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Customised TAA cations as counter ions in silicates and related systems

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CUSTOMISED TAA CATIONS AS COUNTER IONS IN SILICATES AND RELATED SYSTEMS

A THESIS SUBMITTED TO THE UNIVERSITY OF WALES, BANGOR



BY

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Abstract

This thesis reports the structure directing effects of various tetraalkylammonium ions upon the structures found within silicate, aluminosilicate and borate solutions. Structures were identified using a series of NMR techniques, most notably, ²⁹Si, ²⁷Al and ¹¹B NMR.

The preparation and silicate speciation within 10 TAA silicate solutions is reported. Sophisticated NMR techniques were utilised in order to quantify and determine the silicate structures found within two previously reported and 8 novel TAA silicates.

A series of previously unreported TAA aluminosilicates were prepared and the structures found within discussed. Using the complimentary techniques of ²⁹Si and ²⁷Al NMR, the speciation of structures observed within solution is reported.

Using organo-boronic and organo-borinic acid precursors, a series of novel TAA organoborate structures were prepared. A systematic route to their synthesis along with their characterisation by ¹¹B NMR, elemental analysis and, in three cases, single crystal X-ray analysis is reported.

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Contents

1.	Introduction	1
1.1	1. Introduction	2
1.2	2. Aims of the study	2
1.3	3. Silicon and silicates	3
	1.3.1 General background of silicon and silica	3
	1.3.2 Water soluble silicates	3
	1.3.3 Experimental techniques used in the study of silicate	4
	solutions	
	1.3.4 Nomenclature and conventions used	6
	1.3.5 Specific structure of silicate anions in solution	7
	1.3.6 Solid-state silicate structures	13
1.4	4. Aluminosilicates and zeolites	16
	1.4.1 General background of aluminosilicates & zeolites	16
	1.4.2 Composition and structure of zeolites	17
	1.4.3 Preparation of zeolites	18
	1.4.4 Structure determination of zeolites/aluminosilicates	19
	1.4.5 Tetramethylammonium (TMA) aluminosilicate solutions	22
1.5	5. Boron and borates	27
	1.5.1 General background of boron and borates	27
	1.5.2 Boron-oxygen compounds	27
1.6	5. Nuclear magnetic resonance (NMR) spectroscopy	32
	1.6.1 Introduction	32
	1.6.2 Nuclear spin	33
	1.6.3 Abundance	34
	1.6.4 Chemical shift and shielding	35
	1.6.5 Magnetogyric ratio	36

2. Synthesis and characterisation of aqueous silicate systems	38
2.1. Introduction	39
2.2. Aims	41
2.3 Results and discussion	42
2.3.1 Synthesis of tetraalkylammonium halide salts	42
2.3.2 Optimisation of nuclear magnetic resonance (NMR)	45
techniques	
2.3.3 Solution studies of aqueous silicates using ²⁹ Si NMR	48
2.3.4 Tetramethylammonium (1) and choline (2) silicates	56
2.3.5 Functionalised TAA cations with longer alkyl or aromatic	60
groups, (3), (4), (8) and (9)	
2.3.6 Hydroxy-functionalised TAA silicates, (5), (6) and (7)	64
2.3.7 X-Ray studies	65
2.3.8 TAA cation-water and TAA cation-silicate interactions	68
2.3.9 Silicates containing mixed cations	69
2.3.10 The effect of temperature on silicate speciation	77
2.3.11 Dried solutions and solid-state analysis	86
2.3.12 Additional analysis	93
2.4. Conclusions	94
3. Synthesis and characterisation of aqueous aluminosilicate	96
systems	
3.1 Introduction	97
3.2 Aims	97
3.3 Results and discussion	98
3.3.1 Synthesis of [TAA][aluminates]	98
3.3.2 Solution studies of aqueous aluminosilicates using ²⁹ Si &	99
²⁷ Al NMR	
3.4 Conclusion	109

v

4.	Synthesis and characterisation of novel TAA organoborate species	110
	4.1 Introduction	111
	4.2 Aims	111
	4.3 Results and discussion	112
	4.3.1 Preparation of TAA organoborate salts	112
	4.4 Conclusions	122
5.	Experimental	124
	5.1 General	125
	5.2 NMR parameters	125
	5.3 Preparation of tetraalkylammonium halides	128
	5.3 Preparation of silicate solutions	133
	5.4 Preparation of [TAA][aluminate] & [TAA][aluminosilicate] solutions	139
	5.5 Preparation of tetraalkylammonium borates	148
6.	References	151
	Appendix	158

List of Figures

Figure 1	Condensation of silicic acid giving rise to a silioxane bridge	7
Figure 2	²⁹ Si NMR spectra of a commercially available sodium silicate, Na:Si is 1:1.65	8
Figure 3	²⁹ Si NMR spectra of sodium silicate solutions. (a) $[SiO_2] = 4M$, Na/Si = 0.6, (b) $[SiO_2] = 4M$, Na/Si = 1	9
Figure 4	Closed silicate ring structure found in the mineral benitoite.	14
Figure 5	Schematic representation and examples of various chain metasilicates, $[SiO_3]_{\infty}$, with repeat distances in pm.	15
Figure 6	Planar network formed by extended 2D condensation of rings of six [SiO ₄] tetrahedral	16
Figure 7	The zeolite building units. Two SiO ₄ /AlO ₄ tetrahedra linked by an oxygen bridge in a corner-sharing manner.	17
Figure 8	The framework of zeolite-A built up from sodalite units.	18
Figure 9	The five possible local environments of a silicon atom together with their characteristic chemical shift ranges. The inner boxes represent the ²⁹ Si shift ranges suggested in early literature whereas the outer boxes represent ²⁹ Si shift ranges which are more unusual.	21
Figure 10	Borate anions known to exist in solution	32

vii

Figure 11	Energy levels for a nucleus with spin quantum number $\frac{1}{2}$	33
Figure 12	Circulating electron, e, in an s-orbital, producing an opposing magnetic field.	35
Figure 13	A spinning charge with angular momentum, J, such as a proton, gives rise to a magnetic dipole.	36
Figure 14	General reaction scheme for the synthesis of quaternary ammonium salts.	42
Figure 15	1,3-Bis-[<i>N,N,N</i> ,-(2-hydroxy-ethyl)-dimethyl-ammonium]- propan-2-ol dichloride	43
Figure 16	Quaternisation of dimethylethanolamine via an epoxy ring opening reaction in water.	44
Figure 17	²⁹ Si NMR spectra of (a) sodium silicate solution 1:1, 2.5M and (b) choline silicate solution 1:1, 2.43M	49
Figure 18	TAA cations used in the synthesis of some known and some novel quaternary ammonium silicate solutions.	50
Figure 19	²⁹ Si NMR spectra of (a) Sodium silicate solution with a sodium/silicon ratio of 1:1.95 and (b) TMA silicate solution with a TMA/silicon ratio of 1:2.	59
Figure 20	²⁹ Si NMR spectra of (a) choline (2) silicate 1:1 and (b) ethyl- choline (3) silicate 1:1	61
Figure 21	Crystal structure of [NMe ₄] ₈ [Si ₈ O ₂₀].69 H ₂ O	66

viii

- Figure 22 ²⁹Si NMR of (a) commercial sodium silicate 1:1.425 and (b) 70 the same silicate with added TAA cations to give a 1:1 solution.
- Figure 23 (a) TMA silicate solution 1:1 and (b) the same solution after 78 having been heated for 1 hour at 75°C.
- **Figure 24** (a) Choline silicate solution 1:1 and (b) the same solution after 80 having been heated for 1 hour at 75°C.
- Figure 25 (a) DPHEDMA silicate solution 1:1 and (b) the same solution 81 after having been heated for 1 hour at 75°C.
- Figure 26 29 Si NMR Spectra of Choline silicate 1:1 obtained at 85 increasing temperatures with resonances associated with the cubic octamer, Q_{8}^{3} , and prismatic hexamer, Q_{6}^{3} , highlighted.
- Figure27(a) A choline silicate solid-state NMR spectrum. (b)88Deconvoluted Spectrum. (c) Residual fit spectrum.
- Figure 28Synthetic strategy for TAA aluminosilicate preparation97
- Figure 29²⁷Al NMR of an aqueous TMA aluminate solution.99
- Figure 30 Diagram showing TAA aluminate (monodispersed) and Q_{8}^{3} silicate (monodispersed) to illustrate the premise of any 100 observable changes, if any, that may be seen.
- Figure 31
 Octameric anion consisting of 4 parts silica and 4 parts
 104

 aluminate
 104

Figure 32	General reaction schemes for the preparation of the 1	13
	organoborate salts	
Figure 33	X-ray crystal structure of [(CH ₃) ₃ N(CH ₂ CH ₂ OH)][Ph ₄ B ₃ O ₃] 1	15
Figure 34	Reaction yielding triethylammonium triphenyl hydroxy 1	19
	boroxine salt	
Figure 35	Crystal structure of triethylammonium triphenyl hydroxy 1 boroxine	20
Figure 36	Crystal structure of triethylammonium triphenyl hydroxy 1	21
Figure 37	Diagram of the coaxial type NMR tube assembly used for the 1 acquisition of ²⁹ Si NMR spectra	.26

List of Tables

Table 1	²⁹ Si chemical shifts, δ , of silicate anions identified is silicate solutions	10
Table 2	Common names of silicate minerals and their associated Q numbers	13
Table 3	Structures of the Cubic octamer, Q_{8}^{3} , found in TMA aluminosilicates following Lowenstein's rule.	23
Table 4	Interpretation of the observed four resonance lines of the TMA aluminosilicate solutions	26
Table 5	Examples of borate structures found in the solid state. Units containing B in planar BO ₃ coordination only	29
Table 6	Examples of borate structures found in the solid state. Units containing B in tetrahedral BO ₄ coordination only	30
Table 7	Examples of borate structures found in the solid state. Units containing B in both BO_3 and BO_4 coordination	31
Table 8	Relevant properties of the ²⁹ Si nucleus. ^a Assigned as 0ppm with high frequency shifts given as positive. ^b Scaled so that the ¹ H resonance of TMS is at exactly 250 MHz.	45
Table 9	A summary of silicate speciation within a number of TAA silicate solutions.	51

Table 10	A summary of silicate speciation within a number of commercially available silicate solutions	58
Table 11	Distribution of silicate species present in the starting sodium silicate and the three sodium/TAA mixed silicates	72
Table 12	Cation mixing ratio's within the mixed TAA silicate systems	75
Table 13	Speciation of silicate species within TAA silicates before and after heating for 1 hour at 75° C	82
Table 14	Comparison of solution and solid-state NMR for two silicates.	91
Table 15	Summary of TAA aluminosilicate solutions prepared to investigate the effects of aluminate and silicate composition.	102
Table 16	Summary of Choline aluminosilicate solutions prepared to investigate the effects of aluminate to silicate mixing ratio.	103
Table 17	Quantities used in the synthesis of [TAA][silicate] solutions	134
Table 18	Viscosity and ²⁹ Si NMR data of the silicate solutions prepared using [TAA][OH]	135
Table 19	Quantities used in the synthesis of TAA silicate solutions containing mixed cations	137
Table 20	Quantities used in the synthesis of [TAA][aluminosilicate] solutions	141

xii

Table 2127 Al NMR and 29 Si NMR data of the aluminosilicate 143
solutions prepared using three TAA hydroxides



1.1. Introduction

This thesis is partly concerned with the structure directing effects (SDE) of tetraalkylammonium (TAA) cations on silicate species present in solution. Firstly a number of TAA cations were synthesised and characterised using well established methods. The hydroxy forms of these organic cations in the aqueous phase were then used to produce a series of silicate solutions. The silicate structures found in these solutions were investigated by nuclear magnetic resonance (NMR) spectroscopy. Addition of aluminate solutions to these silicate solutions was then investigated in a similar way. Finally the systematic synthesis of a number of tetraalkylammonium borates was investigated using TAA solutions and organoborate precursors.

This chapter contains a literature overview of silicates, aluminosilicates and borates as well as their investigation by NMR. Chapter two focuses on the preparation and characterisation of a number of silicate species formed in solution and in the solid-state. Chapter three looks at the preparation of a select number of aluminosilicates in solution and their characterisation. Chapter four looks at the preparation of a number of novel tetraalkylammonium borates while Chapter five features the experimental methods used.

1.2. Aims of the study

The first aim of the research described within this thesis was to synthesise a number of hydroxy functionalised TAA cations. The second aim was to use these TAA hydroxides to synthesis a number of new and some previously described TAA silicate solutions and to study these solutions using ²⁹Si NMR spectroscopy. The third aim was to investigate the speciation of silicate structures within TAA silicate solutions and to study the SDE of the various TAA cations.

The fourth aim was to study the nature of analogous TAA aluminosilicate solutions and the speciation of structures therein as well as the nature of the cage structures formed in relation to silicon and aluminium environments. The fifth aim of the research was to systematically synthesise a number of novel TAA organoborate salts and to observe the SDE, if any, of the TAA cations upon borate ring structures.

1.3. Silicon and silicates

1.3.1 General background of silicon and silica

The discovery of silicon is generally credited to Jöns Jacob Berzelius, a Swedish chemist, who in 1824 found that by heating chips of potassium in a silica container and then carefully washing away the residual by-products a new element was obtained.¹ Silicon is the seventh most abundant element in the universe and, accounting for approximately 27.5% by weight, the second most abundant in the earth's crust.¹ Silicon dioxide (SiO₂), silicon's most familiar compound, is more frequently referred to as silica. It commonly takes the form of ordinary sand, but also exists as quartz, rock crystal, amethyst, agate, opal, jasper and flint. The last example is also the source of the elements name as it is derived from the Latin word for flint which is *'silicis'*. The properties and abundance of silica and polysilicate minerals has led to massive industrial interest in their applications across the globe. From their use as drilling fluids to their applications in glass technology the use of silicates and their associated chemistry is an area under much investigation.

1.3.2 Water soluble silicates

It has been known since the seventeenth century that sand (silica) and soda ash (sodium or potassium carbonate) react at high temperatures to form a watersoluble silicate known as "water glass".² Even before 1850, alkali silicates were being proposed as useful components in adhesives, cements and fireproof paints, and by 1855 water glass was being made commercially, both in Europe and America.³ In the early 20th century water glass was even used in the preservation of eggs. The bacteria-resistant solution of sodium silicate, discouraged the entrance of spoilage organisms and evaporation of water from eggs. It did not penetrate the egg shell, imparted no odour or taste to the eggs and was considered to have somewhat antiseptic properties.

Today there are perhaps three major types of uses of water soluble silicates 3 :-

- Cleaners and detergents that depend on controlled alkalinity are made generally from silicates, especially *meta-* and *ortho-*silicates.
- Adhesive, binder and deflocculant applications, which depend on the presence of polysilicate ions.
- For the production of precipitated silicas, sols and gels.

It is this third use, which is of particular relevance to glass technology. Such sols and gels may be engineered to give a variety of cosmetic and physical properties to glass structures.

1.3.3 Experimental techniques used in the study of silicate solutions

Many techniques, both chemical and physical, have been employed in attempts to elucidate the chemical structure of the species present in silicate solutions, and in investigations into the polymerisation of silicic acid.⁴ Physical techniques were, as a rule, the earliest to be used, and rely on the observation of a characteristic property of the solution. Amongst others, techniques such as, turbidity, viscosity and pH measurements were employed to elucidate silicate structures present in solution. Realistically, these techniques may only shed light on the composition and physical attributes of the solutions being studied. For example, the measured pH values correspond to the composition of solution as far as the higher the pH value, the higher the content of alkalis therein. Past such rudimentary conclusions, the use of these techniques to analyse silicate structures in solution is very limited.

Chemical methods have also been applied. Perhaps the most important being trimethylsilylation followed by chromatographic separation. The use of trimethylsilanol to inhibit further reaction of SiOH groups, thus allowing the chromatographic separation of the dissolved species, was introduced by Lentz and is often referred to as the Lentz method.⁵ This method allowed the determination of various structures present at differing molar ratios of SiO_2 : R_2O (R = Li, Na, K and TMA). Units containing up to eight silicon atoms were identified as well as determining that a large amount of the silica is present as polymeric anions.

More recently spectroscopic techniques such as infrared (IR), Raman and nuclear magnetic resonance (NMR) spectroscopy have evolved and been applied to the determination of silicate structures and speciation of silicate solutions. The signals obtained from IR and Raman spectroscopy of silicate solutions arise from the relevant Si-OH and Si-O-Si vibrations. These techniques are of limited value however, since the absorption of H₂O in the IR range is relatively high. Nevertheless, the work of Roggendorf et al. identified two distinctive regions where silicates may be investigated by IR.⁶ Firstly the adsorption band of the OH stretching vibration (3700 to 2600 cm⁻¹) of alkaline silicate solutions is broadened compared to pure water, especially the lower frequency side is shifted towards lower wave numbers. This kind of frequency shift is typically associated with hydrogen bonding. Secondly, there is a peak observed at approximately 2200 to 2100 cm⁻¹. Two interpretations are offered for this observation. The absorption may be due to the deformation vibration of water molecules, but, another interpretation arises from IR spectroscopic studies on water-containing glasses.⁷ Here, the band is associated to hydrogen bonding between isolated Si(OH)₄ tetrahedra and the silicate network.

NMR spectroscopy measures a different parameter altogether. As the chemical environment of a given silicon nucleus is affected, the electron density around that nucleus is changed. Therefore, whereas IR and Raman spectroscopy may provide information about the degree of protonation found in simple silicate species, they are of limited value in the determination of the Si-O-Si framework found in aqueous silicate solutions. Structural variation in the siloxane skeleton will have a marked influence on the electron density around specific silicon atoms. Hence, ²⁹Si NMR permits the direct determination of the structure and relative concentration of a series of distinct silicate anions and silicate structural units present in silicate solutions.

1.3.4 Nomenclature and conventions used

Aqueous silicate solutions may be thought of as having three major constituents.

- 1. Silica (in the form of silicate anions),
- 2. Cation (in the form of a basic oxide)
- 3. Water

With this in mind, silicate solutions may be classified according to three basic parameters.

- 1. The concentration of silica in solution
- 2. The ratio of silica to basic oxide
- 3. The cation associated with the basic oxide

Due to trends of nomenclature adopted by industry, silicate solutions are nearly always referred to as a ratio. These ratios are, at best, confusing to understand if one is not very familiar with their usage. In commercially available silicate solutions, the ratios relate to the molar quantity of silica (SiO_2) to the molar quantity of metal oxide (M_2O) present in solution with water. For the purposes of this work the following terminology will be adopted. When a ratio is discussed it will refer to the molar quantity of cation present to the molar quantity of silicon atoms present in solution.

For example, a typical, commercial sodium silicate is referred to as a 3.3 solution. This means that the Na_2O : SiO_2 is 1 : 3.3 and the $[cation]^+$: SiO_2 ratio is 1 : 1.65. Hereinafter all solutions will be defined in terms of their cation : silicon ratios. This system is found to be more convenient particularly when considering organic base silicate solutions.

The nature of silicate structure in solution may be thought of as silicon surrounded by oxygen in an almost regular tetrahedron. Pure silicic acid, Si(OH)₄, however, does not exist in solution. Condensation reactions, such as those shown in **Figure 1**, occur between such units giving rise to silioxane (Si-O-Si) bridges.



Figure 1 Condensation of silicic acid giving rise to a siloxane bridge

The silicon-oxygen tetrahedra may therefore share a corner which, in turn, gives rise to a wide variety of silicate structures in solution.

In order to describe such structures it is convenient to adopt the 'Q' nomenclature used by Englehardt *et al.*⁸ The "Q-unit" (for quadrifunctional) represents a SiO₄ group with the number of other Q-units directly attached to the one under consideration, indicated by a superscript. Taking the example of the condensation reaction shown above in **Figure 1**, the silicic acid species would be denoted as a Q^0 species as the silicon has no siloxane bridges to any other silicon atoms. The dimer formed from the condensation reaction however, would be denoted as Q^1_2 as each silicon atom is bonded to one other via a siloxane bridge. Additional condensation reactions give rise to a wide variety of silicate structures, groups of which may be assigned a Q number and hence easily referred to.

1.3.5 Specific structure of silicate anions in solution

NMR has been extensively used in the elucidation of solution structures. The total range of ²⁹Si chemical shifts observed in the ²⁹Si NMR spectra of silicate and silicic acid solutions extends from approximately -60 to -120 ppm relative to tetramethylsilane. Within this region, five well separated subdivisions have been found which correspond to five possible Q^n building units.⁷ The peak of the monomeric silicate anion Q^0 appears at the low-field side of the spectrum, followed in a regular sequence by the Q^1 to Q^4 units. Each increasing Q^n unit is found to be shifted high field by approximately 10ppm as each additional Si-O-Si

bond is formed. As an example the ²⁹Si NMR of a commercially available sodium silicate, 1:1.65, is shown in **Figure 2**.





No information on individual silicate anion structures may be obtained from this spectrum but the signals of the five types of Q^n units are highlighted. As shown, the linewidth of the Q^n peaks increases as n is increasing. Reasons for this include: -

- 1. Dynamic exchange processes between silicate anions
- 2. Exchange between protonated and unprotonated species
- 3. Effects of paramagnetic impurities
- 4. Overlapping resonance lines with slightly differing chemical shift

The overlapping of numerous resonance lines with slightly different chemical shifts due to different structural environments of the Q^n group is illustrated in **Figure 3**.⁸



Figure 3 29 Si NMR spectra of sodium silicate solutions. (a) [SiO₂] = 4M, Na/Si = 0.6, (b) [SiO₂] = 4M, Na/Si = 1

As **Figure 3** shows, the number of resonance lines found within a typical sodium silicate seems overwhelming to interpret. Thanks to the work of Engelhardt and Michel however, using silicon-29 enriched samples, the specific chemical shift of many silicate anion structures has been determined.⁸ These are highlighted in **Table 1**.

Table 1 29 Si chemical shifts, δ , of silicate anions identified is
silicate solutions 8

^a Silicon atoms are marked by a black dot, oxygen atoms are omitted

^b Values from 1.4M potassium silicate solution with K:Si = 1:1

^c Tentative assignment

^d Value from 0.63M potassium silicate solution with K:Si = 1.5:1

Silicate species	Structure ^a	Q ⁿ site	-ð (ppm) ^b
Monomer	•	Q ⁰	71.3
Dimmer	••	Q ¹	79.81
Linear Trimer	••	$\begin{array}{c} Q^1 \\ Q^2 \end{array}$	79.34 88.22
Cyclic Trimer	\bigtriangleup	Q ²	81.43
Linear Tetramer	• • • •	$\begin{array}{c} Q^1 \\ Q^2 \end{array}$	79.55 ^c 87.47 ^d
Cyclic Tetramer		Q^2	87.29
Monosubstituted Cyclic Trimer	, L	$\begin{array}{c} Q^1 \\ Q^2 \\ Q^3 \end{array}$	79.22 81.08 89.39 ^c
Bridged Cyclic Tetramer		Q^2 Q^3	85.50 93.24
Monosubstituted Cyclic Tetramer	B A	$\begin{array}{c} Q^1\\ Q^2(A)\\ Q^2(B)\\ Q^3 \end{array}$	79.16 87.06 ^d 87.38 ^c 95.29
Bicyclic Pentamer	B A	$\begin{array}{c} Q^2(A) \\ Q^2(B) \\ Q^3 \end{array}$	81.16 87.58 88.41
Prismatic Hexamer		Q ³	88.38

			N
Tricyclic Hexamer I	C A B	Q^{2} $Q^{3}(A)$ $Q^{3}(B)$ $Q^{3}(C)$	87.42 87.94 88.81 96.04
Tricyclic Hexamer IIa		$\begin{array}{c} Q^2 \\ Q^3 \end{array}$	81.80 88.10 ^{c,d}
Tricyclic Hexamer IIb	$< \square >$	$\begin{array}{c} Q^2 \\ Q^3 \end{array}$	82.11 89.15
Doubly Bridged Cyclic Tetramer		$\begin{array}{c} Q^2 \\ Q^3 \end{array}$	85.87 92.74
Pentacyclic Heptamer	A	$\begin{array}{c} Q^2 \\ Q^3(A) \\ Q^3(B) \end{array}$	90.23 89.23
Cubic Octamer		Q ³	98.61
Hexacyclic Octamer		Q ³ (A) Q ³ (B) Q ³ (C)	89.02 91.82 98.01
Prismatic Decamer		Q ³	98.45

Thanks to such detailed work, the quantitative distribution of silicate species in solution may be estimated from the integrated intensities of the corresponding

signals of the ²⁹Si NMR spectra.⁹ This technique allows insight into the nature of silicate solutions and the anions present therein.

1.3.6 Solid-state silicate structures

Almost invariably silicon is coordinated tetrahedrally by four oxygen atoms forming SiO_4 units. Within naturally occurring silicate minerals alone, the diversity of solid-state silicate structures is immense.¹⁰ As with borates the SiO_4 units may be built up into chains, ribbons, rings, sheets and three-dimensional networks. The various mineral types are summarized in **Table 2**.¹¹

Name	Unit	Valence	Q ⁿ
Neso-silicates	Discrete [SiO ₄]	No O atoms shared	Q^0
Soro-silicates	Discrete [Si ₂ O ₇]	1 O atoms shared	Q^1
Cyclo-silicates	Closed ring structures	1, 2 or 3 O atoms shared	Q ¹⁻³
Ino-silicates	Ribbons or continuous chains	1, 2 or 3 O atoms shared	Q ¹⁻³
Phyllo-	Continuous sheets	3 or 4 O atoms shared	Q ³⁻⁴
silicates			
Tecto-silicates	Continuous 3D networks	3 or 4 O atoms shared	Q ³⁻⁴

 Table 2
 Common names of silicate minerals and their associated Q numbers

Discrete $[SiO_4]$ units occur in orthosilicates with the general formula $[M_2^{II}SiO_4]$. Examples include $[Be_2^{II}SiO_4]$, $[Mg_2^{II}SiO_4]$, $[Mn_2^{II}SiO_4]$, $[Fe_2^{II}SiO_4]$ and $[Zn_2^{II}SiO_4]$.¹² Disilicates, containing the discrete $[Si_2O_7]$ unit, are rare. One example is the mineral thorvenite, $[Sc_2Si_2O_7]$, which features octahedral Sc^{III} along with a linear Si-O-Si bond between staggered tetrahedra. There is also a series of lanthanide disilicates, $[Ln_2Si_2O_7]$ in which the Si-O-Si angle decreases progressively from 180° to 130° . Closed ring structures, such as those found in cyclic metasilicates may be exemplified by the mineral benitoite, $[BaTi{Si_3O_9}]$ as shown in **Figure 4**. Minerals containing 3, 4, 6, or 8 tetrahedra are known but those containing 3 or 6 tetrahedral units are the most common.



Figure 4 Closed silicate ring structure found in the mineral benitoite.

Ribbon structures, $[SiO_3]_{\infty}$, formed by corner sharing of SiO₄ tetrahedra are particularly prevalent in nature. Despite the apparent simplicity of their structure considerable structural diversity is encountered because of the differing conformations that can be adopted by the linked tetrahedra. As a result the repeat distance along the chain-axis can be 1, 2, 3, 4, 5, 6, 7, 9 or 12 tetrahedra as illustrated in **Figure 5**.



Figure 5Schematic representation and examples of various chain
metasilicates, $[SiO_3]_{\infty}$, with repeat distances in pm. 11

Silicates with layer structures include some of the most familiar and important minerals known to man.¹³ An example of such a 2D planar network is shown in **Figure 6**. The physical and chemical properties of these minerals can be directly

related to the details of their crystal structure. An example of such a mineral is petalite, $[LiAlSi_4O_{10}]$.



Figure 6Planar network formed by extended 2D condensation of
rings of six [SiO4] tetrahedra

Layers may be joined by sharing of oxygen atoms between tetrahedra giving rise to more extensive 3D networks. The most familiar of such networks are found in structures such as zeolites.

1.4. Aluminosilicates and Zeolites

1.4.1 General background of aluminosilicates & zeolites

Zeolites were first described as a mineral group by the Swedish mineralogist Baron Axel Cronstedt in 1756.¹⁴ They are a class of crystalline aluminosilicates based on a rigid anionic framework with well defined channels and cavities. Most regularly, these cavities contain exchangeable metal cations such as sodium or potassium, but they may also contain removable and replaceable guest molecules. For example, in naturally occurring zeolites, this may be water. It is their ability to lose water that earned them their name. It was observed that upon heating they hissed and bubbled as though they were boiling. Cronstedt named them zeolites from the Greek words 'zeo', to boil and 'lithos', stone.

1.4.2 Composition and structure of zeolites

The general formula for the composition of a zeolite is $M_{x/n}[(AlO_2)_x(SiO_2)_y].mH_2O$, where cations M of valence *n* neutralize the negative charges on the aluminosilicate framework.

The primary building units of zeolites are $[SiO_4]^{4-}$ and $[AIO_4]^{5-}$ tetrahedra. As is the case for silicate structures, these building units are linked together through bent oxygen bridges in a corner-sharing arrangement such as the example shown in **Figure 7**. Silicon-oxygen tetrahedra are electronically neutral when connected in a three dimensional network where all Si atoms are in a Q⁴ environment such as quartz. The substitution of Si(IV) by Al(III) in such a structure, however, creates an electrical imbalance, and to preserve overall electrical neutrality, each $[AIO_4]^$ tetrahedron requires a balancing positive charge. This is provided by exchangeable cations held electrostatically within the zeolite.



Figure 7The zeolite building units. Two SiO₄/AlO₄ tetrahedra linked
by an oxygen bridge in a corner-sharing manner.

Just as with silicate structures discussed previously, it is possible for these tetrahedra to link by sharing two, three, or all four corners, thus forming a variety of structures. A synthetic zeolite, *zeolite-A* (also called Linde A) is shown in

Figure 8. Here the straight lines depict either Si-O-Si bridges, as for silicates, or, Si-O-Al bridges. They do not represent Al-O-Al bridges as these may not be formed in accordance with Lowenstein's rule.¹⁵



Figure 8 The framework of zeolite-A built up from sodalite units.

The formula of *zeolite-A* is $Na_{12}[(SiO_2)_{12}(AIO_2)_{12}].27H_2O$. From this formula we can see that the ratio of silicon to aluminium is 1 : 1 but some zeolites have quite high Si:Al ratios. ZSM-5 (Zeolite Socony-Mobil) for example, can have a Si:Al ratio ranging from 20:1 to ∞ :1, the later being pure SiO₂. This ratio far exceeds that of mordenite, the most siliceous naturally occurring zeolite, with a Si:Al ratio of 5.5:1. Clearly, changing the Si:Al ratio of a zeolite also changes its cation content when solidified. The fewer the aluminium atoms there are, the fewer exchangeable cations will be present. Although such discussions on zeolite composition deal only with the solid state structures of aluminosilicates, the comparisons and similarities between rigid Si/Al-O frameworks and their associated cations to structures found in aluminosilicate solutions must be considered.

1.4.3 Preparation of zeolites

Zeolites are prepared from solutions containing sodium silicates and aluminates, $[Al(OH)_4]^-$, at high pH, obtained by using an alkali metal hydroxide and/or an

organic base.^{16,17} A gel, which is then heated to form the condensed zeolites, is formed through co-polymerisation of the silicate and aluminate ions. The product obtained is determined by the synthesis conditions used. Temperature, time, pH and mechanical mixing are all possible variables. However, when forming silicon rich zeolites the presence of organic bases is extremely useful. The formation of such silicon rich zeolites has been facilitated by the use of templates such as large quaternary ammonium cations in the place of sodium cations.¹⁷

The structure directing effects of quaternary ammonium cations on silicate solutions is discussed in Chapter 2. When applied to the synthesis of zeolites, the size and functionality of the cation used directly relates to the aluminosilicate structure formed. For example, the tetramethylammonium cation, $[N(CH_3)_4]^+$, is used to synthesis the zeolite ZK-4. The aluminosilicate framework condenses around this large cation, which can subsequently be removed by chemical or thermal decomposition. The structure of ZK-4 has the same framework structure as *zeolite-A* as shown in **Figure 8**. ZSM-5 is produced in a similar way, but using tetra-n-propyl ammonium, $[N(CH_2CH_2CH_3)_4]^+$, as a cation.

1.4.4 Structure determination of zeolites/aluminosilicates

The structures of zeolite frameworks, such as those described above, have been determined by X-ray and neutron crystallographic techniques.¹⁸ Unfortunately, it is extremely difficult for diffraction techniques to determine a structure unequivocally. X-rays are scattered by the electron cloud around a nucleus and as aluminium and silicon sit next to each other in the third row of the periodic table, they each scatter X-rays almost equally making them virtually indistinguishable. Therefore, using crystallographic techniques, such as X-ray diffraction, it is possible to build a picture of the framework adopted by an aluminosilicate as it forms a zeolite but not possible to identify the position of the various aluminium and silicon atoms found within this structure. The positions of the aluminium and silicon atoms have always been assigned by applying Lowenstein's rule.¹⁵ The rule forbids the formation of Al-O-Al linkages within the aluminosilicate framework. As a consequence of this, the amount of aluminium found within an aluminosilicate structure has a practical limit imposed upon it. When the Si:Al

ratio is at 1:1 the aluminium content is at a maximum as the silicon and aluminium atoms alternate throughout the structure.

One of the techniques used to elucidate zeolite structures is solid-state, magic angle spinning (MAS) NMR spectroscopy.⁸ Hence, the use of NMR spectroscopy to investigate aluminosilicate structures present in solution may be applied as follows. ²⁹Si has a nuclear spin of ¹/₂ and so gives sharp spectral lines with no quadrupole broadening or asymmetry. Work in the late 1970's using MAS NMR on various zeolites showed that five separate peaks could be observed in the ²⁹Si NMR spectra.¹⁹ As described in the case of silicate solutions, Q^0 to Q^4 , these peaks corresponded to different silicon environments found within the structure of various zeolites. As with the method of Q nomenclature described previously, the five environments found within aluminosilicate structures may be thought of as follows. Each silicon atom is attached to four oxygen atoms, but each oxygen atom may then form a bridge with either another silicon atom or an aluminium atom thus giving rise to five separate environments: Si(OAl₄), Si(OAl₃(OSi), Si(OAl)₂(OSi)₂, Si(OAl)(OSi)₃ and Si(OSi)₄. Additionally, each environment described above was shown to have a characteristic range, as with silicate solutions, allowing further structural investigations into other aluminosilicates. These ranges are shown in Figure 9.





