~B}_{10} \mathrm{~N}_{4} \mathrm{O}_{24} \mathrm{Cu}$ |
| :--- | :--- |
| Formula weight | 720.03 |
| Temperature | $100(2) \mathrm{K}$ |
| Wavelength | $0.71073 \AA$ |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a=11.1860(5) \AA \quad$  <br>  $b=11.4551(8) \AA$ <br>  $c=12.2830(6) \AA$ <br> Volume $1420.35(15) \AA \AA^{3}$ <br> $Z$ 2 <br> Density (calculated) $1.684 \mathrm{Mg} / \mathrm{m}^{3}$ |


| Absorption coefficient | $0.872 \mathrm{~mm}^{-1}$ |
| :--- | :--- |
| $F(000)$ | 742 |
| Crystal | Block; Purple |
| Crystal size | $0.230 \times 0.110 \times 0.050 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $1.966-27.776^{\circ}$ |
| Index ranges | $-14 \leq h \leq 14,-14 \leq k \leq 13,-15 \leq l \leq 15$ |
| Reflections collected | 24265 |
| Independent reflections | $6574\left[R_{\text {int }}=0.0178\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | $99.7 \%$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.946 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | $6574 / 24 / 438$ |
| Goodness-of-fit on $F^{2}$ | 1.028 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R l=0.0243, w R 2=0.0665$ |
| $R$ indices (all data) | $R 1=0.0252, w R 2=0.0669$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.397 and $-0.402 \mathrm{e} \AA \AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha(0.71073 \AA)$ |

Special details: The coordinated diamines were found to be disordered over two positions resulting in the need to use various geometrical (SAME) and displacement (RIGU) restraints, with the lesser component carbon atoms left isotropic. To facilitate suitable hydrogen bonding, the nitrogen atoms were split into the two different components but constrained to be identical using the EADP and EXYZ commands.


Figure 3.9 Diagram showing the structure and the numbering scheme of $\mathbf{2 2}$.

The $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]^{+}$in $\mathbf{2 2}$ has $\mathrm{Cu}-\mathrm{N}$ distances of 1.9714(11)-2.0115(12) $\AA$ [av.
3.9. Although there is a sixth axially weakly coordinated $\mathrm{H}_{2} \mathrm{O}$ 'ligand' at $2.785 \AA$, the complex is best considered as a 5 -coordinate square based pyramid. This confirmed by a $T^{5}$ value of 0.8000. A $\tau$ index ${ }^{182}$ of 0.0013 for this cation supports a square-based pyramidal rather than a trigonal bipyramidal 5-coordinate geometry.

The two pentaborate(1-) anions are structurally similar and are not notably different from other transition metal complex cation pentaborate(1-) anion structure systems involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions. ${ }^{136,181}$ However, one of the two pentaborate(1-) anion is coordinated to the central metal atom copper by O 9 and acts as a monodentate ligand. The coordination site of the pentaborate is from a hydroxyl oxygen atom $(\beta)$ rather than from a bridging oxygen atom ( $\alpha$ or $\gamma$ ). B-O bonds to the 3 -coordinate boron centres for the uncoordinated pentaborate(1-) anion ranges from 1.3419(17) - 1.3848(17) A [av. $1.3585 \AA$ ], and are not significantly different from those of the coordinated pentaborate which range from 1.3447 (17) - $1.3824(17) \AA$ [av. $1.3592 \AA$ ]. These distances are significantly shorter than those involving the 4-coordinate B11 and B1 centres of both uncoordinated and coordinated pentaborate(1-) anions, which range from $1.4474(16)$ to $1.4666(16) \AA$ [av. $1.4585 \AA$ ], and from 1.4547 (16) to $1.4645(15) ~ \AA$ [av. $1.4615 \AA$ ], respectively. B-O distances involving 3-coordinate boron centres and terminal hydroxyl groups are at the shorter end of the range from 1.3465(17) to 1.3545 (16) $\AA$ [av. $1.3504 \AA$ ] for the uncoordinated pentaborate(1-) anion and from $1.3447(17)$ to $1.3551(16) \AA$ [av. $1.3512 \AA$ ] for the coordinated pentaborate(1-) anion. B-O distances involving the oxygen atoms distal from the 4 -coordinate boron centre for uncoordinated pentaborate(1-) anion (O12, O15) and for the coordinated pentaborate(1-) anion $(\mathrm{O} 2, \mathrm{O} 5)$ are at the longer end of the range from $1.3692(16)$ to $1.3848(17) \AA$ [av. $1.3788 \AA$ ], and from $1.3662(16)$ to $1.3824(17) \AA$ [av. $1.3762 \AA$ ], respectively. Bond angles at the B11 and B1 centres range from $107.60(10)$ to $111.31(10)$, and from $107.84(10)$ to $111.91(10)$, respectively while angles at the other ring atoms are range from 116.43(12) to 122.66(12) for the uncoordinated pentaborate(1-) anion and from 116.41(11) to 122.49(12) for the coordinated pentaborate(1-) anion. The bond lengths and angles are given in Appendix I (Table 11, and Table 12).

In 22 the uncoordinated pentaborate(1-) anion has ten H -bond interactions (4 H -bond donors and six H-bond acceptors) without any connections at O12 and O15. The coordinated pentaborate(1-) anion is involved with 12 H -bond interactions ( 4 H -bond donors and 8 H -bond acceptors) with one coordination bond to the central (copper) metal atom. Interestingly, O5 in the $\gamma$ position of the coordinated boroxyl ring has no further connections.

In 22 the 4 H -bond donor sites of the uncoordinated pentaborate(1-) anion are involved with H-bond acceptor oxygens of three different pentaborate(1-) anions (O17-H17…O1*, O18$\mathrm{H} 18 \cdots \mathrm{O} 3^{*}$ and $\mathrm{O} 20-\mathrm{H} 20 \cdots \mathrm{O} 16^{*}$ ) and H -bond acceptor oxygen of one water molecule (O19$\mathrm{H} 19 \cdots \mathrm{O} 23^{*}$ ). The 4 H -bond donor sites of the coordinated pentaborate(1-) anion are involved with H-bonds acceptor oxygen of three different pentaborate(1-) anions ( $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 11^{*}$, O8$\mathrm{H} 8 \cdots \mathrm{O} 13^{*}$ and $\mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O} 18^{*}$ ), and a H -bond acceptor oxygen of one water molecule (O10$\mathrm{H} 10 \cdots \mathrm{O} 22^{*}$ ). The H -bond acceptor sites arising from H -bond donor sites of free and coordinated pentaborate(1-) anions of $\mathbf{2 2}$ are $\alpha \alpha \alpha \omega$ and $\alpha \alpha \beta \omega$, respectively, where $\alpha$ and $\beta$ are pentaborate acceptor sites, and $\omega$ is water acceptor site..$^{77,98}$ The direction of the 4 H -bond donor sites in the free pentaborate(1-) anion are three 'in' (O17-H17, O18-H18, and O20-H20) and one 'out' (O19H19), while the direction of the 4 H -bond donor sites of the coordinated pentaborate(1-) anion are two 'in' (O7-H7 and O8-H8) and two 'out' (O9-H9 and O10-H10) (Figure 3.9). Details of the H -bonds interactions are listed in Table 3.10.

Table 3.10 H-bonds [ $\AA$ and ${ }^{\circ}$ ] in 22.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| N1-H1A $\cdots$ O24 ${ }^{\text {i }}$ | 3.1835(13) | O7-H7 ..O11 ${ }^{\text {v }}$ | 2.7538(13) |
| N1-H1B $\cdots$ O24 ${ }^{\text {ii }}$ | 3.1841(15) | O8-H8…O13 ${ }^{\text {vi }}$ | 2.7084(12) |
| N1B-H1BA $\cdots{ }^{\text {a }}{ }^{\text {i }}$ | 3.1835(13) | O9-H9 ..-O18 ${ }^{\text {iv }}$ | $2.6635(12)$ |
| N1B-H1BB $\cdots$ O24 ${ }^{\text {ii }}$ | 3.1841(15) | O10-H10..O22 ${ }^{\text {vii }}$ | 2.7376 (18) |
| $\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A} \cdots{ }^{\text {O }}{ }^{\text {iii }}$ | 3.0483(14) | O17-H17...O1 $1^{\text {viii }}$ | 2.7638(13) |
| N2-H2B...O22 | 2.9840(13) | O18-H18...O3 ${ }^{\text {ix }}$ | 2.6848(12) |
| N2B-H2BA $\cdots{ }^{\text {O }}{ }^{\text {iii }}$ | 3.0483(14) | O19-H19...O23 | $2.7907(11)$ |
| N2B-H2BB...O22 | 2.9840(13) | O20-H20‥O16(x) | 2.7023(13) |
| N11-H11A $\cdots$ O4 | 3.0360(14) | $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O}^{\text {iii }}$ | 2.8264(12) |
| N11-H11B... $8^{\text {iii }}$ | $3.1757(14)$ | O21-H21B $\cdots$ O14 | $2.7367(12)$ |
| N11B-H11C..O4 | 3.0360(14) | O23-H23A $\cdots \mathrm{O} 10^{\mathrm{i}} 1$ | 2.9141(12) |
| N11B-H11D...O8 ${ }^{\text {iii }}$ | 3.1757(14) | O23-H23B $\cdots \mathrm{O}^{6}{ }^{\text {iii }}$ | 2.8287(11) |
| $\mathrm{N} 12-\mathrm{H} 12 \mathrm{~A} \cdots \mathrm{O} 24^{\mathrm{ii}}$ | 2.9242(16) | $\mathrm{O} 22-\mathrm{H} 22 \mathrm{~A} \cdots \mathrm{O} 20{ }^{\text {i }}$ | 2.7639(12) |
| N12-H12B $\cdots$ O12 ${ }^{\text {iv }}$ | 3.0944(14) | O22-H22B $\cdots$ O 4 | 2.9367(13) |
| N12B-H12C...O24 ${ }^{\text {ii }}$ | 2.9242(16) | O24-H24A $\cdots{ }^{\text {O }} 23$ | 2.813 |
| N2B-H12D $\cdots$ O12 ${ }^{\text {iv }}$ | 3.0944(14) | $\mathrm{O} 24-\mathrm{H} 24 \mathrm{~B} \cdots \mathrm{O} 21^{\mathrm{ii}}$ | (v) $x-1, y, z$ <br> (vi) $x-1, y+1, z$ <br> (xii) $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$ |
| (i) $x, y, z+1$ (ii) $-x+1,-y,-z+1$ (iii) $-x,-y+1,-z+1$ (iv) $-x+1,-y,-z+2$  <br> $-x,-y+1,-z+2$ (viii) $x+1, y, z$ (xi) $x+1, y-1, z$ (x) $-x+2,-y,-z+1$ (xi) $x+1, y, z-1$ |  |  |  |

A view of a plane of $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions in 22 is shown in Figure 3.10. Within the plane a chain of uncoordinated and coordinated pentaborate(1-) anions alternate and are linked by $R_{2}{ }^{2}(8)$ motif connections. An expanded view of the chain is shown in Figure 3.11. The two reciprocal- $\alpha \mathrm{R}_{2}{ }^{2}(8)$ connections are formed between pentaborate(1-) anions by one boroxyl
$\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ ring of both pentaborate (1-) anions. The second boroxyl $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ ring of the uncoordinated pentaborate(1-) anion is cross linked to another uncoordinated pentaborate (1-) anion by a further reciprocal- $\alpha \mathrm{R}_{2}^{2}(8)$ interaction. The second boroxyl ring of the coordinated pentaborate(1-) anions is linked to other chain by bridging water molecules.


Figure 3.10 H-bonded $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$network for 22. Dashed blue lines represent H -bonds.

The $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\} \mathrm{H}_{2} \mathrm{O}\right]^{+}$cations, $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions, and $\mathrm{H}_{2} \mathrm{O}$ molecules of crystallization of $\mathbf{2 2}$ are connected through a complex series of H-bond interactions, with the anion network templated by the cations (Figure 3.12).


Figure 3.11 The $\mathrm{R}_{2}{ }^{2}(8)$ connections between free and coordinate pentaborate(1-) anions in $\mathbf{2 2}$.


Figure 3.12 A diagram shows the structure of $\mathbf{2 2}$ viewed along the c direction of the unit cell. The polyborate groups are arranged in a plane and 'cavities' are filled by the $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]^{+}$cations and water molecules.

The plane shown in Figure $\mathbf{3 . 1 2}$ is connected to the neighbouring planes by further H bond interactions, forming a three-dimensional network. The $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}{ }_{6}(\mathrm{OH})_{4}\right\}\right]^{+}$cation is included within the supramolecular framework structure. The cation in 22, $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]^{+}$, has eight amino H -atoms and which form eight donor H -bonds: four
to water molecules, three to neighbouring $\beta \gamma \gamma$ pentaborate(1-) sites and one intramolecular H bond to the coordinated pentaborate (1-) $\alpha$-site (N11H11A...O4*); details of which can be found in the legend to Figure 3.9.

### 3.3.5.3 Structural characterisation of $\left[\mathrm{Cu}(\right.$ TMEDA $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (23)

Crystallographic data for $\mathbf{2 3}$ are listed in Table 3.11. Crystals of 23 are monoclinic, $P 2_{1} / c$ and consists of a neutral transition metal complex $\left[\mathrm{Cu}(\right.$ TMEDA $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ with six water molecules of crystallization as shown in Figure 3.13.


Figure 3.13 Diagram showing the structure and the numbering scheme of $\mathbf{2 3}$.

Table 3.11 Crystal data and structure refinement details of $\mathbf{2 3}$.

| Empirical formula | $\mathrm{C}_{6} \mathrm{H}_{34} \mathrm{~B}_{6} \mathrm{~N}_{2} \mathrm{O}_{19} \mathrm{Cu}$ |
| :--- | :--- |
| Formula weight | 566.75 |
| Temperature | $100(2) \mathrm{K}$ |
| Wavelength | $0.71073 \AA$ |
| Crystal system | Monoclinic |


| Space group | $P 2{ }_{1} / c$ |
| :---: | :---: |
| Unit cell dimensions | $a=15.4209(3) \AA$ $\alpha=90^{\circ}$ <br> $b=17.0706(3) \AA$ $\beta=90.861(2)^{\circ}$ <br> $c=8.88230(10) \AA$ $\gamma=90^{\circ}$ |
| Volume | $2337.95(7) \AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.610 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.021 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 1180 |
| Crystal | Hexagonal Prism; Blue |
| Crystal size | $0.130 \times 0.080 \times 0.060 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $1.780-27.633^{\circ}$ |
| Index ranges | $-19 \leq h \leq 20,-22 \leq k \leq 22,-11 \leq l \leq 11$ |
| Reflections collected | 9533 |
| Independent reflections | 9533 |
| Completeness to $\theta=25.242^{\circ}$ | 99.8\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.872 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 9533 / 147 / 380 |
| Goodness-of-fit on $F^{2}$ | 1.109 |
| Final $R$ indices [ $\left.F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0354, w R 2=0.1326$ |
| $R$ indices (all data) | $R 1=0.0381, w R 2=0.1405$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.621 and $-0.650 \mathrm{e}^{\text {® }}{ }^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha$ |

Special details: This structure was refined as a two-component twin. Component two rotated by $-179.9844^{\circ}$ around [1.00-0.00 0.00] (reciprocal) or [1.00-0.00 0.03] (direct). The amine was found to be disordered and as such it resulted in the need to use various geometrical (SAME, DFIX, DANG, BUMP) and displacement (DELU, RIGU) restraints, along with a displacement (EADP) constraint.

The neutral complex in compound 23 arises from the coordination of a tridentate hexaborate(2-) $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ ligand to a $[\mathrm{Cu}(\text { TMEDA })]^{2+}$ centre. The 5-coordinate copper(II) centre in 23 has a $\tau$ index of $0.02,{ }^{182}$ consistent with a square-based pyramidal structure. The copper(II) centre has the bidentate diamine ligand within the square plane and the tridentate hexaborate(2-) anion completes the two remaining coordination sites of the square plane and the one axial site ( O 4 ). Compound $\mathbf{2 3}$ has $\mathrm{Cu}-\mathrm{N}$ distances of 2.035(6) $\AA(\mathrm{N} 1)$ and 2.069(10) $\AA$ (N2). The Cu-O distances with the place are $1.9802(16) \AA(\mathrm{O} 2)$ and $1.9934(16) \AA(\mathrm{O} 3)$, whilst the $\mathrm{Cu}-\mathrm{O}$ axial distance is $2.1871(16) \AA(\mathrm{O} 4)$.

To date, most of the synthesised and characterised borate salts have been pentaborates. In contrast, relatively fewer hexaborate(2-) anion compounds are known. ${ }^{135,153,154,183,184}$ The hexaborate(2-) anion has been observed as a tridentate ligand coordinated to cobalt(II) ${ }^{135,153,154}$ and zinc(II) ${ }^{184}$ but has not been previously observed in copper(II) chemistry. The hexaborate(2) anion in $\mathbf{2 3}$ acts as a tridentate ligand in to the copper(II) centre, with an average Cu - O distance
$2.054 \AA$, while the $N, N, N^{\prime}, N^{\prime}$-tetramethyl ethylenediamine ligand acts as a bidentate ligand. The copper(II) centre has a coordination number of five and a square base pyramidal geometry (Figure 3.13).

The hexaborate (2-) anion consist of a three fused 6-membered boroxyl rings in which three tetrahedral boron centres (B1, B2, B3) and three trigonal boron centres (B4, B5, B6). The $B 1, B 2$, and B3 centres are connected to three oxygen atoms and one hydroxyl group while B4, B5, and B6 centres are connected to two oxygen atoms and one hydroxyl group. The hexaborate(2-) anion in $\mathbf{2 3}$ is structurally similar to other reported transition metal complex cation hexaborates. ${ }^{135,153}$ The shorthand designation of the $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ anion is $[6: 3 \Delta+3 \mathrm{~T}]$ according to the Christ and Clark ${ }^{163}$ and Heller ${ }^{27}$ crystal chemical classification schemes. The B-O distances to the tetrahedral B1, B2, B3 centres are in the range of 1.436(3)-1.513(3) $\AA$, $1.436(3)-1.513(3) \AA$, and $1.453(3)-1.516(3) \AA$, respectively and these are significantly longer than those involving the trigonal B4, B5, B6 centres: The B-O distances to B4, B5, and B6 centres are in the range of $1.358(3)-1.375(3) \AA, 1.359(3)-1.368(3) \AA$ and $1.360(3)-1.368(3)$ $\AA$ A , respectively. The B-OH bonds involving tetrahedral B1, B2, and B3 centres are 1.483(3), 1.482(3), and $1.455(3) \AA$, respectively while the B-OH bonds involving trigonal B4, B5, and B6 centres are significantly shorter at $1.375(3), 1.368(3)$, and $1.368(3) \AA$, respectively. Bond angles at the tetrahedral centres B1, B2, and B3 range from $106.17(18)^{\circ}-112.8(18)^{\circ}, 106.91(17)^{\circ}$ $-111.15(18)^{\circ}$, and $105.61(16)^{\circ}-112.49(19)^{\circ}$, respectively while the bond angles at the trigonal B4, B5, and B6 centres range from $117.9(2)^{\circ}-123.3(2)^{\circ}, 117.6(2)^{\circ}-123.2(2)^{\circ}$, and $118.0(2)^{\circ}-$ $122.5(2)^{\circ}$, respectively. The bond lengths and angles are given in Appendix I (Table 13, and Table 14).

The four chemically non-equivalent oxygen sites of the isolated hexaborate(2-) anion are labelled A-D by using a similar nomenclature system to that previously described (Figure 3.14). ${ }^{98,77}$ This labelling system has been used to classify the H -bond interactions between different neighbouring $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ anions and to differentiate between the available sites.

In 23 the hexaborate(2-) anion has six potential H -bond donor sites ( B and C ) which are also capable of accepting H -bond interactions, and a further seven potential H -bond acceptor sites (A and D). The hexaborate(2-) anion has thirteen H-bond interactions (six H-bond donors and seven H -bond acceptors). In addition, there are three coordination bonds to the copper metal. The bridging O atoms (A, D; O1, O5, and O6), are not involved in further stabilizing interactions.


Figure 3.14 Diagram showing oxygen labelling and the H -bond acceptor sites for the hexaborate(2-) anions in 23.

Table 3.12 H-bonds [ $\AA$ and ${ }^{\circ}$ ] in 23.

| $D-\mathrm{H} \cdots{ }^{\text {a }}$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| O11-H11..-O22 ${ }^{\text {i }}$ | 2.742(2) | O24-H24B $\cdots{ }^{\text {O }} 11^{\text {v }}$ | 2.7320 (19) |
| O12-H12..- $6^{\text {ii }}$ | 3.154(2) | O22-H22A $\cdots$ O21 ${ }^{\text {vi }}$ | 2.805(2) |
| O12-H12...O7 $7^{\mathrm{ii}}$ | 2.779(2) | O22-H22B $\cdots{ }^{\text {O }} 1^{\text {vii }}$ | 2.8056(19) |
| O13-H13 ..O10 ${ }^{\text {iii }}$ | 2.736 (2) | O23-H23A $\cdots$ O13 ${ }^{\text {iii }}$ | 2.7240 (19) |
| O2-H2..O24 | 2.6837(17) | O23-H23B $\cdots{ }^{\text {O }}$ 2 ${ }^{\text {i }}$ | 2.772 |
| O3-H3..O22 | 2.7326 (18) | O25-H25A $\cdots$ O26 ${ }^{\text {viii }}$ | 2.795(2) |
| O4-H4...O25 | 2.8679(17) | O25-H25B $\cdots \mathrm{O}^{\text {iv }}$ | 2.9236(18) |
| O21-H21A $\cdots$ O12 ${ }^{\text {iv }}$ | 2.718(2) | O26-H26A $\cdots \mathrm{O}^{9}{ }^{\text {ix }}$ | 2.7906(19) |
| O21-H21B $\cdots$ O25 | 2.859 | O26-H26B $\cdots$ O23 | 2.794 |
| O24-H24A $\cdots 23$ | 2.784 |  |  |
| (i) $x,-y+3 / 2, z-1 / 2$ <br> (vi) $-x+2, y+1 / 2,-z+1 / 2$ | (ii) $-x+2,-y+1,-z$ <br> (iii) $-x+1,-y+1,-z$ <br> (iv) $x,-y+1 / 2, z+1 / 2$ <br> (v) $x,-y+3$ <br> (vii) $-\mathrm{x}+2,-\mathrm{y}+1,-\mathrm{z}+1$ <br> (viii) $-\mathrm{x}+1, \mathrm{y}-1 / 2,-\mathrm{z}+1 / 2$ <br> (xi) $-\mathrm{x}+1, \mathrm{y}+1 / 2,-\mathrm{z}+1 / 2$ |  |  |

In 23 all six potential H -bond donor sites partake in H -bond interaction: three coordinated hydroxyl groups are H -bonded to $\mathrm{H}_{2} \mathrm{O}$ molecules ( $\mathrm{O} 2-\mathrm{H} 2 \cdots \mathrm{O} 24^{*}$, $\mathrm{O} 3-\mathrm{H} 3 \cdots \mathrm{O} 22^{*}$, $\mathrm{O} 4-\mathrm{H} 4 \cdots \mathrm{O} 25^{*}$ ) and the three uncoordinated hydroxyl groups are H -bonded to one $\mathrm{H}_{2} \mathrm{O}$ and two hexaborates. However, $\mathbf{2 3}$ does not possess any amino hydrogen atoms in the TMEDA ligand, and this leads to only hexaborate(2-)-hexaborate (2-) interactions between neighbouring $\left[\mathrm{Cu}(\right.$ TMEDA $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ units. The units are linked into infinite chains through tworeciprocal $\mathrm{R}_{2}{ }^{2}(8)$ interactions: $\mathrm{O} 13-\mathrm{H} 13 \cdots \mathrm{O} 10^{*} / \mathrm{O} 13^{*}-\mathrm{H} 13^{*} \cdots \mathrm{O} 10$ and $\mathrm{O} 12-\mathrm{H} 12 \cdots \mathrm{O} 7^{*} / \mathrm{O} 12^{*}-$ $\mathrm{H} 12^{*} \cdots \mathrm{O} 7$ (Figure 3.15). Details of the H -bonding interactions are given in Table 3.12.


Figure 3.15 The $\mathrm{R}_{2}{ }^{2}(8)$ interactions between $\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ molecules in 23.

The $\left[\mathrm{Cu}(\right.$ TMEDA $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ units and $\mathrm{H}_{2} \mathrm{O}$ molecules of the $\mathbf{2 3}$ compound are connected through a complex series of H -bond interactions to produce planes (Figure 3.16) which are further linked to produce a three-dimension network.


Figure 3.16 Diagram showing a 'plane' of $\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ (viewed along the $c$ direction of the unit cell) and water molecules in 23.

### 3.3.5.4 Structural characterisation of $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Cu}(\text { dach })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$

 (24)Crystallographic data of $\mathbf{2 4}$ are listed in Table 3.13. Crystals of $\mathbf{2 4}$ are monoclinic, $C 2 / c$. Compound $\mathbf{2 4}$ is a salt and comprised of two copper(II) complex cations, two heptaborate (2-) anions, and four waters of crystallization.

Table 3.13 Crystal data and structure refinement details of $\mathbf{2 4}$.

| Empirical formula | $\mathrm{C}_{12} \mathrm{H}_{39} \mathrm{~B}_{7} \mathrm{~N}_{4} \mathrm{O}_{17} \mathrm{Cu}$ |
| :---: | :---: |
| Formula weight | 650.68 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $\begin{array}{ll} \hline a=22.4696(9) \AA & \alpha=90^{\circ} \\ b=10.8711(3) \AA & \beta=108.267(4)^{\circ} \\ c=23.0016(7) \AA & \gamma=90^{\circ} \\ \hline \end{array}$ |
| Volume | 5335.4(3) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.620 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.903 \mathrm{~mm}^{-1}$ |
| F(000) | 2712 |
| Crystal | Blade; Purple |
| Crystal size | $0.090 \times 0.050 \times 0.020 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.175-27.483^{\circ}$ |
| Index ranges | $-28 \leq h \leq 27,-13 \leq k \leq 14,-29 \leq l \leq 29$ |
| Reflections collected | 26756 |
| Independent reflections | $6106\left[R_{\text {int }}=0.0378\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.9\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.799 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 6106 / 940 / 525 |
| Goodness-of-fit on $F^{2}$ | 1.045 |
| Final $R$ indices [ $\left.F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0522, w R 2=0.1330$ |
| $R$ indices (all d ata) | $R 1=0.0656, w R 2=0.1404$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.516 and $-0.557 \mathrm{e}^{\text {® }}{ }^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha$ |

Special details: Both the 1,2-diaminocyclohexane ligands were successfully modelled as disordered over two positions. As such various geometrical (SAME, SADI) and displacement (RIGU, SIMU) restraints were applied.

The copper(II) complex cations in 24 each contain both the ( $1 S, 2 S$ )-1,2diaminocyclohexane and ( $1 R, 2 R$ )-1,2-diaminocyclohexane ligands in a square-planar arrangement. Additionally, both cations connect to two mutually trans $\mathrm{H}_{2} \mathrm{O}$ molecules yielding formally 6 -coordinate metal cations. However, due to the Jahn-Teller effect, one cation has both
the axial Cu-O distances at a long distance of $2.836 \AA$. This complex is best considered as a 4coordinate square-planar $\left\{T=0.70,{ }^{172} \mathrm{Cu}-\mathrm{N}\right.$ distances range from 1.963(7)-2.013(8) $\left.\AA\right\}$. The other cation has both axial Cu-O distances at 2.381(3) A and designated elongated octahedron $\left\{T=0.80,{ }^{172} \mathrm{Cu}-\mathrm{N}\right.$ distances range from $1.910(13)-1.923(11) \AA$. Each cation is partnered by a $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]^{2-}$ anion and an additional water of crystallization. The anions and cations are shown in Figure 3.17.

The heptaborate(2-) anion, $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$, contains four fused 6 -membered rings with three tetrahedral boron centres (B1, B2, B3) and four trigonal boron centres (B4, B5, B6, B7). The B2 and B3 centres are surrounded by four bridging oxygen atoms, while B4, B5, B6, B7 centres are connected to two bridging oxygen atoms and one hydroxyl group. B1 is unique and is connected to three bridging oxygen atoms and one hydroxyl group (Figure 3.17).


Figure 3.17 Diagram showing the complex cations and heptaborate(2-) anion in 24. The water molecules containing O22 are in octahedral positions around Cu 2 (bonds not shown in the diagram).

The structure of the heptaborate(2-) anions in $\mathbf{2 4}$ is essentially the same as those reported for $\left[\mathrm{H}_{3} \mathrm{~N}\left(\mathrm{CH}_{2}\right)_{7} \mathrm{NH}_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot \mathrm{H}_{2} \mathrm{O},{ }^{97}\left[\text { cyclo }-\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NH}_{3}\right]_{2}\left[\mathrm{~B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O} \cdot \mathrm{B}(\mathrm{OH})_{3}$, and $\left[\text { cyclo }-\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NH}_{3}\right]_{2}\left[\mathrm{~B} 7 \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O} \cdot 2 \mathrm{~B}(\mathrm{OH})_{3},{ }^{77}$ and can be considered as a hexaborate (2-) anion condensed with an additional $\mathrm{B}(\mathrm{OH})_{3}$ molecule forming a fused tetracyclic (four boroxyl) ring system with one bridgehead (formally positively charged) 3-coordinate oxygen site, and three bridgehead (formally negatively charged) 4-coordinate boron sites. The $\mathrm{B}-\mathrm{O}$ distances for the 3-coordinate boron centres range from 1.355(4) - 1.376(3) $\AA$, and B-O distances around the 4-coordinate boron centres range from 1.436(3) - 1.471(3) A. The $\mathrm{O}-\mathrm{B}-\mathrm{O}$ angles for the 3coordinate boron centres range from $114.8(3)-123.4(2)^{\circ}$ and $\mathrm{O}-\mathrm{B}-\mathrm{O}$ angles at the 4 coordinate boron centres range from $106.0(2)-112.1(2)^{\circ}$ (Appendix I, Table 15, and Table 16). These distances and angles are as expected for $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3}$ hybridized boron centres. ${ }^{6}$ The ring $\mathrm{B}-\mathrm{O}-\mathrm{B}$ angles range from $110.7(2)-122.8(2)^{\circ}$ indicating $\mathrm{sp}^{2}$ hybridized oxygen atoms. The central three-coordinate oxygen centre is pyramidal $\left(349.39^{\circ}=\right.$ angles sum and $0.288 \AA$ out of the B1B2B3 plane, with B-O bond lengths [av. $1.59 \AA$ ] longer than typically expected for oxygen atoms bound to four-coordinate boron centres $(\sim 1.48 \AA) .{ }^{77}$ The three-coordinate oxygen centres, O 1 , are transoid relative to the OH group of B 1 .

In 24 the heptaborate(2-) anion has five potential H -bond donor sites which are also capable of accepting H -bond interactions, and nine further potential H -bond acceptor sites. According to Christ and Clark's ${ }^{163}$ and Heller's ${ }^{27}$ crystal chemical classification schemes, the shorthand notification of $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]^{2-}$ is $[7: 4 \Delta+3 \mathrm{~T}]$. A labelling scheme was introduced by Beckett ${ }^{77}$ to differentiate between the available sites of the H -bonding interactions between $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ anions. The seven chemically distinct O sites are labelled $\mathrm{A}-\mathrm{G}$, (Figure 3.18). By analogy with Schubert's pentaborate labelling sites A, D and E are $\alpha$ to 4-coordinate boron centres, whilst sites B and F are on 3-coordinate boron centres and $\beta$ to 4-coordinate boron centres. Sites C and G do not have corresponding sites on pentaborate(1-) anions. All the H bonds data are listed in Table 3.14.


Figure 3.18 Diagram showing the H -bond acceptor sites of the heptaborate(2-) anions in 24.

Table 3.14 H-bonds [ $\AA$ and ${ }^{\circ}$ ] in 24.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O} 22^{\text {iii }}$ | 2.698(4) | N11B-H11C...O10 ${ }^{\text {iv }}$ | 3.09(2) |
| O21-H21B..O9 | 3.067(3) | N11B-H11D...O21 ${ }^{\text {i }}$ | 3.35(3) |
| O21-H21B $\ldots$ O14 | $2.996(4)$ | N11B-H11D $\cdots$ O9 ${ }^{\text {i }}$ | 2.99(2) |
| N1-H1A...O14 ${ }^{\text {i }}$ | $3.211(9)$ | N12B-H12C...O23 | 3.01(4) |
| N1-H1B..O12 ${ }^{\text {i }}$ | 3.200 (6) | N12B-H12D $\ldots \mathrm{O}^{\text {O }}{ }^{\text {v }}$ | 2.93(4) |
| N2-H2A $\cdots$ O8 | 3.027(6) | O10-H10...O2 ${ }^{\text {vi }}$ | 2.724(3) |
| N1B-H1BA $\cdots$ O14 ${ }^{\text {i }}$ | 2.975(16) | O11-H11F...O6 $6^{\text {vii }}$ | 2.717(3) |
| N2B-H2BA $\cdots$ O7 | 2.971(10) | O12-H12F...O4 $4^{\text {viii }}$ | 2.740(3) |
| $\mathrm{N} 11-\mathrm{H} 11 \mathrm{~A} \ldots \mathrm{O} 10^{\text {iv }}$ | 3.027(8) | O13-H13...O5 ${ }^{\text {ix }}$ | 2.693 (3) |
| N11-H11B $\ldots \mathrm{O}^{\text {i }}$ | 3.002(9) | $\mathrm{O} 22-\mathrm{H} 22 \mathrm{~A} \cdots \mathrm{O} 23^{\text {ii }}$ | 2.775 (5) |
| N12-H12A $\cdots$ O23 | 3.091(14) | O22-H22B..O11(x) | 2.867(4) |
| N12-H12B $\cdots$ O13 ${ }^{\text {v }}$ | 2.869(15) | O23-H23A $\cdots \mathrm{O} 12$ | 2.790(3) |
| (i) $-x+3 / 2,-y+3 / 2,-z+1$ <br> (v) $x-1 / 2, y+1 / 2, z$ <br> (xi) $-x+3 / 2,-y+1 / 2,-z+1$ | (ii) $-\mathrm{x}+1,-\mathrm{y}+2,-\mathrm{z}+1$ <br> (vi) $-x+2, y,-z+3 / 2$ <br> (x) $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$ | (iii) $x+1 / 2, y-1 / 2, z$ <br> (vii) $-x+3 / 2, y-1 / 2,-z+3 / 2$ | $\begin{aligned} & \text { (iv) } \mathrm{x}-1 / 2,-\mathrm{y}+3 / 2, \mathrm{z}-1 / 2 \\ & \text { (viii) }-\mathrm{x}+3 / 2, \mathrm{y}+1 / 2,-\mathrm{z}+3 / 2 \end{aligned}$ |

A view of a plane of a heptaborate(2-) anions found in 24 is given in Figure 3.19. Four out of the five donor sites in $\mathbf{2 4}$ are involved in H-bonding to four different heptaborate(2-) anions involving a reciprocal $\mathrm{R}_{2}{ }^{2}(8)$ interaction $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 2^{*}$, a reciprocal $\mathrm{R}_{2}{ }^{2}(12) \mathrm{O} 13-$ $\mathrm{H} 13 \cdots \mathrm{O} 5^{*}$, and two non-reciprocal $\mathrm{R}_{2}{ }^{2}(8)$ interactions $\mathrm{O} 11-\mathrm{H} 11 \cdots \mathrm{O} 6^{*} / \mathrm{O} 12^{*}-\mathrm{H} 12^{*} \cdots \mathrm{O} 4$ and
 coordinate boron center (B1) is transoid to O 1 and is not involved in H -bonding.


Figure 3.19 The reciprocal connection (viewed along the $c$ direction of the unit cell) in $\mathbf{2 4}$.


Figure 3.20 The two $\mathrm{R}_{2}{ }^{2}(8)$ and $\mathrm{R}_{2}{ }^{2}(12) \mathrm{H}$-bond motif connections between heptaborate(2-) anions in 24.

The heptaborate(2-) anions are further held within the second coordination spheres of both the $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ and $\left[\mathrm{Cu}(\text { dach })_{2}\right]^{2+}$ cations via H -bonds involving the amino hydrogen atoms. The $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ cation forms two five-point H -bond contacts with its neighbouring heptaborate(2-) anions $\mathrm{N} 1-\mathrm{H} 1 \mathrm{~B} \cdots{ }^{\circ} \mathrm{O}^{*} 1^{*}$, $\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A}^{\cdots}{ }^{\circ} \mathrm{O}^{*}$, $\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A} \cdots{ }^{\cdots} \mathrm{O}^{*}$, O21$\mathrm{H} 21 \mathrm{~B} \cdots{ }^{\cdots}{ }^{*}$, $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~B} \cdots \mathrm{O} 14^{*}$ and this is likely to be involved in structure directing the formation of this compound from aqueous solution. Likewise a $\mathrm{R}_{2}{ }^{2}(8)$ interaction, where the heptaborate(2-) is a double acceptor is present for the square-planar copper(II) center (Figure 3.21).


Figure 3.21 The $\mathrm{R}_{2}{ }^{2}(8)$ interaction in between the heptaborate(2-) anion and $\left[\mathrm{Cu}(\mathrm{dach})_{2}\right]^{2+}$ cation in 24.

### 3.3.5.5 Structural characterisation of $\left[\mathrm{Cu}(N, N-d m e n)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathbf{3 H}_{2} \mathrm{O}$ (27)

Crystallographic data for $\mathbf{2 7}$ compound are listed in Table 3.15. Crystals of $\mathbf{2 7}$ are triclinic, $P-1$ and 27 is an ionic compound with one transition metal complex cation $[\mathrm{Cu}(N, N-$ dmen $\left.)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$ partnered with two $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions (A and B) and three water molecules of crystallization (Figure 3.22).

Table 3.15 Crystal data and structure refinement of 27.

| Empirical formula | $\mathrm{C}_{8} \mathrm{H}_{40} \mathrm{~B}_{10} \mathrm{~N}_{4} \mathrm{O}_{24} \mathrm{Cu}$ |
| :--- | :--- |
| Formula weight | 748.08 |
| Temperature | $100(2) \mathrm{K}$ |


| Wavelength | 0.71073 A |
| :---: | :---: |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a=11.7189(4) \AA$ $\alpha=80.468(3)^{\circ}$ <br> $b=11.7226(4) \AA$ $\beta=66.245(3)^{\circ}$ <br> $c=12.9108(4) \AA$ $\gamma=78.270(3)^{\circ}$ |
| Volume | $1582.49(9) \AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.57 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.786 \mathrm{~mm}^{-1}$ |
| Crystal | Prism; purple |
| Crystal size | $0.210 \times 0.150 \times 0.110 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.366-27.484^{\circ}$ |
| Index ranges | $-15 \leq h \leq 14,-15 \leq k \leq 13,-16 \leq l \leq 16$ |
| Reflections collected | 26183 |
| Independent reflections | 7230 [ $\left.R_{\text {int }}=0.0230\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.9\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.868 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 7230 / 0 / 509 |
| Goodness-of-fit on $F^{2}$ | 1.068 |
| Final $R$ indices [ $F^{2}>2 \sigma\left(F^{2}\right)$ ] | $R 1=0.0248, w R 2=0.0657$ |
| $R$ indices (all d ata) | $R 1=0.0258, w R 2=0.0664$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.336 and $-0.521 \mathrm{e}^{\text {A }}{ }^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha$ |

The $\left[\mathrm{Cu}(N, N-d m e n)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$ in 27 has $\mathrm{Cu}-\mathrm{N}$ distances ranging from 1.9937(11)$2.0781(11) \AA$ with a fifth ligand $\left(\mathrm{H}_{2} \mathrm{O}\right)$ at a distance of $2.3368(10) \AA$. This $\mathrm{Cu}-\mathrm{O}$ distance is significantly shorter than that found in $\mathbf{2 0}$ and since the nearest potential oxygen donor on the other axial site is at $3.55 \AA$ the complex is best considered as a 5 -coordinate square based pyramid $\left(T^{5}=0.87, \tau\right.$ index $\left.=0.12\right) .{ }^{172,182}$

The two pentaborate(1-) anions A (B1-B5) and B (B11-B15) are structurally similar to other transition metal complex polyborate structure systems involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ anions. ${ }^{136,181}$ The B-O distances to the 4-coordinate B1 and B11 centres range from 1.4596(15) $-1.4859(15) \AA$ and $1.4712(15)-1.4763(15) \AA$, respectively, and these are longer than those involving the trigonal boron centres of pentaborate(1-) anions A and B which range from $1.3502(16)-1.3915(16) \AA$ and $1.3533(16)-1.3870(15) \AA$, respectively. B-O bonds involving trigonal boron atoms and terminal OH groups are at the shorter end of the range [av. $1.359 \AA$ and av. $1.358 \AA$ for A and B, respectively], whilst B-O bonds involving trigonal boron atoms and the distal oxygen atoms for anion $\mathrm{A}(\mathrm{O} 2$ and O 5$)$ and $\mathrm{B}(\mathrm{O} 12$ and O 15$)$ are at the longer end of the range [av. $1.384 \AA$ and av. $1.385 \AA$, respectively]. Bond angles at the tetracoordinate B1 of anion A range from $107.69(10)^{\circ}-111.80(10)^{\circ}$, and angles at the other ring boron atoms
range from $115.72(11)^{\circ}-123.72(11)^{\circ}$. Bond angles at the tetracoordinate B 11 of anion B range from $108.17(9)^{\circ}-110.64(9)^{\circ}$, and angles at the other ring boron atoms range from $115.07(11)^{\circ}$ $-123.78(11)^{\circ}$ consistent with $\mathrm{sp}^{3}$ and $\mathrm{sp}^{2}$ hybridisation, respectively. Specific bond lengths and bond angles of the pentaborate anion are listed in Appendix I (Table 17, and Table 18).


Figure 3.22 Diagram showing the complex cation, pentaborate anions and water molecules in 27 and the adopted numbering scheme.

In 27 the pentaborate(1-) anion (A) contains eleven H -bond interactions (four H -bond donors and seven H-bond acceptors) but there are no H-bond interactions at O5. The four H bond donor sites of pentaborate(1-) anion are involved with H -bonds acceptor oxygen of four different pentaborate(1-) anions (O9-H9 $\cdots \mathrm{O}_{1} 7^{*}, \mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 15^{*}, \mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O} 13^{*}$ and $\mathrm{O} 7-$ $\mathrm{H} 7 \cdots \mathrm{O} 11^{*}$ ). This may be described as $\alpha \alpha \beta \gamma$, where $\alpha, \beta$, and $\gamma$ are pentaborate acceptor sites. ${ }^{77,98}$ The hydrogen atoms in pentaborate (A) on the $\beta$-oxygens may be described as two 'in' and two
'out', whilst these on pentaborate (B) are four 'in'. This unusual conformation results in a $\alpha \alpha \alpha \alpha$ H-bond arrangement (O17-H17 $\cdots \mathrm{O}^{*}$, O18-H18 $\cdots \mathrm{O} 3^{*}$, O19-H19 $\cdots \mathrm{O} 14$ * and O20-H20 $\cdots \mathrm{O} 16^{*}$ ). All H-bonds data for 27 are listed in Table 3.16.

Table 3.16 H-bonds [ $\AA$ and ${ }^{\circ}$ ] of $\mathbf{2 7}$

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| O21-H21A-O24 ${ }^{\text {i }}$ | 2.7351(15) | O18-H18-O3 ${ }^{\text {iii }}$ | 2.7543(13) |
| O21-H21B-O7 ${ }^{\text {ii }}$ | 2.8634(14) | O19-H19-O14 ${ }^{\text {vii }}$ | 2.6890 (13) |
| N1-H1A-O24 ${ }^{\text {i }}$ | 2.9310 (15) | O20-H20-O16 ${ }^{\text {vi }}$ | 2.7479(12) |
| N1-H1B-O12 ${ }^{\text {iii }}$ | $3.1078(14)$ | O22-H22A-O10 | 2.8290 (15) |
| N11-H11A-O23 ${ }^{\text {iv }}$ | 3.0038(16) | O22-H22B-O19 ${ }^{\text {vi }}$ | 2.7987 (14) |
| N11-H11B-O2ii | 2.9404(14) | $\mathrm{O} 23-\mathrm{H} 23 \mathrm{~A}-\mathrm{O} 4^{\text {v }}$ | $2.7606(14)$ |
| O7-H7-011 ${ }^{\text {v }}$ | 2.7453(12) | O23-H23B-O20 ${ }^{\text {vi }}$ | 3.0021(15) |
| O8-H8-O13iii | 2.6992(13) | O24-H24A-O3 | $3.2303(14)$ |
| O9-H9-O17 | 2.7347(13) | O24-H24A-O6 | 2.9429(14) |
| O10-H10-O15 ${ }^{\text {vi }}$ | 3.0075(13) | O24-H24B-O22 ${ }^{\text {i }}$ | 2.7119(15) |
| O17-H17-O1 ${ }^{\text {v }}$ | 2.6443(12) |  |  |

$i=1-x,-y, 1-z ; \quad$ ii $=1+x,+y,-1+z ; \quad$ iii $=1-x, 1-y, 1-z ; \quad$ iv $=1+x,+y,+z ; \quad v=-x, 1-y, 1-z ; \quad v i=$ $1-x, 1-y,-z ; \quad$ vii $=1-x, 2-y,-z$


Figure 3.23 The two $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond motif connections and $\mathrm{R}_{3}{ }^{3}(16)$ interaction in 27. Dashed blue lines represent H -bonds.

The pentaborate(1-) anions are linked together in a chain and a section of this chain is shown in Figure 3.23. The $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion (A) within the chain is connected by two $\mathrm{R}_{2}{ }^{2}(8)$ interactions: $\mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O} 13^{*} / \mathrm{O} 18^{*}-\mathrm{H} 18^{*} \cdots \mathrm{O} 3$ and $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 11^{*} / \mathrm{O} 17^{*}-\mathrm{H} 17^{*} \cdots \mathrm{O} 1$. Each pentaborate(1-) anion (A) is further linked to another pentaborate(1-) anions by a $\mathrm{R}_{3}{ }^{3}(16)$ interactions. The three $\mathrm{R}_{3}{ }^{3}(16)$ interactions are $\mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O} 17^{* *}$, $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 15^{*}$, and $\mathrm{O} 20^{*}$ $\mathrm{H} 20^{*} \cdots \mathrm{O} 16^{*}$.

The pentaborate(1-) anions (B) are linked by many H-bond interactions as shown in Figure 3.24. Each $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion $(\mathrm{B})$ is connected by four $\mathrm{R}_{2}{ }^{2}(8)$ interactions: O17$\mathrm{H} 17 \cdots \mathrm{O} 1^{*} / \mathrm{O} 7^{*}-\mathrm{H}^{*} \cdots \mathrm{O} 11, \mathrm{O} 18-\mathrm{H} 18 \cdots \mathrm{O} 3^{*} / \mathrm{O} 8^{*}-\mathrm{H} 8^{*} \cdots \mathrm{O} 13, \mathrm{O} 19-\mathrm{H} 19 \cdots \mathrm{O} 14 * / \mathrm{O} 19^{*}-\mathrm{H} 19^{*} \cdots \mathrm{O} 14$ and O20-H20 $\cdots \mathrm{O} 16^{*} / \mathrm{O} 20^{*}-\mathrm{H} 20^{*} \cdots \mathrm{O} 16$.


Figure 3.24 The four $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond motif connections between pentaborate(1-) anions in 27.

A view of a plane of a pentaborate(1-) anions found in 27 is given in Figure 3.25.


Figure 3.25 Extended H-bonded $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$plane (viewed along the $b$ direction of the unit cell) for 27.


Figure 3.26 Diagram showing a 'plane' of polyborate anions (viewed along the $b$ direction of the unit cell) with $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\mathrm{dmen})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$ and $\mathrm{H}_{2} \mathrm{O}$ molecules shown in the 'cavities' in 27.

The solid-state structures of all transition metal complex polyborate compounds involve H-bonded supramolecular polyborate giant anions, with 'cavities' and 'channels', which can involve the transition metal complex cation. The $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\mathrm{dmen})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$ cations, $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions, and the $\mathrm{H}_{2} \mathrm{O}$ molecules of crystallization of 27 are connected through a complex series of H-bond interactions as shown in Figure 3.26. The connection of the plane shown in Figure $\mathbf{3 . 2 5}$ to the neighbouring planes is formed by further H-bond interactions, forming a three-dimensional network.

Each $\left[\mathrm{Cu}(N, N-d m e n)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$ cation connects to two $\mathrm{H}_{2} \mathrm{O}$ molecules and one pentaborate(1-) anion (Figure 3.27), in the secondary coordination sphere and these units are held there by six H -bonds $\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A} \cdots \mathrm{O} 24^{*}$, $\mathrm{N} 1-\mathrm{H} 1 \mathrm{~B} \cdots \mathrm{O} 12^{*}$, N11-H11A $\cdots \mathrm{O} 23^{*}$, N11H11B $\cdots \mathrm{O} 2^{*}$, O21-H21A $\cdots{ }^{\circ} 4^{*}$, and O21-H21B $\cdots{ }^{\circ} 7^{*}$ (Table 3.16).


Figure 3.27 The H-bond connections of $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N}-\mathrm{dmen})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$ cation in 27

### 3.3.5.6 Structural characterisation of $\left[\mathrm{Cu}(N, N-d m e n)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}(28)$

Crystallographic data for $\mathbf{2 8}$ are listed in Table 3.17. Crystals of $\mathbf{2 8}$ are monoclinic, $P 2_{1} / n$ and consists of a neutral transition metal complex $\left[\mathrm{Cu}(N, N-d m e n)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ with four interstitial water molecules as shown in Figure 3.28.


Figure 3.28 Diagram showing the structure and the numbering scheme of $\mathbf{2 8}$.

Table 3.17 Crystal data and structure refinement details of $\mathbf{2 8}$.

| Empirical formula | $\mathrm{C}_{4} \mathrm{H}_{26} \mathrm{~B}_{6} \mathrm{~N}_{2} \mathrm{O}_{17} \mathrm{Cu}$ |
| :---: | :---: |
| Formula weight | 502.67 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | $P 2_{1} / n$ |
| Unit cell dimensions | $\begin{array}{ll} a=12.75604(17) \AA & \alpha=90^{\circ} \\ b=9.86582(12) \AA & \beta=103.2331(14) \\ c=15.7331(2) \AA & \gamma=90^{\circ} \end{array}$ |
| Volume | 1927.41(5) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.732 \mathrm{~g} / \mathrm{cm}^{3}$ |
| Absorption coefficient | $1.219 \mathrm{~mm}^{-1}$ |
| Crystal | Prism; deep blue |
| Crystal size | $0.110 \times 0.100 \times 0.050 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.456-27.480^{\circ}$ |
| Index ranges | $-16 \leq h \leq 16,-12 \leq k \leq 12,-20 \leq l \leq 20$ |
| Reflections collected | 24614 |
| Independent reflections | 4397 [ $\left.R_{\text {int }}=0.0195\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.9\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.844 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 4397 / 12 / 337 |


| Goodness-of-fit on $F^{2}$ | 1.066 |
| :--- | :--- |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0221, w R 2=0.0597$ |
| $R$ indices (all data) | $R 1=0.0231, w R 2=0.0604$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.348 and $-0.404 \mathrm{e} \AA^{-3}$ |
| Radiation source (wavelength) | $\mathrm{Mo}-\mathrm{K} \alpha$ |

The neutral complex in compound 28 arises from the coordination of tridentate hexaborate(2-) $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ ligands to a cationic $[\mathrm{Cu}(\mathrm{L}-\mathrm{L})]^{2+}$ centre $\{\mathrm{L}-\mathrm{L}=N, N-\mathrm{dmen}\}$. The 5-coordinate copper(II) centre in 28 has a $\tau$ index of $0.19,{ }^{182}$ demonstrating that its structure is best represented as square-based pyramidal structure. The slightly disordered square-based pyramidal copper(II) centre has a bidentate diamine ligand is within the square plane and the tridentate hexaborate(2-) anion completes the two remaining coordination sites of the square plane and the one axial site (O9). Compound 28 has Cu-N distances of 2.0011(11) $\AA$ (N1) and $2.0478(11) \AA(\mathrm{N} 2)$. The square plane $\mathrm{Cu}-\mathrm{O}$ distances are 2.0052(9) $\AA(\mathrm{O} 8)$ and $1.9566(9) \AA$ (O10), whilst the $\mathrm{Cu}-\mathrm{O}$ axial distance is slightly longer at $2.2481(9) \AA(\mathrm{O} 9)$.

The hexaborate(2-) anion in 28 acts as a tridentate ligand (same as in 24) to the copper(II) centre, with an average $\mathrm{Cu}-\mathrm{O}$ distance $2.070 \AA$, whilst the $N, N,-$ dimethylethylenediamine ligand acts as a bidentate ligand. The copper(II) centre has a coordination number of five and a square based pyramidal geometry (Figure 3.28).

The hexaborate(2-) anion consist of a three fused 6-membered boroxyl rings containing 3 tetrahedral boron centres (B1, B2, B3) and 3 trigonal boron centres (B4, B5, B6) (see Section 3.3.5.3 for more details). The hexaborate(2-) anion in $\mathbf{2 8}$ is structurally similar to other reported hexaborate compounds. ${ }^{135,153,154,184}$ The B-O distances to the tetrahedral B1, B2, B3 centres are in the range of $1.4381(16)-1.5161(16) \AA[\mathrm{av} .1 .472 \AA$ ], 1.4437(17) - $1.5142(16) \AA$ [av. 1.474 $\AA$ ], and $1.4409(16)-1.5199(15) \AA$ [av. $1.470 \AA$ ], respectively and these are significantly longer than those involving the trigonal B4, B5, B6 centres: the B-O distances to B4, B5, and B6 centres are in the range of $1.3582(17)-1.3770(17) \AA$ [av. $1.368 \AA], 1.3561(17)-1.3750(17) \AA$ [av. $1.368 \AA$ ], and $1.3619(17)-1.3756(17) \AA$ [av. $1.367 \AA$ ], respectively. The B-OH bond lengths involving tetrahedral B1, B2, and B3 centres are 1.4818(16), 1.4437(17), and $1.4674(16)$ Å, respectively while B-OH bond lengths involving trigonal B4, B5, and B6 centres are significantly shorter at $1.3713(17), 1.3750(17)$, and $1.3756(17) \AA$, respectively. Bond angles at the tetrahedral centres B1, B2, and B3 range from $107.95(10)^{\circ}-111.18(10)^{\circ}, 106.07(10)^{\circ}-$ $113.30(11)^{\circ}$ and $106.25(10)^{\circ}-112.11(10)^{\circ}$, respectively while the bond angles at the trigonal B4, B5, and B6 centres range from $117.21(12)^{\circ}-122.97(12)^{\circ}, 115.95(12)^{\circ}-123.92(12)^{\circ}$, and
$117.20(12)^{\circ}-122.69(12)^{\circ}$, respectively. The bond lengths and angles are given in Appendix I (Table 19, and Table 20).

