

**A new polyborate anion, [B<sub>7</sub>O<sub>9</sub>(OH)<sub>6</sub>]<sup>3-</sup>: Self assembly, XRD and thermal properties of s-fac-[Co(dien)<sub>2</sub>][B<sub>7</sub>O<sub>9</sub>(OH)<sub>6</sub>]-9H<sub>2</sub>O**

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# A new polyborate anion, $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$ : self assembly, XRD and thermal properties of *s-fac*- $[\text{Co}(\text{dien})_2][\text{B}_7\text{O}_9(\text{OH})_6].9\text{H}_2\text{O}$ .

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Keywords:  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$ , Heptaborate(3-); *s-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ , Self-assembly, XRD structure,

Abstract: The title compound, *s-fac*- $[\text{Co}(\text{dien})_2][\text{B}_7\text{O}_9(\text{OH})_6].9\text{H}_2\text{O}$  (**1**) (dien =  $\text{HN}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$ ), has been prepared as a crystalline solid in moderate yield (35%) from the reaction of  $\text{B}(\text{OH})_3$  with  $[\text{Co}(\text{dien})_2][\text{OH}]_3$  in aqueous solution (10:1 ratio). The structure contains a novel polyborate anion  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  which is structurally based on the known ‘ribbon’ isomer of  $[\text{B}_7\text{O}_9(\text{OH})_5]^{2-}$ , with an additional  $[\text{OH}]^-$  group coordinated to a B atom in one of the outer boroxole rings. Compound **1** is formed by a self-assembly process in which the cation and anion mutually template themselves from equilibrium mixtures under reaction conditions. The  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anions are H-bonded to each other in layers with ‘cavities’ suitable for the  $[\text{Co}(\text{dien})_2]^{3+}$  complex. Three  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anions are in the secondary coordination sphere (via H-bonds) of each cation, with each anion H-bonded to three cations.

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Polyborate anions are conveniently classified as either ‘condensed’ (polymeric chains, sheets or networks) or ‘isolated’ with discrete anionic moieties. Salts containing polyborate anions have attracted recent attention due to their possible applications as luminescent, second harmonic generation, ferroelectric, flame retardant and non-linear optical materials [1]. Isolated polyborate anions are readily synthesised by solvothermic methods [2] or by the addition of  $\text{B}(\text{OH})_3$  to a basic aqueous solution containing a potential templating cation [3]. Self-assembled products arise since  $\text{B}(\text{OH})_3$  in basic aqueous solution exists as a dynamic combinatorial library of a number of polyborate anions [4]. In general, pentaborate(1-) salts (containing the  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  anion) are formed because these salts have a strong H-bonded anionic lattice and this lattice is sufficiently flexible to accommodate many small to medium sized cations [5]. Salts containing polyborate anions other than pentaborate(1-) are relatively rare [6]. We are interested in the synthesis of structurally novel polyborate anions and have adopted a strategy of templating such species by the use of sterically demanding and/or highly charged cations [7]. Herein, we report the self-assembly of a salt containing a novel isolated heptaborate(3-) anion, partnered with cationic transition-metal coordination complex. This salt’s thermal properties, and its structure as determined by single-crystal XRD are also reported.

The addition of 10 equivalents of  $\text{B}(\text{OH})_3$  to 1 equivalent of  $[\text{Co}(\text{dien})_2][\text{OH}]_3$  in aqueous solution, prepared by anion exchange from  $[\text{Co}(\text{dien})_2]\text{Cl}_3$ , results in a moderate (35 %) yield of *s-fac*- $[\text{Co}(\text{dien})_2][\text{B}_7\text{O}_9(\text{OH})_6].9\text{H}_2\text{O}$  (**1**) [8]. Compound **1** was initially characterized by elemental analysis, IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$ ) spectroscopy, and by