²⁷Al has a 100% natural abundance and a nuclear spin of 5/2. Aluminium, therefore, gives a strong resonance which is unfortunately broadened due to quadrupolar effects. In accordance with Lowenstein's rule, Al-O-Al linkages do not occur. Therefore, every tetrahedral aluminium is in the same environment, Al(OSi)₄. Consequently only a single resonance is observed for this species and the specific shift of this resonance is characteristic of the zeolites in solid-state NMR. In addition to this, ²⁷Al NMR may be used to distinguish between three types of aluminium coordination, which may be found in aluminosilicate species. Octahedrally coordinated Al, $[Al(H_2O)_6]^{3+}$, is used as a reference and hence

shows a resonance at 0ppm. In aqueous solutions with four-coordinated aluminium, the aluminate anion, $[Al(OH)_4]^-$, is found at 80ppm, whereas, the central AlO₄ tetrahedron of the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (commonly referred to as Al₁₃) cation may be found at 62.5ppm.²⁰

Tetrahedral aluminium within the aluminosilicate framework gives a peak in the range 50-65ppm.^{20,21,22,23} The central AlO₄ tetrahedron in Al₁₃ appears at 62.5ppm and is linked by the corners with twelve distorted AlO₆ octahedra, which in the ²⁷Al NMR spectra are not detectable.

1.4.5 Tetramethylammonium (TMA) aluminosilicate solutions

Having described the study of solid aluminosilicates by NMR techniques, the emphasis must shift to the study of quaternary ammonium aluminosilicate solutions. Early studies focused on the species present in TMA aluminosilicate solutions.²⁴ In the study by Hoebbel *et al.*, various crystalline TMA aluminosilicates were obtained from diluted TMA aluminate and TMA silicate solutions. Mixtures of aluminate and silicate were prepared in order to give varying Si:Al ratios, which through cooling, yielded crystalline products. Using the Lentz method, it was shown that, in a TMA aluminosilicate solution, the formation of the cubic octameric species, Q_{8}^{3} , was preferred as in the case of the aluminium free TMA silicate. In the case of the TMA aluminosilicate however, the aluminium atoms found within the cubic octamer was determined by ratio of Si:Al in the starting aluminate/silicate mixture. Considering Lowenstein's rule, the number of aluminosilicate structures possible within the confines of the cubic species, Q_{8}^{3} , is limited to five. These are highlighted in **Table 3**.




With the first TMA aluminosilicate species in solution established Mueller *et al.* further investigated the aluminium/silicon relationship by combining and comparing ²⁹Si and ²⁷Al NMR spectroscopic data.²⁵ They observed for the first time that in TMA aluminosilicate solutions, additional ²⁷Al resonances could be distinguished in the range 64 to 80ppm. By taking TMA aluminosilicate solutions with varying N:Si:Al ratios, up to four separate ²⁷Al signals could be identified. Apart from the signal observed at 79.5ppm, which was assigned to the TMA aluminate species, all their TMA aluminosilicate solutions showed additional resonances at 69.5 and 64.8ppm. Furthermore, a fourth resonance at 74.8ppm was observed in a TMA aluminosilicate solution with a N:Si:Al ratio of 2.0:0.6:1. Due to overlapping of the signals however, this signal could not be separated in the higher Si:Al ratio solutions.

It was also shown that in solutions with increasing Si:Al ratios, the intensity of the TMA aluminate signal (79.5ppm), was found to diminish as more ²⁷Al resonances were seen. The additional resonances were attributed to the increasing number of more shielded Al atoms which may be formed in two ways. Firstly, the condensation of AlO₄ tetrahedra, or secondly, the formation of Al-O-Si bonds. Studies using ²⁹Si NMR in both silicates and aluminosilicates have shown that the substitution of one neighbouring silicon atom by aluminium affects a low field shift of the ²⁹Si resonance of \approx 5ppm.²⁶ Dependant on the number of neighbouring Al atoms, the ranges of different Q units can overlap thus rendering a defined correlation of the ²⁹Si NMR peaks to structural groups more difficult.

For example, the Q^3 signal in a typical sodium silicate may be located at ~-100ppm. Should this Q^3 Si be neighboured by two Al atoms, the observed effect would be one of a 10ppm shift towards low-field, thus giving a signal at ~-90ppm. Unfortunately, the Q^2 signal found within a typical sodium silicate is located at ~-90ppm. Hence the distinction between $Q^3(2Al)$ and Q^2 becomes one of interpretation. This leaves room for a substantial amount of ambiguity when assigning spectra and hence makes the structural conclusions of aluminosilicate solutions more difficult to draw.

Nevertheless, it is reasoned that, with an increasing number of bridging oxygen atoms at the aluminium, an increase of the shielding is expected. This is supported in the study by Mueller *et al.* where it was suggested that monomeric $[Al(OH)_4]^$ anions (*pseudo* Q^0) would show a resonance in the ²⁷Al NMR spectra in the region of weakest shielding for AlO₄ tetrahedra at 80ppm.²⁵ The range of ²⁷Al chemical shifts for Al atoms then extends up to 62.5ppm for the *pseudo* O^4 type aluminium found in pure aluminium-oxygen compounds such as the central tetrahedron of the [Al₁₃O₄₀] species. However, the substitution of neighbouring Al atoms by Si atoms will also effect the shielding of the Al nucleus. As discussed above, the formation of Si-O-Al bridges by substitution of neighbouring Si atoms by Al atoms causes a decrease of the shielding of the silicon nucleus under study. Therefore, in the case of Al-O-Al bridges, the incorporation of Si atoms corresponds to an increase in the shielding of the Al nucleus. This may be understood in terms of the different electronegativities of the substituted Al and Si atoms and their effect on the Al-O and Si-O bonds found within the Al-O-Si bridges.

The degree of condensation of the silicon-oxygen and aluminium-oxygen tetrahedra and the number of Si-O-Al bridges affect the ²⁷Al and ²⁹Si NMR shifts in different ways. In ²⁹Si NMR they act in contrary directions thus causing $Q^n(xAl)$ (n = 0 - 4, x = n - 1 - 4) species to be found at lower field shifts when compared to their Q^n equivalence. However, in the case of ²⁷Al NMR both the number of oxygen bridges and the number of silicon atoms bridged to the aluminium effect the chemical shift. More oxygen bridges and more substituted silicon atoms affect a chemical shift towards high-field.

Distinguishing between these two effects when looking at the ²⁷Al NMR spectra is not possible without additional information. Comparison of an alkali aluminate and a TMA aluminate however, yields significant help and when coupled with Lowenstein's rule a reasonable explanation may be offered. It is considered highly unlikely that during the addition of a TMA silicate to a dilute TMA aluminate that additional Al-O-Al bonds should originate. This, coupled with Lowenstein's rule forbidding Al-O-Al bonds within an aluminosilicate leaves five aluminium environments which Mueller assigned as shown in **Table 4**.²⁵ Aluminium *pseudo*

 $Q^4(4Si)$ units are not shown in the table, though they are to be expected in the range of ~55ppm they were not found to be present in solutions of TMA aluminosilicates.

²⁷ Al chemical shift (ppm)	Structural unit	
79.5	Q ⁰ isolated AlO ₄ tetrahedron	——A1———
74.3	Q ¹ (1Si) chain end groups	—A1OSi
69.5	Q ² (2Si) middle groups of chains or rings	—SiOAIOSi
64.2	Q ³ (3Si) chain branching sites	SiOAIOSi

Table 4Interpretation of the observed four resonance lines of the
TMA aluminosilicate solutions 25

The key to better understanding of the chemical and physical properties of aluminosilicate materials lies in the detailed knowledge of their framework structure. The use of ²⁷Al and ²⁹Si NMR to investigate zeolites has yielded much information on the species present in aluminosilicate solutions. With these complimentary techniques, studies have identified five structures found in a typical tetramethylammonium aluminosilicate solution. Structure, composition and configuration of these aluminosilicates may all be inferred by particular ²⁹Si

and ²⁷Al chemical shifts making NMR spectroscopy a powerful tool in the study of tetraalkylammonium aluminosilicate solutions.

1.5. Boron and Borates

1.5.1 General background of boron and borates

Boron compounds have been known for thousands of years, but the element was not isolated until 1808 by Sir Humphry Davy, Joseph-Louis Gay-Lussac and Louis Jaques Thénard). This was accomplished through the reaction of boric acid (H_3BO_3) with potassium. Boron is comparatively unabundant in the universe and as elemental boron does not exist by itself in nature. However, in the form of borate minerals its structural complexity is surpassed only by that of silicate minerals. When considering borides, boranes, carboranes, metallocarboranes, boron-nitrogen and boron-oxygen compounds, it has been argued that the inorganic chemistry of boron is more diverse and complex than that of any other element in the periodic table.²⁷

1.5.2 Boron-oxygen compounds

Boron, like silicon, invariably occurs in nature as oxo-compounds and is almost never found directly bonded to any other element than oxygen. The structural chemistry of B-O containing compounds possesses an extraordinary complexity and diversity rivaling that of borides and boranes.¹¹ Of particular interest amongst the class of boron-oxygen compounds is the chemistry of borates. The phase relations, stoichiometry and structural chemistry of the metal borates have been extensively studied because of their geochemical implications and technological importance.²⁹ Borates are known in which the structural unit is mononuclear (1B atom) bi-, tri-, tetra- or penta-nuclear, or in which there are poly-dimensional networks.

Crystalline mineral and synthetic borates exhibit considerable structural variety and complexity. More than two hundred borate minerals and hundreds more synthetic borates are known. The main structural principles underlying the bonding in crystalline borates may be considered as follows:²⁸

- 1. Boron can link either three oxygens to form a triangle or four oxygens to form a tetrahedron.
- 2. Polynuclear anions are formed by corner-sharing only of boron-oxygen triangles and tetrahedral in such a manner that a compact insular group results.

Despite the apparent simplicity of these fundamental units, borate structures are often quite complex. As for silicates, these units may exist as isolated anions, link together by sharing oxygen bridges to form rings and cages, further polymerise into chains, sheets, or extended networks. Furthermore, borate anions interact with cations in complex ways and often display extensive hydrogen-bonding integrating their structures.

In the solid-state, the diversity of structures found in a plethora of minerals is extensive, as highlighted in **Table 5**, 6 and 7.

Table 5Examples of borate structures found in the solid state. Units
containing B in planar BO3 coordination only

Compound	Structure	Structural Unit
Rare earth orthoborates M ^{III} BO ₃ e.g. Mg ₃ (BO ₃) ₂		[BO ₃] ³⁻
Pyroborates e.g. Mg ₂ B ₂ O ₅		$[B_2O_5]^{4-}$
Metaborates M3B3O3 E,g, Na3B3O6		[B ₃ O ₆] ⁶⁻
Polynuclear Linkage e.g. Ca(BO ₂) Tourmaline		[(BO ₂) ⁻] _n
• = Boron	O = Oxygen	○—• = OH

Table 6Examples of borate structures found in the solid state. Units
containing B in tetrahedral BO4 coordination only

 $\{l\}$

Compound	Structure	Structural Unit
Monomeric tetrahedral e.g Ta ^v BO ₄		[BO ₄] ⁵⁻
e.g. Na ₂ [B(OH) ₄]Cl		[B(OH) ₄] ⁻
Binuclear tetrahedral unit e.g. Mg[B ₂ O(OH) ₆]		[B ₂ O(OH) ₆] ²⁻
Binuclear tetrahedral structure e.g. Na ₂ [B ₂ (O ₂) ₂ (OH) ₄].6H ₂ O		[B ₂ (O ₂) ₂ (OH) ₄] ²⁻
• = Boron	🔿 = Oxygen	○—• = OH

Table 7Examples of borate structures found in the solid state. Units
containing B in both BO3 and BO4 coordination



Despite such a diversity of solid state structures being known, titrimetric, temperature jump relaxation method and ¹¹B NMR experiments have shown that aqueous solution borate species are restricted to only a few anions.^{29,30,31,32,33} These are namely, $[B(OH)_4]^-$, the triborate anions $[B_3O_3(OH)_4]^-$ and $[B_3O_3(OH)_5]^2$, the tetraborate anion $[B_4O_5(OH)_4]^{2-}$, and the pentaborate anion $[B_5O_6(OH)_4]^-$. These species are shown in **Figure 10**.



Figure 10 Borate anions known to exist in solution

The investigation into these anionic species present in aqueous solution is relatively untouched, particularly when compared to the extensive study of the solid-state borate minerals. Analogous borate anions with aryl substituents have been reported, but are relatively few in number.^{34,35} The synthesis of borate salts containing an aryl borate anion with an organic cation has also been reported but few studies on such organoborate salts have been performed.³⁶ The systematic synthesis of organoborate anions using tetraalkylammonium cations has not been investigated.

1.6. Nuclear Magnetic Resonance (NMR) Spectroscopy

1.6.1 Introduction

NMR is a powerful and theoretically complex analytical tool. Although affected by many factors, it is worth emphasising that NMR information is obtained from observations at the specific nuclei being studied. The chemical environment of specific nuclei is decided from information obtained about those nuclei. Before applying NMR spectroscopy to the analyses of structures, certain properties of the nucleus must be considered.

1.6.2 Nuclear spin

Electrons, protons and neutrons can be imagined as though they were spinning on their axes. As NMR spectroscopy deals only with the nucleus we need only consider the case of protons and neutrons. In many atoms these spins are paired against each other such that the nucleus has no overall spin. However, in some atoms this is not the case, resulting in the nucleus possessing an overall spin. To determine whether a nucleus has spin, the following three statements may be considered.

- 1. If the number of neutrons and the number of protons are both even, then the nucleus has no spin. This renders the nucleus NMR inactive.
- 2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
- 3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

Both of these last two rules would give an NMR active nucleus as they both give nuclei with overall spin, often referred to as '*I*'. The overall spin *I* is important as quantum mechanics tells us that a nucleus of spin I will have (2I + 1) possible orientations. For example, a nucleus of spin $\frac{1}{2}$ will have two possible orientations.



Figure 11 Energy levels for a nucleus with spin quantum number 1/2

In the absence of a magnetic field, these orientations are of equal energy but if a magnetic field is applied then these energy levels split due to the alignment of

spin with or against the magnetic field. The lower energy level will contain slightly more nuclei due to the thermodynamics of the Boltzmann distribution. Nuclei are excited to the higher energy state by electromagnetic radiation. The energy emitted by these nuclei as they relax is observed during the NMR experiment.

1.6.3 Abundance

As described above, a nucleus must possess an overall spin in order to be NMR active. Taking silicon as an example, it has an atomic number of 14 and an average atomic mass of 28.08. With 14 protons and 14 neutrons the silicon-28 nucleus would have no overall spin and hence be NMR inactive. Silicon however also has an isotope of ²⁹Si. This isotope possesses a spin ½ nucleus and hence may be observed by NMR spectroscopy. The amount of this heavy isotope in existence is referred to as its 'natural abundance'. For reasons discussed above, the abundance of an NMR active isotope is clearly of great importance when considering the observations made during an NMR experiment. ²⁹Si has a natural abundance of 4.7%, making it difficult, but not impossible, to observe by NMR spectroscopy. The net result of this effect sets a practical limit to the sensitivity of NMR spectroscopy when applied to ²⁹Si.

¹¹B and ²⁷Al are also NMR active with natural abundances of 80.9% and 100% respectively.¹¹ With such a high percentage of boron and all the aluminium nuclei being NMR active, the issue of sensitivity is not readily applied to their spectra. Unlike ²⁹Si, which has a nuclear spin of $\frac{1}{2}$, ²⁷Al has I = 5/2 and ¹¹B has I = 3/2 and therefore a nuclear quadrupole moment. The peculiarities of quadrupolar nuclei raise many additional complications at the experimental and theoretical level. Due to their complexity, the theoretical issues are not discussed but are generally reviewed by Englehardt.⁸ The most striking effect of such quadrupolar nuclei is their quadrupole moment. This may cause severe line broadening, particularly in solid-state spectra, due to quadrupolar interactions. This leads to difficulties when interpreting results. However, the sensitivity and relaxation times of both ¹¹B and ²⁷Al, generally lead to good solution NMR spectra of these two nuclei.

1.6.4 Chemical shift and shielding

The magnetic field at the nucleus is not equal to the applied magnetic field. When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field as shown in **Figure 12**.



by circulating electron

Figure 12 Circulating electron, e, in an s-orbital, producing an opposing magnetic field.

The magnetic field at the nucleus, B, is therefore generally less than the applied field, B_0 , by a fraction σ .

$$\mathbf{B} = \mathbf{B}_0 \left(1 - \boldsymbol{\sigma}\right)$$

The easiest example of this is that of an s-orbital as shown in **Figure 12**. In some cases however, such as the π -electron in a benzene ring, the electrons create a magnetic field which enhances the applied field 'B₀' (i.e. the electric field produced by the electrons is in the same direction as the applied magnetic field, thus having a complementary effect). These observable effects are known as 'shielding' and 'deshielding' respectively.

The electron density around any given nucleus in a molecule varies according to the types of nuclei and the bonds in the molecule. This is often referred to as the chemical environment. As this environment changes, so does the strength and direction of the opposing magnetic field at the nucleus. The variation of the effective magnetic field at each nucleus is known as 'chemical shift' and is defined as the difference in the absorption spectrum of a particular nucleus from the absorption position of a reference nucleus.

1.6.5 Magnetogyric ratio

Having established that an NMR active nucleus possesses some element of spin they must correspondingly have a magnetic dipole.³⁷ Since atomic nuclei are associated with charge, a spinning nucleus generates a small electric current. Therefore, it has associated with it a finite magnetic field known as its magnetic dipole, μ . Since the nucleus is a mass rotating about an axis possesses a degree of angular momentum, *J*. In a magnetic field its axis of rotation precesses around the direction of the field, like a gyroscope. These effects are represented pictorially in **Figure 13**.³⁸



Figure 13A spinning charge with angular momentum, J, such as a
proton, gives rise to a magnetic dipole.

The magnetogyric ratio is the ratio of the angular momentum to the magnetic dipole and is characteristic for each nucleus. It is important when considering magnetic field strength to consider this characteristic factor. Considering a spin ¹/₂

nucleus, the difference between the two spin states, hv, in a magnetic field is proportional to the strength of the magnetic field at the nucleus, B, with a proportionality constant that is characteristic of the nucleus, the Magnetogyric ratio, γ .

$$\mathbf{E} = h\mathbf{v} = \frac{\gamma \mathbf{B}h}{2\pi}$$

Considering magnetogyric ratios, a stronger magnetic field as possible is preferred when using NMR spectroscopy as fine structure and splitting may be observed. By definition however, chemical shift does not change with increasing field strength.



SYNTHESIS & CHARACTERISATION OF AQUEOUS SILICATE SYSTEMS

2.1. Introduction

Tetraalkylammonium (TAA) cations may exert remarkable structure forming effects on the silicate anions present in crystalline tetraalkylammonium silicates and aqueous tetraalkylammonium solutions. Under appropriate conditions (Si concentration, TAA/Si ratio, temperature) mainly double four-membered ring cage anions, $[Si_8O_{20}]^{8-}$ are present in tetramethylammonium silicates,³⁹ and their solutions.^{40,41} This is often referred to as the "cubic octamer" structure and denoted as Q³₈. Double three-membered rings, [Si₆O₁₅]⁶⁻, ("prismatic hexamer", Q_{6}^{3}) dominate in crystalline solids and solutions of tetraethylammonium silicate.⁴² In crystalline tetrabutylammonium silicates however, double five-membered ring anions, [Si₁₀O₂₅]¹⁰⁻, ("prismatic decamer") are found to be present.⁴³ On the other hand, a broad distribution of different silicate anions has been found in sodium and potassium silicate solutions of comparable cation/Si ratio and Si concentration.^{44,45,46,47} It has been concluded that water-clathrate like frameworks are formed in the tetraalkylammonium silicate solutions, which causes the preferred formation of the double ring silicate anions. This conclusion has found strong support by the dependence on temperature,⁴⁸ and tetraalkylammonium cation concentration^{40,42} observed for the double ring silicate formation in tetraalkylammonium silicate solution.

In the study by Engelhardt and Rademacher, the quantitative distribution of silicate species in solution was estimated from the integrated intensities of the corresponding signals of the ²⁹Si NMR spectra.⁹ They found that in a solution containing a 1:1 ratio of Si: tetramethylammonium, the double four ring cubic silicate ion is highly predominant. By dropping the amount of tetramethylammonium cation however, and increasing the sodium value, the concentration of this cubic anion dropped sharply. Essentially they observed that in a solution with a cation to Si ratio of 1:1, the decrease in tetraalkylammonium concentration was accompanied by an increase in the distribution of different silicate anions. This was visible by the increasing number and intensity of the NMR signals for the various Q^n units.

Although it was noted that the diminution of the cubic silicate concentration starts with only slight replacement of tetramethylammonium cations by sodium cations, the cubic silicate was found to be increasingly stable during crystalisation.⁹ It was found that the complex cubic silicate Na_{1.6}H_{2.2}TMA_{4.2}Si₈O₂₀.4H₂O crystallises from the mixed tetramethylammonium/sodium silicate solution TMA_{0.3}Na_{0.7}Si.⁴⁹ Although other silicate ions are present in solution, the pure double four ring silicate is found to crystallise. This is not the only study on the distribution of silicate anions in solutions containing organic quaternary ammonium cations and alkali metal cations.^{50,51} Since these studies were made with ²⁹Si NMR however, the quantitative variation in the distribution of low-molecular weight species by the addition of alkali metal cations was not so clear.

This problem was addressed by Hasegawa et al. in 1987.⁵² They used the trimethylsilylation technique, described by Lentz,⁵ combined with gas-liquid chromatography to study the distribution of low-molecular weight silicate species in solution. They found that the distribution of soluble silicate anions in silicate solutions varies with the addition of sodium ions. As mentioned above, the recovery of the cubic octamer decreases with increasing Na : TAA ratio and becomes almost zero when the Na : TAA ratio is more than two. In other words, the cubic octamer is not formed when the sodium to TMA ratio is greater than 2:1. On the other hand it was found that recoveries of the monomer, dimer and linear trimer increase with increasing Na : Si ratio. These facts suggest that the depolymerisation from higher molecular weight species to lower molecular weight species occurs with the increase of the Na : Si ratio. This had been suggested before, ^{5,9,49,50,51,52} but perhaps the most important discovery of this study came from the realisation that water plays an important role in selective structure formation. In the case of mixed sodium/tetraalkylammonium silicate solutions, water may be consumed via hydration of sodium ions. This effect would be attributed to the destruction of the interaction between tetramethylammonium ions and water due to the hydration of sodium ions.

In addition to effects caused by increased sodium 'poisoning' as described above, it has also been shown that these tetraalkylammonium silicates also have a temperature dependence with regards to the species present in solution.⁵³ The

work of Kinrade *et al.* showed that the abundance of the cubic octamer Q_8^3 and prismatic hexamer Q_6^3 species decreases significantly as temperature is increased. In a variable temperature NMR experiment they found that as the temperature was increased the presence and nature of the smaller species were similar to those observed for alkali metal silicates. Thus the breakdown of the larger cyclic species to smaller silicate units is clearly affected by temperature.

Two more important observations were also made during this study. Firstly, it was noted that while other quaternary ammonium cations exhibit similar control over silicate speciation, the degree of control decreases as smaller alkyl groups are replaced by larger organic substituents. For example it was shown that although tetramethylammonium silicate contained only the Q_8^3 octamer, the degree of speciation control had disappeared when all four alkyl groups were C₄ or bigger. Secondly, it was noted that the addition of miscible organic solvents to tetraalkylammonium silicate solutions shifts the equilibria in favour of the Q_6^3 and Q_8^3 species. Again in the case of tetramethylammonium silicates, equilibria were displaced entirely toward the Q_8^3 species. In addition to this, it was shown that organic co-solvents cause the symmetric Q_6^3 and Q_8^3 cages to be favoured even in solutions containing very large quaternary ammonium ions (i.e., all substituents \geq C₄). In the absence of organic cations however, it was found that the addition of organic co-solvents simply increases the overall extent of oligomerisation with no species being uniquely favoured.

2.2. Aims

The purpose of this study is to further elucidate the observations outlined above. The relationship between larger TAA cations and the silicate speciation associated with their solution was to be investigated. By functionalising TAA cations with hydroxy alkyl groups, the structure directing effect (SDE) of these cations was to be investigated by ²⁹Si NMR.

Firstly, a number of hydroxy-functionalised TAA cations needed to be synthesised. Secondly, these TAA hydroxides were to be used to synthesise some previously unreported TAA silicate solutions. These solutions along with some previously reported TAA silicates were to be studied using NMR. Thirdly, the speciation of mixed alkali metal/TAA silicate solutions was to be investigated in a similar manner and fourthly, the rudimentary energetics of a few TAA silicate systems was to be explored.

2.3 Results and Discussion

2.3.1 Synthesis of tetraalkylammonium halide salts

Using the general reaction scheme shown below, it was possible to synthesise a number of quaternary ammonium halides. This method has been used in the synthesis of many such derivatives but the derivatives reported here are previously unreported.



Figure 14 General reaction scheme for the synthesis of quaternary ammonium salts.

With a variety of compounds, with the general formula R_3N and R'X, commercially available it was possible to synthesise a diverse series of tetraalkylammonium salts. Firstly the reactions of dimethylethanolamine, $[(CH_3)_2N(CH_2CH_2OH)]$, with methyl iodide, bromoethane and 1-bromopropane were each found to yield the corresponding ammonium salts with satisfactory elemental analysis. The three alkyl groups were chosen so as to provide a progressive series of functionalised tetraalkylammonium ions each of which contained a varying chain length ($R = CH_3$, CH_3CH_2 , $CH_3CH_2CH_2$). These reactions gave the desired tetraalkylammonium salts in relatively good yield (62 - 98%).

The reactions performed using methyldiethanolamine, same were [(CH₃)N(CH₂CH₂OH)₂] and triethanolamine, [N(CH₂CH₂OH)₃]. In general the reactions with methyldiethanolamine were successful. The methyl iodide and bromoethane reactions were found to proceed smoothly. The reaction with bromopropane was more troublesome however, and did not yield the pure tetraalkylammonium salt. This was most probably due to the relative effectiveness of the electrophile used for the alkylation and steric factors associated with the amine and the alkyl group. It is known that primary alkyl halides do undergo alkylation reactions well, but they are not as favoured as reactants as methyl or allyl halides. In addition to this, the steric hindrance of two ethanol groups on the attack of the propyl alkylating group, would have also contributed to the overall yield of the reaction. For these primary reasons the reactions with triethanolamine were also largely unsuccessful. The methylation of triethanolamine however, was found to give the quaternary ammonium salt, [(CH₃)N(CH₂CH₂OH)₃]I.

Ammonium salts containing benzene rings were also prepared. Dimethylethanolamine and methyldiethanolamine were reacted with benzylbromide to give the corresponding ammonium halide salts containing a substituted benzene ring. In addition to the ammonium salts containing one positive charge a diammonium ion was synthesised using two equivalets of dimethylethanolamine with one equivalents of [(ClCH₂CHOHCH₂Cl)] to give the di-ionic ammonium salt (Figure 15).



Figure 15 1,3-Bis-[*N*,*N*,*N*,-(2-hydroxy-ethyl)-dimethyl-ammonium]propan-2-ol dichloride

The only ammonium cations not synthesised in this manner were made using the epoxy compound, CH_2OCHCH_2OH , commonly known as glycidol. Reactions of R'₃N and glycidol were shown, in some part, to yield the tetraalkylammonium hydroxide.⁵⁴ An example of this reaction is shown in **Figure 16** : -



Figure 16 Quaternisation of dimethylethanolamine by an epoxy ring opening reaction in water.

The percentage of quaternisation was dependant on the structure of the amine. In the study by Lovett it was found that, increasing the number of 2-hydroxethyl groups and substitution of 3-hydroxypropyl for 2-hydroxyethyl decreased the percentage of quaternisation.⁵⁴ For this reason reactions of methyldiethanolamine and triethanolamine were not attempted. It was also shown that the use of water as a solvent for this reaction, suppressed oligomerisation of the ring opened epoxy group and promoted quaternisation of the amine to give the quaternary ammonium hydroxide.

The synthesis of such a hydroxy-functionalised tetraalkylammonium hydroxide was particularly beneficial. It was found, early in the investigation, that in order to synthesise a stable tetraalkylammonium silicate solution, the hydroxy form of the cation must be used. Quaternary ammonium halides, because they do not have an unshared electron pair on the nitrogen atom, cannot act as bases. Silica will only dissolve in strongly basic solutions.³ Quaternary ammonium hydroxides, however, are strong bases. In solution they exist entirely as quaternary ammonium cations and hydroxyl anions thus making them as basic as sodium or potassium hydroxides.

In the case of all cations, except the last example, this meant the use of an anion exchange resin to yield the corresponding tetraalkylammonium hydroxide. Although this method was successful, the use of such a resin was cumbersome and inefficient. This was largely due to the quantities of resin required to exchange a relatively small amount of the tetraalkylammonium halide. Despite taking the utmost care and precaution, the loss of a significant quantity of product occurred when the exchange resin was used. Hence, the direct synthesis of the tetraalkylammonium hydroxide (**Figure 16**) was of significant importance.

Although a relatively simple method of synthesis, a finite number of functionalised TAA hydroxides were chosen to proceed to the investigation of silicate solutions. This was primarily due to the need to allocate research time efficiently. Having synthesised a reasonable number of TAA hydroxides there was felt to be no need to over specialize in this area. Although many more TAA hydroxides may have been synthesised, the academic value of such an in-depth investigation was considered less relevant to the overall aims of the study.

2.3.2 Optimisation of nuclear magnetic resonance (NMR) techniques

Some relevant properties of the ²⁹Si nucleus are shown in **Table 8**.

Isotone	Natural	Spin	Magnetic Moment	Standard	

Isotope	Natural	Spin	Magnetic Moment	Standard	NMR
	Abundance		μ/μΝ	Reference ^a	Frequency ^b
²⁹ Si	4.7 %	1/2	-0.9609	Tetramethylsilane	49.7 MHz

Table 8Relevant properties of the ²⁹Si nucleus. ^a Assigned as 0ppm with
high frequency shifts given as positive. ^b Scaled so that the ¹H
resonance of TMS is at exactly 250 MHz.

The study of silicate solutions by ²⁹Si NMR has, associated with it, a number of advantages and disadvantages. As it is a spin half nucleus, resonances observed appear as sharp lines, hence individual chemical environments may be distinguished as long as they are not found at almost identical chemical shifts. Unfortunately, with the natural abundance of the NMR active nucleus being so low, the analytical limitations of the technique seem to be unavoidable. In the extensive work by Knight,⁴ the use of isotopically enriched silica along with doubly distilled deuterium oxide was applied in order to investigate the nature of silicate structures in aqueous solution. Such techniques were not practical or applicable during this study and hence the natural abundance technique was optimised as outlined below.

In any NMR spectrometer system, it is imperative that the magnetic field be as strong as possible, extremely stable and homogeneous over the sample volume. The strength of the applied magnetic field, B_0 , is limited by the superconducting magnet present in the system. Field stability and homogeneity may be observed and improved however, through the use of a deuterated solvent acting as a 'lock'. In the case of silicate solutions however, most common deuterated solvents were found to be immiscible. The use of D_2O was often not possible due to stability and mixing issues. As many silicate solutions are quite viscous the mixing of D_2O was often impractical. Also, the slight variation in pH caused by the addition of solvent may affect the stability of the solution being studied. To avoid these affects the use of a coaxial system was employed to run the NMR spectra of the silicate solutions. A 5mm O/D sample tube, containing D_2O , was placed inside a larger 10mm O/D NMR sample tube containing the sample to be studied. This system allowed the use of a deuterated solvent as a 'lock signal' without the problems associated with mixing and/or synthesis.

Although the use of a coaxial system improved field stability during the NMR experiments it also had an unwanted affect on the spectral window being observed. Glassware used as well as glass found in the NMR probe itself contains a significant quantity of ²⁹Si atoms. These may be observed in the NMR spectrum and appear as a broad hump ranging from -80 to -130ppm. Unfortunately, the signals associated with Q structural units found in silicate solutions are to be

found in the region -60 to -120ppm. It is for this reason that literature studies of silicate solutions almost always ignore the presence of the Q⁴ units, treating them as indistinguishable from signals generated from the glassware used. The use of synthetic quartz NMR sample tubes was found to reduce the intensity and width of this Q⁴²⁹Si signal. This, coupled with a mathematical subtraction programme, allowed the cosmetic removal of the 'glass hump' to give better insight into the structural nature of the solutions studied. The removal of said 'glass hump' meant that the relative intensities of the Q species present could be integrated. This allowed a degree of quantitative analysis on the solutions being studied. Due to the use of a mathematical subtraction program however, the information obtained may not be classed as fully quantitative as inevitably, slight discrepancies will occur during analysis. Therefore results discussed will be referred to as semiquantitative for Q^0-Q^3 signals. The analysis of any Q^4 signals will only be classed as qualitative. Although Q^4 signals can be observed to be present within certain silicate solutions, the relative intensity and hence abundance of such species may not be assessed mathematically. Therefore any reference to Q⁴ species will be made purely through inspection of the ²⁹Si NMR spectra and hence will only be a qualitative description of the speciation therein.