In 28 the hexaborate(2-) anion has six potential H-bond donor sites which are also capable of accepting H -bond interactions, and a further seven potential H -bond acceptor sites. The hexaborate(2-) anion in $\mathbf{2 8}$ has fourteen H -bond interactions (six H-bond donors and eight H -bond acceptors), and three coordination to the copper (II) metal. There are no further stabilizing interactions at $\mathrm{O} 1, \mathrm{O} 2$, and O 5 .

Table 3.18 H-bonds [ $\AA$ and ${ }^{\circ}$ ] in 28.

| $D-\mathbf{H} \cdots A$ | $d(D \cdots A)$ | $D-\mathrm{H} \cdots \mathrm{A}$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| O8-H8-O23 ${ }^{\text {i }}$ | 2.8424(13) | O22-H22A-O21 | $2.7745(15)$ |
| O9-H9-O22 ${ }^{\text {ii }}$ | 2.7567(14) | O22-H22B-O24 | $2.7061(15)$ |
| O10-H10-O12 ${ }^{\text {iii }}$ | 2.6839(13) | O23-H23A-O22 | $2.7305(15)$ |
| O11-H11-O24 ${ }^{\text {i }}$ | 2.8009 (14) | O23-H23B-O3ii | $2.8629(13)$ |
| O12-H12-O23 | $2.6816(14)$ | O21-H21A-O3 | 2.8478(14) |
| O13-H13-O2 ${ }^{\text {iv }}$ | $3.1168(13)$ | O21-H21B-O4 ${ }^{\text {2ii }}$ | $2.8749(14)$ |
| O13-H13-O7 ${ }^{\text {iv }}$ | 2.8027(13) | O24-H24A-O21 ${ }^{\text {vi }}$ | $2.7793(15)$ |
| N1-H1A-O6 ${ }^{\text {iii }}$ | 2.9064(14) | O24-H24B-O13 ${ }^{\text {vii }}$ | $2.8025(14)$ |
| N1-H1B-O11 ${ }^{\text {v }}$ | 3.0385(15) |  |  |
| $\begin{aligned} & =+x, 1+y,+z \\ & =1-x, 2-y, 1-z \end{aligned}$ | $\begin{array}{ccc} \text { ii }=1-x, 1-y, 1-z ; & \text { iii }=3 / 2-x, 1 / 2+y, 1 / 2-z ; & \text { iv }=2-x, 2-y, 1-z ; \\ v i=3 / 2-x,-1 / 2+y, 3 / 2-z ; & \text { vii }=2-x, 1-y, 1-z & \end{array}$ |  |  |

All six potential H-bond donor sites in the hexaborate(2-) anion in $\mathbf{2 8}$ are involved in donor interactions: the three coordinated hydroxyl groups H-bond to one hexaborate(2-) (from O 10 ) and two $\mathrm{H}_{2} \mathrm{O}$ molecules (from O 8 and O 9 ), whilst the three uncoordinated hydroxyl groups H-bond to two hexaborate(2-) anions and one $\mathrm{H}_{2} \mathrm{O}$ molecule. Therefore each $[\mathrm{Cu}(N, N-$ dmen) $\left.\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ unit has three other such units in its secondary coordination sphere, facilitated through H -bond interactions. The hexaborate(2-)-hexaborate(2-) interactions (O13$\mathrm{H} 13 \cdots \mathrm{O} 7^{*} / \mathrm{O} 13^{*}-\mathrm{H} 13^{*} \cdots \mathrm{O} 7$ ) in 28 can be designated as reciprocal $\mathrm{R}_{2}^{2}(8)$. The two amino hydrogens on the coordinated nitrogen of the $N, N$-dmen ligand in $\mathbf{2 8}$ are also both involved in H -bonding to neighbouring hexaborate(2-) anions. This results in an unusual reciprocal $\mathrm{R}_{2}{ }^{2}(16)$ $\left\{\mathrm{N} 1-\mathrm{H} 1 \mathrm{~B} \cdots \mathrm{O} 11^{*} / \mathrm{N} 1^{*}-\mathrm{H} 1 \mathrm{~B}^{*} \cdots \mathrm{O} 11\right.$ (Figure 3.29) $\}$ motif in 28 and an unusual $\mathrm{R}_{2}{ }^{2}(10)$ motif in which a neighboring hexaborate(2-) is a double acceptor from donor hydrogen atoms on coordinated O 10 and N 1 atoms $\left\{\mathrm{O} 10^{*}-\mathrm{H} 10^{*} \cdots \mathrm{O} 12 / \mathrm{N}^{*}-\mathrm{H} 1 \mathrm{~A}^{*} \cdots \mathrm{O} 6 ; \mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 12{ }^{*} / \mathrm{N} 1-\right.$ H1A…O6* (Figure 3.30) \}; both motifs includes the copper(II) center within their rings. The hexaborate(2-) anion in 28 is also linked by eight water molecules via eight H-bond interactions $\mathrm{O} 23-\mathrm{H} 23 \mathrm{~B} \cdots \mathrm{O} 3^{*}, ~ \mathrm{O} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O} 3^{*}, \mathrm{O} 21-\mathrm{H} 21 \mathrm{~B} \cdots \mathrm{O} 4^{*}, ~ \mathrm{O} 8^{*}-\mathrm{H} 8^{*} \cdots \mathrm{O} 23, ~ \mathrm{O} 9^{*}-\mathrm{H} 9^{*} \cdots \mathrm{O} 22$,
$\mathrm{O} 11^{*}-\mathrm{H} 11^{*} \cdots \mathrm{O} 24, \mathrm{O} 12^{*}-\mathrm{H} 12^{*} \cdots \mathrm{O} 23$, and $\mathrm{O} 24-\mathrm{H} 24 \mathrm{~B} \cdots \mathrm{O} 13^{*}$. Details of the H -bonding interactions are given in Table 3.18.


Figure 3.29 The reciprocal $\mathrm{R}_{2}{ }^{2}(8)$ and reciprocal $\mathrm{R}_{2}{ }^{2}(16)$ interactions in 28.


Figure 3.30 The two $\mathrm{R}_{2}{ }^{2}(10)$ interactions in 28. Dashed blue lines represent H-bonds.

The $\left[\mathrm{Cu}(N, N-\mathrm{dmen})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]\right.$, and $\mathrm{H}_{2} \mathrm{O}$ molecules of 28 are connected through a complex series of H -bond interactions to produce the three-dimension network linking the hexaborates.

### 3.4 Conclusion and summary

The first aim of this chapter was to prepare and investigate new $\mathrm{Cu}(\mathrm{II})$ polyborate compounds. Nine polyborate compounds 20-28 containing different polyborate anions (triborate(1-), tetraborate(2-), pentaborate(1-), hexaborate(2-), and heptaborate(2-) anions have been templated in aqueous solution from boric acid using a set of sterically demanding $\mathrm{Cu}(\mathrm{II})$ complex cations. Six of these salts have been characterized by single-crystal XRD (20, 22-24, 27-28) studies.

The polyborate anions of compounds $\mathbf{2 0 - 2 8}$ show a number of bands in their IR spectra. The pentaborate(1-) anion of $\mathbf{2 0}$ shows peaks at 1094, 927 , and $776 \mathrm{~cm}^{-1}$, tetraborate(2-) anion in 21 has peaks at 1042, 943, and $806 \mathrm{~cm}^{-1}$, hexaborate(2-) anion in 23 has peaks at 1086, 953, and $809 \mathrm{~cm}^{-1}$, while the heptaborate(2-) anion in 24 has bands at 1134,949 , and $854 \mathrm{~cm}^{-1}$. The higher energy bands may be assigned to asymmetric $\mathrm{B}_{(3)}-\mathrm{O}$ stretching whilst the lower energy peaks may be assigned to symmetric $\mathrm{B}_{(3)}-\mathrm{O}$ and symmetric $\mathrm{B}_{(4)}-\mathrm{O}$, respectively. ${ }^{140}$ These peaks may become diagnostic once more compounds of those class have been prepared.

Thermal properties of the copper(II) complex polyborate compounds were analysed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The analysis of $\mathbf{2 0}$ and 22-28 confirmed the presence of a three-stage decomposition to give anhydrous copper(II) borates. The first mass-loss step is associated with the release of interstitial water molecules. The second stage of decomposition is due to the interionic condensation of polyborate network. The third step is related to the oxidation of the ligands of the copper(II) complex. Compound 21 showed only a two-stage decomposition profile due to the absence of interstitial water molecules.

The second aim was to evaluate the structure directing effects of copper(II) complex cations in solid-state supramolecular structures. Typical structure directing effects encountered in crystal engineering are stoichiometry, steric effects (crystal packing), and interionic interactions.

Anion-anion H -bond interactions have been shown to play a dominant role in non-metal cation pentaborate(1-) chemistry. ${ }^{5}$ Inspection of the crystallographic data outlined in this Chapter show that cation-anion H-bond play a dominant role in the templating of the reported solid-state structures. In particular, the polyborate anions are found within the secondary coordination shell of $\mathbf{2 0}, \mathbf{2 4}$, and $\mathbf{2 7}$ by amino hydrogen H -bonds and these display unusual H bond ring interactions e.g. $\mathrm{R}_{2}{ }^{2}(8)$ involving the copper(II) centre (Figure 3.21). In compounds 22, 23 and 28 the polyborate anion is found within the primary coordination shell and here the hexaborate (2-) anions form 3 dative coordinate bonds to the copper(II) centres, in addition to H -bond interactions to neighbouring complexes.

Reaction of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]^{2+}$ with boric acid in a 1:10 ratio produced a compounds containing the pentaborate(1-) anion (20), while the reaction in 1:5 ratio afforded a compound containing the tetraborate(2-) anion (21). Reaction of $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]^{2+}$ in a 1:5 ratio afforded a tetraborate(2-) salt (26) whereas in a $1: 10$ ratio a compound containing two isolated polyborate anions (triborate(1-) and pentaborate(1-)) was obtained (25). These results show that the products obtained are also dependent upon the reaction stoichiometry.

## Chapter Four

## Nickel(II) complex

 polyborate salts
### 4.1 Introduction

Over the past few years, polyborate anions with nickel(II) complex counter ions have been the focus of relatively few studies within the area of crystal engineering and supramolecular chemistry fields. Salts containing isolated polyborate anions partnered with nickel(II) complex cations are known in the literature but these are limited to $\left[\mathrm{Ni}(\mathrm{en})_{2}\right.$ pip $\left.^{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2},{ }^{181} \quad\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{CH}_{3} \mathrm{CO}_{2},{ }^{136}$ $\left[\mathrm{Ni}(\mathrm{en})_{2}\left(\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{~N}_{2}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2},{ }^{113}$ and $\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O} .{ }^{115}$

In this chapter we report the synthesis and characterisation of eight new polyborate compounds (seven polyborate salts of nickel(II) complex cations and one neutral nickel(II) complex containing the hexaborate(2-) anion). Five of these compounds have been characterised by single-crystal XRD studies: four of these contain either isolated pentaborate(1) anions (three) or isolated heptaborate(2-) anion (one), and one of these, $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, contains the $\left[\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]^{2-}$ anion coordinated as a bidentate ligand via two hydroxyl oxygen centres of the hexaborate(2-) anion.

### 4.2 Aims

The aim of this research was to synthesise and characterise a new series of polyborate compounds containing nickel(II) complex cations. A series of the cationic nickel(II) coordination complexes of ethylenediamine (en), 1,2-diaminopropane (pn), 1,2diaminocyclohexane (dach), diethylenetriamine (dien), triethylenetetramine (trien), 2,4-dimethyl-1-(3-azapropyl)-1,5,8-triazaocta-2,4-dienato (AEN) and $N$-(2-hydroxyethyl) ethylenediamine (hn) ligands were prepared to template formation of the polyborates.

Nickel(II) complex cations were chosen due to their relatively high charge, their sterically bulky structure, and their potential to form many H -bond interactions to moieties within their secondary coordination sphere.

### 4.3 Result and discussion

### 4.3.1 Synthesis of nickel(II) complex compounds

The known nickel(II) complexes: $\left[\mathrm{Ni}(\mathrm{en})_{3}\right] \mathrm{Cl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(\mathbf{2 9}),{ }^{185}[\mathrm{Ni}(\mathrm{AEN})] \mathrm{Cl} \cdot \mathrm{H}_{2} \mathrm{O}(\mathbf{3 0}),{ }^{186}$ $\left[\begin{array}{lllll}\left.\mathrm{Ni} \text { (trans } \text {-dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{Cl}_{2} & (\mathbf{3 1}),{ }^{187} \quad\left[\mathrm{Ni}(\mathrm{hn})_{2}\right] \mathrm{Cl}_{2} & (\mathbf{3 2}),{ }^{188} \quad\left[\mathrm{Ni}(\text { dien })_{2}\right] \mathrm{Cl}_{2} \cdot \mathrm{H}_{2} \mathrm{O} & (\mathbf{3 3}),{ }^{189}\end{array}\right.$
$\left[\mathrm{Ni}(\mathrm{pn})_{3}\right] \mathrm{Cl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(34),{ }^{185}$ and $\left[\mathrm{Ni}_{2}(\text { (trien })_{3}\right] \mathrm{Cl}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}(35),{ }^{190}$ were all prepared by standard literature methods. Physical properties of the prepared complexes were all in accord with literature data.

Compounds 29-35 were all prepared as their chloride salts and it was therefore necessary to convert these chloride salts to the corresponding hydroxide salts before reaction with boric acid. The hydroxide salts were prepared as outlined in Chapter two. The experiment details are given in Chapter 6.

### 4.3.2 Preparation of Nickel(II) complex polyborate compounds

A series of nickel(II) complex polyborate compounds 36, 38-43 have been prepared as crystalline solids from nickel(II) complex hydroxides. Boric acid was added in a ratio of 1:10 to the hydroxide solutions. The solutions were then stirred, concentrated using a rotary evaporator and cooled to yield polyborate compounds as solid crude products (36,38-43). The crude products were isolated by filtration and dried.

Compound 37 was prepared by mixing ethylenediamine, nickel(II) sulphate hexahydrate and barium hydroxide octahydrate in water. The mixture was stirred and then filtered to remove the barium sulphate which had formed. Boric acid was added to the filtrate with stirring. Followed by work up as outlined above.

Crystals suitable for single-crystal X-ray diffraction studies of the nickel(II) complex polyborate compounds were prepared by recrystallization of the crude products from distilled water. The recrystallized products were isolated by slow evaporation from aqueous solution or by vapour diffusion from aqueous solution using ethanol and/or methanol.

Seven new nickel(II) complex polyborate compounds (37-43) were prepared. Characterisation data reported for the previously prepared 36 is limited to ${ }^{11} \mathrm{~B}$ NMR, p-XRD, and magnetic properties. ${ }^{115}$ This compound was re-synthesised by a new method. Spectroscopic data for this compound is discussed in the next sections and are reported in the experimental chapter. The recrystallized yields of the nickel(II) complex polyborate compounds (36-43) and their formula are shown in Table 4.1.

Table 4.1 Yields and formula of nickel(II) complex polyborate compounds.

| Compound | Formula | \% Yeeld |
| :---: | :--- | :---: |
| $\mathbf{3 6}$ | $\left[\mathrm{Ni}(\text { en })_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | 63 |
| $\mathbf{3 7}$ | $\left.\left[\mathrm{Ni}(\mathrm{en})^{2} \mathrm{~B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ | 33 |
| $\mathbf{3 8}$ | $[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ | 38 |
| $\mathbf{3 9}$ | $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Ni}(\text { dach })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ | 47 |
| $\mathbf{4 0}$ | $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}$ | 37 |
| $\mathbf{4 1}$ | $s-f a c-\left[\mathrm{Ni}\left(\mathrm{Nien}_{6}\right)_{2}\right]\left[\mathrm{B} 5 \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}$ | 34 |
| $\mathbf{4 2}$ | $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ | 47 |
| $\mathbf{4 3}$ | $\left[\mathrm{Ni} 2(\text { trien })_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}_{2} \cdot \mathrm{CH}_{3} \mathrm{OH} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ | 28 |

### 4.3.3 Characterisation of nickel(II) complex polyborate compounds

The nickel(II) complexes and their polyborate compounds are generally paramagnetic with exception of $\mathbf{3 0}$ and $\mathbf{3 8}$ which are diamagnetic. The mass susceptibility $\left(\chi_{\mathrm{g}}\right)$, molar susceptibility $\left(\chi_{\mathrm{m}}\right)$, diamagnetic susceptibility ( $\chi_{\mathrm{d}}$ ), paramagnetic susceptibility ( $\chi_{\mathrm{p}}$ ), and effective magnetic moment ( $\mu_{\text {eff }}$ ) of compounds 29-43 are shown in Table 4.2. There is no significant diagnostic change between the magnetic properties of the starting nickel(II) complexes and their polyborate compounds. The experimentally determined effective magnetic moment values are very close to those calculated using the 'spin-only' formula for square planar ( $\mathbf{3 0}$ and 38) or octahedral ( $\mathbf{2 9}, \mathbf{3 1 - 3 7}, \mathbf{3 9 - 4 3 )}$ complexes. The $\mu_{\text {eff }}$ values of $\mathrm{Ni}(\mathrm{II})$ complexes and their polyborate compounds are in agreement with literature data for other $\mathrm{Ni}(\mathrm{II})$ complexes. ${ }^{180,191}$

Table 4.2 Magnetic properties of nickel(II) complexes and their polyborate compounds at 24 ${ }^{\circ} \mathrm{C}$.

| Compo <br> und | $\chi_{\mathrm{g}}$ <br> $\left(\mathrm{cm}^{3} \cdot \mathrm{~g}^{-1}\right)$ | $\chi_{\mathrm{m}}$ <br> $\left(\mathrm{cm}^{3} \cdot \mathrm{~mol}^{-1}\right)$ | $\chi_{\mathrm{d}}$ | $\chi_{\mathrm{p}}$ | $\mu_{\text {eff }}$ <br> Bohr <br> magneton | N |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{2 9}$ | $9.8 \times 10^{-6}$ | $3390 \times 10^{-6}$ | $-170 \times 10^{-6}$ | $3563 \times 10^{-6}$ | 2.91 | 2.08 |
| $\mathbf{3 0}$ | $-0.2 \times 10^{-6}$ | $-56 \times 10^{-6}$ | - | - | - | - |
| $\mathbf{3 1}$ | $7.7 \times 10^{-6}$ | $3040 \times 10^{-6}$ | $-190 \times 10^{-6}$ | $3237 \times 10^{-6}$ | 2.77 | 1.96 |
| $\mathbf{3 2}$ | $9.5 \times 10^{-6}$ | $3200 \times 10^{-6}$ | $-168 \times 10^{-6}$ | $3368 \times 10^{-6}$ | 2.82 | 2.00 |
| $\mathbf{3 3}$ | $7.9 \times 10^{-6}$ | $2790 \times 10^{-6}$ | $-177 \times 10^{-6}$ | $2967 \times 10^{-6}$ | 2.65 | 1.83 |
| $\mathbf{3 4}$ | $7.7 \times 10^{-6}$ | $3010 \times 10^{-6}$ | $-194 \times 10^{-6}$ | $3204 \times 10^{-6}$ | 2.76 | 1.94 |
| $\mathbf{3 5}$ | $3.9 \times 10^{-6}$ | $2906 \times 10^{-6}$ | $-366 \times 10^{-6}$ | $3269 \times 10^{-6}$ | 2.78 | 1.95 |
| $\mathbf{3 6}$ | $4.0 \times 10^{-6}$ | $2844 \times 10^{-6}$ | $-355 \times 10^{-6}$ | $3199 \times 10^{-6}$ | 2.75 | 1.94 |
| $\mathbf{3 7}$ | $5.7 \times 10^{-6}$ | $2588 \times 10^{-6}$ | $-225 \times 10^{-6}$ | $2813 \times 10^{-6}$ | 2.58 | 1.81 |
| $\mathbf{3 8}$ | $-0.4 \times 10^{-6}$ | $-170 \times 10^{-6}$ | - | - | - | - |
| $\mathbf{3 9}$ | $2.3 \times 10^{-6}$ | $3030 \times 10^{-6}$ | $-645 \times 10^{-6}$ | $3675 \times 10^{-6}$ | 2.95 | 2.11 |
| $\mathbf{4 0}$ | $4.8 \times 10^{-6}$ | $3430 \times 10^{-6}$ | $-350 \times 10^{-6}$ | $3780 \times 10^{-6}$ | 2.99 | 2.14 |


| $\mathbf{4 1}$ | $5.0 \times 10^{-6}$ | $3516 \times 10^{-6}$ | $-350 \times 10^{-6}$ | $3856 \times 10^{-6}$ | 3.02 | 2.18 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{4 2}$ | $3.3 \times 10^{-6}$ | $2810 \times 10^{-6}$ | $-426 \times 10^{-6}$ | $3236 \times 10^{-6}$ | 2.76 | 1.94 |
| $\mathbf{4 3}$ | $2.6 \times 10^{-6}$ | $3125 \times 10^{-6}$ | $-601 \times 10^{-6}$ | $3721 \times 10^{-6}$ | 2.97 | 2.12 |

The elemental analysis data of the new nickel(II) complex polyborate compounds (37$43)$ and the starting nickel(II) complexes $(\mathbf{3 0}, \mathbf{3 4}, \mathbf{3 5})$ are listed in Table 4.3. Elemental analysis data of the nickel(II) complex polyborate compounds were consistent with their formulation.

Table 4.3 CHN analysis of nickel(II) complex polyborate compounds.

| Compound | Calculated (\%) |  |  | Experimental (\%) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | C | H | N | C | H | N |
| $\mathbf{3 0}$ | 36.5 | 7.1 | 18.9 | 37.1 | 6.7 | 18.8 |
| $\mathbf{3 4}$ | 27.9 | 8.8 | 21.7 | 28.1 | 8.9 | 21.7 |
| $\mathbf{3 5}$ | 29.5 | 8.0 | 22.9 | 29.6 | 8.1 | 22.4 |
| $\mathbf{3 7}$ | 5.3 | 4.5 | 6.2 | 5.4 | 4.5 | 6.2 |
| $\mathbf{3 8}$ | 22.6 | 5.3 | 11.7 | 22.7 | 5.4 | 11.7 |
| $\mathbf{3 9}$ | 22.3 | 6.1 | 8.7 | 21.8 | 6.3 | 8.4 |
| $\mathbf{4 0}$ | 13.7 | 4.6 | 8.0 | 13.7 | 4.7 | 8.0 |
| $\mathbf{4 1}$ | 13.7 | 4.9 | 12.0 | 14.0 | 5.4 | 12.1 |
| $\mathbf{4 2}$ | 15.5 | 6.3 | 9.9 | 15.5 | 6.6 | 10.0 |
| $\mathbf{4 3}$ | 19.0 | 6.5 | 14.0 | 18.9 | 6.3 | 13.7 |

The chemical shift ( $\delta$ ) of ${ }^{11} \mathrm{~B}$ NMR spectra of nickel(II) complex polyborate salts obtained in $\mathrm{D}_{2} \mathrm{O}$ are listed in Table 4.4. ${ }^{11}$ B NMR spectroscopy of nickel(II) complex polyborate compounds showed that the pentaborate salts $(\mathbf{4 0}-\mathbf{4 2}, 43)$ contained the characteristic three peaks. ${ }^{149-151}$ These peaks correspond to the $\mathrm{B}(\mathrm{OH})_{3} / \mathrm{B}(\mathrm{OH})_{4}{ }^{-}, \quad\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right]^{-}$and the four coordinate centre of the $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion (for more details see Section 2.3.3), whilst the pentaborate(1-) salts $\mathbf{3 6}$ and $\mathbf{3 8}$ show two signals and only one signal, respectively. ${ }^{11} \mathrm{~B}$ NMR spectra of the hexaborate (37) and heptaborate (39) compounds are quantitatively different from the spectra observed in the pentaborate salts with only one (averaged and exchanging) signal observed. The observed chemical shift for the hexaborate(2-) complex (37) is similar to that observed for hexaborate(2-) copper(II) complex salts $(\mathbf{2 3}, 28)$ described in Section 3.3.3. Likewise, the observed chemical shift for the heptaborate(2-) nickel(II) complex compound (39) is comparable to that of the copper(II) complex heptaborate salt (24) described in Section 3.3.3.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were not obtained due to the paramagnetic properties of the $\mathrm{Ni}^{2+}$ cations. However, compound 38 was diamagnetic and ${ }^{1} \mathrm{H}$ NMR: 2, 2.5, 3.2, and 4.8 ppm , ${ }^{13}$ C NMR: $19.9,43,53.6$, and 160.5 ppm . These data agree with reported literature data of the cation. ${ }^{186}$

Table 4.4 The chemical shift ( $\delta$ ) of ${ }^{11}$ B NMR spectra of nickel(II) complex polyborate compounds.

| Compound | ${ }^{11} \mathrm{~B} / \mathrm{ppm}$ |
| :---: | :---: |
| $\mathbf{3 6}$ | $13.4(16 \%), 16.1(84 \%)$ |
| $\mathbf{3 7}$ | 17.7 |
| $\mathbf{3 8}$ | 16.3 |
| $\mathbf{3 9}$ | 15.8 |
| $\mathbf{4 0}$ | $1.2(3 \%), 13.4(23 \%), 18.0(74 \%)$ |
| $\mathbf{4 1}$ | $1.5(1 \%), 13.3(13 \%), 17.4(86 \%)$ |
| $\mathbf{4 2}$ | $1.5(2 \%), 13.8(20 \%), 16.8(78 \%)$ |
| $\mathbf{4 3}$ | $1.2(3 \%), 13.8(30 \%), 16.5(67 \%)$ |

Infra-red spectroscopic investigation confirmed that the nickel(II) complex salts contained polyborate anions. The FT-IR data for B-O stretches for compounds 36-43 (Table 4.5) have been assigned by comparison with data of Jun et al. ${ }^{140}$ for related polyborate anions.

Table 4.5 Selected FT-IR spectroscopic data for nickel(II) polyborate compounds.

| Comp. | $\begin{aligned} & \hline \mathrm{v}(\mathrm{O}-\mathrm{H}), \\ & \mathrm{v}(\mathrm{~N}-\mathrm{H}) \end{aligned}$ | $v$ C-H) | $\begin{gathered} v_{\mathrm{as}} \\ \left(\mathrm{~B}_{(3)}-\mathrm{O}\right) \\ \hline \end{gathered}$ | $\begin{gathered} \delta \\ (\mathrm{B}-\mathrm{O}-\mathrm{H}) \\ \hline \end{gathered}$ | $\begin{gathered} v_{\text {as }} \\ \left(\mathrm{B}_{(4)}-\mathrm{O}\right) \\ \hline \end{gathered}$ | $\begin{gathered} v_{\mathrm{s}} \\ \left(\mathrm{~B}_{(3)}-\mathrm{O}\right) \end{gathered}$ | $\begin{gathered} v_{\mathrm{s}} \\ \left(\mathrm{~B}_{(4)}-\mathrm{O}\right) \end{gathered}$ | $\begin{gathered} \gamma \\ \left(\mathrm{B}_{(3)}-\mathrm{O}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 36 | $\begin{aligned} & 3344(\mathrm{~s}), \\ & 3297(\mathrm{~s}) \end{aligned}$ | 2947(w) | $\begin{aligned} & \text { 1407(s) } \\ & 1315(\mathrm{~s}) \end{aligned}$ | 1168(m) | 1026(s) | 921(s) | $\begin{gathered} 851 \mathrm{w} \\ 775(\mathrm{~m}) \\ \hline \end{gathered}$ | 706(w) |
| 37 | $\begin{aligned} & 3400(\mathrm{~s}), \\ & 3350(\mathrm{~s}) \end{aligned}$ | $\begin{aligned} & \hline \text { 2924(w), } \\ & \text { 2854(w) } \\ & \hline \end{aligned}$ | $\begin{gathered} \hline 1420(\mathrm{~m}), \\ 1380(\mathrm{~s}) \\ \hline \end{gathered}$ | 1133(s) | 1044(s) | 955(m) | $\begin{gathered} \hline 852(\mathrm{w}), \\ 809(\mathrm{~s}) \\ \hline \end{gathered}$ | 696(w) |
| 38 | $\begin{aligned} & 3377(\mathrm{~s}), \\ & 3326(\mathrm{~s}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { 2983(w), } \\ & 2963(\mathrm{w}) \end{aligned}$ | $\begin{aligned} & \text { 1416(s), } \\ & 1393(\mathrm{~s}) \end{aligned}$ | 1129(m) | 1019(m) | 924(s) | $\begin{aligned} & \hline 820(\mathrm{w}), \\ & 778(\mathrm{~m}) \\ & \hline \end{aligned}$ | 708(w) |
| 39 | $\begin{aligned} & \hline 3663(\mathrm{~s}), \\ & 3271(\mathrm{~s}) \\ & \hline \end{aligned}$ | $\begin{aligned} & 2929(\mathrm{~m}), \\ & 2863(\mathrm{~m}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { 1453(s), } \\ & 1350(\mathrm{~s}) \\ & \hline \end{aligned}$ | 1180(s) | 1066(s) | 948(w) | $\begin{aligned} & \hline 854(\mathrm{~m}), \\ & 807(\mathrm{~m}) \\ & \hline \end{aligned}$ | 716(w) |
| 40 | $\begin{aligned} & \hline 3375(\mathrm{~s}), \\ & 3288(\mathrm{~s}) \end{aligned}$ | 2962(w) | $\begin{aligned} & \text { 1410(s), } \\ & 1321(\mathrm{~s}) \end{aligned}$ | 1141(s) | 1022(s) | 919(s) | $\begin{gathered} \hline 846(\mathrm{w}), \\ 774(\mathrm{~s}) \\ \hline \end{gathered}$ | 706(s) |
| 41 | $\begin{aligned} & 3333(\mathrm{~s}), \\ & 3297(\mathrm{~s}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { 2988(w), } \\ & 2950(\mathrm{w}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { 1412(s), } \\ & 1330(\mathrm{~s}) \\ & \hline \end{aligned}$ | 1135(m) | 1042(m) | 915(s) | $\begin{gathered} 809(\mathrm{w}), \\ 774(\mathrm{~s}) \\ \hline \end{gathered}$ | 707(s) |
| 42 | $\begin{aligned} & \hline 3336(\mathrm{~s}), \\ & 3235(\mathrm{~s}) \\ & \hline \end{aligned}$ | 2974(w) | $\begin{gathered} \hline 1434(\mathrm{~s}), \\ 1305(\mathrm{~s}) \end{gathered}$ | 1156(s) | 1044(s) | 916(s) | $\begin{gathered} \hline 820(\mathrm{w}), \\ 777(\mathrm{~s}) \\ \hline \end{gathered}$ | 708(m) |
| 43 | $\begin{aligned} & 3290(\mathrm{~s}), \\ & 3238(\mathrm{~s}) \end{aligned}$ | 2951(w) | $\begin{aligned} & \text { 1410(s), } \\ & 1313(\mathrm{~s}) \end{aligned}$ | 1163(m) | 1057(m) | 920(s) | $\begin{aligned} & \hline 822(\mathrm{w}), \\ & 773(\mathrm{~m}) \\ & \hline \end{aligned}$ | 705(m) |

$\mathrm{b}=$ broad, $\mathrm{m}=$ middle, $\mathrm{s}=$ strong, $\mathrm{w}=$ weak, $\mathrm{sh}=$ shoulder, $\mathrm{B}_{(3)}=$ three coordinate boron, $\mathrm{B}_{(4)}=$ four coordinate boron, $\mathrm{v}=$ stretching frequency, $v_{s}=$ symmetrical stretching frequency, $v_{a s}=$ asymmetrical stretching frequency, $\delta=$ bending frequency.

### 4.3.4 Thermal properties of nickel(II) complex polyborate compounds

TGA and DSC analysis were used to investigate the thermal properties of the nickel(II) complex polyborate compounds. Samples were heated in an alumina $\left(\mathrm{Al}_{2} \mathrm{O}_{3}\right)$ crucible at a temperature ramp rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ between $25-800^{\circ} \mathrm{C}$ under a flow air ( $100 \mathrm{~mL} / \mathrm{min}$.). The thermal dissociation stages of compounds 36-43 are described in Table 4.6. The new polyborate compounds 36-39, $\mathbf{4 2}$ and $\mathbf{4 3}$ followed the expected multi pathway step for decomposition (for more details see Section 2.3.4), with observed mass loss agreeing with the calculated values. Compounds 40 and 41 showed fewer mass-loss steps (Figure 4.1 and Figure 4.2).

All the dehydration processes are endothermic while the complex cation oxidation processes are exothermic and occur at higher temperatures. All the nickel(II) complex polyborate compounds $\mathbf{3 6 - 4 3}$ followed the expected path of decomposition to the residual anhydrous metal borates, with observed mass losses agreeing with calculated values. The thermal behaviour of these compounds were in accord with published data describing thermal decomposition of other related transition metal complex polyborates. ${ }^{113}$

Table 4.6 TGA data for nickel(II) polyborate compounds 36-43.*

| Comp. | $\begin{aligned} & \hline \text { Step } \\ & \text { No. } \\ & \hline \end{aligned}$ | The thermal reactions | Temp. Range ${ }^{\circ} \mathrm{C}$ | $\begin{gathered} \hline \hline \text { Expt } \\ (\%) \end{gathered}$ | $\begin{gathered} \hline \hline \text { Calc. } \\ (\%) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 36 | 1 | $\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}+2 \mathrm{H}_{2} \mathrm{O}$ | 70-180 | 4.9 | 5.1 |
|  | 2 | $\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \rightarrow\left[\mathrm{Ni}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+4 \mathrm{H}_{2} \mathrm{O}$ | 180-280 | 15.0 | 15.2 |
|  | 3 | $\left[\mathrm{Ni}(\text { en })_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{NiB}_{10} \mathrm{O}_{16}+$ volatile oxidation products | 280-800 | 38.1 | 40.6 |
|  |  | Residue $\mathrm{NiB}_{10} \mathrm{O}_{16}$ |  | 61.9 | 59.4 |
| 37 | 1 | $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]+3 \mathrm{H}_{2} \mathrm{O}$ | 100-180 | 10.8 | 12.0 |
|  | 2 | $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH}) 6\right\}\right] \rightarrow[\mathrm{Ni}(\mathrm{en})]\left[\mathrm{B}_{6} \mathrm{O}_{10}\right]$ | 180-280 | 24.3 | 23.9 |
|  | 3 | [ $\mathrm{Ni}(\mathrm{en}$ ) $]\left[\mathrm{B}_{6} \mathrm{O}_{10}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{NiB}_{6} \mathrm{O}_{10}+$ volatile oxidation products | 280-700 | 38.6 | 37.2 |
|  |  | Residue $\mathrm{NiB}_{6} \mathrm{O}_{10}$ |  | 61.4 | 62.8 |
| 38 | 1 | $[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O} \rightarrow[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]+\mathrm{H}_{2} \mathrm{O}$ | 100-180 | 2.5 | 3.7 |
|  | 2 | $[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH}) 4\right] \rightarrow[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{8}\right]+2 \mathrm{H}_{2} \mathrm{O}$ | 180-280 | 10.0 | 11.3 |
|  | 3 | $[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{8}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{NiB}_{5} \mathrm{O}_{8}+$ volatile oxidation products | 280-700 | 46.1 | 48.0 |
|  |  | Residue $\mathrm{NiB}_{5} \mathrm{O}_{8}$ |  | 53.9 | 52.0 |
| 39 | 1 | $\begin{aligned} & \hline\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Ni}(\text { dach })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Ni}(\text { dach })_{2}\right]_{2} \\ & {\left[\mathrm{~B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2}+6 \mathrm{H}_{2} \mathrm{O}} \end{aligned}$ | 100-190 | 7.5 | 8.4 |
|  | 2 | $\left[\mathrm{Ni}(\text { dach })_{2}\right]_{2}\left[\mathrm{~B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2}+6 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Ni}(\text { dach })_{2}\right]_{2}\left[\mathrm{~B}_{14} \mathrm{O}_{23}\right]+5 \mathrm{H}_{2} \mathrm{O}$ | 190-270 | 15.0 | 15.3 |
|  | 3 | $\left[\mathrm{Ni}(\text { dach })_{2}\right]_{2}\left[\mathrm{~B}_{14} \mathrm{O}_{23}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{Ni}_{2} \mathrm{~B}_{14} \mathrm{O}_{23}+$ volatile oxidation products | 270-720 | 48.2 | 50.7 |
|  |  | Residue $\mathrm{Ni}_{2} \mathrm{~B}_{14} \mathrm{O}_{23}$ |  | 51.8 | 49.3 |
| 40 | 1 | $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \rightarrow\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+4 \mathrm{H}_{2} \mathrm{O}$ | 230-290 | 10.3 | 10.2 |
|  | 2 | [ $\left.\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{NiB}_{10} \mathrm{O}_{16}+$ volatile oxidation products | 290-700 | 37.9 | 39.9 |
|  |  | Residue $\mathrm{NiB}_{10} \mathrm{O}_{16}$ |  | 62.1 | 60.1 |
| 41 | 1 | $\left[\mathrm{Ni}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \rightarrow\left[\mathrm{Ni}(\text { dien })_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+4 \mathrm{H}_{2} \mathrm{O}$ | 100-200 | 14.9 | 10.2 |
|  | 2 | $\left[\mathrm{Ni}(\text { dien })_{2}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{NiB}_{10} \mathrm{O}_{16}+$ volatile oxidation products | 200-650 | 40.3 | 39.7 |
|  |  | Residue $\mathrm{NiB}_{10} \mathrm{O}_{16}$ |  | 59.7 | 60.3 |
| 42 | 1 | $\begin{aligned} & \left.\hline \hline \mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \cdot 5 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}+ \\ & 5 \mathrm{H}_{2} \mathrm{O}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \end{aligned}$ | 100-160 | 17.0 | 16.0 |


|  | 2 | $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \rightarrow\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+4 \mathrm{H}_{2} \mathrm{O}$ | 160-260 | 23.4 | 24.3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 3 | $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right]+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{NiB}_{10} \mathrm{O}_{16}+$ volatile oxidation products | 260-900 | 48.8 | 50.5 |
|  |  | Residue $\mathrm{NiB}_{10} \mathrm{O}_{16}$ |  | 51.2 | 49.5 |
| 43 | 1 | $\begin{aligned} & \hline\left[\mathrm{Ni}_{2}(\text { trien })_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{Cl}_{2} \cdot \mathrm{CH}_{3} \mathrm{OH} \cdot 6 \mathrm{H}_{2} \mathrm{O} \rightarrow\left[\mathrm{Ni}_{2}(\text { trien })_{3}\right] \\ & {\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{Cl}_{2}+\mathrm{CH}_{3} \mathrm{OH}+6 \mathrm{H}_{2} \mathrm{O}} \end{aligned}$ | 100-160 | 10.2 | 11.6 |
|  | 2 | $\left[\mathrm{Ni}_{2}(\text { (trien })_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{Cl}_{2} \rightarrow\left[\mathrm{Ni}_{2}(\text { (trien })_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \cdot \mathrm{Cl}_{2}+4 \mathrm{H}_{2} \mathrm{O}$ | 160-240 | 17.9 | 17.6 |
|  | 3 | $\left[\mathrm{Ni}_{2}(\text { (trien })_{3}\right]\left[\mathrm{B}_{10} \mathrm{O}_{16}\right] \cdot \mathrm{Cl}_{2}+$ excess $\mathrm{O}_{2} \rightarrow \mathrm{Ni}_{2} \mathrm{~B}_{10} \mathrm{O}_{16} \mathrm{Cl}_{2}+$ volatile oxidation products | 240-700 | 54.9 | 54.1 |
|  |  | Residue $\mathrm{Ni}_{2} \mathrm{~B}_{10} \mathrm{O}_{16} \mathrm{Cl}_{2}$ |  | 45.2 | 46.0 |

Calculated values and experimental values are given as totals relative to $100 \%$, and include the process described and earlier mass loss process.


Figure 4.1 TGA diagram for the thermal decomposition of nickel(II) complex polyborate compounds 36-39.


Figure 4.2 TGA diagram for the thermal decomposition of nickel(II) complex polyborate compounds 40-43.

### 4.3.5 Structural characterisation of nickel(II) complex polyborate compounds

### 4.3.5.1 Structural characterisation of $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}(37)$

Crystallographic data for $\mathbf{3 7}$ are listed in Table 4.7. Crystals of $\mathbf{3 7}$ are triclinic, $P-1$ and the compound consists of an uncharged transition metal complex $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right]$ and one interstitial water molecule as shown in Figure 4.3.


Figure 4.3 Diagram showing the 37 and the adopted numbering scheme. Colour code (used throughout this chapter): green ( Ni ), blue ( N ), red ( O ), pink (B), dark grey (C) and light grey (H).

Table 4.7 Crystal data and structure refinement of $\mathbf{3 7}$.

| Empirical formula | $\mathrm{C}_{2} \mathrm{H}_{20} \mathrm{~B}_{6} \mathrm{~N}_{2} \mathrm{O}_{16} \mathrm{Ni}$ |
| :--- | :--- |
| Formula weight | 451.77 |
| Temperature | $100(2) \mathrm{K}$ |
| Wavelength | $0.71073 \AA$ |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a=8.5116(7) \AA \quad \alpha \quad \alpha=89.873(5)^{\circ}$ |
|  | $b=9.7946(5) \AA \quad \beta=82.902(7)^{\circ}$ |
|  | $c=9.8073(8) \AA \quad \gamma=74.372(6)^{\circ}$ |
| Volume | $780.93(10) \AA^{3}$ |
| $Z$ | 2 |
| Density (calculated) | $1.921 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.333 \mathrm{~mm}{ }^{-1}$ |
| Crystal | light blue, blade |
| Crystal size | $0.130 \times 0.030 \times 0.015 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.094-27.572^{\circ}$ |
| Reflections used | 5320 |
| Independent reflections | 5883 |
| Completeness to $\theta=25.242^{\circ}$ | $99.9 \%$ |
| Absorption correction | Semi-empirical from equivalents |


| Max. and min. transmission | 1.000 and 0.886 |
| :--- | :--- |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | $5883 / 289 / 291$ |
| Goodness-of-fit on $F^{2}$ | 1.027 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0682, w R 2=0.1838$ |
| $R$ indices (all data) | $R 1=0.0745, w R 2=0.1906$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 1.876 and $-0.864 \mathrm{e} \AA^{-3}$ |
| Radiation source (wavelength) | $\mathrm{Mo}-\mathrm{K} \alpha$ |

The majority of synthesised and characterised borate salts to date are pentaborates, whereas, fewer hexaborate(2-) anion compounds are known. ${ }^{135,153,154,183,184}$ The hexaborate(2-) anion in $\mathbf{3 7}$ acts as a bidentate ligand to the $\left[\mathrm{Ni}(\mathrm{en})\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ centre, trans to the bidentate ethylenediamine ligand. The nickel(II) centre has a coordination number of six and a distorted octahedral geometry (Figure 4.3), with the two remaining ligands water molecules mutually trans. Compound $\mathbf{3 7}$ has $\mathrm{Ni}-\mathrm{N}$ distances of $2.086(4) \AA(\mathrm{N} 1)$ and $2.085(4) \AA(\mathrm{N} 2)$. The square plane Ni-O distances to hexaborate(2-) anion are 2.065(3) $\AA(\mathrm{O} 8)$ and $2.065(3) \AA(\mathrm{O} 9)$, whilst the $\mathrm{Ni}-\mathrm{O}$ axial distances to water molecules are 2.096(3) $\AA(\mathrm{O} 21)$ and $2.082(3) \AA(\mathrm{O} 22)$.

The hexaborate(2-) anion possess three fused six-membered rings with three tetrahedral $\mathrm{BO}_{4}$ centres and three trigonal $\mathrm{BO}_{3}$ centres (see Section 3.3.5.3 for more details). The B-O distances to the four-coordinate tetrahedral B1, B2, B3 centres are $1.460(6)-1.498(6) \AA$, $1.441(6)-1.515(6) \AA$, and $1.439(6)-1.538(6) \AA$, respectively, and these are significantly longer than those involving the trigonal B4, B5, B6 centres. The B-O distances to B4, B5, and B6 centres are $1.327(6)-1.391(7) \AA, 1.360(7)-1.367(7) \AA$, and $1.365(6)-1.370(7) \AA$, respectively. The B-OH bonds involving tetrahedral B1, B2, and B3 centres are 1.468(6), 1.470(6), and 1.455(6) A, respectively while the B-OH bonds involving trigonal B4, B5, and B6 centres are significantly shorter at 1.327(6), 1.367(7), and 1.370(7) A., respectively. Bond angles at the tetrahedral centres B1, B2, and B3 range from $108.9(4)^{\circ}-111.2(4)^{\circ}, 106.3(4)^{\circ}-$ $112.2(4)^{\circ}$, and $108.1(4)^{\circ}-111.7(4)^{\circ}$, respectively while the bond angles at the trigonal B4, B5, and B6 centres are $118.6(4)^{\circ}-122.1(5)^{\circ}, 114.8(5)^{\circ}-122.9(5)^{\circ}$, and $117.8(5)^{\circ}-122.2(5)^{\circ}$, respectively. The bond lengths and angles are listed in Appendix I (Table 21, and Table 22).

In 37 the hexaborate(2-) anion has six potential H-bond donor sites and thirteen potential H -bond acceptor sites. The hexaborate(2-) anion in 37 has twenty two H -bond interactions (six H -bond donor and sixteen H -bond acceptor), and two coordination bonds to the nickel metal. Surprisingly, the potential acceptor atoms O 1 and O 5 are not involved in any H -bond interactions.

Table 4.8 H-bonds [ $\AA$ and ${ }^{\circ}$ ] in 37.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| O8-H8 $\cdots{ }^{\text {a }}{ }^{\text {i }}$ | $2.786(5)$ | O22-H22A $\cdots{ }^{\text {a }}{ }^{\text {ii }}$ | 2.724(5) |
| O9-H9...O3ii | $2.831(5)$ | $\mathrm{O} 22-\mathrm{H} 22 \mathrm{~B} \cdots{ }^{\text {a }}{ }^{\text {i }}$ | $2.744(5)$ |
| O10-H10 $\cdots$ O8 | $3.227(5)$ | N1-H1AA $\cdots{ }^{\text {2 }}{ }^{\text {i }}$ | 3.017(5) |
| O10-H10.. ${ }^{2} 21$ | $2.704(5)$ | N1-H1BC $\cdots{ }^{\text {O }}{ }^{\text {i }}$ | $3.171(5)$ |
| O11-H11 $\cdots$ O10 ${ }^{\text {iii }}$ | $2.805(5)$ | N1-H1BD $\cdots$ O31B | 2.993(12) |
| O12-H12 $\cdots \mathrm{O}^{\text {iv }}$ | $2.799(6)$ | N2-H2AA $\cdots$ O10 ${ }^{\text {vii }}$ | 3.281(6) |
| O13-H13A $\cdots{ }^{\text {O }}$ 12 ${ }^{\text {v }}$ | 2.960 (5) | $\mathrm{N} 2-\mathrm{H} 2 \mathrm{AB} \cdots \mathrm{O} 4{ }^{\text {iii }}$ | 3.189(6) |
| O13-H13 $\cdots$ O13 ${ }^{\text {vi }}$ | 2.684(9) | N2-H2BD $\cdots{ }^{\text {O }}{ }^{\text {ii }}$ | $2.997(5)$ |
| O21-H21A $\cdots$ O31 | 2.871(9) | O31-H31A $\cdots$ O11 ${ }^{\text {i }}$ | $2.715(9)$ |
| O21-H21A $\cdots$ O31B | 2.841(8) | O31-H31A $\cdots$ O31 ${ }^{\text {viii }}$ | 3.01(3) |
| O21-H21B $\cdots{ }^{\text {O }}{ }^{\text {vii }}$ | $3.087(5)$ | O31-H31B $\cdots$ O11 ${ }^{\text {ix }}$ | 2.993(13) |
| O21-H21B $\cdots \mathrm{O}^{\text {dii }}$ | $2.807(5)$ | O31B-H31C $\cdots$ O11 ${ }^{\text {i }}$ | 2.812(9) |

The H-bond interactions in 37 are complicated due to the presence of additional coordinated and uncoordinated water molecules and the NH centres of the ethylenediamine ligand, and H-atom disorders. These interactions may be described as eight reciprocal connections \{two $\mathrm{R}_{2}^{2}(8)$, five $\mathrm{R}_{2}{ }^{2}(12)$, and one unusual $\left.\mathrm{R}_{2}{ }^{2}(16)\right\}$, two $\mathrm{C}(8)$ connections, and one D (dimer) interaction. The two reciprocal $\mathrm{R}_{2}{ }^{2}(8)$ interactions are $\mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O} 2^{*} / \mathrm{O} 8^{*}-$ $\mathrm{H} 8 * \cdots \mathrm{O} 2$ and $\mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O} 3^{*} / \mathrm{O} 9^{*}-\mathrm{H} 9^{*} \cdots \mathrm{O} 3$. As an example, one of the two $\mathrm{R}_{2}{ }^{2}(8)$ interactions is illustrated in Figure 4.4. The five reciprocal $\mathrm{R}_{2}{ }^{2}(12)$ interactions are $\mathrm{N} 1-\mathrm{H} 1 \mathrm{AA} \cdots \mathrm{O} 2^{*} / \mathrm{N} 1^{*}-$ H1AA ${ }^{*} \cdots \mathrm{O} 2$, O22-H22B $\cdots \mathrm{O}^{*} / \mathrm{O} 22^{*}-\mathrm{H} 22 \mathrm{~B}^{*} \cdots \mathrm{O} 7, ~ \mathrm{O} 12-\mathrm{H} 12 \cdots \mathrm{O} 6^{*} / \mathrm{O} 12^{*}-\mathrm{H} 12^{*} \cdots \mathrm{O} 6$, O22$\mathrm{H} 22 \mathrm{~A} \cdots \mathrm{O} 4^{*} / \mathrm{O} 22^{*}-\mathrm{H} 22 \mathrm{~A}^{*} \cdots \mathrm{O} 4$, and $\mathrm{N} 2-\mathrm{H} 2 \mathrm{BD} \cdots \mathrm{O} 3^{*} / \mathrm{N} 2^{*}-\mathrm{H} 2 \mathrm{BD}{ }^{*} \cdots \mathrm{O} 3$, and the reciprocal $\mathrm{R}_{2}{ }^{2}(16)$ interaction is $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~B} \cdots \mathrm{O} 10^{*} / \mathrm{O} 21^{*}-\mathrm{H} 21 \mathrm{~B}^{*} \cdots \mathrm{O} 10$. An example one of the five $\mathrm{R}_{2}{ }^{2}(12)$ interaction and a $\mathrm{R}_{2}{ }^{2}(16)$ interaction are shown in Figure 4.5 and 4.6, respectively. The two $\mathrm{C}(8)$ connections are $\mathrm{O} 13-\mathrm{H} 13 \mathrm{~A} \cdots \mathrm{O} 12^{*}$ and $\mathrm{O} 11-\mathrm{H} 11 \cdots \mathrm{O} 10^{*}$ (Figure 4.7). The D interaction is $\mathrm{O} 13-\mathrm{H} 13 \cdots \mathrm{O} 13^{*}$ (Figure 4.8).


Figure 4.4 One of the two reciprocal $\mathrm{R}^{2}(8)$ interactions in 37. Dashed blue lines represent H bonds.


Figure 4.5 One of the five reciprocal $\mathrm{R}_{2}{ }^{2}(12)$ interactions in 37 .


Figure 4.6 The reciprocal $\mathrm{R}_{2}{ }^{2}(16) \mathrm{H}$-bond interaction in 37. Dished blue lines represent H bonds.


Figure 4.7 One of the two $\mathrm{C}(8) \mathrm{H}$-bonds connections in 37.


Figure 4.8 The dimer H -bond interaction in 37.

The $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]\right.$, and $\mathrm{H}_{2} \mathrm{O}$ molecules of $\mathbf{3 7}$ are connected through a complex series of H -bond interactions to produce the three-dimension network linking the hexaborates (Figure 4.9). The hexaborate(2-) anion in 37 are linked to three water molecules via three H -bond interactions $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O} 31 \mathrm{~B}^{*}$, O31B-H31D $\cdots \mathrm{O} 11^{*}$, and O31$\mathrm{H} 31 \mathrm{~A} \cdots \mathrm{O} 11^{*}$. Details of the H -bonding interactions are given in Table 4.8.


Figure 4.9 Diagram showing a 'plane' of $\left[\mathrm{Ni}_{1}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]\right.$ (viewed along the $a$ direction of the unit cell) and water molecule in 37.

### 4.3.5.2 Structural characterisation of $[\mathrm{Ni}(\mathrm{EAN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O}(38)$

Crystallographic data of $\mathbf{3 8}$ are given in Table 4.9. The crystals of $\mathbf{3 8}$ are triclinic, $P-1$ and compound 38 is an ionic compound with one transition metal complex cation $[\mathrm{Ni}(\mathrm{EAN})]^{+}$ partnered with one $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions and one water molecule as shown in Figure 4.10. The $[\mathrm{Ni}(\mathrm{EAN})]^{+}$cation in $\mathbf{3 8}$ has Ni-N distances ranging from 1.8504(14) - 1.9284(16) A. The $\mathrm{Ni}(\mathrm{II})$ complex cation in 38 is best considered as a 4-coordinate distorted square-planar geometry.


Figure 4.10 Diagram showing the complex cation, pentaborate anion and water molecule in 38 and the adopted numbering scheme.