thermal (TGA/DSC) analysis (air). The thermal and spectroscopic data indicated that **1** was not a pentaborate(1-) salt. In particular, the compound displayed several BO bands in the IR spectra but the diagnostic pentaborate(1-) peak ( $926\text{ cm}^{-1}$ ) [9] was absent. At ‘infinite’ dilution its  $^{11}\text{B}$  NMR spectrum gave a single peak at  $+12.3\text{ ppm}$ , rather than at  $+16.1$  [5] which would be indicative of pentaborate(1-). This higher field  $^{11}\text{B}$  signal would be more consistent with a lower B/charge ratio (2.3 rather than 5). Compound **1** was obtained as a crystalline material and was subjected to a single-crystal XRD study [10,11]. This study revealed its identity as *s-fac*-[Co(dien) $_2$ ][B $_7$ O $_9$ (OH) $_6$ ].9H $_2$ O. Compound **1** possesses a hitherto unseen isolated polyborate anion of composition [B $_7$ O $_9$ (OH) $_6$ ] $^{3-}$ . The structure of this anion is shown schematically in Figure 1a and is discussed in more fully below.

The synthesis of **1** can be rationalized since the addition of B(OH) $_3$  to water results in a complex set of equilibria involving a variety of mono and polyborate species which are pH and concentration dependent [4]. Polyborate salts may be crystal engineered through self-assembly *via* cation templating processes. Interestingly, the stereochemistry of the cation is also in dynamic equilibrium under reaction (basic) conditions with the starting material displaying an equilibrium mixture of three geometric isomers with % ratios *mer* (65%) : *u-fac* (28%) : *s-fac* (7%) [12]. The product is prepared in good yield (35%) with the geometrical isomer present exclusively *s-fac*. This indicates a mutual self-assembly process with crystallization driven by solid-state energetics and H-bond interactions in particular (*vide infra*).

Compound **1** was also characterized spectroscopically.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for **1** were obtained in D $_2$ O solution. The  $^{13}\text{C}$ -( $^1\text{H}$ ) spectrum displayed 2 signals for the dien ligand, whilst the  $^1\text{H}$  spectrum displayed 2 broad multiplets in the methylene region for the dien ligand and an additional signal at  $\delta 4.79$  assigned to exchanging NH/BOH/H $_2$ O protons. The relative intensities of the peaks in the methylene region were 1:3. The *s-fac* arrangement of the dien ligands give rise to prochiral ethylene carbon centres and 4 inequivalent H atom sites and three of which overlap in the highfield signal. The data we have found for our complex is in agreement with that reported for *s-fac*-[Co(dien) $_2$ ][Cl $_2$ (Bz)H $_2$ O] [13]. IR spectra gave broad O-H and N-H bands and a series of three strong lower energy bands centered at  $1400$ ,  $1050$  and  $860\text{ cm}^{-1}$  which might be assigned to the heptaborate(3-) moiety. In particular bands at  $1415$ ,  $1385$ , and  $1331\text{ cm}^{-1}$  may be assigned to  $\nu_{\text{as}}(\text{B}_{\text{trig}}\text{-O})$ ,  $1134$ ,  $1084$ , and  $1047\text{ cm}^{-1}$  to  $\nu_{\text{as}}(\text{B}_{\text{tet}}\text{-O})$ ,  $932\text{ cm}^{-1}$  to  $\nu_{\text{s}}(\text{B}_{\text{trig}}\text{-O})$ , and  $861\text{ cm}^{-1}$  to  $\nu_{\text{s}}(\text{B}_{\text{tet}}\text{-O})$  modes [14]. The spectra is largely similar to that reported for the ribbon isomer of [B $_7$ O $_9$ (OH) $_5$ ] $^{2-}$  (**2**) (Figure 1b) but **1** exhibits an additional strong band at  $861\text{ cm}^{-1}$ , which may be associated with the anion [15]. The  $^{11}\text{B}$  signal at  $\delta 12.3\text{ ppm}$  gives a calculated B/charge ratio of 2.36 which is consistent with that expected (2.33) for [B $_7$ O $_9$ (OH) $_6$ ] $^{3-}$ .

Elemental analysis data for **1** were consistent with the XRD formulation and the TGA/DSC data in air, were now explainable in terms of a three step process: loss of lattice water ( $< 120\text{ }^\circ\text{C}$ ), dehydration of the polyborate ( $250\text{-}300\text{ }^\circ\text{C}$ ), and oxidation of organics ( $300\text{-}600\text{ }^\circ\text{C}$ ). The final product was a glassy solid of composition CoB $_7$ O $_{12}$ . The DSC trace reveals that the first two processes were endothermic, whereas the oxidation of the diethylenetriamine ligands was exothermic. This is consistent with TGA/DSC traces of metal containing polyborate salts such as [Zn(dien) $_2$ ][B $_5$ O $_6$ (OH) $_5$ ] $_2$  [16].