As highlighted above, ²⁹Si has a relatively low natural abundance. Hence, the use of larger sample volumes is beneficial when studying aqueous silicate solutions. It was found that the use of 10mm O/D coaxial quartz/quartz systems obtained on a Bruker AC 250 CP/MAS NMR spectrometer, operating at 49.7MHz for ²⁹Si, produced better spectra when compared to those obtained using a 5mm O/D coaxial quartz/PTFE system on a Bruker AVANCE 500 NMR spectrometer, operating at 99.4 MHz for ²⁹Si. This 'trade off' between magnetic field strength and sample volume meant that all aqueous silicate solutions were studied using the Bruker AC 250 CP/MAS NMR spectrometer.

In the silicate solutions previously studied, the relaxation time, T_1 , of the Si nuclei were found to vary depending on the sample composition.⁴⁰ In order to optimise the spectra, it was suggested in one case, that the samples should be pulsed only once a minute. This was calculated from the relaxation time multiplied by three.

Over the course of this study, it has been found that the number of scans used is more important than the pulse delay applied. This was shown by taking a single commercial sodium silicate solution and observing the spectra obtained using different combinations of pulse delay, D1, and number of scans, NS. It has been found that a spectra obtained from 125 scans with a pulse delay of 60sec generally looked the same as to ones obtained using the same number of scans with only a 5sec delay. It was found however, that spectra obtained from many more scans showed a much higher signal to noise ratio as well as allowing finer detail with regards to signal multiplicity to be observed. The most practical compromise between time and quality of spectra obtained was found to be ~1500 scans with a 3.0sec pulse delay. This was reduced further to a 1.5sec pulse delay when applied to tetraalkylammonium silicates as these have been shown to relax very quickly.⁴

2.3.3 Solution studies of aqueous silicates using ²⁹Si NMR

Unlike alkali metal cations, certain tetraalkylammonium (TAA) cations may exert specific structure directing effects on the silicate anions present in solution. This is clearly demonstrated by the ²⁹Si NMR of sodium and choline, $[(CH_3)_3N(CH_2CH_2OH)]$, silicate solutions as shown in **Figure 17**. Although the silica concentrations and cation/silica ratios of both solutions are comparable, a broad distribution of silicate anions is observed in the sodium silicate solution but a single anionic species predominates in the choline silicate solution.



Figure 17 ²⁹Si NMR spectra of (a) sodium silicate solution 1:1, 2.5M and (b) choline silicate solution 1:1, 2.43M

As described in Chapter 1, the appearance of the sodium silicate spectra is down to the overlapping of many resonance lines each of which corresponds to a specific silicate anion present in solution. In the case of the choline silicate solution an intense peak may be observed at -100ppm, which may be assigned to the cubic octameric anion, Q_{8}^3 . Past studies have investigated the speciation of silicate anions in a number of TAA silicate solutions. In addition to these, the TAA cations used in the synthesis of the silicate solutions described within this thesis are shown in **Figure 18**.



Figure 18TAA cations used in the synthesis of some known and some novel
quaternary ammonium silicate solutions.

Using these TAA hydroxides a number of quaternary ammonium silicates were synthesised and the speciation of silicate structures was investigated by 29 Si NMR. The results obtained are summarised in **Table 9.** In previous studies, only TAA silicates of 1 and 2 have been synthesised and investigated in this manner. TAA silicates of 3 - 10 have not been previously reported.

Cation	Cation : Si	$\approx c[SiO_2]$	pH	Q ⁰ (%)	Q ¹ (%)	Q ² ₃ (%)	Q ² (%)	Q ³ (%)	Additional	
				-73ppm	-81/82ppm	-83ppm	-87/91ppm	-100ppm		
1	- 1:1	1.02M	10	0	0	0	0	100	Q ⁴ ,	Accounts for all the Q ³ Signal observed Absent
1	1:2	5.1M	10	0	0	0	6	94	Q ²	Slightly broad signal observed Accounts for all the Q ³ Signal observed Absent
2	1:1	2.42M	10	Trace	Trace	Trace	Trace	100	Q4	Accounts for all the Q ³ Signal observed Absent

							×		5	
Cation	Cation : Si	$\approx c[SiO_2]$	рH	Q⁰(%) -73ppm	Q¹ (%) -81/82ppm	Q ² 3 (%) -83ppm	Q² (%) -87/91ppm	Q³ (%) -100ppm		Additional
2	1:2	4.1M	10	Trace	Trace	0	15	85	Q^2 \square Q^4	Slightly broad signal observed Accounts for all the Q ³ Signal observed Absent
2	2:1	1.04M	10	Trace	0	0	Trace	100	[]] Q⁴	Accounts for all the Q ³ Signal observed Absent
3	1:1	1.12M	10	9.4	5.7	3.8	20.8	60.4	Q4	Accounts for all the Q ³ Signal observed Absent
4	1:1	0.91M	10	6	13	6	31	44		Apart from Q^0 , no specific structures can be identified from the spectra

Cation	Cation : Si	≈ c[SiO2]	pН	Q ⁰ (%)	Q ¹ (%)	Q ² ₃ (%)	Q ² (%)	Q ³ (%)		Additional
				-73ppm	-81/82ppm	-83ppm	-87/91ppm	-100ppm		
8	-1:1	0.7M	10	Trace	Trace	Trace	58	42		No specific structures can be identified from the spectra
5	1:1	1.6M	10	4.5	0	0	15	79.5	Q ²	Slightly broad signal observed
		1 (1992) 2010 (1997) (1992) (1	503.0ve		2. 1005 2. 2.	A25			0 ⁴	Accounts for all the Q ³ Signal observed
9	1:1	2.7M	10	Trace	Trace	0	31	69		Accounts for 8% of the signal observed for Q^2 Accounts for 23% of the signal observed for Q^2
				2					Q4	 Accounts for all the Q³ signal observed Absent

Cation	Cation : Si	≈ c[SiO2]	pH	Q ⁰ (%)	Q ¹ (%)	Q ² ₃ (%)	Q ² (%)	Q ³ (%)		Additional	
				-73ppm	-81/82ppm	-83ppm	-87/91ppm	-100ppm			
6	1:1	3.97M	10	Trace	Trace	0	10	90	Q^2 Q^2 Q^4	Broad signal observed Accounts for all the Q ³ Signal observed Absent	
7	1:1	2.42M	10	4	0	0	5	91	↓ <p< td=""><td>Accounts for 5% Accounts for all the Q³ Signal observed Absent</td></p<>	Accounts for 5% Accounts for all the Q ³ Signal observed Absent	
10	1:2	3.01M	11	3	Trace	Trace	14	83	Q^2 Q^2 Q^4	Slightly broad signal observed Accounts for all the Q ³ Signal observed Absent	

As outlined in Chapter 1, the use of the Lentz method to identify specific structural units within a silicate solution has led to a better understanding of the speciation of anions therein. Using the optimised NMR techniques described in section 2.3.2, the silicate structures found within a range of TAA silicate solutions was investigated. Although the specific chemical shift of many silicate anions is known, as outlined in Table 1, the resolution of the ²⁹Si NMR experiment meant that a comprehensive analysis of all anionic structures present within many of the silicate solutions was not possible. For this reason, **Table 9** refers to the speciation and relevant intensity of specific regions within the NMR spectra. Although these regions are rather broad, specific structural detail has been highlighted when possible. For example, the inclusion of the cyclic trimer, Q_{3}^{2} , in **Table 9** occurs due to the isolated chemical shift at which this species occurs. Thanks to the detailed work of Engelhardt et al., the only silicate species which has been shown to have a resonance at -83ppm (10ppm upfield of Q^0) is the Q^2_3 species. Therefore, the presence of this Q^2_3 species may be confirmed by the observation of a ²⁹Si resonance at this specific chemical shift. In the same way, the absence of this resonance would automatically imply that none of the cyclic trimer species was present in the solution being studied.

A similar reasoning may be applied to the additional structural information displayed in **Table 9**. The sharp resonance occurring at a chemical shift of -100pm, is caused by the presence of the Q_8^3 species. Again this is known from previous studies. The ²⁹Si NMR spectra of a silicate solution containing almost solely the cubic octameric species would show quite different character from that of a polydispersed silicate solution (**Figure 17**). The sharpness and intensity of the resonance associated with the Q_8^3 species means that the relevant abundance of this silicate structure could be semi-quantitatively determined even when additional resonances were observed within the Q^3 region. In addition to this and where possible, the semi-quantitative analysis of the prismatic hexamer, Q_{6}^3 , and cyclic tetramer, Q_{4}^2 , has also been highlighted. The data displayed in **Table 9** is presented in an order of increasing cation complexity/functionality and does not easily convey the trends shown. Therefore the observations made are discussed below.

2.3.4 Tetramethylammonium (1) and choline (2) silicates

Tetramethylammonium (TMA), [(CH₃)₄N] and choline, [(CH₃)₃N(CH₂CH₂OH)], silicate solutions have been shown to consist of mainly Q_8^3 species.^{39,55,56} The primary observation made when analysing TMA and choline silicate solutions with a cation/silicon ratio of 1:1 was the intensity and abundance of the Q_8^3 silicate anion in solution. In both cases the anion was the by far the major structure present in solution. In the case of TMA silicate, it is reasonable to suggest that, the only silicate structure adopted in solution is that of the cubic octamer. This seems a reasonable assumption as not even trace amounts of any other Q species could be observed within the NMR spectra. In addition to this, the presence of Q^4 species is also extremely unlikely on the basis of qualitative analysis of the ²⁹Si spectra obtained. Although not a new observation, such a sample serves as a useful example of the structure-directing effects of TAA cations upon silicate speciation.

In the case of the choline silicate solution, the Q_{8}^{3} anion is found to be dominant within solution. Apart from the presence of trace amounts of smaller Q species, the solution, it may be argued, contains only the cubic anion. This was also found to be the case should the cation/silicon ratio exceed 1:1. i.e. the ratio of cation/silicon was greater than 1.This observation was of particular interest when compared with past studies on cation/silicon ratios in sodium silicate solutions. It has been shown that the ratio of sodium/silicon directly affects the speciation of anions present in solution.^{8,57} In studies by Engelhardt *et al.* and Kinrade *et al.* it was concluded that depolymerisation of the silicate anions present in alkali metal silicate solutions increases with decreasing cation/silicon ratios and increasing silica concentration.^{8,53} In these studies, a series of sodium silicate solutions with cation/silicon ratios varying from 0.5:1 up to 40:1 were investigated by ²⁹Si NMR. It was shown that in a solution with a large excess of sodium ions to silicon atoms, the monomeric Q⁰ species became increasingly favoured up to a point whereby almost pure silicic acid was present in solution. Although the ratios of TAA/silicon are not comparable to the extreme example of a 40:1 sodium/silicon solution, the effect of excess cation on silicate speciation does appear to be quite different. Rather than seeing a shift towards the smaller monomeric species, as with sodium silicates, the choline silicate containing excess cation/silicon shows an unchanged monodispersed solution containing only the Q_8^3 anionic species. This supports the idea of this TAA cation having a pronounced SDE on silicate speciation.

Following on from such a line of investigation, the effect of excess silicon/cation was also explored by observing the distribution and intensity of Q species in solution with NMR. The situation whereby the cation/silicon ratio is less than 1:1 may be likened to the composition of most commercially available alkali metal silicate solutions. Using a similar format to that shown in **Table 9**, the composition of a number of commercially available alkali metal silicate solutions is summarised in **Table 10**. Studies into the speciation of alkali metal silicate solutions are amongst the oldest and most extensive in this field of chemistry and have been thoroughly discussed in Chapter 1. **Table 10** therefore, merely serves to highlight two important trends. Firstly, regardless of concentration, cation or cation/silicon ratio, alkali metal silicates show a wide distribution of silicate species to be present in solution. Secondly, that Q^4 species are present and may be qualitatively observed by NMR spectroscopy.

Comparison of TMA and choline silicate solutions, with a cation/silicon ratio of 1:2, with an analogous sodium silicate solution, shows some interesting differences amongst the speciation of silicates therein (**Figure 19**). The observation of Q^4 species in the sodium silicates has been explained as arising from increased polymerisation of smaller silicate anions due to the higher silica content when compared to the number of alkali metal cations present. The distribution of species remains consistent with the patterns observed for all alkali metal silicates. While the smaller anionic species may vary in quantity, the majority of silicate species seem to be Q^2 and Q^3 structures. This is not the case with TMA silicate solution (**Figure 19**) or choline silicate solution.

Cation	Cation : Si	$\approx c[SiO_2]$	pН	Q ⁰ (%)	Q ¹ (%)	Q ² ₃ (%)	Q ² (%)	Q ³ (%)	Additional	
				-73ppm	-81/82ppm	-83ppm	-87/91ppm	-100ppm		
Na	1:1.03	7.01M	12	2.3	14.1	4.6	44	35	Q^4	Trace
Na	1:1.29	7.75M	12	0.8	11	1.6	45.6	43.2	Q^4	Present
Na	1:1.425	7.88M	12	Trace	10.2	1	42.5	46.5	Q^4	Present
Na	1:1.65	6.53M	12	0	4	0	30	66	Q^4	Present
Na	1:1.95	8.9M	13	1.8	9.1	Trace	34.5	52.7	Q ⁴	Present
K	1:1.12	8.2M	12	1	10	3	44	40	Q^4	Trace
K	1:1.6	5.17M	12	Trace	12	Trace	34	54	Q^4	Trace

Table 10A summary of silicate speciation within a number of commercially available silicate solutions


1

Figure 19 ²⁹Si NMR spectra of (a) Sodium silicate solution with a sodium/silicon ratio of 1:1.95 and (b) TMA silicate solution with a TMA/silicon ratio of 1:2.

The difference in speciation when comparing the TAA silicates to the sodium silicate example is clear to see. In 1:2 ratio solution, [Si₈O₂₀]⁸⁻ is still the dominant structure although it may exist in protonated forms with a reduced charge e.g. $[Si_8O_{20}H]^7$, $[Si_8O_{20}H_2]^{6-}$, $[Si_8O_{20}H_3]^{5-}$, etc., and these forms are likely to be indistinguishable by ²⁹Si NMR. The 'excess' SiO₂ or Si(OH)₄ in these solutions may be solubilised as silicate anions by acting as Brønsted acids to the $[Si_8O_{20}]^{8-}$ anion. Thus additional Q⁰ to Q^4 species should be observable due to condensation of the anion [Si(OH)₃O]⁻ with neutral silicate moieties. This was not the case however, and the only observable difference between these higher Si : cation ratio solutions and those described in the preceding paragraphs is the appearance of a broad Q^2 environment accounting for a small fraction of the observable silicon species. Another possible explanation may be found by considering larger silicate species. Should the increase in silicon content lead to a growth in the number of larger polymeric anions then a O^4 signal. similar to that described in the case of sodium silicate, should be observed. Again this was not the case and hence the nature and structure of the excess silica content may only be assumed from the spectroscopic evidence. It seems apparent that the additional silica present in the higher modulus solutions is present as predominantly Q_{8}^{3} species with a smaller fraction forming an array of Q^{2} type species in solution. Why such Q^2 species should be formed is unclear, but the experimental evidence clearly supports the idea that TMA and choline cations exert strong SDE on silicate speciation in solutions containing an excess of silica compared to the cation content.

2.3.5 Functionalised TAA cations with longer alkyl or aromatic groups, (3), (4),(8) and (9)

Comparison of these early examples with those cations possessing longer alkyl chains agrees with observations made previously in the literature.⁸ Engelhardt describes the observations made when studying tetramethyl-, tetraethyl-, tetrapropyl- and tetrabutylammonium silicate solutions using ²⁹Si NMR. The observed trend showed

an increase in silicate speciation as the alkyl chain lengths became larger. TMA silicate, as discussed, showed predominantly the Q_8^3 species but as the chain lengths grew so did the diversity of silicate species found within solution. This continued up to a point whereby the distribution found within a tetrapropyl- or tetrabutylammonium silicate was comparable to that found within an alkali metal silicate solution. This trend was mirrored in the new TAA silicate solutions shown in **Table 9**. Comparison of the choline (2) silicate with silicates of (3) and (4) illustrates this fact well (**Figure 20**).



Figure 20 ²⁹Si NMR spectra of (a) choline (2) silicate 1:1 and (b) ethyl-choline (3) silicate 1:1

Although the steric and structural differences between these cations are subtle, their effect on silicate speciation is pronounced. The ethyl derivatised choline cation (3) still shows a tendency towards the Q_8^3 anion. However, the presence of a substantial amount of Q^2 species along with clear quantities of Q^0 , Q^1 and Q_3^2 highlights the increased diversity of silicate species expected from a TAA cation with a longer alkyl chain (Figure 20). This effect was found to be more dramatic in the case of the propyl derivatised choline cation (4). Despite being only subtly different from cations (2) and (3), all degrees of structure control were found to have been lost when the TAA silicate was studied using NMR. No specific structural units could be identified from the spectral data obtained, which resembled that of a comparable sodium silicate solution. A broad distribution of species was found to be present suggesting that all the SDE of this particular TAA had been lost. Although such effects were likely from previously described studies, the severity and rapid loss of structure control was still unexpected to such a degree when considering the small differences between the cations being looked at.

With subtle changes to the cations structure, functionality and size causing such pronounced effects on anionic distribution, the expected speciation found in TAA silicates, 1:1, of (8) and (9) could be postulated. In the case of the aromatic choline derivative (8) all structure directing effects would most likely be lost and an alkali metal type distribution observed. This was found to be only partly true however, as the speciation of silicates did not mirror that of an analogous sodium silicate solution. The distribution of Q^2 and Q^3 species was 'typical' of an alkali metal silicate solution. Q² species were found to be more abundant in solution when compared to Q³ but no specific structures of either type could be identified from the observed spectra, which showed only broad peaks in the relative regions of the spectral window. Interestingly, the distinct lack of smaller Q species, Q⁰ to Q²₃, was an unexpected and previously unreported effect of using such an aromatic derivatised TAA in a silicate solution.

was supported by the study of a dihydroxy-aromatic functionalised TAA silicate (9). The absence of smaller anionic structures was again found suggesting that aromatic TAA cations possess a degree of structure control on silicate speciation. In addition to this, the specific structures accounting for the Q^2 and Q^3 signals could be assigned from the spectral information obtained. As highlighted in **Table 9**, the predominant structure found in the silicate of (9) is the Q^3_8 octameric species. Additionally the Q^3_6 hexamer and Q^2_4 tetramer were present and accounted for 23% and 8% of the species found in solution respectively.

As both these TAA silicates were previously unreported their effect upon silicate speciation in solution was previously unknown. As described above however, it seemed reasonable to suggest that they would display little or no control on the structural units found in their silicate solutions as they are both larger and more complex than the ethyl and propyl choline derivatives discussed above. In the case of the TAA silicate (8), the lack of smaller Q species was novel and hinted at the idea of some structure control taking place, namely a preference for larger silicate species to form in the presence of this cation. This observation was further supported by the speciation found in the TAA silicate (9), where a similar lack of smaller species was seen. This solution also showed a predominance of the Q_8^3 octamer which, despite the size of the alkyl groups present, suggested that structure control was indeed taking place. The SDE however, were not towards a monodispersed silicate solution, but more towards the formation of larger silicate species in solution.

2.3.6 Hydroxy-Functionalised TAA Silicates, (5), (6) and (7)

Having discussed the effects of increasing chain length and aromatising the TAA cation, the effects of the polyhydroxy TAA cations upon silicate speciation were not predictable. Comparison of the propyl derivatised cation (4) with the dihydroxy functionalised cation (5) would seem acceptable as the relative chain lengths in both quaternary ammonium compounds are similar. This led to a prediction that the dihydroxy cation (5) would show little or no SDE and that the silicate species present in this solution would be varied and diverse, ranging from Q^0-Q^3 . This was not the case however, and the speciation found in these two solutions was very different. Rather than showing a broad distribution of many Q species, as found in the propyl derivative (4), the dihydroxy cation (5), showed the majority of silicate units to be of the Q³ type, with the Q³₈ octamer accounted for the entire Q³ signal suggesting that rather than having no SDE, the cation (5) favoured the formation of the octameric species as previously obtained with TMA and choline.

Analysis of additional hydroxy functionalised TAA silicates, (6) and (7), showed more unexpected speciation to be present in their solutions. Despite the increased alkyl chain length, both TAA silicates contained predominantly the Q_8^3 structure, with the octamer accounting for at least 90% of all silicates species present in solution. These observations are against the trends discussed in the preceding paragraphs which lead to a simple suggestion. It appears that, as previously reported, increasing alkyl chain length, counteracts the SDE of TAA cations in silicate solutions. But, should these longer alkyl chains be hydroxy functionalised, then the degree of structure control increases, favouring once again the Q_8^3 species. The degree of structure control is not as great as in the case of TMA or choline silicates but, although measurable, the amount of Q^0 , Q^1 and/or Q^2 present in solution is small enough to justify the idea that the cations (5), (6) and (7) exhibit SDE towards the Q_8^3 species in solution. The suggestion of hydroxy-functionalisation favouring the Q_8^3 silicate species is further supported by the SDE observed for the dication (10). The formation of a stable TAA silicate solution containing a large and dicationic species lends itself to the potential of hydrogen bonding within silicate solutions being very important in the structure control seen and described above. It may be expected that such a sterically bulky cation would show little or no structure control but the inclusion of the hydroxy groups seems to favour once again the octameric species, which accounts for the large majority of anionic structures present.

2.3.7 X-ray studies

The interactions between TAA cations, silicates and the water present as solvent has been discussed since the first TAA silicates were synthesised. Wiebcke et al. obtained first crystal structure of TMA silicate only 11 years the ago as [NMe₄]₈[Si₈O₂₀].65H₂O.⁵⁸ The importance of the interaction between the clathrate structure of water, the organic cation and the silicate species has been further described by Shantz et al.⁵⁹ All the solutions described above may be considered as mixed heteronetwork structures which are formed by both covalent and non-covalent interactions between the water, inorganic and organic species. In many of the solutions described, the predominant silicate species found is that of a silicate cube, Q_{8}^{3} , which in the case of the 1:1 solutions certainly is charge compensated by the cationic organic molecules present in solution. Single crystal studies obtained from solutions of (1) have shown that these silicate cubes are bridged by water molecules which hydrogen-bond to other water molecules. In the case of TMA, the small cation is encased within a water clathrate structure. The structure of the crystal obtained from the solution of (1), [NMe₄]₈[Si₈O₂₀].69 H₂O, is shown in Figure 21 and has slightly more waters of crystallisation than that reported by Wiebcke et al.58



Figure 21 Crystal structure of [NMe₄]₈[Si₈O₂₀].69 H₂O

The structure shown in Figure 21 represents the common structure found within TMA silicate 1:1 crystals. The triclinic crystal system contains a symmetric central cubic structure. As shown, the oxygen bridges between interstitial silicon atoms are not straight but rather, slightly bent. The bond angles between, for example Si3-O8-Si4, are measured as 150.5° as opposed to a straight bridge which would measure 180°. This in turn allows each silicon atom to adopt a tetrahedral geometry with the O5-Si2-O4 bond angle measured as 110°. The Si-O⁻ bond lengths are found to be slightly shorter than those found within Si-O-Si bridges. This may have been expected as the increased electron density upon the negatively charged oxygen may give partial double bond character to the sp³ hybridised silicon causing a shortening of the observed bond length. This is found to be the case at each silicon centre. Each tetrahedral TMA cation is found to be comparable with the C-N bond length and C-N-C bond angles all measuring the same within the parameters of experimental error. Comparison of this structure with that reported by Wiebcke et al. is limited owing to the amount of data published within the initial study.⁵⁸ Both the crystal systems reported are triclinic and possess the same space group, P1. However, owing to the different number of waters of crystallisation, 69 c.f. 65, the unit cell dimensions, as expected, are slightly different. As there is no discussion of bond length or bond angles within Wiebcke's study further comparison is not possible.

2.3.8 TAA cation-water and TAA cation-silicate interactions

Although the observable effects of TAA cations within silicate solutions have been discussed above, in order to understand the nature of such chemistry, attention must be applied to the various interactions within solution. The structure control exerted by certain TAA cations seems to be unpredictable but the stability of silicate species formed may be explained by considering two principal factors. Primarily, strong hydrogen-bonding between the water molecules and the silicate species are responsible for stabilising the silicate hydrates formed. Although secondary in nature, the forces between the cationic organic molecules and the water molecules and anionic silicate species are also important. Hydrogen-bonding interactions along with electrostatic interactions and van der Waals contacts influence how the organic molecules organise themselves in the solvent. This organisation is the most likely cause for the relative stability of structures observed.

For example, the TMA silicate shown in **Figure 21** contains a small organic cation with relatively high charge density. The cation may arrange itself within the solvent molecules of the solvated anions, hereafter referred to as the solvent shell, more easily than a larger organic cation, i.e. there is no preferred orientation of the cation in the solvent. The coulombic force generated between the cation and the silicate cube plays an important role in the stabilisation of silicate hydrates.⁵⁹ It follows on from this suggestion, that a cation with larger organic, hydrophobic substituents will arrange themselves so as to minimise their unfavourable interaction with the polar water molecules. This change in orientation will not only affect the electrostatic interaction between silicate cage and organic cation but also the nature of the hydrogen-bonding present, as the solvent shell must adapt to the adopted geometry of the cation. This process may destabilise the silicate hydrate and hence lead to the observed loss of structure control.

Considering the above hypothesis, the increased structure control obtained by hydroxy functionalisation of larger alkyl groups may be better reasoned. The interaction between the polar water molecules and hydroxy functionalised alkyl chains will clearly have a stabilising affect to the dynamics of the hydrogen-bonded clathrate system described above. Thus, the structure control regained by hydroxy functionalisation of larger alkyl groups, it may be argued, is caused by the favourable cation-water interactions present which provide a stabilising effect on the silicate species found in solution.

2.3.9 Silicates containing mixed cations

As described by Hasegawa *et al.* the distribution of soluble silicate anions in TMA silicate solutions varies with addition of sodium ions.⁵² In this study it was also suggested that should the sodium/TMA ratio exceed 2:1 then no Q_8^3 would be present in solution. The effect of 'sodium poisoning' on some of the new TAA cation silicates discussed earlier was not previously investigated. As commercially available sodium silicates were readily available the change in silicate speciation upon addition of TAA cations was to be investigated.

Although section 2.3.3 describes ten different TAA cations, the focus of the investigation from here on centres around three particular cations, TMA(1), choline(2) (2,3-dihydroxy-propyl)-(2-hydroxy-ethyl)-dimethyl-ammonium and (DPHEDMA) (7). The commercial silicate used contained a sodium/silicon ratio of 1.425:1 and displayed wide range silicate speciation as is characteristic of alkali metal silicates (Figure 22a). TAA cations were added so as to effect a change in cation/silicon ratio resulting in a 1:1 solution. The change in the silicate speciation was observed by NMR (Figure 22b). The addition of sodium ions to this solution should show an increased Q^0 signal since, as described previously, the addition of alkali metal cations favours depolymerisation of the larger silicate species towards the smaller Q units. Upon initial inspection a similar effect is shown by the addition of TAA cations. In the case of TMA and choline, the Q^2 and Q^3 signals clearly account for considerably less of the observed speciation present in solution. Whereas, in all three cases, the observable Q⁴ signal present in the starting solution has clearly been removed supporting the idea that there are no larger Q^4 species present in the 1:1 solutions.



Figure 22 ²⁹Si NMR of (a) commercial sodium silicate 1:1.425 and (b) the same silicate with added TAA cations to give a 1:1 solution.

More interesting is the appearance of greater fine structure upon the addition of TAA cations to the sodium silicate solution. This is best illustrated by the appearance of a sharp peak at -100ppm, associated with the Q_8^3 octamer. Although the octamer is present in all three solutions, the speciation of silicate anions observed was largely unexpected at this (sodium/TAA/silicate) ratio. The solutions shown in **Figure 22b** contain a cation/silicon ration of 1:1. To give this ratio, a quantity of TAA hydroxide in aqueous solution was added to a commercially available sodium silicate which contained a sodium/TAA ratio of 2.09:1. In the study by Hasegawa *et al.*, the effects of sodium poisioning are described as being destructive to the Q_8^3 species and with a sodium/TAA ratio exceeding 2:1 no Q_8^3 would be expected.⁵² A sharp resonance associated with the octamer was observed however, and although present with varying degrees of intensity, the cubic structure was found to be present in all three solutions (**Figure 22b**). The distribution of silicate species present within the starting sodium silicate and the mixed sodium/TAA solutions is highlighted in **Table 11**.

The Q_8^3 species was found to be least abundant in the mixed sodium/choline silicate solution which, although present, accounted for only 2.5% of the total silicate species observed. The most predominant structures found within this solution were of the Q^2 type which accounted for 43% of the observed speciation. Similarly, in the mixed sodium/TMA silicate the Q^2 species were most abundant and again accounted for 43% of the observed speciation. Similarly, in the mixed sodium/TMA silicate the Q^2 species were most abundant and again accounted for 43% of the observed speciation. The increased intensity of the Q_8^3 signal however, suggested that the ocatmeric anion was present in considerably greater concentration than in the sodium/choline silicate solution. The octamer accounted for almost four times the number of silicate species present in solution, consisting of 8% of all silicate anions therein. The most pronounced effect on silicate speciation was observed upon addition of the trihydroxy-cation DPHEDMA (7). Unlike the previous two examples, there was found to be little increase in the number of smaller Q^n species present in solution of the starting sodium silicate. Additionally, Q^2 species accounted for a smaller number of anionic structures whereas no Q^4 structures were observed at all.

Cation	Cation : Si	≈ c[SiO2]	pH	Q ⁰ (%)	Q ¹ (%)	Q ² ₃ (%)	Q ² (%)	Q³ (%)	Additional	
Na	1:1.425	7.88M	12	Trace	10.2	1	42.5	46.5	Q ⁴	Present
Na & (1)	1:1	2.7M	11	8	16	10	43	23		Accounts for 8% of the total spectra observed
									Q^4	Absent
Na & (2)	1:1	2.0M	10	12	21	9	43	15		Accounts for 2.5% of the total spectra observed
									Q^4	Absent
Na & (7)	1:1	3.0M	11	3	9.5	3	37	47.5		Accounts for 24% of the total spectra observed
									Q^4	Absent

Distribution of silicate species present in the starting sodium silicate and the three sodium/TAA mixed silicates

Table 11

Of the Q^3 signal observed, over half of these species were the Q^3_8 octamer which contributed to 24% of all silicate species observed. This suggests that the depolymerisation of larger silicate species does occur, but rather than an increase in the number of smaller, Q^0 , Q^1 and Q^2 species, the Q^4 structures which were present have formed additional Q^3 units, a large amount of which are the Q^3_8 anion. The formation of the Q^3_8 species in all three cases supports the role of TAA cations as structure directing agents when they are added to a sodium silicate. A newly observed effect of such TAA cations is their ability to influence the speciation of silicates even when the sodium/TAA ratio exceeds 2:1.

A similar explanation to that offered for the SDE of hydroxy functionalised TAA cations may be applied to explain these observations. As discussed previously, water plays an important role in the stability of silicate hydrates. In the case of mixed sodium/TMA silicates however, it has been reported that, water may be consumed via hydration of sodium ions.⁵² The interaction of water with the sodium ions, it has been argued, disrupts the interaction between the TAA cation. the silicate anion and the solvent shell. This may be observed by the formation of lower molecular weight species within solution at the expense of the Q³₈ octamer. Because of this it was reasoned that all structure control would be lost when sodium is present in more than twice the quantity of TAA. This has been shown not to be the case however, with all three mixed sodium/TAA silicate solutions showing a quantity of the Q_8^3 octamer to be present. A possible explanation for these observations may be found by considering the role of the hydroxy functionalised alkyl groups on the TAA cations. As the hydrogen bonding between the solvent shell and silicate anion is affected by sodium ion concentration, it seems reasonable to suggest that the hydroxy groups present on the functionalised TAA cations may adopt a similar stabilising role to that of the consumed water molecules described by Hasegawa et al. The effects of this alternative hydrogen bonding between the hydroxy functionalised TAA cation and the depleted solvent shell may serve to stabilise the Q38 octameric anion as well as the larger Q species initially present. Hence, the hydroxy functionalised TAA cations may now possess a two fold stabilising effect. The coulombic interactions $(N^{+...}O)$ serve to stabilise the anionic silicate structures, particularly the Q_8^3

octamer. The hydrogen bonding however, may interact and stabilise the solvent shell, counter acting the effects of sodium poisioning. It would therefore follow, that a multi functionalised TAA cation would show the greatest degree of structure control and stabilisation upon a mixed sodium/TAA silicate.

This was found to be the case as the TAA cation, DPHEDMA (7), showed the greatest quantity of the Q_8^3 octamer to be present when added to a commercial sodium silicate. As described above, the speciation present in this mixed solution showed quite different character when compared to the mixed sodium/TMA and sodium/choline silicates. Following from this, it may be expected that the quantity and intensity of the Q_8^3 octamer would decrease as the TAA functionalisation was reduced, being lowest for the mixed sodium/TMA silicate solution. This was not found to be the case however, with the sodium/choline silicate showing the least Q_8^3 character. This inconsistent result may be due to the low silica concentration present in the sodium/choline solution. It has been shown, that in a sodium silicate solution of decreasing silica concentration, the speciation of anionic structures favours smaller Q^n species to be present.⁵² The concentration of silica in the mixed sodium/choline is relatively low, and may explain the distribution of silicate species observed. A sodium silicate of comparable silica concentration may similarly be expected to show predominantly smaller Q^n species. The structure control provided by the addition of the choline cation has shown itself to be present in the form of a small percentage of Q³₈ formed. The effect may be less pronounced however, due to the dilute nature of the silicate solution and the sodium content therein.