Table 4.9 Crystal data and structure refinement of $\mathbf{3 8}$.

| Empirical formula | $\mathrm{C}_{9} \mathrm{H}_{25} \mathrm{~B}_{5} \mathrm{~N}_{4} \mathrm{O}_{11} \mathrm{Ni}$ |
| :---: | :---: |
| Formula weight | 478.09 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a=8.5589(3) \AA \quad \alpha=115.895(3)^{\circ}$ |
|  | $b=11.3670(4) \AA \quad \beta=101.639(3)^{\circ}$ |
|  | $c=11.9017(4) \AA \quad \gamma=99.641(3)^{\circ}$ |
| Volume | 976.36(6) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.626 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.057 \mathrm{~mm}^{-1}$ |
| F(000) | 496 |
| Crystal | Block; Pink |
| Crystal size | $0.050 \times 0.040 \times 0.040 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.539-27.485^{\circ}$ |
| Index ranges | $-11 \leq h \leq 11,-14 \leq k \leq 11,-15 \leq l \leq 15$ |
| Reflections collected | 16234 |
| Independent reflections | 4479 [ $\left.R_{\text {int }}=0.0256\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.9\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.797 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 4479 / 0 / 280 |
| Goodness-of-fit on $F^{2}$ | 1.056 |
| Final $R$ indices [ $F^{2}>2 \sigma\left(F^{2}\right)$ ] | $R 1=0.0291, w R 2=0.0768$ |
| $R$ indices (all data) | $R 1=0.0329, w R 2=0.0788$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.876 and $-0.864 \mathrm{e}^{\text {® }}{ }^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha$ |

The pentaborate anion is structurally similar to other pentaborate systems involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions. ${ }^{136,181}$ The B-O distances to the 4-coordinate tetrahedral B1 centre are $1.4595(18)-1.4782(18) \AA$ and they are significantly longer than those involving the trigonal boron centres which range from 1.3429(19) - 1.4049(19) A. B-O bonds involving trigonal boron atoms and terminal OH groups are at the shorter end of this range [av. $1.356 \AA$ ] whilst B-O bonds involving trigonal boron atoms and distal $(\mathrm{O} 2, \mathrm{O} 5)$ to the 4 -coordinate B 1 centre are at the longer end of this range [av. $1.3919 \AA$ A ]. Bond angles at the B 1 centre range from $108.42(12)^{\circ}$ $-110.63(12)^{\circ}$, and angles at the other ring atoms range from $116.75(13)^{\circ}-122.77(14)^{\circ}$ for boron centres consistent with $\mathrm{sp}^{3}$ and $\mathrm{sp}^{2}$ hybridisation, respectively. The bond lengths and bond angles of $\mathbf{3 8}$ are listed in Appendix I (Table 23 and 24).

In 38 the four H -bond donor sites of pentaborate(1-) anion are involved with H -bonds to $\alpha$ oxygen acceptor sites of two pentaborate anions (O9-H9 $\cdots 4^{*}$, and $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 6^{*}$ ), a $\gamma$
oxygen acceptor site of a pentaborate(1-) anion ( $\mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O} 2^{*}$ ), and one water molecule ( $\mathrm{O} 7-$ $\mathrm{H} 7 \cdots \mathrm{O} 11^{*}$ ), so this molecule displays $\alpha \alpha \gamma \omega$ interactions. ${ }^{77,98}$ The direction of four donor sites in pentaborate anion are two 'in' and two 'out' (Figure 4.10). All the H -bonds data are given in Table 4.10.

Table 4.10 H-bonds [ $\AA{ }^{\circ}$ and $^{\circ}$ ] of $\mathbf{3 8}$.

| $\boldsymbol{D}-\mathbf{H} \cdots \boldsymbol{A}$ | $\boldsymbol{d}(\boldsymbol{D} \cdots \boldsymbol{A})$ | $\boldsymbol{D}-\mathbf{H} \cdots \boldsymbol{A}$ | $\boldsymbol{d}(\boldsymbol{D} \cdots \boldsymbol{A})$ |
| :--- | :--- | :--- | :---: |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{C} \cdots 5^{\mathrm{i}}$ | $2.9648(17)$ | $\mathrm{O}^{\mathrm{i}}-\mathrm{H} 9 \cdots \mathrm{O}^{4 \mathrm{iv}}$ | $2.7016(15)$ |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{D} \cdots \mathrm{O}^{\mathrm{ii}}$ | $3.3848(18)$ | $\mathrm{O}^{\mathrm{ii}} 0-\mathrm{H} 10 \cdots \mathrm{O}^{\mathrm{i}}$ | $2.7642(15)$ |
| $\mathrm{N} 4-\mathrm{H} 4 \mathrm{~A} \cdots \mathrm{O}^{\mathrm{ii}}$ | $2.9598(17)$ | $\mathrm{O}^{\mathrm{ii}}$ | $11-\mathrm{H} 11 \mathrm{~A} \cdots \mathrm{O}^{\mathrm{v}}$ |
| $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 11$ | $2.6613(17)$ | $\mathrm{O} 11-\mathrm{H} 11 \mathrm{~B} \cdots \mathrm{O}^{\mathrm{iii}}$ | $2.7460(15)$ |
| $\mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O} 2^{\mathrm{iii}}$ | $2.7994(15)$ |  | $2.7889(16)$ |

A view of part of the layered structure of $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions in $\mathbf{3 8}$ is shown in Figure 4.11 illustrating a ribbon structure between adjacent pentaborate(1-) anions where each $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion is connected via two reciprocal $\mathrm{R}_{2}{ }^{2}(8)$ connections. Each $\mathrm{R}_{2}{ }^{2}(8)$ connection is formed between neighbouring pentaborate(1-) anions as follows: O9-H9A $\cdots 4^{*} / \mathrm{O}^{*}{ }^{*}$ $\mathrm{H} 9 \mathrm{~A}^{*} \cdots \mathrm{O} 4$ and $\mathrm{O} 10^{*}-\mathrm{H} 10^{*} \cdots \mathrm{O} 6 / \mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O}^{*}$. The other boroxyl $\left(\mathrm{B}_{3} \mathrm{O}_{3}\right)$ rings of the pentaborate(1-) anion ribbon are linked to a further pentaborate(1-) anion, cross links the ribbons by a third reciprocal $\mathrm{R}_{2}{ }^{2}(8)$ interaction. This $\mathrm{R}_{2}{ }^{2}(8)$ connection is $\mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O}^{*} / \mathrm{O} 8^{*}$ $\mathrm{H} 8^{*} \cdots \mathrm{O} 2$. The fourth donor hydroxyl group of each $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anion acts to crosslinks the planes via a $\beta \rightarrow \omega$ interaction with a water molecule $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 11^{*}$.

As shown in Figure $\mathbf{4 . 1 2}$ the supramolecular layered structure of $\mathbf{3 8}$ the water molecules and the $[\mathrm{Ni}(\mathrm{EAN})]^{+}$cations connect pentaborate(1-) anion ribbons by complex series of H -bond interactions. This cation is involved in H -bonding to water molecules. The $[\mathrm{Ni}(\mathrm{EAN})]^{+}$cation acts as H -bond donors to two pentaborate(1-) anions via three H -bond interactions N 4 $\mathrm{H} 4 \mathrm{~A} \cdots \mathrm{O} 1^{*}$, $\mathrm{N} 1-\mathrm{H} 1 \mathrm{C} \cdots \mathrm{O} 5^{*}$, and $\mathrm{N} 1-\mathrm{H} 1 \mathrm{D} \cdots \mathrm{O}^{*}$. All $\mathrm{H}-$ bonds data for 38 are listed in Table 4.10.


Figure 4.11 The three $\mathrm{R}_{2}{ }^{2}(8) \mathrm{H}$-bond motif connections in 38. Dashed blue lines represent H bonds.


Figure 4.12 Diagram showing a 'plane' of polyborate anions (viewed along the a direction of the unit cell) and water molecule with $[\mathrm{Ni}(\mathrm{EAN})]^{+}$cations in 38.

### 4.3.5.3 Structural characterisation of $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Ni}(\text { dach })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$

 (39)Crystallographic data of $\mathbf{3 9}$ are listed in Table 4.11. The crystals of $\mathbf{3 9}$ are monoclinic, $C 2 / c$. The structure of $\mathbf{3 9}$ contains two different nickel(II) complex cations: $\left[\mathrm{Ni}(\text { dach })_{2}\right]^{2+}$ and $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$. Both of these cations contain one ( $1 \mathrm{~S}, 2 \mathrm{~S}$ )-1,2-diaminocyclohexane (dach) and one $(1 R, 2 R)$-1,2-diaminocyclohexane ligand in a distorted square-planar arrangement. One cation contains two mutually trans $\mathrm{H}_{2} \mathrm{O}$ molecules yielding a 6-coordinate metal cation. Compound 39 has Ni-N distances of 2.113(9) $\AA(\mathrm{N} 1), 2.108(8) \AA(\mathrm{N} 2), 2.036(15) \AA(\mathrm{N} 1 \mathrm{~B})$, and $2.015(14) \AA(\mathrm{N} 2 \mathrm{~B})$ [av. $2.068 \AA$ ], which are the same for both cations. The Ni-O axial distances are $2.1352(15) \AA$ and $2.1353(15) \AA$ [av. $2.1353 \AA$ ]. Each cation is partnered by a crystallographically identical $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]^{2-}$ anion and an additional water of crystallization. The anions and cations in $\mathbf{3 9}$ are shown in Figure 4.13.


Figure 4.13 Diagram showing the complex cation, heptaborate(2-) anion and water molecule in 39 and the adopted numbering scheme.

Table 4.11 Crystal data and structure refinement of $\mathbf{3 9}$.

| Empirical formula | $\mathrm{C}_{24} \mathrm{H}_{78} \mathrm{~B}_{14} \mathrm{~N}_{8} \mathrm{O}_{34} \mathrm{Ni}_{2}$ |
| :---: | :---: |
| Formula weight | 1291.70 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $a=22.2909(7) \AA \quad \alpha=90^{\circ}$ |
|  | $b=10.9861(3) \AA$ ® $\quad \beta=107.744(3)^{\circ}$ |
|  | $c=22.8446(7) \AA \quad \gamma=90^{\circ}$ |
| Volume | 5328.3(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.610 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.812 \mathrm{~mm}^{-1}$ |
| F(000) | 2704 |
| Crystal | Prism; Orange |
| Crystal size | $0.150 \times 0.150 \times 0.090 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.165-27.483^{\circ}$ |
| Index ranges | $-27 \leq h \leq 28,-14 \leq k \leq 14,-29 \leq l \leq 29$ |
| Reflections collected | 33681 |
| Independent reflections | $6102\left[R_{\text {int }}=0.0275\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | 99.9\% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.921 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | 6102 / 1165 / 525 |
| Goodness-of-fit on $F^{2}$ | 1.049 |
| Final $R$ indices [ $\left.F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0391, w R 2=0.1084$ |
| $R$ indices (all data) | $R 1=0.0415, w R 2=0.1099$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.851 and -0.727 e $\AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha$ |

Special details: Both the 1,2 -diaminocyclohexane ligands were modelled as disordered over two positions and as a result various geometrical (SAME, SADI) and displacement (RIGU, SIMU) restraints were required.

The heptaborate(2-) anion contains four fused six-membered rings containing three tetrahedral boron centres and four trigonal boron centres (for more details see Section 3.3.5.4). The structure of the heptaborate(2-) anions in 39 is essentially the same as those reported for $\left[\mathrm{H}_{3} \mathrm{~N}\left(\mathrm{CH}_{2}\right)_{7} \mathrm{NH}_{3}\right]\left[\mathrm{B} 7 \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot \mathrm{H}_{2} \mathrm{O},{ }^{97} \quad\left[\text { cyclo- } \mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NH}_{3}\right]_{2}\left[\mathrm{~B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O} \cdot \mathrm{B}(\mathrm{OH})_{3}, \quad$ and $\left[\text { cyclo }-\mathrm{C}_{7} \mathrm{H}_{13} \mathrm{NH}_{3}\right]_{2}\left[\mathrm{~B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O} \cdot 2 \mathrm{~B}(\mathrm{OH})_{3}{ }^{77}$ The $\mathrm{B}-\mathrm{O}$ distances around the threecoordinate boron centres range from 1.356(2) - 1.374(2) $\AA$ [av. $1.366 \AA$ ], and B-O distances around the four-coordinate boron centres range from $1.435(2)-1.512(2) \AA$ [av. $1.468 \AA$ ]. The $\mathrm{O}-\mathrm{B}-\mathrm{O}$ angles for the three-coordinate boron centres range from 114.6(17) - 123.61(17) ${ }^{\circ}$ [av. $119.99^{\circ}$ ] and $\mathrm{O}-\mathrm{B}-\mathrm{O}$ angles at the four-coordinate boron centres range from 106.06(14) $112.17(15)^{\circ}$ [av. $109.45^{\circ}$ ]. The ring B-O-B angles range from $110.72(13)-123.15(15)^{\circ}[\mathrm{av}$.
$119.77^{\circ}$ ] indicating $\mathrm{sp}^{2}$ hybridised oxygen atoms. The central three-coordinate oxygen centres is pyramidal ( $349.68^{\circ}$ angle sum) and $0.283 \AA$ out of the B1B2B3 plane, with B-O bond lengths, [av. $1.509 \AA$ ]. This distance is longer than typically expected for oxygen atoms bound to fourcoordinate boron centres ( $\sim 1.48 \AA$ ). ${ }^{77}$ The three-coordinate oxygen centre, O1, are trans-oid relative to the OH group of B1. The bond lengths and angles are listed in Appendix I (Table 25 and Table 26).

In 39 the heptaborate(2-) anion has an opportunity to form many H -bond interactions. It has 5 potential H-bond donor sites and 14 potential H-bond acceptor sites. The labelling scheme of heptaborate(2-) anion is illustrated in Section 3.3.5.4. The BBFFG hydroxyl group donor sites of heptabotrate(2-) anion form H -bond donor interactions to four different heptaborate(2-) anions. Whilst the G site is not involved in any donor H-bond interactions. These four interactions are $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 8^{*}$, $\mathrm{O} 12-\mathrm{H} 12 \mathrm{~F} \cdots \mathrm{O} 9^{*}, \mathrm{O} 13-\mathrm{H} 13 \cdots \mathrm{O} 7^{*}$, and $\mathrm{O} 11-$ $\mathrm{H} 11 \mathrm{~F} \cdots 5^{*}$ (Figure 4.14). All the H -bonds data in 39 are listed in Table 4.12.


Figure 4.14 The four H-bond donor interactions of each heptaborate(2-) anion in 39.

Table 4.12 H-bond interactions [ $\AA$ and ${ }^{\circ}$ ] in 39.

| $D-\mathrm{H} \cdots{ }^{\text {a }}$ | $d(D \cdots A)$ | $D-\mathrm{H} \cdots{ }^{\text {a }}$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O} 22^{\text {iii }}$ | 2.693(2) | N12-H12B $\cdots$ O23 ${ }^{\text {v }}$ | 3.10(2) |
| $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~B} \cdots{ }^{\text {O }}{ }^{\text {i }}$ | 3.203(2) | N11B-H11C...O3ii | 2.98(2) |
| O21-H21B $\cdots$ O14 ${ }^{\text {i }}$ | 2.974(2) | N11B-H11D $\cdots \mathrm{O}^{\text {1 }}{ }^{\text {iv }}$ | 3.08(2) |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A} \cdots \mathrm{O} 22^{\mathrm{ii}}$ | 3.251(18) | N12B-H12C...O10 | 2.99(2) |
| N1-H1B...O14 ${ }^{\text {i }}$ | 3.182(17) | N12B-H12D $\cdots{ }^{\text {O }}{ }^{\text {a }}$ | 2.85(3) |
| N2-H2B..O2 | 3.098(13) | O10-H10...O8 ${ }^{\text {vi }}$ | 2.6854(19) |
| N2-H2B $\cdots$ O6 | $2.935(8)$ | O11-H11F...O5 ${ }^{\text {vii }}$ | 2.7034(19) |
| N1B-H1BA $\cdots{ }^{\text {O }} 2^{\text {ii }}$ | 3.25(3) | O12-H12F...O9 $9^{\text {viii }}$ | 2.7629(19) |
| N1B-H1BB $\ldots$ O14 ${ }^{\text {i }}$ | 3.19(3) | O13-H13..O7 $7^{\text {ix }}$ | 2.6831(18) |
| N2B-H2BB $\cdots$ O2 | 3.269(19) | $\mathrm{O} 22-\mathrm{H} 22 \mathrm{~A} \cdots{ }^{\text {O }} 23^{v}$ | 2.829 |
| N2B-H2BB $\ldots$ O6 | 2.976 (13) | $\mathrm{O} 22-\mathrm{H} 22 \mathrm{~B} \cdots \mathrm{O} 13^{\text {x }}$ | 2.801(2) |
| N11-H11A $\cdots{ }^{\text {a }} 3^{\text {ii }}$ | 2.970 (8) | O23-H23A $\cdots$ O12 | 2.7857(19) |
| N11-H11B $\cdots$ O11 ${ }^{\text {iv }}$ | 2.992(8) | O23-H23B $\cdots$ O11 ${ }^{\text {viii }}$ | 2.806(2) |
| N12-H12A $\cdots \mathrm{O} 10$ | 2.811(9) |  |  |


| (i) $-x+3 / 2,-y+1 / 2,-z+1$ | (ii) $-x+1,-y+1,-z+1$ | (iii) $x+1 / 2, y-1 / 2, z$ | (iv) $x,-y+1, z+1 / 2$ | (v) |
| :--- | :--- | :---: | :---: | ---: |
| $x-1 / 2, y+1 / 2, z$ | (vi) $-x+3 / 2,-y+3 / 2,-z+1$ | (vii) $-x+1, y,-z+1 / 2$ | (viii) $-x+3 / 2, y-1 / 2,-z+1 / 2$ | (xi) |
| $-x+3 / 2, y+1 / 2,-z+1 / 2$ | (x) $x-1 / 2, y-1 / 2, z$ |  |  |  |

Detailed inspection of Figure $\mathbf{4 . 1 5}$ shows that each $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ anion is connected by two $\mathrm{R}_{2}{ }^{2}(8)$ and one reciprocal $\mathrm{R}_{2}{ }^{2}(12)$ interaction. The two $\mathrm{R}_{2}{ }^{2}(8)$ connections are $\mathrm{O} 11-$ $\mathrm{H} 11 \mathrm{~F} \cdots \mathrm{O} 5^{*} / \mathrm{O} 11^{*}-\mathrm{H} 11 \mathrm{~F}^{*} \cdots \mathrm{O} 5$ and $\mathrm{O} 12-\mathrm{H} 12 \mathrm{~F} \cdots \mathrm{O} 9^{*} / \mathrm{O} 13^{*}-\mathrm{H} 13^{*} \cdots \mathrm{O} 7^{*}$, while the reciprocal $\mathrm{R}_{2}{ }^{2}(12)$ connection is $\mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 8^{*} / \mathrm{O} 10^{*}-\mathrm{H} 10^{*} \cdots \mathrm{O} 8$. All the H-bonds data in 39 are listed in Table 4.12.

A three-dimensional network is formed by connecting the plane shown in Figure 4.16 (part of which is shown in Figure 4.15) to the neighbouring planes by further H-bond interactions. The $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ and $\left[\mathrm{Ni}(\text { dach })_{2}\right]^{2+}$ cations act as H -bond donors to two $\left[\mathrm{B}_{7} \mathrm{O} 9(\mathrm{OH})_{5}\right]^{2-}$ anions and two water molecules. The connection of $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ and $\left[\mathrm{Ni}(\text { dach })_{2}\right]^{2+}$ cations to the $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]^{2-}$ anions occur by seven H-bond interactions $\mathrm{N} 1-$ H1B $\cdots \mathrm{O} 14^{*}$, N2-H2B $\cdots \mathrm{O} 2^{*}$, N2B-H2BB $\cdots \mathrm{O}^{*}$, N11-H11A $\cdots \mathrm{O} 3^{*}$, N12-H12A $\cdots \mathrm{O} 10^{*}$, O21$\mathrm{H} 21 \mathrm{~B} \cdots \mathrm{O} 14^{*}$, and N11-H11D $\cdots \mathrm{O} 11^{*}$. The connection of the cations to the interstitial water molecules occur by three H-bond interactions: N12-H12D..O23*, N1B-H1BA…O22*, and $\mathrm{O} 21-\mathrm{H} 21 \mathrm{~A} \cdots \mathrm{O} 22^{*}$. Details of the H-bonding interactions are given in Table 4.12.


Figure 4.15 The $\mathrm{R}_{2}{ }^{2}(8)$ and $\mathrm{R}_{2}{ }^{2}(12)$ connections between heptaborate anions.


Figure 4.16 A plane of heptaborate anions and $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ and $\left[\mathrm{Ni}(\text { dach })_{2}\right]^{2+}$ cations in plane H -bond interactions in 39.

### 4.3.5.4 Structural characterisation of $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}(40)$

Crystallographic data of $\mathbf{4 0}$ are listed in Table 4.13. The crystals of $\mathbf{4 0}$ are monoclinic, $P 2{ }_{1} / c$ and it is an ionic compound with one transition metal complex cation $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]^{+2}$ partnered with two crystallographically identical $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions as shown in Figure 4.17. The $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]^{+2}$ in $\mathbf{4 0}$ has Ni-N distances ranging from 2.064(15) - 2.140(6) $\AA$ [av. $\left.2.94 \AA\right]$, whilst the Ni-O distances are $2.087(7) \AA(\mathrm{O} 11)$ and $2.072(8) \AA(\mathrm{O} 11 \mathrm{~B})$ [av. $2.080 \AA$ ]. The nickel(II) centre in $\mathbf{4 0}$ has a coordination number of six with a distorted octahedral geometry.


Figure 4.17 Diagram showing the complex cation and pentaborate(1-) anion in $\mathbf{4 0}$ and the adopted numbering scheme.

Table 4.13 Crystal data and structure refinement of $\mathbf{4 0}$.

| Empirical formula | $\mathrm{C}_{8} \mathrm{H}_{32} \mathrm{~B}_{10} \mathrm{~N}_{4} \mathrm{O}_{22} \mathrm{Ni}$ |
| :--- | :--- |
| Formula weight | 703.18 |
| Temperature | $100(2) \mathrm{K}$ |
| Wavelength | $0.71073 \AA$ |
| Crystal system | Monoclinic |
| Space group | $P 2_{1} / c$ |
| Unit cell dimensions | $a=8.3887(3) \AA \quad \alpha=90^{\circ}$ |
|  | $b=11.6644(4) \AA \quad \beta=90.046(3)^{\circ} \AA$ |
|  | $c=14.3061(5) \AA \quad \gamma=90^{\circ} \AA$ |
| Volume | $1399.84(8) \AA^{3}$ |
| $Z$ | 2 |


| Density (calculated) | $1.668 \mathrm{Mg} / \mathrm{m}^{3}$ |
| :--- | :--- |
| Absorption coefficient | $0.792 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 724 |
| Crystal | Rod; Lilac |
| Crystal size | $0.340 \times 0.050 \times 0.040 \mathrm{~mm}^{3}$ |
| $\theta$ range for data collection | $2.848-27.499^{\circ}$ |
| Index ranges | $-10 \leq h \leq 10,-15 \leq k \leq 15,-18 \leq l \leq 18$ |
| Reflections collected | 6244 |
| Independent reflections | $6244\left[R_{\text {int }}=?\right]$ |
| Completeness to $\theta=25.242^{\circ}$ | $99.9 \%$ |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.798 |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Data / restraints / parameters | $6244 / 14 / 223$ |
| Goodness-of-fit on $F^{2}$ | 1.044 |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R l=0.0444, w R 2=0.1113$ |
| $R$ indices (all data) | $R 1=0.0518, w R 2=0.1154$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 1.018 and $-0.468 \mathrm{e} \AA^{-3}$ |
| Radiation source (wavelength) | Mo-K $\alpha$ |

Special details: This structure was refined as a two-component twin (Component two was rotated by $179.9835^{\circ}$ around [-0.45 -0.00 0.89] (reciprocal) or [-0.83-0.00 0.56] (direct) axis). The $\mathrm{N}-(2-$ hydroxyethyl)ethylenediamine ligand was successfully modelled as disordered over positions and as such various geometrical (SADI, DFIX, DANG) and displacement (EADP) restraints were applied.

The two pentaborate anions are structurally similar and are not notably different from other transition metal complex cation pentaborate anion structure systems involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions. ${ }^{136,181}$ The B-O distances to the four-coordinate tetrahedral B1 centres range from $1.462(3)-1.476(3) \AA$ [av. $1.47 \AA$ ] and these are significantly longer than those involving the trigonal boron centres which range from 1.348(3)-1.389(3) Å [av. $1.365 \AA$ A. BO bonds involving trigonal boron atoms and terminal OH groups are at the shorter end of this range [av. $1.358(3) \AA$ A whilst B-O bonds involving trigonal boron atoms and distal (O2, O5) to the 4-coordinate B1 centre are at the longer end of this range [av. 1.380 (3) A $\AA$ ]. Bond angles at the B1 range from $108.04(19)^{\circ}-111.66(18)^{\circ}$, and angles at the other ring atoms range from $116.1(2)^{\circ}-122.8(2)^{\circ}$. The bond lengths and bond angles of $\mathbf{4 0}$ are listed in Appendix I (Tables 27 and Table 28).

In 40 the four H -bond donor sites of pentaborate(1-) anion are involved with H -bonds to $\alpha$ oxygen acceptor sites of three different pentaborate (1-) anions (O8-H8‥O3*, O9-H9 $\cdots{ }^{*} 6^{*}$ and $\mathrm{O} 10-\mathrm{H} 10 \cdots 4^{*}$ ) and an H -bond to a $\beta$ oxygen acceptor site of the fourth pentaborate(1-) anion ( $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 8^{*}$ ), so this molecule displays $\alpha \alpha \alpha \beta$ interactions to neighbouring pentaborate(1-) anions. ${ }^{77,98}$ The direction of four H-bond donor sites of pentaborate(1-) anion
in 40 are three 'in' and one 'out' (Figure 4.17). All the H-bond interactions data of $\mathbf{4 0}$ are listed in Table 4.14.

Table 4.14 H-bonds [ ${ }^{\AA}$ and ${ }^{\circ}$ ] in 40


Detailed inspection of Figure $\mathbf{4 . 1 8}$ shows that the $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ions are connected by two $\mathrm{R}_{2}{ }^{2}(8)$ interactions $\mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O}^{*} / \mathrm{O} 10^{*}-\mathrm{H} 10^{*} \cdots \mathrm{O} 4$ and $\mathrm{O} 9^{*}-\mathrm{H} 9^{*} \cdots \mathrm{O} 6 / \mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 4^{*}$ forming a chain. The pentaborate(1-) anion chains are linked to other pentaborate(1-) anion chains by two reciprocal H -bond interactions forming a three-dimensional network. The first reciprocal interaction is $\mathrm{R}_{2}{ }^{2}(8) \mathrm{O} 8-\mathrm{H} 8 \cdots \mathrm{O}^{*} / \mathrm{O} 8^{*}-\mathrm{H} 8^{*} \cdots \mathrm{O} 3$. The second reciprocal interaction is $\mathrm{R}_{2}{ }^{2}(12) \mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 8^{*} / \mathrm{O} 7^{*}-\mathrm{H} 7^{*} \cdots \mathrm{O} 8$.


Figure 4.18 The $\mathrm{R}_{2}{ }^{2}(8)$ and $\mathrm{R}_{2}{ }^{2}(12)$ connections between two layers of pentaborate(1-) ion in 40.

Two structural motifs that commonly occur in pentaborate giant structures containing the $\alpha \alpha \alpha \beta$ acceptor sites are called herringbone (HB) and brickwall (BW). However these motifs involve a $\mathrm{C}(8)$ chain $\beta$-interaction and structure 40 has a reciprocal-pair $\mathrm{R}_{2}{ }^{2}(12) \beta$-interaction (Figure 4.19), and so it is neither of these structures. This motif is not as common as the other two but has been previously observed in a few examples $\left[\mathrm{MeHN}\left(\mathrm{CH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NMe}^{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]$, $\left[\mathrm{Me}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NMe}_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}, 2-\mathrm{Et}-4-\mathrm{MeC}_{3} \mathrm{~N}_{2} \mathrm{H}_{3}$, and $2-{ }^{\mathrm{i}} \mathrm{PrC}_{3} \mathrm{~N}_{2} \mathrm{H}_{4} .{ }^{170,192}$


Figure 4.19 H -bonded $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$network for $\mathbf{4 0}$ view perpendicular to the large channels (viewed along the $a$ direction of the unit cell).

The solid-state structures of all transition metal complex polyborate compounds involve H-bonded supramolecular polyborate anion networks, with cavities and channels, which occlude the transition metal complex cations. The $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]^{2+}$ cations and $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions of crystallisation of $\mathbf{4 0}$ are connected through a complex series of H -bond interactions (Figure 4.20), with the anion network templated by the cations.


Figure 4.20 A plane of pentaborate(1-) anions and $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]^{2+}$ cations in plane of H -bond interactions in 40 (viewed along the $a$ direction of the unit cell).

The $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]^{2+}$ cation acts as H -bond donors to four pentaborate(1-) anions via eight H-bond interactions N11-H11D...O1*, O11-H11…O7*, N11B-H11E $\cdots \mathrm{O} 7^{*}$, N12-H12 $\cdots \mathrm{O} 9^{*}$,
 Details of the H -bonding interactions are given in Table 4.14.

### 4.3.5.5 Structural characterisation of $s$-fac- $\left[\mathrm{Ni}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}(41)$

Crystallographic data of $\mathbf{4 1}$ are listed in Table 4.15. Crystals of $\mathbf{4 1}$ are triclinic, $P-1$ and compound 41 is an ionic compound with one transition metal complex cation $\left[\mathrm{Ni}(\text { dien })_{2}\right]^{+2}$ partnered with two crystallographically identical $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions as shown in Figure 4.21. The $\left[\mathrm{Ni}(\text { dien })_{2}\right]^{+2}$ in $\mathbf{4 1}$ has $\mathrm{Ni}-\mathrm{N}$ distances ranging from 2.095(8) - 2.161(8) $\AA$ [av. $2.142 \AA$ A . The nickel(II) centre in $\mathbf{4 1}$ has a coordination number of six with a distorted octahedral geometry.


Figure 4.21 Diagram showing the complex cation and pentaborate(1-) anion in 41 and the adopted numbering scheme.

Table 4.15 Crystal data and structure refinement of 41.

| Empirical formula | $\mathrm{C}_{8} \mathrm{H}_{34} \mathrm{~B}_{10} \mathrm{~N}_{6} \mathrm{O}_{20} \mathrm{Ni}$ |
| :--- | :--- |
| Formula weight | 701.22 |
| Temperature | $100(2) \mathrm{K}$ |
| Wavelength | $0.6889 \AA$ |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a=8.5579(11) \AA \quad \alpha=78.099(10)^{\circ} \quad \beta=89.109(10)^{\circ}$ |
|  | $b=9.2772(11) \AA \quad \gamma=89.054(10)^{\circ}$ |
|  | $c=9.3422(10) \AA \quad \AA \quad 725.61(15) \AA^{3}$ |
| Volume | 1 |
| $Z$ | $1.605 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Density (calculated) | $0.702 \mathrm{~mm}{ }^{-1}$ |
| Absorption coefficient | Blade; orange |
| Crystal | $0.020 \times 0.020 \times 0.010 \mathrm{~mm}^{3}$ |
| Crystal size | $2.160-26.572^{\circ}$ |
| $\theta$ range for data collection | 6369 |
| Reflections collected | $3184\left[R_{\text {int }}=0.0479\right]$ |
| Independent reflections | $99.9 \%$ |
| Completeness to $\theta=25.242^{\circ}$ | Semi-empirical from equivalents |
| Absorption correction | 1.000 and 0.703 |
| Max. and min. transmission | Full-matrix least-squares on $F^{2}$ |
| Refinement method | $3184 / 278 / 282$ |
| Data / restraints / parameters |  |


| Goodness-of-fit on $F^{2}$ | 1.070 |
| :--- | :--- |
| Final $R$ indices $\left[F^{2}>2 \sigma\left(F^{2}\right)\right]$ | $R 1=0.0794, w R 2=0.2215$ |
| $R$ indices (all data) | $R 1=0.0907, w R 2=0.2358$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 1.188 and $-1.069 \mathrm{e} \AA^{-3}$ |
| Radiation source (wavelength) | $\mathrm{Mo}-\mathrm{K} \alpha$ |

The two pentaborate anions are structurally similar to other transition metal complex cation pentaborate anion structure systems involving isolated $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions. ${ }^{136,181}$ The B-O distances to the 4-coordinate tetrahedral B1 centres range from 1.361(7)-1.484(7) A and these are significantly longer than those involving the trigonal boron centres which range from 1.343(5) - 1.407(16) Å. B-O bonds involving trigonal boron atoms and terminal OH groups are at the shorter end of this range [av. $1.365 \AA$ A ] whilst B-O bonds involving trigonal boron atoms and distal ( $\mathrm{O} 2, \mathrm{O} 5$ ) to the 4 -coordinate B 1 centre are at the longer end of this range [av. 1.39 $\AA$ A. Bond angles at the B1 range from $107.8(4)^{\circ}-111.6(3)^{\circ}$, and angles at the other ring atoms range from 114.9(6)-123.0(5) . The bond lengths and bond angles of $\mathbf{4 1}$ are listed in Appendix I (Tables 29 and Table 30).

In 41 the four H -bond donor sites of pentaborate(1-) anion are involved with H -bonds to $\alpha$ oxygen acceptor sites of three different pentaborate(1-) anions (O8-H8 $\cdots 3^{*}, \mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O} 4^{*}$ and $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{Ol}^{*}$ ) and an H -bond to $\beta$ oxygen acceptor site of the fourth pentaborate(1-) anion (O10-H10‥O9*). ${ }^{77,98}$ This compound displays $\alpha \alpha \alpha \beta$ interactions to neighbouring four different pentaborate(1-) anions (Figure 4.22). The hydrogen bonding motif is identical to that observed for compound 40. The direction of four H -bond donor sites of pentaborate(1-) anion in 41 are three 'in' and one 'out' (Figure 4.21). All the H-bond interactions data of 41 are listed in Table

### 4.16.

Table 4.16 H-bonds [ $\AA$ and ${ }^{\circ}$ ] in 41.

| $D-H \cdots A$ | $d(D \cdots A)$ | $D-H \cdots A$ | $d(D \cdots A)$ |
| :---: | :---: | :---: | :---: |
| O7-H7 $\cdots \mathrm{Ol}^{\text {i }}$ | 2.737(6) | N3A-H3AB $\cdots$ O6 ${ }^{\text {vii }}$ | 3.280(9) |
| O8-H8 $\cdots{ }^{\text {O }}{ }^{\text {ii }}$ | 2.718(5) | N1B-H1BA $\cdots \mathrm{O}^{2 i}$ | 3.360 (12) |
| O9-H9 $\cdots$ O $4^{\text {iii }}$ | 2.683(3) | N1B-H1BB $\cdots \mathrm{O}^{\text {v }}$ | 3.300 (11) |
| O10-H10 ${ }^{\text {a }}$ O $9^{\text {iv }}$ | $2.820(4)$ | N2B-H2B $\cdots \mathrm{O}^{\text {vi }}$ | 2.886(11) |
| N1A-H1AA $\cdots{ }^{\text {O }}{ }^{\text {v }}$ | 2.970 (8) | N3B-H3BA $\cdots$ O10 ${ }^{\text {vii }}$ | 2.926(11) |
| N1A-H1AB $\cdots \mathrm{O}^{\text {vi }}$ | 3.198(10) | N3B-H3BB $\cdots{ }^{\text {O }}{ }^{\text {ii }}$ | 3.209(11) |
| N2A-H2A $\cdots$ O8 ${ }^{\text {ii }}$ | $2.910(9)$ |  |  |



Figure 4.22 H-bonded $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$network for 41 view perpendicular to the large channels (viewed along the $a$ direction of the unit cell).

Detailed inspection of Figure $\mathbf{4 . 2 3}$ shows that the $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$ions are connected by two reciprocal- $\alpha \mathrm{R}_{2}{ }^{2}(8)$ interactions $\mathrm{O} 8-\mathrm{H} 8 \cdots 3^{*} / \mathrm{O} 8^{*}-\mathrm{H} 8^{*} \cdots \mathrm{O} 3$ and $\mathrm{O} 7-\mathrm{H} 7 \cdots \mathrm{O} 1^{*} / \mathrm{O} 7^{*}-\mathrm{H} 7^{*} \cdots \mathrm{O} 1$ forming a chain. The pentaborate(1-) anion chains are linked to other pentaborate(1-) anion chains by two reciprocal H -bond interactions forming a three-dimensional network. The first interaction is a reciprocal- $\alpha \mathrm{R}_{2}{ }^{2}(8) \mathrm{O} 9-\mathrm{H} 9 \cdots \mathrm{O} 4^{*} / \mathrm{O} 9^{*}-\mathrm{H} 9^{*} \cdots \mathrm{O} 4$, while the second interaction is a reciprocal- $\beta \mathrm{R}_{2}{ }^{2}(12) \mathrm{O} 10-\mathrm{H} 10 \cdots \mathrm{O} 9^{*} / \mathrm{O} 10^{*}-\mathrm{H} 10^{*} \cdots \mathrm{O} 9$.

The $\left[\mathrm{Ni}(\text { dien })_{2}\right]^{2+}$ cations and $\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]^{-}$anions of crystallisation of 41 are connected through a complex series of H -bond interactions (Figure 4.24), with the anion network templated by the cations. The $\left[\mathrm{Ni}(\text { dien })_{2}\right]^{2+}$ cation acts as H -bond donors to four pentaborate(1) anion molecules via nine H -bond interactions N1A-H1AA $\cdots \mathrm{O} 10^{*}$, N1A-H1AB $\cdots \mathrm{O}^{*}$, N2AH2A $\cdots{ }^{\circ} 8^{*}$, N3A-H3AB $\cdots$ O $^{*}$, N1B-H1BA $\cdots 2^{*}$, N1B-H1BB $\cdots 0^{*}$, N2B-H2B $\cdots 7^{*}$, N3BH3BA $\cdots \mathrm{O} 10^{*}$, and N3B-H3BB $\cdots \mathrm{O}^{*}$. Details of the H -bonding interactions are given in Table 4.16.


Figure 4.23 The $\mathrm{R}_{2}{ }^{2}(8)$ and $\mathrm{R}_{2}{ }^{2}(12)$ connections between two layers of pentaborate(1-) ion in
41.


Figure 4.24 A plane of pentaborate(1-) anions and $\left[\mathrm{Ni}(\text { dien })_{2}\right]^{2+}$ cations in plane of H -bond interactions in 41 (viewed along the $a$ direction of the unit cell).

### 4.4 Conclusion and summary

The main aim of this chapter of the thesis was to prepare and investigate new polyborate compounds contains nickel(II) cations. Eight polyborate compounds $\mathbf{3 6 - 4 3}$ containing different polyborate anions (pentaborate(1-), hexaborate(2-), and heptaborate(2-) anions) have been prepared and templated from aqueous solution from boric acid using a series of nickel(II) complex cations. Five of these salts have been characterized by single-crystal XRD (37-41) studies.

New polyborate anion structural architecture has been identified within this Chapter. The hexaborate(2-) anion in 37 coordinates as a bidentate ligand with nickel(II) cation. Compound 39 is a rare example of a crystallographically characterized compound containing the isolated heptaborate(2-) anion.

Reaction of $\left[\mathrm{Ni}(\mathrm{en})_{2}\right]^{2+}$ with boric acid in a 1:10 ratio produced compounds containing the pentaborate(1-) anion (36), while the reaction in 1:7 ratio afforded a compound containing the hexaborate(2-) anion (37). These results show that the products obtained are also dependent upon the reaction stoichiometry.

## Chapter Five

## General Conclusion

And Future Work

### 5.1 General conclusion

This thesis has been concerned with the synthesis of polyborate salts partnered with transition metal cations. With non-metal cations, pentaborate(1-) salts are commonly observed. Each pentaborate(1-) anion has four H -bond donor sites. All of them are always used as an H bond donor to other pentaborate anions and form supramolecular 3D frameworks. The cations in many of these structures are 'innocent', in that they interact weakly with the anions and do not significantly influence the structure, which is dominated by the anion-anion H -bond interactions.

The first aim of this study was to synthesise novel transition metal borate complexes with the synthesis of unique 'isolated' borate anions and anions other than the pentaborate(1-) anion. The second aim of this study was to investigate the structural feature of the transition metal complex polyborate compounds and evaluate the solid-state structure directing effects operating within these compounds. The strategy used to break the domination of pentaborate compounds and achieve these aims were:
(i) The use of inert 'non-innocent' cations (e.g. multi-H-bond donor transition metal complexes such as $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ ), to improve cation-anion H-bonds formation and reduce anion-anion H -bond interactions.
(ii) The use of relatively high charged cations (e.g. $\mathrm{Co}^{3+}, \mathrm{Cu}^{2+}$, and $\mathrm{Ni}^{2+}$ complexes) with unusual or non-spherical shapes, in order to change the stoichiometry of the salt.
(iii) The use of very large cations (e.g. $\left.[\mathrm{Co}(\mathrm{diNOsar})]^{3+}\right)$ to see how this influences the structures of the products.
(iv) The use of different boric acid ratios to evaluate the effect of the ratio on reaction products.

The aims of this study were achieved as demonstrated by:
(i) Two unique polyborate anions, $\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right]^{3-}(\mathbf{1 1})$ and $\left.\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right)\right]^{2-}(6)$ have been prepared by using inert transition metal cations $\left[\mathrm{Co}(\text { dien })_{2}\right]^{3+}$ and $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$, respectively.
(ii) Structures containing a variety of polyborate ions (e.g. triborate(1-) (12), tetraborate(2-) (9), pentaborate(1-) (6, 20, 22, 27, 38, 40, 41), hexaborate(2-) (23, $\mathbf{2 8}, \mathbf{3 7})$, and heptaborate(2-) $(\mathbf{2 4}, \mathbf{3 9}))$ have also been prepared and their structures have been investigated by single-crystal X-ray diffraction studies.
(iii) The solid-state structures of transition metal complex polyborate compounds all display multiple cation-anion H -bond interactions and these undoubtable play a major role in the energetics of engineering these structures. For instance, in compound 9 , all eighteen of the amino hydrogen atoms of the $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ cation are involved in secondary coordination to anions via H -bonds.
(iv) New polyborate anion structural architectures have been identified within this thesis. The hexaborate(2-) anion in 37 coordinates as a bidentate ligand with a $\mathrm{Ni}^{2+}$ cation, and in $\mathbf{2 3}$ and $\mathbf{2 8}$ it acts as a tridentate ligand with a $\mathrm{Cu}^{2+}$ cation. The pentaborate(1) anion in (22) coordinates as a monodentate ligand with the copper(II) cation.
(v) Reaction of transition metal complex cations with boric acid in different ratios produced compounds containing different polyborate anions, e.g. reaction of $[\mathrm{Co}(\text { diNOsar })]^{3+}: \mathrm{B}(\mathrm{OH})_{3}$ in a 1:5 or 1:10 ratio gave rise to the triborate(1-) (12) or pentaborate(1-) salt (13), respectively.

### 5.2 Future work

This thesis has focused on structural aspects of transition metal polyborate compounds however their potential applications have not been investigated or explored. Such application may include fire retardant additives, wide band-gap semi-conductor, fluorescent, piezoelectric and SHG materials. Future work could investigate their physical properties and potential industrial applications.

Further synthetic work could focus on transition metal complexes with high oxidation state metals (e.g. $\mathrm{Pt}^{4+}$ ) as templating cations and the inclusion of metals (e.g. $\mathrm{Al}^{3+}$ ) in the polyborate framework. Work will also focus on employing larger and magnetically interesting polymetallic cages as the cationic counter parts to borate anions. Here we would be able to assess how cation size influences the type of borate obtained within the resultant salt.

## Chapter six

## Experimental

### 6.1 Material analysis

All material reagents were obtained commercially from Sigma-Aldrich (UK) or Lancaster Synthesis (UK) and unless specified were used without further purification. Solvents were standard reagent grade and were used as supplied unless otherwise stated.

NMR spectra were acquired using a Bruker Ultrashield ${ }^{\mathrm{TM}}$ plus 400 , using the TopSpin ${ }^{\mathrm{TM}} 3.2$ software package, operating at: 400 MHz for ${ }^{1} \mathrm{H}, 100 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$, and 128 MHz for ${ }^{11} \mathrm{~B}$, with $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{Si}$ as an external standard for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$, and $\mathrm{BF}_{3}$. $\mathrm{OEt}_{2}$ for ${ }^{11} \mathrm{~B}$. All chemical shifts are given in ppm. Deuterium oxide was used as a solvent unless otherwise stated. Spectra were analysed using Master Re-Nova, version: 6.0.2-5475 software. Elemental analysis ( $\mathrm{C}, \mathrm{H}$, and N ) was carried out at external laboratories, OEA laboratories Ltd in Callington, Cornwall and Elemtex Ltd. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were obtained on an SDT Q600 V4.1 build 59 instruments. Samples were heated in an $\left(\mathrm{Al}_{2} \mathrm{O}_{3}\right)$ alumina crucible at a temperature ramp rate of $10{ }^{\circ} \mathrm{C} / \mathrm{min}$ between $25-800^{\circ} \mathrm{C}$ under a flow air ( $100 \mathrm{~mL} / \mathrm{min}$.). Fourier transform infra-red (FTIR) spectra were performed on a Perkin Elmer 100 FT-IR spectrometer over $4000-400 \mathrm{~cm}^{-1}$. Samples were analysed as KBr pellets. Powder X-ray diffraction (p-XRD) analyses were performed on an XPert PRO Phillips 3040/60 XRD diffractometer instrument. Spectra were analysed and recorded using the Phillips X' Pert Data Collector software package. UV/Vis spectra were performed on Perkin Elmer lambda 35 UV/Vis spectrophotometer. Samples were analysed at a concentration of $1 \times 10^{-3} \mathrm{M}$. Molar magnetic susceptibility values of the prepared compounds were performed on a magnetic susceptibility balance, Johnson Matthey Equipment Limited. Melting point values were performed on a Stuart SMP10 melting point apparatus. Single-crystals were analysed by single-crystal X-ray diffraction at the EPSRC National Crystallography service centre at the University of Southampton (UK).

### 6.2 Preparation of cobalt(III) complexes

### 6.2.1 Preparation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right] \mathrm{Cl}_{3} \cdot \mathbf{2 H}_{2} \mathrm{O}$ (1)

Compound 1 was prepared using a modified version of a previously published procedure. ${ }^{155}$ To an ice bath cooled solution of ethylenediamine (en) ( $20.00 \mathrm{~g}, 30 \%, 99.83$ $\mathrm{mmol})$ was added hydrochloric acid $(5.7 \mathrm{~mL}, 6 \mathrm{M})$. The resulting mixture was poured into a solution of cobalt(III) chloride hexahydrate $(8.00 \mathrm{~g}, 33.60 \mathrm{mmol})$ in distilled water $(25 \mathrm{~mL})$ and
activated charcoal ( 0.90 g ). The cobalt(II) was oxidized to cobalt(III) by bubbling a vigorous stream of air through the solution for 7 hours. The resulting mixture was filtered to remove the charcoal. The mixture was heated in an evaporating dish on a steam bath until a crystalline crust began to form over the surface. After cooling, a solution of concentrated hydrochloric acid ( 5 mL ) and ethanol ( 10 mL ) were added. The orange crystals were collected by filtration, washed with ethanol until the washings were colourless before being dried in an oven at $90^{\circ} \mathrm{C}$ for 24 hours to yield $1(9.80 \mathrm{~g}, 76 \%)$. M.p. $=253-255{ }^{\circ} \mathrm{C}($ dec. $) . \chi_{m}=-155 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. ${ }^{1} \mathrm{H} / \mathrm{ppm}: 2.9\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{CH}_{2}\right), 4.8\left(\mathrm{~s}, 16 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 44.5$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right)$ : 3409(m), 3204(s), 3092(s), 1615(w), 1561(s), 1463(s), 1365(m), 1327(m), 1300(w), 1279(m), 1255(m), 1209(w), 1158(m), 1126(m), 1059(s), 1007(w), 895(w), 786(m), 740(w) 495(w), 466(w). [Lit. 3510-3440, 3195-3060, 1619, 1591-1563, 1466, 1366, 1325, 1302, 1277, 1251, 1215, 1163, 1122, 1057, 1002, 894, 782, 744, 490, 465]. ${ }^{193}$ [Lit. 3210, 3160, 3100]. ${ }^{194}$ UV-Vis $\lambda / \mathrm{nm}\left(\varepsilon / \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right): 337$ (72), 464 (80). [Lit. 338 (68), 466 (75)]. ${ }^{162}$

### 6.2.2 Preparation of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$ (2)

Compound 2 was prepared by a modified version of a literature procedure. ${ }^{156}$ To a hot solution of ammonium chloride ( $7.00 \mathrm{~g}, 130 \mathrm{mmol}$ ) in distilled water ( 14 mL ) was added cobalt(III) chloride hexahydrate $(10.00 \mathrm{~g}, 42 \mathrm{mmol})$. The reaction mixture was stirred to dissolve all the precipitate, and then activated charcoal $(1.00 \mathrm{~g})$ was added. The reaction mixture was cooled to room temperature, and then ammonium hydroxide solution ( $22 \mathrm{~mL}, 35 \%$ ) was added. The oxidation of cobalt(II) to cobalt(III) was carried out by bubbling a stream of air through the solution for 4 hours. The mixture was carefully heated to $60^{\circ} \mathrm{C}$ for 20 minutes. The product mixture was cooled in an ice bath, and the precipitate was collected by filtration. The product was dissolved in a hot solution of hydrochloric acid ( $80 \mathrm{~mL}, 0.5 \mathrm{M}$ ). The charcoal was removed by filtration of the hot solution and concentrated hydrochloric acid ( 12 mL ) was added to the filtrate. The solution was cooled in an ice bath to yield orange crystals of $\mathbf{2}(8.20 \mathrm{~g}, 73 \%)$. M.p. $=237-240{ }^{\circ} \mathrm{C}(\mathrm{dec}.) . \chi_{m}=-123 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3412(\mathrm{~m}), 3233(\mathrm{~s}), 3160(\mathrm{~s})$, 1616(m), 1328(vs), 830(s), 620(m), 495(sh), 475(w). [Lit. 3240, 3170]. ${ }^{194}$ [Lit. 1610(m), 1330(vs), 830(s), 499(vw), 476(vw)]. ${ }^{195}$

### 6.2.3 Preparation of $\left[\mathrm{Co}(\text { dien })_{2}\right] \mathrm{Cl}_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ (3)

Compound $\mathbf{3}$ was prepared by the method of Searle and Keene as described below. ${ }^{13}$ Diethylenetriamine (dien) ( $3.45 \mathrm{~g}, 30 \mathrm{mmol}$ ) and diethylenetriamine trihydrochloric acid ( 1.45 $\mathrm{g}, 60 \mathrm{mmol})$ were added to a solution of cobalt(II) chloride hexahydrate ( $4.76 \mathrm{~g}, 20 \mathrm{mmol}$ ) in distilled water ( 25 mL ) and activated charcoal ( 2.50 g ). A vigorous stream of air was passed through the solution for 24 hours, then the reaction mixture was filtered to remove charcoal. The filtrate volume was reduced to 5 mL using a rotary evaporator. The resulting mixture was cooled in an ice bath and a small amount of ethanol was then added to complete the precipitation of the crude product. The crude product was isolated by filtration, washed with ethanol, recrystallized from ethanol and acetone, and then dried in an oven at $60{ }^{\circ} \mathrm{C}$ for 60 minutes to yield orange crystals of $3(6.90 \mathrm{~g}, 85 \%)$. M.p. $=224-225^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-83 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. ${ }^{1} \mathrm{H} / \mathrm{ppm}: 3.0\left(\mathrm{~m}, 16 \mathrm{H}, \mathrm{CH}_{2}\right), 4.8\left(\mathrm{~s}, 14 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}\right)$. [Lit. $3.0\left(\mathrm{~m}, \mathrm{CH}_{2}\right), 4.8\left(\mathrm{~s}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}\right)$ ]. ${ }^{13}$ ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 38.5,42.2,43.5,45.9,47.2,50.4,53.2,54.9$. IR (KBr/cm ${ }^{-1}$ ): 3398(s), 3166(s), 3063(s), 2961(s), 2886(s), 1610(m), 1556(m), 1476(m), 1359(m), 1325(m), 1189(m), 1153(m), 1127(m), 1081(m), 1046(s), 896(w), 878(w), 777(m), 666(m), 570(m), 519(m).