The X-ray diffraction study of **1** revealed that it contains discrete *s-fac*-[Co(dien) $_2$ ] $^{3+}$  cations, novel [B $_7$ O $_9$ (OH) $_6$ ] $^{3-}$  anions, and 9 H $_2$ O molecules of crystallization (two of the waters were disordered over 2 positions), held together by an extensive H-bond network. The structure is shown in Figure 2, together with the associated numbering scheme.

The *s-fac* geometry for the octahedral  $[\text{Co}(\text{dien})_2]^{3+}$  cation has been previously characterized crystallographically and Co-N bond lengths and bond angles in **1** are 1.969(2)-1.956(2) Å and 85.58(9)-95.19(9)° and 177.72(9)-178.31(8)°, respectively, and are not significantly different from previously reported data [13,17]. All 10 cation NH atoms are involved in H-bonding and form 8 H-bonds to heptaborate anions, and 2 H-bonds to H<sub>2</sub>O molecules, in a secondary co-ordination sphere. Three heptaborate(3-) anions interact through H-bonds with each cation and each heptaborate(3-) anion H-bonds to 3 cations. Details of these H-bond interactions can be found in the supplementary data.

The  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anion has never been previously observed in minerals or in synthetic borates. It is comprised of three almost planar (half-chair, B1 and O1 are both ca. 0.2 Å out of best-planes) boroxole rings ( $\text{B}_3\text{O}_3$ ) which link together by sharing two 4-coordinate B centres, in a similar way to that observed for one of the known isomers of  $[\text{B}_7\text{O}_9(\text{OH})_5]^{2-}$  (**2**) (Figure 1b)[15]. However, the  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  found in **1** (Figure 1) has an additional 4 co-ordinate B centre formed by the addition of  $[\text{OH}]^-$  to a 3 coordinate B centre on a terminal boroxole ring in **2**. The new heptaborate(3-) anion may be described, using the Christ and Clark convention as 7:4Δ+3T [18]. Bond lengths and bond angles for the anion in **1** are similar to those found in other polyborate anions [19], and generally not significantly different to those found in the **2** [15] with the exception of data associated with the outer boroxole ring containing the additional hydroxyl group. Here B7 is 4 coordinate with longer B-O bonds [1.448(3)-1.516(3) Å] and angles [104.40(19)-112.0(2)°] appropriate for a tetrahedral geometry [19]. The inclusion of the additional  $[\text{OH}]^-$  ligand has little structural effects on other parameters within this boroxole ring, other than shortening B6-O8 [1.365(3) Å] relative to that observed in **2** [1.393(7) Å] [14]. This data is similar to that for  $[\text{B}_3\text{O}_4(\text{OH})_4]^-$  [20] and with adduct formation in boroxine ring systems [21] since O8B6  $\pi$ -bonding increases in **1** as the 4 coordinate B7 can no longer partake in  $\pi$ -bonding. This outer boroxole ring in **1** has a similar bondlength distribution to that found in  $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot\text{H}_2\text{O}$  (meyerhofferite) which contains a boroxole ring with two 4 coordinate boron centres [22].

The heptaborate anions are arranged as a series of ‘planes’ and the H-bonds associated with these planes are shown in Figure 3. All heptaborate anions are equivalent by symmetry and the ‘central’ anion of the diagram is involved in H-bonding to 4 neighbouring heptaborate(3-) anions. There is a C(10) chain interaction [23] involving O11H11...O14’ H-bonds and there are also two reciprocal  $R_2^2(8)$  interactions involving O12H12...O8’ and O13H13...O6’ which crosslink the C(10) chains to form a plane (Figure 4). The heptaborate(3-) network possess cavities and these cavities are sufficiently large to accommodate *s-fac*- $[\text{Co}(\text{dien})_2]^{3+}$  cations, which are H-bonded to three heptaborate(3-) anions. The H<sub>2</sub>O molecules link between planes which follow a repeating AA’ sequence with A’ being displaced relative to A.