The newly observed effects of structure control on sodium silicate solution upon addition of TMA hydroxide may also be in some part due to the water content of the final solution. The TMA hydroxide was added as a 25% w/w solution to the commercial sodium silicate. The mixture formed was not stable and readily formed a precipitate which was found to re-dissolve upon addition of water. The addition of water to the solution may provide sufficient water molecules to both hydrate the sodium ions while maintaining the solvent shell around the TMA cation. Thus the silicate structure remains stabilised but also speciation is shifted towards the Q_{8}^{3} anion due to the SDE of the TAA cation.

A similar observation was made when studying a synthetic silicate containing mixed cationic content. A solution of sodium hydroxide was mixed with a solution of TMA hydroxide so that the molar ratio of sodium/TMA was 1:1. The mixed solution was then used to synthesise a mixed silicate containing a cation/silica ratio of 1:1. The resulting solution showed a broad distribution of silicate species to be present with those of a Q^2 nature being most abundant. Due to the quantities of TMA present however, a substantial quantity of the Q_8^3 anion was observed which, even in a solution containing equal quantities of sodium, was not expected due to the poisoning effects described in the literature. It seems reasonable to therefore suggest that, although sodium poisoning will affect silicate speciation, the silica concentration and nature of the TAA cation may counteract the loss of structure control observed in earlier studies.

The effects of using a combination of TAA cations to produce a mixed silicate solutions had not previously been studied. Therefore a series of TAA silicate solutions were prepared and analysed by ²⁹Si NMR. In all solutions studied the cation/silicon ratio was a constant 1:1, but the nature of the cation mixtures varied with respect to each other. The solutions studied are shown in **Table 12**.

Silicate	TMA	Choline	DPHEDMA	SiO ₂
11	1	1	0	2
12	1	4	0	5
13	1	0	1	2
14	1	0	4	5

 Table 12
 Cation mixing ratio's within the mixed TAA silicate systems

These solutions showed the distinctive speciation associated with most of the TAA silicates described earlier. The Q_8^3 octamer was exclusively present in solutions (11), (12), and (13). Solution (14) showed trace amounts of Q^0 to be present but considering the series overall, the effect of mixing these three TAA cations to synthesise TAA silicates showed no alternative character to their mono-cationic derivatives discussed previously. There would therefore seem to be no discernable interactions taking place within such solutions that have not been discussed in the previous section.

2.3.10 The effect of temperature on silicate speciation

The relationship between sodium/TAA content within mixed silicates has already shown some interesting, newly observed effects. From the same study which described the effects of sodium 'poisoning', it was also shown that tetraalkylammonium silicates have a temperature dependence with regards to the species present in solution.⁵³ The work of Kinrade *et al.* showed that in TMA silicate, the abundance of the cubic octamer, Q^3_{8} , and prismatic hexamer, Q^3_{6} , species decreases significantly as temperature is increased. In a variable temperature (VT) NMR experiment they found that as the temperature was increased the presence and nature of the smaller species were similar to those observed for alkali metal silicates. Thus the breakdown of the larger cyclic species to smaller silicate units is clearly affected by temperature. To investigate this further, solutions of TMA, Choline and DPHEDMA silicate were synthesised with a cation/silicon ratio of 1:1. The effect of temperature upon silicate speciation, within these solutions, was investigated by ²⁹Si NMR.

The change of silicate speciation within a TMA silicate is quite pronounced (Figure 23). In this 1:1 solution, as described previously, the single silicate structure found is that of the Q_8^3 octamer (Figure 23a). This solution was then heated on a water bath at 75°C for 1hour. The silicate speciation was found to have significantly changed within this time period (Figure 23b). The distribution of silicates found within the post heated solution showed a large degree of thermal rearrangement had taken place. Unlike the monodispersed starting solution, the resultant speciation shows a profile more closely associated with that of an alkali metal silicate. The 29 Si NMR shows a percentage of Q⁰, Q¹, Q² and Q³ to be present. The most intense peak observed appears at $\delta = -90.6$ ppm and is rather broad. This suggests that the majority of silicate structures have rearranged to a Q^2 type geometry and not a Q_{6}^{3} type structure although the presence of the prismatic hexamer may not be ruled out. In addition to this, there are a significant number of Q^0 and Q^1 structures present along with a small quantity of Q^3 . The residual Q^3 peak is also broad suggesting that the Q^3 structures which are present are not solely the Q_8^3 octamer.



(b)

Figure 23(a) TMA silicate solution 1:1 and (b) the same solutionafter having been heated for 1 hour at 75°C.

Interestingly, there is no observable Q^4 signal in either of the spectra. Although a large degree of silicate redistribution has occurred there are no Q^4 type species observed before or after the heating of the solution. This observation supports the

idea that thermal instability will favour the formation of smaller silicate species as the structure control is lost within a TMA silicate solution. Should a random redistribution of silicate structures occur it might be expected that some smaller silicate structures may agglomerate giving rise to a Q^4 type signal. This has not been observed however, with the ²⁹Si NMR spectrum showing an increased intensity for smaller silicate species only. These smaller species have been formed at the apparent expense of the Q^3_8 octamer. This redistribution of silicate species, along with an associated loss of structure control, is consistent with observations previously reported.⁵³

The behaviour of analogous choline and DPHEDMA silicate solutions under identical conditions could not be more different. As with the example of TMA silicate described above, the thermal stability of these two silicate solutions was investigated by ²⁹Si NMR. Spectra were recorded of the starting solutions and then again after they had been heated to a temperature of 75°C for one hour (**Figure 24 & Figure 25**). The speciation found within all three solutions before and after heat treatment is tabulated in **Table 13**.

As shown, the larger, hydroxy functionalised, TAA silicates have undergone no thermal rearrangement. The speciation observed within both solutions before and after heating overwhelmingly favours the Q_8^3 octameric anion. This observation suggests that, in the case of these two TAA silicates at least, the solutions are thermally stable to a temperature of 75°C. This behaviour is clearly different from that of TMA silicate solution and again, this increased stability may be attributed to the interaction of additional hydrogen bonding. The stability of silicate species with respect to the TAA/silicate/water system has already been described in section **2.3.8**, but, the increased thermal stability of the two functionalised TAA silicates may be explained in a similar manner. The hydrogen bonding between the solvent shell and the hydroxy functionalised TAA cations may be serving to stabilise the Q_8^3 structure more so than in the previously studied TMA silicate. This additional interaction has been found to increase the thermal stability of choline and DPHEDMA silicates.



Figure 24(a) Choline silicate solution 1:1 and (b) the same solutionafter having been heated for 1 hour at 75°C.



Figure 25(a) DPHEDMA silicate solution 1:1 and (b) the same
solution after having been heated for 1 hour at 75°C.

Cation	Cation : Si	$\approx c[SiO_2]$	Q ⁰ (%)	Q ¹ (%)	Q ² ₃ (%)	Q ² (%)	Q ³ (%)	Additional	
			-73ppm	-81/82ppm	-83ppm	-87/91ppm	-100ppm		
TMA	1:1	2.78M	0	0	0	0	100	Q ³ 8	Accounts for all the Q ³ Signal observed
								Q ⁴	Absent
TMA After Heating	1:1	2.78M	5.4	9.6	2.7	79	4.1	04	Slightly broad signals observed
								Q	Adsent
Choline	1:1	2.42M	Trace	Trace	Trace	Trace	100	Q ³ ₈	Accounts for all the Q ³ Signal observed
-								Q^4	Absent
Choline After Heating	1:1	2.42M	Trace	Trace	Trace	Trace	100		No Observable change in speciation
								Q_{6}^{3}	Accounts for 5%
DPHEDMA	1:1	2.42M	4	0	0	5	91	Q ³ ₈	Accounts for all the Q ³ Signal observed
		-						Q^4	Absent
DPHEDMA After Heating	1:1	2.42M	4	0	0	5	91		No Observable change in speciation

Table 13Speciation of silicate species within TAA silicates before and after heating for 1 hour at 75°C

The nature of silicate solutions and the speciation present therein has been shown to be dependant on many factors. The nature of any solution however, is one of a dynamic equilibrium and this is true for all the silicate solutions described previously. The time taken for a silicate solution to reach a point of equilibrium has been discussed.⁶⁰

It has been shown by Knight *et al.* that, although alkali metal silicates may reach equilibrium rapidly, TMA silicate solutions may take in excess of two weeks to attain an equilibrium state. It was also suggested in this study that, firstly a number of smaller anionic species would be formed. These species would agglomerate and grow over time leading to the final cubic anion Q_8^3 suggesting that, in TMA silicate, the Q_8^3 octamer was a thermodynamic product formed after/from a number of shorter lived kinetic products. In a separate study on TAA silicate solutions by Kinrade *et al.* the effect of increased temperature was found to have a destructive effect on the Q_8^3 species found within TMA silicates.⁵³

These two observations however, initially seem to be opposed to each other. Should, as suggested by Knight et al., the cubic anion be the thermodynamic product, then a heated solution, which showed a redistribution of silicate speciation, should, after time, return to a monodispersed TMA silicate solution. If the octameric anion, Q_{8}^{3} , is the thermodynamic product then it should reform after infinite time. Although this can not be ruled out, the heat treated TMA silicate (Figure 23) did not show any further silicate redistribution after cooling even after a period of four weeks. This observation suggests that the thermal instability described by Kinrade et al. results in a permanent redistribution of silicate anions within solution. The speciation of silicate anions observed within a heated sample of TMA silicate 1:1, seems to be as a result of a number of decomposition reactions rather than thermal rearrangement. The type of decomposition reaction taking place may not be categorically inferred from the spectroscopic evidence. However, the redistribution of anions observed is clearly not a reversible process and hence, the processes involved within the thermal rearrangement observed are not a matter of solely kinetics as should this be the case, the thermodynamic product, Q³₈, would be expected to reform after time.

The relationship between the formation of a kinetic product and the thermodynamic product was investigated using a VT NMR experiment. By taking a freshly prepared choline silicate, 1:1, and performing a VT NMR experiment, the speciation and formation of kinetic and thermodynamic products was studied in-situ. By recording the NMR of the silicate solution at a number of increasing temperatures, the effect of applying increasing energy to the system was observed (**Figure 26**). At each measurement, a set of identical experimental parameters were used once the temperature had stabilised. This system allowed the qualitative analysis of the silicate speciation present to be performed.



Figure 26

²⁹Si NMR Spectra of Choline silicate 1:1 obtained at increasing temperatures with resonances associated with the cubic octamer, Q_{8}^{3} , and prismatic hexamer, Q_{6}^{3} , highlighted.

As shown in the lowest spectra, recorded at ambient room temperature, the predominant species found within the freshly prepared choline silicate was that of the prismatic hexamer, Q_6^3 (-90ppm). The Q_8^3 octamer (-100ppm) is also clearly present, but in significantly smaller amounts. What is seen as the temperature of the sample is increased is a shift in silicate speciation. This shift moves away from Q_{6}^{3} being the predominant species present towards an increased intensity of the signal associated with the Q_8^3 structure. At a temperature of 348K the distribution of the two species is approximately 1:1, and by a temperature of 363K the octameric anion is now the predominant silicate structure found in solution. The solution was then allowed to cool to room temperature and after 24 hours the spectra recorded again. It was found after this time had elapsed that the Q_8^3 octamer was the sole silicate anion present in solution, thus suggesting that the observed change in speciation with temperature was not a reversible process. Such an observation signifies that, the Q_6^3 hexameric anion present in the starting solution is a kinetic product. The Q_8^3 anion is however, the thermodynamic and hence most stable product when considering the case of choline silicate 1:1. Although the DPHEDMA silicate was not analysed in the same way, it might seem reasonable to suppose that the nature of anions therein behave in a similar manner, forming a kinetic product before the thermodynamic Q³₈ anion. However, TMA silicate was found not to revert back to the Q_8^3 octamer with time hence the thermal rearrangement observed must be as a consequence of some form of decomposition reaction.

2.3.11 Dried solutions and solid-state analysis

Alkali metal silicates are applied to a host of commercial applications. In just one example, aqueous silicates are condensed through a complicated drying process to form a clear intumescent gel. Given that all silicate structures thus far discussed within this study are formed via condensation reactions, the effect of further condensation is not fully understood as the variation in solid-state silicate structures is immense within minerals and most comparably zeolites. The speciation within alkali metal silicate solutions will, most likely, have a corresponding effect on the nature and structure of the solid-state anions formed when dried. To investigate this concept, a polydispersed sodium silicate and a monodispersed TAA silicate were dried and the resultant solids analysed by ²⁹Si NMR.

Solid-state ²⁹Si NMR has associated with it a number of advantages and disadvantages when compared to the solution characterisation discussed earlier. Solid-state ²⁹Si NMR involves no use of a deuterated lock solvent or any glassware which leads to simpler sample preparation and removal of glass contamination in the observed spectra. As samples are more concentrated, the difficulties associated with silicon-29's low natural abundance are also less pronounced. However, an unfortunate consequence of solid-state NMR spectroscopy is that relaxation times of the nuclei may increase along with undesirable signal broadening which occurs due to spin-spin interactions. A typical spectrum obtained is shown in **Figure 27a** and shows four resonances to be present.

The use of solid-state ²⁹Si NMR has allowed the Q⁴ signal to be interpreted along with the Q⁰-Q³ resonances observed within the solution analysis which was not previously possible, due to the glass contamination present in the NMR probe. With the new information present in the NMR spectrum, every effort in improving the analysis was made in a similar vein to the improvements that were yielded from the solution NMR investigation. With the use of a deconvolution package available on WinNMRTM, it was possible to analyse the four peaks believed to be present. The interpretation of the spectrum using deconvolution may best be illustrated in **Figure 27**. The four coloured peaks show the four signals believed to be present in the original spectrum (**Figure 27b**). The dotted outline shows the original spectrum and the black line shows the sum of the deconvoluted peaks. The peaks may now be more easily integrated to give an idea of quantity of silicate species present. In addition to this, the residual spectrum is also shown to give a sense of how good the deconvoluted fit is (**Figure 27c**).





Using this method it was possible to analyse two dried silicate solutions. The purpose of which, was to compare the Q species present in solution with those found in a dried sample (Table 14), the chemical shifts of which may be directly compared with those found in the solution NMR of the same silicate. The spectrum above shows the presence of a Q^2 (~ -90ppm), two Q^3 peaks (~ -95ppm & ~ -100ppm) and the presence of a Q^4 (~ -110ppm). In the case of the sodium silicate, the 3% Q⁴ observed represents a minor part of the various species present. As it is not possible to say whether this value of 3% is an increase from that present in solution, it is difficult to assign a sure explanation. When looking at the smaller Qⁿ species however, it is clear to see that the smaller species present in solution, are no longer present in the dry silicate. The most likely explanation for such observations follows a similar reasoning described in the previous section discussing solution speciation within alkali metal silicates. As water is removed, condensation reactions, which were at an equilibrated state, are driven further leading to smaller anionic species combining into larger Q^2 and Q^3 units. Due to the diverse nature of silicate species present in the initial solution, this agglomeration of anions leads to a diverse but highly populated Q^3 resonance along with a substantial Q^2 region. The increase in Q^3 species at the expense of the Q^2 species supports the theory that condensation reactions cause an overall increase in the number of high Q^n species due to the smaller species combining. The observed shift towards the Q^3 type structure would suggest that an increase in Q^4 type species had also occurred through this forced condensation but such a conclusion may not be made owing to the unknown nature of the initial solution.

In the case of the choline silicate 1:2 solution the amount of Q^2 present in both solid and solution spectra are similar. The intensity of the Q^3 signal has decreased however, seemingly due to the emergence of a strong Q^4 signal. Such a strong signal could not be due to experimental errors and so must have been formed during the drying process. It would seem that in the case of the choline silicate, the Q^3 species which dominate in solution ($Q^3_6 \& Q^3_8$) have condensed, in part, to give rise to Q^4 species. This may be seen to support the concept discussed above whereby existing silicate anions are forced to come together due to the forced condensation during drying. Given the speciation present within the initial TAA silicate, it is not possible for smaller Q^n species to combine as they are not present. This leaves only the Q^3 species present to condense together forming a substantial number of Q^4 type silicon centres. This would be observed as a decrease of the Q^3 resonance intensity following drying when compared to the initial solutions speciation. This is indeed what is seen and is tabulated in **Table 14**.

The comparison of these two samples suggests that species present in solution undergo condensation reactions when dried. It also suggests that speciation present within any silicate solution affects the nature and structures found upon drying. By narrowing silicate speciation within solution to mainly Q^3 type structures, substantially greater numbers of Q^4 type species will form upon further forced condensation. Again therefore, the nature of these dried silicates may be associated with the nature of the cation present within the initial solution.

Cation	Cation : Si	≈ c[SiO2]	Q⁰(%) -73ppm	Q¹ (%) -81/82ppm	Q ² ₃ (%)	Q² (%) -87/91ppm	Q³ (%)	Q⁴ (%)	Additional
Choline Solution	1:2	4.1M	Trace	Trace	0	15	85	0	Q ² Slightly broad signal observed Accounts for all the Q ³ Signal observed Q ⁴
Choline Solid-state	1:2	n/a	0	0	0	14	70	16	The Q^3 region contained two clear signals. The sharpest peak, contributing ~29%, was found at the same shift as the Q^3_8 octamer in solution.
Na+ Solution	1:1.65	2.5M	1.85	9.3	Trace	38.9	50	None Observed	Q2Both of these signals were noted as being very broad
Na+ Solid-state	1:1.65	n/a	0	0	0	10	. 87	3	A large, broad Q^3 signal was observed as well as a small amount of Q^4

Table 14

Comparison of solution and solid-state NMR for two silicates.

2.3.12 Additional analysis

Although the use of NMR has been by far the major form of analysis, other techniques such as viscometry, high performance particle sizing (HPPS) and IR spectroscopy were employed to investigate the TAA silicate solutions described above. Owing to the nature of viscometry, the physical characteristics observed are closely related to the composition of the solution. Since the solutions discussed in this chapter are of varying silica concentration, it is not possible to hold responsible the nature of the TAA cation with the observed viscosity of the silicate. Although some solutions were considerably more viscous, the most reasonable explanation is that this is associated purely with the higher silica concentration within said TAA silicates.

The use of HPPS also proved inconclusive. It was hoped that in the case of TMA silicate, where NMR supported the idea of a monodispersed solution, the particle sizes within said solution would be correspondingly narrow. From the crystal structure (**Figure 21**), the particle size of the octameric anion is 1nm. Hence, in a solution containing almost entirely this species, a corresponding particle size distribution would be found. However, despite a number of TAA silicates showing an extremely narrow particle size distribution at ca. 1nm, the technique was found to be not entirely reliable. Data obtained from a single solution was found to consistently vary over a series of runs. The distribution, number of and size of particles within solution was therefore not discussed and the results of HPPS analysis not included within this study.

As discussed within Chapter 1, IR spectroscopy is not particularly useful when applied to aqueous silicate characterisation. As discussed by Rogendorf *et al.* two distinctive regions of the spectra may be observed.⁶ Firstly the adsorption band, when compared to pure water, is seen to broaden within alkali silicate solutions, particularly towards the lower frequency side. This observed shift is attributed to hydrogen bonding interactions and is observed within all of the TAA silicates studied. Secondly, and additionally, an adsorption observed at c.a. 2100 cm⁻¹ was observed to a significant intensity within all solutions. Within previous literature, two interpretations are offered for this observation. It has been suggested that this

adsorption band is associated with hydrogen bonding between isolated Si(OH)₄ tetrahedra and the silicate network.⁷ However, the Si(OH)₄ unit (Q^0) would be observable within the ²⁹Si NMR spectrum. As described above, in many of the TAA silicates studied there is clearly no Q^0 resonance observed which therefore leads to the conclusion that there are no Si(OH)₄ units present. The IR spectra of these TAA silicates do however show the adsorption band at c.a. 2100 cm⁻¹. Such an observation lends itself to the conclusion that such an explanation of hydrogen bonding can not be the case. Therefore, the second interpretation, which assigns the adsorption band to the deformation vibration of the water molecule, must be considered as the most probable explanation in the light of the supporting evidence described within this study. Other than this, IR spectroscopic analysis of the TAA silicate solutions yielded no greater insight into the speciation therein.

2.4. Conclusions

A series of TAA hydroxides were synthesised using an established synthetic route. These in turn, were then used to prepare two previously reported and eight novel TAA silicate solutions. The distribution of silicate species within these silicate solutions was then investigated by ²⁹Si NMR and found to be directly related to the nature and quantity of the TAA cation present.

It was found that hydroxy-functionalisation of the longer alkyl chains upon the ammonium cations has a favourable effect towards the structure directing effects reported for smaller TAA cations, particularly when compared to analogous TAA silicates. It was found that the hydroxy functionalised cation, DPHEDMA, exerted a pronounced degree of structure control when added to a sodium silicate solution. TMA, choline and DPHEDMA were found to exert some SDE on a sodium silicate despite being present in relatively small quantities, showing them to be less susceptible to the effects of sodium poisoning than had been previously reported.

In the case of choline and DPHEDMA silicate the Q_8^3 octamer, found in many of the novel TAA silicates, was found to be the thermodynamic product. These two TAA silicates also showed much greater thermal stability when compared with previous studies on TMA silicate. Finally the speciation within a dried silicate has been seen to be directly related to the distribution of silicate species observed within the initial aqueous silicate solution.
Chapter 3

SYNTHESIS & CHARACTERISATION OF AQUEOUS ALUMINOSILICATE SYSTEMS

3.1 Introduction

As discussed in Chapter 1, the most extensive research associated with the chemistry of aluminosilicates features the preparation and characterisation of zeolites. The use of TAA cations in zeolites synthesis is frequently reported but still not completely understood.^{17,16} The preliminary studies by Hoebbel *et al.* and Muller *et al.* describe the possible structures formed within TMA silicates.^{61,62} Following the work of Hoebbel *et al.* the synthesis of all aluminosilicate solutions described hereafter follows the scheme shown in **Figure 28**.



Figure 28 Synthetic strategy for TAA aluminosilicate preparation

3.2 Aims

The systematic analysis of a number of aluminosilicate solutions was to be performed in order to further explore the nature of silicate speciation within solutions. With the analysis of TMA, choline and DPHEDMA silicates being the most extensive within this study, these cations were chosen to investigate the further nature of TAA aluminosilicate solutions.

3.3 Results and discussion

3.3.1 Synthesis of [TAA][aluminates]

The synthesis of the three [TAA][aluminates] used in this study (i.e. [TMA][aluminate], [choline][aluminate] and [DPHEDMA][aluminate]) was largely uncomplicated. Previous literature on such compounds is limited however, with TMA aluminate only appearing in a select number of early papers as cited above.^{61,62} Choline aluminate is reported within a few patents for zeolite synthesis but has not been previously isolated.¹⁶ DPHEDMA aluminate has not been reported before this study was undertaken. The aluminates formed were characterised by ²⁷Al NMR with references being made to sodium aluminate analogues and those cited in the early literature.

In all cases the aluminates were prepared by dissolving aluminium powder into a hot aqueous solution of the relevant TAA hydroxide in a ratio of 1 to 1.5. It was found that using more concentrated solutions caused undesirable side reactions to occur. Primarily, the high viscosities involved led to difficulties with mixing and solubility. Therefore, additional water was added to each reaction to minimise the reaction times and aid solubility. The removal of water under reduced pressure after the aluminium had dissolved gave a more concentrated TAA aluminate solution. The need to reduce reaction times arose because of the limited stability of the TMA aluminate solutions. Although the aluminate was formed relatively easily, the solution was found to be stable for only a short time. After ca. 45 minutes a white precipitate of $Al(OH)_3$ was seen to form. Choline aluminate was found to be considerably more stable and would not regularly form a precipitate before *ca.* 10 days. DPHEDMA aluminate was found to be most stable of the three aluminates synthesised. A freshly prepared aluminate was found to be stable for a period of at least 6 months.

The ratio of TAA/aluminium was also found to be crucial to the reaction conditions. It was observed that 1:1 reactions did not form the corresponding aluminate. It was established that excess TAA hydroxide was required to fully

dissolve the aluminium, and a minimum TAA/aluminium ratio was found as 1.3:1. These aluminates were found to be less stable when formed, compared to solutions containing a 1.5:1 ratio, and regularly precipitated $Al(OH)_3$ from solution. Ratios of TAA/aluminium up to 5:1 were synthesised but it was found that these higher ratios were no more stable than those containing a 1.5:1 TAA/aluminium ratio and the effect of adding substantial amounts of 'free' TAA hydroxide solution was not beneficial. Although the effect of TAA cations on silicates has been established (cation/silica ratio >1), their behaviour when added to new aluminosilicate mixtures was unknown. For this reason, all TAA aluminates synthesised contain a 1.5:1 TAA aluminium ratio.

3.3.2 Solution studies of aqueous aluminosilicates using ²⁹Si & ²⁷Al NMR

Having established the speciation within the three TAA silicates to be almost uniform, it was necessary to establish the characteristic properties of these new TAA aluminates. As reported in the literature, TMA aluminate shows a resonance at 79.5ppm within its ²⁷Al NMR spectrum (**Figure 29**).⁶² It was possible to confirm this and this was also found to be the case for both the choline and DPHEDMA aluminates.



Figure 29 ²⁷Al NMR of an aqueous TMA aluminate solution.

It was anticipated that any change to the chemical environment of the aluminium would manifest itself in the form of a chemical shift observable within the ²⁷Al NMR spectrum. Should the aluminate interact in any way upon addition to a prepared silicate solution, the nature of the interaction may be investigated by the corresponding change in the ²⁷Al NMR spectra. Similarly, any observable change in the silicate speciation may also be used to investigate aluminate/silicate interaction when they are mixed together. It was hoped that by starting from a monodispersed silicate solution and a monodispersed aluminate solution the effect of any aluminosilicate formation would be clearly observable by NMR. This strategy is illustrated in **Figure 30** with possible outcomes 1-3.

Figure 30 Diagram showing TAA aluminate (monodispersed) and Q_8^3 silicate (monodispersed) to illustrate the premise of any observable changes, if any, that may be seen.



As represented by the scheme above, the three most possible outcomes of any aluminate/silicate interaction within solution are as follows: -

- The octameric anion becomes substituted by aluminium atoms. The degree of silicon replacement will depend on the ratio of silicate/aluminate in the mixing solution. This possibility was suggested in the earlier literature and is reviewed in Chapter 1.⁶²
- 2. The octameric species present within the initial silicate solution is forced to break up. As it does so, a number of smaller silicate anions form, leading to a polydispersed solution as found in alkali metal silicates. Any of the smaller anionic species formed may contain oxygen bridges to aluminium centres thus leading to a polydispersed aluminosilicate solution.
- 3. The aluminium centres act as a cross-linking units between neighbouring octameric anions leading to a long range order within the aluminosilicate solution.

In all three cases we may predict the probable observations made when studying the ²⁹Si and ²⁷Al NMR spectra of the newly formed aluminosilicate solution. In the light of previous studies, particularly those featuring solid-state NMR analysis of zeolites, the structural properties of these newly formed species may be inferred. To explore the nature of aluminosilicate interactions within solution, a number of new TAA aluminates ([TMA][aluminate], [choline][aluminate] and [DPHEDMA][aluminate]) were mixed with the well characterised TAA silicates ([TMA][silicate], [choline][silicate] and [DPHEDMA][silicate], [choline][silicate] and [DPHEDMA][silicate]. In all cases the silicate was of a 1:1 cation/silica ratio and all aluminates were of a 1.5:1 cation/aluminium ratio. The nature of the aluminate and silicate was varied along with the ratio of one to the other to give a relatively broad cross-section of possible aluminosilicate complexes. The solutions prepared are summarised in **Tables 15** and **16**.

	TAA silicate	TAA Aluminate	Ratio Si:Al
15	TMA	/	8:0
16	TMA	TMA	7:1
17	TMA	Choline	7:1
18	TMA	DPHEDMA	7:1
19	TMA	Na	7:1
20	TMA	TMA	4:4
21	TMA	Choline	4:4
22	TMA	DPHEDMA	4:4
23	TMA	Na	4:4
24	Choline	1	8:0
25	Choline	TMA	7:1
26	Choline	Choline	7:1
27	Choline	DPHEDMA	7:1
28	Choline	Choline	4:4
29	Choline	DPHEDMA	4:4
30	DPHEDMA	1	8:0
31	DPHEDMA	TMA	7:1
32	DPHEDMA	Choline	7:1
33	DPHEDMA	DPHEDMA	7:1
34	DPHEDMA	Choline	4:4
35	DPHEDMA	DPHEDMA	4:4

Table 15Summary of TAA aluminosilicate solutions prepared to investigate
the effects of aluminate and silicate composition.

	TAA silicate	TAA Aluminate	Ratio Si:Al
24	Choline	Choline	8:0
26	Choline	Choline	7:1
36	Choline	Choline	6:2
37	Choline	Choline	5:3
28	Choline	Choline	4:4

Table 16Summary of Choline aluminosilicate solutions prepared toinvestigate the effects of aluminate to silicate mixing ratio.

To begin, let us consider the case described in Chapter 1 whereby the aluminium finds itself substituting silicon atoms within the octameric species (**option 1**). For this reason only the solutions tabulated above are quoted with a ratio totalling eight. As the degree of silicon substitution was also believed to be directly related to the ratio of silicon/aluminium mixing, the ratios refer, in principle, to the composition of the octameric anion formed upon silicate/aluminate mixing. These arrangements however, seem energetically unfavourable as, in order for such substitution reactions to take place, the octameric anions would have to open and reform. The driving force for such processes would appear to be lacking since heating was not involved, and such thermal rearrangements seem unlikely. Also, the steric interactions do not favour the aluminium substituted structures more than the initial silicate species. However, the expected shifts observed within the NMR spectra of the aluminosilicates may be predicted.

Should we look at TMA silicate/TMA aluminate system as an example then we would expect the following spectroscopic evidence to support the idea of substitution of silicon centres by aluminium centres. The speciation observed for the initial TMA silicate showed a monodispersed solution containing $100\% Q_8^3$ anion. This may be thought of as a silicate/aluminate ratio of 8:0. Similarly the TMA aluminate was shown to contain only the tetrahedral [Al(OH)₄]⁻ anion with a sharp resonance at 79.8ppm appearing in the ²⁷Al NMR. Should the ratio of

silicate to aluminate be mixed in equal quantities, 4:4, the resulting octameric anion should show very specific spectroscopic evidence. Following Lowenstein's rule, all aluminium atoms would be found to be within the same chemical environment and hence show the same chemical shift.¹⁵ As all aluminium atoms must be oxygen bridged to three silicon atoms, the only possible geometry of the cubic octamer is shown in **Figure 31**.



Figure 31 Octameric anion consisting of 4 parts silica and 4 parts aluminate where $= SiO_{4/2} = AlO_{4/2}$

The effect on chemical shift for the aluminium resonance would be observed as a 15ppm shift towards high-field with each aluminium atom, bridged via oxygen, to three silicon atoms. This corresponds to a shift of 5ppm per silicon as suggested by Mueller *et al.*⁶² This would result in a single resonance within the ²⁷Al NMR found at ~ 65.8ppm. Similarly, each silicon environment would observe a 5ppm chemical shift towards low-field for each neighbouring aluminium atom thus resulting in a single resonance at ~ -85ppm.⁶³

This was not observed to be the case however, as both the ²⁷Al and ²⁹Si NMR spectra showed multiple environments to be present (**Table 21, Chapter 5**). The ²⁹Si NMR did show a broad signal at -84ppm which would agree with the predicted resonance above. There was also a sharp resonance at -100ppm however, corresponding with the Q_8^3 silicate species. This suggests that not all the octameric anions have undergone aluminium substitution. This is further supported by the ²⁷Al NMR of the solution. A resonance of substantial intensity was observed at 79.8ppm corresponding with the initial aluminate species. Additional resonances were also observed at ~ 71ppm, 67ppm and 65ppm

suggesting that an array of aluminosilicate species were present. The resonance at 71ppm would agree with an aluminium species bridged to two neighbouring silicon atoms whereas the resonance at 67ppm and 65ppm may concur with the predicted structure described previously. The presence of a tetra-substituted octameric anion may not be ruled out as both the ²⁷Al and ²⁹Si NMR do show resonances which may be attributed to this structure. Should there be a number of unreacted species still present in solution, this may account for the TMA aluminate and Q³₈ silicate observed in the ²⁷Al and ²⁹Si NMR respectively. The aluminium resonance at 71ppm does not fall into either of these categories however, suggesting that this explanation does not fully cover the nature of aluminosilicate interaction present in solution.

A similar discussion may be applied to solutions containing varying TAA cations. In the case of both the choline aluminate/choline silicate and DPHEDMA aluminate/DPHEDMA silicate the 4:4 solutions displayed similar spectral properties. While the characteristic resonances for the tetra-substituted aluminosilicate octamer (**Figure 31**) were observed, quantities of unreacted aluminate and silicate were also found to be present along with resonances that could not be explained by this explanation alone. This trend continued for solutions prepared from the mixed TAA aluminates and TAA silicates as highlighted in **Table 15**.

An interesting yet subtle observation made during the analysis of these mixed TAA aluminosilicate solutions was the effect that hydroxy functionalised TAA aluminates had on the overall speciation. Although a quantity of 'unreacted' Q_8^3 and TAA aluminate were observed in almost all cases, the intensity of the Q_8^3 resonance diminished as hydroxy functionalised TAA cations were used. In the case of the choline aluminosilicate solution, 4:4, the intensity and hence quantity of the Q_8^3 silicate anion and the aluminate anion were observed to be less than that found within the analogous TMA aluminosilicate. These resonances were found to be less intense again in the case of DPHEDMA aluminosilicate. Owing to the subtlety of the variation in speciation, no clear trend may be observed with every differing aluminosilicate solution. For example, the observed change in speciation

between solutions (20) and (21) are too subtle to comment on the nature of these solutions.