### 6.2.4 Preparation of $[\mathrm{Co}(\mathrm{diNOsar})] \mathrm{Cl}_{3}$ (4)

Compound $\mathbf{4}$ was prepared following a previously published procedure. ${ }^{157}$ To a stirred solution of $\mathbf{1}(2.45 \mathrm{~g}, 6.41 \mathrm{mmol})$ and anhydrous sodium carbonate $\mathrm{Na}_{2} \mathrm{CO}_{3}(1.20 \mathrm{~g}, 11.3 \mathrm{mmol})$ in distilled water ( 25 mL ) was added formaldehyde ( $20 \mathrm{~mL}, 37 \%$ ) followed by nitromethane $(2.85 \mathrm{~g}, 37.0 \mathrm{mmol})$. The reaction mixture was placed in a water bath and the solution was maintained without stirring at $35-40{ }^{\circ} \mathrm{C}$ for 90 minutes. The colour rapidly changed from clear yellow to dark brown. The mixture was allowed to stand at $0{ }^{\circ} \mathrm{C}$ for 48 hours. The orange crystals of the "chloride carbonate" salt were filtered off. The resulting chloride carbonate solid was cautiously dissolved in hot hydrochloric acid ( $7 \mathrm{~mL}, 3 \mathrm{M}$ ). After cooling in an ice bath the fine crystals of $\mathbf{4}$ were isolated by filtration, air dried and placed in a vacuum desiccator to yield orange crystals ( $1.45 \mathrm{~g}, 42 \%$ ). M.p. $=274-275^{\circ} \mathrm{C}($ dec. $) \cdot \chi_{m}=-167 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} .{ }^{1} \mathrm{H} / \mathrm{ppm}: 3.4$, 3.9 (AB doublet of doublet, $12 \mathrm{H}, J=12 \mathrm{~Hz}, \mathrm{CH}_{2}$ Caps), 3.0, 3.6 (complex AA'BB' coupling pattern, $12 \mathrm{H}, J=8 \mathrm{~Hz}, \mathrm{CH}_{2}$ of en), $4.8\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NH}_{2}\right)$. [Lit. two overlapping quartet, associated with AB or $\mathrm{AA}^{\prime} \mathrm{BB}^{\prime}$ patterns of cap and en methylene groups, 3.4, 4.1, 3.1, and 3.6]. ${ }^{162}$ ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 51.2,54.7,87.4$. IR (KBr/cm ${ }^{-1}$ ): 3459(s), 3034(s), 2864(s), 1558(s), 1452(m), 1344(s), 1078(m), 1058(m), 812(m), 469(m). [Lit. 1555(s), 1353(s)]. ${ }^{157}$

### 6.2.5 Preparation of $\left[\mathrm{Co}(\mathrm{pn})_{3}\right] \mathrm{Cl}_{3}(5)$

Compound 5 was prepared as described in the literature. ${ }^{158}$ Cobalt(III) chloride hexahydrate ( $3.55 \mathrm{~g}, 14.9 \mathrm{mmol}$ ), hydrochloric acid ( $3 \mathrm{~mL}, 5 \mathrm{M}$ ), and 1,2-diaminopropane ( pn ) $(3.70 \mathrm{~g}, 49.9 \mathrm{mmol})$ were mixed together and dissolved in distilled water ( 7.5 mL ). Cobalt(II) was oxidized to cobalt(III) by passing a stream of air through the solution at room temperature for 24 hours. The resulting mixture was filtered to remove charcoal and the filtrate was acidified with a few drops of concentrated hydrochloric acid. The resulting solution was gently evaporated to dryness using a rotary evaporator to yield a dark green powder of $\mathbf{5}$ which was then recrystallized using ethanol ( $4.50 \mathrm{~g}, 78 \%$ ). M.p. $=237-240{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-133 \times 10^{-6} \mathrm{~cm}^{3}$ $\mathrm{mol}^{-1} .{ }^{1} \mathrm{H} / \mathrm{ppm}: 1.3\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{CH}_{3}\right.$ of pn), $2.5\left(\mathrm{t}, 3 \mathrm{H}, J=13.2 \mathrm{~Hz}, J=26.4 \mathrm{~Hz}, \mathrm{H}_{\mathrm{a}}\right.$ of $\mathrm{CH}_{2}$ of pn), $2.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{Hb}_{\mathrm{b}}\right.$ of $\mathrm{CH}_{2}$ of pn$), 3.0(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}$ of pn$)$, and $4.8\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NH}_{2}\right)$. [Lit. $3.1(\mathrm{~m}, 3 \mathrm{H}$, CH of pn$), 2.9\left(\mathrm{dd}, 3 \mathrm{H}, \mathrm{H}_{\mathrm{b}}\right.$ of $\mathrm{CH}_{2}$ of pn), $2.5\left(\mathrm{t}, 3 \mathrm{H}, \mathrm{H}_{\mathrm{a}}\right.$ of $\mathrm{CH}_{2}$ of pn), $1.4\left(\mathrm{~d}, 9 \mathrm{H}, \mathrm{CH}_{3}\right.$ of $\mathrm{pn})] .{ }^{160}{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 16.5\left(\mathrm{CH}_{3}\right.$ of pn$), 49.9(\mathrm{CH}$ of pn$)$, and $53.9\left(\mathrm{CH}_{2}\right.$ of pn$)$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right)$ : 3393(s), 3190(s), 3081(s), 2971(m), 1554(m), 1459(m), 1394(w), 1346(w), 1243(w), 1137(w), 1110(m), 1047(w), 1016(w), 917(w), 781(w).

### 6.3 Preparation of cobalt(III) complex polyborate compounds

### 6.3.1 Preparation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{8} \mathrm{O}_{10}(\mathrm{OH})_{6}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}$ (6)

A solution of compound $\mathbf{1}(1.00 \mathrm{~g}, 2.7 \mathrm{mmol})$ in water $(10 \mathrm{~mL})$ was added to an aqueous suspension solution of excess activated Dowex $550 \mathrm{~A}(50 \mathrm{~g})$ monosphere anion exchange resin in water ( 40 mL ). The resulting mixture was stirred at room temperature for 24 hours. The Dowex 550A resin was separated by filtration with a Buchner funnel and washed four times with a distilled water $(4 \times 5 \mathrm{~mL})$. The solution of $\left[\mathrm{Co}(\mathrm{en})_{3}\right](\mathrm{OH})_{3}$ was reduced to a volume of 15 mL using a rotary evaporator. Methanol ( 15 mL ) was added to the concentrated solution, followed by boric acid ( $2.46 \mathrm{~g}, 39.9 \mathrm{mmol}$ ). The reaction mixture was gently warmed for 3 hours. The solution volume was reduced to 5 mL using a rotary evaporator. The concentrated solution was left for 40 days in NMR tubes for crystallization to yield orange crystals of $\mathbf{6}$ ( 0.97 g, $41 \%$ ). M.p. $=264-267{ }^{\circ} \mathrm{C}(\mathrm{dec}.) \cdot \chi_{m}=-101 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{6} \mathrm{H}_{44} \mathrm{~B}_{13} \mathrm{CoN}_{6} \mathrm{O}_{31}$. Anal. Calc.: $\mathrm{C}=8.0 \%, \mathrm{H}=4.9 \%, \mathrm{~N}=9.4 \%$. Found: $\mathrm{C}=8.2 \%, \mathrm{H}=5.0 \%, \mathrm{~N}=9.6 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 2.7(\mathrm{~m}, 12 \mathrm{H}$, $\mathrm{CH}_{2}$ of en), 4.8 (s, $\left.32 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 44.6 .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 13.4$ ( $15 \%$ ), 16.5 ( $85 \%$ ). IR (KBr/cm ${ }^{-1}$ ): 3461(s), 3265(s), 3149(s), 2960(w), 1611(w), 1394(s), 1324(s), 1170(s), 1059(s), 1033(m), 939(m), 863(m), 811(m), 779(m), 710(w). p-XRD d-spacing/Å (\% rel. int.):
8.47 (53), 7.60 (54), 6.35 (73), 5.76 (100), 3.64 ( $370,3.33$ (53). TGA: $100-150{ }^{\circ} \mathrm{C}$, loss of five interstitial $\mathrm{H}_{2} \mathrm{O}: 9.7 \% ~\left(10.1 \%\right.$ calc.); 150-250 ${ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of five further $\mathrm{H}_{2} \mathrm{O}: 20.5 \%$ ( $20.1 \%$ calc.); 250-800 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $41.0 \%$ ( $40.3 \%$ calc.); residual $\mathrm{CoB}_{13} \mathrm{O}_{21} 59.0 \%$ ( $59.7 \%$ calc.).

### 6.3.2 Preparation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ (7)

The preparation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right] \mathrm{Cl}(\mathrm{OH})_{2}$ was carried out using the same method as described above for the preparation of $\mathbf{6}$ from $\mathbf{1}(1.00 \mathrm{~g}, 2.66 \mathrm{mmol})$. Dowex ( 25 g ), and boric $\operatorname{acid}(1.64 \mathrm{~g}, 26.6 \mathrm{mmol})$ was carefully added. The reaction mixture was gently warmed for 2 hours. The solution volume was reduced to $(5 \mathrm{~mL})$ using a rotary evaporator. The final mixture was sealed in an autoclave stainless steel reactor with a Teflon liner at $140{ }^{\circ} \mathrm{C}$ for 7 days before being cooled to ambient temperature to yield orange crystals of $7(1.15 \mathrm{~g}, 57 \%)$. M.p. $=294-$ $295^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-230 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{6} \mathrm{H}_{38} \mathrm{~B}_{10} \mathrm{ClCoN}_{6} \mathrm{O}_{23}$. Anal. Calc.: $\mathrm{C}=9.4 \%, \mathrm{H}=5.0 \%$, $\mathrm{N}=11.0 \%$. Found: $\mathrm{C}=9.7 \%, \mathrm{H}=4.8 \%, \mathrm{~N}=10.5 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 2.7\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{CH}_{2}\right.$ of en), $4.8(\mathrm{~s}$, $\left.26 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 44.3 .{ }^{11} \mathrm{~B} / \mathrm{ppm}$ : 1.2 (8\%), 12.9 (33\%), and 17.4 (59\%). IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3267(s), 3167(s), 2945(w) 1613(w), 1409(s), 1302(s), 1154(m), 1057(m), 1007(m), 986(m), $916(\mathrm{~m}), 895(\mathrm{~m}), 785(\mathrm{~m}), 709(\mathrm{~m})$. UV-Vis, $\lambda / \mathrm{nm}\left(\varepsilon / \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right): 337(180), 462(180) . \mathrm{p}-$ XRD d-spacing/Å (\% rel. int.): 7.33 (55), 5.96 (100), 4.68 (11), 4.31 (20), 3.72 (5). TGA: 100$180^{\circ} \mathrm{C}$, loss of three interstitial $\mathrm{H}_{2} \mathrm{O}: 7.8 \%\left(7.1 \%\right.$ calc.); $180-280^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 17.7 \%$ ( $16.5 \%$ calc.); 280-800 ${ }^{\circ} \mathrm{C}$, oxidation of organic component $40.0 \%$ ( $40.1 \%$ calc.); residual $\mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl} 60.0 \%$ ( $59.9 \%$ calc.).

### 6.3.3 Preparation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6} \cdot \cdot 6 \mathrm{H}_{2} \mathrm{O}(8)\right.$

The preparation of $\left[\mathrm{Co}(\mathrm{en})_{3}\right](\mathrm{OH})_{3}$ was carried out exactly in the same method as described above for the preparation of $\mathbf{6}$ from $\mathbf{1}(1.00 \mathrm{~g}, 2.66 \mathrm{mmol})$, Dowex ( 50 g ), and boric $\operatorname{acid}(1.64 \mathrm{~g}, 26.6 \mathrm{mmol})$. The reaction mixture was gently warmed for 3 hours. The solution volume was reduced to 5 mL using a rotary evaporator. The final mixture was left for 7 days at room temperature for crystallization to yield orange crystals of $8(0.80 \mathrm{~g}, 45 \%)$. M.p. $=242-$ $244{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-255 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{6} \mathrm{H}_{42} \mathrm{~B}_{7} \mathrm{CoN}_{6} \mathrm{O}_{21}$. Anal. Calc.: $\mathrm{C}=10.8 \%, \mathrm{H}=6.4 \%$, $\mathrm{N}=12.3 \%$. Found: $\mathrm{C}=10.7 \%, \mathrm{H}=6.3 \%, \mathrm{~N}=12.6 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 2.7\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{CH}_{2}\right.$ of en), 4.8 (s, 30H, $\left.\mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 44.2 .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 13.0$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3413(s), 3253(s), 2926(w), 2855(w), 1637(w), 1618(w), 1385(s), 1322(s), 1162(m), 1058(s), 1005(s), 930(m),

825(w), 757 (w), $702(\mathrm{w})$. p-XRD d-spacing/Å (\% rel. int.): 8.35 (74), 8.00 (31), 6.62 (100), 6.22 (31), 5.46 (39), 4.54 (39). TGA: $70-180{ }^{\circ} \mathrm{C}$, loss three of six interstitial $\mathrm{H}_{2} \mathrm{O}: 15.0 \%(16.1 \%$ calc.); $180-280{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of three further $\mathrm{H}_{2} \mathrm{O}: 23.2 \%(24.1 \%$ calc.); 280-800 ${ }^{\circ} \mathrm{C}$, oxidation of organic component $49.8 \%$ ( $51.2 \%$ calc.); residual $\mathrm{CoB}_{7} \mathrm{O}_{12}$ $50.2 \%$ ( $48.8 \%$ calc.).

### 6.3.4 Preparation of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{~B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right]_{3} \cdot 11 \mathrm{H}_{2} \mathrm{O}(9)$

The preparation of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right](\mathrm{OH})_{3}$ was carried out exactly in the same method as described previously for the preparation of 6 from $2(0.71 \mathrm{~g}, 2.66 \mathrm{mmol})$ and Dowex ( 50 g ). Boric acid ( $1.64 \mathrm{~g}, 26.6 \mathrm{mmol}$ ) was added to the solution, which was gently warmed with stirring for 2 hours. The solvent was evaporated to 5 mL using a rotary evaporator before being the product was crystalized from solution. The product was filtered off and allowed to dry for 3 hours in an oven at $40^{\circ} \mathrm{C}$ to yield orange crystals of $9(0.60 \mathrm{~g}, 41 \%)$. M.p. $=258-260^{\circ} \mathrm{C}(\mathrm{dec}$.$) .$ $\chi_{m}=-330 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{B}_{12} \mathrm{Co}_{2} \mathrm{H}_{70} \mathrm{~N}_{12} \mathrm{O}_{38}$. Anal. Calc.: $\mathrm{H}=6.4 \%, \mathrm{~N}=15.4 \%$. Found: $\mathrm{H}=$ $6.5 \%, \mathrm{~N}=15.4 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 10.4$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3400(\mathrm{~s}), 3308(\mathrm{~s}), 1636(\mathrm{~m}), 1421(\mathrm{~s}), 1384(\mathrm{~s})$, 1339(s),1190(s), 1015(s), 995(s), 943(m), 809(m), 704(w). p-XRD d-spacing/Å (\% rel. int.): 4.95 (99), 4.83 (100), 3.47 (34). TGA: $70-150^{\circ} \mathrm{C}$, condensation of polyborate which loss of eleven $\mathrm{H}_{2} \mathrm{O}: 17.8 \%$ ( $18.1 \%$ calc.); $150-350{ }^{\circ} \mathrm{C}$, oxidation of ammonia molecules $46.5 \%$ ( $46.7 \%$ calc.); residual $\mathrm{Co}_{2} \mathrm{~B}_{12} \mathrm{O}_{21} 53.5 \%$ ( $53.3 \%$ calc.).

### 6.3.5 Preparation of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right] \mathrm{Cl} \cdot 5 \mathrm{H}_{2} \mathrm{O}(10)$

The preparation of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}(\mathrm{OH})_{2}$ was carried out exactly in the same method as described previously for the preparation of $\mathbf{6}$ from $2(1.00 \mathrm{~g}, 3.73 \mathrm{mmol})$ and Dowex ( 30 g ). Boric acid ( $2.30 \mathrm{~g}, 27.3 \mathrm{mmol}$ ) was added to the solution which was gently warmed with stirring for 2 hours. The solvent was evaporated to ( 5 mL ) using a rotary evaporator. The product was isolated by filtration before being allowed to dry for 3 hours in an oven at $40^{\circ} \mathrm{C}$ to yield orange crystals of $10(0.80 \mathrm{~g}, 36 \%)$. M.p. $=249-251{ }^{\circ} \mathrm{C}($ dec. $) . \chi_{m}=-37 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{B}_{7} \mathrm{CoH}_{33} \mathrm{~N}_{6} \mathrm{O}_{19} \mathrm{Cl}$. Anal. Calc.: $\mathrm{H}=5.6 \%, \mathrm{~N}=14.2 \%$. Found: $\mathrm{H}=5.6 \%, \mathrm{~N}=14.1 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm}$ : 13.4. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3477(s), 3407(s), 3320(s), 1639(w), 1440(s), 1401(m), 1353.1(s), 1164(m), 1114(s), 1037(s), 954(m), 852(m), 800(m), 767(w), 732(w), 699(w), 653(w). p-XRD d-spacing/Å (\% rel. int.): 8.04 (33), 6.20 (44), 5.84 (100), 5.24 (64), 4.11 (34), 2.03 (46). TGA: $70-150{ }^{\circ} \mathrm{C}$, loss of five interstitial $\mathrm{H}_{2} \mathrm{O}: 14.1 \%$ ( $15.2 \%$ calc.); 180- $250{ }^{\circ} \mathrm{C}$, condensation of
polyborate which loss of two and half further $\mathrm{H}_{2} \mathrm{O}: 21.4 \%$ ( $22.8 \%$ calc.); 250-650 ${ }^{\circ} \mathrm{C}$, oxidation of ammonia molecules $39.0 \%$ ( $40.0 \%$ calc.); residual $\mathrm{CoB}_{7} \mathrm{O}_{11.5} \mathrm{Cl} 61.0 \%$ ( $60.0 \%$ calc.).

### 6.3.6 Preparation of $\left[\mathrm{Co}(\text { dien })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{6}\right] \cdot \mathbf{9 H}_{2} \mathrm{O}(11)$

The preparation of $\left[\mathrm{Co}(\operatorname{dien})_{2}\right](\mathrm{OH})_{3}$ was carried out in the same method as described previously for the preparation of $\mathbf{6}$ from $3(1.00 \mathrm{~g}, 2.45 \mathrm{mmol})$ and Dowex ( 50 g ). Boric acid $(1.51 \mathrm{~g}, 24.5 \mathrm{mmol})$ was added with stirring. The reaction mixture was stirred for 3 hours at room temperature. The solvents were evaporated to 5 mL using a rotary evaporator, then the concentrated solution was left for 25 days in several NMR tubes for crystallization to yield yellow crystals of $11(0.65 \mathrm{~g}, 35 \%)$. M.p. $=238-240{ }^{\circ} \mathrm{C}($ dec. $) . \chi_{m}=-120 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{8} \mathrm{H}_{50} \mathrm{~B}_{7} \mathrm{CoN}_{6} \mathrm{O}_{24}$. Anal. Calc.: $\mathrm{C}=12.8 \%, \mathrm{H}=6.7 \%, \mathrm{~N}=11.2 \%$. Found: $\mathrm{C}=13.4 \%, \mathrm{H}=7.2 \%$, $\mathrm{N}=11.1 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 3.0\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{CH}_{2}\right), 3.2\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 4.8\left(\mathrm{~s}, 34 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}\right)$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 43.3,55.0,{ }^{11} \mathrm{~B} / \mathrm{ppm}: 12.3$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3432(s), 3201(s), 3095(s), 2950(m), 1631(w), 1415(s), 1385(s), 1331(s), 1134(m), 1084(s), 1047(s), 932(m), 861(m), 750(w), $656(\mathrm{w})$. p-XRD d-spacing/Å (\% rel. int.): 3.87 (100), 2.02 (55), 1.43 ( 90 ), 1.22 (30). TGA: 70$200{ }^{\circ} \mathrm{C}$, loss of nine interstitial $\mathrm{H}_{2} \mathrm{O}: 19.5 \%$ ( $21.7 \%$ calc.); 200-280 ${ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of three further $\mathrm{H}_{2} \mathrm{O}: 28.4 \%$ ( $28.9 \%$ calc.); 280-800 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $56.9 \%$ ( $56.5 \%$ calc.); residual $\mathrm{CoB}_{7} \mathrm{O}_{12} 43.1 \%$ ( $43.5 \%$ calc.).

### 6.3.7 Preparation of $\left[\mathrm{Co}(\text { diNOsar })_{2}\left[\mathrm{~B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \mathrm{Cl}_{5} \cdot \mathbf{4 . 7}^{2} \mathbf{7 5 H}_{2} \mathrm{O}\right.$ (12)

The preparation of $[\mathrm{Co}(\mathrm{diNOsar})] \mathrm{Cl}_{2} \mathrm{OH}$ was carried out in the same method as described previously in the preparation of $\mathbf{6}$ using $\mathbf{4}(1.00 \mathrm{~g}, 1.85 \mathrm{mmol})$ and Dowex ( 20 g ). Boric acid ( $0.57 \mathrm{~g}, 9.25 \mathrm{mmol}$ ) was added to the aqueous solution which was stirred for 2 hours at room temperature. The solution volume was reduced in volume by gently evaporation at 45 ${ }^{\circ} \mathrm{C}$ to 5 mL before being left for 4 weeks in several NMR tubes for crystallization to yield orange needle crystals of $\mathbf{1 2}(0.12 \mathrm{~g}, 10 \%)$. M.p. $=283-285{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-25 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{28} \mathrm{H}_{73.5} \mathrm{~B}_{3} \mathrm{Cl}_{5} \mathrm{Co}_{2} \mathrm{~N}_{16} \mathrm{O}_{19.75}$. Anal. Calc.: $\mathrm{C}=26.4 \%, \mathrm{H}=5.8 \%, \mathrm{~N}=17.5 \%$. Found: $\mathrm{C}=25.6 \%$, $\mathrm{H}=6.5 \%, \mathrm{~N}=16.7 \% .^{1} \mathrm{H} / \mathrm{ppm}: 3.3,3.9$ (AB doublet of doublet, $12 \mathrm{H}, J=12 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Caps}$ ), 2.9, 3.5 (complex AA'BB' coupling pattern, $12 \mathrm{H}, \mathrm{CH}_{2}$ of en), 4.8 (s, $19.5 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}$ ). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}$ : $51.4\left(\mathrm{CH}_{2}\right.$ group of the en), $55.1\left(\mathrm{CH}_{2}\right.$ group of the capping units), 87.9 (tertiary $\mathrm{C}-\mathrm{NO}_{2}$ of the caps). ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 16.2$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3552(s), 3475(s), 3413(s), 3236(m), 3014(m), 2866(m), 1617(s), 1559(s), 1432(m), 1343(m), 1179(w), 1134(w), 1076(m), 1018(w),

988(w), 952(w), 873(w), 847(w), 812(w), 780(w), and 620(m). p-XRD d-spacing/ $\AA$ (\% rel. int.): 8.81 (4), 8.21 (4), 7.85 (4), 7.25 (5), 4.86 (3), 3.17 (100). TGA: $70-150{ }^{\circ} \mathrm{C}$, loss of five interstitial $\mathrm{H}_{2} \mathrm{O}: 7.8 \%$ ( $6.7 \%$ calc.); $150-250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of two further $\mathrm{H}_{2} \mathrm{O}: 11.0 \%$ ( $9.5 \%$ calc.); $250-800{ }^{\circ} \mathrm{C}$, oxidation of organic content $68.8 \%$ ( $68.1 \%$ calc.); residual $\mathrm{Co}_{2} \mathrm{~B}_{3} \mathrm{O}_{5} \mathrm{Cl}_{5} 31.3 \%$ ( $31.9 \%$ calc.).

### 6.3.8 Preparation of $[\mathrm{Co}($ diNOsar $)]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ (13)

The preparation of $[\mathrm{Co}($ diNOsar $)] \mathrm{Cl}(\mathrm{OH})_{2}$ was carried out in the same method as described previously in the preparation of $\mathbf{6}$ using $\mathbf{4}(1.00 \mathrm{~g}, 1.85 \mathrm{mmol})$ and Dowex ( 30 g ). Boric acid ( $1.14 \mathrm{~g}, 18.5 \mathrm{mmol}$ ) was added to the aqueous solution which was gently warmed with stirring for 60 minutes. The solution volume was reduced using a rotary evaporator to 8 mL before being left for 3 weeks to yield orange crystals of $\mathbf{1 3}(0.95 \mathrm{~g}, 54 \%)$. M.p. $=283-285$ ${ }^{\circ} \mathrm{C}($ dec. $) \cdot \chi_{m}=-50 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{14} \mathrm{H}_{44} \mathrm{~B}_{10} \mathrm{ClCoN}_{8} \mathrm{O}_{27}$. Anal. Calc.: $\mathrm{C}=18.4 \%, \mathrm{H}=5.1 \%, \mathrm{~N}$ $=12.3 \%$. Found: $\mathrm{C}=18.3 \%, \mathrm{H}=5.0 \%, \mathrm{~N}=12.4 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 3.4,3.7(\mathrm{AB}$ doublet of doublet, $12 \mathrm{H}, J=12 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Caps}$ ), 2.8, 3.6 (complex AA'BB' coupling pattern, $12 \mathrm{H}, \mathrm{CH}_{2}$ of en), 4.8 (s, $\left.20 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}$ : $51.3\left(\mathrm{CH}_{2}\right.$ group of the en), $55.0\left(\mathrm{CH}_{2}\right.$ group of the capping units), 87.8 (tertiary $\mathrm{C}-\mathrm{NO}_{2}$ of the caps). ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 15.9$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): $3437(\mathrm{~s})$, 3025(s), 2859(s),1634(s), 1558(s),1447(s), 1348(s), 1100(m), 1078(m), 925(m), 810(m), 696(w). p-XRD d-spacing/Å (\% rel. int.): 8.66 (16), 7.36 (33), 6.04 (19), 4.88 (14), 3.19 (100). TGA: $70-150{ }^{\circ} \mathrm{C}$, loss of four interstitial $\mathrm{H}_{2} \mathrm{O}: 7.9 \%$ ( $7.9 \%$ calc.); $150-250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 15.0 \%$ ( $15.7 \%$ calc.); 250-800 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $59.1 \%$ ( $59.1 \%$ calc.); residual $\mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl} 40.9 \%$ ( $40.9 \%$ calc.).

### 6.3.9 Preparation of $\left[\mathrm{Co}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}^{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ (14)

The preparation of $\left[\mathrm{Co}(\mathrm{pn})_{3}\right] \mathrm{Cl}(\mathrm{OH})_{2}$ was carried out as described previously in the preparation of 6 using $5(1.00 \mathrm{~g}, 2.58 \mathrm{mmol})$ and Dowex ( 30 g ). Boric acid ( $1.59 \mathrm{~g}, 25.8 \mathrm{mmol}$ ) was added to the aqueous solution which was gently warmed with stirring for 2 hours. A rotary evaporator was used to reduce the solution volume to 5 mL . The final mixture was sealed in a Teflon lined stainless steel autoclave, and heated at $140^{\circ} \mathrm{C}$ for 3 days. The product was isolated by filtration, and left overnight to dry in a desiccator. The crude result was recrystallized using mix-solvent $\mathrm{H}_{2} \mathrm{O}: \mathrm{EtOH}(2: 8)$ to yield bright orange crystals of 14 ( $1.05 \mathrm{~g}, 50 \%$ ). M.p. $=294-$ $295{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-200 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{9} \mathrm{H}_{44} \mathrm{~B}_{10} \mathrm{ClCoN}_{6} \mathrm{O}_{23}$. Anal. $\mathrm{Calc} .: \mathrm{C}=13.4 \%, \mathrm{H}=$
$6.5 \%, \mathrm{~N}=10.4 \%$. Found: $\mathrm{C}=13.6 \%, \mathrm{H}=6.3 \%, \mathrm{~N}=10.4 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 1.3\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{CH}_{3}\right.$ of pn$)$, $2.5\left(\mathrm{t}, 3 \mathrm{H}, J=13.2 \mathrm{~Hz}, J=26.4 \mathrm{~Hz}, \mathrm{C}_{\mathrm{b}}\right.$ of $\mathrm{CH}_{2}$ of pn$), 2.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{H}_{\mathrm{a}}\right.$ of $\mathrm{CH}_{2}$ of pn), $3.0(\mathrm{~m}$, $3 \mathrm{H}, \mathrm{CH}$ of pn), and $4.8\left(\mathrm{~s}, 26 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}$ : $16.5\left(\mathrm{CH}_{3}\right.$ of pn$), 49.9(\mathrm{CH}$ of $\mathrm{pn}), 53.9\left(\mathrm{CH}_{2}\right.$ of pn). ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 1.2(11 \%), 13.2(33 \%)$, and $16.6(56 \%)$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3437(\mathrm{~s})$, 3249(m), 2925(m), 1638(w), 1435(s), 1352(s), 1238(w), 1091(m), 1023(m), 925(m), 780(w), 692(w). p-XRD d-spacing/Å (\% rel. int.): 2.34 (93), 2.03 (98), 1.43 (60), 1.22 (100). TGA: 70$160^{\circ} \mathrm{C}$, loss of three interstitial $\mathrm{H}_{2} \mathrm{O}: 7.2 \%\left(6.7 \%\right.$ calc.); $160-250^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 16.0 \%$ ( $15.6 \%$ calc.); $250-800{ }^{\circ} \mathrm{C}$, oxidation of organic content $44.8 \%$ ( $43.2 \%$ calc.); residual $\mathrm{CoB}_{10} \mathrm{O}_{16} \mathrm{Cl} 55.2 \%$ ( $56.8 \%$ calc.).

### 6.4 Preparation of copper(II) complexes

### 6.4.1 Preparation of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]_{\mathrm{SO}_{4}}$ (15)

Compound 15 was prepared as described in the literature. ${ }^{174} \mathrm{~A}$ slight excess of the ethylenediamine (en) $(2.10 \mathrm{~g}, 70 \%, 24.45 \mathrm{mmol})$ was added to an aqueous solution of copper(II) sulphate pentahydrate $(4.00 \mathrm{~g}, 16.02 \mathrm{mmol})$ in distilled water $(10 \mathrm{~mL})$. The solution was concentrated by gentle evaporation on a warm water bath before being cooled in an ice bath to yield navy crystals of $15(3.70 \mathrm{~g}, 83 \%)$. M.p. $=240-241{ }^{\circ} \mathrm{C} . \chi_{m}=1210 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3307(s), 3218(s), 3145(s), 2967(w), 2953(w), 2887(w), 1586(s), 1472(w), 1453(w), 1394(w), 1321(w), 1277(m), 1165(m), 1111(m), 1089(m), 1045(s), 1020(m), 988(m), 975(m), 671(m), 527(s), 469(m). [Lit. 968, 1050, 1062, 1120]. ${ }^{174}$

### 6.4.2 Preparation of $\left[\mathrm{Cu}(\mathrm{pn})_{2}\right]_{\mathrm{SO}_{4}}{ }_{4}(\mathbf{1 6 )}$

Compound 16 was prepared following a previously published procedure. ${ }^{175}$ A solution of 1,2-propanediamine ( pn ) $(2.37 \mathrm{~g}, 32.04 \mathrm{mmol})$ in distilled water $(3 \mathrm{~mL})$ was added to an aqueous solution of copper(II) sulphate pentahydrate ( $4.00 \mathrm{~g}, 16.02 \mathrm{mmol}$ ) in distilled water $(10 \mathrm{~mL})$. The solution volume was reduced to $(4 \mathrm{~mL})$ by gentle evaporation on a warm water bath before being cooled in an ice bath. The resulting product, which formed over the cooling period, was filtered, washed with $\mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH}$ and dried at $50{ }^{\circ} \mathrm{C}$ to yield purple crystals of $\mathbf{1 6}$ $(3.80 \mathrm{~g}, 77 \%)$. M.p. $=232-235^{\circ} \mathrm{C}(\mathrm{dec}.) \cdot \chi_{m}=1380 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3431(\mathrm{~s})$, 3248(s), 3134(s), 2933(w), 2879(w), 1592(s), 1460(w), 1394(w), 1280(w),1125(sh), 1115(s),

1057(m), 1022(m), 912(w) 699(m), and 618(s). [Lit. 3431, 3214, 3130, 2940, 2886, 1582, 1466, 1401, 1281, 1121, 1027, 913, 619]. ${ }^{175}$

### 6.4.3 Preparation of $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{Cl}_{2}$ (17)

Compound $\mathbf{1 7}$ was prepared by a method as described by Pariya. ${ }^{176}$ To a solution of copper(II) chloride di-hydrate ( $2.00 \mathrm{~g}, 11.73 \mathrm{mmol}$ ) in ethanol ( 100 mL ) was added 1,2diaminocyclohexane (dach) ( $2.68 \mathrm{~g}, 23.46 \mathrm{mmol}$ ). The solution volume was reduced by gentle evaporation on a warm water bath before being cooled in an ice bath. The resulting product, which formed over the cooling period, was isolated by filtration, washed with $\mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH}$ and dried at $40^{\circ} \mathrm{C}$ to yield pink crystals of $17(3.00 \mathrm{~g}, 66 \%)$. M.p. $=238-240^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=1270 \times 10^{-}$ ${ }^{6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. IR (KBr/cm ${ }^{-1}$ ): 3470(s), 3360(s), 3256(s), 3222(s), 3135(s), 2930(s), 2857(s), 1591(s), 1447(s), 1399(m), 1184(m), 1168(m), 1132(s), 170(s), 156(s), 136(s), 987(s), 946(w), 912(w), 875(w), 859(w), 717(w). [Lit. 3270, 3230, 3150, 1592]. ${ }^{196}$

### 6.4.4 Preparation of $\left[\mathrm{Cu}(\operatorname{tn})_{2}\right] \mathrm{SO}_{4} \cdot \mathbf{0 . 5 H}_{2} \mathrm{O}$ (18)

Compound 18 was prepared by the same procedure as was used for compound 15. ${ }^{197,198}$ Copper(II) sulphate pentahydrate ( $3.00 \mathrm{~g}, 18.7 \mathrm{mmol}$ ) and 1,3-diaminopropane (tn) ( 2.78 g , $37.6 \mathrm{mmol})$ were added to water ( 10 mL ) and then the addition of ethanol $(25 \mathrm{~mL})$ yielded purple crystals of $18(4.10 \mathrm{~g}, 69 \%)$. M.p. $=264-265^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=1170 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{CuC}_{6} \mathrm{H}_{21} \mathrm{O}_{4.5} \mathrm{~N}_{4} \mathrm{~S}$. Anal. Calc.: $\mathrm{C}=23.0 \%, \mathrm{H}=6.7 \%, \mathrm{~N}=17.6 \%$. Found: $\mathrm{C}=23.0 \%, \mathrm{H}=6.7 \%$, $\mathrm{N}=17.1 \%$. IR (KBr/cm ${ }^{-1}$ ): 3427(s), 3212(s), 2938(m), 2884(m), 1575(s), 1441(w), 1401(w), 1321(w), 1282(w), 1179(s), 1115(s), 1025(w), 991(m), 912(m), 883(w), 688(w), and 618(s). [Lit. 3300-3200, 2920, 2890, 1580, 1450, 1400, 1320, 1270, 1160, 1010, 1000, 900, 870, 730, 670]. ${ }^{199}$

### 6.4.5 [ $\left.\mathrm{Cu}(N, N-\text {-dmen })_{2}\right] \mathrm{Cl}_{2} \quad(19)$

Compound 19 was prepared by a procedure modified from Cui et al. ${ }^{177}$ Copper chloride dihydrate ( $4.00 \mathrm{~g}, 24 \mathrm{mmol}$ ) was dissolved in ethanol $(40 \mathrm{~mL})$ and gave a clear green solution. An ethanolic solution ( 10 mL ) of $N, N$-dimethylethylenediamine ( $4.14 \mathrm{~g}, 47 \mathrm{mmol}$ ) was added dropwise to the green solution with stirring and was left to stir for a further 10 minutes and gave a dark blue solution. The solution was placed in an ice bath for 2 hours until a dark blue
precipitate had formed. Precipitate was collected by suction filtration and washed with $2 \times 5$ mL of diethyl ether and dried for 30 minutes in a desiccator. Crude yield: $75.6 \%$. M.p.: 145$147^{\circ} \mathrm{C} . \chi_{\mathrm{m}}=960 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}, \mathrm{C}_{8} \mathrm{H}_{24} \mathrm{CuN}_{4} \mathrm{Cl}_{2}$. Anal. Calc.: $\mathrm{C}=30.9 \%, \mathrm{H}=7.8 \%, \mathrm{~N}=18.0 \%$. Found: $\mathrm{C}=31.2 \%, \mathrm{H}=7.8 \%, \mathrm{~N}=18.0 \%$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): $3460(\mathrm{~m}), 3407(\mathrm{~m}), 3204(\mathrm{~s}), 3112$ (s), 3069 (m), 2969 (m), 2872 (m), 1635 (w), 1592 (m), 1472 (m), 1448 (m), 1397 (m), 1339 (w), 1319 (w), 1281 (w), 1224 (w), 1170 (s), 1131 (m), 1082 (m), 1066 (m), 1051 (m), 1025 (m), 995 (m), 901 (w), 830 (w), 792 (w), 735 (w), 681 (w), 583 (w), 550 (w), 471 (w).

### 6.5 Preparation of copper(II) complex polyborate salts

### 6.5.1 Preparation of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(20)$

A stoichiometric amount of compound $15(1.00 \mathrm{~g}, 3.57 \mathrm{mmol})$ and barium hydroxide octahydrate ( $1.13 \mathrm{~g}, 3.57 \mathrm{mmol}$ ) were dissolved in distilled water $(25 \mathrm{~mL})$. The mixture was rapidly stirred at room temperature for 10 minutes, then the white precipitate of barium sulphate was completely removed by gravity filtration (twice). Boric acid ( $2.20 \mathrm{~g}, 35.7 \mathrm{mmol}$ ) was added to the filtrate. After stirring for 30 minutes, volume of the solution was reduced to 5 mL by gentle evaporation on a warm water bath. The crude precipitate was collected by filtration and recrystallized using water/ethanol mixture 1:1. The product was carefully washed with ethanol then with acetone and dried at $50{ }^{\circ} \mathrm{C}$ for 5 hours to yield purple crystals of $20(1.20 \mathrm{~g}, 52 \%)$. M.p. $=283-285^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=1134 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{4} \mathrm{H}_{28} \mathrm{CuB}_{10} \mathrm{~N}_{4} \mathrm{O}_{22}$. Anal. Calc.: $\mathrm{C}=7.5 \%$, $\mathrm{H}=4.1 \%, \mathrm{~N}=8.8 \%$. Found: $\mathrm{C}=7.4 \%, \mathrm{H}=4.4 \%, \mathrm{~N}=8.6 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm} 1.3(2 \%), 13.4$ (25\%), 17.3 (72\%). IR (KBr/cm ${ }^{-1}$ ): 3459(s), 3328(s), 3282(s), 2956(w), 2904(w), 1614(m), 1416(s), 1314(s), 1139(s), 1094(s), 1041(s), 927(s), 776(s), 708(s), 549(m), 464(m). p-XRD d-spacing/Å (\% rel. int.): 7.20 (62), 6.33 (64), 5.65 (66), 5.26 (75), 3.92 (100), 3.23 (41). TGA: 70-180 ${ }^{\circ} \mathrm{C}$, loss of two interstitial $\mathrm{H}_{2} \mathrm{O}: 6.0 \%$ ( $5.5 \%$ calc.); 180-280 ${ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 16 \%$ ( $16.5 \%$ calc.); $280-600{ }^{\circ} \mathrm{C}$, oxidation of organic content $32.9 \%$ ( $34.9 \%$ calc.); residual $\mathrm{CuB}_{10} \mathrm{O}_{16} 67.1 \%$ ( $65.1 \%$ calc.).

### 6.5.2 Preparation of $\left[\mathrm{Cu}(\mathrm{en})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{~B}(\mathrm{OH})_{3}(21)$

Compound 21 was prepared by a modified literature method. ${ }^{137}$ The preparation of complex hydroxide solution was carried out in the same method as described previously in the preparation of $\mathbf{2 0}$ from $\mathbf{1 5}(1.00 \mathrm{~g}, 3.57 \mathrm{mmol})$ and barium hydroxide ( $1.12 \mathrm{~g}, 3.57 \mathrm{mmol})$. Boric $\operatorname{acid}(1.10 \mathrm{~g}, 17.85 \mathrm{mmol})$ was directly added to the filtrate. After stirring for 30 minutes the
solution volume was reduced to 5 mL using a rotary evaporator. The crude precipitate was collected by filtration. The product was recrystallized using $\mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH} 1: 1$ mixture to yield navy crystals of 21 ( $1.05 \mathrm{~g}, 59 \%$ ). M.p. $=275-276{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=1007 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{4} \mathrm{H}_{26} \mathrm{CuB}_{6} \mathrm{~N}_{4} \mathrm{O}_{15}$. Anal. Calc.: $\mathrm{C}=9.6 \%, \mathrm{H}=5.2 \%, \mathrm{~N}=11.2 \%$. Found: $\mathrm{C}=9.7 \%, \mathrm{H}=5.4 \%$, $\mathrm{N}=11.4 \%$. [Lit. $\mathrm{C}=9.4 \%, \mathrm{H}=4.6 \%, \mathrm{~N}=10.6 \%$ ]. ${ }^{137}{ }^{11} \mathrm{~B} / \mathrm{ppm}: 13.9$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3513(\mathrm{~s})$, 3346(s), 3252(s), 2960(s), 2920(m), 1612(w), 1466(s), 1432(s), 1363(s), 1219(m), 1147(m), 1042(s), 1005(s), 943(m), 882(m), 806(m), 707(m), 681(m), 524(m), 494(m), 461(m). p-XRD d-spacing/Å (\% rel. int.): 7.26 (76), 6.37 (81), 5.67 (73), 5.28 (93), 4.21 (54), 3.92 (100). TGA: $100-200{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of five $\mathrm{H}_{2} \mathrm{O}: 18.9 \%$ ( $18.1 \%$ calc.); 200-550 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $41.2 \%$ ( $42.2 \%$ calc.); residual $\mathrm{CuB}_{6} \mathrm{O}_{10} 58.8 \%$ ( $57.8 \%$ calc.).

### 6.5.3 Preparation of $\left[\mathrm{Cu}(\mathrm{pn})_{2}\left\{\mathrm{~B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right\}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (22)

The preparation of $\left[\mathrm{Cu}(\mathrm{pn})_{2}\right](\mathrm{OH})_{2}$ was carried out using the method described previously for the preparation of $\mathbf{2 0}$ from $\mathbf{1 6}(1.00 \mathrm{~g}, 3.24 \mathrm{mmol})$ and barium hydroxide ( 1.02 $\mathrm{g}, 3.24 \mathrm{mmol}$ ). Boric acid ( $2.00 \mathrm{~g}, 32.4 \mathrm{mmol}$ ) was added to the filtrate solution. After stirring for 30 minutes the solution volume was concentrated to 5 mL by gentle evaporation on a warm water bath. The crude precipitate was collected by filtration, and recrystallized by using water/ethanol. The product was carefully washed with ethanol and then acetone and then dried at $40^{\circ} \mathrm{C}$ for 5 hours to yield purple crystals of $22(1.30 \mathrm{~g}, 56 \%)$. M.p. $=296-298^{\circ} \mathrm{C}(\mathrm{dec}.) \cdot \chi_{m}=$ $1094 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{6} \mathrm{H}_{36} \mathrm{~B}_{10} \mathrm{CuN}_{4} \mathrm{O}_{24}$. Anal. Calc.: $\mathrm{C}=10.0 \%, \mathrm{H}=5.0 \%, \mathrm{~N}=7.8 \%$. Found: $\mathrm{C}=10.1 \%, \mathrm{H}=5.4 \%, \mathrm{~N}=7.6 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 1.5(2 \%), 13.2(24 \%), 16.9(74 \%) . \operatorname{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right)$ : 3405(s), 3305(s), 2974(s), 1615(w), 1423(s), 1380(s), 1336(s), 1305(s), 1121(m), 1061(s), 1019(s), 921(s), 778(s), 708(s). p-XRD d-spacing/Å (\% rel. int.): 7.57 (33), 6.21 (17), 5.39 (18), 4.69 (100), 3.39 (51), 2.03 (20). TGA: $70-180{ }^{\circ} \mathrm{C}$, loss of four interstitial $\mathrm{H}_{2} \mathrm{O}: 9.1 \% ~(10 \%$ calc.); $180-250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 18.2 \%$ ( $20 \%$ calc.); $250-650{ }^{\circ} \mathrm{C}$, oxidation of organic content $38.1 \%$ ( $40.6 \%$ calc.); residual $\mathrm{CuB}_{10} \mathrm{O}_{16} 61.9 \%$ (59.4\% calc.).

### 6.5.4 Preparation of $\left[\mathrm{Cu}(\mathrm{TMEDA})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right]\right]_{6} \cdot 6 \mathrm{H}_{2} \mathrm{O}(23)$

A solution of $N, N, N^{\prime}, N^{\prime}$,-tetramethyl ethylendiamine (TMEDA) ( $3.72 \mathrm{~g}, 32.04 \mathrm{mmol}$ ) in water ( 3 mL ) was added to an aqueous solution of copper(II) sulphate pentahydrate ( 4.00 g , $16.02 \mathrm{mmol})$ in distilled water $(10 \mathrm{~mL})$. The reaction mixture was stirred at room temperature
for 60 minutes, and then a solution of barium hydroxide octahydrate ( $5.05 \mathrm{~g}, 16.02 \mathrm{mmol}$ ) in water $(15 \mathrm{~mL})$ was added. The reaction mixture was stirred for a further 30 minutes and then filtered by gravity (twice). A solution of boric acid $(9.90 \mathrm{~g}, 160.2 \mathrm{mmol})$ in water $(10 \mathrm{~mL})$ was added to the filtrate and the solution was stirred at room temperature for 3 hours. The volume of the solution was reduced to 20 mL by using a rotary evaporator. The solution was distributed over a few small vials and left for 10 days to yield bright blue crystals of 23 ( $4.80 \mathrm{~g}, 53 \%$ ). M.p. $=243-245^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=1320 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{6} \mathrm{H}_{34} \mathrm{~B}_{6} \mathrm{CuN}_{2} \mathrm{O}_{19}$. Anal. Calc.: $\mathrm{C}=12.7 \%, \mathrm{H}=$ $6.1 \%, \mathrm{~N}=4.9 \%$. Found: $\mathrm{C}=12.8 \%, \mathrm{H}=6.2 \%, \mathrm{~N}=5.0 \%$. ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 15.3$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right)$ : 3399(s), 2926(w), 1638(w), 1470(m), 1419(s), 1366(s), 1133(s), 1086(s), 1037(s), 953(s), 902(m), 852(m), 809(s), 694(w), p-XRD d-spacing/Å (\% rel. int.): 8.57 (100), 7.75 (66), 7.04 (28), 5.75 (75), 4.29 (28), 2.03 (48), 1.22 (30). TGA: $70-180{ }^{\circ} \mathrm{C}$, loss of six interstitial $\mathrm{H}_{2} \mathrm{O}$ : $19.4 \%$ ( $19.1 \%$ calc.); $180-250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of three further $\mathrm{H}_{2} \mathrm{O}$ : $28.6 \%$ ( $28.6 \%$ calc.); $250-650^{\circ} \mathrm{C}$, oxidation of organic content $48.1 \%$ ( $49.2 \%$ calc.); residual $\mathrm{CuB}_{6} \mathrm{O}_{10} 51.9 \%$ (50.8\% calc.).

### 6.5.5 Preparation of $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Cu}(\text { dach })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (24)

The preparation of $\left[\mathrm{Cu}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right](\mathrm{OH})_{2}$ was carried out following the same method as described previously in the preparation of $\mathbf{6}$ from $\mathbf{1 7}(1.00 \mathrm{~g}, 2.5 \mathrm{mmol})$ and Dowex ( 30 g ). Boric acid ( $1.55 \mathrm{~g}, 25 \mathrm{mmol}$ ) was added to the $\mathrm{H}_{2} \mathrm{O} / \mathrm{MeOH}$ solution which was gently warmed with stirring for 3 hours. The solution volume was reduced to 5 mL using a rotary evaporator. The product was collected by filtration and allowed to dry overnight in an oven at $40^{\circ} \mathrm{C}$ to yield purple crystals of $24(0.84 \mathrm{~g}, 52 \%)$. M.p. $=263-265^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=1145 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{12} \mathrm{H}_{39} \mathrm{~B}_{7} \mathrm{CuN}_{4} \mathrm{O}_{17}$. Anal. Calc.: $\mathrm{C}=22.2 \%, \mathrm{H}=6.0 \%, \mathrm{~N}=8.6 \%$. Found: $\mathrm{C}=22.0 \%, \mathrm{H}=6.1 \%$, $\mathrm{N}=8.5 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm} 14.7$. IR (KBr/cm ${ }^{-1}$ ): 3480(s), 3304(s), 3245(s), 2931(s), 2863(m), 1603(w), 1468(m), 1454(s), 1350(s), 1183(s), 1134(s), 1059(s), 987(w), 949(w), 919(w), 854(s), 815(s), 686(w). p-XRD d-spacing/Å (\% rel. int.): 10.80 (71), 9.76 (100), 6.27 (45), 5.95 (36), 5.31 (36), 4.25 (40), 3.77 (41). TGA: $70-190{ }^{\circ} \mathrm{C}$, loss of four interstitial $\mathrm{H}_{2} \mathrm{O}$ : and two coordinate $\mathrm{H}_{2} \mathrm{O}$ : $9.0 \%$ ( $8.3 \%$ calc.); $190-250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of five further $\mathrm{H}_{2} \mathrm{O}$ : $16.0 \%$ ( $15.2 \%$ calc.); $250-650{ }^{\circ} \mathrm{C}$, oxidation of organic content $51.0 \%$ ( $50.4 \%$ calc.); residual $\mathrm{CuB}_{7} \mathrm{O}_{11.5} 49.0 \%$ (49.6\% calc.).

### 6.5.6 Preparation of $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]\left[\mathrm{B}_{3} \mathrm{O}_{3}(\mathrm{OH})_{4}\right] \cdot 2 \mathrm{~B}(\mathrm{OH})_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ (25)

The preparation of $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right](\mathrm{OH})_{2}$ was carried out following the same method as described previously in the preparation of $\mathbf{2 0}$ from $\mathbf{1 8}(1.10 \mathrm{~g}, 3.57 \mathrm{mmol})$ and barium hydroxide $(1.13 \mathrm{~g}, 3.57 \mathrm{mmol})$. Boric acid $(2.20 \mathrm{~g}, 35.7 \mathrm{mmol})$ was added to the filtrate solution. After stirring for 30 minutes the solution volume was concentrated to 5 mL by gentle evaporation on a warm water bath. The crude precipitate was collected by filtration and recrystallized using a water/ethanol solution. The product was collected by filtration and carefully washed with cold water and then acetone and then dried at $40^{\circ} \mathrm{C}$ for 1 hour to yield blue crystals $\mathbf{2 5}(1.20 \mathrm{~g}, 52 \%)$. M.p. $=277-278^{\circ} \mathrm{C}($ dec. $) \cdot \chi_{m}=1365 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{CuC}_{6} \mathrm{H}_{38} \mathrm{O}_{25} \mathrm{~N}_{4} \mathrm{~B} 10$. Anal. $\mathrm{Calc} .: \mathrm{C}=10.1 \%$, $\mathrm{H}=5.4 \%, \mathrm{~N}=7.6 \%$. Found: $\mathrm{C}=9.8 \%, \mathrm{H}=5.2 \%, \mathrm{~N}=7.6 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 16.7$. $\mathrm{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right)$ : 3385(s), 3333(s), 2961(w), 1615(w), 1405(m), 1362(s), 1114(s), 1086(s), 1041(sh), 954(m), 911(w), 809(s), 696(w), 626(w). p-XRD d-spacing/Å (\% rel. int.): 4.95 (99), 4.83 (100), 3.47 (34). TGA: 70-200 ${ }^{\circ} \mathrm{C}$, loss of two interstitial $\mathrm{H}_{2} \mathrm{O}: 5.8 \% ~\left(4.9 \%\right.$ calc.); 200- $250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of seven further $\mathrm{H}_{2} \mathrm{O}: 21.8 \%$ ( $21.9 \%$ calc.); $250-850{ }^{\circ} \mathrm{C}$, oxidation of organic content $42.5 \%$ ( $42.1 \%$ calc.); residual $\mathrm{CuB}_{10} \mathrm{O}_{16} 57.5 \%$ ( $57.9 \%$ calc.).

### 6.5.7 Preparation of $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right]\left[\mathrm{B}_{4} \mathrm{O}_{5}(\mathrm{OH})_{4}\right] \cdot \mathrm{B}(\mathrm{OH})_{3} \cdot \mathbf{6 H}_{2} \mathrm{O}(26)$

The preparation of $\left[\mathrm{Cu}(\mathrm{tn})_{2}\right](\mathrm{OH})_{2}$ was carried out exactly in the same method as described for the preparation of $\mathbf{2 0}$ from $\mathbf{1 8}(1.00 \mathrm{~g}, 3.57 \mathrm{mmol})$ and barium hydroxide ( 1.13 g , $3.57 \mathrm{mmol})$. Boric acid ( $1.10 \mathrm{~g}, 17.85 \mathrm{mmol}$ ) was added to the filtrate solution. After stirring for 30 minutes the solution volume was concentrated to 5 mL by gently evaporation on a warm water bath. The crude product was collected by filtration and recrystallized by using water/ethanol solution to yield navy crystals of $26(0.45 \mathrm{~g}, 22 \%)$. M.p. $=270-272{ }^{\circ} \mathrm{C}$ (dec.). $\mathrm{C}_{6} \mathrm{H}_{39} \mathrm{~B}_{5} \mathrm{CuN}_{4} \mathrm{O}_{18}$. Anal. Calc.: $\mathrm{C}=12.6 \%, \mathrm{H}=6.9 \%, \mathrm{~N}=9.8 \%$. Found: $\mathrm{C}=12.9 \%, \mathrm{H}=6.8 \%$, $\mathrm{N}=9.5 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 14.4 . \operatorname{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3429(\mathrm{~s}), 3350(\mathrm{~s}), 2961(\mathrm{~s}), 1626(\mathrm{w}), 1450(\mathrm{~s}), 1403(\mathrm{~s})$, 1380(m), 1164(m), 1112(m), 1027(s), 933(m), 873(w), 818(m), 708(w), 671(w). TGA: 70-200 ${ }^{\circ} \mathrm{C}$, loss of six interstitial $\mathrm{H}_{2} \mathrm{O}: 17.0 \%$ ( $18.8 \%$ calc.); 200-300 ${ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of seven further $\mathrm{H}_{2} \mathrm{O}: 27.1 \%$ ( $29.8 \%$ calc.); $300-700^{\circ} \mathrm{C}$, oxidation of organic content $55.5 \%$ ( $55.8 \%$ calc.); residual $\mathrm{CuB}_{5} \mathrm{O}_{8.5} 44.5 \%$ ( $44.2 \%$ calc.).