To conclude, the salt *s-fac*- $[\text{Co}(\text{dien})_2][\text{B}_7\text{O}_9(\text{OH})_6]\cdot 9\text{H}_2\text{O}$  (**1**) has been synthesized in moderate yield. A single crystal XRD study of **1** revealed that the salt possess a previously unknown heptaborate (3-)  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anion. This anion is formed under strongly basic conditions and possesses three boroxole rings linked together by two 4 coordinate B centres. One of the two outer rings has a further 4 coordinate B centre with two terminal OH groups.

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## Supporting information.

CCDC 1407542 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via [www.cam.ac.uk/conts/retrieving.html](http://www.cam.ac.uk/conts/retrieving.html), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; fax (+44)1223-336033; or email [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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- [8]  $[\text{Co}(\text{en})_3]\text{Cl}_3$  (1.0 g, 2.45 mmol) was added an aqueous suspension (50 g) of  $[\text{OH}]^-$  activated mesosphere anion exchange resin (Dowex 550A), and stirred for 24 h. The resin was separated (filtered) and the washed with  $\text{H}_2\text{O}$  (4 x 5 ml).  $\text{B}(\text{OH})_3$  (1.51 g, 24.5 mmol) was then added to the filtrate, reduced to 15 ml, containing  $[\text{Co}(\text{en})_3][\text{OH}]_3$ . The reaction mixture was stirred for 3 h at room temperature before concentrating to ca. 5 ml, and transferred to 4 NMR tubes for crystallization. After 25 d yellow crystals of **1** were collected (filtered) and dried in air (0.65 g, 35.4%). **1**: m. pt. 240 °C (dec.). Elem. Anal for  $\text{C}_8\text{H}_{50}\text{B}_7\text{CoN}_6\text{O}_{24}$  Calc: (%) C, 12.8; H 6.7; N 11.2; Found: (%) C, 13.4; H 7.2; N, 11.1. IR (KBr disc,  $\nu_{\text{max}}/\text{cm}^{-1}$ ): 3432(s), 3201(s), 3095(s), 1631(w), 1415(vs), 1331(vs), 1134 (m), 1084(s), 1047(vs), 932(m), 861(m), 750(w), 656(w). NMR ( $\text{D}_2\text{O}$ ):  $^1\text{H}$  (400 MHz)  $\delta^1\text{H}/\text{ppm}$ : 3.00 (m, 12H), 3.24(m, 4H), 4.79 (s, 34H).  $^{11}\text{B}$  (128 MHz)  $\delta^{11}\text{B}/\text{ppm}$ : 12.3.  $^{13}\text{C}$  (101 MHz)  $\delta^{13}\text{C}/\text{ppm}$ : 43.29, 55.04. TGA: <120 °C, loss of 9 $\text{H}_2\text{O}$  (18.7%, Calc, 21.7%); 250-300 °C loss of 3 $\text{H}_2\text{O}$  (7.4%, 7.3% calc.); 300-600 °C, oxidation of organics (27.7%, 27.6% calc) to  $\text{CoB}_7\text{O}_{12}$  residue (46.9%, 43.5% calc).
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- [10] A *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with VHF *Varimax* optics (70 $\mu\text{m}$  focus) was used. X-ray data for **1**:

$C_8H_{50}B_7CoN_6O_{24}$ ,  $M = 749.14$ ; monoclinic, space group  $P2_1/n$ ;  $a = 11.7755(3) \text{ \AA}$ ,  $b = 15.3238(3) \text{ \AA}$ ,  $c = 17.3965(7) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 96.515(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $U = 3118.85(16) \text{ \AA}^3$ ,  $Z = 4$ .  $T = 100(2) \text{ K}$ , Wavelength  $0.71075 \text{ \AA}$ . Density (calculated)  $1.595 \text{ Mg / m}^3$ . Absorption coefficient  $0.651 \text{ mm}^{-1}$ .  $F(000) 1576$ . Crystal: Cut Blade, orange; size =  $0.150 \times 0.080 \times 0.010 \text{ mm}^3$ .  $\theta$  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 [ $R_{int} = 0.0491$ ]. Completeness to  $\theta = 25.242^\circ$ , 99.9%. Absorption correction: semi-empirical from equivalents. Max. and min. transmission 1.00000 and 0.79667. 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 [ $F^2 > 2\sigma(F^2)$ ]  $RI = 0.0483$ ,  $wR2 = 0.1159$ ;  $R$  indices (all data)  $RI = 0.0711$ ,  $wR2 = 0.1258$ ; Extinction coefficient n/a; Largest diff. peak and hole 1.214 and  $-0.801 \text{ e \AA}^{-3}$ .