A similar explanation to that offered in the earlier chapter may be applied here. In the case of TAA silicates containing a silicon/TAA ratio > 1, the stability of solution, it was argued, was due to an improved interaction with both the charged anionic silicate and the solvent shell due to the increased hydroxy functionalisation. In the case of any aluminosilicate structures formed the charge on the anionic species increases for each substitution of a silicon atom by aluminium. The charge on the aluminium centre within the tetrahedron is -1. Should this be found within the octameric anion, the charged aluminium along with the eight O⁻ peripheral atoms leads to an overall anionic charge of -9 unless protonated. As the degree of aluminium substitution increases the charge of the corresponding anion will also increase. Therefore, should the octameric anion exist within a 4:4 aluminate/silicate mix, the overall charge of the species would be -12, unless protonated, which may lead to a destabilisation of the cage. The TMA aluminosilicate may contain 'unreacted' Q38 silicate and TAA aluminate as the substituted species may not form a stable solution. The formation of larger proportions of the substituted structure in the case of choline and DPHEDMA mixtures may be explained by considering the effects of charge stabilisation. The hydroxy functionalisation leads to better charge stabilisation along with improved interaction with the solvent shell due to an increase in hydrogen bonding. This additional stabilisation allows a greater percentage of the tetra-substituted aluminosilicate anion to form leading to the observed decrease in residual starting silicate and aluminate species. Hence, the solution containing DPHEDMA aluminate and DPHEDMA silicate, 4:4, shows the smallest amounts of 'unreacted' species within the ²⁷Al and ²⁹Si NMR as the greatest number of stabilising hydroxy groups are present.

For solutions containing varying silicate/aluminate ratios, the nature of any anionic substitution may again be discussed in terms of the predicted chemical shifts which may infer the presence of certain aluminosilicate species. Previous literature has suggested that the degree of aluminium substitution, within the octameric anion, may be controlled through the ratio of aluminate to silicate

mixing.⁶² To investigate this further a number of choline aluminosilicate solutions were prepared with varying silicate/aluminate ratios as shown in Table 16. Once again, Lowenstein's rule along with the predicted anionic structure allowed the use of the observed NMR spectra to investigate this hypothesis. Comparison of solutions (24), (26), (28), (36) and (37) with Table 1 in Chapter 1 highlights the structural effects which may be inferred. Solutions (24), (26), (37) and (28) may only adopt a single geometry should the octameric anion remain intact. The speciation of solution (24) and (28) has been discussed previously. In the case of solution (26), the substitution of a single silicon atom by aluminium would lead to two ²⁹Si and one ²⁷Al NMR resonance. The ²⁷Al spectra should only contain a resonance associated with the Al(OSi)₃ environment appearing at a chemical shift of ~ 65ppm. The observed spectra however, show resonances appearing at 80 -65ppm. These resonances correspond with the initial aluminate structure along with the Al(OSi) and Al(OSi)₂ geometries suggesting that a monodispersed. monosubstituted solution is not present. Inspection of the ²⁹Si NMR spectrum supports this conclusion. Multiple resonances along with those characteristic of Q^0 , Q^1 , Q^2_3 , Q^2 and Q^3_8 silicate species are observed. A weak resonance at -95ppm was observed which may be indicative of a Q_8^3 Si(OAl) species. Such a resonance should be observed if the monosubstituted anion were present in solution but is not clear evidence that this structure is formed. Much like the situation described for the 4:4 aluminosilicate solutions, the resonances, which would be characteristic of a monosubstituted anion, are observed but only in the presence of additional ²⁷Al and ²⁹Si chemical environments. This is not only the case for a choline aluminosilicate, 7:1, but is also found for the mixed TAA aluminosilicates with an identical mixing ratio.

In the case of choline aluminosilicate 6:2 and 5:3, solutions (36) and (37), the substituted octameric anion may be formed but only in the presence of additional aluminate/silicate structures. The spectroscopic evidence for such comment arises from a similar discussion to that outlined above whereby the expected chemical shifts for both the silicon and aluminium centres within such a structure were not observed to be the only signals within their respective NMR spectra. In the light of such evidence it is not possible to rule out the formation of substituted octameric species within the mixed aluminosilicate solutions. However, as the

observed spectra have additional peaks, the alternative outcomes described in **Figure 30** must be considered.

Should the octameric anion be fractured upon addition of the aluminate solution (option 2), a much broader distribution of species may be observed when compared to the scenario described previously. The redistribution of speciation within solution may be likened to the effects observed upon addition of sodium. The addition of the aluminate leads to a splintering of many of the octameric anions leading to an increase in the number of smaller silicate species. Such a scenario would agree with the observed ²⁹Si NMR spectra which in the case of all solutions studied showed a more dispersed pattern of speciation compared to the starting silicate solution. It is also possible that many of the newly formed smaller silicate species may contain one or more aluminium centres. For example, a newly formed silicate dimer, [Si₂O₇]⁻⁶, (Q¹) may also be aluminium substituted forming, [SiO₇Al]⁻⁷. In such a solution additional resonances would be observed in the ²⁹Si NMR spectra at -81ppm, Q^1 silicon, and, ~ -76ppm for the Si(OAl) analogue.⁶³ Similarly, the ²⁷Al NMR spectra should show the presence of the new Al(OSi) species at a chemical shift of ~ 76ppm.⁶³ Such spectroscopic evidence is seen for solutions (18), (26), (27), (33) and (36) where both the ²⁹Si and ²⁷Al NMR's show resonances at these chemical shifts. In addition to this example, let us consider the case of many substituted silicate structures being formed upon aluminate addition. This would result in diverse speciation due to the fractured octameric anion, and additional resonances corresponding to aluminium substituted anions arising within the ²⁹Si NMR spectrum. These resonances may overlap with other Q species leading to a complex spectrum from which no specific structural information may be inferred. When studying the ²⁷Al NMR spectrum, the range of resonances most likely correspond to Al(OH)4, Al(OSi), Al(OSi)2, Al(OSi)3 and possibly Al(OSi)₄. Similarly, such species may arise due to the varied nature of aluminosilicate structures suggested above whereby a large number of silicate structures may be partially substituted by aluminium centres. Even by combining these techniques, the speciation and nature of the aluminate/silicate interactions may not be fully determined.

The third option (**option 3**), which may not be ruled out, is the role of aluminium as a cross-linking agent between silicate cages. It is possible that aluminium centres may combine with up to four silicate species to form a cross-linked aluminosilicate network akin to a zeolite. This situation would lead to an excess of unreacted aluminate material along with a variety of $Al(OSi)_x$ (x = 1-4) species. Such spectroscopic evidence for such a scenario is observed within the ²⁷Al NMR but, as described above, may also be accounted for by either of the two previous explanations. Similarly, the increased silicate speciation may be due to the additional silicon environments arising due to the Si-O-Al-O-Si bridge but again may not be distinguished from the scenarios described above. X-ray diffraction studies may yield information upon any long range order found within a solid sample of analogous composition but given the dynamic nature of such a solution the speciation present may not be the same as in the solid-state.

In the work of Engelhardt *et al.*, the use of the modified Lentz method followed by chromatographic separation led to the identification of the silicate anions discussed in the previous chapter.⁸ Crude attempts at a similar technique were employed to trap and identify some of these unknown anionic structures. They were unfortunately unsuccessful but with further research the speciation and structure of these aluminosilicate mixes may be further understood by this method.

3.4 Conclusion

In the light of the evidence presented above, the most likely conclusion is that a combination of all three options is operating. The aluminate may form a cross-linking bridge between silicates as well as forming an array of partially substituted silicate anions a percentage of which may retain the octameric geometry of the initial silicate species. The use of ²⁷Al and ²⁹Si NMR to study such solutions has not led to a complete understanding of the anionic speciation present therein but it has suggested some previously undescribed possibilities regarding the nature of aluminate/silicate interactions within these solutions.

Chapter 4

SYNTHESIS & CHARACTERISATION OF NOVEL TAA ORGANOBORATE SPECIES

4.1 Introduction

As highlighted in Chapter 1, the parallels between silicate and borate chemistry are clear to see. Despite the variety of structures found within the solid-state, the diversity of borate species within solution is limited to four general anionic forms, $[B(OH)_4]^-$, $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$ and $[B_5O_6(OH)_4]^-$.

The structure directing effects of organic cations on oxoborate anion chemistry has recently been observed in the solid-state structures of the guanidinium and imidazolium oxoborates, where the salts $[C(NH_2)_4]_3[B_9O_{12}(OH)_6]$ and $[C_{3}H_{5}N_{2}]_{3}[B_{9}O_{12}(OH)_{6}]$ containing the previously unreported $[B_{9}O_{12}(OH)_{6}]^{3-1}$ anion were obtained.⁶⁴ This novel anionic structure is believed to occur primarily because of the influence of H-bonding interactions which are unavailable to cations.65,66 ammonium metal tetraalkyl or The structure of [NMe₄][B₅O₆(OH)₄].0.25H₂O has recently been reported and the water of crystallisation plays an important role in the solid-state lattice.⁶⁷ Organoborate analogues of $[B_5O_6(OH)_4]^{-1}$ have been observed in $[Rh(PMe_3)_4][B_5O_6Ar_4]$ (Ar = C_6H_4OMe-4 , $C_6H_3Me_2-2$,6), obtained from the unusual reaction of the arylboronic acids ArB(OH)₂ with the aryloxorhodium complex [(PMe₃)₃Rh(OC₆H₄Me-4)] in a 5:1 ratio, with $[(PMe_3)_3Rh(OC_6H_4Me-4)]$ slowly hydrolysed to [Rh(PMe₃)₄][B₅O₆(OH)₄] in acetone solution at room temperature.⁶⁸ The anion $[B_3O_3Ph_4]$ which is an organoborate analogue of $[B_3O_3(OH)_4]$ has been prepared from 1:4:2 mixtures of Ph2BOBPh2, PhB(OH)2 and [NMe4][OH] or serendipitously as $[(^{t}Bu_{3}PAu)_{4}P][B_{3}O_{3}Ph_{4}].CH_{2}Cl_{2}$ from attempted an crystallisation of [(^tBu₃PAu)₄P][BPh₄].^{69,70}

4.2 Aims

Using the NMR techniques discussed previously along with the characterised structure directing effects of TAA cations upon silicate speciation, the preparation and characterisation of a number of novel organoborate salts was attempted through the systematic mixing of organoborate precursors. The structure directing

effects of potentially hydrogen-bonding cations with borate anions was to be investigated. The synthesis of a range of aromatically substituted organoborate salts was to be attempted by adopting a similar approach to that reported for the preparation of condensed borate anions.

4.3 Results and Discussion

4.3.1 Preparation of TAA Organoborate Salts

In a general scheme, quantities of phenylboronic acid, diphenylborinic acid and TAA hydroxide were mixed in order to synthesise a variety of organoborate structures (Figure 32). With a number of boronic acid derivatives commercially available, the preparation of a number of TAA organoborate salts was attempted. With the general properties of these novel organoborates unknown, the reaction conditions required along with the nature of the TAA cation used was investigated. Similarly, owing to the preparation of solid products, the methods of characterisation varied slightly to those that have gone before. Elemental analysis (C, H, N) was utilised along with, where possible, single crystal X-ray analysis. As with previous discussions however, NMR spectroscopy featured greatly when characterising and analysing the novel borate salts. Within the structures targeted, characteristic resonances may be observed within the ¹¹B NMR spectra. A four coordinate boron centre would typically show a resonance at a chemical shift between 2-5ppm, whereas a three coordinate boron centre would be observed within the range 27-30ppm. As the intensity of either resonance is representative of the number of these species present, the ratio of one to the other will be directly comparable to the expected ratio found within a specific target compound.





Firstly reactions of TMA hydroxide with [PhB(OH)₂] and [Ph₂B(OH)] were attempted. In a typical reaction, stoichiometric quantities of the three components were mixed and then allowed to stand in order for the products formed to precipitate from the solution. Despite numerous attempts, no target borates were obtained in this manner. To obtain a product of any sort, complete removal of solvents in vacuo was required, followed by thorough washing with diethyl ether. Where a solid product was obtained, the resulting powder was found to be insoluble in all available organic solvents. Similar reactions involving choline hydroxide in the place of TMA hydroxide yielded similar results.

In the case of all four reactions shown in Figure 32, it was found that reactions involving TMA or choline as the counter cation, yielded a solid product in the form of a grey powder. Analysis of the solid products by elemental analysis suggested that the target compounds were not successfully synthesised as the observed values for C, H and N were considerably outside the values calculated for the respective borates. ¹¹B NMR analysis also suggested a negative result as the observed spectra showed no boron resonances within the region of 27-30ppm. This infers that there is a complete absence of three coordinate boron atoms within the solid product obtained, and hence implies that the target ions had not been formed. A single strong resonance was observed within the ¹¹B NMR spectra, and was centred in the region of 1.5ppm. A resonance found at such a chemical shift is characteristically associated with the borate anion, [B(OH)₄]⁻. In general it was found that reactions of phenyl substituted boric acids with aqueous TAA hydroxides did not proceed smoothly and in view of the analysis obtained it would seem reasonable to suggest that, in aqueous solution, the condensation of phenylboronic and diphenylborinic acid precursors does not readily occur, but rather the hydrolysis of all boron centres leads to the formation of an impure borate anion product.

For the range of TAA cations discussed previously in Chapter 2, the supporting medium in all cases was aqueous solution. Given the negative preliminary findings with aqueous reaction conditions, the application of a range of TAA cations was therefore restricted. However, two commercially available TAA hydroxides, TMA and choline hydroxide, were available with methanol as a supporting medium.

For reactions of the type shown in (1), a literature method describing the reaction of diphenylborinic acid anhydride, phenylboronic acid and TMA hydroxide in ethanol was available.⁶⁹ With choline hydroxide solution in methanol available, it was found that substitution of the TMA cation for choline yielded the corresponding triborate structure under comparable reaction conditions. Elemental analysis found the relevant quantities of C, H and N to be in agreement with the calculated values expected for the appropriate borate species $[(CH_3)_3N(CH_2CH_2OH)][Ph_4B_3O_3]$. ¹¹B NMR showed the relative ratio of B/B⁻ to be 2:1. This is also in agreement with the relevant number of three-to-four coordinate boron centres expected within the desired structure. The crystalline product was also characterised by single-crystal X-ray analysis, the structure obtained is shown in **Figure 33**.



Figure 33 X-ray crystal structure of [(CH₃)₃N(CH₂CH₂OH)][Ph₄B₃O₃]

The structure shown is that of the target compound, however, unlike in a typical boroxine ring, the trioxo triborate ring is not planar but is slightly puckered. The orientation of the choline cation is in a plane perpendicular to that of the triborate ring and as shown the hydroxyl group is hydrogen bonded to one of the oxygen atoms within the trioxo triborate ring. Analysis has shown that the B-O bonds are interestingly not all of the same length. The bond length between B2-O1 (1.337Å) and B3-O3 (1.341Å) is found to be considerably shorter than the B1-O3 (1.517Å) and B1-O1 (1.498Å) bonds. An explanation for this observation may be offered by considering the electron density upon the oxygen atoms and the geometry of

the p_z -orbitals within the ring. The free electron pair within the p_z -orbital of the oxygen atoms, O3 and O1, may donate electron density to the empty p_z -orbital upon the boron atom, B3 and B2 respectively. This would lead to partial doublebond character between the observed atoms and hence account for the shorter bond lengths observed. Following on from this, it may be expected that further differences between bond lengths may be observed between B3-O3 and B2-O1 due to the hydrogen bond interaction with the O3 atom. As described above, this hydrogen-bond sits perpendicular to the plane of the boroxine ring and may therefore be expected to further interact with the p_z -orbital of the O3 atom. Such an interaction may lead to the observed bond length between B3-O3 (1.341Å) being slightly longer than that seen for the B2-O1 (1.337Å) bond. Although this is indeed found to be the case, the observed difference is found to be within experimental margins of error and hence may not be categorically confirmed by this crystal structure. The complete structural data may be found within the appendix.

Owing to the availability of a number of derivitised phenylboronic acid compounds, analogous reactions performed using were metaacid. methoxyphenylboronic ortho-methoxyphenylboronic acid and ferrocenylboronic acid in the place of phenylboronic acid. These reactions proceeded in a similar manner and were found to yield analogous crystalline products. These products were characterised by elemental analysis and ¹¹B NMR. Although, not entirely satisfactory, the observed values for the C, H and N analysis were in close agreement with the calculated values for the target molecule. ¹¹B NMR analysis showed appropriate resonances to suggest that both three and four coordinate boron centres were present, and additionally, the correct B/B⁻ ratio, 2:1, was observed. Unfortunately, no single crystal of sufficient quality was obtained in order to further characterise the respective structures using single crystal X-ray characterisation. However, by comparing the analysis obtained with that described for the previously discussed organoborate, along with the crystal structure described in Figure 33, it would seem reasonable to suggest that the target borates had been successfully synthesised in all three cases.

Reactions of the type (2) shown in Figure 32 were found to not proceed smoothly. Under the same reaction conditions as those used in type (1) reactions, choline hydroxide with diphenylborinic acid and phenylboronic acid did not yield the expected borate anion. Despite repetition of the reaction on a number of occasions, a solid crystalline product was not obtained at any time. Analysis of the resulting crude material gave C, H and N values to be well outside those calculated for the target structure. The ¹¹B NMR showed resonances associated with both three and four coordinate boron centres to be present, but the relevant intensity of one to the other was not characteristic of that expected should the target molecule have been synthesised. The NMR analysis suggested that rather than a pentaphenyl triborate anion being formed, under these reaction conditions, a significant quantity of the tetraphenyl triborate structure described above had been formed. It was found that the resultant crude product contained a ratio of three-to-four coordinate boron centres but the B/B⁻ ratio was nearer 2:1 than 1:2. A suggestion offered for such an observation is that rather than form the desired target molecule, an amount of the tetraphenyl triborate anion is produced and is found along with a quantity of unreacted starting materials. The inference that such a di-anionic triborate anion is not easily formed may be partially explained by considering the steric crowding that would occur in a pentaphenyl triborate structure. As seen in Figure 33, the tetraphenyl triborate anion is already a relatively 'crowded' structure. It may be therefore, that such a pentaphenyl triborate derivative is simply too sterically unfavourable to form a stable structure in solution. Possibly for this reason, the synthetic route to borate anions as described in the type (2) reactions, Figure 32, were found not to be successful.

Synthesis of an organic tetraphenyl tetraborate type derivative, such as that described in reaction type (3), Figure 32, was attempted by reacting four equivalents of phenylboronic acid with two equivalents of choline hydroxide in methanol. Interestingly, the compound obtained behaved differently from the two examples that had gone before. In the case of the products obtained from reactions of type (1) and (2), Figure 32, ¹¹B NMR of the crystalline product had been recorded using d₆-acetone as a solvent. However, the product obtained from reaction but completely soluble in D_2O . The ¹¹B NMR spectra recorded showed two now

familiar resonances to be present and, in accordance with the desired structure, the relative intensity of both three and four coordinate boron species were found to be 1:1. Elemental analysis also supported the formation of the desired tetraphenyl tetraborate compound, with the observed values for C, H and N satisfactorily matching the values calculated. A suitable crystal to perform single crystal X-ray charcterisaction was not obtained, however, with the spectroscopic analysis conforming to the expected structure, coupled with the compounds stability in aqueous solution, it seems reasonable to suggest that a route to a novel organic tetraborate di-anion with choline counter ions has been found.

Although *spiro*-pentaborate structures similar to that depicted in reaction type (4), Figure 32, have been reported, their preparation through stoichiometric mixing of precursors has not been previously attempted. To this end, quantities of phenylboronic acid, trimethoxyborate and TAA hydroxide were mixed in methanol in an attempt to synthesise a spiro-pentaborate species. It was found that when TMA or choline hydroxide were present, a small quantity of crystalline material was obtained from the reaction mixture. However, analysis of this crystalline material did not confirm the formation of the desired spiro-pentaborate species. The quantities of C, H and N obtained from elemental analysis of the crystalline product were found to be not even remotely comparable with the values calculated for the spiro-anion. Furthermore, although ¹¹B NMR analysis showed characteristic resonances of both three and four coordinate boron centres to be present, the relative ratio of B/B⁻ did not agree with the 4:1 ratio associated with the desired pentaborate anion. Upon closer inspection, the NMR data obtained suggests the possible presence of a quantity of a tetraphenyl triborate species, as a 2:1 ratio of three-to-four coordinate boron centres, characteristic of such a triborate anion, was observed. A further resonance may be found within the ¹¹B NMR spectra, at a chemical shift of 1.5 ppm. Such a resonance may be associated with the presence of the borate anion, $[B(OH)_4]$, as mentioned above. In order to explain the presence of such an anion, one must consider the possible reactions involving the trimethoxyborate species. As the analysis suggests that the desired spiro-pentaborate anion has not been formed, it may be possible that the trimethoxyborate species has been hydrolysed in the presence of water leading to the observation of a borate anion, $[B(OH)_4]$. The source of this unwanted

hydrolysis may be due to the presence of 'wet' solvent, in this case methanol, within the reaction conditions. Alternatively, the condensation of all the borate species highlighted in reaction types (1)-(4), Figure 32, leads to a number of associated water molecules produced during the reaction. These may, in some part, lead to the hydrolysis of the trimethoxyborate species and hence give rise to the borate anion, $[B(OH)_4]^{-}$, described above. Whether either of these possibilities is the case remains unclear, but what is apparent from the results obtained, is that reactions of type (4), Figure 32, do not yield the desired spiro-pentaborate species under the described reaction conditions.

Although the tetraphenyl tetraborate structure synthesised from reactions of type (3), Figure 32, has shown a 'tolerance' to the presence of water, in general, the synthesis of borate anions was limited due to the lack of availability of TAA hydroxides supported in organic solvents. To this end, triethylamine in ether was employed as an alternative supporting medium for the condensation reactions of phenyl- boronic/borinic acids. It was found, serendipitously, that reaction of three equivalents of phenylboronic acid with one equivalents of triethylamine in ether yielded a triethylammonium triphenyl hydroxy boroxine salt (Figure 34).



Figure 34 Reaction yielding triethylammonium triphenyl hydroxy boroxine salt

As with the borates described previously, the pure compound was a white crystalline material which was characterised by ¹¹B NMR as well as single-crystal X-ray analysis. The NMR spectra showed a now familiar ratio of three-to-four coordinate boron centres, 2:1. This was further confirmed by the X-ray analysis obtained from the resulting material (**Figure 35**).



Figure 35 Crystal structure of triethylammonium triphenyl hydroxy boroxine

The preparation of this structure is of interest as there are no similar compounds reported within the literature. However, the compound may be likened to the tetraphenyl triborate anion shown in **Figure 33** as, once again, the boroxine ring is not planar but is slightly puckered. Similarly, the length of B1-O2 (1.344 Å) and B3-O3 (1.337 Å) bonds is found to again be considerably shorter than B2-O3 (1.490 Å) and B2-O2 (1.507Å) bonds. This may also be explained by considering the electron density transfer between the comparable p_z -orbital on the O3 and O2 atoms and the empty p_z -orbital on the boron atoms B3 and B1 respectively. Once again, such an electron transfer may impart partial double bond character upon the B3-O3 and B1-O2 bond and hence explain their shorter bond lengths. It has also been noted that as well as these varying bond lengths within the triborate ring, the relative bond lengths of this triphenyl hydoxy boroxine are directly comparable

with those measured in the tetraphenyl triborate anion shown in **Figure 33**. For example, the 'shorter' B-O bond lengths found within both structures have been measured in the region of 1.33-1.34 Å again highlighting the similarities shared by both structures.

The differences between the tetraphenyl triborate and triphenyl hydroxy boroxine structures (Figure 33 & 35) may only be discussed when considering the hydrogen-bonding interactions present in each case. Although not clear in Figure 35, the hydrogen-bonds present in the triphenyl hydroxy boroxine structure lead to the formation of a dimer (Figure 36).



Figure 36 Crystal structure of triethylammonium triphenyl hydroxy boroxine dimer

In the case of the tetraphenyl triborate structure Figure 33, the hydrogen bond between the choline cation and triborate anion lay in a plane perpendicular to the triborate ring. In the case of the triphenyl hydroxy boroxine dimer, Figure 36, the hydrogen-bond between the cation and borate now lies in a distorted plane. Furthermore, the hydrogen-bond is now interacting with the peripheral hydroxyl group (O4) and not, as before, with the oxygen atom within the triborate ring (O2). This oxygen atom (O2), found within the triborate ring, is still found to be hydrogen bonded but now interacts with the hydroxyl group (O4) on an adjacent boroxine, thus giving rise to the dimer species shown in Figure 36. As discussed in the case of the tetraphenyl triborate anion, such hydrogen-bonding may be observed to increase the B2-O2 bond length (1.507Å), when compared to the B2-O3 bond length (1.490Å). As before, this is found to be the case but once again the margin of experimental error disallows this conclusion to be drawn beyond doubt. In general, it seems reasonable to state that, even though this two-fold hydrogen bonding is found within the triphenyl hydroxy boroxine compound, the structural properties of the triborate ring are largely the same in both the tetraphenyl triborate and triphenyl hydroxy triborate structures. Although not attempted within this study, it may be reasoned that a number of new derivatives may be synthesised using the many boronic acid derivatives available.

4.4 Conclusions

Over the course of the investigation presented above, a systematic approach to a number of novel organoborate anions has been attempted. The preparation of a number of organoborate derivatives containing a trioxo-triborate ring species has been shown to proceed in the presence of choline cations in methanol. An interesting tetraorgano-tetraborate 'borax' structure has also been prepared and was found to be water tolerant unlike the smaller boroxine ring systems. The preparation of spiro-type pentaborate derivatives was not successful with the resulting mixture containing a number of decomposition products. Although being similar to the tetraphenyl triborate anion, a new and previously unreported triphenyl hydroxy triborate species has been prepared in the presence of triethylamine.

Although TAA hydroxides have been shown to exert strong structure directing effects upon silicate speciation within aqueous solution, the effect of the counter ion has been found to be less pronounced within comparable organic phase borate chemistry. Furthermore, the involvement of solvent molecules, discussed at length in Chapter 2 and referred to as the 'solvent shell', has been observed to be almost non-existent. However, such a statement may not be categorically confirmed without further investigation. The structure of the borate anion formed has been seen to be more dependent on the stoichiometry of the initial mixture rather than the TAA cation present.



EXPERIMENTAL

5.1 General

All materials and solvents were of standard reagent grade and were used without further purification unless otherwise stated. Reagents were purchased from Aldrich Chemical Company, Acros Fine Chemicals and Lancaster Synthesis Ltd and used as supplied.

Elemental analysis (C, H, N) was obtained on a Carlo-Erba MOD-1108 machine using helium as a carrier gas. Calculated values are in parenthesis. NMR data was obtained as described in Section **5.2**. IR spectroscopy was performed using a Perkin-Elmer 1600 series FTIR spectrometer. Samples were analysed by being placed between NaCl plates.

5.2 NMR Parameters

¹H and ¹³C NMR Parameters

¹H and ¹³C NMR spectra were acquired using a Bruker 250 CP/MAS spectrometer operating at 250MHz and 62.9MHz respectively. Appropriate deuterated solvents were used to lock and shim the magnetic field. Chemical shifts are given in ppm with positive values towards high frequency (downfield) of SiMe₄ (TMS).

²⁹Si NMR Parameters

The ²⁹Si solution spectra were acquired using a Bruker 250 CP/MAS spectrometer operating at 49.7MHz. The spectral field was locked and shimmed through the use of a coaxial arrangement as shown in **Figure 37**. Deuterium oxide was placed in a 5mm O.D. quartz NMR tube to act as an internal lock signal. This was then placed inside a 10mm O.D. quartz NMR tube containing the sample solution. The inner tube was held in place through the use of a PTFE coaxial spacer.



Figure 37 Diagram of the coaxial type NMR tube assembly used for the acquisition of ²⁹Si NMR spectra

Spectra were obtained using a pulse angle of 90° achieved through a 10μ s pulse at 0dB. A sweep width of 20,000Hz was used with a pulse delay of 1.5sec. The number of scans employed to acquire an adequate signal/noise ratio varied with sample concentration and composition. Typically 1500 scans were attained per sample. Chemical shifts are given in ppm with positive values towards high frequency (downfield) of SiMe₄ (TMS).

Solid-state ²⁹Si NMR were acquired using a Bruker 500 AVANCE spectrometer operating at 99.4MHz. Spectra were obtained using MAS and a 5.0µs pulse at 3dB. A sweep width of 44,642Hz was used with a pulse delay of 10.0sec. Typically 1000 scans were attained per sample with a total accumulation time of 2.7 hours.

²⁷Al NMR Parameters

The ²⁷Al solution spectra were acquired using a Bruker 500 AVANCE spectrometer operating at 130.3MHz. The spectral field was locked and shimmed using an internal solvent lock of deuterium oxide where possible. Spectra were obtained using a pulse angle of 30° achieved through a 7.5µs pulse at 1dB. A sweep width of 80,645Hz was used with a pulse delay of 2.0sec. Typically 512 scans were attained per sample, with a total accumulation time of 17 minutes.

Solid-state ²⁷Al NMR were acquired using a Bruker 500 AVANCE spectrometer operating at 130.3MHz. Spectra were obtained using MAS and a 5.0µs pulse at 3dB. A sweep width of 44,642Hz was used with a pulse delay of 2.0sec. Typically 200 scans were attained per sample, with a total accumulation time of 6.5 minutes.

¹¹B NMR Parameters

The ¹¹B solution spectra were acquired using a Bruker 500 AVANCE spectrometer operating at 160.5MHz. The spectral field was locked and shimmed using an internal solvent lock of d_6 -acetone. 5mm O.D. quartz NMR sample tubes were used to minimise the presence of borosilicate glass. Spectra were obtained using a pulse angle of 30° achieved through a 10.0µs pulse at 0dB. A sweep width of 80,645Hz was used with a pulse delay of 200 msec. Typically 512 scans were attained per sample, with a total accumulation time of 1.7 minutes.

5.3 Preparation of tetraalkylammonium halides

Preparation of [(CH₃)₃N(CH₂CH₂OH)]I (2I)

Dimethylethanolamine (40ml, 35.44g, 0.39mol) was cooled in a round bottom flask on an ice bath. To this, methyl iodide (24.3ml, 55.35g, 0.39mol) was slowly added. The reaction was allowed to cool for 5mins before methanol (40ml) was added. The solution was then heated to *ca*. 60°C overnight. All solvents were then removed on a rotary evaporator to give the white crystalline solid. Yield = 55.85g (62%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 7.31 (1H, s), 6.65 (2H, d t), 6.1 (2H, t), 5.77 (9H, s). $\delta(^{13}\text{C})$ /ppm: 69.8 (CH₂OH), 58.1 (3 x CH₃), 56.5 (CH₂). Required for C₅H₁₄INO: C, 26.0; H, 6.1; N, 6.1. Found: C, 25.6; H, 5.7; N, 6.1.

Preparation of [(CH₃)₂(CH₃CH₂)N(CH₂CH₂OH)]Br (**3Br**)

Dimethylethanolamine (30ml, 26.58g, 0.29mol) was cooled in a round bottom flask on an ice bath. To this, bromoethane (22.1ml, 32.3g, 0.29mol) was slowly added. Water (50ml) was added and the solution was then heated to ca. 60°C overnight. All solvents were then removed on a rotary evaporator to give a brown gummy solid. This was redissolved in methanol before being dried again. THF (50ml) was then added and the mixture stirred for 30mins. The THF was then decanted and the solid dried.

Yield = 40.3g(70%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 7.32 (2H, d), 6.57 (2H, d), 6.0 (2H, dt), 5.7 (1H, s), 5.64 (6H, s), 3.9 (3H, t). $\delta(^{13}\text{C})/\text{ppm}$: 66.6 (CH₂), 63.3 (CH₂), 57.6 (2 x CH₂), 53.1 (CH₂), 9.9 (CH₃). Required for C₆H₁₆BrNO: C, 36.4; H, 8.1; N, 7.1. Found: C, 35.9; H, 8.2; N, 7.1.

Preparation of [(CH₃)₂(CH₃CH₂CH₂)N(CH₂CH₂OH)]Br (4Br)

Dimethylethanolamine (20ml, 17.72g, 0.2mol) was cooled in a round bottom flask on an ice bath. To this, bromopropane (18ml, 24.35g, 0.2mol) was slowly added. Methanol (90ml) was then added and the solution heated to reflux (*ca.* 60° C) overnight. All solvents were then removed on a rotary evaporator to give the white crystalline solid.

Yield = 41.54g (98%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 7.31 (1H, s), 6.55 (2H, bs), 6.1 (2H, t), 5.9 (2H, t), 5.6 (6H, s), 4.35 (2H, d t), 3.45 (3H, t). $\delta(^{13}\text{C})/\text{ppm}$: 69.0 (CH₂..O), 67.1 (CH₂..C), 57.6 (2 x CH₂), 53.6 (CH₂OH), 17.9 (CH₂), 12.1 (CH₃). Required for C₇H₁₈BrNO: C, 39.6; H, 8.6; N, 6.6. Found: C, 38.7; H, 8.9; N, 6.5.

Preparation of [(CH₃)₂N(CH₂CH₂OH)₂]I (5I)

Methyldiethanolamine (20ml, 20.8g, 0.17mol) was cooled in a round bottom flask on an ice bath. To this, methyl iodide (10.9ml, 24.83g, 0.17mol) was slowly added. The reaction was allowed to cool for 5mins before methanol (80ml) was added. The solution was then heated to *ca*. 60°C overnight. All solvents were then removed on a rotary evaporator to give a yellow oil as the product. This was crystallised in small amounts using acetone to give crops of white crystals. Yield = 40.12g (90%)

NMR $\delta(^{1}H)/ppm$: 7.32 (2H, s), 6.9 (4H, dd), 6.25 (4H, t), 5.9 (6H, s). $\delta(^{13}C)/ppm$: 68.8 (2 x CH₂OH), 58.1 (2 xCH₃), 55.2 (2 x CH₂). Required for C₆H₁₆INO₂: C, 27.6; H, 6.2; N, 5.4. Found: C, 27.6; H, 6.3; N, 5.4.