### 6.5.8 $\left[\mathrm{Cu}(\mathrm{N}, \mathrm{N} \text {-dmen })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ (27)

$\left[\mathrm{Cu}(N, N-\mathrm{dmen})_{2}\right] \mathrm{Cl}_{2}(1.00 \mathrm{~g}, 3 \mathrm{mmol})$, and $\mathrm{Ag}_{2} \mathrm{O}(0.746 \mathrm{~g}, 3 \mathrm{mmol})$ were rapidly stirred in $\mathrm{H}_{2} \mathrm{O}(25 \mathrm{~mL})$ at room temperature for 30 minutes and the precipitate which had formed $(\mathrm{AgCl})$ was removed by filtration. $\mathrm{B}(\mathrm{OH})_{3}(1.99 \mathrm{~g}, 32 \mathrm{mmol})$ was added to the dark blue filtrate and left to stir for a further 30 mins. The reaction mixture was filtered twice by gravity and the filtrate was placed in small vials and left to allow for slow evaporation of solvent. After 12 h , purple crystals of $\mathbf{2 7}$ had formed and these were collected by filtration and dried in desiccator ( $1.19 \mathrm{~g}, 53 \%$ ). M.p. $=>300^{\circ} \mathrm{C} . \chi_{\mathrm{m}}=820 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{8} \mathrm{H}_{40} \mathrm{CuN}_{4} \mathrm{~B}_{10} \mathrm{O}_{24}$. Anal. Calc.: $\mathrm{C}=$ $12.8 \%, \mathrm{H}=5.4 \%, \mathrm{~N}=7.5 \%$. Found: $\mathrm{C}=13.0 \%, \mathrm{H}=5.3 \%, \mathrm{~N}=7.3 .{ }^{11} \mathrm{~B} / \mathrm{ppm} 16.5$. $\mathrm{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-}\right.$ ${ }^{1}$ ): 3587 (m), 3336 (m), 3271 (m), 1614 (w), 1421 ( s , 1308 ( s$), 1158$ (m), 1125 (m), 1065 (m), 1017 (m), 918 (m), 812 (w), 776 (m), 708 (m), 529 (w), 479 (w). P-XRD: d-spacing/Å (\% rel. int.): 6.67 (15.82), 5.71 (100.00), 5.51 (12.12), 4.54 (24.80), 3.73 (40.37), 3.34 (11.56), 2.03 (13.06). TGA: $30-90^{\circ} \mathrm{C}$, loss of three interstitial and one coordinated $\mathrm{H}_{2} \mathrm{O}: 9.8 \% ~(9.6 \%$ calc.); $90-250{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 21.3 \%$ ( $19.2 \%$ calc.); $250-630{ }^{\circ} \mathrm{C}$, oxidation of organic content $45.1 \%$ ( $42.7 \%$ calc.); residual $\mathrm{CuB}_{10} \mathrm{O}_{16} 54.9 \%$ (57.3\% calc.).

### 6.5.9 $\left[\mathrm{Cu}(N, N-\right.$ dmen $\left.)\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (28)

$\left[\mathrm{Cu}(N, N \text {-dmen })_{2}\right] \mathrm{Cl}_{2}(1.00 \mathrm{~g}, 3 \mathrm{mmol})$ was dissolved in $\mathrm{H}_{2} \mathrm{O}(25 \mathrm{ml})$ to a dark blue solution. Dowex monosphere 550A ion exchange resin ( 60 g ) was added to the solution which was left to stir for 24 hours. The ion exchange resin was removed by filtration and $\mathrm{B}(\mathrm{OH})_{3}(1.99$ $\mathrm{g}, 30 \mathrm{mmol}$ ) was added to the filtrate which was then left to stir for 30 minutes. The dark blue reaction mixture was filtered into vials and left to allow for slow evaporation of $\mathrm{H}_{2} \mathrm{O}$ to occur. After 1 week, the blue crystals of $\mathbf{2 8}$ which had formed and were collected filtration $(0.61 \mathrm{~g}$, $41 \%)$. M.p. $=>300{ }^{\circ} \mathrm{C} . \chi_{\mathrm{m}}=880 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{4} \mathrm{H}_{26} \mathrm{CuN}_{2} \mathrm{~B}_{6} \mathrm{O}_{17}$. Anal. Calc.: $\mathrm{C}=9.5 \%, \mathrm{H}=$ $5.2 \%, \mathrm{~N}=5.6 \%$. Found: $\mathrm{C}=9.7 \%, \mathrm{H}=5.2 \%, \mathrm{~N}=5.5 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm} 16.9$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3340$ (b), 3254 (b), 2931 (w), 2859 (w), 2814 (w), 1641 (w), 1586 (w), 1467 (sh), 1423 (s), 1366 (s), 1269 ( s ), 1137 ( s ), 1091 ( s$), 1052$ ( s$), 1007$ (m), 958 (m), 892 (m), 859 (m), 808 ( s$), 784$ (m), 694 (m), 574 (w). P-XRD d-spacing/Å (\% rel. int.): 10.87 (100.00), 8.64 (24.76), 7.30 (27.96), 3.65 (22.86). TGA: $30-120^{\circ} \mathrm{C}$, loss of four interstitial $\mathrm{H}_{2} \mathrm{O}: 14.2 \%$ ( $14.3 \%$ calc.); $120-250^{\circ} \mathrm{C}$, condensation of polyborate which loss of three further $\mathrm{H}_{2} \mathrm{O}: 26.0 \%$ ( $25.0 \%$ calc.); $250-650{ }^{\circ} \mathrm{C}$, oxidation of organic content $44.3 \%$ ( $22.5 \%$ calc.); residual $\mathrm{CuB}_{6} \mathrm{O}_{10} 55.7 \%$ ( $57.5 \%$ calc.).

### 6.6 Preparation of nickel(II) complexes

### 6.6.1 Preparation of $\left[\mathrm{Ni}(\mathrm{en})_{3}\right] \mathrm{Cl}_{2} \cdot \mathbf{2 H}_{2} \mathrm{O}$ (29)

Compound 29 was prepared as described in the literature. ${ }^{185}$ Nickel(II) chloride hexahydrate ( $5.75 \mathrm{~g}, 24.19 \mathrm{mmol}$ ) was dissolved in distilled water ( 25 mL ) and then ethylenediamine ( $7.00 \mathrm{~g}, 70 \%, 81.25 \mathrm{mmol}$ ) was added to the nickel solution. The reaction mixture was stirred at room temperature for 2 hours, then gently evaporated on steam bath to 10 mL . Two drops of ethylene diamine were added. The solution was cooled in an ice bath and the crude produced was collected by filtration and recrystallized from distilled water to yield purple crystals of $29(6.50 \mathrm{~g}, 78 \%)$. M.p. $=243-245^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=3390 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3294(s), 3246(s), 3158(s), 2960(m), 2878(m), 1588(m), 1457(m), 1369(m), 1331(m), 1273(m), 1155(m), 1102(m), 1029(s), 860, 668(s), 524(m), 501(m). [Lit. 3250, 2940-$2875,1587,1457,1369,1330,1275,1140-1118-1100,1026-974,865,662,522] .{ }^{193}$

### 6.6.2 Preparation of $[\mathrm{Ni}(\mathrm{AEN})] \mathrm{Cl} \cdot \mathrm{H}_{2} \mathrm{O}$ (30)

Compound 30 was prepared as described in the literature. ${ }^{186}$ The 2,4-dimethyl-1-(3-azapropyl)-1,5,8-triazaocta-2,4-dienato (AEN) ligand was synthesized by dissolving ethylene diamine ( $12.00 \mathrm{~g}, 200 \mathrm{mmol}$ ) and acetyl acetone ( $10.00 \mathrm{~g}, 100 \mathrm{mmol}$ ) in acetic acid ( 400 mL , $20 \%$ ). The reaction mixture was left for 24 hours and a solution of nickel(II) chloride hexahydrate ( $23.80 \mathrm{~g}, 100 \mathrm{mmol}$ ) in distilled water $(100 \mathrm{~mL})$ was added. The reaction mixture was stirred vigorously and during the stirring sodium hydroxide ( $175 \mathrm{~g}, 4.37 \mathrm{~mol}$ ) was steadily added. The solution was left overnight, and then the reaction mixture was gently heated to redissolve the crude product. The hot solution was filtered and the solution was cooled for 24 hours at $0{ }^{\circ} \mathrm{C}$ to yield red crystals of $\mathbf{3 0}(8.40 \mathrm{~g}, 29 \%)$. M.p. $=242-244{ }^{\circ} \mathrm{C}($ dec. $) \cdot \chi_{m}=-56 \times 10^{-6}$ $\mathrm{cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{NiC}_{9} \mathrm{H}_{21} \mathrm{ON}_{4} \mathrm{Cl}$. Anal. Calc.: $\mathrm{C}=36.5 \%, \mathrm{H}=7.1 \%, \mathrm{~N}=18.9 \%$. Found: $\mathrm{C}=37.1 \%$, $\mathrm{H}=6.7 \%, \mathrm{~N}=18.8 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 2\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.5\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right.$ of en), $3.2\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right.$ of en), and $4.8\left(\mathrm{~s}, 7 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{CH}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 20.1,43.2,53.6,160.8$. IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): $3447(\mathrm{~s})$, 3250(m), 3172(s), 3080(s), 2983(m), 2945(m), 2888(w), 2822(s), 1613(w), 1558(s), 1527(s), 1475(s), 1439(s), 1420(s), 1330(s), 1276(s), 1149(s), 1089(s), 1031(s), 732(m), 570(w).

### 6.6.3 Preparation of $\left[\mathrm{Ni}(\text { trans-dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{Cl}_{2}(31)$

Compound 31 was prepared as described in the literature ${ }^{187}$ by adding excess amount of the mixture cis and trans-1,2-diaminocyclohexane (dach) ligand ( $2.88 \mathrm{~g}, 25.24 \mathrm{mmol}$ ) to a solution of nickel(II) chloride hexahydrate ( $2.00 \mathrm{~g}, 8.41 \mathrm{mmol}$ ) in water ( 15 mL ). The solution was stirred for 2 hours and then cooled in an ice bath for two hours. The resulting crystals which formed over the cooling period were filtered, washed with cold distilled water and dried at 40 ${ }^{\circ} \mathrm{C}$. The crude product was re-crystallized from hot water to yield violet crystals of $\mathbf{3 1}(1.30 \mathrm{~g}$, $40 \%$ ). M.p. $=253-255^{\circ} \mathrm{C}($ dec. $) . \chi_{m}=3040 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3459(\mathrm{~s}), 3342(\mathrm{~s})$, 3278(s), 3262(sh), 3158(m), 2932(s), 2857(m), 1583(m), 1450(m), 1401(w), 1164(w), 1120(m), 1017(s), 985(m), 924(w), 860(w), 670(m), and 656(m). [Lit. 3340, 3260, 3180, 1605, $669,661] .{ }^{196}$

### 6.6.4 Preparation of $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]_{\mathrm{Cl}_{2}}$ (32)

Compound 32 was synthesized by a method analogous to that described for $\left[\mathrm{Ni}(\mathrm{hn})_{3}\right] \mathrm{Br}_{2} .{ }^{188} \mathrm{~N}$-hydroxy ethyl ethylenediamine (hn) $(2.63 \mathrm{~g}, 25.2 \mathrm{mmol})$ was added to an aqueous solution of nickel(II) chloride hexahydrate ( $3.00 \mathrm{~g}, 12.6 \mathrm{mmol}$ ) in distilled water ( 15 $\mathrm{mL})$. The solution was stirred for 2 hours at room temperature. The solution volume was reduced by gently evaporation on a warm water bath and then cooled in an ice bath. The resulting crystals were filtered, washed with cold $\mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH}$ and dried at $50^{\circ} \mathrm{C}$ to yield purple crystals of $\mathbf{3 2}(4.40 \mathrm{~g}, 79 \%)$. M.p. $=174-175^{\circ} \mathrm{C}($ dec. $) \cdot \chi_{m}=3200 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-}\right.$ ${ }^{1}$ ): 3390(s), 3304(s), 3275(s), 3237(s), 3188(s), 3166(s), 3050(sh), 2976(sh), 2921(s), 2874(s), 2807(m), 1596(s), 1470(s), 1457(s), 1442(s), 1408(m), 1397(m), 1357(m), 1330(s), 1313(s), 1281(w), 1237(w), 1201(w), 1107(s), 1090(s), 1063(s), 1041(s), 1024.7(s), 982(s), 907(m), 889(m), 881(m), 859(s), 820(m), 790.1(m), 671(m), 646(m), 631(m). [Lit. 3315(sh), 3232(s), 3160(s), 3070(m)]..$^{200}$

### 6.6.5 Preparation of $\left[\mathrm{Ni}(\text { dien })_{2}\right] \mathrm{Cl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}(33)$

Compound 33 was prepared along a previously published procedure. ${ }^{189}$ An aqueous solution of nickel(II) chloride hexahydrate ( $2.00 \mathrm{~g}, 8.4 \mathrm{mmol}$ ) in distilled water ( 10 mL ) was added to an aqueous solution of diethylentriamine (dien) ( $1.75 \mathrm{~g}, 17 \mathrm{mmol}$ ) in distilled water $(10 \mathrm{~mL})$. The reaction mixture was gently heated on water bath with stirring for 30 minutes and
then cooled in an ice bath. The resulting crystals were filtered, washed with cold water and dried at $50{ }^{\circ} \mathrm{C}$. The product was re-crystallized from $\mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH}$ to yield blue crystals of $\mathbf{3 3}$ $(1.90 \mathrm{~g}, 64 \%)$. M.p. $=235-237^{\circ} \mathrm{C} .\left[\right.$ Lit. 232-232.5 $\left.{ }^{\circ} \mathrm{C}\right] .{ }^{194} \chi_{m}=2790 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. IR $\left(\mathrm{KBr} / \mathrm{cm}^{-}\right.$ ${ }^{1}$ ): 3436(s), 3422(sh), 3378(sh), 3349(s), 3323(s), 3287(s), 3265(s), 3186(s), 3169(s), 2948(m), 2917(m), 2873(m), 1633(w), 1586(s), 1489(w), 1475(m), 1449(s), 1385(m), 1333(sh), 1322(s), 1315(m), 1282(w), 1252(m), 1145(m), 1093(s), 1060(s), 1027(sh), 1013(s), 980(s), 909(w), 890(s), 865(w), 825(w). [Lit. 3420(s), 3378(s), 3340(m), 3315(s), 3278(s), 3255(s), 3180(s), 3160(s), 1490(w), 1475(w), 1450(m), 1380(w), 1333(m), 1322(m), 1315(w), 1264(w), 1131(m), 1098(m), 1078(s), 1048(s), 1027(sh), 1014(s), 980(s), 910(w), 892(s), 867(w), $827(\mathrm{w})] .{ }^{201}$

### 6.6.6 Preparation of $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right] \mathrm{Cl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ (34)

Compound 34 was prepared as described in the literature. ${ }^{185}$ To a solution of nickel(II) chloride hexahydrate ( $5.75 \mathrm{~g}, 24.19 \mathrm{mmol}$ ) in distilled water ( 25 mL ) was added propylenediamine (pn) $(6.00 \mathrm{~g}, 80.94 \mathrm{mmol})$. The reaction mixture was stirred at room temperature for 2 hours and then gently evaporated on a steam bath to ( 10 mL ). Propylenediamine ( 1 mL ) was added to the reaction mixture. The solution was cooled in an ice bath, and the crude product was collected by filtration and recrystallized by distilled water to yield purple crystals of $34(7.10 \mathrm{~g}, 76 \%)$. M.p. $=247-248{ }^{\circ} \mathrm{C}(\mathrm{dec}.) \cdot \chi_{m}=3010 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{NiC}_{9} \mathrm{H}_{34} \mathrm{O}_{2} \mathrm{~N}_{6} \mathrm{Cl}_{2}$. Anal. Calc.: $\mathrm{C}=27.9 \%, \mathrm{H}=8.8 \%, \mathrm{~N}=21.7 \%$. Found: $\mathrm{C}=28.1 \%, \mathrm{H}=8.9 \%$, $\mathrm{N}=21.7 \%$. IR (KBr/cm ${ }^{-1}$ ): 3725(sh), 3435(s), 3257(vs), 3165(s), 2965(s), 2940(s), 2878(s), 1598(s), 1461(s), 1394(s), 1375(s), 1307(m), 1269(w), 1202(m), 1158(s), 1074(m), 1047(s), 1019(vs), 934(m), 838(m), and 645(s). [Lit. 3743(w), 3449(w), 3256(vs), 3141(m), 2955(m), 2925(m), 2863(m), 1566(vs), 1450(m), 1381(vs), 1304(w), 1265(w), 1196(w), 1142(w), $1065(\mathrm{~m}), 1011(\mathrm{vs}), 926(\mathrm{w}), 825(\mathrm{w})$, and $640(\mathrm{~m})] .{ }^{202}$

### 6.6.7 Preparation of $\left[\mathrm{Ni}_{2}(\text { trien })_{3}\right] \mathrm{Cl}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}(35)$

Compound 35 was prepared as described in the literature. ${ }^{190}$ To a solution of nickel(II) chloride hexahydrate ( $5.00 \mathrm{~g}, 21.04 \mathrm{mmol}$ ) in distilled water ( 25 mL ) was added triethylenetetramine (trien) ( $6.14 \mathrm{~g}, 41.99 \mathrm{mmol}$ ). The solution mixture was stirred at room temperature for 2 hours, then the solution was evaporated on a steam bath to dryness. The crude product was collected and washed using a mixture of methanol $(40 \mathrm{~mL})$ and ether $(20 \mathrm{~mL})$. The
crude product was recrystallized by $\mathrm{MeOH} /$ ether mixture. The product was dried in an oven at $65^{\circ} \mathrm{C}$ for 3 hours to yield light pink crystals of $35(5.10 \mathrm{~g}, 66 \%)$. M.p. $=248-250^{\circ} \mathrm{C}$ (dec.). $\chi_{m}$ $=2906 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{NiC}_{18} \mathrm{H}_{58} \mathrm{O}_{2} \mathrm{~N}_{12} \mathrm{Cl}_{4}$. Anal. Calc.: $\mathrm{C}=29.5 \%, \mathrm{H}=8.0 \%, \mathrm{~N}=22.9 \%$. Found: $\mathrm{C}=29.6 \%, \mathrm{H}=8.1 \%, \mathrm{~N}=22.4 \%$. $\mathrm{IR}\left(\mathrm{KBr} / \mathrm{cm}^{-1}\right): 3368(\mathrm{~s}), 3323(\mathrm{~s}), 3239(\mathrm{~s}), 3159(\mathrm{~s})$, 2932(m), 2879(m), 1653(w), 1596(w), 1462(m), 1335(m), 1134(m), 1086(s), 1064(s), 1016(m), 966(s). UV-Vis $\lambda / \mathrm{nm}$ : 350,540, 880. [Lit. 346, 539]. ${ }^{203}$ [Lit. 353, 535, 877]. ${ }^{204}$

### 6.7 Preparation of nickel(II) complex polyborate salts

### 6.7.1 Preparation of $\left[\mathrm{Ni}(\mathrm{en})_{3}\right]_{\left[B_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(36)}$

Compound 36 was prepared by a modified literature method. ${ }^{115}$ The preparation of $\left[\mathrm{Ni}(\mathrm{en})_{3}\right](\mathrm{OH})_{2}$ was carried out as described previously for the preparation of $\mathbf{6}$ from $29(0.92$ $\mathrm{g}, 2.66 \mathrm{mmol}$ ) and Dowex ( 40 g ). Boric acid ( $1.64 \mathrm{~g}, 26.6 \mathrm{mmol}$ ) was added to the aqueous solution which was then gently warmed with stirring for 3 hours. A rotary evaporator was used to reduce the volume of the solution to 5 mL and the resulting solution was sealed in a Teflon lined stainless steel autoclave, and heated at $140^{\circ} \mathrm{C}$ for 3 days. The crystals were collected by filtration and left overnight to dry in a desiccator to yield light blue crystals of $\mathbf{3 6}(1.20 \mathrm{~g}, 63 \%)$. M.p. $=294-295{ }^{\circ} \mathrm{C}(\mathrm{dec}.) . \chi_{m}=2844 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 13.4$ ( $16 \%$ ), 16.1 ( $84 \%$ ). IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3344(s), 3297(s), 2947(w), 1607(w), 1407(s), 1314(s), 1168(m), 1026(s), 921(s), 851(w), 775(m), 706(w), 668(w), 484(w). [Lit. 3426, 3352, 3299, 2952, 1622, 1407, 1317, 923, $1168,1025,851,775,713,478] .{ }^{115}$ p-XRD d-spacing/Å (\% rel. int.): 6.12 (36), 5.75 (62), 5.55 (100), 4.30 (22), 3.93 (26), 3.86 (35), 3.71 (54). TGA: $70-180{ }^{\circ} \mathrm{C}$, loss of two interstitial $\mathrm{H}_{2} \mathrm{O}$ : $4.9 \%$ ( $5.1 \%$ calc.); $180-280{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}$ : $15.0 \%$ ( $15.2 \%$ calc.); $280-800{ }^{\circ} \mathrm{C}$, oxidation of organic content $38.1 \%$ ( $40.6 \%$ calc.); residual $\mathrm{NiB}_{10} \mathrm{O}_{16} 61.9 \%$ (59.4\% calc.).

### 6.7.2 Preparation of $\left[\mathrm{Ni}(\mathrm{en})\left\{\mathrm{B}_{6} \mathrm{O}_{7}(\mathrm{OH})_{6}\right\}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ (37)

An aqueous solution of ethylenediamine ligand ( $2.30 \mathrm{~g}, 70 \%, 26.79 \mathrm{mmol}$ ) was added to an aqueous solution of nickel(II) sulphate hexahydrate ( $2.12 \mathrm{~g}, 8.06 \mathrm{mmol}$ ) in water ( 10 mL ). The reaction mixture was stirred for 5 minutes, then a solution of barium hydroxide octahydrate $(2.54 \mathrm{~g}, 8.06 \mathrm{mmol})$ in water $(10 \mathrm{~mL})$ was added. The reaction mixture was stirred for 30 minutes and then filtered. A solution of boric acid ( $3.48 \mathrm{~g}, 56.42 \mathrm{mmol}$ ) in water ( 10 mL ) was
added to the filtrate with stirring. The reaction mixture was stirred at room temperature for 2 hours. The solution was then distributed in several aliquots (vials) and left for 10 days to yield faint blue crystals of $37(1.20 \mathrm{~g}, 33 \%)$. M.p. $=245-247^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=2588 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{2} \mathrm{H}_{20} \mathrm{~B}_{6} \mathrm{NiN}_{2} \mathrm{O}_{16}$. Anal. Calc.: $\mathrm{C}=5.3 \%, \mathrm{H}=4.5 \%, \mathrm{~N}=6.2 \%$. found: $\mathrm{C}=5.4 \%, \mathrm{H}=4.5 \%, \mathrm{~N}$ $=6.2 \%{ }^{11} \mathrm{~B} / \mathrm{ppm}: 17.7$. IR (KBr/cm ${ }^{-1}$ ): 3400(s), 3350(s), 2924(w), 2854(w), 1600(w), 1420(m), 1380(s), 1360(s), 1133(s), 1095(s), 1044(s), 955(m), 908(m), 852(w), 809(s), 696(w), 537(w), 427(w). p-XRD d-spacing/Å (\% rel. int.): 9.78 (100), 8.26 (24), 6.77 (53), 4.88 (48), 3.99 (34), 3.38 (30), 2.74 (47). TGA: $100-180{ }^{\circ} \mathrm{C}$, loss of one interstitial $\mathrm{H}_{2} \mathrm{O}$ : and two coordinated water molecules $0.8 \%$ ( $12 \%$ calc.); $180-280^{\circ} \mathrm{C}$, condensation of polyborate which loss of three further $\mathrm{H}_{2} \mathrm{O}: 24.3 \%$ ( $23.9 \%$ calc.); $280-700{ }^{\circ} \mathrm{C}$, oxidation of organic content $38.6 \%$ ( $37.2 \%$ calc.); residual $\mathrm{NiB}_{6} \mathrm{O}_{10} 61.4 \%$ ( $62.8 \%$ calc.).

### 6.7.3 Preparation of $[\mathrm{Ni}(\mathrm{AEN})]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ (38)

The replacement of chloride in $\mathbf{3 8}$ with hydroxide was carried out as described previously in the preparation of $\mathbf{6}$ from $30(2.10 \mathrm{~g}, 7.2 \mathrm{mmol})$ and Dowex ( 25 g ). Boric acid ( $2.22 \mathrm{~g}, 36 \mathrm{mmol}$ ) was added to the aqueous solution which was gently warmed with stirring for 3 hours. A rotary evaporator was used to reduce the solution volume to 5 mL . The solution was then distributed in a few NMR tubes for crystallization and left for 10 days to yield dark red crystals of 38 ( $1.30 \mathrm{~g}, 38 \%$ ). M.p. $=279-280{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=-170 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{9} \mathrm{H}_{25} \mathrm{~B}_{5} \mathrm{NiN}_{4} \mathrm{O}_{11}$. Anal. Calc.: $\mathrm{C}=22.6 \%, \mathrm{H}=5.3 \%, \mathrm{~N}=11.7 \%$. Found: $\mathrm{C}=22.7 \%, \mathrm{H}=5.4 \%$, $\mathrm{N}=11.7 \%$. ${ }^{1} \mathrm{H} / \mathrm{ppm}: 2\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.5\left(\mathrm{t}, 4 \mathrm{H}, J=6 \mathrm{~Hz}, \mathrm{CH}_{2}\right.$ of en), $3.2\left(\mathrm{t}, 4 \mathrm{H}, J=6 \mathrm{~Hz}, \mathrm{CH}_{2}\right.$ of en), 4.8 (s, 11H, NH2, $\left.\mathrm{H}_{2} \mathrm{O}, \mathrm{OH}, \mathrm{CH}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 19.9,43,53.6,160.5$. ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 16.3$. IR (KBr/cm ${ }^{-1}$ ): 3601(m), 3377(s), 3326(s), 3288(s), 3246(s), 3169(s), 2983(w), 2963(w), 1615(m), 1566(m), 1536(m), 1476(s), 1442(s), 1416(s), 1393(s), 1333(s), 1295(s), 1129(m), 1094(s), 1072(m), 1019(m), 924(s), 820(w), 778(m), 747(w), 725(w), 708(w), p-XRD dspacing/Å (\% rel. int.): 5.65 (69), 5.38 (100), 4.14 (46), 3.89 (33), 3.81 (53), 3.65 (58), 2.03 (41), 1.43 (33). TGA: $100-180^{\circ} \mathrm{C}$, loss of one interstitial $\mathrm{H}_{2} \mathrm{O}: 2.5 \%$ ( $3.7 \%$ calc.); $180-280{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of two further $\mathrm{H}_{2} \mathrm{O}: 10.0 \%$ ( $11.3 \%$ calc.); 280-700 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $46.1 \%$ ( $48.0 \%$ calc.); residual $\mathrm{NiB}_{5} \mathrm{O}_{8.5} 53.9 \%$ ( $52.0 \%$ calc.).

### 6.7.4 Preparation of $\left[\mathrm{Ni}(\text { dach })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left[\mathrm{Ni}(\text { dach })_{2}\right]\left[\mathrm{B}_{7} \mathrm{O}_{9}(\mathrm{OH})_{5}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (39)

The replacement of chloride in $\mathbf{3 9}$ by hydroxide was carried out as described previously in the preparation of $\mathbf{6}$ from $\mathbf{3 1}(1.00 \mathrm{~g}, 2.53 \mathrm{mmol})$ and Dowex $(40 \mathrm{~g})$. Boric acid $(1.56 \mathrm{~g}, 25.3$ mmol ) was added to the solution which was then gently warmed with stirring for 3 hours. The solution volume was reduced to 5 mL using a rotary evaporator. The product was isolated by filtration, and then allowed to dry in an oven at $40^{\circ} \mathrm{C}$ for 3 hours to yield orange prismatic crystals of $39(0.78 \mathrm{~g}, 47 \%)$. M.p. $=270-272{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=3030 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{24} \mathrm{H}_{78} \mathrm{~B}_{14} \mathrm{~N}_{8} \mathrm{Ni}_{2} \mathrm{O}_{34}$. Anal. Calc.: $\mathrm{C}=22.3 \%, \mathrm{H}=6.1 \%, \mathrm{~N}=8.7 \%$. Found: $\mathrm{C}=21.8 \%, \mathrm{H}=$ $6.3 \%, \mathrm{~N}=8.4 \% .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 15.8$. IR (KBr/ $\mathrm{cm}^{-1}$ ): 3663(s), 3271(s), 2929(m), 2863(m), 1603(w), 1468(m), 1453(s), 1350(s), 1180(s), 1125(m), 1066(s), 986(w), 948(w), 918(w), 854(m), 807(m), 716(w), 685(w). p-XRD d-spacing/Å (\% rel. int.): 10.67 (100), 9.81 (89), 6.25 (58), 5.35 (70), 4.26 (48), 3.74 (55), 2.03(59). TGA: $100-190{ }^{\circ} \mathrm{C}$, loss of four interstitial and two coordinated $\mathrm{H}_{2} \mathrm{O}: 7.5 \%$ ( $8.4 \%$ calc.); 190- $270^{\circ} \mathrm{C}$, condensation of polyborate which loss of five further $\mathrm{H}_{2} \mathrm{O}: 15.0 \%$ ( $15.3 \%$ calc.); 270- $720{ }^{\circ} \mathrm{C}$, oxidation of organic content $48.2 \%$ ( $50.7 \%$ calc.); residual $\mathrm{Ni}_{2} \mathrm{~B}_{14} \mathrm{O}_{23} 51.8 \%$ ( $49.3 \%$ calc.).

### 6.7.5 Preparation of $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}(40)$

The preparation of $\left[\mathrm{Ni}(\mathrm{hn})_{2}\right](\mathrm{OH})_{2}$ was carried out as described previously in the preparation of $\mathbf{6}$ from $32(1.00 \mathrm{~g}, 2.95 \mathrm{mmol})$ and Dowex ( 40 g ). Boric acid ( $1.83 \mathrm{~g}, 29.6 \mathrm{mmol}$ ) was added with stirring. The reaction mixture was stirred for a further 2 hours at room temperature. The solvent was then evaporated to 5 mL using a rotary evaporator, then the resulting solution was left for 10 days in a few NMR tubes for crystallization to yield purple crystals of $40(0.76 \mathrm{~g}, 37 \%)$. M.p. $=288-289{ }^{\circ} \mathrm{C}($ dec. $) . \chi_{m}=3430 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{C}_{8} \mathrm{H}_{32} \mathrm{~B}_{10} \mathrm{NiN}_{4} \mathrm{O}_{22}$. Anal. Calc.: $\mathrm{C}=13.7 \%, \mathrm{H}=4.6 \%, \mathrm{~N}=8.0 \%$. Found: $\mathrm{C}=13.7 \%, \mathrm{H}=4.7 \%$, $\mathrm{N}=8.0 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 2.8\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.9\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.6\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) 4.8$ (s, 16H, NH2, OH). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 37.9,46.1,49.5,58.9 .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 1.2$ (3\%), 13.4 (23\%), 18.0 (74\%). IR (KBr/cm ${ }^{-1}$ ): 3375(s), 3288(s), 3322(s), 2962(w), 1410(s), 1321(s), 1196(m), 1141(s), 1022(s), 980(w), 919(s), 846(w), 774(s), 722(w), 706(s), 669(w). p-XRD d-spacing/ $\AA$ (\% rel. int.): 6.18 (40), 5.88 (75), 5.50 (100), 3.94 (26), 3.78 (38), 3.66 (25). TGA: 230-290 ${ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four $\mathrm{H}_{2} \mathrm{O}: 10.3 \%$ ( $10.2 \%$ calc.); 290-700 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $37.9 \%$ ( $39.9 \%$ calc.); residual $\mathrm{NiB}_{10} \mathrm{O}_{16} 62.1 \%$ ( $60.1 \%$ calc.).

### 6.7.6 Preparation of $s-f a c-\left[\mathrm{Ni}(\text { dien })_{2}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2}$ (41)

The preparation of $\left[\mathrm{Ni}(\text { dien })_{2}\right](\mathrm{OH})_{2}$ was carried out as described previously for the preparation of $\mathbf{6}$ from $33(1.05 \mathrm{~g}, 2.97 \mathrm{mmol})$ and Dowex ( 40 g ). Boric acid ( $1.83 \mathrm{~g}, 29.7 \mathrm{mmol}$ ) was added to the $\mathrm{H}_{2} \mathrm{O} / \mathrm{MeOH}$ solution which was then gently warmed with stirring for 3 hours. The solution was concentrated to 5 mL using a rotary evaporator and the concentrated solution was left few days for crystallization. The produced crystals were carefully recovered by filtration and dried in air to yield purple crystals of $41(0.70 \mathrm{~g}, 34 \%)$. M.p. $=287-289{ }^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=3516 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1} . \mathrm{C}_{8} \mathrm{H}_{34} \mathrm{~B}_{10} \mathrm{NiN}_{6} \mathrm{O}_{20}$. Anal. Calc.: $\mathrm{C}=13.7 \%, \mathrm{H}=4.9 \%, \mathrm{~N}=12.0 \%$. Found: $\mathrm{C}=14.0 \%, \mathrm{H}=5.4 \%, \mathrm{~N}=12.1 \%$. ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 1.5$ ( $1 \%$ ), 13.3 ( $13 \%$ ), 17.4 ( $86 \%$ ). IR (KBr/cm ${ }^{-1}$ ): 3362(s), 3333(s), 3297(s), 3263(s), 2988(w), 2950(w), 2903(w), 1615(w), 1594(w), 1412(s), 1330(s), 1303(s), 1186(w), 1135(m), 1059(m), 1042(m), 1028(m), 964(m), 931(m), 915(s), 809(w), 774(s), 772(m), 707(s), 677(w). p-XRD d-spacing/Å (\% rel. int.): 6.22 (24), 5.88 (100), 5.57 (94), 4.27 (15), 3.79 (19), 3.71 (28), 2.94 (17). TGA: $100-200{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four $\mathrm{H}_{2} \mathrm{O}: 14.9 \%$ ( $10.2 \%$ calc.); 200-650 ${ }^{\circ} \mathrm{C}$, oxidation of organic content $40.3 \%$ ( $39.7 \%$ calc.); residual $\mathrm{NiB}_{8} \mathrm{O}_{13} 59.7 \%$ ( $60.3 \%$ calc.).

### 6.7.7 Preparation of $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \cdot \mathrm{C}_{2} \mathrm{H}_{5}-\mathrm{OH} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ (42)

The preparation of $\left[\mathrm{Ni}(\mathrm{pn})_{3}\right](\mathrm{OH})_{2}$ was carried out exactly in the same method as described previously for the preparation of $\mathbf{6}$ from $34(1.55 \mathrm{~g}, 4 \mathrm{mmol})$ and Dowex ( 40 g ). Boric acid ( $2.47 \mathrm{~g}, 40 \mathrm{mmol}$ ) was added to the aqueous solution which was gently warmed with stirring for 2 hours. A rotary evaporator was used to reduce the volume of the solution to 5 mL and the resulting mixture was sealed in a Teflon lined stainless steel autoclave, and heated at $140{ }^{\circ} \mathrm{C}$ for 5 days. The crystals which had formed were isolated by filtration, and left overnight to dry in a desiccator as yield light grey bluish crystals of $\mathbf{4 2}(1.60 \mathrm{~g}, 47 \%) . \mathrm{M} . \mathrm{p} .=289-290^{\circ} \mathrm{C}$ (dec.). $\chi_{m}=2810 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{NiC}_{11} \mathrm{H}_{54} \mathrm{O}_{26} \mathrm{~N}_{6} \mathrm{~B} 10$. Anal. $\mathrm{Calc} .: \mathrm{C}=15.5 \%, \mathrm{H}=6.3 \%, \mathrm{~N}=$ $9.9 \%$. Found: $\mathrm{C}=15.5 \%, \mathrm{H}=6.6 \%, \mathrm{~N}=10.0 \% .{ }^{1} \mathrm{H} / \mathrm{ppm}: 1.1\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{CH}_{3}\right.$ of pn$), 1.2(\mathrm{t}, 3 \mathrm{H}, J$ $=1.2 \mathrm{~Hz}, J=2.4 \mathrm{~Hz}, \mathrm{CH}_{3}$ of EtOH$), 2.8(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}$ of pn$), 3.2\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right.$ of EtOH$), 3.6(\mathrm{~d}$, $6 \mathrm{H}, J=6 \mathrm{~Hz}, \mathrm{CH}_{2}$ of pn), and 4.8 ( $\mathrm{s}, 30 \mathrm{H}, \mathrm{NH}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{OH}$ ). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} / \mathrm{ppm}: 39.5 .{ }^{11} \mathrm{~B} / \mathrm{ppm}: 1.5$ (2\%), 13.8 (20\%), and 16.8 ( $78 \%$ ). IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3336(s), 3235(s), 2974(w), 1593(m), 1434(s), 1305(s), 1156(s), 1080(m), 1044(s), 1015(s), 916(s), 820(w), 777(s), 723(m), 708(m), 464(w). p-XRD d-spacing/Å (\% rel. int.): 8.40 (39), 5.62 (48), 5.39 (43), 4.35 (40), 3.61 (100), 2.03 (66), 1.22 (36). TGA: $100-160^{\circ} \mathrm{C}$, loss of five interstitial $\mathrm{H}_{2} \mathrm{O}$ : and $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} 17.0 \%$ ( $16.0 \%$
calc.); $160-260{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four further $\mathrm{H}_{2} \mathrm{O}: 23.4 \%$ ( $24.3 \%$ calc.); $260-900{ }^{\circ} \mathrm{C}$, oxidation of organic content $48.8 \%$ ( $50.5 \%$ calc.); residual $\mathrm{NiB}_{10} \mathrm{O}_{16} 51.2 \%$ ( $49.5 \%$ calc.).

### 6.7.8 Preparation of $\left[\mathrm{Ni}_{2}(\text { trien })_{3}\right]\left[\mathrm{B}_{5} \mathrm{O}_{6}(\mathrm{OH})_{4}\right]_{2} \mathrm{Cl}_{2} \cdot \mathrm{CH}_{3} \mathrm{OH} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (43)

The preparation of $\left[\mathrm{Ni}(\text { trien })_{3}\right](\mathrm{OH})_{2}$ was carried out as described previously for the preparation of $\mathbf{6}$ from $35(2.00 \mathrm{~g}, 2.72 \mathrm{mmol})$ and Dowex ( 20 g ). Boric acid ( $1.68 \mathrm{~g}, 27.2 \mathrm{mmol}$ ) was added to the aqueous solution which was gently warmed with stirring for 3 hours. A rotary evaporator was used to reduce the volume of the solution to 5 mL and the final mixture was sealed in a Teflon lined stainless steel autoclave and heated at $140{ }^{\circ} \mathrm{C}$ for 4 days. The crystals which had formed were isolated by filtration, and left overnight to dry in a desiccator to afford light purple crystals of $43(0.90 \mathrm{~g}, 28 \%)$. M.p. $=287-288^{\circ} \mathrm{C}($ dec. $) \cdot \chi_{m}=3125 \times 10^{-6} \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$. $\mathrm{NiC}_{13} \mathrm{H}_{48} \mathrm{O}_{21} \mathrm{~N}_{8} \mathrm{~B}_{10}$. Anal. Calc.: $\mathrm{C}=19.0 \%, \mathrm{H}=6.5 \%, \mathrm{~N}=14.0 \%$. Found: $\mathrm{C}=18.9 \%, \mathrm{H}=$ $6.3 \%, \mathrm{~N}=13.7 \%$. ${ }^{11} \mathrm{~B} / \mathrm{ppm}: 1.2(3 \%), 13.8$ (30\%), and 16.5 ( $67 \%$ ). IR ( $\mathrm{KBr} / \mathrm{cm}^{-1}$ ): 3290(s), 3238(s), 2951(w), 1410(s), 1313(s), 1163(m), 1057(m), 1022(m), 920(s), 822(w), 773(m), 705(m), 490(m). p-XRD d-spacing/Å (\% rel. int.): 6.13 (20), 5.79 (100), 5.49 (12), 3.98 (14), 3.76 (22), 3.52 (13). TGA: $100-160{ }^{\circ} \mathrm{C}$, loss of interstitial $\mathrm{CH}_{3} \mathrm{OH}$ and six $\mathrm{H}_{2} \mathrm{O}: 10.2 \%$ ( $11.6 \%$ calc.); $160-240{ }^{\circ} \mathrm{C}$, condensation of polyborate which loss of four $\mathrm{H}_{2} \mathrm{O}: 17.9 \%$ ( $17.6 \%$ calc.); $240-700{ }^{\circ} \mathrm{C}$, oxidation of organic content $54.9 \%$ ( $54.1 \%$ calc.); residual $\mathrm{Ni}_{2} \mathrm{~B}_{10} \mathrm{O}_{16} \mathrm{Cl}_{2} 45.2 \%$ ( $46.0 \%$ calc.).

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## Appendix I

## Crystallographic details

Diffractometer: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an $F R-E+$ SuperBright molybdenum rotating anode generator with HF Varimax optics (100 m focus). Cell determination and data collection: CrystalClear-SM Expert 3.1 b27 (Rigaku, 2013). Data reduction, cell refinement and absorption correction: CrystalClearSM Expert 3.1 b27 (Rigaku, 2012). Structure solution : SUPERFLIP (Palatinus, L. \& Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.) Structure refinement: SHELXL-2013 (G Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.). Graphics: ORTEP3 for Windows (L. J. Farrugia, J. Appl. Crystallogr. 1997, 30, 565).

Table 1 Bond lengths [ $\AA$ ] in 6.

| Co1-N6 | 1.869(19) | C11-C12 | 1.507(5) | C26-H26B | 0.9900 | B12-O11 | 1.543(3) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Co1-N26 | 1.937(17) | C11-H11A | 0.9900 | C27-N27 | $1.485(15)$ | B13-O21 | 1.423(3) |
| Co1-N16 | 1.945(16) | C11-H11B | 0.9900 | C27-H27A | 0.9900 | B13-O17 | 1.453(3) |
| Co1-N22 | 1.961(2) | C12-N12 | 1.501(4) | C27-H27B | 0.9900 | B13-O15 | 1.475 (3) |
| Co1-N12 | 1.966(3) | C12-H12A | 0.9900 | N26-H26C | 0.9900 | B13-O11 | 1.565(3) |
| Co1-N17 | 1.966(15) | C12-H12B | 0.9900 | N26-H26D | 0.9900 | B14-O13 | 1.354(3) |
| Co1-N2 | 1.969(3) | N11-H11C | 0.9900 | N27-H27C | 0.9900 | B14-O12 | 1.372 (3) |
| Co1-N21 | 1.977(3) | N11-H11D | 0.9900 | N27-H27D | 0.9900 | B14-O22 | 1.385(3) |
| Co1-N1 | 1.979(2) | N12-H12C | 0.9900 | B1-O4 | 1.459(4) | B15-O15 | 1.366 (3) |
| Co1-N11 | 1.981(3) | N12-H12D | 0.9900 | B1-O1 | 1.467(4) | B15-O23 | 1.368 (3) |
| Co1-N7 | 1.993(18) | C16-C17 | 1.490 (15) | B1-O3 | 1.468(4) | B15-O14 | 1.373(3) |
| Co1-N27 | 2.028(16) | C16-N16 | 1.501(14) | B1-O6 | 1.491(4) | B16-O17 | 1.368 (3) |
| C1-N1 | 1.494(4) | C16-H16A | 0.9900 | B2-O1 | 1.359(4) | B16-O24 | 1.375(3) |
| C1-C2 | 1.511(5) | C16-H16B | 0.9900 | B2-O7 | 1.363(4) | B16-O16 | 1.379(3) |
| C1-H1A | 0.9900 | C17-N17 | 1.466(14) | B2-O2 | 1.374(4) | B17-O25 | 1.357(4) |
| C1-H1B | 0.9900 | C17-H17A | 0.9900 | B3-O3 | 1.357(4) | B17-O18 | 1.359(4) |
| C2-N2 | 1.492(4) | C17-H17B | 0.9900 | B3-O8 | 1.363(4) | B17-O19 | 1.388(4) |
| C2-H2A | 0.9900 | N16-H16C | 0.9900 | B3-O2 | 1.388(4) | B18-O26 | 1.344(4) |
| C2-H2B | 0.9900 | N16-H16D | 0.9900 | B4-O4 | 1.354(4) | B18-O20 | 1.369(4) |
| N1-H1C | 0.9900 | N17-H17C | 0.9900 | B4-O9 | 1.358(4) | B18-O19 | $1.398(4)$ |
| N1-H1D | 0.9900 | N17-H17D | 0.9900 | B4-O5 | $1.376(4)$ | $\mathrm{O} 21-\mathrm{H} 21$ | 0.8400 |
| N2-H2C | 0.9900 | C21-N21 | 1.499(6) | B5-O6 | 1.354(4) | $\mathrm{O} 22-\mathrm{H} 22$ | 0.8400 |
| N2-H2D | 0.9900 | C21-C22 | 1.506(6) | B5-O10 | 1.365(4) | $\mathrm{O} 23-\mathrm{H} 23$ | 0.8400 |
| C6-C7 | 1.480 (15) | C21-H21A | 0.9900 | B5-O5 | 1.391(4) | O24-H24 | 0.8400 |
| C6-N6 | 1.503(14) | C21-H21B | 0.9900 | O7-H7 | 0.8400 | $\mathrm{O} 25-\mathrm{H} 25$ | 0.8400 |
| C6-H6A | 0.9900 | C22-N22 | 1.469(6) | O8-H8 | 0.8400 | O26-H26 | 0.8400 |
| C6-H6B | 0.9900 | C22-H22A | 0.9900 | O9-H9 | 0.8400 | O41-H41A | 0.8501 |
| C7-N7 | 1.481(15) | C22-H22B | 0.9900 | O10-H10 | 0.8400 | O41-H41B | 0.8501 |
| C7-H7A | 0.9900 | N21-H21C | 0.9900 | B11-O20 | 1.439(4) | O42-H42A | 0.8497 |
| C7-H7B | 0.9900 | N21-H21D | 0.9900 | B11-O12 | 1.446(3) | O42-H42B | 0.8500 |
| N6-H6C | 0.9900 | N22-H22C | 0.9900 | B11-O18 | 1.472(4) | O43-H43A | 0.8497 |
| N6-H6D | 0.9900 | N22-H22D | 0.9900 | B11-O11 | 1.554(3) | O43-H43B | 0.8500 |
| N7-H7C | 0.9900 | C26-N26 | 1.491(15) | B12-O13 | 1.443(3) | O44-H44A | 0.8499 |
| N7-H7D | 0.9900 | C26-C27 | 1.495(16) | B12-O14 | 1.469(3) | O44-H44B | 0.8498 |
| C11-N11 | 1.494(4) | C26-H26A | 0.9900 | B12-O16 | 1.472(3) | $\mathrm{O} 51-\mathrm{H} 51 \mathrm{~A}$ O51-H51B | $0.8500$ |

Table 2 Bond angles [ ${ }^{\circ}$ ] in 6.

| N6-Co1-N26 | 91.5(8) | C11-C12-H12A | 110.4 | Col-N27-H27D | 109.3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N6-Co1-N16 | 96.8(7) | N12-C12-H12B | 110.4 | H27C-N27-H27D | 108.0 |
| N26-Co1-N16 | 92.1(7) | C11-C12-H12B | 110.4 | O4-B1-O1 | 108.0(2) |
| N22-Co1-N12 | 92.28(11) | H12A-C12-H12B | 108.6 | O4-B1-O3 | 109.6(2) |
| N6-Co1-N17 | 95.8(8) | C11-N11-Co1 | 109.14(19) | O1-B1-O3 | 112.2(2) |
| N26-Co1-N17 | 172.5(7) | C11-N11-H11C | 109.9 | O4-B1-O6 | 112.4(2) |
| N16-Co1-N17 | 85.2(6) | Co1-N11-H11C | 109.9 | O1-B1-O6 | 107.1(2) |
| N22-Co1-N2 | 89.36(11) | C11-N11-H11D | 109.9 | O3-B1-O6 | 107.7(2) |
| N12-Co1-N2 | 91.40(11) | Co1-N11-H11D | 109.9 | O1-B2-O7 | 120.8(3) |
| N22-Co1-N21 | 85.69(10) | H11C-N11-H11D | 108.3 | $\mathrm{O} 1-\mathrm{B}-\mathrm{O} 2$ | 122.0(3) |
| N12-Co1-N21 | 91.74(11) | C12-N12-Col | 109.61(19) | O7-B2-O2 | 117.1(3) |
| N2-Co1-N21 | 174.24(11) | C12-N12-H12C | 109.7 | O3-B3-08 | 122.6(2) |
| N22-Co1-N1 | 92.30(11) | $\mathrm{Co} 1-\mathrm{N} 12-\mathrm{H} 12 \mathrm{C}$ | 109.7 | O3-B3-O2 | 121.2(2) |
| N12-Co1-N1 | 174.45(11) | C12-N12-H12D | 109.7 | O8-B3-O2 | 116.1(2) |
| N2-Co1-N1 | 85.52(10) | Co1-N12-H12D | 109.7 | O4-B4-O9 | 119.0(3) |
| N21-Co1-N1 | 91.72(10) | H12C-N12-H12D | 108.2 | O4-B4-O5 | 121.5(3) |
| N22-Co1-N11 | 175.88(11) | C17-C16-N16 | 107.6(14) | O9-B4-O5 | 119.5(3) |
| N12-Col-N11 | 85.32(11) | C17-C16-H16A | 110.2 | O6-B5-O10 | 120.9(3) |
| N2-Co1-N11 | 94.04(11) | N16-C16-H16A | 110.2 | O6-B5-O5 | 121.2(3) |
| N21-Co1-N11 | 91.02(11) | C17-C16-H16B | 110.2 | O10-B5-O5 | 117.9(3) |
| N1-Co1-N11 | 90.28(11) | N16-C16-H16B | 110.2 | B2-O1-B1 | 122.5(2) |
| N6-Col-N7 | 87.3(6) | H16A-C16-H16B | 108.5 | B2-O2-B3 | 119.0(2) |
| N26-Co1-N7 | 92.6(8) | N17-C17-C16 | 108.5(13) | B3-O3-B1 | 122.9(2) |
| N16-Co1-N7 | 173.7(7) | N17-C17-H17A | 110.0 | B4-O4-B1 | 122.4(2) |
| N17-Co1-N7 | 89.7(7) | C16-C17-H17A | 110.0 | B4-O5-B5 | 119.6(2) |
| N6-Co1-N27 | 172.0(7) | N17-C17-H17B | 110.0 | B5-O6-B1 | 121.5(2) |
| N26-Co1-N27 | 84.1(6) | C16-C17-H17B | 110.0 | B2-O7-H7 | 109.5 |
| N16-Co1-N27 | 90.0(7) | H17A-C17-H17B | 108.4 | B3-O8-H8 | 109.5 |
| N17-Co1-N27 | 88.9(7) | C16-N16-Co1 | 108.4(11) | B4-O9-H9 | 109.5 |
| N7-Co1-N27 | 86.3(7) | C16-N16-H16C | 110.0 | B5-O10-H10 | 109.5 |
| N1-C1-C2 | 107.5(2) | Co1-N16-H16C | 110.0 | O20-B11-O12 | 109.3(2) |
| N1-C1-H1A | 110.2 | C16-N16-H16D | 110.0 | O20-B11-O18 | 112.2(2) |
| C2-C1-H1A | 110.2 | Co1-N16-H16D | 110.0 | O12-B11-O18 | 108.7(2) |
| N1-C1-H1B | 110.2 | H16C-N16-H16D | 108.4 | O20-B11-O11 | 110.3(2) |
| C2-C1-H1B | 110.2 | C17-N17-Co1 | 111.5(10) | O12-B11-O11 | 107.0(2) |
| H1A-C1-H1B | 108.5 | C17-N17-H17C | 109.3 | O18-B11-O11 | 109.1(2) |
| N2-C2-C1 | 106.9(3) | Co1-N17-H17C | 109.3 | O13-B12-O14 | 108.8(2) |
| N2-C2-H2A | 110.3 | C17-N17-H17D | 109.3 | O13-B12-O16 | 111.3(2) |
| C1-C2-H2A | 110.3 | Co1-N17-H17D | 109.3 | O14-B12-O16 | 110.0(2) |
| N2-C2-H2B | 110.3 | H17C-N17-H17D | 108.0 | O13-B12-O11 | 111.1(2) |
| C1-C2-H2B | 110.3 | N21-C21-C22 | 107.5(4) | O14-B12-O11 | 108.46(19) |
| H2A-C2-H2B | 108.6 | N21-C21-H21A | 110.2 | O16-B12-O11 | 107.12(19) |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{Co} 1$ | 109.27(19) | C22-C21-H21A | 110.2 | O21-B13-O17 | 109.0(2) |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{H} 1 \mathrm{C}$ | 109.8 | N21-C21-H21B | 110.2 | O21-B13-O15 | 111.2(2) |
| Col-N1-H1C | 109.8 | C22-C21-H21B | 110.2 | O17-B13-O15 | 111.0(2) |
| C1-N1-H1D | 109.8 | H21A-C21-H21B | 108.5 | O21-B13-O11 | 112.3(2) |
| Col-N1-H1D | 109.8 | N22-C22-C21 | 107.0(4) | O17-B13-O11 | 107.92(19) |
| H1C-N1-H1D | 108.3 | N22-C22-H22A | 110.3 | O15-B13-O11 | 105.34(19) |
| $\mathrm{C} 2-\mathrm{N} 2-\mathrm{Co} 1$ | 109.6(2) | C21-C22-H22A | 110.3 | O13-B14-O12 | 122.3(2) |
| C2-N2-H2C | 109.8 | N22-C22-H22B | 110.3 | O13-B14-O22 | 119.2(2) |
| Col-N2-H2C | 109.8 | C21-C22-H22B | 110.3 | O12-B14-O22 | 118.5(2) |
| C2-N2-H2D | 109.8 | H22A-C22-H22B | 108.6 | O15-B15-O23 | 121.1(2) |
| Co1-N2-H2D | 109.8 | C21-N21-Co1 | 108.3(3) | O15-B15-O14 | 121.3(2) |
| H2C-N2-H2D | 108.2 | C21-N21-H21C | 110.0 | O23-B15-O14 | 117.6(2) |
| C7-C6-N6 | 107.0(13) | Co1-N21-H21C | 110.0 | O17-B16-O24 | 117.7(2) |
| C7-C6-H6A | 110.3 | C21-N21-H21D | 110.0 | O17-B16-O16 | 122.3(2) |
| N6-C6-H6A | 110.3 | Co1-N21-H21D | 110.0 | O24-B16-O16 | 120.0(2) |
| C7-C6-H6B | 110.3 | H21C-N21-H21D | 108.4 | O25-B17-O18 | 121.7(3) |
| N6-C6-H6B | 110.3 | C22-N22-Co1 | 109.8(3) | O25-B17-O19 | 117.6(2) |
| H6A-C6-H6B | 108.6 | C22-N22-H22C | 109.7 | O18-B17-O19 | 120.7(3) |
| C6-C7-N7 | 108.1(15) | Co1-N22-H22C | 109.7 | O26-B18-O20 | 122.5(3) |


| C6-C7-H7A | 110.1 | C22-N22-H22D | 109.7 | O26-B18-O19 | $116.6(2)$ |
| :--- | ---: | :--- | ---: | ---: | ---: |
| N7-C7-H7A | 110.1 | Co1-N22-H22D | 109.7 | O20-B18-O19 | $120.8(3)$ |
| C6-C7-H7B | 110.1 | H22C-N22-H22D | 108.2 | B12-O11-B11 | $115.79(19)$ |
| N7-C7-H7B | 110.1 | N26-C26-C27 | $109.2(19)$ | B12-O11-B13 | $108.60(18)$ |
| H7A-C7-H7B | 108.4 | N26-C26-H26A | 109.8 | B11-O11-B13 | $120.15(19)$ |
| C6-N6-Co1 | $110.4(12)$ | C27-C26-H26A | 109.8 | B14-O12-B11 | $122.8(2)$ |
| C6-N6-H6C | 109.6 | N26-C26-H26B | 109.8 | B14-O13-B12 | $123.2(2)$ |
| Co1-N6-H6C | 109.6 | C27-C26-H26B | 109.8 | B15-O14-B12 | $118.6(2)$ |
| C6-N6-H6D | 109.6 | H26A-C26-H26B | 108.3 | B15-O15-B13 | $124.1(2)$ |
| Co1-N6-H6D | 109.6 | N27-C27-C26 | $107.7(19)$ | B16-O16-B12 | $122.5(2)$ |
| H6C-N6-H6D | 108.1 | N27-C27-H27A | 110.2 | B16-O17-B13 | $119.8(2)$ |
| C7-N7-Co1 | $106.1(10)$ | C26-C27-H27A | 110.2 | B17-O18-B11 | $122.1(2)$ |
| C7-N7-H7C | 110.5 | N27-C27-H27B | 110.2 | B17-O19-B18 | $118.6(2)$ |
| Co1-N7-H7C | 110.5 | C26-C27-H27B | 110.2 | B18-O20-B11 | $121.3(2)$ |
| C7-N7-H7D | 110.5 | H27A-C27-H27B | 108.5 | B13-O21-H21 | 109.5 |
| Co1-N7-H7D | 110.5 | C26-N26-Co1 | $108.9(19)$ | B14-O22-H22 | 109.5 |
| H7C-N7-H7D | 108.7 | C26-N26-H26C | 109.9 | B15-O23-H23 | 109.5 |
| N11-C11-C12 | $106.8(3)$ | Co1-N26-H26C | 109.9 | B16-O24-H24 | 109.5 |
| N11-C11-H11A | 110.4 | C26-N26-H26D | 109.9 | B17-O25-H25 | 109.5 |
| C12-C11-H11A | 110.4 | Co1-N26-H26D | 109.9 | B18-O26-H26 | 109.5 |
| N11-C11-H11B | 110.4 | H26C-N26-H26D | 108.3 | H41A-O41-H41B | 109.5 |
| C12-C11-H11B | 110.4 | C27-N27-Co1 | $111.5(13)$ | H42A-O42-H42B | 109.5 |
| H11A-C11-H11B | 108.6 | C27-N27-H27C | 109.3 | H43A-O43-H43B | 109.5 |
| N12-C12-C11 | $106.6(3)$ | Co1-N27-H27C | 109.3 | H44A-O44-H44B | 109.5 |
| N12-C12-H12A | 110.4 | C27-N27-H27D | 109.3 | H51A-O51-H51B | 109.5 |