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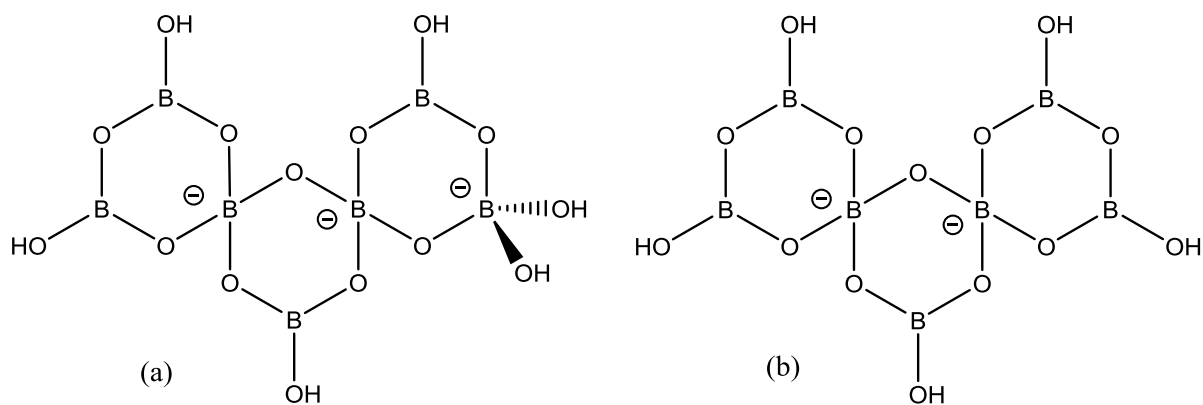
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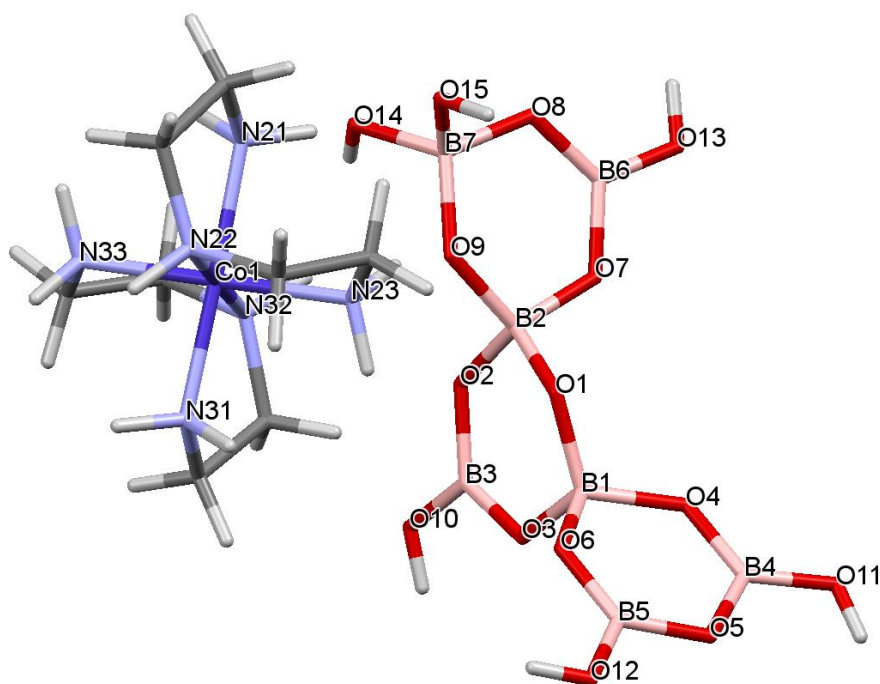
**Figure 1.**

Schematic drawing on the polyborate anion,  $[B_7O_9(OH)_6]^{3-}$  anion which is found in **1**,  $[Co(dien)_2][B_7O_9(OH)_6] \cdot 9H_2O$ , and a related triborate anion,  $[B_7O_9(OH)_5]^{2-}$  (**2**).