Preparation of $[(CH_3)N(CH_2CH_2OH)_3]I(6I)$

Triethanolamine (20ml, 22.48g, 0.15mol) was cooled in a round bottom flask on an ice bath. To this, methyl iodide (9.3ml, 21.29g, 0.15mol) was slowly added. The reaction was allowed to cool for 5mins before methanol (80ml) was added. The solution was then heated to *ca*. 60° C overnight. All solvents were then removed on a rotary evaporator to give a yellow oil as the product. This was crystallised in small amounts using acetone to give crops of white crystals. Yield = 34.2g (69%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 7.34 (3H, s), 6.61 (6H, m), 6.28 (6H, t), 5.85 (3H, q). $\delta(^{13}\text{C})/\text{ppm}$: 66.9 (3 x CH₂ OH), 57.7 (3 x CH₂N), 52.66 (CH₃). Required for C₇H₁₈INO₃: C, 28.9; H, 6.2; N, 4.8. Found: C, 28.1; H, 6.5; N, 4.4.

Preparation of [(CH₃)₂N(CH₂CH₂OH)(CH₂CHOHCH₂OH)]OH (7OH)⁵⁴

Glycidol (20.4ml, 22.78g, 0.3mol) was added slowly to dimethylethanolamine (28.2ml, 24.98g, 0.28mol) with cooling supplied by a water bath at 20°C. To this, water (50ml) was added. Caution: below 20°C the reaction proceeds very slowly but above 35°C an uncontrollable exotherm occurs. The solution was left to stir for a minimum of 4 hours but preferably 12-18 hours. After this time the viscosity of the solution had increased. Chloroform (3 x 20ml) was used to remove any unreacted amine and/or glycidol. A 1ml aliquot of the resulting solution (total volume = 45.4ml) was titrated with HCl (0.1M) to establish its cationic content and hence the concentration of the solution (2.025M).

Calculated yield = 18.36g(36%)

NMR $\delta(^{13}C)$ /ppm: 70.42, 69.0 (CH₂N), 68.1 (CHOH), 66.6 (3-CH₂OH), 57.2 (2-CH₂OH), 54.4 (2 x CH₃N). Ref ⁵⁴ 69.6, 68.2 (CH₂N), 67.7 (CHOH), 65.8 (3-CH₂OH), 56.6 (2-CH₂OH), 53.8 (2 x CH₃N).

Preparation of [(CH₃)₂(CH₂Ph)N(CH₂CH₂OH)]Br (8Br)

Dimethylethanolamine (11.1ml, 9.81g, 0.11mol) was cooled in a round bottom flask on an ice bath. To this, benzylbromide (13.1ml, 18.8g 0.11mol) was slowly added. Methanol (60ml) was then added and the solution heated to reflux (*ca*. 60°C) overnight. All solvents were then removed on a rotary evaporator to give a yellow oil as the product. This was crystallised in small amounts using acetone to give crops of white crystals.

Yield = 19.42g(68%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 10.1 (5H, s), 7.4 (1H, s), 7.1 (2H, s), 6.56 (2H, bs), 6.0 (2H, bs), 5.6 (6H, s). $\delta(^{13}\text{C})/\text{ppm}$: 135.4(ArC), 133.1 (2 x ArCH), 131.5 (2 x ArCH), 129.4 (ArC), 71.5(CH₂), 67.6 (CH₂OH), 57.7(2 x CH₃), 52.6 (CH₂). Required for C₁₁H₁₈BrNO: C, 50.8; H, 7.0; N, 5.4. Found: C, 50.7; H, 7.1; N, 5.4.

Preparation of [(CH₃)(CH₂Ph)N(CH₂CH₂OH)₂]Br (9Br)

Methyldiethanolamine (8.6ml, 7.66g, 0.086mol) was cooled in a round bottom flask on an ice bath. To this, benzylbromide (10.2ml, 14.71g, 0.086mol) was slowly added. Methanol (60ml) was then added and the solution heated to reflux (*ca.* 60° C) overnight. All solvents were then removed on a rotary evaporator to give a white crystalline product.

Yield = 20.1g(80%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 10.1 (5H, s), 7.3 (1H, s), 7.1 (2H, s), 6.6 (4H, bs), 6.1 (4H, bs), 5.6 (3H, s). $\delta(^{13}\text{C})/\text{ppm}$: 136.2(ArC), 133.2 (2 x ArCH), 131.6 (2 x ArCH), 129.2 (ArCH), 70.0 (CH₂OH), 65.3 (CH₂OH), 57.6 (2 x CH₂), 50.8 (CH₃). Required for C₁₂H₂₀BrNO₂: C, 49.7; H, 6.8; N, 4.9. Found: C, 49.1; H, 6.8; N, 4.9.
Preparation of [(CH₃)₂(CH₂CH₂OH)NCH₂CH(OH)CH₂N(CH₃)₂(CH₂CH₂OH)₂].2Cl (**10Cl**)

Dimethylethanolamine (11.1ml, 9.81g, 0.11mol) was cooled in a round bottom flask on an ice bath. To this, 1,3-dichloro-2-propanol (7.09g, 55mmol) was slowly added. Methanol (60ml) was then added and the solution heated to reflux (*ca*. 60° C) overnight. All solvents were then removed on a rotary evaporator to give a yellow oil as the product. This was crystallised in small amounts using acetone to give crops of white crystals.

Yield = 7.4g(44%)

NMR $\delta(^{1}\text{H})/\text{ppm}$: 7.51 (1H, s), 7.32 (2H, s), 6.85 (1H, m), 6.62 (4H, t), 6.24 (4H, d), 6.13 (4H, t), 5.74 (6H, s). $\delta(^{13}\text{C})/\text{ppm}$: 69.0 (2 x CH₂OH), 67.1 (CHOH), 64.2(NCH₂C), 57.7 (3 x CH₂N), 55.1 (4 x CH₃). Required for C₁₁H₂₈Cl₂NO₃: C, 43.8; H, 7.4; N, 9.3. Found: C, 43.8; H, 7.1; N, 8.9.

Preparation of tetraalkylammonium hydroxides

The TAA halides described previously were converted to the equivalent hydroxide using the anion exchange resin, Dowex 550. The general procedure is described in detail for the exchange of choline iodide to choline hydroxide.

The resin (30g) was activated using NaOH before being thoroughly washed with distilled water. To this was added $[(CH_3)_3N(CH_2CH_2OH)]I$ (1.99g/ 8mmol) in distilled water (50ml). This was then agitated on a mixing plate for 24 hours. The resin was removed by filtration and further washed with distilled water (4 x 15ml). The filtrate and washings were reduced on a rotary evaporator to a volume of 8ml. The filtrate was shown to contain no halide using the silver nitrate test. An aliquot of the solution (1ml) was diluted with water (9ml) and titrated with HCl (0.1M) to establish the hydroxide content as 1.0M. Calculated yield = 0.96g (99%) (1M solution)

Using such a procedure, TAA hydroxides of the TAA halides were prepared respectively.

5.3 Preparation of silicate solutions

Preparation of synthetic sodium silicate solutions

Two silicate solutions were synthesised using sodium hydroxide and silica. The cation/silicon ratios prepared were 1:1 and 1:1.65. The general synthesis is described for the sodium silicate 1:1. Quantities used to synthesise the 1:1.65 sodium silicate are written below.

NaOH (1.6g, 41.5mmol) was dissolved in water (6ml) in a narrow high-sided beaker and stirred using a homogeniser rotating at 11500 rpm. To this, fumed silica (2.5g, 41.5mmol) was added gradually over 30 minutes. The mixture was left to mix for a further 45 minutes.

To synthesise a 1:1.65 ratio sodium silicate, NaOH (1g, 25.2mmol) was dissolved in water (5ml) and mixed with silica (2.5g, 41.5mmol) as described above. After a minimum of 4 days the solutions were analysed by ²⁹Si NMR.

NMR $\delta(^{29}Si)$ /ppm: -73.3 (Q⁰), -81.7 (Q¹), -83.5 (Q²₃), -90.3 (Q²), -98.9 (Q³)

Preparation of [TAA][silicate] solutions

A series of silicate solutions were prepared using the TAA hydroxides described previously. The cation/silicon ratio was varied in some of the early solutions. The general synthesis is described in detail for the 1:1 TMA silicate. Quantities used for the series are shown in **Table 17**.

[(CH₃)₄N]OH 25% w/w (15ml, 41.5mmol) was placed in a narrow high-sided beaker and stirred using a homogeniser rotating at 11500 rpm. To this, fumed silica (2.5g, 41.5mmol) was added gradually over 30 minutes. The mixture was left to mix for a further 45 minutes. After a minimum of 4 days the solution was analysed by ²⁹Si NMR. Viscosity and ²⁹Si NMR spectroscopy data is tabulated in **Table 18**.

Cation	Cation:Silicon	Volume	Conc. [TAA]	SiO ₂
		[TAA][OH]	[OH] in H ₂ O	
1	1:1	8.97 ml	25% w/w	1.5g / 25mmol
1	1:2	4.49 ml	25% w/w	1.5g / 25mmol
2	1:1	5.65 ml	50% w/w	1.5g / 25mmol
2	1:2	2.82 ml	50% w/w	1.5g / 25mmol
2	2:1	11.29 ml	50% w/w	1.5g / 25mmol
3	1:1	22 ml	1.12 M	1.48g / 24mmol
4	1:1	24 ml	0.91 M	1.32g / 22mmol
8	1:1	14 ml	0.7 M	0.59g / 9.8mmol
5	1:1	11 ml	1.6 M	1.06g / 17.6mmol
9	1:1	10 ml	2.7 M	1.62g / 27mmol
6	1:1	6.8 ml	3.97 M	1.62g / 27mmol
7	1:1	30 ml	2.025 M	3.65g / 60mmol
10	1:1	27 ml	1.51 M	4.92g / 82mmol

Table 17	Quantities used in the synthesis of [TAA][silicate] solutions
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Cation	Cation:Silicon	Viscosity/ CPs	NMR δ(²⁹ Si)/ppm
1	1:1	5.9	-100.3; Q ³ ₈ Si
1	1:2	25.0	-90.8 ; Q ² Si -100.6 ; Q ³ ₈ Si
2	1:1	6.2	-100.3 ; Q ³ ₈ Si
2	1:2	14.7	-90.4 ; Q ² Si -100.4 ; Q ³ ₈ Si
2	2:1	3.74	-100.3 ; Q ³ ₈ Si
3	1:1	1.6	-73.1 ; Q^0 Si -81.7 ; Q^1 Si -83.3 ; Q^2_3 Si -90.3 ; Q^2 Si -99.9 ; Q^3_8 Si
4	1:1	1.6	-73.1 ; Q^0 Si -81.8 ; Q^1 Si -83.5 ; Q^2_3 Si -89.8 ; Q^2 Si -99.6 ; Q^3 Si
8	1:1	1.5	-89.4 ; Q ² Si -99.3 ; Q ³ Si

Table 18	Viscosity and ²⁹ Si	NMR	data	of the	silicate	solutions	prepared
	using [TAA][OH]						

			$-73.1:0^{0}$ Si
			-90.4 ; Q^2_4 Si
5	1:1	2.9	-91.4 ; Q ³ ₆ Si
			-99.8 ; Q ³ ₈ Si
			-90.4 ; Q ² ₄ Si
9	1-1	72.4	-91.2 ; Q ³ ₆ Si
	1.1	12.1	-99.6 ; Q ³ ₈ Si
			2
6	1:1	65.6	-90.0 ; Q ² Si
1.965	SUC2YALT-PHI	39994907003078	-99.8 ; Q ³ ₈ Si
-			-73.1 ; Q° Si
7	1:1	125.9	-90.9 ; Q ³ ₆ Si
			-99.9 ; Q ³ ₈ Si
			72 1. 00 8.
10	1.1	40.9	$-73.1; Q^2 Si$
10	1:1	40.8	-90.7; Q ² S1
			-100.0; Q ⁵ ₈ Si

Preparation of [TAA][silicate] solutions containing mixed cationic content

A series of silicate solutions were prepared using the following TAA hydroxides, [(CH₃)₄N]OH 25% w/w, [(CH₃)₃N(CH₂CH₂OH)]OH 50% w/w and [(CH₃)₂N(CH₂CH₂OH)(CH₂CH(OH)CH₂OH)]OH 2.025M in aqueous solution. The cation/silicon ratio in all cases was 1:1. The ratio of TAA(a)/TAA(b) was either 1:1 or 1:4. The general synthesis is described in detail for the mixed TMA/choline silicate 1:1:2. Quantities used for the series are shown in **Table 19**.

[(CH₃)₄N]OH 25% w/w (3.038g, 8.3mmol) and [(CH₃)₃N(CH₂CH₂OH)]OH 50% w/w (2.0196g, 8.3mmol) were mixed together using a homogeniser rotating at

11500 rpm. To this, fumed silica (1.0g, 16.6mmol) was added gradually over 30 minutes. The mixture was left to mix for a further 45 minutes. After a minimum of 4 days the solution was analysed by 29 Si NMR.

Table 19	Quantities	used	in	the	synthesis	of	TAA	silicate	solutions
	containing	mixed	cati						

Silicate	TMA	choline	DPHEMA	SiO ₂	NMR
	25% w/w in	50 w/w in	2.025M in		δ(²⁹ Si)/ppm
	H_2O	H_2O	H_2O		
	3.038g /	2.019g /		1.0g /	-100.7 ppm
11	8mmol	8mmol		16mmol	
	1.166g /	3.1g/		1.0g /	-100.5 ppm
12	3.2mmol	12.8mmol		16mmol	
	3.038g /		4.1ml /	1.0g /	-100.4 ppm
13	8mmol	—	8mmol	16mmol	
	1.166g /		6.32ml /	1.0g /	-100.1 ppm
14	3.2mmol	_	12.8mmol	16mmol	

Modified Lentz Trimethylsilylation leading to the preparation of Q8M8

The general method of Lentz trimethylsilylation is described in detail for the [TAA][silicate] DPHEDMA silicate 1:1, which in this case gave a good yield of Q8M8. Dimethylformamide (250ml), hexamethyldisiloxane (125ml) and trimethylchlorosiliane (125ml) were vigorously stirred in a flask equipped with a calcium chloride guard tube at ambient temperature for 30 minutes. [DPHEDMA][silicate] (4.0g, of a 2.025M solution) was added and the mixture stirred for a further 2 hours. Ice (200g) was added to decompose excess trimethylchlorosiliane. The organic layer was isolated, washed to neutrality and dried over magnesium sulphate. The mixture was then filtered before all solvents were removed *in vacuo* yielding a clear/white crystalline product.

Mass of product = 1.2g	
NMR δ(²⁹ Si)/ppm _(Chloroform) :	-100.2 (Q ³ ₈),
NMR δ(²⁹ Si)/ppm _(Solid-state) :	11.1 (Q8M8, s), -108.9 (Q8M8, d),
	-109.8 (Q8M8,d)

Required for C₂₄H₇₂O₂₀Si₁₆ : C, 25.5; H, 6.4; Found: C, 25.9; H, 6.2;

Solid-state sample preparation

A series of silicate solutions were dried and prepared for solid-state analysis. Typically, silicate solution, 5g (~4.5ml), was concentrated using a rotary evaporator with a water bath temperature of 65°C. The viscous solution was poured onto a clock glass coated with a non-stick PTFE tape. This was further dried in a desiccated oven at 80°C for 12 hours. After this time, the solid mass was chilled using liquid nitrogen before being ground to a fine powder using a pestle and mortar. The prepared sample was stored in a vacuum desiccator to prevent absorption of atmospheric moisture.

Single crystal x-ray analysis of [NMe₄]₈[Si₈O₂₀].69 H₂O

[(CH₃)₄N]OH 25% w/w (15ml, 41.5mmol) was placed in a narrow high-sided beaker and stirred using a homogeniser rotating at 11500 rpm. To this, fumed silica (2.5g, 41.5mmol) was added gradually over 30 minutes. The mixture was mixed for a further 45 minutes before being left to stand. After a period of two weeks a crystalline precipitation was observed. A crystal was collected and used for x-ray analysis. Full data is given in the appendix with selected data discussed in Chapter 2.

5.4 Preparation of [TAA][aluminate] & [TAA][aluminosilicate] solutions

Preparation of [TMA][aluminate]

[(CH₃)₄N]OH 25% w/w solution (20.2ml, 55.5mmol) was heated on a hot plate to ca. 75°C. To this, powdered aluminium (1g, 37mmol) was added (CAUTION:-flammable gas evolved) and the solution stirred until all the aluminium had dissolved. This was denoted by the arresting of effervescence. The resulting solution was filtered to remove any undissolved impurities.

NMR $\delta(^{27}Al)/ppm$: 79.8

Preparation of [choline][aluminate]

[(CH₃)₃(CH₂CH₂OH)N]OH 50% w/w solution (12.53ml, 55.5mmol) and water (20ml) were heated on a hot plate to *ca*. 75°C. To this, powdered aluminium (1g, 37mmol) was added (CAUTION:- flammable gas evolved) and the solution stirred until all the aluminium had dissolved. This was denoted by the arresting of effervescence. The resulting solution was filtered to remove any undissolved impurities and concentrated under vacuum.

NMR $\delta(^{27}Al)/ppm:$ 79.5

Preparation of [DPHEDMA][aluminate]

[(CH₃)₂N(CH₂CH₂OH)(CH₂CH(OH)CH₂OH)]OH 2.025M solution (27.4ml, 55.5mmol) and water (50ml) were heated on a hot plate to *ca*. 75°C. To this, powdered aluminium (1g, 37mmol) was added (CAUTION:- flammable gas evolved) and the solution stirred until all the aluminium had dissolved. This was denoted by the arresting of effervescence. The resulting solution was filtered to remove any undissolved impurities and concentrated under vacuum.

NMR δ(²⁷Al)/ppm: 79.6

Preparation of [TAA][aluminosilicate] solutions

A series of [TAA][aluminosilicate] solutions were prepared using the [TAA] [aluminates] and some of the [TAA][silicates] described previously. The ratios quoted refer to the silicate/aluminate ratio. This was varied as was the nature of the TAA cation. The general synthesis is described in detail for a [choline] [aluminosilicate] 1:1. Quantities used for the series are shown in **Table 20**.

A mixture of $[(CH_3)_3(CH_2CH_2OH)N]$ [silicate] 2.42M (20ml, 48.4mmol) and $[(CH_3)_3(CH_2CH_2OH)N]$ [aluminate] 2.5M (19.36ml, 48.4mmol) were placed in a narrow high-sided beaker and stirred using a homogeniser rotating at 11500 rpm for 30 minutes The resulting solution was left to stand and after a minimum of 4 days the solution was analysed by ²⁹Si NMR and ²⁷Al NMR spectroscopy. Results are tabulated in **Table 21**.

	Silicat	te	Alun	Ratio	
Solution	Cation	SiO ₂	Cation	Al	Si:Al
	TMA (25%)	2g,			
15	12.15ml,	33.3mmol	1	1	8:0
	33.3mmol				
	TMA (25%)	2g,	TMA	0.128g,	
16	12.15ml,	33.3mmol	2.6g,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	TMA (25%)	2g,	choline	0.128g,	
17	12.15ml,	33.3mmol	2.6g,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	TMA (25%)	2g,	DPHEDMA	0.128g,	
18	12.15ml,	33.3mmol	3.4ml,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	TMA (25%)	2g,	Na	0.128g,	
19	12.15ml,	33.3mmol	0.29g,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	TMA (25%)	2g,	TMA	0.90g,	
20	12.15ml,	33.3mmol	18.2g,	33.3mmol	4:4
	33.3mmol		49.95mmol		
	TMA (25%)	2g,	choline	0.90g,	
21	12.15ml,	33.3mmol	12.1g,	33.3mmol	4:4
	33.3mmol		49.95mmol		
	TMA (25%)	2g,	DPHEDMA	0.90g,	
22	12.15ml,	33.3mmol	15.9ml,	33.3mmol	4:4
	33.3mmol		49.95mmol		
	TMA (25%)	2g,	Na	0.90g,	
23	12.15ml,	33.3mmol	2g,	33.3mmol	4:4
	33.3mmol		49.95mmol		

Table 20Quantities used in the synthesis of [TAA][aluminosilicate]
solutions

	choline (50%)	2g,			
24	8.1ml,	33.3mmol	1	1	8:0
	33.3mmol				
	choline (50%)	2g,	TMA	0.128g,	
25	8.1ml,	33.3mmol	2.6g,	4.76mmol	7:1
5	33.3mmol 7.		7.14mmol		
	choline (50%)	2g,	choline	0.128g,	
26	8.1ml,	33.3mmol	2.6g,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	choline (50%)	2g,	DPHEDMA	0.128g,	
27	8.1ml,	33.3mmol	3.4ml,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	choline	2g,	choline	0.90g,	
28	(50%)8.1ml,	33.3mmol	12.1g,	33.3mmol	4:4
	33.3mmol		49.95mmol		
	choline (50%)	2g,	DPHEDMA	0.90g,	
29	8.1ml,	33.3mmol	15.9ml,	33.3mmol	4:4
	33.3mmol		49.95mmol		
	DPHEDMA	2g,			
30	(2.1M) 15.8ml,	33.3mmol	1	/	8:0
	33.3mmol				
	DPHEDMA	2g,	TMA	0.128g,	
31	(2.1M) 15.8ml,	33.3mmol	2.6g,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	DPHEDMA	2g,	choline	0.128g,	
32	(2.1M) 15.8ml,	33.3mmol	2.6g,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	DPHEDMA	2g,	DPHEDMA	0.128g,	
33	(2.1M) 15.8ml,	33.3mmol	3.4ml,	4.76mmol	7:1
	33.3mmol		7.14mmol		
	DPHEDMA	2g,	choline	0.90g,	
34	(2.1M) 15.8ml,	33.3mmol	12.1g,	33.3mmol	4:4
	33.3mmol		49.95mmol		

	DPHEDMA	2g,	DPHEDMA	0.90g,	
35	(2.1M) 15.8ml,	33.3mmol	15.9g,	33.3mmol	4:4
	33.3mmol		49.95mmol		
	choline (50%)	2g,	choline	0.29g,	
36	8.1ml,	33.3mmol	4.0g,	11.1mmol	6:2
	33.3mmol		16.65mmol		
	choline (50%)	2g,	choline	0.53g,	
37	8.1ml,	33.3mmol	7.3g,	19.98mmol	5:3
	33.3mmol		29.97mmol		

Table 2127 Al NMR and 29 Si NMR data of the aluminosilicate solutionsprepared using three TAA hydroxides

Solution	Al:Si	NMR δ(²⁷ Al)/ppm	NMR δ(²⁹ Si)/ppm
15	8:0	1	-100.3 ; Q ³ ₈ Si
16	7:1	75.0 ; Al(OSi) 69.1 ; Al(OSi) ₂ 64.1 ; Al(OSi) ₃	-100.5 ; Q_8^3 Si -95.68 ; Q^3 Si(OAl) -90.3 ; Q^2 Si -83.2 ; Q_3^2 Si -81.4 ; Q^1 Si -72.9 ; Q^0 Si
17	7:1	74.7 ; Al(OSi) 69.5 ; Al(OSi) ₂ 64.5 ; Al(OSi) ₃	-100.4 ; $Q_8^3 Si$ -95.4 ; $Q^3 Si(OAI)$ -90.4 ; $Q^2 Si$ -83.2 ; $Q_3^2 Si$ -81.2 ; $Q^1 Si$ -72.9 ; $Q^0 Si$

		1	
18	7:1	74.9 ; Al(OSi) 69.1 ; Al(OSi) ₂ 64.5 ; Al(OSi) ₃ 61.4 ; Al(OSi) ₄	-100.5 ; Q_8^3 Si -95.7 ; Q^3 Si(OAl) -90.5 ; Q^2 Si -83.3 ; Q_3^2 Si -81.3 ; Q^1 Si -73.1 ; Q^0 Si
19	7:1	64.1 ; Al(OSi) ₃ 57.5 ; Al(OSi) ₄	-100.3 ; Q_8^3 Si -89.4 ; Q^2 Si -83.1 ; Q_3^2 Si -81.4 ; Q^1 Si -72.8 ; Q^0 Si
20	4:4	78.9 ; Al(OH) ₄ 71.2 ; Al(OSi) ₂ 65.2 ; Al(OSi) ₃	-100.4 ; Q ³ ₈ Si -84.0 ; Q ³ Si(OAl) ₃
21	4:4	78.9 ; Al(OH) ₄ ⁻ 71.1 ; Al(OSi) ₂ 64.5 ; Al(OSi) ₃	-100.8 ; Q ³ ₈ Si -86.5 ; Q ³ Si(OAl) ₃ -82.4 ; Q ¹ Si
22	4:4	76.7 ; Al(OSi) 69.5 ; Al(OSi) ₂ 64.6 ; Al(OSi) ₃	-100.4 ; Q ³ ₈ Si -91.2 ; Q ² Si -86.7 ; Q ³ Si(OAl) ₃ -82.9 ; Q ¹ Si

24	8:0	/	-100.3 ; Q ³ ₈ Si
25	7:1	68.1 ; Al(OSi) ₂ 63.8 ; Al(OSi) ₃ 59.1 ; Al(OSi) ₄	-100.5 ; Q_8^3 Si -95.7 ; Q^3 Si(OAl) -90.9 ; Q^2 Si -87.7 ; Q^3 Si(OAl) ₃ -83.3 ; Q_3^2 Si -81.5 ; Q^1 Si -73.5; Q^0 Si
26	7:1	68.2 ; Al(OSi) ₂ 64.2 ; Al(OSi) ₃ 59.8 ; Al(OSi) ₄	-100.1 ; Q_8^3 Si -95.2 ; Q^3 Si(OAl) -89.9 ; Q^2 Si -83.1 ; Q_3^2 Si -81.3 ; Q^1 Si -72.9 ; Q^0 Si
27	7:1	63.8 ; Al(OSi) ₃ 59.5 ; Al(OSi) ₄	-100.4 ; Q_8^3 Si -95.6 ; Q^3 Si(OAl) -90.7 ; Q^2 Si -83.4 ; Q_3^2 Si -81.7 ; Q^1 Si -73.2 ; Q^0 Si
28	4:4	76.1 ; Al(OSi) 69.4 ; Al(OSi) ₂ 64.1 ; Al(OSi) ₃	-100.5 ; Q ³ ₈ Si -86.4 ; Q ³ Si(OAl) ₃

29	4:4	68.9 ; Al(OSi) ₂ 63.8 ; Al(OSi) ₃	-99.6 ; Q ² Si -86.2 ; Q ³ Si(OAl) ₃ -82.5 ; Q ¹ Si
30	8:0	/	-99.7 ; Q ³ ₈ Si
31	7:1	68.9 ; Al(OSi) ₂ 63.7 ; Al(OSi) ₃	-100.2 ; Q_8^3 Si -95.3 ; Q^3 Si(OAl) -90.4 ; Q^2 Si -83.3 ; Q_3^2 Si -81.6 ; Q^1 Si -73.0 ; Q^0 Si
32	7:1	67.9 ; Al(OSi) ₂ 63.2 ; Al(OSi) ₃	-99.7 ; Q ³ ₈ Si -94.7 ; Q ³ Si(OAl) -90.4 ; Q ² Si -81.7 ; Q ¹ Si -73.1 ; Q ⁰ Si
33	7:1	76.1 ; Al(OSi) 69.4 ; Al(OSi) ₂ 64.1 ; Al(OSi) ₃	-99.6 ; Q_8^3 Si -94.9 ; Q^3 Si(OAl) -90.4 ; Q^2 Si -83.3 ; Q_3^2 Si -81.7 ; Q^1 Si -73.1 ; Q^0 Si

35	4:4	76.8 ; Al(OSi) 69.5 ; Al(OSi) ₂	-100.6 ; Q ³ ₈ Si
		64.6 ; Al(OSi) ₃	-86.8 ; Q ³ Si(OAl) ₃
36	6:2	74.8 ; Al(OSi) 68.9 ; Al(OSi) ₂ 64.4 ; Al(OSi) ₃	-100.2 ; Q ³ ₈ Si -95.3 ; Q ³ Si(OAI) -89.4 ; Q ² Si -85.9 ; Q ³ Si(OAI) ₃ -80.9 ; Q ¹ Si -73.4 ; Q ⁰ Si
37	5:3	75.6 ; Al(OSi) 69.3 ; Al(OSi) ₂ 64.6 ; Al(OSi) ₃	-100.4 ; Q ³ ₈ Si -86.5 ; Q ³ Si(OAl) ₃ -82.1 ; Q ¹ Si

5.5 Preparation of tetraalkylammonium borates

Preparation of [Ph₂BOBPh₂]⁷¹

Diphenylborinic acid ethanolamine ester, $[Ph_2BOCH_2CH_2NH_2]$ (2.0g, 8.88mmol), was dissolved in 1:1 acetone/methanol (30ml) and treated with diluted hydrochloric acid (5ml). The mixture was extracted with ether and the solvent evaporated. A yellow oil, diphenylborinic acid, $[Ph_2BOH]$, remained which crystallised into the anhydride, $[Ph_2BOBPh_2]$, under vacuum. Yield = 1.43g (92.8%)

Mpt = 137-140 °C (lit. 135-140°C)⁷¹. NMR δ (¹¹B)/ppm: 45.09 (1B).

Preparation of $[(CH_3)_3N(CH_2CH_2OH)][Ph_4B_3O_3]$

Choline hydroxide, $[(CH_3)_3N(CH_2CH_2OH)][OH]$ 45% w/w solution in MeOH (0.31g, 1.156mmol) was added to diphenylborinic acid anhydride, $[Ph_2BOBPh_2]$, (0.2g, 0.578mmol) and phenylboronic acid, $[PhB(OH)_2]$, (0.28g, 2.31mmol). The mixture was dissolved in a further 5 ml of methanol which, after a short while, afforded a precipitate. The crude product was recrystallised using acetone to give a white crystalline product, $[(CH_3)_3N(CH_2CH_2OH)][Ph_4B_3O_3]$. Yield = 0.6g (52.6%)

Mpt: 189°C. NMR δ(¹¹B)/ppm: 4.19 (1B), 29.05 (2B). Required for C₂₉H₃₄B₃NO₄: C, 70.7; H, 7.0; N, 2.8. Found: C, 70.3; H, 6.5; N, 2.1.

Preparation of $[(CH_3)_3N(CH_2CH_2OH)][(Ph_2BO)(3-MeOC_6H_4BO)_2]$

Choline hydroxide, $[(CH_3)_3N(CH_2CH_2OH)][OH]$, 45% w/w solution in MeOH (0.31g, 1.156mmol) was added to diphenylborinic acid anhydride, $[Ph_2BOBPh_2]$, (0.2g, 0.578mmol) and *m*-methoxy phenylboronic acid, $[(3-MeOC_6H_4)B(OH)_2]$ (0.35g, 2.31mmol). The mixture was dissolved in a further 5 ml of methanol which, after a short while, afforded a precipitate. The crude product was

recrystallised using acetone to give a white crystalline product, $[(CH_3)_3N(CH_2CH_2OH)][(Ph_2BO)(3-MeOC_6H_4BO)_2].$ Yield = 0.46g (36.2%)

NMR $\delta(^{11}B)$ /ppm: 3.6 (1B), 27.69(2B). Required for $C_{31}H_{38}B_3NO_6$: C, 67.3; H, 6.9; N, 2.5. Found: C, 68.9; H, 6.5; N, 2.4.

Preparation of $[(CH_3)_3N(CH_2CH_2OH)]$ $[(Ph_2BO)(2-MeOC_6H_4BO)_2]$

Choline hydroxide, $[(CH_3)_3N(CH_2CH_2OH)][OH]$, 45% w/w solution in MeOH (0.31g, 1.156mmol) was added to diphenylborinic acid anhydride, $[Ph_2BOBPh_2]$, (0.2g, 0.578mmol) and *o*-methoxy phenylboronic acid, $[(2-MeOC_6H_4)B(OH)_2]$ (0.35g, 2.31mmol). The mixture was dissolved in a further 5 ml of methanol which, after a short while, afforded a precipitate. The crude product was recrystallised using acetone to give a white crystalline product, $[(CH_3)_3N(CH_2CH_2OH)][((Ph_2BO)(2-MeOC_6H_4BO)_2]$ Yield = 0.3g (23.6%)

NMR δ(¹¹B)/ppm: 3.45 (1B), 28.19(2B). Required for C₃₁H₃₈B₃NO₆: C, 67.3; H, 6.9; N, 2.5. Found: C, 69.4; H, 7.3 ; N, 2.0.

Preparation of $[(CH_3)_3N(CH_2CH_2OH)]_2$ [Ph₄B₄O₅]

Choline hydroxide, $[(CH_3)_3N(CH_2CH_2OH)][OH]$, 45% w/w solution in MeOH (0.31g, 1.156mmol) was added to phenylboronic acid, $[PhB(OH)_2]$, (0.28g, 2.31mmol). The mixture was dissolved in a further 5 ml of methanol which, after a short while, was removed under vacuum. The crude product was recrystallised using acetone to give a white crystalline product, $[(CH_3)_3N(CH_2CH_2OH)]_2$ $[Ph_4B_4O_5]$ Yield = 0.3g (23.6%)

NMR δ(¹¹B)/ppm: 3.02 (2B), 28.62(2B). Required for C₃₄H₄₈B₄N₂O₇: C, 63.8; H, 7.6; N, 4.4. Found: C, 63.5; H, 7.9; N, 4.0.

Choline hydroxide, $[(CH_3)_3N(CH_2CH_2OH)][OH]$, 45% w/w solution in MeOH (0.156g, 0.57mmol) was added to diphenylborinic acid anhydride, $[Ph_2BOBPh_2]$, (0.1g, 0.28mmol) and ferrocenylboronic acid, $[FcB(OH)_2]$, (0.257g, 1.12mmol). The mixture was dissolved in a further 5 ml of methanol which, after a short while, was removed under vacuum. The crude product was recrystallised using acetone to give an orange crystalline product, $[(CH_3)_3N(CH_2CH_2OH)][(Ph_2BO)(FcBO)_2]$.