Table 3 Bond lengths [ $A ̊$ ] in 9.

| B1-06 | 1.4469(19) | O17-H17 | 0.8400 | N3-H3A | 0.9100 | N21-H21A | 0.9100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| B1-O5 | 1.455(2) | O18-H18 | 0.8400 | N3-H3B | 0.9100 | N21-H21B | 0.9100 |
| B1-O4 | 1.500(2) | O19-H19 | 0.8400 | N3-H3C | 0.9100 | N21-H21C | 0.9100 |
| B1-O1 | 1.5104(19) | B21-O26 | 1.437(2) | N4-H4A | 0.9100 | N22-H22A | 0.9100 |
| B2-O1 | 1.367(2) | B21-O25 | 1.470(2) | N4-H4B | 0.9100 | N22-H22B | 0.9100 |
| B2-O2 | 1.376(2) | B21-O21 | 1.498(2) | N4-H4C | 0.9100 | N22-H22C | 0.9100 |
| B2-07 | 1.378(2) | B21-O24 | 1.5042(19) | N5-H5A | 0.9100 | N23-H23A | 0.9100 |
| B3-08 | 1.452(2) | B22-O22 | 1.364(2) | N5-H5B | 0.9100 | N23-H23B | 0.9100 |
| B3-05 | 1.4648(19) | B22-O21 | 1.374(2) | N5-H5C | 0.9100 | N23-H23C | 0.9100 |
| B3-O3 | 1.494(2) | B22-027 | 1.376(2) | N6-H6A | 0.9100 | O41-H41A | 0.848(9) |
| B3-O2 | 1.5011(19) | B23-O28 | 1.452(2) | N6-H6B | 0.9100 | O41-H41B | 0.852(9) |
| B4-O3 | 1.370(2) | B23-O25 | 1.469(2) | N6-H6C | 0.9100 | O42-H42A | 0.856(9) |
| B4-09 | 1.372(2) | B23-O22 | 1.486(2) | Co11-N13 ${ }^{\text {i }}$ | $1.9625(14)$ | O42-H42B | 0.854(9) |
| B4-O4 | 1.377(2) | B23-O23 | 1.512(2) | Co11-N13 | $1.9625(14)$ | O43-H43A | 0.846(9) |
| O6-H6 | 0.8400 | B24-O23 | 1.366(2) | Co11-N11 | $1.9705(14)$ | O43-H43B | 0.848(9) |
| O7-H7 | 0.8400 | B24-O24 | 1.375(2) | Co11-N11 ${ }^{\text {i }}$ | $1.9706(14)$ | O44-H44A | 0.849(9) |
| O8-H8 | 0.8400 | B24-O29 | 1.376(2) | Co11-N12 ${ }^{\text {i }}$ | $1.9820(14)$ | O44-H44B | 0.851(9) |
| O9-H9 | 0.8400 | O26-H26 | 0.8400 | Co11-N12 | 1.9820 (14) | O45-H45A | 0.857(9) |
| B11-O16 | 1.4519(19) | O27-H27 | 0.8400 | N11-H11A | 0.9100 | O45-H45B | 0.850(9) |
| B11-O15 | 1.471(2) | O28-H38 | 0.8400 | N11-H11B | 0.9100 | O46-H46A | 0.853(9) |
| B11-O14 | 1.485(2) | O29-H29 | 0.8400 | N11-H11C | 0.9100 | O46-H46B | 0.846(9) |
| B11-O11 | 1.507(2) | Col-N5 | $1.9625(13)$ | N12-H12A | 0.9100 | O47-H47A | 0.858(9) |
| B12-O12 | 1.364(2) | Co1-N6 | $1.9646(14)$ | N12-H12B | 0.9100 | O47-H47B | 0.830(9) |
| B12-O11 | 1.366(2) | Col-N1 | 1.9679(13) | N12-H12C | 0.9100 | O48-H48A | 0.858(9) |
| B12-O17 | 1.383(2) | Co1-N4 | 1.9681(14) | N13-H13A | 0.9100 | O48-H48B | 0.858(9) |
| B13-O18 | 1.438(2) | $\mathrm{Co} 1-\mathrm{N} 2$ | $1.9720(14)$ | N13-H13B | 0.9100 | O49-H49A | 0.850(9) |
| B13-O15 | 1.4770(19) | Co1-N3 | $1.9738(13)$ | N13-H13C | 0.9100 | O49-H49B | 0.856(9) |
| B13-O12 | 1.486(2) | N1-H1A | 0.9100 | Co21-N23 | 1.9646(13) | O50-H50A | 0.853(9) |
| B13-O13 | 1.512(2) | N1-H1B | 0.9100 | Co21-N23ii | 1.9646 (13) | O50-H50B | 0.849(9) |
| B14-O13 | 1.373(2) | N1-H1C | 0.9100 | Co21-N21 | 1.9680 (13) | O51-H51A | 0.844(9) |
| B14-O14 | 1.374(2) | N2-H2A | 0.9100 | Co21-N21ii | 1.9680 (13) | O51-H51B | 0.844(9) |
| B14-O19 | 1.376(2) | N2-H2B | 0.9100 | Co21-N22 | $1.9759(14)$ |  |  |
| O16-H16 | 0.8400 | N2-H2C | 0.9100 | Co21-N22ii | 1.9760 (14) |  |  |

Table 4 Bond angles [ ${ }^{\circ}$ ] in 9.

| O6-B1-O5 | 113.76(13) | O23-B24-O29 | 117.02(15) | N11-Co11-N12 ${ }^{\text {i }}$ | 92.42(6) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| O6-B1-O4 | 106.19(13) | O24-B24-O29 | 120.90(15) | N11 ${ }^{\text {i }}$-Co11-N12 ${ }^{\text {i }}$ | 87.58(6) |
| O5-B1-O4 | 111.11(13) | B22-O21-B21 | 121.26(13) | N13 ${ }^{\text {i }}$-Co11-N12 | 88.48(6) |
| O6-B1-O1 | 112.01(13) | B22-O22-B23 | 115.77(13) | N13-Co11-N12 | 91.52(6) |
| O5-B1-O1 | 107.89(12) | B24-O23-B23 | 121.40(13) | N11-Co11-N12 | 87.58(6) |
| O4-B1-O1 | 105.61(12) | B24-O24-B21 | 116.45(13) | N11 ${ }^{\text {i}}$-Co11-N12 | 92.42(6) |
| O1-B2-O2 | 122.91(14) | B23-O25-B21 | 110.55(12) | N12 ${ }^{\text {i }}$ Col1-N12 | 180.0 |
| O1-B2-07 | 120.43(15) | B21-O26-H26 | 109.5 | Co11-N11-H11A | 109.5 |
| O2-B2-O7 | 116.66(14) | B22-O27-H27 | 109.5 | Col1-N11-H11B | 109.5 |
| O8-B3-O5 | 112.18(12) | B23-O28-H38 | 109.5 | H11A-N11-H11B | 109.5 |
| O8-B3-O3 | 109.67(13) | B24-O29-H29 | 109.5 | Co11-N11-H11C | 109.5 |
| O5-B3-03 | 109.21(12) | N5-Col-N6 | 91.56(6) | H11A-N11-H11C | 109.5 |
| O8-B3-O2 | 108.12(12) | N5-Col-N1 | 89.12(5) | H11B-N11-H11C | 109.5 |
| O5-B3-02 | 109.11(13) | N6-Co1-N1 | 179.19(5) | Co11-N12-H12A | 109.5 |
| O3-B3-O2 | 108.49(12) | N5-Co1-N4 | 89.93(6) | Co11-N12-H12B | 109.5 |
| O3-B4-O9 | 117.15(15) | N6-Co1-N4 | 88.85(6) | H12A-N12-H12B | 109.5 |
| O3-B4-O4 | 122.08(14) | N1-Co1-N4 | 90.72(6) | Co11-N12-H12C | 109.5 |
| O9-B4-O4 | 120.77(15) | N5-Co1-N2 | 88.65(6) | H12A-N12-H12C | 109.5 |
| B2-O1-B1 | 119.43(13) | N6-Co1-N2 | 89.92(6) | H12B-N12-H12C | 109.5 |
| B2-O2-B3 | 117.90(12) | $\mathrm{N} 1-\mathrm{Co} 1-\mathrm{N} 2$ | 90.52(6) | Co11-N13-H13A | 109.5 |
| B4-O3-B3 | 119.58(13) | $\mathrm{N} 4-\mathrm{Co} 1-\mathrm{N} 2$ | 178.10(6) | Co11-N13-H13B | 109.5 |
| B4-O4-B1 | 118.55(13) | N5-Co1-N3 | 177.72(6) | H13A-N13-H13B | 109.5 |
| B1-O5-B3 | 111.66(12) | N6-Co1-N3 | 89.19(6) | Co11-N13-H13C | 109.5 |
| B1-O6-H6 | 109.5 | N1-Co1-N3 | 90.14(6) | H13A-N13-H13C | 109.5 |
| B2-07-H7 | 109.5 | N4-Co1-N3 | 92.24(6) | H13B-N13-H13C | 109.5 |
| B3-O8-H8 | 109.5 | N2-Co1-N3 | 89.19(6) | N23-Co21-N23ii | 180.00(3) |
| B4-O9-H9 | 109.5 | Co1-N1-H1A | 109.5 | N23-Co21-N21 | 90.08(6) |
| O16-B11-O15 | 112.64(13) | Co1-N1-H1B | 109.5 | N23ii-Co21-N21 | 89.92(6) |
| O16-B11-O14 | 108.57(13) | H1A-N1-H1B | 109.5 | N23-Co21-N21ii | 89.92(6) |
| O15-B11-O14 | 108.68(13) | $\mathrm{Co1-N1-H1C}$ | 109.5 | N23ii-Co21-N2 ${ }^{\text {ii }}$ | 90.08(6) |
| O16-B11-O11 | 108.41(13) | $\mathrm{H} 1 \mathrm{~A}-\mathrm{N} 1-\mathrm{H} 1 \mathrm{C}$ | 109.5 | N21-Co21-N21 ${ }^{\text {ii }}$ | 180.0 |
| O15-B11-O11 | 109.90(13) | H1B-N1-H1C | 109.5 | N23-Co21-N22 | 89.26(6) |
| O14-B11-O11 | 108.56(13) | $\mathrm{Co1-N2-H2A}$ | 109.5 | N23 ${ }^{\text {ii }}$-Co21-N22 | 90.74(6) |
| O12-B12-O11 | 122.95(15) | Col-N2-H2B | 109.5 | N21-Co21-N22 | 87.91(6) |
| O12-B12-O17 | 116.31(14) | $\mathrm{H} 2 \mathrm{~A}-\mathrm{N} 2-\mathrm{H} 2 \mathrm{~B}$ | 109.5 | N21 ${ }^{\text {ii }}$-Co21-N22 | 92.09(6) |
| O11-B12-O17 | 120.74(14) | $\mathrm{Co1-N2-H2C}$ | 109.5 | N23-Co21-N22ii | 90.74(6) |
| O18-B13-O15 | 113.40(13) | $\mathrm{H} 2 \mathrm{~A}-\mathrm{N} 2-\mathrm{H} 2 \mathrm{C}$ | 109.5 | N23ii-Co21-N22 ${ }^{\text {ii }}$ | 89.26(6) |
| O18-B13-O12 | 106.85(13) | $\mathrm{H} 2 \mathrm{~B}-\mathrm{N} 2-\mathrm{H} 2 \mathrm{C}$ | 109.5 | N21-Co21-N22ii | 92.09(6) |
| O15-B13-O12 | 109.13(13) | Co1-N3-H3A | 109.5 | N2 ${ }^{1 i}$-Co21-N22 ${ }^{\text {ii }}$ | 87.91(6) |
| O18-B13-O13 | 111.02(13) | Co1-N3-H3B | 109.5 | N22-Co21-N22ii | 180.0 |
| O15-B13-O13 | 107.54(13) | H3A-N3-H3B | 109.5 | Co21-N21-H21A | 109.5 |
| O12-B13-O13 | 108.81(13) | $\mathrm{Co1-N3-H3C}$ | 109.5 | Co21-N21-H21B | 109.5 |
| O13-B14-O14 | 122.78(16) | H3A-N3-H3C | 109.5 | H21A-N21-H21B | 109.5 |
| O13-B14-O19 | 121.51(15) | H3B-N3-H3C | 109.5 | Co21-N21-H21C | 109.5 |
| O14-B14-O19 | 115.71(15) | $\mathrm{Co1-N4-H4A}$ | 109.5 | H21A-N21-H21C | 109.5 |
| B12-O11-B11 | 118.07(12) | Co1-N4-H4B | 109.5 | H21B-N21-H21C | 109.5 |
| B12-O12-B13 | 120.22(12) | H4A-N4-H4B | 109.5 | Co21-N22-H22A | 109.5 |
| B14-O13-B13 | 118.62(13) | $\mathrm{Co1-N4-H4C}$ | 109.5 | Co21-N22-H22B | 109.5 |
| B14-O14-B11 | 119.11(13) | H4A-N4-H4C | 109.5 | H22A-N22-H22B | 109.5 |
| B11-O15-B13 | 111.10(12) | H4B-N4-H4C | 109.5 | Co21-N22-H22C | 109.5 |
| B11-O16-H16 | 109.5 | Co1-N5-H5A | 109.5 | H22A-N22-H22C | 109.5 |
| B12-O17-H17 | 109.5 | Co1-N5-H5B | 109.5 | H22B-N22-H22C | 109.5 |
| B13-O18-H18 | 109.5 | H5A-N5-H5B | 109.5 | Co21-N23-H23A | 109.5 |
| B14-O19-H19 | 109.5 | Co1-N5-H5C | 109.5 | Co21-N23-H23B | 109.5 |
| O26-B21-O25 | 113.87(13) | H5A-N5-H5C | 109.5 | H23A-N23-H23B | 109.5 |
| O26-B21-O21 | 107.12(13) | H5B-N5-H5C | 109.5 | Co21-N23-H23C | 109.5 |
| O25-B21-O21 | 109.23(13) | Co1-N6-H6A | 109.5 | H23A-N23-H23C | 109.5 |
| O26-B21-O24 | 110.35(13) | Col-N6-H6B | 109.5 | H23B-N23-H23C | 109.5 |
| O25-B21-O24 | 108.64(13) | H6A-N6-H6B | 109.5 | H41A-O41-H41B | 107.0(14) |
| O21-B21-O24 | 107.43(12) | Co1-N6-H6C | 109.5 | H42A-O42-H42B | 106.5(14) |
| O22-B22-O21 | 122.49(15) | H6A-N6-H6C | 109.5 | H43A-O43-H43B | 108.8(14) |


| O22-B22-O27 | $118.02(15)$ | H6B-N6-H6C | 109.5 | H44A-O44-H44B | $106.8(14)$ |
| :--- | :--- | :--- | ---: | ---: | ---: |
| O21-B22-O27 | $119.49(15)$ | N13i-Co11-N13 | 180.0 | H45A-O45-H45B | $106.2(12)$ |
| O28-B23-O25 | $113.02(13)$ | N13-Co11-N11 | $91.02(6)$ | H46A-O46-H46B | $106.1(13)$ |
| O28-B23-O22 | $108.24(13)$ | N13-Co11-N11 | $88.98(6)$ | H47A-O47-H47B | $106.7(14)$ |
| O25-B23-O22 | $109.42(13)$ | N13-Co11-N11 | $88.98(6)$ | H48A-O48-H48B | $106.0(14)$ |
| O28-B23-O23 | $109.15(13)$ | N13-Co11-N11 | i | $91.02(6)$ | H49A-O49-H49B |
| O25-B23-O23 | $108.99(13)$ | N11-Co11-N11 ${ }^{\mathrm{i}}$ | 180.0 | H50A-O50-H50B | $106.9(14)$ |
| O22-B23-O23 | $107.89(12)$ | N13-Co11-N12 | $106.2(14)$ |  |  |
| O23-B24-O24 | $122.07(14)$ | N13-Co11-N12 | $91.52(6)$ | H51A-O51-H51B | $108.1(13)$ |

Table 5 Bond lengths [ $\AA$ ] in $\mathbf{1 1}$.

| Co1-N23 | $1.956(2)$ | O10-H10 | 0.8400 | C32-H32A | 0.9900 | C34-H34A | 0.9900 |
| :--- | :--- | :--- | ---: | :--- | ---: | :--- | :--- |
| Co1-N32 | $1.957(2)$ | O11-H11 | 0.8400 | C32-H32B | 0.9900 | C34-H34B | 0.9900 |
| Co1-N22 | $1.960(2)$ | O12-H12 | 0.8400 | C33-N32 | $1.489(3)$ | N31-H31C | 0.9900 |
| Co1-N21 | $1.963(2)$ | O13-H13 | 0.8400 | C33-C34 | $1.515(4)$ | N31-H31D | 0.9900 |
| Co1-N31 | $1.967(2)$ | O14-H14 | 0.8400 | C33-H33A | 0.9900 | N32-H32 | 1.0000 |
| Co1-N33 | $1.969(2)$ | O15-H15 | 0.8400 | C33-H33B | 0.9900 | N33-H33C | 0.9900 |
| B1-O1 | $1.424(3)$ | C21-N21 | $1.493(3)$ | C34-N33 | $1.491(4)$ | N33-H33D | 0.9900 |
| B1-O3 | $1.473(4)$ | C21-C22 | $1.518(3)$ | C34-H34A | 0.9900 | O51-H51A | 0.8706 |
| B1-O4 | $1.486(3)$ | C21-H21A | 0.9900 | C34-H34B | 0.9900 | O51-H51B | 0.8702 |
| B1-O6 | $1.507(3)$ | C21-H21B | 0.9900 | N31-H31C | 0.9900 | O52-H52A | 0.8701 |
| B2-O9 | $1.444(3)$ | C22-N22 | $1.490(3)$ | N31-H31D | 0.9900 | O52-H52B | 0.8703 |
| B2-O1 | $1.453(3)$ | C22-H22A | 0.9900 | N32-H32 | 1.0000 | O53-H53A | 0.8700 |
| B2-O7 | $1.492(3)$ | C22-H22B | 0.9900 | N33-H33C | 0.9900 | O53-H53B | 0.8704 |
| B2-O2 | $1.508(4)$ | C23-N22 | $1.497(3)$ | N33-H33D | 0.9900 | O54-H54A | 0.8698 |
| B3-O2 | $1.356(3)$ | C23-C24 | $1.515(3)$ | N21-H21D | 0.9900 | O54-H54B | 0.8703 |
| B3-O3 | $1.367(3)$ | C23-H23A | 0.9900 | N22-H22 | 1.0000 | O55-H55A | 0.8696 |
| B3-O10 | $1.371(4)$ | C23-H23B | 0.9900 | N23-H23C | 0.9900 | O55-H55B | 0.8703 |
| B4-O11 | $1.348(3)$ | C24-N23 | $1.483(4)$ | N23-H23D | 0.9900 | O56-H56A | 0.8706 |
| B4-O4 | $1.357(3)$ | C24-H24A | 0.9900 | C31-N31 | $1.489(4)$ | O56-H56 | 0.8702 |
| B4-O5 | $1.400(3)$ | C24-H24B | 0.9900 | C31-C32 | $1.516(3)$ | O57-H57A | 0.8704 |
| B5-O6 | $1.347(3)$ | N21-H21C | 0.9900 | C31-H31A | 0.9900 | O57-H57B | 0.8701 |
| B5-O12 | $1.361(3)$ | N21-H21D | 0.9900 | C31-H31B | 0.9900 | O58-H58A | 0.8699 |
| B5-O5 | $1.385(3)$ | N22-H22 | 1.0000 | C32-N32 | $1.497(3)$ | O58-H58B | 0.8702 |
| B6-O7 | $1.354(3)$ | N23-H23C | 0.9900 | C32-H32A | 0.9900 | O88-H88A | 0.8699 |
| B6-O8 | $1.365(3)$ | N23-H23D | 0.9900 | C32-H32B | 0.9900 | O88-H88B | 0.8699 |
| B6-O13 | $1.366(3)$ | C31-N31 | $1.489(4)$ | C33-N32 | $1.489(3)$ | O59-H59A | 0.8699 |
| B7-O9 | $1.448(3)$ | C31-C32 | $1.516(3)$ | C33-C34 | $1.515(4)$ | O59-H59B | 0.8704 |
| B7-O15 | $1.464(4)$ | C31-H31A | 0.9900 | C33-H33A | 0.9900 | O89-H89A | 0.8698 |
| B7-O14 | $1.471(3)$ | C31-H31B | 0.9900 | C33-H33B | 0.9900 | O89-H89B | 0.8702 |
| B7-O8 | $1.516(3)$ | C32-N32 | $1.497(3)$ | C34-N33 | $1.491(4)$ |  |  |

Table 6 Bond angles [ ${ }^{\circ}$ ] in 11.

| N23-Co1-N33 | $177.72(9)$ | B7-O15-H15 | 109.5 | H31A-C31-H31B | 108.3 |
| :--- | ---: | :--- | ---: | :--- | ---: |
| N32-Co1-N33 | $86.65(9)$ | N21-C21-C22 | $109.2(2)$ | N32-C32-C31 | $110.2(2)$ |
| N22-Co1-N33 | $95.19(9)$ | N21-C21-H21A | 109.8 | N32-C32-H32A | 109.6 |
| N21-Co1-N33 | $90.38(9)$ | C22-C21-H21A | 109.8 | C31-C32-H32A | 109.6 |
| N31-Co1-N33 | $88.56(9)$ | N21-C21-H21B | 109.8 | N32-C32-H32B | 109.6 |
| O1-B1-O3 | $113.0(2)$ | C22-C21-H21B | 109.8 | C31-C32-H32B | 109.6 |
| O1-B1-O4 | $113.7(2)$ | H21A-C21-H21B | 108.3 | H32A-C32-H32B | 108.1 |
| O3-B1-O4 | $108.5(2)$ | N22-C22-C21 | $109.4(2)$ | N32-C33-C34 | $109.7(2)$ |
| O1-B1-O6 | $108.0(2)$ | N22-C22-H22A | 109.8 | N32-C33-H33A | 109.7 |
| O3-B1-O6 | $105.42(19)$ | C21-C22-H22A | 109.8 | C34-C33-H33A | 109.7 |
| O4-B1-O6 | $107.77(18)$ | N22-C22-H22B | 109.8 | N32-C33-H33B | 109.7 |
| O9-B2-O1 | $111.7(2)$ | C21-C22-H22B | 109.8 | C34-C33-H33B | 109.7 |
| O9-B2-O7 | $110.52(19)$ | H22A-C22-H22B | 108.2 | H33A-C33-H33B | 108.2 |
| O1-B2-O7 | $110.13(19)$ | N22-C23-C24 | $109.6(2)$ | N33-C34-C33 | $108.1(2)$ |
| O9-B2-O2 | $109.6(2)$ | N22-C23-H23A | 109.8 | N33-C34-H34A | 110.1 |
| O1-B2-O2 | $109.80(19)$ | C24-C23-H23A | 109.8 | C33-C34-H34A | 110.1 |


| O7-B2-O2 | $104.9(2)$ | N22-C23-H23B | 109.8 | N33-C34-H34B | 110.1 |
| :--- | ---: | :--- | ---: | :--- | ---: |
| O2-B3-O3 | $122.9(3)$ | C24-C23-H23B | 109.8 | C33-C34-H34B | 110.1 |
| O2-B3-O10 | $117.5(2)$ | H23A-C23-H23B | 108.2 | H34A-C34-H34B | 108.4 |
| O3-B3-O10 | $119.6(2)$ | N23-C24-C23 | $107.0(2)$ | C31-N31-Co1 | $111.75(15)$ |
| O11-B4-O4 | $118.3(2)$ | N23-C24-H24A | 110.3 | C31-N31-H31C | 109.3 |
| O11-B4-O5 | $120.5(2)$ | C23-C24-H24A | 110.3 | Co1-N31-H31C | 109.3 |
| O4-B4-O5 | $121.2(2)$ | C22-N22-C23 | $114.9(2)$ | C31-N31-H31D | 109.3 |
| O6-B5-O12 | $123.2(2)$ | N23-C24-H24B | 110.3 | Co1-N31-H31D | 109.3 |
| O6-B5-O5 | $120.8(2)$ | C23-C24-H24B | 110.3 | H31C-N31-H31D | 107.9 |
| O12-B5-O5 | $116.0(2)$ | H24A-C24-H24B | 108.6 | C33-N32-C32 | $116.0(2)$ |
| O7-B6-O8 | $124.3(2)$ | C21-N21-Co1 | $112.58(14)$ | C33-N32-Co1 | $108.63(16)$ |
| O7-B6-O13 | $115.1(2)$ | C21-N21-H21C | 109.1 | C32-N32-Co1 | $108.24(16)$ |
| O8-B6-O13 | $120.7(2)$ | Co1-N21-H21C | 109.1 | C33-N32-H32 | 107.9 |
| O9-B7-O15 | $110.6(2)$ | C21-N21-H21D | 109.1 | C32-N32-H32 | 107.9 |
| O9-B7-O14 | $112.0(2)$ | Co1-N21-H21D | 109.1 | Co1-N32-H32 | 107.9 |
| O15-B7-O14 | $104.40(19)$ | H21C-N21-H21D | 107.8 | C34-N33-Co1 | $110.75(15)$ |
| O9-B7-O8 | $111.29(19)$ | C22-N22-Co1 | $108.76(16)$ | C34-N33-H33C | 109.5 |
| O15-B7-O8 | $109.2(2)$ | C23-N22-Co1 | $108.30(15)$ | Co1-N33-H33C | 109.5 |
| O14-B7-O8 | $109.04(19)$ | C22-N22-H22 | 108.3 | C34-N33-H33D | 109.5 |
| B1-O1-B2 | $125.1(2)$ | C23-N22-H22 | 108.3 | Co1-N33-H33D | 109.5 |
| B3-O2-B2 | $122.5(2)$ | Co1-N22-H22 | 108.3 | H33C-N33-H33D | 108.1 |
| B3-O3-B1 | $120.7(2)$ | C24-N23-Co1 | $110.15(15)$ | H51A-O51-H51B | 109.4 |
| B4-O4-B1 | $124.41(18)$ | C24-N23-H23C | 109.6 | H52A-O52-H52B | 109.4 |
| B5-O5-B4 | $118.79(19)$ | Co1-N23-H23C | 109.6 | H53A-O53-H53B | 109.5 |
| B5-O6-B1 | $124.81(19)$ | C24-N23-H23D | 109.6 | H54A-O54-H54B | 109.5 |
| B6-O7-B2 | $123.01(19)$ | Co1-N23-H23D | 109.6 | H55A-O55-H55B | 109.5 |
| B6-O8-B7 | $120.71(19)$ | H23C-N23-H23D | 108.1 | H55A-O556-H56B | 109.5 |
| B2-O9-B7 | $129.20(18)$ | N31-C31-C32 | $109.2(2)$ | H57A-O57-H57B | 109.5 |
| B3-O10-H10 | 109.5 | N31-C31-H31A | 109.8 | H58A-O58-H58B | 109.5 |
| B4-O11-H11 | 109.5 | C32-C31-H31A | 109.8 | H88A-O88-H88B | 109.5 |
| B5-O12-H12 | 109.5 | N31-C31-H31B | 109.8 | H59A-O59-H59B | 109.5 |
| B6-O13-H13 | 109.5 | C32-C31-H31B | 109.8 | H89A-O89-H89B | 109.5 |
| B7-O14-H14 | 109.5 |  |  |  |  |
|  |  |  |  |  |  |

Table $\mathbf{7}$ Bond lengths [ $\AA$ ] in $\mathbf{1 2}$.

| Co1-N15 | $1.966(2)$ | N18-O1 | $1.212(3)$ | C42-N35 | $1.496(3)$ | C18-H18B | 0.9900 |
| :--- | :--- | :--- | ---: | :--- | ---: | :--- | ---: |
| Co1-N16 | $1.969(2)$ | N18-O13 | $1.226(3)$ | C42-C43 | $1.504(4)$ | C19-N14 | $1.487(3)$ |
| Co1-N12 | $1.970(2)$ | C31-C41 | $1.518(4)$ | C42-H42A | 0.9900 | C19-H19A | 0.9900 |
| Co1-N11 | $1.972(2)$ | C31-C33 | $1.526(4)$ | C42-H42B | 0.9900 | C19-H19B | 0.9900 |
| Co1-N13 | $1.972(2)$ | C31-C37 | $1.528(3)$ | C43-N36 | $1.486(3)$ | C20-N14 | $1.487(3)$ |
| Co1-N14 | $1.975(2)$ | C31-N37 | $1.529(3)$ | C43-H43A | 0.9900 | C20-H20A | 0.9900 |
| Co2-N31 | $1.963(2)$ | C32-C40 | $1.518(4)$ | C43-H43B | 0.9900 | C20-H20B | 0.9900 |
| Co2-N36 | $1.965(2)$ | C32-C44 | $1.526(4)$ | C44-N36 | $1.486(3)$ | C21-N15 | $1.490(3)$ |
| Co2-N35 | $1.967(2)$ | C32-C36 | $1.528(3)$ | C44-H44A | 0.9900 | C21-H21A | 0.9900 |
| Co2-N33 | $1.970(2)$ | C32-N38 | $1.531(3)$ | C44-H44B | 0.9900 | C21-H21B | 0.9900 |
| C02-N34 | $1.971(2)$ | C33-N31 | $1.478(3)$ | N31-H31 | 1.0000 | C22-N15 | $1.493(3)$ |
| C02-N32 | $1.973(2)$ | C33-H33A | 0.9900 | N32-H32 | 1.0000 | C22-C23 | $1.495(4)$ |
| B1-O1 | $1.466(4)$ | C33-H33B | 0.9900 | N33-H33 | 1.0000 | C22-H22A | 0.9900 |
| B1-O5 | $1.467(3)$ | C34-N31 | $1.489(3)$ | N34-H34 | 1.0000 | C22-H22B | 0.9900 |
| B1-O4 | $1.468(3)$ | C34-C35 | $1.510(4)$ | N35-H35 | 1.0000 | C23-N16 | $1.486(3)$ |
| B1-O3 | $1.471(4)$ | C34-H34A | 0.9900 | N36-H36 | 1.0000 | C23-H23A | 0.9900 |
| B2-O1 | $1.351(3)$ | C34-H34B | 0.9900 | N37-O31 | $1.211(3)$ | C23-H23B | 0.9900 |
| B2-O6 | $1.359(4)$ | C35-N32 | $1.481(3)$ | N37-O32 | $1.226(3)$ | C24-N16 | $1.484(3)$ |
| B2-O2 | $1.380(4)$ | C35-H35A | 0.9900 | N38-O33 | $1.209(3)$ | C24-H24A | 0.9900 |
| B3-O3 | $1.347(4)$ | C35-H35B | 0.9900 | N38-O34 | $1.219(3)$ | C24-H24B | 0.9900 |
| B3-O7 | $1.357(4)$ | C36-N32 | $1.491(3)$ | O51-H51A | 0.8496 | N11-H11 | 1.0000 |
| B3-O2 | $1.386(4)$ | C36-H36A | 0.9900 | O51-H51A | 0.8496 | N12-H12 | 1.0000 |
| O4-H4 | 0.8400 | C36-H36B | 0.9900 | C13-H13B | 0.9900 | N13-H13 | 1.0000 |
| O5-H5 | 0.8400 | C37-N33 | $1.493(3)$ | C14-N11 | $1.495(3)$ | N14-H14 | 1.0000 |
| O6-H6 | 0.8400 | C37-H37A | 0.9900 | C14-C15 | $1.503(4)$ | N15-H15 | 1.0000 |
| O7-H7 | 0.8400 | C37-H37B | 0.9900 | C14-H14A | 0.9900 | O51-H51B | 0.8495 |


| C11-C17 | $1.519(4)$ | C38-N33 | $1.486(3)$ | C14-H14B | 0.9900 | O52-H52A | 0.8496 |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | :--- |
| C11-C21 | $1.522(4)$ | C38-C39 | $1.500(4)$ | C15-N12 | $1.492(3)$ | O52-H52B | 0.8502 |
| C11-C13 | $1.525(3)$ | C38-H38A | 0.9900 | C15-H15A | 0.9900 | O53-H53A | 0.8496 |
| C11-N17 | $1.527(3)$ | C38-H38B | 0.9900 | C15-H15B | 0.9900 | O53-H53B | 0.8505 |
| C12-C16 | $1.505(4)$ | C39-N34 | $1.495(3)$ | C16-N12 | $1.493(3)$ | O54-H54A | 0.8501 |
| C12-C24 | $1.528(3)$ | C39-H39A | 0.9900 | C16-H16A | 0.9900 | O54-H54B | 0.8501 |
| C12-C20 | $1.531(3)$ | C39-H39B | 0.9900 | C16-H16B | 0.9900 | O55-H55A | 0.8500 |
| C12-N18 | $1.531(3)$ | C40-N34 | $1.485(3)$ | C17-N13 | $1.494(3)$ | O55-H55B | 0.8494 |
| C13-N11 | $1.487(3)$ | C40-H40A | 0.9900 | C17-H17A | 0.9900 | O61-H61A | 0.8500 |
| C13-H13A | 0.9900 | C40-H40B | 0.9900 | C17-H17B | 0.9900 | O61-H61B | 0.8499 |
| N16-H16 | 1.0000 | C41-N35 | $1.495(3)$ | C18-N13 | $1.492(3)$ |  |  |
| N17-O12 | $1.212(3)$ | C41-H41A | 0.9900 | C18-C19 | $1.502(4)$ |  |  |
| N17-O11 | $1.223(3)$ | C41-H41B | 0.9900 | C18-H18A | 0.9900 |  |  |

Table 8 Bond angles $\left[^{\circ}\right]$ in 12.

| N15-Co1-N16 | 86.43(9) | N14-C20-C12 | 110.6(2) | N32-C36-C32 | 111.5(2) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N15-Col-N12 | 92.58(9) | N14-C20-H20A | 109.5 | N32-C36-H36A | 109.3 |
| N16-Co1-N12 | 90.39(9) | C12-C20-H20A | 109.5 | C32-C36-H36A | 109.3 |
| N15-Co1-N11 | 90.78(9) | N14-C20-H20B | 109.5 | N32-C36-H36B | 109.3 |
| N16-Co1-N11 | 175.79(9) | C12-C20-H20B | 109.5 | C32-C36-H36B | 109.3 |
| N12-Co1-N11 | 86.58(9) | H20A-C20-H20B | 108.1 | H36A-C36-H36B | 108.0 |
| N15-Col-N13 | 90.32(9) | N15-C21-C11 | 111.8(2) | N33-C37-C31 | 111.0(2) |
| N16-Co1-N13 | 92.05(9) | N15-C21-H21A | 109.3 | N33-C37-H37A | 109.4 |
| N12-Co1-N13 | 176.33(9) | C11-C21-H21A | 109.3 | C31-C37-H37A | 109.4 |
| N11-Co1-N13 | 91.12(9) | N15-C21-H21B | 109.3 | N33-C37-H37B | 109.4 |
| N15-Col-N14 | 176.54(9) | C11-C21-H21B | 109.3 | C31-C37-H37B | 109.4 |
| N16-Co1-N14 | 91.25(9) | H21A-C21-H21B | 107.9 | H37A-C37-H37B | 108.0 |
| N12-Col-N14 | 90.00(9) | N15-C22-C23 | 106.4(2) | N33-C38-C39 | 107.8(2) |
| N11-Co1-N14 | 91.67(9) | N15-C22-H22A | 110.5 | N33-C38-H38A | 110.2 |
| N13-Co1-N14 | 87.20(9) | C23-C22-H22A | 110.5 | C39-C38-H38A | 110.2 |
| N31-Co2-N36 | 176.86(9) | N15-C22-H22B | 110.5 | N33-C38-H38B | 110.2 |
| N31-Co2-N35 | 90.61(9) | C23-C22-H22B | 110.5 | C39-C38-H38B | 110.2 |
| N36-Co2-N35 | 87.52(9) | H22A-C22-H22B | 108.6 | H38A-C38-H38B | 108.5 |
| N31-Co2-N33 | 91.96(9) | N16-C23-C22 | 106.9(2) | N34-C39-C38 | 106.4(2) |
| N36-Co2-N33 | 90.56(9) | N16-C23-H23A | 110.4 | N34-C39-H39A | 110.4 |
| N35-Co2-N33 | 90.24(9) | C22-C23-H23A | 110.4 | C38-C39-H39A | 110.4 |
| N31-Co2-N34 | 91.98(9) | N16-C23-H23B | 110.4 | N34-C39-H39B | 110.4 |
| N36-Co2-N34 | 90.02(9) | C22-C23-H23B | 110.4 | C38-C39-H39B | 110.4 |
| N35-Co2-N34 | 176.12(8) | H23A-C23-H23B | 108.6 | H39A-C39-H39B | 108.6 |
| N33-Co2-N34 | 86.78(9) | N16-C24-C12 | 112.3(2) | N34-C40-C32 | 111.7(2) |
| N31-Co2-N32 | 86.84(9) | N16-C24-H24A | 109.1 | N34-C40-H40A | 109.3 |
| N36-Co2-N32 | 90.69(9) | C12-C24-H24A | 109.1 | C32-C40-H40A | 109.3 |
| N35-Co2-N32 | 91.21(9) | N16-C24-H24B | 109.1 | N34-C40-H40B | 109.3 |
| N33-Co2-N32 | 178.12(10) | C12-C24-H24B | 109.1 | C32-C40-H40B | 109.3 |
| N34-Co2-N32 | 91.82(9) | H24A-C24-H24B | 107.9 | H40A-C40-H40B | 107.9 |
| O1-B1-O5 | 109.8(2) | C13-N11-C14 | 112.5(2) | N35-C41-C31 | 111.7(2) |
| O1-B1-O4 | 108.3(2) | C13-N11-Co1 | 118.41(16) | N35-C41-H41A | 109.3 |
| O5-B1-O4 | 108.3(2) | C14-N11-Co1 | 106.96(15) | C31-C41-H41A | 109.3 |
| O1-B1-O3 | 112.3(2) | C13-N11-H11 | 106.0 | N35-C41-H41B | 109.3 |
| O5-B1-O3 | 108.8(2) | C14-N11-H11 | 106.0 | C31-C41-H41B | 109.3 |
| O4-B1-O3 | 109.2(2) | Co1-N11-H11 | 106.0 | H41A-C41-H41B | 107.9 |
| O1-B2-O6 | 122.9(3) | C15-N12-C16 | 112.5(2) | N35-C42-C43 | 107.0(2) |
| O1-B2-O2 | 121.6(3) | C15-N12-Co1 | 107.50(16) | N35-C42-H42A | 110.3 |
| O6-B2-O2 | 115.5(2) | C16-N12-Co1 | 118.58(16) | C43-C42-H42A | 110.3 |
| O3-B3-O7 | 123.7(3) | C15-N12-H12 | 105.8 | N35-C42-H42B | 110.3 |
| O3-B3-O2 | 121.6(3) | C16-N12-H12 | 105.8 | C43-C42-H42B | 110.3 |
| O7-B3-O2 | 114.7(2) | Co1-N12-H12 | 105.8 | H42A-C42-H42B | 108.6 |
| B2-O1-B1 | 122.2(2) | C18-N13-C17 | 112.02(19) | N36-C43-C42 | 107.1(2) |
| B2-O2-B3 | 118.8(2) | C18-N13-Co1 | 106.79(15) | N36-C43-H43A | 110.3 |
| B3-O3-B1 | 122.4(2) | C17-N13-Co1 | 118.35(16) | C42-C43-H43A | 110.3 |
| B1-O4-H4 | 109.5 | C18-N13-H13 | 106.3 | N36-C43-H43B | 110.3 |


| B1-O5-H5 | 109.5 | C17-N13-H13 | 106.3 | C42-C43-H43B | 110.3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| B2-O6-H6 | 109.5 | Co1-N13-H13 | 106.3 | H43A-C43-H43B | 108.5 |
| B3-O7-H7 | 109.5 | C19-N14-C20 | 112.0(2) | N36-C44-C32 | 111.3(2) |
| C17-C11-C21 | 112.4(2) | C19-N14-Co1 | 106.89(15) | N36-C44-H44A | 109.4 |
| C17-C11-C13 | 112.3(2) | C20-N14-Col | 119.12(16) | C32-C44-H44A | 109.4 |
| C21-C11-C13 | 113.3(2) | C19-N14-H14 | 106.0 | N36-C44-H44B | 109.4 |
| C17-C11-N17 | 108.1(2) | C20-N14-H14 | 106.0 | C32-C44-H44B | 109.4 |
| C21-C11-N17 | 105.3(2) | Co1-N14-H14 | 106.0 | H44A-C44-H44B | 108.0 |
| C13-C11-N17 | 104.8(2) | C21-N15-C22 | 113.1(2) | C33-N31-C34 | 113.33(19) |
| C16-C12-C24 | 113.3(2) | C21-N15-Co1 | 118.40(16) | C33-N31-Co2 | 118.36(16) |
| C16-C12-C20 | 112.9(2) | C22-N15-Co1 | 107.74(16) | C34-N31-Co2 | 107.43(16) |
| C24-C12-C20 | 112.1(2) | C21-N15-H15 | 105.5 | C33-N31-H31 | 105.6 |
| C16-C12-N18 | 108.1(2) | C22-N15-H15 | 105.5 | C34-N31-H31 | 105.6 |
| C24-C12-N18 | 103.8(2) | Co1-N15-H15 | 105.5 | Co2-N31-H31 | 105.6 |
| C20-C12-N18 | 105.8(2) | C24-N16-C23 | 113.6(2) | C35-N32-C36 | 113.03(19) |
| N11-C13-C11 | 111.6(2) | C24-N16-Co1 | 117.49(15) | C35-N32-Co2 | 106.92(16) |
| N11-C13-H13A | 109.3 | C23-N16-Co1 | 106.97(16) | C36-N32-Co2 | 117.78(15) |
| C11-C13-H13A | 109.3 | C24-N16-H16 | 106.0 | C35-N32-H32 | 106.1 |
| N11-C13-H13B | 109.3 | C23-N16-H16 | 106.0 | C36-N32-H32 | 106.1 |
| C11-C13-H13B | 109.3 | Col-N16-H16 | 106.0 | Co2-N32-H32 | 106.1 |
| H13A-C13-H13B | 108.0 | O12-N17-O11 | 124.1(2) | C38-N33-C37 | 113.2(2) |
| N11-C14-C15 | 106.5(2) | O12-N17-C11 | 119.3(2) | C38-N33-Co2 | 107.63(15) |
| N11-C14-H14A | 110.4 | O11-N17-C11 | 116.6(2) | C37-N33-Co2 | 118.47(15) |
| C15-C14-H14A | 110.4 | O14-N18-O13 | 124.5(2) | C38-N33-H33 | 105.5 |
| N11-C14-H14B | 110.4 | O14-N18-C12 | 117.5(2) | C37-N33-H33 | 105.5 |
| C15-C14-H14B | 110.4 | O13-N18-C12 | 117.9(2) | Co2-N33-H33 | 105.5 |
| H14A-C14-H14B | 108.6 | C41-C31-C33 | 112.7(2) | C40-N34-C39 | 113.00(19) |
| N12-C15-C14 | 106.4(2) | C41-C31-C37 | 112.7(2) | C40-N34-Co2 | 117.52(16) |
| N12-C15-H15A | 110.5 | C33-C31-C37 | 113.1(2) | C39-N34-Co2 | 106.91(15) |
| C14-C15-H15A | 110.5 | C41-C31-N37 | 107.9(2) | C40-N34-H34 | 106.2 |
| N12-C15-H15B | 110.5 | C33-C31-N37 | 104.6(2) | C39-N34-H34 | 106.2 |
| C14-C15-H15B | 110.5 | C37-C31-N37 | 105.2(2) | Co2-N34-H34 | 106.2 |
| H15A-C15-H15B | 108.6 | C40-C32-C44 | 113.7(2) | C41-N35-C42 | 113.05(19) |
| N12-C16-C12 | 111.3(2) | C40-C32-C36 | 112.8(2) | C41-N35-Co2 | 117.75(16) |
| N12-C16-H16A | 109.4 | C44-C32-C36 | 111.3(2) | C42-N35-Co2 | 106.41(15) |
| C12-C16-H16A | 109.4 | C40-C32-N38 | 107.0(2) | C41-N35-H35 | 106.3 |
| N12-C16-H16B | 109.4 | C44-C32-N38 | 106.5(2) | C42-N35-H35 | 106.3 |
| C12-C16-H16B | 109.4 | C36-C32-N38 | 104.8(2) | Co2-N35-H35 | 106.3 |
| H16A-C16-H16B | 108.0 | N31-C33-C31 | 111.5(2) | C44-N36-C43 | 113.1(2) |
| N13-C17-C11 | 111.7(2) | N31-C33-H33A | 109.3 | C44-N36-Co2 | 118.52(16) |
| N13-C17-H17A | 109.3 | C31-C33-H33A | 109.3 | C43-N36-Co2 | 106.96(15) |
| C11-C17-H17A | 109.3 | N31-C33-H33B | 109.3 | C44-N36-H36 | 105.8 |
| N13-C17-H17B | 109.3 | C31-C33-H33B | 109.3 | C43-N36-H36 | 105.8 |
| C11-C17-H17B | 109.3 | H33A-C33-H33B | 108.0 | Co2-N36-H36 | 105.8 |
| H17A-C17-H17B | 107.9 | N31-C34-C35 | 106.4(2) | O31-N37-O32 | 124.3(2) |
| N13-C18-C19 | 107.6(2) | N31-C34-H34A | 110.4 | O31-N37-C31 | 119.1(2) |
| N13-C18-H18A | 110.2 | C35-C34-H34A | 110.4 | O32-N37-C31 | 116.5(2) |
| C19-C18-H18A | 110.2 | N31-C34-H34B | 110.4 | O33-N38-O34 | 123.6(2) |
| N13-C18-H18B | 110.2 | C35-C34-H34B | 110.4 | O33-N38-C32 | 118.6(2) |
| C19-C18-H18B | 110.2 | H34A-C34-H34B | 108.6 | O34-N38-C32 | 117.6(2) |
| H18A-C18-H18B | 108.5 | N32-C35-C34 | 106.9(2) | H51A-O51-H51B | 109.5 |
| N14-C19-C18 | 107.1(2) | N32-C35-H35A | 110.3 | H52A-O52-H52B | 109.5 |
| N14-C19-H19A | 110.3 | C34-C35-H35A | 110.3 | H53A-O53-H53B | 109.5 |
| C18-C19-H19A | 110.3 | N32-C35-H35B | 110.3 | H54A-O54-H54B | 109.5 |
| N14-C19-H19B | 110.3 | C34-C35-H35B | 110.3 | H55A-O55-H55B | 109.4 |
| C18-C19-H19B | 110.3 | H35A-C35-H35B | 108.6 | H61A-O61-H61B | 109.5 |
| H19A-C19-H19B | 108.5 |  |  |  |  |

Table 9 Bond lengths [ $\AA$ ] in 20.

| $\mathrm{Cu} 1-\mathrm{N} 2$ | $2.0044(14)$ | B2-O7 | $1.356(2)$ | B5-O10 | $1.365(2)$ | C1-H1B | 0.9900 |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | ---: |
| $\mathrm{Cu} 1-\mathrm{N} 2^{\mathrm{i}}$ | $2.0044(14)$ | B2-O2 | $1.393(2)$ | B5-O5 | $1.388(2)$ | C2-N2 | $1.487(2)$ |
| $\mathrm{Cu} 1-\mathrm{N} 1$ | $2.0195(14)$ | B3-O8 | $1.366(2)$ | O7-H7 | 0.8400 | C2-H2 | 0.9900 |
| $\mathrm{Cu} 1-\mathrm{N} 1$ | $2.0195(14)$ | B3-O3 | $1.370(2)$ | O8-H8 | 0.8400 | C2-H2 | 0.9900 |
| $\mathrm{~B} 1-\mathrm{O} 1$ | $1.455(2)$ | B3-O2 | $1.377(2)$ | O9-H9 | 0.8400 | N1-H1C | 0.9900 |
| $\mathrm{~B} 1-\mathrm{O} 6$ | $1.463(2)$ | B4-O9 | $1.359(2)$ | O10-H10 | 0.8400 | N1-H1D | 0.9900 |
| B1-O4 | $1.4725(19)$ | B4-O4 | $1.360(2)$ | C1-N1 | $1.487(2)$ | N2-H2C | 0.9900 |
| B1-O3 | $1.487(2)$ | B4-O5 | $1.384(2)$ | C1-C2 | $1.519(2)$ | N2-H2D | 0.9900 |
| B2-O1 | $1.355(2)$ | B5-O6 | $1.360(2)$ | C1-H1A | 0.9900 | O21-H21A | 0.8500 |
|  |  |  |  |  | O21-H21B | 0.8501 |  |

Table $\mathbf{1 0}$ Bond angles [ ${ }^{\circ}$ ] in 20.

| $\mathrm{N} 2-\mathrm{Cu} 1-\mathrm{N} 2^{\text {i }}$ | 180.0 | O4-B4-O5 | 120.77(14) | N2-C2-C1 | 107.59(13) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N2-Cu1-N1 | 84.80(6) | O6-B5-O10 | 122.71(14) | N2-C2-H2A | 110.2 |
| N2 ${ }^{\text {i }}$-Cu1-N1 | 95.20(6) | O6-B5-O5 | 121.31(15) | C1-C2-H2A | 110.2 |
| $\mathrm{N} 2-\mathrm{Cu} 1-\mathrm{N} 1^{\text {i }}$ | 95.20(6) | O10-B5-O5 | 115.96(15) | N2-C2-H2B | 110.2 |
| $\mathrm{N} 2{ }^{\text {i }}$-Cu1-N1 $1^{\text {i }}$ | 84.80(6) | B2-O1-B1 | 125.52(13) | C1-C2-H2B | 110.2 |
| $\mathrm{N} 1-\mathrm{Cu} 1-\mathrm{N} 1^{\text {i }}$ | 180.0 | B3-O2-B2 | 119.10(14) | H2A-C2-H2B | 108.5 |
| O1-B1-O6 | 109.30(13) | B3-O3-B1 | 122.03(13) | $\mathrm{C} 1-\mathrm{N} 1-\mathrm{Cu} 1$ | 107.07(10) |
| O1-B1-O4 | 108.70(12) | B4-O4-B1 | 123.68(13) | C1-N1-H1C | 110.3 |
| O6-B1-O4 | 111.51(13) | B4-O5-B5 | 119.34(14) | Cu1-N1-H1C | 110.3 |
| O1-B1-O3 | 110.56(13) | B5-O6-B1 | 123.30(12) | C1-N1-H1D | 110.3 |
| O6-B1-O3 | 109.02(12) | B2-O7-H7 | 109.5 | Cu1-N1-H1D | 110.3 |
| O4-B1-O3 | 107.74(13) | B3-O8-H8 | 109.5 | H1C-N1-H1D | 108.6 |
| O1-B2-O7 | 118.31(15) | B4-O9-H9 | 109.5 | C2-N2-Cu1 | 110.10(10) |
| O1-B2-O2 | 119.97(15) | B5-O10-H10 | 109.5 | C2-N2-H2C | 109.6 |
| O7-B2-O2 | 121.68(16) | N1-C1-C2 | 107.37(13) | Cu1-N2-H2C | 109.6 |
| O8-B3-O3 | 120.77(15) | N1-C1-H1A | 110.2 | C2-N2-H2D | 109.6 |
| O8-B3-O2 | 117.12(15) | C2-C1-H1A | 110.2 | Cu1-N2-H2D | 109.6 |
| O3-B3-O2 | 122.09(15) | N1-C1-H1B | 110.2 | H2C-N2-H2D | 108.2 |
| O9-B4-O4 | 122.10(15) | C2-C1-H1B | 110.2 | H21A-O21-H21B | 109.5 |
| O9-B4-O5 | 117.12(15) | H1A-C1-H1B | 108.5 |  |  |