**Figure 2.**

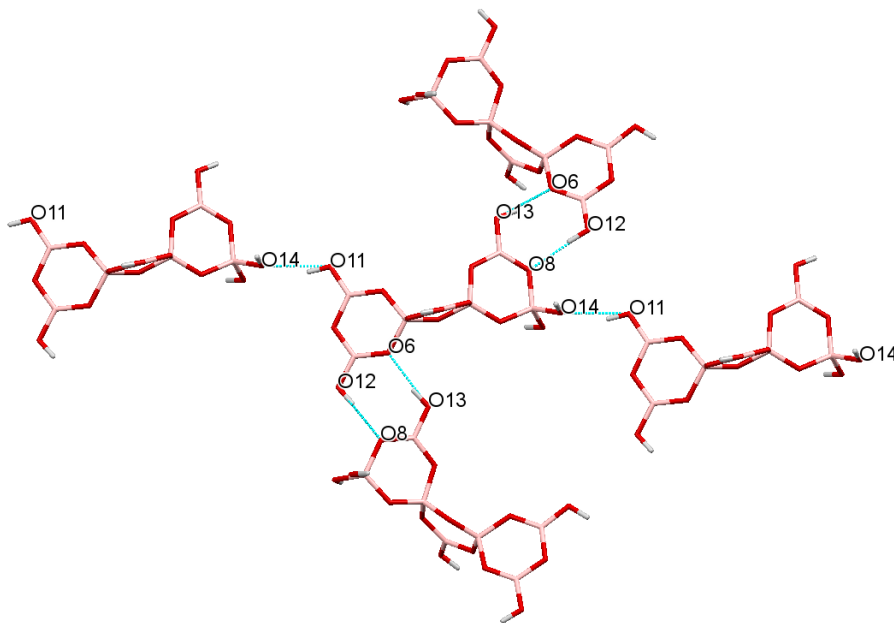
View of **1** showing atomic numbering scheme for the anion and cation. There are 9 additional H<sub>2</sub>O of crystallization which are omitted for clarity.





**Figure 3**

Anion-anion H-bond interactions found with a 'plane' of heptaborate(3-) anions. The central  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anion has a C(10) interaction forming a ribbon with its neighbours left and right [ $d(\text{O11}-\text{H11})$  0.84 Å;  $d(\text{H11}\dots\text{O14}')$  1.84 Å;  $d(\text{O11}\dots\text{O14}')$  2.645(2) Å;  $\angle\text{O11H11O14}'$  159.4°] and  $R_2^2(8)$  interactions with neighbours above and below [ $\text{O12H12}\dots\text{O8}'$ ,  $d(\text{O12}-\text{H12})$  0.84 Å;  $d(\text{H12}\dots\text{O8}')$  1.93 Å;  $d(\text{O12}\dots\text{O8}')$  2.767(2) Å;  $\angle\text{O12H12O8}'$  173.5° and  $\text{O13H13}\dots\text{O6}'$   $d(\text{O13}-\text{H13})$  0.84 Å;  $d(\text{H13}\dots\text{O6}')$  1.77 Å;  $d(\text{O13}\dots\text{O6}')$  2.605(2) Å;  $\angle\text{O13H13O6}'$  169.7°].



**Figure 4**

Diagram showing a 'plane' of heptaborate (viewed along *c*) with  $[\text{Co}(\text{dien})_2]^{3+}$  cations. The  $[\text{Co}(\text{dien})_2]^{3+}$  cation forms H-bonds to its three neighbouring  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anions, and each  $[\text{B}_7\text{O}_9(\text{OH})_6]^{3-}$  anion is H-bonded to three  $[\text{Co}(\text{dien})_2]^{3+}$  cations.