Yield = 0.12g(66.6%)

NMR δ(¹¹B)/ppm: 3.17 (1B), 29.53(2B). Required for C₃₇H₃₄B₃Fe₂NO₄: C, 63.4; H, 4.9; N, 2.0. Found: C, 63.0; H, 4.7; N, 2.4.

Preparation of [(CH₃CH₂)₃NH] [Ph₃B₃O₃OH]

Triethylamine, $[N(Et)_3]$, (0.17g, 1.6mmol) and phenylboronic acid, $[PhB(OH)_2]$, (0.49, 4.8mmol) were dissolved in diethyl ether (10ml). The solvent was evaporated and the remaining white crystalline powder recrystallised from diethyl ether to give $[(CH_3CH_2)_3NH]$ $[Ph_3B_3O_3OH]$. Yield = 0.38g (49%)

NMR δ(¹¹B)/ppm: 4.57(1B), 29.75(2B). Required for C₂₅H₃₂B₃NO₄: C, 67.8; H, 7.3; N, 3.2. Found: C, 67.2; H, 6.9; N, 2.8.



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- 158 -

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Table 1. Crystal data and structure refinement.

Identification code Empirical formula Formula weight Temperature Wavelength

Crystal system Space group Unit cell dimensions

Volume Z Density (calculated) Absorption coefficient F(000) Crystal Crystal size θ range for data collection Index ranges Reflections collected Independent reflections Completeness to $\theta = 25.03^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices $[F^2 > 2\sigma(F^2)]$ R indices (all data) Largest diff. peak and hole

04src0036 MAB/BST/131 C₃₂H₂₂₂N₈O₈₃Si₈ Si_8O_{20} . 8(N(CH₃)₄) . 63(H₂0) 2272.90 120(2) K 0.71073 Å Triclinic P-1a = 15.5929(4) Å b = 15.5953(4) Å c = 15.8120(4) Å $\gamma = 91.680(2)^{\circ}$ 3089.65(14) Å³ 1 $1.222 \text{ Mg}/\text{m}^3$ 0.189 mm^{-1} 1246 Colourless Block $0.50 \times 0.30 \times 0.15 \text{ mm}^3$ $2.94 - 25.03^{\circ}$ $-18 \le h \le 18, -18 \le k \le 18, -18 \le l \le 18$ 47875 $10884 [R_{int} = 0.0411]$ 99.8 % Semi-empirical from equivalents 0.9722 and 0.9114 Full-matrix least-squares on F^2 10884 / 167 / 777 1.012 R1 = 0.0999, wR2 = 0.2851R1 = 0.1201, wR2 = 0.30402.270 and $-1.224 \text{ e} \text{ Å}^{-3}$

 $\alpha = 109.4100(10)^{\circ}$ $\beta = 118.9040(10)^{\circ}$

Special details: All hydrogen atoms were placed in idealised positions and refined using a riding model.

Diffractometer: Nonius KappaCCD area detector (ϕ scans and ω scans to fill asymmetric unit sphere). Cell determination: DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) Data collection: Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). Data reduction and cell refinement: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. 276: Macromolecular Crystallography, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). Absorption correction: SORTAV (R. H. Blessing, Acta Cryst. A51 (1995) 33-37; R. H. Blessing, J. Appl. Cryst. 30 (1997) 421-426). Structure solution: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A46 467-473). Structure refinement: SHELXL97 (G. M. Sheldrick (1997), University of Göttingen, Germany). Graphics: Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Atom	x	у	z	U_{eq}	S.o.f.	
		Parameter praticies of the	and 1975 state by instance from the		.u	
Si1	-1317(1)	4879(1)	3037(1)	15(1)	1	
Si2	-489(1)	3221(1)	3603(1)	15(1)	1	
Si3	1677(1)	4510(1)	5086(1)	15(1)	1	
Si4	847(1)	6173(1)	4518(1)	15(1)	1	
O 1	-1782(3)	5200(3)	3780(3)	29(1)	1	
O2	-2095(2)	4797(2)	1880(2)	20(1)	1	
O3	-1056(3)	3878(2)	3006(3)	31(1)	1	
O4	-805(3)	3255(2)	4446(3)	32(1)	1	
05	-775(2)	2181(2)	2783(2)	20(1)	1	
06	711(2)	3654(2)	4232(3)	29(1)	1	
07	2667(2)	4217(2)	5146(2)	20(1)	1	
08	1487(3)	5391(3)	4746(3)	32(1)	1	
09	1339(2)	6860(2)	4241(2)	19(1)	1	
O10	-291(3)	5640(3)	3560(3)	33(1)	1	
N1	-1559(2)	8135(2)	3714(2)	37(1)	1	
C1	-1961(4)	8980(3)	3902(5)	70(1)	1	
C2	-2142(5)	7531(4)	2612(3)	70(1)	1	
C3	-1600(5)	7670(4)	4366(5)	70(1)	1	
C4	-502(4)	8448(5)	4081(5)	70(1)	1	
N2	881(2)	3784(2)	1498(2)	30(1)	1	
C5	33(3)	3252(5)	1429(5)	109(2)	1	
C6	934(5)	4769(3)	1933(5)	109(2)	1	
C7	1808(5)	3543(6)	2159(6)	109(2)	1	
C8	710(6)	3463(6)	439(5)	109(2)	1	
N3	-4060(2)	2438(2)	2073(2)	29(1)	1	
C9	-3857(6)	3341(4)	2919(6)	194(4)	1	
C10	-5114(4)	1993(6)	1490(8)	194(4)	1	
C11	-3430(7)	1860(5)	2560(8)	194(4)	1	
C12	-3736(8)	2634(8)	1418(8)	194(4)	1	
N4	2696(5)	9061(4)	2811(5)	77(2)	ĩ	
C13	2321(9)	9888(7)	2650(10)	172(4)	1	
C14	3737(6)	9195(9)	3112(10)	172(4)	1	
C15	2566(10)	8942(9)	3628(8)	172(4)	1	
C16	2054(9)	8250(7)	1831(7)	172(4)	1	
011	-262(1)	1275(1)	485(2)	65(3)	0.50	
012	-1435(1)	495(4)	-480(1)	64(3)	0.50	
013	605(1)	663(1)	789(4)	48(2)	0.50	
014	3942(1)	1504(1)	5058(3)	61(3)	0.50	
015	-5748(1)	2425(1)	-3050(3)	40(2)	0.50	
016	-6320(1)	-373(1)	73(3)	105(6)	0.50	
017	-3367(1)	301(1)	-915(2)	67(3)	0.50	

Table 2. Atomic coordinates [× 10⁴], equivalent isotropic displacement parameters [Å² × 10³] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

O18	-1545(1)	5623(1)	951(2)	32(1)	1	
019	3037(1)	6708(1)	4326(2)	28(1)	1	
O20	-2622(1)	3224(1)	256(2)	27(1)	1	
O21	-1458(1)	790(1)	3049(2)	36(1)	1	
O22	3711(1)	5221(1)	4806(2)	29(1)	1	
O23	-3846(1)	5133(2)	1400(1)	32(1)	1	
O24	1869(1)	8708(1)	5369(2)	42(1)	1	
O25	327(1)	6871(1)	2284(2)	41(1)	1	
026	4074(1)	4154(1)	6926(2)	37(1)	1	
O27	-3085(1)	6337(1)	-207(1)	38(1)	1	
O28	664(1)	1430(2)	2628(2)	34(1)	1	
029	2587(1)	2465(1)	4095(2)	35(1)	1	
O30	-1961(1)	1732(2)	744(1)	38(1)	1	
O31	-1645(1)	3972(1)	-500(2)	47(1)	1	
O32	5638(1)	5930(1)	6422(2)	41(1)	1	
033	-229(1)	8377(1)	1814(1)	64(1)	1	
034	5995(1)	5081(1)	7751(2)	46(1)	1	
035	-4630(1)	2516(1)	-1106(2)	39(1)	1	
036	-5475(1)	3799(1)	-274(1)	38(1)	1	
O37	3682(1)	2290(1)	3168(2)	50(1)	1	
O38	-4695(1)	-695(2)	1556(2)	48(1)	1	
039	-2267(1)	-1854(1)	394(2)	53(1)	1	
O40	246(1)	10142(1)	3313(1)	57(1)	1	
O41	2517(1)	1204(1)	1113(2)	61(1)	1	
O42	3847(2)	9674(1)	6278(2)	70(2)	1	
043	-3080(1)	-536(1)	1287(2)	70(2)	1	
O44	3103(1)	6446(1)	2571(3)	79(2)	1	
O45	4631(1)	8203(1)	5615(2)	77(2)	1	

Si1–O2	1.589(3)	N1-C2	1.441(4)
Si1-O1	1.615(3)	N1-C4	1.458(6)
Si1-O10	1.615(3)	N1-C3	1.467(6)
Si1-O3	1.617(4)	N1-C1	1.479(5)
Si2-O5	1.584(3)	N2-C6	1.441(4)
Si2–O3	1.615(3)	N2-C8	1.458(6)
Si2-04	1.617(3)	N2-C7	1.467(6)
Si2-06	1.620(3)	N2-C5	1.479(5)
Si3–O7	1.590(3)	N3-C10	1.441(4)
Si3-06	1.610(3)	N3-C12	1.458(6)
Si3–O1 ⁱ	1.618(3)	N3-C11	1.467(6)
Si3-08	1.619(3)	N3-C9	1.479(5)
Si409	1.586(3)	N4-C14	1.441(4)
Si4-O10	1.617(3)	N4-C16	1.458(6)
Si4–O4 ⁱ	1.618(4)	N4-C15	1.467(6)
Si4-08	1.622(3)	N4-C13	1.479(5)
O1–Si3 ⁱ	1.618(3)	O16–O17 ⁱⁱ	1.599(5)
O4–Si4 ⁱ	1.618(4)	O17–O16 ⁱⁱ	1.599(5)
O2-Si1-O1	110.95(18)	Si1–O1–Si3 ⁱ	150.8(2)
O2-Si1-O10	110.52(18)	Si2-O3-Si1	150.6(2)
O1-Si1-O10	108.1(2)	Si2-O4-Si4 ⁱ	150.9(2)
O2-Si1-O3	110.00(18)	Si3-O6-Si2	150.5(2)
O1-Si1-O3	108.0(2)	Si3-O8-Si4	150.6(2)
O10-Si1-O3	109.2(2)	Si1-O10-Si4	150.4(2)
O5-Si2-O3	110.52(18)	C2-N1-C4	112.5(4)
O5-Si2-O4	110.49(18)	C2-N1-C3	111.5(3)
O3-Si2-O4	108.8(2)	C4-N1-C3	107.8(3)
O5-Si2-O6	110.78(18)	C2-N1-C1	109.5(3)
O3-Si2-O6	107.5(2)	C4-N1-C1	107.2(3)
O4-Si2-O6	108.7(2)	C3-N1-C1	108.2(3)
07-Si3-O6	110.33(18)	C6-N2-C8	112.5(4)
O7–Si3–O1 ⁱ	110.22(17)	C6-N2-C7	111.4(3)
O6–Si3–O1 ⁱ	108.6(2)	C8-N2-C7	108.0(3)
O7-Si3-O8	110.73(18)	C6-N2-C5	109.4(3)
O6-Si3-O8	108.3(2)	C8-N2-C5	107.2(3)
01 ⁱ –Si3–O8	108.5(2)	C7-N2-C5	108.1(3)
O9-Si4-O10	110.78(18)	C10-N3-C12	112.6(4)
09–Si4–O4 ⁱ	110.61(18)	C10-N3-C11	111.4(3)
O10–Si4–O4 ⁱ	107.9(2)	C12-N3-C11	107.9(4)
O9–Si4–O8	111.27(18)	C10-N3-C9	109.5(3)
O10-Si4-O8	108.1(2)	C12-N3-C9	107.2(3)
O4 ⁱ –Si4–O8	108.0(2)	C11-N3-C9	108.1(3)

Table 3. Bond lengths [Å] and angles [°].

C14-N4-C16	112.5(4)
C14-N4-C15	111.4(3)
C16-N4-C15	107.9(4)
C14-N4-C13	109.5(3)
C16-N4-C13	107.2(3)
C15-N4-C13	108.1(3)

Symmetry transformations used to generate equivalent atoms: (i) -x, -y+1, -z+1 (ii) -x-1, -y, -z

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
Si1	12(1)	18(1)	12(1)	6(1)	5(1)	1(1)	
Si2	14(1)	16(1)	14(1)	5(1)	6(1)	0(1)	
Si3	12(1)	18(1)	15(1)	7(1)	7(1)	2(1)	
Si4	13(1)	17(1)	14(1)	7(1)	7(1)	1(1)	
O1	22(2)	50(2)	17(2)	12(2)	13(1)	15(2)	
O2	15(2)	25(2)	15(2)	9(1)	5(1)	1(1)	
O3	40(2)	23(2)	18(2)	7(1)	6(2)	12(2)	
O4	49(2)	23(2)	33(2)	5(2)	32(2)	-1(2)	
O5	22(2)	17(2)	19(2)	4(1)	11(1)	1(1)	
06	16(2)	24(2)	30(2)	-1(2)	7(2)	-1(1)	
O 7	15(2)	24(2)	20(2)	9(1)	10(1)	5(1)	
O 8	31(2)	33(2)	57(2)	33(2)	31(2)	18(2)	
09	19(2)	20(2)	20(2)	9(1)	10(1)	2(1)	
O10	19(2)	46(2)	22(2)	17(2)	1(1)	-12(2)	
N1	35(3)	43(3)	42(3)	28(2)	20(2)	12(2)	
C1	83(3)	62(2)	63(2)	23(2)	39(2)	12(2)	
C2	83(3)	62(2)	63(2)	23(2)	39(2)	12(2)	
C3	83(3)	62(2)	63(2)	23(2)	39(2)	12(2)	
C4	83(3)	62(2)	63(2)	23(2)	39(2)	12(2)	
N2	29(2)	37(3)	28(2)	12(2)	18(2)	10(2)	
C5	84(4)	164(6)	82(4)	67(4)	35(3)	45(4)	
C6	84(4)	164(6)	82(4)	67(4)	35(3)	45(4)	
C7	84(4)	164(6)	82(4)	67(4)	35(3)	45(4)	
C8	84(4)	164(6)	82(4)	67(4)	35(3)	45(4)	
N3	22(2)	33(2)	26(2)	14(2)	9(2)	1(2)	
C9	126(7)	195(10)	206(10)	43(8)	74(7)	-22(6)	
C10	126(7)	195(10)	206(10)	43(8)	74(7)	-22(6)	
C11	126(7)	195(10)	206(10)	43(8)	74(7)	-22(6)	
C12	126(7)	195(10)	206(10)	43(8)	74(7)	-22(6)	
N4	106(6)	58(4)	76(5)	29(4)	51(5)	27(4)	
C13	242(11)	142(7)	162(8)	61(6)	127(8)	40(7)	
C14	242(11)	142(7)	162(8)	61(6)	127(8)	40(7)	
C15	242(11)	142(7)	162(8)	61(6)	127(8)	40(7)	
C16	242(11)	142(7)	162(8)	61(6)	127(8)	40(7)	
O 11	73(7)	76(7)	57(6)	22(5)	43(6)	23(6)	
012	62(6)	68(7)	51(6)	14(5)	27(5)	21(5)	
013	30(4)	65(6)	28(4)	-5(4)	16(3)	5(4)	
O14	67(6)	31(4)	31(4)	0(4)	-6(4)	26(4)	
O15	52(5)	32(4)	32(4)	15(3)	17(4)	14(4)	
O16	40(6)	71(7)	127(11)	78(8)	-33(6)	-29(5)	
O17	54(6)	37(5)	64(7)	-2(5)	14(5)	14(4)	

Table 4. Anisotropic displacement parameters $[Å^2 \times 10^3]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2h k a^* b^* U^{12}]$.

O18	31(2)	38(2)	26(2)	16(2)	13(2)	3(2)
019	25(2)	35(2)	34(2)	18(2)	20(2)	9(2)
O20	28(2)	26(2)	22(2)	6(1)	12(2)	4(1)
O21	50(2)	24(2)	41(2)	10(2)	31(2)	2(2)
O22	23(2)	32(2)	37(2)	16(2)	18(2)	4(1)
O23	20(2)	50(2)	24(2)	16(2)	8(2)	13(2)
O24	65(3)	22(2)	49(2)	9(2)	42(2)	5(2)
O25	38(2)	46(2)	29(2)	19(2)	9(2)	-2(2)
O26	33(2)	44(2)	30(2)	14(2)	14(2)	17(2)
O27	41(2)	40(2)	34(2)	20(2)	18(2)	10(2)
O28	29(2)	34(2)	34(2)	2(2)	20(2)	5(2)
O29	30(2)	27(2)	35(2)	1(2)	14(2)	7(2)
O30	42(2)	34(2)	20(2)	4(2)	7(2)	10(2)
O31	51(3)	59(3)	41(2)	24(2)	29(2)	18(2)
O32	30(2)	47(2)	37(2)	10(2)	16(2)	1(2)
O33	95(4)	34(2)	75(3)	27(2)	49(3)	16(3)
O34	35(2)	61(3)	36(2)	18(2)	15(2)	5(2)
O35	29(2)	32(2)	44(2)	8(2)	14(2)	4(2)
O36	30(2)	39(2)	37(2)	14(2)	14(2)	6(2)
O37	33(2)	48(3)	53(3)	2(2)	22(2)	5(2)
O38	36(2)	41(2)	52(3)	13(2)	17(2)	0(2)
O39	67(3)	44(3)	50(3)	18(2)	32(2)	8(2)
O40	65(3)	32(2)	72(3)	15(2)	38(3)	4(2)
O41	68(3)	58(3)	46(3)	12(2)	28(2)	-6(2)
O42	64(3)	62(3)	62(3)	-2(3)	34(3)	1(3)
O43	70(3)	61(3)	64(3)	1(3)	41(3)	-12(3)
O44	81(4)	138(6)	49(3)	51(3)	45(3)	52(4)
O45	44(3)	57(3)	88(4)	4(3)	20(3)	7(2)
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Atom x y z U_{eq} S.o.f. H1A -1558 9395 4649 104 1 H1B -2662 8798 3700 104 1 H1C -1931 9306 3480 104 1 H2A -1881 6967 2490 104 1 H2A -1881 6967 2490 104 1 H2A -1881 6967 2490 104 1 H2A -2847 7357 2398 104 1 H3A -1392 7079 4207 104 1 H3A -2290 7546 4215 104 1 H4B -235 7907 3877 104 1 H4C -119 8774 4849 104 1 H5A 35 2586 1197 163 1 H5C 104 3475 2122 163 1							
H1A -1558 939546491041H1B -2662 879837001041H1C -1931 930634801041H2A -1881 696724901041H2B -2093 785922001041H2A -1881 696724901041H2A -2847 735723981041H3A -1392 707942071041H3B -2290 754642151041H3C -1146 807551111041H4A -444 887437651041H4B -235 790738771041H4C -119 877448491041H5A35258611971631H5C104347521221631H5E -603 33429221631H6A276489515291631H6A276489515291631H7A2391395723041631H7A2391395723041631H7A2391395723041631H8B125438094531631H8B125438094531631H9A -4410 365026552911H9A -510 2	Atom	x	у	z	U_{eq}	S.o.f.	
H1A -1558 939546491041H1B -2662 879837001041H1C -1931 930634801041H2A -1881 696724901041H2B -2093 785922001041H2C -2847 735723981041H3A -1392 707942071041H3B -2290 754642151041H4A -444 887437651041H4B -235 790738771041H4A -444 887437651041H5A35258611971631H5B -603 33429221631H5C104347521221631H6A276489515291631H6B1440511818971631H6C1122496426681631H7A2391395723041631H7B1793289317911631H8A69527941851631H8A69527941851631H8A69527941851631H9B -3226 374031442911H9B -5234 13649862911H10A -5234 1364 </td <td></td> <td></td> <td></td> <td>02 Peol 9 420124</td> <td>the Connect</td> <td></td> <td></td>				02 Peol 9 420124	the Connect		
H1B -2662 8798 3700 104 1 H1C -1931 9306 3480 104 1 H2A -1881 6967 2490 104 1 H2B -2093 7859 2200 104 1 H3A -1392 7079 4207 104 1 H3B -2290 7546 4215 104 1 H3B -2290 7546 4215 104 1 H3C -1146 8075 5111 104 1 H4A -444 8874 3765 104 1 H4B -235 7907 3877 104 1 H4C -119 8774 4849 104 1 H5A 35 2586 1197 163 1 H5B -603 3342 922 163 1 H5C 104 3475 2122 163 1 H6A 276 4895 1529 163 1 H6C 1122 4964 2668 163 1 H7B 1793 2893 1791 163 1 H7B 1793 2893 1791 163 1 H8A 695 2794 185 163 1 H8A 695 2794 185 163 1 H9A -4410 3650 2655 291 1 H9A -510 2361 1112 291 1 H9B </td <td>H1A</td> <td>-1558</td> <td>9395</td> <td>4649</td> <td>104</td> <td>1</td> <td></td>	H1A	-1558	9395	4649	104	1	
H1C -1931 930634801041H2A -1881 696724901041H2B -2093 785922001041H2C -2847 735723981041H3A -1392 707942071041H3B -2290 754642151041H3C -1146 807551111041H4A -444 887437651041H4B -235 790738771041H4C -119 877448491041H5A35258611971631H5B -603 33429221631H6A276489515291631H6A1122496426681631H6C1122496426681631H7A2391395723041631H7B1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H9A -4410 365026552911H9A -5310 236111122911H9B -5224 13649862911H10A -5315 195319782911H10B -5510 <t< td=""><td>H1B</td><td>-2662</td><td>8798</td><td>3700</td><td>104</td><td>1</td><td></td></t<>	H1B	-2662	8798	3700	104	1	
H2A -1881 696724901041H2B -2093 785922001041H2C -2847 735723981041H3A -1392 707942071041H3B -2290 754642151041H3C -1146 807551111041H4A -444 887437651041H4B -235 790738771041H4C -119 877448491041H5A35258611971631H5B -603 33429221631H5C104347521221631H6A276489515291631H6A276489515291631H7A2391395723041631H7A2391395723041631H7C1858361928231631H8B125438094531631H8B125438094531631H9A -4410 365026552911H9B -3226 374031442911H9B -5510 236111122911H10A -5315 195319782911H10A -5316 21718352911H11B -2750 <t< td=""><td>H1C</td><td>-1931</td><td>9306</td><td>3480</td><td>104</td><td>1</td><td></td></t<>	H1C	-1931	9306	3480	104	1	
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H2C -2847 7357 2398 104 1H3A -1392 7079 4207 104 1H3B -2290 7546 4215 104 1H3C -1146 8075 5111 104 1H4A -444 8874 3765 104 1H4B -235 7907 3877 104 1H4C -119 8774 4849 104 1H5A 35 2586 1197 163 1H5B -603 3342 922 163 1H5C 104 3475 2122 163 1H6A 276 4895 529 163 1H6B 1440 5118 1897 163 1H6C 1122 4964 2668 163 1H7A 2391 3957 2304 163 1H7A 2391 3957 2304 163 1H7A 2391 3957 2304 163 1H8A 695 2794 185 163 1H8B 1254 3809 453 163 1H8B 1254 3809 2655 291 1H9A -4410 3650 2655 291 1H9B -3226 3740 3144 291 1H9B -5510 2361 1112 291 1H10C -5315 1953 1978 <	H2B	-2093	7859	2200	104	1	
H3A -1392 707942071041H3B -2290 754642151041H3C -1146 807551111041H4A -444 887437651041H4B -235 790738771041H4C -119 877448491041H5A35258611971631H5B -603 33429221631H6A276489515291631H6A276489515291631H6B1440511818971631H6C1122496426681631H7A2391395723041631H7B1793289317911631H8A69527941851631H8A69527941851631H8B125438094531631H9A -4410 365026552911H9B -3226 374031442911H9C -3801 323235172911H10C -5315 195319782911H10B -5750 224231042911H11A -3721 160728792911H11A -3216 321718352911H112 -4312	H2C	-2847	7357	2398	104	1	
H3B -2290 754642151041H3C -1146 807551111041H4A -444 887437651041H4B -235 790738771041H4C -119 877448491041H5A35258611971631H5B -603 33429221631H5C104347521221631H6A276489515291631H6B1440511818971631H7A2391395723041631H7A2391395723041631H7B1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H9A -4410 365026552911H9B -3226 374031442911H9C -3801 323235172911H10A -5510 236111122911H10A -3721 160728792911H11A -3721 160728792911H11B -2750 224231042911H12A -3216 321718352911H12A -3216 <	H3A	-1392	7079	4207	104	1	
H3C -1146 8075 5111 104 1 H4A -444 8874 3765 104 1 H4B -235 7907 3877 104 1 H4C -119 8774 4849 104 1 H5A 35 2586 1197 163 1 H5B -603 3342 922 163 1 H5C 104 3475 2122 163 1 H6A 276 4895 1529 163 1 H6B 1440 5118 1897 163 1 H7C 1858 3619 2823 163 1 H7R 1793 2893 1791 163 1 H7C 1858 3619 2823 163 1 H8A 695 2794 185 163 1 H8B 1254 3809 453 163 1 H9A -4410 3650 2655 291 1 H9A -5316 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5750 2242 3104 291 1 H11A <td>H3B</td> <td>-2290</td> <td>7546</td> <td>4215</td> <td>104</td> <td>1</td> <td></td>	H3B	-2290	7546	4215	104	1	
H4A -444 887437651041H4B -235 790738771041H4C -119 877448491041H5A35258611971631H5B -603 33429221631H6A276489515291631H6B1440511818971631H6C1122496426681631H7A2391395723041631H7B1793289317911631H7C1858361928231631H8B125438094531631H8C653569 -31 1631H9A -4410 365026552911H9B -3226 374031442911H10A -5234 13649862911H10B -5510 236111122911H11A -3721 160728792911H11A -3721 160728792911H12A -3216 321718352911H12B -4312 26968182911H12C -3461 212111632911H12A -3216 321718352911H12A -3216 321718352911H12A -3216	H3C	-1146	8075	5111	104	1	
H4B -235 7907 3877 104 1H4C -119 8774 4849 104 1H5A 35 2586 1197 163 1H5B -603 3342 922 163 1H5C 104 3475 2122 163 1H6A 276 4895 1529 163 1H6B 1440 5118 1897 163 1H6C 1122 4964 2668 163 1H7A 2391 3957 2304 163 1H7B 1793 2893 1791 163 1H7C 1858 3619 2823 163 1H8A 695 2794 185 163 1H8B 1254 3809 453 163 1H8C 65 3569 -31 163 1H9A -4410 3650 2655 291 1H9B -3226 3740 3144 291 1H9C -3801 3232 3517 291 1H10A -5510 2361 1112 291 1H10A -5750 2242 3104 291 1H11B -2750 2242 3104 291 1H11A -3216 3217 1835 291 1H12A -3216 3217 1835 291 1H12B -4312 2696 818	H4A	-444	8874	3765	104	1	
H4C -119 877448491041H5A35258611971631H5B -603 33429221631H5C104347521221631H6A276489515291631H6B1440511818971631H6C1122496426681631H7A2391395723041631H7B1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H9A -4410 365026552911H9B -3226 374031442911H9C -3801 323235172911H10A -5510 236111122911H10B -5510 236111122911H11A -3721 160728792911H11A -3721 160728792911H11B -2750 224231042911H12A -3216 321718352911H12B -4312 26968182911H12B -4312 26968182911H12C -3461 212111632911H12A -2700 </td <td>H4B</td> <td>-235</td> <td>7907</td> <td>3877</td> <td>104</td> <td>1</td> <td></td>	H4B	-235	7907	3877	104	1	
H5A35258611971631H5B -603 33429221631H5C104347521221631H6A276489515291631H6B1440511818971631H6C1122496426681631H7A2391395723041631H7R1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H9A-4410365026552911H9B-3226374031442911H0C-5315195319782911H10A-523413649862911H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H12C-3461212111632911H12C-3461212111632911H12A-3216321718352911H12A-321632171835 </td <td>H4C</td> <td>-119</td> <td>8774</td> <td>4849</td> <td>104</td> <td>1</td> <td></td>	H4C	-119	8774	4849	104	1	
H5B -603 3342 922 163 1H5C 104 3475 2122 163 1H6A 276 4895 1529 163 1H6B 1440 5118 1897 163 1H6C 1122 4964 2668 163 1H7A 2391 3957 2304 163 1H7B 1793 2893 1791 163 1H7C 1858 3619 2823 163 1H8A 695 2794 185 163 1H8B 1254 3809 453 163 1H8B 1254 3809 453 163 1H9A -4410 3650 2655 291 1H9B -3226 3740 3144 291 1H9C -3801 3232 3517 291 1H10A -5234 1364 986 291 1H10A -52315 1953 1978 291 1H11A -3721 1607 2879 291 1H11B -2750 2242 3104 291 1H11C -3397 1344 2023 291 1H12A -3216 3217 1835 291 1H12B -4312 2696 818 291 1H12B -4312 2696 818 291 1H12C -3461 2121 <td>H5A</td> <td>35</td> <td>2586</td> <td>1197</td> <td>163</td> <td>1</td> <td></td>	H5A	35	2586	1197	163	1	
H5C 104 3475 2122 163 1 H6A 276 4895 1529 163 1 H6B 1440 5118 1897 163 1 H6C 1122 4964 2668 163 1 H7A 2391 3957 2304 163 1 H7B 1793 2893 1791 163 1 H7C 1858 3619 2823 163 1 H8A 695 2794 185 163 1 H8B 1254 3809 453 163 1 H8B 1254 3809 453 163 1 H9A -4410 3650 2655 291 1 H9B -3226 3740 3144 291 1 H9C -3801 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5510 2361 1112 291 1 H11A -3721 1607 2879 291 1 H11B -2750 2242 3104 291 1 H112 -3397 1344 2023 291 1 H12A -3216 3217 1835 291 1 H12A -3216 3217 1835 291 1 H12A -3216 2121 1163 291 1 H12A -3216 2121 1163 291 1 <td>H5B</td> <td>-603</td> <td>3342</td> <td>922</td> <td>163</td> <td>1</td> <td></td>	H5B	-603	3342	922	163	1	
H6A 276 4895 1529 163 1 H6B 1440 5118 1897 163 1 H6C 1122 4964 2668 163 1 H7A 2391 3957 2304 163 1 H7B 1793 2893 1791 163 1 H7C 1858 3619 2823 163 1 H8A 695 2794 185 163 1 H8B 1254 3809 453 163 1 H8B 1254 3809 453 163 1 H9A -4410 3650 2655 291 1 H9B -3226 3740 3144 291 1 H9C -3801 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5510 2361 1112 291 1 H11A -3721 1607 2879 291 1 H11B -2750 2242 3104 291 1 H11B -2750 2242 3104 291 1 H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H12A -3216 2217 1835 291 1 H12A -3216 2217 1835 291 1 </td <td>H5C</td> <td>104</td> <td>3475</td> <td>2122</td> <td>163</td> <td>1</td> <td></td>	H5C	104	3475	2122	163	1	
H6B1440511818971631H6C1122496426681631H7A2391395723041631H7B1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H8C653569-311631H9A-4410365026552911H9B-3226374031442911H9C-3801323235172911H10A-523413649862911H10B-5510236111122911H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12A-3216321718352911H12A-3216321718352911H12A-3216321718352911H12A-3216321718352911H12A-3216321718352911H12A-3216321718352911H12A-32163217	H6A	276	4895	1529	163	1	
H6C1122496426681631H7A2391395723041631H7B1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H8C653569-311631H9A-4410365026552911H9B-3226374031442911H9C-3801323235172911H10A-523413649862911H10B-5510236111122911H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12A-3216212111632911H12A-3216212111632911H12A-3216212111632911H12A-3461212111632911H13A27901026225922581	H6B	1440	5118	1897	163	1	
H7A2391395723041631H7B1793289317911631H7C1858361928231631H8A69527941851631H8B125438094531631H8C653569-311631H9A-4410365026552911H9B-3226374031442911H9C-3801323235172911H10A-523413649862911H10B-5510236111122911H11A-3721160728792911H11B-2750224231042911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H13A27901026225922581	H6C	1122	4964	2668	163	1	
H7B 1793 2893 1791 163 1 H7C 1858 3619 2823 163 1 H8A 695 2794 185 163 1 H8B 1254 3809 453 163 1 H8C 65 3569 -31 163 1 H9A -4410 3650 2655 291 1 H9B -3226 3740 3144 291 1 H9C -3801 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5510 2361 1112 291 1 H10C -5315 1953 1978 291 1 H11A -3721 1607 2879 291 1 H11B -2750 2242 3104 291 1 H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H7A	2391	3957	2304	163	1	
H7C1858 3619 2823 163 1H8A 695 2794 185 163 1H8B 1254 3809 453 163 1H8C 65 3569 -31 163 1H9A -4410 3650 2655 291 1H9B -3226 3740 3144 291 1H9C -3801 3232 3517 291 1H10A -5234 1364 986 291 1H10B -5510 2361 1112 291 1H10C -5315 1953 1978 291 1H11A -3721 1607 2879 291 1H11B -2750 2242 3104 291 1H11C -3397 1344 2023 291 1H12A -3216 3217 1835 291 1H12B -4312 2696 818 291 1H12C -3461 2121 1163 291 1H13A 2790 10262 2592 258 1	H7B	1793	2893	1791	163	1	
H8A 695 2794 185 163 1 H8B 1254 3809 453 163 1 H8C 65 3569 -31 163 1 H9A -4410 3650 2655 291 1 H9B -3226 3740 3144 291 1 H9C -3801 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5510 2361 1112 291 1 H10C -5315 1953 1978 291 1 H11A -3721 1607 2879 291 1 H11B -2750 2242 3104 291 1 H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H7C	1858	3619	2823	163	1	
H8B 1254 3809 453 163 1 H8C 65 3569 -31 163 1 H9A -4410 3650 2655 291 1 H9B -3226 3740 3144 291 1 H9C -3801 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5510 2361 1112 291 1 H10C -5315 1953 1978 291 1 H11A -3721 1607 2879 291 1 H11B -2750 2242 3104 291 1 H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H8A	695	2794	185	163	1	
H8C 65 3569 -31 163 1 H9A -4410 3650 2655 291 1 H9B -3226 3740 3144 291 1 H9C -3801 3232 3517 291 1 H10A -5234 1364 986 291 1 H10B -5510 2361 1112 291 1 H10C -5315 1953 1978 291 1 H11A -3721 1607 2879 291 1 H11B -2750 2242 3104 291 1 H11C -3397 1344 2023 291 1 H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H8B	1254	3809	453	163	1	
H9A-4410365026552911H9B-3226374031442911H9C-3801323235172911H10A-523413649862911H10B-5510236111122911H10C-5315195319782911H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H13A27901026225922581	H8C	65	3569	-31	163	1	
H9B-3226374031442911H9C-3801323235172911H10A-523413649862911H10B-5510236111122911H10C-5315195319782911H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H13A27901026225922581	H9A	-4410	3650	2655	291	1	
H9C -3801 3232 3517 291 1H10A -5234 1364 986 291 1H10B -5510 2361 1112 291 1H10C -5315 1953 1978 291 1H11A -3721 1607 2879 291 1H11B -2750 2242 3104 291 1H11C -3397 1344 2023 291 1H12A -3216 3217 1835 291 1H12B -4312 2696 818 291 1H12C -3461 2121 1163 291 1H13A 2790 10262 2592 258 1	H9B	-3226	3740	3144	291	1	
H10A -5234 13649862911H10B -5510 236111122911H10C -5315 195319782911H11A -3721 160728792911H11B -2750 224231042911H11C -3397 134420232911H12A -3216 321718352911H12B -4312 26968182911H12C -3461 212111632911H13A27901026225922581	H9C	-3801	3232	3517	291	1	
H10B -5510 236111122911H10C -5315 195319782911H11A -3721 160728792911H11B -2750 224231042911H11C -3397 134420232911H12A -3216 321718352911H12B -4312 26968182911H12C -3461 212111632911H13A27901026225922581	H10A	-5234	1364	986	291	1	
H10C-5315195319782911H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H13A27901026225922581	H10B	-5510	2361	1112	291	1	
H11A-3721160728792911H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H13A27901026225922581	H10C	-5315	1953	1978	291	1	
H11B-2750224231042911H11C-3397134420232911H12A-3216321718352911H12B-431226968182911H12C-3461212111632911H13A27901026225922581	H11A	-3721	1607	2879	291	1	
H11C -3397 1344 2023 291 1 H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H11B	-2750	2242	3104	291	1	
H12A -3216 3217 1835 291 1 H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H11C	-3397	1344	2023	291	1	
H12B -4312 2696 818 291 1 H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H12A	-3216	3217	1835	291	1	
H12C -3461 2121 1163 291 1 H13A 2790 10262 2592 258 1	H12B	-4312	2696	818	291	1	
H13A 2790 10262 2592 258 1	H12C	-3461	2121	1163	291	<u>ः</u> 1	
	H13A	2790	10262	2592	258	1	
H13B 2266 10266 3248 258 1	H13B	2266	10266	3248	258	1	
H13C 1657 9683 2002 258 1	H13C	1657	9683	2002	258	1	
H14A 3831 8649 2661 258 1	H14A	3831	8649	2661	258	1	
H14B 4158 9274 3848 258 1	H14B	4158	9274	3848	258	1	
H14C 3931 9754 3033 258 1	H14C	3931	9754	3033	258	ī	

Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [Å² × 10³].