Table 11 Bond lengths [ $\AA$ ] in 22.

| Cu1-N2B | $1.9714(11)$ | N12-H12B | 0.9100 | C11B-C12B | $1.492(12)$ | O11-B12 | $1.3419(17)$ |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | ---: |
| Cu1-N2 | $1.9714(11)$ | N12B-C12B | $1.525(10)$ | C11B-H11G | 0.9900 | O11-B11 | $1.4666(16)$ |
| Cu1-N12B | $1.9832(11)$ | N12B-H12C | 0.9100 | C11B-H11H | 0.9900 | O12-B13 | $1.3794(16)$ |
| Cu1-N12 | $1.9832(11)$ | N12B-H12D | 0.9100 | C12B-C13B | $1.511(18)$ | O12-B12 | $1.3848(17)$ |
| Cu1-N11B | $2.0084(11)$ | C1-C2 | $1.509(2)$ | C12B-H12E | 1.0000 | O13-B13 | $1.3440(16)$ |
| Cu1-N11 | $2.0084(11)$ | C1-H1C | 0.9900 | C13B-H13D | 0.9800 | O13-B11 | $1.4609(16)$ |
| Cu1-N1B | $2.0115(12)$ | C1-H1D | 0.9900 | C13B-H13E | 0.9800 | O14-B14 | $1.3494(17)$ |
| Cu1-N1 | $2.0115(12)$ | C2-C3 | $1.498(3)$ | C13B-H13F | 0.9800 | O14-B11 | $1.4474(16)$ |
| N1-C1 | $1.498(2)$ | C2-H2 | 1.0000 | O1-B2 | $1.3535(17)$ | O15-B15 | $1.3692(16)$ |
| N1-H1A | 0.9100 | C3-H3A | 0.9800 | O1-B1 | $1.4645(15)$ | O15-B14 | $1.3818(17)$ |
| N1-H1B | 0.9100 | C3-H3B | 0.9800 | O2-B3 | $1.3764(16)$ | O16-B15 | $1.3501(16)$ |
| N1B-C1B | $1.366(11)$ | C3-H3C | 0.9800 | O2-B2 | $1.3824(17)$ | O16-B11 | $1.4590(16)$ |
| N1B-H1BA | 0.9100 | C11-C12 | $1.512(2)$ | O3-B3 | $1.3501(16)$ | O17-B12 | $1.3484(17)$ |
| N1B-H1BB | 0.9100 | C11-H11E | 0.9900 | O3-B1 | $1.4628(15)$ | O17-H17 | 0.8400 |
| N2-C2 | $1.4890(19)$ | C11-H11F | 0.9900 | O4-B4 | $1.3474(16)$ | O18-B13 | $1.3545(16)$ |
| N2-H2A | 0.9100 | C12-C13 | $1.515(5)$ | O4-B1 | $1.4640(16)$ | O18-H18 | 0.8400 |
| N2-H2B | 0.9100 | C12-H12 | 1.0000 | O5-B4 | $1.3662(16)$ | O19-B14 | $1.3465(17)$ |
| N2B-C2B | $1.467(13)$ | C13-H13A | 0.9800 | O5-B5 | $1.3800(16)$ | O19-H19 | 0.8400 |
| N2B-H2BA | 0.9100 | C13-H13B | 0.9800 | O6-B5 | $1.3497(16)$ | O20-B15 | $1.3522(17)$ |
| N2B-H2BB | 0.9100 | C13-H13C | 0.9800 | O6-B1 | $1.4547(16)$ | O20-H20 | 0.8400 |
| N11-C11 | $1.4778(19)$ | C1B-C2B | $1.537(13)$ | O7-B2 | $1.3447(17)$ | O21-H21A | 0.8695 |
| N11-H11A | 0.9100 | C1B-H1BC | 0.9900 | O7-H7 | 0.8400 | O21-H21B | 0.8700 |
| N11-H11B | 0.9100 | C1B-H1BD | 0.9900 | O8-B3 | $1.3551(16)$ | O23-H23A | 0.8699 |
| N11B-C11B | $1.483(10)$ | C2B-C3B | $1.482(17)$ | O8-H8 | 0.8400 | O23-H23B | 0.8700 |


| N11B-H11C | 0.9100 | C2B-H2BC | 1.0000 | O9-B4 | $1.3548(16)$ | O22-H22A | 0.8699 |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | :--- |
| N11B-H11D | 0.9100 | C3B-H3BA | 0.9800 | O9-H9 | 0.8400 | O22-H22B | 0.8701 |
| N12-C12 | $1.4799(19)$ | C3B-H3BB | 0.9800 | O10-B5 | $1.3502(17)$ | O24-H24A | 0.8703 |
| N12-H12A | 0.9100 | C3B-H3BC | 0.9800 | O10-H10 | 0.8400 | O24-H24B | 0.8698 |

Table 12 Bond angles [ ${ }^{\circ}$ ] in 22.

| N2B-Cu1-N12B | 175.36(5) | C2-C1-H1D | 110.3 | H13D-C13B-H13E | 109.5 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N2-Cu1-N12 | 175.36(5) | $\mathrm{H} 1 \mathrm{C}-\mathrm{C} 1-\mathrm{H} 1 \mathrm{D}$ | 108.5 | C12B-C13B-H13F | 109.5 |
| N2B-Cu1-N11B | 95.19(4) | N2-C2-C3 | 112.14(14) | H13D-C13B-H13F | 109.5 |
| N12B-Cu1-N11B | 84.75(5) | $\mathrm{N} 2-\mathrm{C} 2-\mathrm{C} 1$ | 106.23(14) | H13E-C13B-H13F | 109.5 |
| N2-Cu1-N11 | 95.19(4) | $\mathrm{C} 3-\mathrm{C} 2-\mathrm{C} 1$ | 112.35(16) | B2-O1-B1 | 122.37(10) |
| N12-Cu1-N11 | 84.75(5) | N2-C2-H2 | 108.7 | B3-O2-B2 | 119.38(11) |
| N2B-Cu1-N1B | 85.56(5) | $\mathrm{C} 3-\mathrm{C} 2-\mathrm{H} 2$ | 108.7 | B3-O3-B1 | 121.64(10) |
| N12B-Cu1-N1B | 94.14(5) | $\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2$ | 108.7 | B4-O4-B1 | 122.98(10) |
| N11B-Cu1-N1B | 175.44(5) | $\mathrm{C} 2-\mathrm{C} 3-\mathrm{H} 3 \mathrm{~A}$ | 109.5 | B4-O5-B5 | 119.17(10) |
| $\mathrm{N} 2-\mathrm{Cu} 1-\mathrm{N} 1$ | 85.56(5) | $\mathrm{C} 2-\mathrm{C} 3-\mathrm{H} 3 \mathrm{~B}$ | 109.5 | B5-O6-B1 | 122.85(10) |
| N12-Cu1-N1 | 94.14(5) | H3A-C3-H3B | 109.5 | B2-07-H7 | 109.5 |
| N11-Cu1-N1 | 175.44(5) | $\mathrm{C} 2-\mathrm{C} 3-\mathrm{H} 3 \mathrm{C}$ | 109.5 | B3-O8-H8 | 109.5 |
| C1-N1-Cu1 | 106.85(9) | H3A-C3-H3C | 109.5 | B4-O9-H9 | 109.5 |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A}$ | 110.4 | H3B-C3-H3C | 109.5 | B5-O10-H10 | 109.5 |
| $\mathrm{Cu} 1-\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A}$ | 110.4 | N11-C11-C12 | 108.20(14) | O6-B1-O3 | 108.66(10) |
| C1-N1-H1B | 110.4 | N11-C11-H11E | 110.1 | O6-B1-O4 | 111.91(10) |
| $\mathrm{Cu} 1-\mathrm{N} 1-\mathrm{H} 1 \mathrm{~B}$ | 110.4 | C12-C11-H11E | 110.1 | O3-B1-O4 | 108.24(10) |
| H1A-N1-H1B | 108.6 | N11-C11-H11F | 110.1 | O6-B1-O1 | 109.21(10) |
| C1B-N1B-Cu1 | 105.1(5) | C12-C11-H11F | 110.1 | O3-B1-O1 | 110.99(10) |
| C1B-N1B-H1BA | 110.7 | H11E-C11-H11F | 108.4 | O4-B1-O1 | 107.84(10) |
| Cu1-N1B-H1BA | 110.7 | N12-C12-C11 | 106.78(13) | O7-B2-O1 | 122.49(12) |
| C1B-N1B-H1BB | 110.7 | N12-C12-C13 | 111.8(3) | O7-B2-O2 | 117.07(12) |
| Cu1-N1B-H1BB | 110.7 | C11-C12-C13 | 112.0(3) | $\mathrm{O} 1-\mathrm{B} 2-\mathrm{O} 2$ | 120.44(12) |
| H1BA-N1B-H1BB | 108.8 | N12-C12-H12 | 108.7 | O3-B3-O8 | 122.43(12) |
| C2-N2-Cu1 | 109.24(9) | C11-C12-H12 | 108.7 | O3-B3-O2 | 121.05(11) |
| C2-N2-H2A | 109.8 | C13-C12-H12 | 108.7 | O8-B3-O2 | 116.41(11) |
| $\mathrm{Cu} 1-\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A}$ | 109.8 | C12-C13-H13A | 109.5 | O4-B4-09 | 117.86(11) |
| C2-N2-H2B | 109.8 | C12-C13-H13B | 109.5 | O4-B4-O5 | 121.31(11) |
| $\mathrm{Cu} 1-\mathrm{N} 2-\mathrm{H} 2 \mathrm{~B}$ | 109.8 | H13A-C13-H13B | 109.5 | O9-B4-O5 | 120.82(11) |
| H2A-N2-H2B | 108.3 | C12-C13-H13C | 109.5 | O6-B5-O10 | 119.29(11) |
| C2B-N2B-Cu1 | 106.6(5) | H13A-C13-H13C | 109.5 | O6-B5-O5 | 121.41(12) |
| C2B-N2B-H2BA | 110.4 | H13B-C13-H13C | 109.5 | O10-B5-O5 | 119.30(11) |
| $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BA}$ | 110.4 | N1B-C1B-C2B | 107.2(9) | B12-O11-B11 | 124.11(10) |
| C2B-N2B-H2BB | 110.4 | N1B-C1B-H1BC | 110.3 | B13-O12-B12 | 118.68(11) |
| $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BB}$ | 110.4 | C2B-C1B-H1BC | 110.3 | B13-O13-B11 | 123.84(10) |
| H2BA-N2B-H2BB | 108.6 | N1B-C1B-H1BD | 110.3 | B14-O14-B11 | 123.18(10) |
| C11-N11-Cu1 | 107.41(9) | C2B-C1B-H1BD | 110.3 | B15-O15-B14 | 119.22(10) |
| C11-N11-H11A | 110.2 | H1BC-C1B-H1BD | 108.5 | B15-O16-B11 | 121.47(10) |
| Cu1-N11-H11A | 110.2 | N2B-C2B-C3B | 105.5(16) | B12-O17-H17 | 109.5 |
| C11-N11-H11B | 110.2 | N2B-C2B-C1B | 105.2(9) | B13-O18-H18 | 109.5 |
| Cu1-N11-H11B | 110.2 | C3B-C2B-C1B | 108.3(15) | B14-O19-H19 | 109.5 |
| H11A-N11-H11B | 108.5 | N2B-C2B-H2BC | 112.5 | B15-O20-H20 | 109.5 |
| C11B-N11B-Cu1 | 108.3(4) | C3B-C2B-H2BC | 112.5 | O14-B11-O16 | 111.31(10) |
| C11B-N11B-H11C | 110.0 | C1B-C2B-H2BC | 112.5 | O14-B11-O13 | 109.53(10) |
| Cu1-N11B-H11C | 110.0 | C2B-C3B-H3BA | 109.5 | O16-B11-O13 | 107.60(10) |
| C11B-N11B-H11D | 110.0 | C2B-C3B-H3BB | 109.5 | O14-B11-O11 | 109.45(10) |
| Cu1-N11B-H11D | 110.0 | H3BA-C3B-H3BB | 109.5 | O16-B11-O11 | 108.23(10) |
| H11C-N11B-H11D | 108.4 | C2B-C3B-H3BC | 109.5 | O13-B11-O11 | 110.71(10) |
| C12-N12-Cu1 | 110.88(9) | H3BA-C3B-H3BC | 109.5 | O11-B12-O17 | 122.66(12) |
| C12-N12-H12A | 109.5 | H3BB-C3B-H3BC | 109.5 | O11-B12-O12 | 120.91(12) |
| $\mathrm{Cu} 1-\mathrm{N} 12-\mathrm{H} 12 \mathrm{~A}$ | 109.5 | N11B-C11B-C12B | 109.4(8) | O17-B12-O12 | 116.43(12) |
| C12-N12-H12B | 109.5 | N11B-C11B-H11G | 109.8 | O13-B13-O18 | 121.68(12) |
| Cu1-N12-H12B | 109.5 | C12B-C11B-H11G | 109.8 | O13-B13-O12 | 121.34(11) |
| H12A-N12-H12B | 108.1 | N11B-C11B-H11H | 109.8 | O18-B13-O12 | 116.94(11) |
| C12B-N12B-Cu1 | 108.2(3) | C12B-C11B-H11H | 109.8 | O19-B14-O14 | 118.94(12) |


| C12B-N12B-H12C | 110.1 | H11G-C11B-H11H | 108.2 | O19-B14-O15 | $120.62(12)$ |
| :--- | ---: | :--- | ---: | :--- | ---: |
| Cu1-N12B-H12C | 110.1 | C11B-C12B-C13B | $112.3(17)$ | O14-B14-O15 | $120.44(12)$ |
| C12B-N12B-H12D | 110.1 | C11B-C12B-N12B | $103.7(8)$ | O16-B15-O20 | $121.50(12)$ |
| Cu1-N12B-H12D | 110.1 | C13B-C12B-N12B | $107(2)$ | O16-B15-O15 | $121.16(12)$ |
| H12C-N12B-H12D | 108.4 | C11B-C12B-H12E | 111.1 | O20-B15-O15 | $117.34(11)$ |
| N1-C1-C2 | $107.11(13)$ | C13B-C12B-H12E | 111.1 | H21A-O21-H21B | 109.5 |
| N1-C1-H1C | 110.3 | N12B-C12B-H12E | 111.1 | H23A-O23-H23B | 109.4 |
| C2-C1-H1C | 110.3 | C12B-C13B-H13D | 109.5 | H22A-O22-H22B | 109.4 |
| N1-C1-H1D | 110.3 | C12B-C13B-H13E | 109.5 | H24A-O22-H24B | 109.5 |

Table 13 Bond lengths [ $A$ ] in 23.

| Cu1-N2A | $1.99(2)$ | O8-B3 | $1.453(3)$ | C3-H3B | 0.9800 | C3A-H3AB | 0.9800 |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | :--- |
| Cu1-O2 | $1.9802(16)$ | O9-B6 | $1.360(3)$ | C3-H3C | 0.9800 | C3A-H3AC | 0.9800 |
| Cu1-O3 | $1.9934(16)$ | O9-B3 | $1.455(3)$ | C4-H4A | 0.9800 | C4A-H4AA | 0.9800 |
| C11-N1 | $2.035(6)$ | O10-B6 | $1.365(3)$ | C4-H4B | 0.9800 | C4A-H4AB | 0.9800 |
| Cu1-N1A | $2.037(10)$ | O10-B1 | $1.453(3)$ | C4-H4C | 0.9800 | C4A-H4AC | 0.9800 |
| Cu1-N2 | $2.069(10)$ | O11-B4 | $1.375(3)$ | C5-H5A | 0.9800 | C5A-H5AA | 0.9800 |
| Cu1-O4 | $2.1871(16)$ | O11-H11 | 0.8400 | C5-H5B | 0.9800 | C5A-H5AB | 0.9800 |
| O1-B1 | $1.513(3)$ | O12-B5 | $1.368(3)$ | C5-H5C | 0.9800 | C5A-H5AC | 0.9800 |
| O1-B2 | $1.513(3)$ | O12-H12 | 0.8400 | C6-H6A | 0.9800 | C6A-H6AA | 0.9800 |
| O1-B3 | $1.516(3)$ | O13-B6 | $1.368(3)$ | C6-H6B | 0.9800 | C6A-H6AB | 0.9800 |
| O2-B1 | $1.483(3)$ | O13-H13 | 0.8400 | C6-H6C | 0.9800 | C6A-H6AC | 0.9800 |
| O2-H2 | $0.872(9)$ | N1-C3 | $1.485(7)$ | N1A-C3A | $1.478(12)$ | O21-H21A | 0.8697 |
| O3-B2 | $1.482(3)$ | N1-C1 | $1.481(7)$ | N1A-C4A | $1.496(12)$ | O21-H21B | 0.8706 |
| O3-H3 | 0.8880 | N1-C4 | $1.498(7)$ | N1A-C1A | $1.496(11)$ | O24-H24A | 0.8699 |
| O4-B3 | $1.455(3)$ | N2-C6 | $1.466(8)$ | N2A-C6A | $1.472(16)$ | O24-H24B | 0.8699 |
| O4-H4 | 0.8683 | N2-C5 | $1.485(8)$ | N2A-C5A | $1.471(14)$ | O22-H22A | 0.8701 |
| O5-B4 | $1.358(3)$ | N2-C2 | $1.496(8)$ | N2A-C2AA | $1.507(14)$ | O22-H22B | 0.8702 |
| O5-B1 | $1.436(3)$ | C1-C2 | $1.512(6)$ | C1A-C2A | $1.488(11)$ | O23-H23A | 0.8695 |
| O6-B4 | $1.362(3)$ | C1-H1A | 0.9900 | C1A-H1AA | 0.9900 | O23-H23B | 0.8704 |
| O6-B2 | $1.436(3)$ | C1-H1B | 0.9900 | C1A-H1AB | 0.9900 | O25-H25A | 0.8699 |
| O7-B5 | $1.367(3)$ | C2-H2A | 0.9900 | C2A-H2AA | 0.9900 | O25-H25B | 0.8701 |
| O7-B2 | $1.451(3)$ | C2-H2B | 0.9900 | C2A-H2AB | 0.9900 | O26-H26A | 0.8696 |
| O8-B5 | $1.359(3)$ | C3-H3A | 0.9800 | C3A-H3AA | 0.9800 | O26-H26B | 0.8699 |

Table 14 Bond angles [ ${ }^{\circ}$ ] in 23.

| N2A-Cu1-O2 | $90.0(4)$ | O5-B4-O6 | $123.3(2)$ | H6B-C6-H6C | 109.5 |
| :--- | ---: | :--- | ---: | :--- | ---: |
| N2A-Cu1-O3 | $175.7(4)$ | O5-B4-O11 | $117.9(2)$ | C3A-N1A-C4A | $108.8(9)$ |
| O2-Cu1-O3 | $89.72(7)$ | O6-B4-O11 | $118.8(2)$ | C3A-N1A-C1A | $109.7(9)$ |
| O2-Cu1-N1 | $176.69(17)$ | O8-B5-O7 | $123.2(2)$ | C4A-N1A-C1A | $109.8(8)$ |
| O3-Cu1-N1 | $91.90(17)$ | O8-B5-O12 | $117.6(2)$ | C3A-N1A-Cu1 | $107.9(7)$ |
| N2A-Cu1-N1A | $87.4(5)$ | O7-B5-O12 | $119.1(2)$ | C4A-N1A-Cu1 | $113.1(7)$ |
| O2-Cu1-N1A | $163.1(3)$ | O9-B6-O10 | $122.5(2)$ | C1A-N1A-Cu1 | $107.4(6)$ |
| O3-Cu1-N1A | $91.6(3)$ | O9-B6-O13 | $118.0(2)$ | C6A-N2A-C5A | $108.6(14)$ |
| O2-Cu1-N2 | $92.3(2)$ | O10-B6-O13 | $119.4(2)$ | C6A-N2A-C2A | $108.7(12)$ |
| O3-Cu1-N2 | $166.8(2)$ | C3-N1-C1 | $109.7(5)$ | C5A-N2A-C2A | $108.7(12)$ |
| N1-Cu1-N2 | $85.4(3)$ | C3-N1-C4 | $108.7(5)$ | C6A-N2A-Cu1 | $114.0(13)$ |
| N2A-Cu1-O4 | $94.4(4)$ | C1-N1-C4 | $111.8(5)$ | C5A-N2A-Cu1 | $112.9(10)$ |
| O2-Cu1-O4 | $91.08(6)$ | C3-N1-Cu1 | $114.5(4)$ | C2A-N2A-Cu1 | $103.8(9)$ |
| O3-Cu1-O4 | $89.97(6)$ | C1-N1-Cu1 | $104.5(4)$ | C2A-C1A-N1A | $109.3(7)$ |
| N1-Cu1-O4 | $91.80(17)$ | C4-N1-Cu1 | $107.7(4)$ | C2A-C1A-H1AA | 109.8 |
| N1A-Cu1-O4 | $105.8(3)$ | C6-N2-C5 | $109.7(7)$ | N1A-C1A-H1AA | 109.8 |
| N2-Cu1-O4 | $103.1(2)$ | C6-N2-C2 | $109.6(6)$ | C2A-C1A-H1AB | 109.8 |
| B1-O1-B2 | $114.76(16)$ | C5-N2-C2 | $109.9(7)$ | N1A-CC1A-H1AB | 109.8 |
| B1-O1-B3 | $119.46(17)$ | C6-N2-Cu1 | $110.7(7)$ | H1AA-C1A-H1AB | 108.3 |
| B2-O1-B3 | $118.68(17)$ | C5-N2-Cu1 | $108.6(5)$ | C1A-C2A-N2A | $110.4(9)$ |
| B1-O2-Cu1 | $118.98(14)$ | C2-N2-Cu1 | $108.4(5)$ | C1A-C2A-H2AA | 109.6 |
| B1-O2-H2 | $108.2(14)$ | N1-C1-C2 | $110.2(4)$ | N2A-C2A-H2AA | 109.6 |
| Cu1-O2-H2 | $124.8(13)$ | N1-C1-H1A | 109.6 | C1A-C2A-H2AB | 109.6 |


| B2-O3-Cu1 | $118.09(14)$ | C2-C1-H1A | 109.6 | N2A-C2A-H2AB | 109.6 |
| :--- | ---: | :--- | ---: | :--- | ---: |
| B2-O3-H3 | 107.3 | N1-C1-H1B | 109.6 | H2AA-C2A-H2AB | 108.1 |
| Cu1-O3-H3 | 127.9 | C2-C1-H1B | 109.6 | N1A-C3A-H3AA | 109.5 |
| B3-O4-Cu1 | $116.32(13)$ | H1A-C1-H1B | 108.1 | N1A-C3A-H3AB | 109.5 |
| B3-O4-H4 | 112.9 | N2-C2-C1 | $108.8(5)$ | H3AA-C3A-H3AB | 109.5 |
| Cu1-O4-H4 | 130.4 | N2-C2-H2A | 109.9 | N1A-C3A-H3AC | 109.5 |
| B4-O5-B1 | $121.34(19)$ | C1-C2-H2A | 109.9 | H3AA-C3A-H3AC | 109.5 |
| B4-O6-B2 | $121.45(19)$ | N2-C2-H2B | 109.9 | H3AB-C3A-H3AC | 109.5 |
| B5-O7-B2 | $123.67(19)$ | C1-C2-H2B | 109.9 | N1A-C4A-H4AA | 109.5 |
| B5-O8-B3 | $120.99(18)$ | H2A-C2-H2B | 108.3 | N1A-C4A-H4AB | 109.5 |
| B6-O9-B3 | $122.69(18)$ | N1-C3-H3A | 109.5 | H4AA-C4A-H4AB | 109.5 |
| B6-O10-B1 | $123.55(18)$ | N1-C3-H3B | 109.5 | N1A-C4A-H4AC | 109.5 |
| B4-O11-H11 | 109.5 | H3A-C3-H3B | 109.5 | H4AA-C4A-H4AC | 109.5 |
| B5-O12-H12 | 109.5 | N1-C3-H3C | 109.5 | H4AB-C4A-H4AC | 109.5 |
| B6-O13-H13 | 109.5 | H3A-C3-H3C | 109.5 | N2A-C5A-H5AA | 109.5 |
| O5-B1-O10 | $109.79(18)$ | H3B-C3-H3C | 109.5 | N2A-C5A-H5AB | 109.5 |
| O5-B1-O2 | $112.08(18)$ | N1-C4-H4A | 109.5 | H5AA-C5A-H5AB | 109.5 |
| O10-B1-O2 | $110.43(19)$ | N1-C4-H4B | 109.5 | N2A-C5A-H5AC | 109.5 |
| O5-B1-O1 | $109.75(18)$ | H4A-C4-H4B | 109.5 | H5AA-C5A-H5AC | 109.5 |
| O10-B1-O1 | $108.49(18)$ | N1-C4-H4C | 109.5 | H5AB-C5A-H5AC | 109.5 |
| O2-B1-O1 | $106.18(17)$ | H4A-C4-H4C | 109.5 | N2A-C6A-H6AA | 109.5 |
| O6-B2-O7 | $109.61(18)$ | H4B-C4-H4C | 109.5 | N2A-C6A-H6AB | 109.5 |
| O6-B2-O3 | $111.55(18)$ | N2-C5-H5A | 109.5 | H6AA-C6A-H6AB | 109.5 |
| O7-B2-O3 | $111.09(18)$ | N2-C5-H5B | 109.5 | N2A-C6A-H6AC | 109.5 |
| O6-B2-O1 | $109.47(18)$ | H5A-C5-H5B | 109.5 | H6AA-C6A-H6AC | 109.5 |
| O7-B2-O1 | $108.11(18)$ | N2-C5-H5C | 109.5 | H6AB-C6A-H6AC | 109.5 |
| O3-B2-O1 | $106.91(17)$ | H5A-C5-H5C | 109.5 | H21A-O21-H21B | 109.5 |
| O8-B3-O9 | $109.32(17)$ | H5B-C5-H5C | 109.5 | H24A-O24-H24B | 109.5 |
| O8-B3-O4 | $112.42(19)$ | N2-C6-H6A | 109.5 | H22A-O22-H22B | 109.4 |
| O9-B3-O4 | $112.49(19)$ | N2-C6-H6B | 109.5 | H23A-O23-H23B | 109.5 |
| O8-B3-O1 | $108.72(18)$ | H6A-C6-H6B | 109.5 | H25A-O25-H25B | 109.5 |
| O9-B3-O1 | $108.06(17)$ | N2-C6-H6C | 109.5 | H26A-O26-H26B | 109.4 |
| O4-B3-O1 | $105.61(16)$ | H6A-C6-H6C | 109.5 |  |  |
|  |  |  |  |  |  |

Table 15 Bond lengths [ $\AA$ ] in 24.

| $\mathrm{Cu} 1-\mathrm{N} 1 \mathrm{~B}^{\text {i }}$ | 1.910(13) | N1B-H1BA | 0.9100 | C11-C16 | 1.518(6) | C15B-H15D | 0.9900 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Cu1-N1B | 1.910(13) | N1B-H1BB | 0.9100 | C11-C12 | 1.524(5) | C16B-H16C | 0.9900 |
| $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}^{\text {i }}$ | 1.923(11) | N2B-C2B | $1.496(7)$ | C11-H11 | 1.0000 | C16B-H16D | 0.9900 |
| Cu1-N2B | 1.923(11) | $\mathrm{N} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BA}$ | 0.9100 | C12-C13 | 1.516(6) | O1-B2 | 1.505(3) |
| $\mathrm{Cu} 1-\mathrm{N} 2$ | 2.073(6) | N2B-H2BB | 0.9100 | C12-H12 | 1.0000 | O1-B1 | 1.511(3) |
| $\mathrm{Cu} 1-\mathrm{N} 2^{\text {i }}$ | 2.073(6) | C1B-C6B | 1.510 (8) | C13-C14 | 1.530(7) | O1-B3 | 1.512(3) |
| $\mathrm{Cu} 1-\mathrm{N} 1$ | 2.076(7) | C1B-C2B | 1.521(8) | C13-H13A | 0.9900 | O2-B4 | 1.373(3) |
| $\mathrm{Cu} 1-\mathrm{N} 1^{\text {i }}$ | 2.076(7) | C1B-H1BC | 1.0000 | C13-H13B | 0.9900 | O2-B1 | 1.464(3) |
| $\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 2.381(3) | C2B-C3B | 1.516(8) | C14-C15 | 1.509(6) | O3-B4 | $1.355(4)$ |
| $\mathrm{Cu} 1-\mathrm{O} 21$ | 2.381(3) | C2B-H2BC | 1.0000 | C14-H14A | 0.9900 | O3-B2 | 1.436 (3) |
| O21-H21A | 0.8681 | C3B-C4B | 1.529(9) | C14-H14B | 0.9900 | O4-B6 | 1.367(3) |
| O21-H21B | 0.8685 | C3B-H3BA | 0.9900 | C15-C16 | 1.537(6) | O4-B2 | 1.467(3) |
| N1-C1 | 1.475(6) | C3B-H3BB | 0.9900 | C15-H15A | 0.9900 | O5-B6 | 1.366 (3) |
| N1-H1A | 0.9100 | C4B-C5B | 1.514(8) | C15-H15B | 0.9900 | O5-B3 | 1.468(3) |
| N1-H1B | 0.9100 | C4B-H4BA | 0.9900 | C16-H16A | 0.9900 | O6-B5 | 1.376 (3) |
| N2-C2 | 1.480(6) | C4B-H4BB | 0.9900 | C16-H16B | 0.9900 | O6-B2 | 1.471(3) |
| N2-H2A | 0.9100 | C5B-C6B | 1.547(9) | N11B-C11B | 1.485(8) | O7-B5 | 1.359(3) |
| N2-H2B | 0.9100 | C5B-H5BA | 0.9900 | N11B-H11C | 0.9100 | O7-B3 | 1.461(3) |
| C1-C6 | 1.511(6) | C5B-H5BB | 0.9900 | N11B-H11D | 0.9100 | O8-B7 | $1.360(4)$ |
| C1-C2 | 1.516(6) | C6B-H6BA | 0.9900 | N12B-C12B | 1.483(8) | O8-B3 | 1.437(3) |
| C1-H1 | 1.0000 | C6B-H6BB | 0.9900 | N12B-H12C | 0.9100 | O9-B7 | 1.371(4) |
| C2-C3 | 1.512(6) | $\mathrm{Cu} 2-\mathrm{N} 11^{\mathrm{ii}}$ | 1.963(7) | N12B-H12D | 0.9100 | O9-B1 | 1.439(3) |
| C2-H2 | 1.0000 | $\mathrm{Cu} 2-\mathrm{N} 11$ | 1.963(7) | C11B-C16B | 1.520(9) | O10-B4 | 1.373(4) |
| C3-C4 | 1.523(7) | $\mathrm{Cu} 2-\mathrm{N} 12 \mathrm{~B}^{\text {ii }}$ | 1.999(19) | C11B-C12B | 1.524(8) | O10-H10 | 0.8400 |
| C3-H3A | 0.9900 | $\mathrm{Cu} 2-\mathrm{N} 12 \mathrm{~B}$ | 1.999(19) | C11B-H11E | 1.0000 | O11-B6 | 1.370(3) |
| C3-H3B | 0.9900 | $\mathrm{Cu} 2-\mathrm{N} 12$ | $2.013(8)$ | C12B-C13B | 1.516(9) | O11-H11F | 0.8400 |


| C4-C5 | $1.510(7)$ | Cu2-N12ii | $2.013(8)$ | C12B-H12E | 1.0000 | O12-B5 | $1.372(3)$ |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | ---: |
| C4-H4A | 0.9900 | Cu2-N11Bi | $2.070(18)$ | C13B-C14B | $1.528(9)$ | O12-H12F | 0.8400 |
| C4-H4B | 0.9900 | Cu2-N11B | $2.070(18)$ | C13B-H13C | 0.9900 | O13-B7 | $1.364(4)$ |
| C5-C6 | $1.528(7)$ | N11-C11 | $1.483(6)$ | C13B-H13D | 0.9900 | O13-H13 | 0.8400 |
| C5-H5A | 0.9900 | N11-H11A | 0.9100 | C14B-C15B | $1.509(9)$ | O14-B1 | $1.461(4)$ |
| C5-H5B | 0.9900 | N11-H11B | 0.9100 | C14B-H14C | 0.9900 | O14-H14 | 0.8400 |
| C6-H6A | 0.9900 | N12-C12 | $1.481(6)$ | C14B-H14D | 0.9900 | O22-H22A | 0.8495 |
| C6-H6B | 0.9900 | N12-H12A | 0.9100 | C15B-C16B | $1.540(9)$ | O22-H22B | 0.8500 |
| N1B-C1B | $1.478(7)$ | N12-H12B | 0.9100 | C15B-H15C | 0.9900 | O23-H23A | 0.8490 |
|  |  |  |  |  | O23-H23B | 0.8518 |  |

Table 16 Bond angles [ ${ }^{\circ}$ ] in 24.

| N1B ${ }^{\text {i }}$-Cu1-N1B | 180.0 | N1B-C1B-H1BC | 107.0 | Cu2-N11B-H11C | 110.5 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N1B ${ }^{\text {i }}$ - $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}^{\text {i }}$ | 89.8(4) | C6B-C1B-H1BC | 107.0 | C11B-N11B-H11D | 110.5 |
| N1B-Cu1-N2B ${ }^{\text {i }}$ | 90.2(4) | $\mathrm{C} 2 \mathrm{~B}-\mathrm{C} 1 \mathrm{~B}-\mathrm{H} 1 \mathrm{BC}$ | 107.0 | Cu2-N11B-H11D | 110.5 |
| N1B ${ }^{\text {i }}$ - $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}$ | 90.2(4) | N2B-C2B-C3B | 112.8(8) | H11C-N11B-H11D | 108.6 |
| N1B-Cu1-N2B | 89.8(4) | N2B-C2B-C1B | 105.8(7) | C12B-N12B-Cu2 | 112.3(9) |
| N2B ${ }^{\text {i }}$ - $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}$ | 180.0(5) | C3B-C2B-C1B | 110.2(8) | C12B-N12B-H12C | 109.1 |
| $\mathrm{N} 2-\mathrm{Cu} 1-\mathrm{N} 2^{\text {i }}$ | 180.0 | N2B-C2B-H2BC | 109.3 | Cu2-N12B-H12C | 109.1 |
| N2-Cu1-N1 | 81.3(2) | C3B-C2B-H2BC | 109.3 | C12B-N12B-H12D | 109.1 |
| N2 ${ }^{\text {i }}$ - ${ }^{\text {Cu1-N1 }}$ | 98.7(2) | $\mathrm{C} 1 \mathrm{~B}-\mathrm{C} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BC}$ | 109.3 | Cu2-N12B-H12D | 109.1 |
| $\mathrm{N} 2-\mathrm{Cu} 1-\mathrm{N} 1^{\text {i }}$ | 98.7(2) | C2B-C3B-C4B | 110.2(8) | H12C-N12B-H12D | 107.9 |
| $\mathrm{N} 2^{\mathbf{i}}-\mathrm{Cu} 1-\mathrm{N} 1^{\text {i }}$ | 81.3(2) | C2B-C3B-H3BA | 109.6 | N11B-C11B-C16B | 112.6(9) |
| $\mathrm{N} 1-\mathrm{Cu} 1-\mathrm{N} 1^{\text {i }}$ | 180.0 | C4B-C3B-H3BA | 109.6 | N11B-C11B-C12B | 108.1(9) |
| N1B ${ }^{\text {i }}$ - $\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 101.4(5) | C2B-C3B-H3BB | 109.6 | C16B-C11B-C12B | 109.8(9) |
| N1B-Cu1-O21 ${ }^{\text {i }}$ | 78.6(5) | C4B-C3B-H3BB | 109.6 | N11B-C11B-H11E | 108.8 |
| $\mathrm{N} 2 \mathrm{~B}^{\mathrm{i}}-\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 105.1(4) | H3BA-C3B-H3BB | 108.1 | C16B-C11B-H11E | 108.8 |
| $\mathrm{N} 2 \mathrm{~B}-\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 74.9(4) | C5B-C4B-C3B | 112.5(9) | C12B-C11B-H11E | 108.8 |
| $\mathrm{N} 2-\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 85.33(18) | C5B-C4B-H4BA | 109.1 | N12B-C12B-C13B | 114.0(10) |
| $\mathrm{N} 2^{\mathrm{i}}$ - $\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 94.67(18) | C3B-C4B-H4BA | 109.1 | N12B-C12B-C11B | 107.0(10) |
| $\mathrm{N} 1-\mathrm{Cu} 1-\mathrm{O} 21^{\text {i }}$ | 86.6(3) | C5B-C4B-H4BB | 109.1 | C13B-C12B-C11B | 110.2(9) |
| $\mathrm{N} 1{ }^{\text {i }}$ - $\mathrm{Cu} 1-\mathrm{O} 21{ }^{\text {i }}$ | 93.4(3) | C3B-C4B-H4BB | 109.1 | N12B-C12B-H12E | 108.5 |
| N1Bi-Cu1-O21 | 78.6(5) | H4BA-C4B-H4BB | 107.8 | C13B-C12B-H12E | 108.5 |
| N1B-Cu1-O21 | 101.4(5) | C4B-C5B-C6B | 109.5(8) | C11B-C12B-H12E | 108.5 |
| N2Bi-Cu1-O21 | 74.9(4) | C4B-C5B-H5BA | 109.8 | C12B-C13B-C14B | 109.9(10) |
| N2B-Cu1-O21 | 105.1(4) | C6B-C5B-H5BA | 109.8 | C12B-C13B-H13C | 109.7 |
| N2-Cu1-O21 | 94.67(18) | C4B-C5B-H5BB | 109.8 | C14B-C13B-H13C | 109.7 |
| $\mathrm{N} 2{ }^{\mathrm{i}}$ - $\mathrm{Cu} 1-\mathrm{O} 21$ | 85.33(18) | C6B-C5B-H5BB | 109.8 | C12B-C13B-H13D | 109.7 |
| N1-Cu1-O21 | 93.4(3) | H5BA-C5B-H5BB | 108.2 | C14B-C13B-H13D | 109.7 |
| $\mathrm{N} 1^{\mathrm{i}}$-Cu1-O21 | 86.6(3) | C1B-C6B-C5B | 110.3(8) | H13C-C13B-H13D | 108.2 |
| $\mathrm{O} 21{ }^{\mathrm{i}}-\mathrm{Cu} 1-\mathrm{O} 21$ | 180.0 | C1B-C6B-H6BA | 109.6 | C15B-C14B-C13B | 111.9(10) |
| $\mathrm{Cu} 1-\mathrm{O} 21-\mathrm{H} 21 \mathrm{~A}$ | 110.3 | C5B-C6B-H6BA | 109.6 | C15B-C14B-H14C | 109.2 |
| Cu1-O21-H21B | 110.0 | C1B-C6B-H6BB | 109.6 | C13B-C14B-H14C | 109.2 |
| H21A-O21-H21B | 108.5 | C5B-C6B-H6BB | 109.6 | C15B-C14B-H14D | 109.2 |
| C1-N1-Cu1 | 111.5(4) | H6BA-C6B-H6BB | 108.1 | C13B-C14B-H14D | 109.2 |
| C1-N1-H1A | 109.3 | $\mathrm{N} 11^{\text {ii }}-\mathrm{Cu} 2-\mathrm{N} 11$ | 180.0 | H14C-C14B-H14D | 107.9 |
| $\mathrm{Cu} 1-\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A}$ | 109.3 | $\mathrm{N} 12 \mathrm{~B}{ }^{\mathrm{ii}}-\mathrm{Cu} 2-\mathrm{N} 12 \mathrm{~B}$ | 180.0 | C14B-C15B-C16B | 110.3(9) |
| C1-N1-H1B | 109.3 | $\mathrm{N} 11^{\text {iii }}-\mathrm{Cu} 2-\mathrm{N} 12$ | 94.00(17) | C14B-C15B-H15C | 109.6 |
| Cu1-N1-H1B | 109.3 | N11-Cu2-N12 | 86.01(17) | C16B-C15B-H15C | 109.6 |
| H1A-N1-H1B | 108.0 | $\mathrm{N} 11^{\text {iii }}-\mathrm{Cu} 2-\mathrm{N} 12{ }^{\text {ii }}$ | 86.01(17) | C14B-C15B-H15D | 109.6 |
| C2-N2-Cu1 | 109.5(3) | $\mathrm{N} 11-\mathrm{Cu} 2-\mathrm{N} 12^{\text {ii }}$ | 93.99(17) | C16B-C15B-H15D | 109.6 |
| $\mathrm{C} 2-\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A}$ | 109.8 | N12-Cu2-N12 ${ }^{\text {ii }}$ | 180.0 | H15C-C15B-H15D | 108.1 |
| $\mathrm{Cu} 1-\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A}$ | 109.8 | $\mathrm{N} 12 \mathrm{~B}^{\text {ii }}-\mathrm{Cu} 2-\mathrm{N} 11 \mathrm{~B}^{\text {ii }}$ | 83.5(4) | C11B-C16B-C15B | 108.7(9) |
| C2-N2-H2B | 109.8 | N12B-Cu2-N11B ${ }^{\text {ii }}$ | 96.5(4) | C11B-C16B-H16C | 110.0 |
| Cu1-N2-H2B | 109.8 | N12B ${ }^{\text {ii }}-\mathrm{Cu} 2-\mathrm{N} 11 \mathrm{~B}$ | 96.5(4) | C15B-C16B-H16C | 110.0 |
| H2A-N2-H2B | 108.2 | N12B-Cu2-N11B | 83.5(4) | C11B-C16B-H16D | 110.0 |
| N1-C1-C6 | 114.8(5) | $\mathrm{N} 11 \mathrm{~B}^{\mathrm{i}}-\mathrm{Cu} 2-\mathrm{N} 11 \mathrm{~B}$ | 180.0 | C15B-C16B-H16D | 110.0 |
| N1-C1-C2 | 109.0(5) | $\mathrm{C} 11-\mathrm{N} 11-\mathrm{Cu} 2$ | 110.3(4) | H16C-C16B-H16D | 108.3 |
| C6-C1-C2 | 110.7(5) | C11-N11-H11A | 109.6 | B2-O1-B1 | 119.42(19) |
| N1-C1-H1 | 107.3 | $\mathrm{Cu} 2-\mathrm{N} 11-\mathrm{H} 11 \mathrm{~A}$ | 109.6 | B2-O1-B3 | 110.7(2) |
| C6-C1-H1 | 107.3 | C11-N11-H11B | 109.6 | B1-O1-B3 | 119.13(19) |


| C2-C1-H1 | 107.3 | Cu2-N11-H11B | 109.6 | B4-O2-B1 | 120.3(2) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N2-C2-C3 | 113.5(5) | H11A-N11-H11B | 108.1 | B4-O3-B2 | 122.7(2) |
| N2-C2-C1 | 107.0(4) | C12-N12-Cu2 | 107.2(4) | B6-O4-B2 | 121.3(2) |
| C3-C2-C1 | 111.4(5) | C12-N12-H12A | 110.3 | B6-O5-B3 | 120.3(2) |
| N2-C2-H2 | 108.3 | Cu2-N12-H12A | 110.3 | B5-O6-B2 | 119.0(2) |
| C3-C2-H2 | 108.3 | C12-N12-H12B | 110.3 | B5-07-B3 | 120.8(2) |
| C1-C2-H2 | 108.3 | Cu2-N12-H12B | 110.3 | B7-08-B3 | 122.8(2) |
| C2-C3-C4 | 111.4(6) | H12A-N12-H12B | 108.5 | B7-09-B1 | 120.7(2) |
| C2-C3-H3A | 109.3 | N11-C11-C16 | 113.3(5) | B4-O10-H10 | 109.5 |
| C4-C3-H3A | 109.3 | N11-C11-C12 | 107.8(5) | B6-O11-H11F | 109.5 |
| C2-C3-H3B | 109.3 | C16-C11-C12 | 109.9(4) | B5-O12-H12F | 109.5 |
| C4-C3-H3B | 109.3 | N11-C11-H11 | 108.5 | B7-O13-H13 | 109.5 |
| H3A-C3-H3B | 108.0 | C16-C11-H11 | 108.5 | B1-O14-H14 | 109.5 |
| C5-C4-C3 | 111.1(6) | C12-C11-H11 | 108.5 | O9-B1-O14 | 108.4(2) |
| C5-C4-H4A | 109.4 | N12-C12-C13 | 114.6(5) | O9-B1-O2 | 111.3(2) |
| C3-C4-H4A | 109.4 | N12-C12-C11 | 108.2(5) | $\mathrm{O} 14-\mathrm{B} 1-\mathrm{O} 2$ | 111.5(2) |
| C5-C4-H4B | 109.4 | C13-C12-C11 | 111.1(4) | O9-B1-O1 | 107.5(2) |
| C3-C4-H4B | 109.4 | N12-C12-H12 | 107.6 | O14-B1-O1 | 112.1(2) |
| H4A-C4-H4B | 108.0 | C13-C12-H12 | 107.6 | O2-B1-O1 | 106.0(2) |
| C4-C5-C6 | 113.4(6) | C11-C12-H12 | 107.6 | O3-B2-O4 | 110.2(2) |
| C4-C5-H5A | 108.9 | C12-C13-C14 | 110.2(5) | O3-B2-O6 | 111.0(2) |
| C6-C5-H5A | 108.9 | C12-C13-H13A | 109.6 | O4-B2-O6 | 111.4(2) |
| C4-C5-H5B | 108.9 | C14-C13-H13A | 109.6 | O3-B2-O1 | 109.7(2) |
| C6-C5-H5B | 108.9 | C12-C13-H13B | 109.6 | O4-B2-O1 | 107.1(2) |
| H5A-C5-H5B | 107.7 | C14-C13-H13B | 109.6 | O6-B2-O1 | 107.3(2) |
| C1-C6-C5 | 109.9(5) | H13A-C13-H13B | 108.1 | O8-B3-07 | 112.0(2) |
| C1-C6-H6A | 109.7 | C15-C14-C13 | 111.4(5) | O8-B3-O5 | 109.8(2) |
| C5-C6-H6A | 109.7 | C15-C14-H14A | 109.4 | O7-B3-05 | 111.0(2) |
| C1-C6-H6B | 109.7 | C13-C14-H14A | 109.4 | O8-B3-O1 | 109.5(2) |
| C5-C6-H6B | 109.7 | C15-C14-H14B | 109.4 | O7-B3-O1 | 108.1(2) |
| H6A-C6-H6B | 108.2 | C13-C14-H14B | 109.4 | O5-B3-O1 | 106.3(2) |
| C1B-N1B-Cu1 | 107.6(6) | H14A-C14-H14B | 108.0 | O3-B4-O10 | 117.0(2) |
| C1B-N1B-H1BA | 110.2 | C14-C15-C16 | 111.5(5) | O3-B4-O2 | 123.4(2) |
| Cu1-N1B-H1BA | 110.2 | C14-C15-H15A | 109.3 | O10-B4-O2 | 119.5(3) |
| C1B-N1B-H1BB | 110.2 | C16-C15-H15A | 109.3 | O7-B5-O12 | 116.9(2) |
| Cu1-N1B-H1BB | 110.2 | C14-C15-H15B | 109.3 | O7-B5-O6 | 123.0(2) |
| H1BA-N1B-H1BB | 108.5 | C16-C15-H15B | 109.3 | O12-B5-O6 | 120.1(2) |
| C2B-N2B-Cu1 | 103.8(6) | H15A-C15-H15B | 108.0 | O5-B6-04 | 121.9(2) |
| C2B-N2B-H2BA | 111.0 | C11-C16-C15 | 109.0(4) | O5-B6-O11 | 117.2(2) |
| $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BA}$ | 111.0 | C11-C16-H16A | 109.9 | O4-B6-O11 | 121.0(2) |
| C2B-N2B-H2BB | 111.0 | C15-C16-H16A | 109.9 | O8-B7-O13 | 122.4(2) |
| $\mathrm{Cu} 1-\mathrm{N} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BB}$ | 111.0 | C11-C16-H16B | 109.9 | O8-B7-09 | 122.8(2) |
| H2BA-N2B-H2BB | 109.0 | C15-C16-H16B | 109.9 | O13-B7-O9 | 114.8(3) |
| N1B-C1B-C6B | 115.4(8) | H16A-C16-H16B | 108.3 | H22A-O22-H22B | 109.5 |
| N1B-C1B-C2B | 109.9(7) | C11B-N11B-Cu2 | 106.4(9) | H23A-O23-H23B | 109.5 |
| C6B-C1B-C2B | 110.1(7) | C11B-N11B-H11C | 110.5 |  |  |

Table 17 Bond lengths [ $A$ ] in 27.

| Cu1-O21 | $2.3368(10)$ | N12-C14 | $1.4819(16)$ | O5-B5 | $1.3771(18)$ | O13-B13 | $1.3619(15)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Cu1-N1 | $1.9998(11)$ | C1-C2 | $1.5077(18)$ | O6-B1 | $1.4596(15)$ | O14-B11 | $1.4715(15)$ |
| Cu1-N2 | $2.0781(11)$ | C11-C12 | $1.5173(18)$ | O6-B5 | $1.3570(16)$ | O14-B14 | $1.3606(15)$ |
| Cu1-N11 | $1.9937(11)$ | O1-B1 | $1.4859(15)$ | O7-B2 | $1.3629(16)$ | O15-B14 | $1.3842(16)$ |
| Cu1-N12 | $2.0755(11)$ | O1-B2 | $1.3586(15)$ | O8-B3 | $1.3502(16)$ | O15-B15 | $1.3844(16)$ |
| N1-C1 | $1.4822(17)$ | O2-B2 | $1.3813(16)$ | O9-B4 | $1.3519(18)$ | O16-B11 | $1.4728(15)$ |
| N2-C2 | $1.4854(15)$ | O2-B3 | $1.3915(16)$ | O10-B5 | $1.3703(17)$ | O16-B15 | $1.3615(15)$ |
| N2-C3 | $1.4811(16)$ | O3-B1 | $1.4773(15)$ | O11-B11 | $1.4712(15)$ | O17-B12 | $1.3609(15)$ |
| N2-C4 | $1.4810(16)$ | O3-B3 | $1.3586(15)$ | O11-B12 | $1.3599(15)$ | O18-B13 | $1.3533(16)$ |
| N11-C11 | $1.4864(17)$ | O4-B1 | $1.4620(16)$ | O12-B12 | $1.3829(15)$ | O19-B14 | $1.3590(16)$ |
| N12-C12 | $1.4903(16)$ | O4-B4 | $1.3608(16)$ | O12-B13 | $1.3870(15)$ | O20-B15 | $1.3607(16)$ |
| N12-C13 | $1.4806(16)$ | O5-B4 | $1.3866(17)$ | O13-B11 | $1.4763(15)$ |  |  |
|  |  |  |  |  |  |  |  |

Table 18 Bond angles [ ${ }^{\circ}$ ] in 27.

| N1-Cu1-O21 | $94.53(4)$ | N11-C11-C12 | $108.35(10)$ | O10-B5-O5 | $120.30(12)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| N1-Cu1-N2 | $85.96(4)$ | N12-C12-C11 | $109.81(10)$ | B12-O11-B11 | $123.29(10)$ |
| N1-Cu1-N12 | $93.87(4)$ | B2-O1-B1 | $122.41(10)$ | B12-O12-B13 | $119.25(10)$ |
| N2-Cu1-O21 | $90.55(4)$ | B2-O2-B3 | $119.98(10)$ | B13-O13-B11 | $124.20(9)$ |
| N11-Cu1-O21 | $94.35(4)$ | B3-O3-B1 | $123.04(10)$ | B14-O14-B11 | $123.70(10)$ |
| N11-Cu1-N1 | $171.11(5)$ | B4-O4-B1 | $124.01(10)$ | B14-O15-B15 | $119.02(10)$ |
| N11-Cu1-N2 | $94.23(4)$ | B5-O5-B4 | $118.58(10)$ | B15-O16-B11 | $123.18(9)$ |
| N11-Cu1-N12 | $85.65(4)$ | B5-O6-B1 | $122.24(10)$ | O11-B11-O13 | $110.64(9)$ |
| N12-Cu1-O21 | $91.37(4)$ | O3-B1-O1 | $110.12(9)$ | O11-B11-O14 | $109.31(10)$ |
| N12-Cu1-N2 | $178.08(4)$ | O4-B1-O1 | $107.69(10)$ | O11-B11-O16 | $108.62(9)$ |
| C1-N1-Cu1 | $109.19(8)$ | O4-B1-O3 | $109.15(10)$ | O14-B11-O13 | $108.17(9)$ |
| C2-N2-Cu1 | $103.59(7)$ | O6-B1-O1 | $109.64(10)$ | O14-B11-O16 | $110.39(9)$ |
| C3-N2-Cu1 | $111.18(8)$ | O6-B1-O3 | $108.43(10)$ | O16-B11-O13 | $109.72(10)$ |
| C3-N2-C2 | $110.40(10)$ | O6-B1-O4 | $111.80(10)$ | O11-B12-O12 | $121.67(11)$ |
| C4-N2-Cu1 | $115.25(8)$ | O1-B2-O2 | $120.54(11)$ | O11-B12-O17 | $122.70(11)$ |
| C4-N2-C2 | $108.45(10)$ | O1-B2-O7 | $123.58(11)$ | O17-B12-O12 | $115.63(10)$ |
| C4-N2-C3 | $107.87(10)$ | O7-B2-O2 | $115.86(11)$ | O13-B13-O12 | $120.20(11)$ |
| C11-N11-Cu1 | $110.72(8)$ | O3-B3-O2 | $120.54(11)$ | O18-B13-O12 | $116.01(11)$ |
| C12-N12-Cu1 | $103.84(8)$ | O8-B3-O2 | $115.72(11)$ | O18-B13-O13 | $123.78(11)$ |
| C13-N12-Cu1 | $110.43(8)$ | O8-B3-O3 | $123.72(11)$ | O14-B14-O15 | $120.87(11)$ |
| C13-N12-C12 | $110.66(10)$ | O4-B4-O5 | $120.46(12)$ | O19-B14-O14 | $122.36(11)$ |
| C13-N12-C14 | $107.63(10)$ | O9-B4-O4 | $117.52(12)$ | O19-B14-O15 | $116.75(11)$ |
| C14-N12-Cu1 | $114.99(8)$ | O9-B4--O5 | $122.01(12)$ | O16-B15-O15 | $121.41(11)$ |
| C14-N12-C12 | $109.27(10)$ | O6-B5-O5 | $122.75(12)$ | O20-B15-O15 | $115.07(11)$ |
| N1-C1-C2 | $107.67(10)$ | O6-B5-O10 | $116.95(12)$ | O20-B15-O16 | $123.51(11)$ |
| N2-C2-C1 | $110.03(10)$ |  |  |  |  |
|  |  |  |  |  |  |