H15A	3226	9096	4269	258	1
H15B	2230	8293	3381	258	1
H15C	2154	9359	3779	258	1
H16A	1636	8459	1272	258	1
H16B	1622	7870	1925	258	1
H16C	2475	7877	1639	258	1
H01	-340(1)	1371(9)	1028(2)	50	0.50
H02	258(5)	1004(6)	628(7)	50	0.50
H03	-898(1)	371(11)	-519(5)	50	0.50
H04	-1184(12)	800(60)	207(5)	50	0.50
H05	575(1)	1187(3)	677(7)	50	0.50
H06	1241(3)	624(6)	1012(12)	50	0.50
H07	3688(1)	1943(2)	4833(4)	50	0.50
H08	3548(11)	1339(12)	5265(17)	50	0.50
H09	-5188(1)	2592(6)	-3035(4)	50	0.50
H010	-5950(7)	2955(3)	-2912(16)	50	0.50
H011	-5823(1)	-503(5)	575(5)	50	0.50
H012	-6816(7)	-403(19)	199(13)	50	0.50
H013	-2967(1)	870(1)	-498(7)	50	0.50
H014	-3542(15)	150(12)	-516(8)	50	0.50
H015	-1424(1)	5196(3)	510(3)	50	1
H016	-1705(16)	6053(7)	680(9)	50	1
H017	2520(1)	6820(3)	4409(2)	50	1
H018	3205(8)	6242(7)	4534(12)	50	1
H019	-2294(1)	3393(2)	-14(2)	50	1
H020	-2374(6)	2750(5)	401(9)	50	1
H021	-811(1)	779(2)	3406(9)	50	1
H022	-1444(6)	1300(8)	2916(15)	50	1
H023	3805(1)	4810(4)	4329(3)	50	1
H024	3326(9)	4871(4)	4895(9)	50	1
H025	-3916(1)	5320(20)	1955(1)	50	1
H026	-3189(3)	5170(19)	1677(4)	50	1
H027	1578(1)	8807(5)	5747(2)	50	1
H028	1644(15)	8098(3)	4973(15)	50	1
H029	-243(1)	6431(1)	1858(7)	50	1
H030	169(9)	7331(12)	2660(20)	50	1
H031	3812(1)	3545(1)	6667(9)	50	1
H032	3655(8)	4422(5)	7101(14)	50	1
H033	-3026(1)	6625(5)	414(1)	50	1
H034	-2670(8)	5952(7)	-95(5)	50	1
H035	164(1)	1638(8)	2690(7)	50	1
H036	1202(6)	1710(20)	3273(8)	50	1
H037	1972(2)	2241(2)	3523(4)	50	1
H038	2586(9)	3051(7)	4426(14)	50	1
H039	-1530(1)	1587(14)	532(3)	50	1
H040	-1574(7)	1960(40)	1443(1)	50	1
H041	-1220(1)	4323(2)	-544(3)	50	1
	the state of the s	and the second			
H042	-1688(15)	3392(2)	-894(16)	50	1
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H043	4987(1)	5788(2)	6198(3)	50	1
H044	5731(1)	5416(2)	6044(2)	50	1
H045	-610(1)	8576(1)	1315(1)	50	1
H046	-143(9)	7842(5)	1464(2)	50	1
H047	5798(1)	5390(3)	7331(3)	50	1
H048	5423(2)	4825(12)	7661(12)	50	1
H049	-4011(1)	2800(6)	-553(4)	50	1
H050	-5011(5)	2886(16)	-970(17)	50	1
H051	-5571(3)	3361(4)	-65(5)	50	1
H052	-5880(30)	3536(12)	-971(3)	50	1
H053	3316(1)	2183(11)	3429(4)	50	1
H054	4260(5)	2149(12)	3540(11)	50	1
H055	-4589(1)	-333(11)	2183(4)	50	1
H056	-4078(2)	-670(30)	1662(9)	50	1
H057	-1819(1)	-2051(6)	225(3)	50	1
H058	-1990(12)	-1800(20)	1058(8)	50	1
H059	-36(2)	9634(2)	2716(2)	50	1
H060	440(14)	10578(5)	3154(6)	50	1
H061	2020(1)	1493(1)	1054(3)	50	1
H062	2630(11)	1260(13)	631(11)	50	1
H063	3417(3)	9156(3)	5731(4)	50	1
H064	4100(30)	9501(10)	6819(7)	50	1
H065	-3334(2)	-35(1)	1397(7)	50	1
H066	-3000(20)	-719(14)	1791(16)	50	1
H067	2656(1)	5948(4)	2382(8)	50	1
H068	3644(5)	6226(4)	2642(15)	50	1
H069	4094(2)	8407(1)	5267(4)	50	1
H070	4570(13)	8160(20)	6130(14)	50	1





University of Southampton · Department of Chemistry EPSRC National Crystallography Service



Table 1. Crystal data and structure refinement.

Identification code Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions Volume Z Density (calculated) Absorption coefficient F(000) Crystal Crystal size

Density (calculated) Absorption coefficient F(000)Crystal Crystal size θ range for data collection Index ranges Reflections collected Independent reflections Completeness to $\theta = 25.03^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final *R* indices $[F^2 > 2\sigma(F^2)]$ *R* indices (all data) Largest diff. peak and hole



Diffractometer: Nonius KappaCCD area detector (ϕ scans and ω scans to fill asymmetric unit sphere). Cell determination: DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) Data collection: Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). Data reduction and cell refinement: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. 276: Macromolecular Crystallography, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). Absorption correction: SORTAV (R. H. Blessing, Acta Cryst. 451 (1995) 33–37; R. H. Blessing, J. Appl. Cryst. 30 (1997) 421–426). Structure solution: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A46 467–473). Structure refinement: SHELXL97 (G. M. Sheldrick (1997), University of Göttingen, Germany). Graphics: Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: All hydrogen atoms were placed in idealised positions and refined using a riding model, except those on hetero atoms which were fully refined.

Atom	x	у	z	U_{eq}	S.o.f.	_
B1	420(1)	3382(2)	3795(1)	26(1)	1	
B2	947(1)	4590(2)	4614(1)	27(1)	Î	
B3	1511(1)	4289(2)	3638(1)	26(1)	î	
O1	1012(1)	3480(1)	3457(1)	30(1)	1	
O2	357(1)	3966(1)	4319(1)	27(1)	1	
O3	1458(1)	4903(1)	4150(1)	28(1)	1	
O4	725(1)	5745(1)	4856(1)	30(1)	1	
C1	-156(1)	2537(2)	3557(1)	26(1)	1	
C2	-63(1)	1822(2)	3049(1)	31(1)	1	
C3	-547(1)	992(2)	2866(1)	37(1)	1	
C4	-1140(1)	873(2)	3183(1)	39(1)	1	
C5	-1250(1)	1581(2)	3683(1)	37(1)	1	
C6	-763(1)	2400(2)	3865(1)	30(1)	1	
C7	1278(1)	3707(2)	5110(1)	27(1)	1	
C8	1289(1)	2456(2)	5041(1)	34(1)	1	
C9	1597(1)	1695(2)	5454(1)	43(1)	1	
C10	1905(1)	2175(2)	5954(1)	46(1)	1	
C11	1902(1)	3402(2)	6035(1)	42(1)	1	
C12	1598(1)	4156(2)	5621(1)	34(1)	1	
C13	2147(1)	4468(2)	3225(1)	26(1)	1	
C14	2285(1)	3722(2)	2739(1)	32(1)	1	
C15	2873(1)	3849(2)	2405(1)	41(1)	1	
C16	3327(1)	4748(2)	2542(1)	42(1)	1	
C17	3202(1)	5519(2)	3013(1)	37(1)	1	
C18	2623(1)	5367(2)	3354(1)	32(1)	1	
N1	-839(1)	2372(1)	5852(1)	27(1)	1	
C19	-1569(1)	2055(2)	5927(1)	34(1)	1	
C20	-1937(1)	1935(2)	5348(1)	58(1)	1	
C21	-444(1)	1451(2)	5511(1)	34(1)	1	
C22	-386(1)	246(2)	5817(1)	50(1)	1	
C23	-541(1)	2666(2)	6450(1)	35(1)	1	
C24	176(1)	3132(2)	6400(1)	48(1)	1	

Table 2. Atomic coordinates [× 10⁴], equivalent isotropic displacement parameters [Å² × 10³] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

D 4 00			
B1-O2	1.344(2)	C7–C12	1.397(2)
B1-O1	1.396(2)	C8–C9	1.390(3)
B1-C1	1.567(3)	C9–C10	1.380(3)
B2–O4	1.456(2)	C10-C11	1.371(3)
B2-O3	1.490(2)	C11-C12	1.385(3)
B2-O2	1.507(2)	C13–C14	1.393(2)
B2-C7	1.617(3)	C13-C18	1.399(2)
B3-O3	1.337(2)	C14–C15	1.389(3)
B3-O1	1.391(2)	C15-C16	1.374(3)
B3-C13	1.571(2)	C16-C17	1.379(3)
C1–C6	1.391(2)	C17-C18	1.384(2)
C1-C2	1.399(2)	N1-C21	1.494(2)
C2–C3	1.388(2)	N1-C19	1.494(2)
C3–C4	1.376(3)	N1-C23	1.497(2)
C4-C5	1.383(3)	C19-C20	1.491(3)
C5–C6	1.382(2)	C21-C22	1.503(3)
C7–C8	1.394(2)	C23-C24	1.511(3)
O2-B1-O1	120.80(16)	C12-C7-B2	121.95(16)
O2-B1-C1	121.08(15)	C9-C8-C7	122.34(18)
O1-B1-C1	118.09(16)	C10-C9-C8	119.97(19)
O4-B2-O3	105.04(14)	C11-C10-C9	119.13(19)
O4-B2-O2	109.48(14)	C10-C11-C12	120.68(19)
O3-B2-O2	108.90(14)	C11-C12-C7	121.99(19)
O4-B2-C7	113.43(14)	C14-C13-C18	116.81(15)
O3-B2-C7	110.12(13)	C14-C13-B3	122.70(15)
O2-B2-C7	109.71(14)	C18-C13-B3	120.42(15)
O3-B3-O1	121.39(15)	C15-C14-C13	121.56(17)
O3-B3-C13	120.14(15)	C16-C15-C14	120.01(18)
O1-B3-C13	118.47(15)	C15-C16-C17	120.05(17)
B3-O1-B1	119.07(14)	C16-C17-C18	119.64(18)
B1O2B2	122.16(13)	C17-C18-C13	121.89(17)
B3-O3-B2	122.19(14)	C21-N1-C19	113.61(14)
C6-C1-C2	117.04(15)	C21-N1-C23	113.63(14)
C6-C1-B1	121.54(15)	C19-N1-C23	109.31(13)
C2C1B1	121.26(15)	C20-C19-N1	113.23(15)
C3-C2-C1	121.58(17)	N1-C21-C22	114.34(15)
C4-C3-C2	119.88(18)	N1-C23-C24	112.07(14)
C3-C4-C5	119.77(17)		
C6-C5-C4	120.05(17)		
C5-C6-C1	121.68(17)		
C8-C7-C12	115.90(17)		
C8-C7-B2	122.09(15)		

Table 3. Bond lengths [Å] and angles [°].

	11	22	33	- 23	13	- 12	
Atom	$U^{\prime\prime}$	U^{zz}	U^{ss}	U^{23}	U^{13}	U^{12}	
D 1	00/1)	04(1)	05(1)	F (1)	1/1)	4/11	
BI	28(1)	24(1)	25(1)	5(1)	-1(1)	4(1)	
B2	28(1)	27(1)	27(1)	-2(1)	5(1)	-5(1)	
B3	28(1)	25(1)	27(1)	5(1)	-1(1)	2(1)	
01	28(1)	34(1)	27(1)	-3(1)	4(1)	-3(1)	
02	24(1)	30(1)	26(1)	-1(1)	2(1)	-2(1)	
03	27(1)	31(1)	26(1)	-2(1)	6(1)	-5(1)	
04	31(1)	28(1)	30(1)	-1(1)	9(1)	-2(1)	
C1	27(1)	26(1)	24(1)	4(1)	-2(1)	2(1)	
C2	32(1)	37(1)	26(1)	4(1)	-3(1)	-2(1)	
C3	44(1)	41(1)	26(1)	-1(1)	-5(1)	-5(1)	
C4	41(1)	41(1)	37(1)	2(1)	-13(1)	-13(1)	
C5	28(1)	45(1)	36(1)	3(1)	-4(1)	-6(1)	
C6	27(1)	32(1)	31(1)	0(1)	-3(1)	0(1)	
C7	21(1)	33(1)	27(1)	-2(1)	5(1)	-3(1)	
C8	32(1)	36(1)	34(1)	2(1)	-2(1)	$-\frac{1}{1}$	
C9	41(1)	37(1)	51(1)	9(1)	1(1)	3(1)	
C10	37(1)	59(2)	41(1)	13(1)	-2(1)	6(1)	
C11	26(1)	68(2)	32(1)	0(1)	-4(1)	2(1)	
C12	25(1)	45(1)	33(1)	-4(1)	4(1)	-2(1)	
C13	27(1)	26(1)	25(1)	5(1)	2(1)	4(1)	
C14	32(1)	36(1)	29(1)	2(1)	2(1)	2(1)	
C15	40(1)	58(1)	27(1)	0(1)	7(1)	11(1)	
C16	30(1)	56(1)	39(1)	16(1)	13(1)	7(1)	
C17	30(1)	35(1)	47(1)	12(1)	5(1)	1(1)	
C18	31(1)	28(1)	37(1)	5(1)	4(1)	4(1)	
N1	26(1)	29(1)	26(1)	1(1)	1(1)	1(1)	
C19	26(1)	34(1)	41(1)	5(1)	4(1)	-1(1)	
C20	33(1)	87(2)	54(1)	3(1)	-8(1)	-13(1)	
C21	33(1)	35(1)	33(1)	-1(1)	2(1)	5(1)	
C22	66(1)	39(1)	45(1)	6(1)	7(1)	16(1)	
C23	34(1)	47(1)	24(1)	-1(1)	2(1)	-4(1)	
C24	38(1)	75(2)	29(1)	-4(1)	-1(1)	-12(1)	

Table 4. Anisotropic displacement parameters $[\text{\AA}^2 \times 10^3]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2h k a^* b^* U^{12}]$.

Atom	x	у	z	U_{eq}	S.o.f.	
TT1	400/11	5710/10	510((10)	52(6)		
HI	408(11)	5/10(19)	5126(10)	53(6)	1	
H2	341	1906	2823	37	1	
H3	-469	507	2523	44	1	
H4	-1473	306	3060	47	1	
H5	-1660	1505	3902	44	1	
H6	-845	2881	4209	36	1	
H8	1078	2110	4700	41	1	
H9	1595	846	5392	51	1	
H10	2116	1661	6238	55	1	
H11	2111	3739	6379	50	1	
H12	1607	5004	5686	41	1	
H14	1969	3110	2634	38	1	
H15	2961	3315	2082	50	1	
H16	3728	4839	2311	50	1	
H17	3511	6151	3104	44	1	
H18	2548	5887	3685	38	1	
H1N	-809(9)	3152(18)	5593(9)	44(5)	1	
H19A	-1604	1282	6148	41	1	
H19B	-1792	2687	6170	41	1	
H20A	-1881	2678	5115	87	1	
H20B	-2419	1797	5425	87	ĩ	
H20C	-1752	1251	5123	87	1	
H21A	17	1769	5439	40	1	
H21B	-662	1331	5117	40	1	
H22A	-148	346	6198	75	1	
H22R	_133	_313	5561	75	1	
H22C	840	-515	5901	75	1	
L122C	-040	-/9	5091	13	1	
1123A	-545	1932	6703	42	1	
H23B	-820	3284	6649	42	1	
1124A	4/0	2472	6278	71	1	
H24B	323	344/	6/88	71	1	
H24C	193	3780	6102	71	1	

Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [Å² × 10³].

$D-H\cdots A$	d(D-H)	$d(H \cdots A)$	$d(D \cdots A)$	\angle (DHA)
· · · · · · · · · · · · · · · · · · ·				
O4–H1…O2 ⁱ	0.87(2)	1.99(2)	2.8425(17)	166(2)
N1–H1N…O4 ⁱ	1.04(2)	1.59(2)	2.6283(19)	173.8(18)
N1–H1N…O3 ⁱ	1.04(2)	2.570(19)	3.2545(18)	122.8(14)

Table 6. Hydrogen bonds [Å and °].

Symmetry transformations used to generate equivalent atoms: (i) -x, -y+1, -z+1







University of Southampton · Department of Chemistry EPSRC National Crystallography Service



 Table 1. Crystal data and structure refinement.

Identification code	03SRC0770 (MAB/LF06)
Empirical formula	$C_{29}H_{34}B_3NO_4$
Formula weight	493.00
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	<i>a</i> = 16.9787(8) Å
	b = 17.2540(6) Å
	c = 18.2709(8) Å
Volume	5352.5(4) Å ³
Ζ	8
Density (calculated)	$1.224 \text{ Mg} / \text{m}^3$
Absorption coefficient	0.078 mm^{-1}
<i>F</i> (000)	2096
Crystal	Colourless shard
Crystal size	$0.14 \times 0.10 \times 0.06 \text{ mm}^3$
θ range for data collection	$3.25 - 25.02^{\circ}$
Index ranges	$-19 \le h \le 19, -16 \le k \le 20, -21 \le l \le 21$
Reflections collected	20261
Independent reflections	$3645 \ [R_{int} = 0.0741]$
Completeness to $\theta = 25.02^{\circ}$	77.2 % (low due to twin overlap)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9953 and 0.9891
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3645 / 0 / 338
Goodness-of-fit on F^2	0.988
Final R indices $[F^2 > 2\sigma(F^2)]$	R1 = 0.0656, wR2 = 0.1609
R indices (all data)	R1 = 0.1088, wR2 = 0.1840
Largest diff. peak and hole	0.793 and $-0.380 \text{ e} \text{ Å}^{-3}$

Diffractometer: Nonius KappaCCD area detector (ϕ scans and ω scans to fill asymmetric unit sphere). Cell determination: DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) Data collection: Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). Data reduction and cell refinement: Denzo (Z. Otwinowski & W. Minor, Methods in Enzymology (1997) Vol. 276: Macromolecular Crystallography, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). Absorption correction: SORTAV (R. H. Blessing, Acta Cryst. A51 (1995) 33–37; R. H. Blessing, J. Appl. Cryst. 30 (1997) 421–426). Structure solution: SHELXS97 (G. M. Sheldrick, Acta Cryst. (1990) A46 467–473). Structure refinement: SHELXL97 (G. M. Sheldrick (1997), University of Göttingen, Germany). Graphics: Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: The crystal was twinned via a small rotation around 100 - so the completeness is low due to data lost via reflection overlap.

Atom	x	у	z	U_{eq}	S.o.f.	
B1	7724(3)	1635(2)	4538(2)	19(1)	1	
B2	8172(3)	431(2)	3931(2)	17(1)	ĩ	
B3	6987(2)	1043(2)	3516(2)	16(1)	î	
01	8215(1)	914(1)	4502(1)	18(1)	ĩ	
O2	7611(2)	542(1)	3378(1)	19(1)	1	
O3	6972(1)	1504(1)	4107(1)	18(1)	1	
C1	7509(2)	1806(2)	5389(2)	17(1)	1	
C2	7995(2)	1539(2)	5954(2)	22(1)	1	
C3	7855(3)	1719(2)	6681(2)	26(1)	1	
C4	7218(3)	2180(2)	6865(2)	29(1)	1	
C5	6725(2)	2455(2)	6328(2)	27(1)	1	
C6	6873(2)	2268(2)	5595(2)	22(1)	1	
C7	8194(2)	2359(2)	4183(2)	17(1)	1	
C8	7800(2)	3001(2)	3889(2)	20(1)	1	
C9	8206(2)	3630(2)	3594(2)	22(1)	1	
C10	9016(2)	3638(2)	3590(2)	23(1)	1	
C11	9425(2)	3021(2)	3887(2)	25(1)	1	
C12	9014(2)	2396(2)	4180(2)	20(1)	1	
C13	8742(2)	-278(2)	3865(2)	16(1)	1	
C14	9242(2)	-468(2)	4441(2)	23(1)	1	
C15	9782(2)	-1070(2)	4386(2)	30(1)	1	
C16	9834(2)	-1491(2)	3750(2)	31(1)	1	
C17	9340(2)	-1322(2)	3172(2)	26(1)	1	
C18	8804(2)	-726(2)	3231(2)	21(1)	1	
C19	6274(2)	1034(2)	2966(2)	18(1)	1	
C20	6181(2)	469(2)	2429(2)	22(1)	1	
C21	5550(2)	485(2)	1948(2)	26(1)	1	
C22	5005(2)	1077(2)	1990(2)	28(1)	1	
C23	5078(2)	1641(2)	2519(2)	26(1)	1	
C24	5703(2)	1616(2)	3002(2)	20(1)	1	
N1	6673(2)	-645(2)	5927(2)	28(1)	1	
O4	5647(2)	845(2)	4829(2)	35(1)	1	
C25	6829(3)	-644(3)	6727(2)	55(2)	1	
C26	6252(3)	-1377(2)	5734(2)	33(1)	1	
C27	7488(3)	-655(3)	5568(3)	49(1)	1	
C28	6222(3)	53(3)	5737(3)	48(1)	1	
C29	6029(3)	117(3)	4910(3)	42(1)	1	

Table 2. Atomic coordinates [× 10⁴], equivalent isotropic displacement parameters [Å² × 10³] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

B101	1.498(5)	C10-C11	1.382(5)
B1-O3	1.517(5)	C11-C12	1.392(5)
B1-C7	1.618(6)	C13-C14	1.392(5)
B1-C1	1.624(5)	C13-C18	1.397(5)
B2-O1	1.337(5)	C14-C15	1.388(5)
B2-O2	1.401(5)	C15-C16	1.374(5)
B2-C13	1.564(6)	C16-C17	1.380(5)
B3-O3	1.341(4)	C17-C18	1.378(5)
B3-O2	1.391(5)	C19-C20	1.393(5)
B3-C19	1.573(5)	C19-C24	1.397(5)
C1-C6	1.394(5)	C20-C21	1.385(5)
C1-C2	1.400(5)	C21-C22	1.381(6)
C2-C3	1.385(5)	C22-C23	1.377(5)
C3-C4	1.384(6)	C23-C24	1.381(5)
C4–C5	1.375(6)	N1-C28	1.469(5)
C5-C6	1.400(5)	N1-C25	1.485(5)
C7-C12	1.392(5)	N1-C26	1.494(5)
C7–C8	1.402(5)	N1-C27	1.532(6)
C8-C9	1.394(5)	O4-C29	1.422(5)
C9–C10	1.376(5)	C28-C29	1.549(6)
O1-B1-O3	108.8(3)	C1-C6-C5	122.0(3)
O1-B1-C7	110.4(3)	C12-C7-C8	116.0(3)
O3-B1-C7	108.8(3)	C12-C7-B1	122.1(3)
O1-B1-C1	108.6(3)	C8-C7-B1	121.8(3)
O3-B1-C1	109.6(3)	C9-C8-C7	121.8(4)
C7-B1-C1	110.7(3)	C10-C9-C8	120.3(4)
O1-B2-O2	120.9(3)	C9-C10-C11	119.4(4)
O1-B2-C13	120.9(3)	C10-C11-C12	119.7(4)
O2-B2-C13	118.1(3)	C7-C12-C11	122.6(3)
O3-B3-O2	121.9(3)	C14-C13-C18	116.8(3)
O3-B3-C19	120.4(3)	C14-C13-B2	120.2(3)
O2-B3-C19	117.7(3)	С18-С13-В2	123.0(3)
B2O1B1	121.4(3)	C15-C14-C13	121.6(3)
B3-O2-B2	118.2(3)	C16-C15-C14	120.0(4)
B3-O3-B1	119.4(3)	C15-C16-C17	119.7(4)
C6-C1-C2	116.5(3)	C18-C17-C16	120.0(4)
C6-C1-B1	122.5(3)	C17-C18-C13	121.9(3)
C2C1B1	120.9(3)	C20-C19-C24	117.3(3)
C3-C2-C1	122.2(4)	С20-С19-В3	123.0(3)
C4–C3–C2	119.7(4)	С24-С19-В3	119.7(3)
C5-C4-C3	120.1(3)	C21-C20-C19	121.4(3)
C4-C5-C6	119.6(4)	C22-C21-C20	119.8(3)

Table 3. Bond lengths [Å] and angles [°].

C23-C22-C21	120.1(4)	
C22-C23-C24	119.7(4)	
C23-C24-C19	121.7(3)	
C28-N1-C25	108.9(3)	
C28-N1-C26	112.9(4)	
C25-N1-C26	108.6(3)	
C28-N1-C27	112.2(3)	
C25-N1-C27	105.1(4)	
C26-N1-C27	108.8(3)	
N1-C28-C29	113.5(4)	
O4-C29-C28	105.1(4)	

Table 4. Anisotropic displacement parameters $[Å^2 \times 10^3]$. The anisotropic displacement

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
B1	19(3)	18(2)	19(2)	-4(2)	-3(2)	3(2)	
B2	14(2)	17(2)	19(2)	3(2)	2(2)	-8(2)	
B 3	18(3)	14(2)	17(2)	4(2)	4(2)	0(2)	
O1	16(2)	16(1)	23(2)	0(1)	-4(1)	2(1)	
O2	18(2)	19(1)	20(1)	-3(1)	-3(1)	3(1)	
O3	16(2)	19(2)	18(1)	-2(1)	-3(1)	1(1)	
C1	16(2)	14(2)	21(2)	2(1)	0(2)	-4(2)	
C2	22(2)	20(2)	25(2)	0(2)	0(2)	-1(2)	
C3	29(3)	29(2)	21(2)	4(2)	-3(2)	-1(2)	
C4	38(3)	32(2)	17(2)	-2(2)	9(2)	-4(2)	
C5	21(2)	33(3)	26(2)	-3(2)	8(2)	-2(2)	
C6	18(2)	22(2)	25(2)	2(2)	-2(2)	-2(2)	
C7	19(2)	19(2)	13(2)	-6(1)	-2(2)	3(2)	
C8	17(2)	21(2)	20(2)	-5(2)	-2(2)	-1(2)	
C9	26(2)	18(2)	23(2)	1(2)	-1(2)	5(2)	
C10	26(3)	21(2)	22(2)	2(2)	4(2)	-4(2)	
C11	17(2)	27(2)	30(2)	-1(2)	3(2)	0(2)	
C12	22(2)	21(2)	18(2)	1(1)	-1(2)	5(2)	
C13	14(2)	16(2)	20(2)	1(1)	2(2)	-2(2)	
C14	23(2)	22(2)	25(2)	1(2)	-4(2)	1(2)	
C15	25(3)	23(2)	42(3)	3(2)	-14(2)	3(2)	
C16	22(2)	14(2)	57(3)	-4(2)	-5(2)	5(2)	
C17	23(2)	19(2)	36(2)	-5(2)	2(2)	-1(2)	
C18	18(2)	17(2)	27(2)	1(2)	-2(2)	-2(2)	
C19	19(2)	16(2)	19(2)	8(1)	3(2)	1(2)	
C20	26(2)	15(2)	25(2)	2(2)	2(2)	-2(2)	
C21	30(3)	22(2)	25(2)	0(2)	-7(2)	-9(2)	
C22	22(2)	27(2)	34(3)	5(2)	-11(2)	-7(2)	
C23	20(2)	19(2)	38(3)	6(2)	-4(2)	1(2)	
C24	23(2)	21(2)	17(2)	2(1)	-2(2)	-1(2)	
N1	42(2)	19(2)	25(2)	-3(1)	-3(2)	-3(2)	
O4	30(2)	25(2)	49(2)	4(1)	10(1)	1(1)	
C25	61(4)	63(4)	41(3)	-10(2)	-20(3)	6(3)	
C26	32(3)	22(2)	44(3)	0(2)	-4(2)	-6(2)	
C27	37(3)	48(3)	61(3)	-2(2)	12(2)	-2(2)	
C28	38(3)	40(3)	66(4)	-3(2)	-9(2)	1(2)	
C29	34(3)	33(3)	57(3)	11(2)	4(2)	1(2)	

factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2h k a^* b^* U^{12}].$

Atom	x	у	z	U_{eq}	S.o.f.	
112	0125	1002	5024	07	ĩ	
HZ H2	8433	1223	3834	27	1	
H3	8196	1528	7052	32	1	
H4	/121	2306	/363	35	1	
HO	6286	2770	6453	32	1	
Ho	6529	2461	5228	26	1	
Hð	7240	3007	3891	24	1	
H9	7922	4054	3396	27	1	
HIU	9293	4065	3384	28	1	
HII	9985	3023	3891	30	1	
H12	9303	1978	4386	24	1	
H14	9214	-179	4883	28	1	
H15	10114	-1191	4789	36	1	
H16	10210	-1897	3708	37	1	
H17	9369	-1617	2734	31	1	
H18	8467	-616	2829	25	1	
H20	6558	64	2390	26	1	
H21	5492	89	1590	31	1	
H22	4578	1095	1654	33	1	
H23	4701	2046	2551	31	1	
H24	5747	2005	3368	24	1	
H4A	5966	1169	4655	52	1	
H25A	7144	-188	6855	83	1	
H25B	7117	-1115	6861	83	1	
H25C	6328	-628	6993	83	1	
H26A	5732	-1381	5968	49	1	
H26B	6558	-1823	5906	49	1	
H26C	6188	-1409	5202	49	1	
H27A	7420	_721	5038	73	1	
H27R	7707	_1096	5767	73	1	
1127D	7750	-1080	5660	15	1	
H2/C	6520	-103	5009	13	1	
1128A	5724	510	588/	38 59	ा. ा	
1120A	5124	33	0017	50	1	
H29A	5/70	98	4014	50	1	
H29B	20/8	-310	4755	50	1	

Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [Å² × 10³].

Table 6. Hydrogen bonds [Å and °].

D–H···A	<i>d</i> (<i>D</i> –H)	$d(H \cdots A)$	$d(D \cdots A)$	\angle (DHA)
O4–H4A…O3	0.84	2.06	2.845(4)	154.7