Table 19 Bond lengths [ $\AA$ ] in 28.

| Cu1-O8 | $2.0052(9)$ | O2-B1 | $1.4381(16)$ | O6-B3 | $1.4529(16)$ | O12-B5 | $1.3750(17)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Cu1-O9 | $2.2481(9)$ | O2-B4 | $1.3582(17)$ | O6-B6 | $1.3619(17)$ | O13-B6 | $1.3756(17)$ |
| Cu1-O10 | $1.9566(9)$ | O3-B2 | $1.4778(16)$ | O7-B1 | $1.4531(16)$ | N1-C1 | $1.4829(18)$ |
| Cu1-N1 | $2.0011(11)$ | O3-B4 | $1.3770(17)$ | O7-B6 | $1.3653(17)$ | N2-C2 | $1.4880(17)$ |
| Cu1-N2 | $2.0478(11)$ | O4-B2 | $1.4623(16)$ | O8-B1 | $1.4818(16)$ | N2-C3 | $1.4785(18)$ |
| O1-B1 | $1.5161(16)$ | O4-B5 | $1.3733(17)$ | O9-B2 | $1.4437(17)$ | N2-C4 | $1.4796(18)$ |
| O1-B2 | $1.5142(16)$ | O5-B3 | $1.4409(16)$ | O10-B3 | $1.4674(16)$ | C1-C2 | $1.5115(19)$ |
| O1-B3 | $1.5199(15)$ | O5-B5 | $1.3561(17)$ | O11-B4 | $1.3713(17)$ |  |  |

Table 20 Bond angles [ ${ }^{\circ}$ ] in 28.

| O8-Cu1-O9 | $83.58(4)$ | B2-O9-Cu1 | $116.51(7)$ | O9-B2-O1 | $106.07(10)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| O8-Cu1-N2 | $177.94(4)$ | B3-O10-Cu1 | $121.92(7)$ | O9-B2-O3 | $112.36(10)$ |
| O10-Cu1-O8 | $90.76(4)$ | C1-N1-Cu1 | $110.26(8)$ | O9-B2-O4 | $113.30(11)$ |
| O10-Cu1-O9 | $91.63(4)$ | C2-N2-Cu1 | $104.20(8)$ | O5-B3-O1 | $108.59(10)$ |
| O10-Cu1-N1 | $166.49(4)$ | C3-N2-Cu1 | $109.86(8)$ | O5-B3-O6 | $110.22(10)$ |
| O10-Cu1-N2 | $90.90(4)$ | C3-N2-C2 | $110.83(11)$ | O5-B3-O10 | $112.11(10)$ |
| N1-Cu1-O8 | $92.91(4)$ | C3-N2-C4 | $108.87(11)$ | O6-B3-O1 | $108.78(10)$ |
| N1-Cu1-O9 | $101.69(4)$ | C4-N2-Cu1 | $113.83(9)$ | O6-B3-O10 | $110.74(10)$ |
| N1-Cu1-N2 | $85.74(5)$ | C4-N2-C2 | $109.19(11)$ | O10-B3-O1 | $106.25(10)$ |
| N2-Cu1-O9 | $95.15(4)$ | N1-C1-C2 | $108.58(11)$ | O2-B4-O3 | $122.97(12)$ |
| B1-O1-B3 | $115.85(9)$ | N2-C2-C1 | $109.65(11)$ | O2-B4-O11 | $119.83(12)$ |
| B2-O1-B1 | $116.15(9)$ | O2-B1-O1 | $108.79(10)$ | O11-B4-O3 | $117.21(12)$ |
| B2-O1-B3 | $119.11(9)$ | O2-B1-O7 | $109.46(11)$ | O4-B5-O12 | $120.12(12)$ |
| B-O2-B1 | $123.69(11)$ | O2-B1-O8 | $11.18(10)$ | O5-B5-O4 | $123.92(12)$ |
| B4-O3-B2 | $119.53(10)$ | O7-B1-O1 | $107.95(10)$ | O5-B5-O12 | $115.95(12)$ |
| B5-O4-B2 | $121.43(10)$ | O7-B1-O8 | $110.822(10)$ | O6-B6-O7 | $12.69(12)$ |
| B5-O5-B3 | $122.73(11)$ | O8-B1-O1 | $108.55(10)$ | O6-B6-O13 | $117.20(12)$ |
| B6-O6-B3 | $121.48(10)$ | O3-B2-O1 | $107.46(10)$ | O7-B6-O13 | $120.09(12)$ |


| B6-O7-B1 | $122.90(10)$ | O4-B2-O1 | $108.92(10)$ |  |
| :--- | :--- | :--- | :--- | :--- |
| B1-O8-Cu1 | $118.29(7)$ | O4-B2-O3 | $108.51(10)$ |  |

Table 21 Bond lengths [ $\AA$ ] in 37

| Ni-O8 | $2.065(3)$ | O2-B1 | $1.468(7)$ | O6-B3 | $1.460(6)$ | O12-B5 | $1.367(7)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | ---: |
| Ni1-O9 | $2.065(3)$ | O2-B4 | $1.391(7)$ | O6-B6 | $1.365(7)$ | O13-B6 | $1.370(7)$ |
| Ni1-O21 | $2.096(3)$ | O3-B2 | $1.464(7)$ | O7-B1 | $1.460(6)$ | N1-C1 | $1.464(13)$ |
| Ni1-O22 | $2.082(3)$ | O3-B4 | $1.382(7)$ | O7-B6 | $1.358(6)$ | N1-C1B | $1.518(12)$ |
| Ni1-N1 | $2.086(4)$ | O4-B2 | $1.441(6)$ | O8-B1 | $1.468(6)$ | N2-C2 | $1.483(13)$ |
| Ni1-N2 | $2.085(4)$ | O4-B5 | $1.364(6)$ | O9-B2 | $1.470(6)$ | N2-C2B | $1.454(12)$ |
| O1-B1 | $1.498(6)$ | O5-B3 | $1.439(6)$ | O10-B3 | $1.455(6)$ | C1-C2 | $1.52(2)$ |
| O1-B2 | $1.515(6)$ | O5-B5 | $1.360(7)$ | O11-B4 | $1.327(6)$ | C1B-C2B | $1.52(2)$ |
| O1-B3 | $1.538(6)$ |  |  |  |  |  |  |

Table 22 Bond angles [ ${ }^{\circ}$ ] in 37

| O8-Ni1-O9 | $90.48(12)$ | B5-O5-B3 | $124.4(4)$ | O9-B2-O1 | $106.3(4)$ |
| :--- | ---: | :--- | :--- | :--- | ---: |
| O8-N11-O21 | $84.84(13)$ | B6-O6-B3 | $122.3(4)$ | O5-B3-O1 | $108.4(4)$ |
| O8-Ni1-O22 | $89.04(14)$ | B6-O7-B1 | $124.1(4)$ | O5-B3-O6 | $109.0(4)$ |
| O8-Ni1-N1 | $93.51(14)$ | B1-O8-Ni1 | $124.8(3)$ | O5-B3-O10 | $109.9(4)$ |
| O8-Ni1-N2 | $175.70(14)$ | B2-O9-Ni1 | $124.8(3)$ | O6-B3-O1 | $108.1(4)$ |
| O9-Ni1-O21 | $85.55(14)$ | C1-N1-Ni1 | $107.7(5)$ | O10-B3-O1 | $109.7(3)$ |
| O9-Ni1-O22 | $88.86(14)$ | C1B-N1-Ni1 | $109.2(5)$ | O10-B3-O6 | $111.7(4)$ |
| O9-Ni1-N1 | $176.01(14)$ | C2-N2-Ni1 | $110.0(5)$ | O3-B4-O2 | $118.6(4)$ |
| O9-Ni1-N2 | $93.21(14)$ | C2B-N2-Ni1 | $108.2(5)$ | O11-B4-O2 | $122.1(5)$ |
| O22-Ni1-O2 | $171.67(12)$ | O2-B1-O1 | $108.9(4)$ | O11-B4-O3 | $119.3(5)$ |
| O22-Ni1-N1 | $91.38(16)$ | O7-B1-O | $110.2(4)$ | O4-B5-O12 | $114.8(5)$ |
| O22-Ni1-N2 | $93.24(16)$ | O7-B1-O2 | $107.8(4)$ | O5-B5-O4 | $122.3(5)$ |
| N1-Ni1-O21 | $94.62(16)$ | O7-B1-O8 | $111.0(4)$ | O5-B5-O12 | $122.9(5)$ |
| N2-Ni1-O21 | $93.23(16)$ | O8-B1-O1 | $107.6(4)$ | O6-B6-O13 | $120.1(4)$ |
| N2-Ni1-N1 | $82.80(14)$ | O8-B1-O2 | $111.2(4)$ | O7-B6-O6 | $122.2(5)$ |
| B1-O1-B2 | $117.7(3)$ | O3-B2-O1 | $108.6(4)$ | O7-B6-O13 | $117.8(5)$ |
| B1-O1-B3 | $119.1(4)$ | O3--B2-O9 | $112.2(4)$ | N1-C1-C2 | $109.3(14)$ |
| B2-O1-B3 | $120.1(4)$ | O4-B2-O1 | $110.04)$ | N2-C2-C1 | $109.4(13)$ |
| B4-O-B1 | $124.1(4)$ | O4-B2-O3 | $108.44)$ | N1-C1B-C2B | $108.7(12)$ |
| B4-O3-B2 | $124.9(4)$ | O4-B2-O9 | $111.4(4)$ | N2-C2B-C1B | $108.2(12)$ |
| B5-O4-B2 | $123.6(4)$ |  |  |  |  |

Table 23 Bond lengths $[\AA ̊]$ in 38.

| C1-N1 | $1.481(2)$ | C6-N3 | $1.473(2)$ | B1-O6 | $1.4643(18)$ | B5-O5 | $1.386(2)$ |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | ---: |
| C1-C2 | $1.511(2)$ | C6-C7 | $1.513(2)$ | B1-O4 | $1.4713(19)$ | N1-Ni1 | $1.9214(14)$ |
| C1-H1A | 0.9900 | C6-H6A | 0.9900 | B1-O3 | $1.4782(18)$ | N1-H1C | 0.9100 |
| C1-H1B | 0.9900 | C6-H6B | 0.9900 | B2-O7 | $1.3445(19)$ | N1-H1D | 0.9100 |
| C2-N2 | $1.472(2)$ | C7-N4 | $1.474(3)$ | B2-O1 | $1.353(2)$ | N2-Ni1 | $1.8506(14)$ |
| C2-H2A | 0.9900 | C7-H7A | 0.9900 | B2-O2 | $1.4049(19)$ | N3-Ni1 | $1.8504(14)$ |
| C2-H2B | 0.9900 | C7-H7B | 0.9900 | B3-O3 | $1.3429(19)$ | N4-Ni1 | $1.9284(16)$ |
| C3-N2 | $1.328(2)$ | C8-H8A | 0.9800 | B3-O8 | $1.3689(19)$ | N4-H4A | 0.9100 |
| C3-C4 | $1.397(2)$ | C8-H8B | 0.9800 | B3-O2 | $1.3921(18)$ | N4-H4B | 0.9100 |
| C3-C8 | $1.507(2)$ | C8-H8C | 0.9800 | B4-O9 | $1.355(2)$ | O7-H7 | 0.8400 |
| C4-C5 | $1.391(2)$ | C9-H9A | 0.9800 | B4-O4 | $1.3597(19)$ | O8-H8 | 0.8400 |
| C4-H4 | 0.9500 | C9-H9B | 0.9800 | B4-O5 | $1.3846(19)$ | O9-H9 | 0.8400 |
| C5-N3 | $1.329(2)$ | C9-H9C | 0.9800 | B5-O10 | $1.3557(19)$ | O10-H10 | 0.8400 |
| C5-C9 | $1.510(2)$ | B1-O1 | $1.4595(18)$ | B5-O6 | $1.3644(19)$ | O11-H11A | 0.8702 |
|  |  |  |  |  |  | O11-H11B | 0.8700 |

Table 24 Bond angles [ ${ }^{\circ}$ ] in 38.

| N1-C1-C2 | 106.36(14) | N4-C7-H7B | 110.3 | O10-B5-O6 | 122.73(14) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N1-C1-H1A | 110.5 | C6-C7-H7B | 110.3 | O10-B5-O5 | 116.75(13) |
| C2-C1-H1A | 110.5 | H7A-C7-H7B | 108.6 | O6-B5-O5 | 120.51(13) |
| N1-C1-H1B | 110.5 | C3-C8-H8A | 109.5 | C1-N1-Ni1 | 107.98(10) |
| C2-C1-H1B | 110.5 | C3-C8-H8B | 109.5 | C1-N1-H1C | 110.1 |
| H1A-C1-H1B | 108.6 | H8A-C8-H8B | 109.5 | Ni1-N1-H1C | 110.1 |
| N2-C2-C1 | 106.92(14) | C3-C8-H8C | 109.5 | C1-N1-H1D | 110.1 |
| N2-C2-H2A | 110.3 | H8A-C8-H8C | 109.5 | Ni1-N1-H1D | 110.1 |
| C1-C2-H2A | 110.3 | H8B-C8-H8C | 109.5 | H1C-N1-H1D | 108.4 |
| N2-C2-H2B | 110.3 | C5-C9-H9A | 109.5 | C3-N2-C2 | 119.26(14) |
| C1-C2-H2B | 110.3 | C5-C9-H9B | 109.5 | C3-N2-Ni1 | 126.48(12) |
| H2A-C2-H2B | 108.6 | H9A-C9-H9B | 109.5 | C2-N2-Ni1 | 113.74(11) |
| N2-C3-C4 | 122.55(15) | C5-C9-H9C | 109.5 | C5-N3-C6 | 118.52(15) |
| N2-C3-C8 | 119.90(15) | O1-B1-O4 | 108.42(12) | Ni1-N4-H4B | 110.3 |
| C4-C3-C8 | 117.54(14) | O6-B1-O4 | 110.63(12) | H4A-N4-H4B | 108.6 |
| C5-C4-C3 | 125.63(15) | O1-B1-O3 | 110.38(12) | B2-O1-B1 | 124.63(12) |
| C5-C4-H4 | 117.2 | O6-B1-O3 | 109.28(12) | B3-O2-B2 | 118.05(12) |
| C3-C4-H4 | 117.2 | O4-B1-O3 | 108.91(12) | B3-O3-B1 | 123.40(12) |
| N3-C5-C4 | 122.64(15) | O7-B2-O1 | 117.85(14) | B4-O4-B1 | 122.81(12) |
| N3-C5-C9 | 119.62(15) | O7-B2-O2 | 121.68(14) | B4-O5-B5 | 119.62(12) |
| C4-C5-C9 | 117.75(14) | O1-B2-O2 | 120.46(13) | B5-O6-B1 | 122.43(12) |
| N3-C6-C7 | 107.40(15) | O3-B3-O8 | 118.34(13) | B2-O7-H7 | 109.5 |
| N3-C6-H6A | 110.2 | O3-B3-O2 | 122.05(13) | B3-O8-H8 | 109.5 |
| C7-C6-H6A | 110.2 | O8-B3-O2 | 119.61(13) | B4-O9-H9 | 109.5 |
| N3-C6-H6B | 110.2 | O9-B4-O4 | 122.77(14) | B5-O10-H10 | 109.5 |
| C7-C6-H6B | 110.2 | O9-B4-O5 | 117.14(13) | H11A-O11-H11B | 109.5 |
| H6A-C6-H6B | 108.5 | O4-B4-O5 | 120.07(14) | N3-Ni1-N2 | 95.19(6) |
| N4-C7-C6 | 107.02(16) | C5-N3-Ni1 | 126.73(12) | N3-Ni1-N1 | 175.84(6) |
| N4-C7-H7A | 110.3 | C6-N3-Ni1 | 114.62(11) | N2-Ni1-N1 | 86.46(6) |
| C6-C7-H7A | 110.3 | C7-N4-Ni1 | 107.05(11) | N3-Ni1-N4 | 85.81(6) |
| H9A-C9-H9C | 109.5 | C7-N4-H4A | 110.3 | N2-Ni1-N4 | 175.94(6) |
| H9B-C9-H9C | 109.5 | Ni1-N4-H4A | 110.3 | N1-Ni1-N4 | 92.81(7) |
| O1-B1-O6 | 109.21(12) | C7-N4-H4B | 110.3 |  |  |

Table 25 Bond lengths $[\AA]$ in 39.

| Ni1-N2B | 2.015(14) | N1B-H1BA | 0.9100 | C11-C12 | 1.518(4) | C15B-H15D | 0.9900 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ni1-N2B ${ }^{\text {i }}$ | 2.015(14) | N1B-H1BB | 0.9100 | C11-C16 | 1.529(5) | C16B-H16C | 0.9900 |
| Ni1-N1B ${ }^{\text {i }}$ | 2.036 (15) | N2B-C2B | 1.485(7) | C11-H11 | 1.0000 | C16B-H16D | 0.9900 |
| Ni1-N1B | 2.036 (15) | N2B-H2BA | 0.9100 | C12-C13 | 1.525(5) | O1-B3 | 1.505(2) |
| $\mathrm{Ni} 1-\mathrm{N} 2^{\text {i }}$ | 2.108(8) | N2B-H2BB | 0.9100 | C12-H12 | 1.0000 | O1-B2 | 1.511(2) |
| Ni1-N2 | 2.108(8) | C1B-C6B | $1.517(7)$ | C13-C14 | 1.528(5) | O1-B1 | 1.512(2) |
| Ni1-N1 ${ }^{\text {i }}$ | 2.113(9) | C1B-C2B | 1.530(6) | C13-H13A | 0.9900 | O2-B4 | 1.357(2) |
| Ni1-N1 | 2.113(9) | C1B-H1BC | 1.0000 | C13-H13B | 0.9900 | O2-B2 | 1.439(2) |
| $\mathrm{Ni} 1-\mathrm{O} 21^{\text {i }}$ | $2.1352(15)$ | C2B-C3B | 1.524(7) | C14-C15 | 1.516(5) | O3-B4 | 1.372(2) |
| Ni1-O21 | $2.1353(15)$ | C2B-H2BC | 1.0000 | C14-H14A | 0.9900 | O3-B1 | 1.443(2) |
| O21-H21A | 0.8542 | C3B-C4B | 1.522(7) | C14-H14B | 0.9900 | O4-B5 | 1.356(2) |
| O21-H21B | 0.8546 | C3B-H3BA | 0.9900 | C15-C16 | 1.531(5) | O4-B3 | 1.435(2) |
| N1-C1 | 1.484(6) | C3B-H3BB | 0.9900 | C15-H15A | 0.9900 | O5-B5 | 1.370(2) |
| N1-H1A | 0.9100 | C4B-C5B | 1.522(6) | C15-H15B | 0.9900 | O5-B1 | 1.461(2) |
| N1-H1B | 0.9100 | C4B-H4BA | 0.9900 | C16-H16A | 0.9900 | O6-B6 | 1.357(2) |
| N2-C2 | 1.475(6) | C4B-H4BB | 0.9900 | C16-H16B | 0.9900 | O6-B2 | 1.459(2) |
| N2-H2A | 0.9100 | C5B-C6B | 1.528(7) | N11B-C11B | 1.479(8) | O7-B6 | 1.373(2) |
| N2-H2B | 0.9100 | C5B-H5BA | 0.9900 | N11B-H11C | 0.9100 | O7-B3 | 1.471(2) |
| C1-C6 | 1.521(6) | C5B-H5BB | 0.9900 | N11B-H11D | 0.9100 | O8-B7 | 1.360(2) |
| C1-C2 | $1.525(5)$ | C6B-H6BA | 0.9900 | N12B-C12B | 1.482(7) | O8-B2 | 1.464(2) |
| C1-H1 | 1.0000 | C6B-H6BB | 0.9900 | N12B-H12C | 0.9100 | O9-B7 | 1.368(2) |
| C2-C3 | 1.522(6) | Ni2-N11 | 1.897(7) | N12B-H12D | 0.9100 | O9-B3 | 1.465(2) |
| C2-H2 | 1.0000 | $\mathrm{Ni} 2-\mathrm{N} 11^{\text {ii }}$ | 1.897(7) | C11B-C16B | 1.521(7) | O10-B4 | 1.364(2) |
| C3-C4 | 1.520(6) | Ni2-N12 ${ }^{\text {ii }}$ | 1.900(6) | C11B-C12B | 1.523(7) | O10-H10 | 0.8400 |
| C3-H3A | 0.9900 | Ni2-N12 | 1.900(6) | C11B-H11E | 1.0000 | O11-B5 | 1.374(2) |
| C3-H3B | 0.9900 | Ni2-N11B | 1.965(17) | C12B-C13B | 1.531(7) | O11-H11F | 0.8400 |
| C4-C5 | 1.516(6) | Ni2-N11Bii | 1.965(17) | C12B-H12E | 1.0000 | O12-B6 | 1.373(2) |
| C4-H4A | 0.9900 | Ni2-N12B ${ }^{\text {ii }}$ | 1.971(16) | C13B-C14B | 1.521(7) | O12-H12F | 0.8400 |
| C4-H4B | 0.9900 | Ni2-N12B | 1.971(16) | C13B-H13C | 0.9900 | O13-B7 | 1.373(2) |
| C5-C6 | $1.526(6)$ | N11-C11 | 1.491(5) | C13B-H13D | 0.9900 | O13-H13 | 0.8400 |
| C5-H5A | 0.9900 | N11-H11A | 0.9100 | C14B-C15B | 1.515(7) | O14-B1 | 1.456(3) |
| C5-H5B | 0.9900 | N11-H11B | 0.9100 | C14B-H14C | 0.9900 | O14-H14 | 0.8400 |
| C6-H6A | 0.9900 | N12-C12 | 1.479(5) | C14B-H14D | 0.9900 | O22-H22A | 0.8507 |
| C6-H6B | 0.9900 | N12-H12A | 0.9100 | C15B-C16B | 1.527(7) | O22-H22B | 0.8507 |
| N1B-C1B | $1.484(7)$ | N12-H12B | 0.9100 | C15B-H15C | 0.9900 | O23-H23A | 0.8497 |
|  |  |  |  |  |  | O23-H23B | 0.8487 |

Table 26 Bond angles [ ${ }^{\circ}$ ] in 39.

| N2B-Ni1-N2B ${ }^{\text {i }}$ | 180.0 | N1B-C1B-H1BC | 108.0 | Ni2-N11B-H11C | 110.3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N2B-Ni1-N1B ${ }^{\text {i }}$ | 95.2(3) | C6B-C1B-H1BC | 108.0 | C11B-N11B-H11D | 110.3 |
| N2B ${ }^{\text {i }}$-Ni1-N1B ${ }^{\text {i }}$ | 84.8(3) | $\mathrm{C} 2 \mathrm{~B}-\mathrm{C} 1 \mathrm{~B}-\mathrm{H} 1 \mathrm{BC}$ | 108.0 | Ni2-N11B-H11D | 110.3 |
| N2B-Ni1-N1B | 84.8(3) | N2B-C2B-C3B | 112.8(8) | H11C-N11B-H11D | 108.6 |
| N2B ${ }^{\text {i }}$-Ni1-N1B | 95.2(3) | N2B-C2B-C1B | 106.4(7) | C12B-N12B-Ni2 | 111.3(8) |
| N1B ${ }^{\text {i }}$-Ni1-N1B | 180.0 | C3B-C2B-C1B | 109.9(6) | C12B-N12B-H12C | 109.4 |
| N2 ${ }^{\text {i }}$-Ni1-N2 | 180.0 | N2B-C2B-H2BC | 109.2 | Ni2-N12B-H12C | 109.4 |
| $\mathrm{N} 2{ }^{\mathrm{i}}-\mathrm{Ni} 11-\mathrm{N} 1^{\text {i }}$ | 81.50(18) | C3B-C2B-H2BC | 109.2 | C12B-N12B-H12D | 109.4 |
| $\mathrm{N} 2-\mathrm{Ni} 1-\mathrm{N} 1^{\text {i }}$ | 98.50(18) | $\mathrm{C} 1 \mathrm{~B}-\mathrm{C} 2 \mathrm{~B}-\mathrm{H} 2 \mathrm{BC}$ | 109.2 | Ni2-N12B-H12D | 109.4 |
| N2 ${ }^{\text {i }}$-Ni1-N1 | 98.50(18) | C4B-C3B-C2B | 110.9(7) | H12C-N12B-H12D | 108.0 |
| N2-Ni1-N1 | 81.50(18) | C4B-C3B-H3BA | 109.5 | N11B-C11B-C16B | 114.6(9) |
| N1 ${ }^{\text {i }}$-Ni1-N1 | 180.0 | C2B-C3B-H3BA | 109.5 | N11B-C11B-C12B | 108.0(8) |
| $\mathrm{N} 2 \mathrm{~B}-\mathrm{Ni} 1-\mathrm{O} 21^{\text {i }}$ | 96.6(6) | C4B-C3B-H3BB | 109.5 | C16B-C11B-C12B | 111.9(8) |
| $\mathrm{N} 2 \mathrm{~B}^{\mathrm{i}}-\mathrm{Ni} 1-\mathrm{O} 21^{\text {i }}$ | 83.4(6) | C2B-C3B-H3BB | 109.5 | N11B-C11B-H11E | 107.4 |
| $\mathrm{N} 1 \mathrm{~B}^{\mathrm{i}}-\mathrm{Ni} 1-\mathrm{O} 21^{\text {i }}$ | 87.2(8) | H3BA-C3B-H3BB | 108.1 | C16B-C11B-H11E | 107.4 |
| N1B-Ni1-O21 ${ }^{\text {i }}$ | 92.8(8) | C3B-C4B-C5B | 111.3(7) | C12B-C11B-H11E | 107.4 |
| $\mathrm{N} 2^{\mathrm{i}}-\mathrm{Ni} 1-\mathrm{O} 21^{1}$ | 88.0(4) | C3B-C4B-H4BA | 109.4 | N12B-C12B-C11B | 107.0(7) |
| N2-Ni1-O21 ${ }^{\text {i }}$ | 92.0(4) | C5B-C4B-H4BA | 109.4 | N12B-C12B-C13B | 113.6(8) |
| $\mathrm{N} 1{ }^{\mathrm{i}}$-Ni1-O21 ${ }^{\text {i }}$ | 87.1(5) | C3B-C4B-H4BB | 109.4 | C11B-C12B-C13B | 109.4(8) |
| N1-Ni1-O21 ${ }^{\text {i }}$ | 92.9(5) | C5B-C4B-H4BB | 109.4 | N12B-C12B-H12E | 108.9 |
| N2B-Ni1-O21 | 83.4(6) | H4BA-C4B-H4BB | 108.0 | C11B-C12B-H12E | 108.9 |


| N2B ${ }^{\text {i }}$-Ni1-O21 | 96.6(6) | C4B-C5B-C6B | 111.3(7) | C13B-C12B-H12E | 108.9 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N1B ${ }^{\text {i- }}$ - ${ }^{\text {il1-O21 }}$ | 92.8(8) | C4B-C5B-H5BA | 109.4 | C14B-C13B-C12B | 108.3(8) |
| N1B-Ni1-O21 | 87.2(8) | C6B-C5B-H5BA | 109.4 | C14B-C13B-H13C | 110.0 |
| N2 ${ }^{\text {i }}$-Ni1-O21 | 92.0(4) | C4B-C5B-H5BB | 109.4 | C12B-C13B-H13C | 110.0 |
| N2-Ni1-O21 | 88.0(4) | C6B-C5B-H5BB | 109.4 | C14B-C13B-H13D | 110.0 |
| N1 ${ }^{\text {i}}$-Ni1-O21 | 92.9(5) | H5BA-C5B-H5BB | 108.0 | C12B-C13B-H13D | 110.0 |
| N1-Ni1-O21 | 87.1(5) | C1B-C6B-C5B | 111.2(7) | H13C-C13B-H13D | 108.4 |
| O21 ${ }^{\text {i }}$-Ni1-O21 | 180.0 | C1B-C6B-H6BA | 109.4 | C15B-C14B-C13B | 112.5(9) |
| Ni1-O21-H21A | 109.3 | C5B-C6B-H6BA | 109.4 | C15B-C14B-H14C | 109.1 |
| Ni1-O21-H21B | 109.6 | C1B-C6B-H6BB | 109.4 | C13B-C14B-H14C | 109.1 |
| H21A-O21-H21B | 109.2 | C5B-C6B-H6BB | 109.4 | C15B-C14B-H14D | 109.1 |
| C1-N1-Ni1 | 110.2(4) | H6BA-C6B-H6BB | 108.0 | C13B-C14B-H14D | 109.1 |
| C1-N1-H1A | 109.6 | N11-Ni2-N11 ${ }^{\text {ii }}$ | 180.0(3) | H14C-C14B-H14D | 107.8 |
| Ni1-N1-H1A | 109.6 | N11-Ni2-N12 ${ }^{\text {ii }}$ | 92.05(16) | C14B-C15B-C16B | 112.1(8) |
| C1-N1-H1B | 109.6 | $\mathrm{N} 11^{\text {iii }}-\mathrm{Ni} 2-\mathrm{N} 12^{\text {ii }}$ | 87.95(16) | C14B-C15B-H15C | 109.2 |
| Ni1-N1-H1B | 109.6 | N11-Ni2-N12 | 87.95(16) | C16B-C15B-H15C | 109.2 |
| H1A-N1-H1B | 108.1 | $\mathrm{N} 11^{\text {iii }}-\mathrm{Ni} 2-\mathrm{N} 12$ | 92.05(16) | C14B-C15B-H15D | 109.2 |
| C2-N2-Ni1 | 108.7(4) | $\mathrm{N} 12^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 12$ | 180.0 | C16B-C15B-H15D | 109.2 |
| C2-N2-H2A | 109.9 | $\mathrm{N} 11 \mathrm{~B}-\mathrm{Ni} 2-\mathrm{N} 11 \mathrm{~B}^{\text {ii }}$ | 180.0 | H15C-C15B-H15D | 107.9 |
| Ni1-N2-H2A | 109.9 | N11B-Ni2-N12B ${ }^{\text {ii }}$ | 94.4(4) | C11B-C16B-C15B | 108.6(8) |
| C2-N2-H2B | 109.9 | $\mathrm{N} 11 \mathrm{~B}^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 12 \mathrm{~B}^{\text {ii }}$ | 85.6(4) | C11B-C16B-H16C | 110.0 |
| Ni1-N2-H2B | 109.9 | N11B-Ni2-N12B | 85.6(4) | C15B-C16B-H16C | 110.0 |
| H2A-N2-H2B | 108.3 | $\mathrm{N} 11 \mathrm{~B}^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 12 \mathrm{~B}$ | 94.4(4) | C11B-C16B-H16D | 110.0 |
| N1-C1-C6 | 113.1(5) | $\mathrm{N} 12 \mathrm{~B}^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 12 \mathrm{~B}$ | 180.0 | C15B-C16B-H16D | 110.0 |
| N1-C1-C2 | 108.5(5) | $\mathrm{C} 11-\mathrm{N} 11-\mathrm{Ni} 2$ | 110.0(4) | H16C-C16B-H16D | 108.3 |
| C6-C1-C2 | 109.8(5) | C11-N11-H11A | 109.7 | B3-O1-B2 | 110.72(13) |
| N1-C1-H1 | 108.4 | Ni2-N11-H11A | 109.7 | B3-O1-B1 | 119.72(13) |
| C6-C1-H1 | 108.4 | C11-N11-H11B | 109.7 | B2-O1-B1 | 119.24(13) |
| C2-C1-H1 | 108.4 | Ni2-N11-H11B | 109.7 | B4-O2-B2 | 123.15(15) |
| N2-C2-C3 | 113.5(5) | H11A-N11-H11B | 108.2 | B4-O3-B1 | 120.25(15) |
| N2-C2-C1 | 108.3(5) | C12-N12-Ni2 | 108.4(3) | B5-O4-B3 | 122.19(15) |
| C3-C2-C1 | 110.9(5) | C12-N12-H12A | 110.0 | B5-O5-B1 | 120.87(15) |
| N2-C2-H2 | 108.0 | Ni2-N12-H12A | 110.0 | B6-O6-B2 | 120.93(15) |
| C3-C2-H2 | 108.0 | C12-N12-H12B | 110.0 | B6-07-B3 | 119.12(14) |
| C1-C2-H2 | 108.0 | Ni2-N12-H12B | 110.0 | B7-O8-B2 | 120.21(15) |
| C4-C3-C2 | 111.1(5) | H12A-N12-H12B | 108.4 | B7-O9-B3 | 121.08(14) |
| C4-C3-H3A | 109.4 | N11-C11-C12 | 105.3(4) | B4-O10-H10 | 109.5 |
| C2-C3-H3A | 109.4 | N11-C11-C16 | 112.3(4) | B5-O11-H11F | 109.5 |
| C4-C3-H3B | 109.4 | C12-C11-C16 | 109.8(4) | B6-O12-H12F | 109.5 |
| C2-C3-H3B | 109.4 | N11-C11-H11 | 109.7 | B7-O13-H13 | 109.5 |
| H3A-C3-H3B | 108.0 | C12-C11-H11 | 109.7 | B1-O14-H14 | 109.5 |
| C5-C4-C3 | 110.8(5) | C16-C11-H11 | 109.7 | O3-B1-O14 | 107.86(15) |
| C5-C4-H4A | 109.5 | N12-C12-C11 | 107.5(4) | $\mathrm{O} 3-\mathrm{B} 1-\mathrm{O} 5$ | 111.44(16) |
| C3-C4-H4A | 109.5 | N12-C12-C13 | 115.9(4) | O14-B1-O5 | 111.96(15) |
| C5-C4-H4B | 109.5 | C11-C12-C13 | 110.9(4) | O3-B1-O1 | 107.29(15) |
| C3-C4-H4B | 109.5 | N12-C12-H12 | 107.4 | O14-B1-O1 | 112.17(15) |
| H4A-C4-H4B | 108.1 | C11-C12-H12 | 107.4 | O5-B1-O1 | 106.06(14) |
| C4-C5-C6 | 112.3(5) | C13-C12-H12 | 107.4 | O2-B2-O6 | 112.08(15) |
| C4-C5-H5A | 109.1 | C12-C13-C14 | 108.5(4) | O2-B2-O8 | 110.02(15) |
| C6-C5-H5A | 109.1 | C12-C13-H13A | 110.0 | O6-B2-08 | 110.99(15) |
| C4-C5-H5B | 109.1 | C14-C13-H13A | 110.0 | O2-B2-O1 | 109.17(14) |
| C6-C5-H5B | 109.1 | C12-C13-H13B | 110.0 | O6-B2-O1 | 108.03(14) |
| H5A-C5-H5B | 107.9 | C14-C13-H13B | 110.0 | O8-B2-O1 | 106.34(14) |
| C1-C6-C5 | 111.1(5) | H13A-C13-H13B | 108.4 | O4-B3-O9 | 110.11(15) |
| C1-C6-H6A | 109.4 | C15-C14-C13 | 112.4(4) | O4-B3-07 | 110.78(15) |
| C5-C6-H6A | 109.4 | C15-C14-H14A | 109.1 | O9-B3-07 | 111.52(15) |
| C1-C6-H6B | 109.4 | C13-C14-H14A | 109.1 | O4-B3-O1 | 110.07(14) |
| C5-C6-H6B | 109.4 | C15-C14-H14B | 109.1 | O9-B3-O1 | 107.11(14) |
| H6A-C6-H6B | 108.0 | C13-C14-H14B | 109.1 | O7-B3-O1 | 107.13(14) |
| C1B-N1B-Ni1 | 107.5(8) | H14A-C14-H14B | 107.9 | O2-B4-O10 | 122.62(17) |
| C1B-N1B-H1BA | 110.2 | C14-C15-C16 | 111.3(4) | O2-B4-O3 | 122.72(17) |
| Ni1-N1B-H1BA | 110.2 | C14-C15-H15A | 109.4 | O10-B4-O3 | 114.60(17) |
| C1B-N1B-H1BB | 110.2 | C16-C15-H15A | 109.4 | O4-B5-O5 | 123.61(17) |


| Ni1-N1B-H1BB | 110.2 | C14-C15-H15B | 109.4 | O4-B5-O11 | $116.65(16)$ |
| :--- | ---: | :--- | ---: | :--- | ---: |
| H1BA-N1B-H1BB | 108.5 | C16-C15-H15B | 109.4 | O5-B5-O11 | $119.73(17)$ |
| C2B-N2B-Ni1 | $108.7(7)$ | H15A-C15-H15B | 108.0 | O6-B6-O7 | $122.91(17)$ |
| C2B-N2B-H2BA | 109.9 | C11-C16-C15 | $108.0(4)$ | O6-B6-O12 | $117.23(17)$ |
| Ni1-N2B-H2BA | 109.9 | C11-C16-H16A | 110.1 | O7-B6-O12 | $119.86(17)$ |
| C2B-N2B-H2BB | 109.9 | C15-C16-H16A | 110.1 | O8-B7-O9 | $122.23(17)$ |
| Ni1-N2B-H2BB | 109.9 | C11-C16-H16B | 110.1 | O8-B7-O13 | $117.28(17)$ |
| H2BA-N2B-H2BB | 108.3 | C15-C16-H16B | 110.1 | O9-B7-O13 | $120.49(17)$ |
| N1B-C1B-C6B | $113.7(8)$ | H16A-C16-H16B | 108.4 | H22A-O22-H22B | 109.4 |
| N1B-C1B-C2B | $107.8(8)$ | C11B-N11B-Ni2 | $107.1(9)$ | H23A-O23-H23B | 109.6 |
| C6B-C1B-C2B | $111.0(7)$ | C11B-N11B-H11C | 110.3 |  |  |

Table 27 Bond lengths $[\AA]$ in 40.

| O1-B2 | $1.348(3)$ | O9-B4 | $1.357(3)$ | O11B-H11 | $0.883(14)$ | C11-H11B | 0.9900 |
| :--- | ---: | :--- | ---: | :--- | ---: | :--- | ---: |
| O1-B1 | $1.462(3)$ | O9-H9 | 0.8400 | N12-H12 | 1.0000 | C14-O11 | $1.41(2)$ |
| O2-B3 | $1.372(3)$ | O10-B5 | $1.350(3)$ | C12-C11 | $1.514(7)$ | C14-H14A | 0.9900 |
| O2-B2 | $1.379(3)$ | O10-H10 | 0.8400 | C12-C11B | $1.514(10)$ | C14-H14B | 0.9900 |
| O3-B3 | $1.357(3)$ | Ni1-N11B | $2.064(15)$ | C12-H12A | 0.9900 | N11-H11C | 0.9100 |
| O3-B1 | $1.472(3)$ | Ni1-N11B | $2.064(15)$ | C12-H12B | 0.9900 | N11-H11D | 0.9100 |
| O4-B4 | $1.350(3)$ | Ni1-O11B | $2.072(8)$ | C12-H12C | 0.9900 | O11-H11 | $0.865(13)$ |
| O4-B1 | $1.476(3)$ | Ni1-O11B | $2.072(8)$ | C12-H12D | 0.9900 | C11B-O11B | $1.42(3)$ |
| O5-B4 | $1.382(3)$ | Ni1-N12 | $2.080(2)$ | C13-C14 | $1.498(7)$ | C11B-H11H | 0.9900 |
| O5-B5 | $1.389(3)$ | Ni1-N12 | $2.080(2)$ | C13-C14B | $1.501(10)$ | C11B-H11I | 0.9900 |
| O6-B5 | $1.352(3)$ | Ni1-O11 | $2.087(7)$ | C13-H13A | 0.9900 | C14B-N11B | $1.51(3)$ |
| O6-B1 | $1.472(3)$ | Ni1-O11 | $2.087(7)$ | C13-H13B | 0.9900 | C14B-H14C | 0.9900 |
| O7-B2 | $1.364(3)$ | Ni1-N11 | $2.140(6)$ | C13-H13C | 0.9900 | C14B-H14D | 0.9900 |
| O7-H7 | 0.8400 | N11-N11 | $2.140(6)$ | C13-H13D | 0.9900 | N11B-H11E | 0.9100 |
| O8-B3 | $1.363(3)$ | N12-C12 | $1.466(4)$ | C11-N11 | $1.51(2)$ | N11B-H11F | 0.9100 |
| O8-H8 | 0.8400 | N12-C13 | $1.497(4)$ | C11-H11A | 0.9900 |  |  |

Table 28 Bond angles [ ${ }^{\circ}$ ] in 40.

| B2-O1-B1 | 122.92(19) | N12-Ni1-O11 ${ }^{\text {i }}$ | 99.43(17) | H13C-C13-H13D | 108.3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| B3-O2-B2 | 119.58(19) | $\mathrm{N} 12^{\mathrm{i}}-\mathrm{Ni} 1-\mathrm{O} 11^{\text {i }}$ | 80.57(17) | N11-C11-C12 | 101.8(13) |
| B3-O3-B1 | 123.24(19) | N12-Ni1-O11 | 80.57(17) | $\mathrm{N} 11-\mathrm{C} 11-\mathrm{H} 11 \mathrm{~A}$ | 111.4 |
| B4-O4-B1 | 123.44(19) | $\mathrm{N} 12^{\mathrm{i}}$-Ni1-O11 | 99.43(17) | C12-C11-H11A | 111.4 |
| B4-O5-B5 | 119.0(2) | O11 ${ }^{\text {i }}$-Ni1-O11 | 180.0 | N11-C11-H11B | 111.4 |
| B5-O6-B1 | 123.68(19) | N12-Ni1-N11 | 81.18(15) | C12-C11-H11B | 111.4 |
| B2-O7-H7 | 109.5 | N12 ${ }^{\text {i }}$-Ni1-N11 | 98.82(15) | $\mathrm{H} 11 \mathrm{~A}-\mathrm{C} 11-\mathrm{H} 11 \mathrm{~B}$ | 109.3 |
| B3-O8-H8 | 109.5 | O11 ${ }^{\text {i}}$-Ni1-N11 | 82.6(3) | O11-C14-C13 | 107.4(12) |
| B4-O9-H9 | 109.5 | O11-Ni1-N11 | 97.4(3) | O11-C14-H14A | 110.2 |
| B5-O10-H10 | 109.5 | N12-Ni1-N11 ${ }^{\text {i }}$ | 98.82(15) | C13-C14-H14A | 110.2 |
| O1-B1-O6 | 109.32(19) | N12 ${ }^{\text {i }}$-Ni1-N11 ${ }^{\text {i }}$ | 81.18(15) | O11-C14-H14B | 110.2 |
| O1-B1-O3 | 111.66(18) | $\mathrm{O} 11^{\text {i }}-\mathrm{Ni} 1-\mathrm{N} 11^{\text {i }}$ | 97.4(3) | C13-C14-H14B | 110.2 |
| O6-B1-O3 | 108.15(18) | O11-Ni1-N11 ${ }^{\text {i }}$ | 82.6(3) | H14A-C14-H14B | 108.5 |
| O1-B1-O4 | 109.46(18) | N11-Ni1-N11 ${ }^{\text {i }}$ | 180.0 | C11-N11-Ni1 | 109.0(12) |
| O6-B1-O4 | 110.20(18) | C12-N12-C13 | 116.1(2) | C11-N11-H11C | 109.9 |
| O3-B1-O4 | 108.04(19) | C12-N12-Ni1 | 108.9(2) | Ni1-N11-H11C | 109.9 |
| O1-B2-07 | 119.4(2) | C13-N12-Ni1 | 106.40(18) | C11-N11-H11D | 109.9 |
| O1-B2-O2 | 121.5(2) | C12-N12-H12 | 108.4 | Ni1-N11-H11D | 109.9 |
| O7-B2-O2 | 119.0(2) | C13-N12-H12 | 108.4 | H11C-N11-H11D | 108.3 |
| O3-B3-08 | 122.6(2) | Ni1-N12-H12 | 108.4 | C14-O11-Ni1 | 116.3(10) |
| O3-B3-O2 | 120.8(2) | N12-C12-C11 | 114.4(11) | C14-O11-H11 | 111(2) |
| O8-B3-O2 | 116.7(2) | N12-C12-C11B | 108.7(17) | Ni1-O11-H11 | 131(2) |
| O4-B4-O9 | 122.8(2) | N12-C12-H12A | 108.7 | O11B-C11B-C12 | 120.3(18) |
| O4-B4-O5 | 121.1(2) | C11-C12-H12A | 108.7 | O11B-C11B-H11H | 107.3 |
| O9-B4-O5 | 116.1(2) | N12-C12-H12B | 108.7 | C12-C11B-H11H | 107.3 |
| O10-B5-O6 | 123.1(2) | C11-C12-H12B | 108.7 | O11B-C11B-H11I | 107.3 |
| O10-B5-O5 | 116.1(2) | H12A-C12-H12B | 107.6 | C12-C11B-H11I | 107.3 |
| O6-B5-O5 | 120.7(2) | N12-C12-H12C | 110.0 | H11H-C11B-H11I | 106.9 |


| N11B-Ni1-N11B ${ }^{\text {i }}$ | 180.0 | C11B-C12-H12C | 110.0 | C13-C14B-N11B | 113(2) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| N11B-Ni1-O11B | 76.1(4) | N12-C12-H12D | 110.0 | C13-C14B-H14C | 108.9 |
| N11B ${ }^{\text {i }}$-Ni1-O11B | 103.9(4) | C11B-C12-H12D | 110.0 | N11B-C14B-H14C | 108.9 |
| N11B-Ni1-O113 ${ }^{\text {i }}$ | 103.9(4) | H12C-C12-H12D | 108.3 | C13-C14B-H14D | 108.9 |
| N11B ${ }^{\text {i }}$-Ni1-O113 ${ }^{\text {i }}$ | 76.1(4) | N12-C13-C14 | 113.1(14) | N11B-C14B-H14D | 108.9 |
| O11B-Ni1-O113 ${ }^{\text {i }}$ | 180.0(2) | N12-C13-C14B | 109(2) | H14C-C14B-H14D | 107.7 |
| N11B-Ni1-N12 | 82.9(3) | N12-C13-H13A | 109.0 | C14B-N11B-Ni1 | 110.1(12) |
| N11Bi-Ni1-N12 | 97.1(3) | C14-C13-H13A | 109.0 | C14B-N11B-H11E | 109.6 |
| O11B-Ni1-N12 | 85.69(19) | N12-C13-H13B | 109.0 | Ni1-N11B-H11E | 109.6 |
| O11B ${ }^{\text {i }}$-Ni1-N12 | 94.31(19) | C14-C13-H13B | 109.0 | C14B-N11B-H11F | 109.6 |
| N11B-Ni1-N12 ${ }^{\text {i }}$ | 97.1(3) | H13A-C13-H13B | 107.8 | Ni1-N11B-H11F | 109.6 |
| N11B ${ }^{\text {i }}$-Ni1-N12 ${ }^{\text {i }}$ | 82.9(3) | N12-C13-H13C | 109.9 | H11E-N11B-H11F | 108.1 |
| O11B-Ni1-N12 ${ }^{\text {i }}$ | 94.31(19) | $\mathrm{C} 14 \mathrm{~B}-\mathrm{C} 13-\mathrm{H} 13 \mathrm{C}$ | 109.9 | C11B-O11B-Ni1 | 106.3(13) |
| O113 ${ }^{\text {i }}$-Ni1-N12 ${ }^{\text {i }}$ | 85.69(19) | N12-C13-H13D | 109.9 | C11B-O11B-H11G | 100(3) |
| N12-Ni1-N12 ${ }^{\text {i }}$ | 180.0 | C14B-C13-H13D | 109.9 | Ni1-O11B-H11G | 130(3) |

Table 29 Bond lengths [ $\AA$ ] in 41.

| O1-B1 | $1.476(7)$ | O6-B1 | $1.466(5)$ | Ni1-N3A | $2.161(8)$ | C3A-C4A | $1.527(13)$ |
| :--- | :--- | :--- | :--- | :--- | ---: | :--- | :--- |
| O1-B2 | $1.361(7)$ | O6-B5 | $1.352(5)$ | Ni1-N1B | $2.152(10)$ | N1B-C1B | $1.496(15)$ |
| O2-B2 | $1.382(8)$ | O7-B2 | $1.359(7)$ | Ni1-N1 | $2.152(10)$ | N2B-C2B | $1.476(15)$ |
| O2-B3 | $1.386(8)$ | O8-B3 | $1.358(8)$ | Ni1-N2B | $2.105(11)$ | N2B-C3B | $1.495(15)$ |
| O3-B1 | $1.484(7)$ | O9-B4 | $1.377(5)$ | Ni1-N2B | $2.105(11)$ | N3B-C4B | $1.490(16)$ |
| O3-B3 | $1.356(6)$ | O10-B5 | $1.364(5)$ | Ni1-N3B | $2.130(10)$ | C1B-C2B | $1.503(15)$ |
| O4-B1 | $1.484(4)$ | Ni1-N1A | $2.103(8)$ | Ni1-N3B | $2.130(10)$ | C3B-C4B | $1.497(16)$ |
| O4-B4 | $1.343(5)$ | Ni1-N1A ${ }^{1}$ | $2.103(8)$ | N1A-C1A | $1.507(15)$ |  |  |
| O5-B4 | $1.392(14)$ | Ni1-N2A ${ }^{1}$ | $2.095(8)$ | N2A-C2A | $1.498(13)$ |  |  |
| O5-B5 | $1.404(17)$ | Ni1-N2A | $2.095(8)$ | N2A-C3A | $1.464(13)$ |  |  |
| O5A-B4 | $1.406(13)$ | Ni1-N3A | $2.161(8)$ | N3A-C4 | $1.472(13)$ |  |  |
| O5A-B5 | $1.407(16)$ |  |  | C1A-C2 | $1.460(14)$ |  |  |
|  |  |  |  |  |  |  |  |

Table $\mathbf{3 0}$ Bond angles [ ${ }^{\circ}$ ] in 41.

| B2-O1-B1 | 123.4(4) | O3-B3-O8 | 123.0(5) | N2A ${ }^{1}$-Ni1-N1A | 99.8(3) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| B2-O2-B3 | 119.5(3) | O8-B3-O2 | 116.0(4) | N2A ${ }^{1}-\mathrm{Ni} 1-\mathrm{N} 1 \mathrm{~A}^{1}$ | 80.2(3) |
| B3-O3-B1 | 123.3(4) | O4-B4-O5 | 119.5(10) | N2A-Ni1-N1A ${ }^{1}$ | 99.8(3) |
| B4-O4-B1 | 123.1(3) | O4-B4-O5A | 121.4(6) | N2A-Ni1-N1A | 80.2(3) |
| B4-O5-B5 | 116.7(13) | O4-B4-O9 | 122.9(3) | N2A ${ }^{1}-\mathrm{Ni1}-\mathrm{N} 2 \mathrm{~A}$ | 180.0 |
| B4-O5A-B5 | 115.5(15) | O9-B4-O5 | 115.9(7) | N2A-Ni1-N3A | 82.4(3) |
| B5-06-B1 | 122.7(3) | O9-B4-05A | 114.9(6) | N2A1-Ni1-N3A ${ }^{1}$ | 82.4(3) |
| O1-B1-O3 | 110.6(3) | O6-B5-05 | 119.9(11) | N2A ${ }^{1}$-Ni1-N3A | 97.6(3) |
| O1-B1-O4 | 108.0(4) | O6-B5-05A | 121.8(7) | N2A-Ni1-N3A ${ }^{1}$ | 97.6(3) |
| O3-B1-O4 | 107.8(4) | O6-B5-O10 | 118.8(4) | N3A ${ }^{1}$-Ni1-N3A | 180.0 |
| O6-B1-O1 | 109.8(4) | O10-B5-O5 | 120.0(8) | N1B-Ni1-N1B ${ }^{1}$ | 180.0 |
| O6-B1-O3 | 109.0(4) | O10-B5-O5A | 118.0(6) | N2B-Ni1-N1B | 82.2(4) |
| O6-B1-O4 | 111.6(3) | N1A-Ni1-N1A ${ }^{1}$ | 180.0 | N2B-Ni1-N1B ${ }^{1}$ | 97.8(4) |
| O1-B2-O2 | 121.0(5) | N1A ${ }^{1}$-Ni1-N3A | 89.1(3) | N2B ${ }^{1}$-Ni1-N1B ${ }^{1}$ | 82.2(4) |
| O7-B2-O1 | 122.4(6) | N1A ${ }^{1}-\mathrm{Ni} 11-\mathrm{N} 3 \mathrm{~A}^{1}$ | 90.9(3) | N2B ${ }^{1}$-Ni1-N1B | 97.8(4) |
| O7-B2-O2 | 116.6(5) | N1A-Ni1-N3A ${ }^{1}$ | 89.1(3) | N2B ${ }^{1}$-Ni1-N2B | 180.0 |
| O3-B3-O2 | 121.0(5) | N1A-Ni1-N3A | 90.9(3) | N2B ${ }^{1}-\mathrm{Ni} 1-\mathrm{N} 3 \mathrm{~B}$ | 99.5(4) |
|  |  |  |  | N2B ${ }^{1}$-Ni1-N3B ${ }^{1}$ | 80.5(4) |

