Synthesis and Structure of Mixed Chloride–Tetrachloroaluminate Salts†

Jaime M. Martell and Michael J. Zaworotko *
Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, B3H 3C3, Canada

Two mixed chloride–tetrachloroaluminate salts of simple ammonium cations, $[NH_3(CH_2Ph)]_4Cl[AlCl_4]_3$ **1** and $[NH_3(C_6H_{11})]_2Cl[AlCl_4]$ **2** have been prepared, crystallized from hydrocarbon solution, and **2** has been characterized *via* single-crystal X-ray crystallography. The salts melt at 109–112 and 107–108 °C, respectively, however the structures are significant in the general context of interionic attractions in ambient-temperature chloroaluminate melts, particularly the basic variety, and are discussed in such a context. Salt **2** exhibits $N-H \cdots Cl^-$ hydrogen bonding [$d_{N \cdots Cl}$ range 3.134(10)–3.203(9) Å] leading to a cationic polymer. Comparisons are made between the structure of **2** and that of **1**, which was communicated earlier.

The field of ambient-temperature halogenoaluminate ionic liquids had its nascence with alkylpyridinium-based salts four decades ago,[1] but did not really gain momentum until the 1-ethyl-3-methylimidazolium chloride–aluminium chloride system was reported in 1982.[2] The latter systems are ambient over a wide range of compositions and possess a wider electrochemical window than their precursors.

Unsurprisingly, a primary focus of such melts has been their utility as electrolytes, but more recent work has shown these materials to be unconventional and interesting aprotic media for the study of inorganic,[3,4] organometallic[5–9] and organic[9–11] solutes. A topic of considerable current interest is the nature of any structure or ordering in the liquid phase, particularly in basic melts (mol fraction $AlCl_3 < 0.5$). Evidence for ordering *via* hydrogen bonding exists from both solid-state X-ray crystallographic[12] and liquid-phase NMR[13–16] and IR[17–19] studies. In this contribution we report the second crystallographic study conducted upon mixed chloride–tetrachloroaluminate salts,[20] an area in which we have become interested because of the tendency of alkylaluminates[21] and chloroaluminates[22] to sustain the 'liquid clathrate' effect in the presence of liquid aromatic hydrocarbon compounds. 'Liquid clathrates' were originally thought to be exclusively sustained by air-sensitive alkylaluminates but recent reports have focused upon tetrafluoroborate,[23] tetraalkylborate,[24] and complex hydrogen halide sustained systems,[25] all of which are more air and moisture stable than first-generation 'liquid clathrates'.

Experimental

Preparation of $[NH_3(CH_2Ph)]_4Cl[AlCl_4]_3$ **1**.—The following is an improved synthesis of salt **1**, which, as was reported earlier,[20] may be isolated in lower yield *via* a slightly different approach. Benzylamine (3.28 cm^3, 0.0300 mol) was dissolved in freshly distilled benzene (50 cm^3) and converted into its hydrochloride salt *via* slow bubbling of dried HCl for 15 min. Aluminium trichloride (4.00 g, 0.0300 mol) was added to the resulting suspension and within minutes a 'liquid clathrate' containing 5.5 mol of benzene per mol of benzylammonium was formed exothermically. Allowing the 'liquid clathrate' to stand for 20 h gave large crystals of salt **1** (7.09 g, 0.007 28 mol, 97.0%) suitable for X-ray crystallography, m.p. 109–112 °C. The reaction may also be conducted in toluene, affording a 'liquid clathrate' containing 2.0 mol of toluene per mol of benzylammonium cation. If the reaction is effected with larger amounts of $AlCl_3$ (*e.g.* 0.0600 mol) the composition of the 'liquid clathrate' phases changes and crystals of **1** are not isolable from the resulting acidic ionic liquid.

Preparation of $[NH_3(C_6H_{11})]_2Cl[AlCl_4]$ **2**.—This was prepared as for salt **1** except that cyclohexylamine (2.00 cm^3, 0.0175 mol) in toluene was used and the resulting 'liquid clathrate', which was formed exothermically, was not stable under ambient conditions. Allowing the reaction mixture to stand for 20 h afforded crystals of salt **2**, suitable for X-ray crystallography, along the sides of the reaction flask, m.p. 107–108 °C. The 'liquid clathrate' obtained from incorporation of 0.0600 mol of $AlCl_3$, which contained 4.0 mol of toluene per mol of cyclohexylammonium cation, appeared indefinitely stable in the absence of moisture and did not produce any crystalline material.

Crystallography.—Crystal data. $C_{12}H_{28}AlCl_5N_2$ **2**, $M = 404.47$, monoclinic, space group $P2_1/c$, $a = 13.319(2)$, $b = 9.379(2)$, $c = 18.396(3)$ Å, $\beta = 110.750(10)°$, $U = 2148.95$ Å^3, $Z = 4$, $D_c = 1.251$ g cm^{-3}, $\mu = 7.1$ cm^{-1}, $F(000) = 848$, λ(Mo-Kα) = 0.7093 Å colourless, air-stable rectangular blocks, dimensions $0.21 \times 0.57 \times 1.36$ mm.

Data collection and processing. CAD4 diffractometer, θ–2θ scan mode, graphite-monochromated Mo-Kα radiation, 3049 reflections measured ($2 < 2\theta < 45°$), 2775 unique, giving 1782 with $I > 2.5\sigma(I)$. Correction was made for absorption but not for extinction. Programs used for data processing and subsequent structure solution and refinement were from the NRCVAX system,[26] implemented locally on an IBM PC–AT computer. Neutral atom scattering factors were taken from ref. 27.

Structure analysis and refinement. Direct methods (Al and Cl atoms) followed by Fourier difference synthesis located all non-hydrogen atoms. Full-matrix least-squares refinement of non-hydrogen atoms with anisotropic thermal parameters, methylene hydrogen atoms placed in calculated positions ($d_{C-H} = 1.08$ Å, isotropic thermal parameters based upon the carbon atom of the methylene moiety), and other hydrogen atoms located and, except for H(N1c) and H(N2c), freely refined gave final values of $R = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.066$ and $R' = [\Sigma w(F_o - F_c)^2/\Sigma F_o^2]^{\frac{1}{2}} = 0.068$. Weights based upon counting statistics were used, the weight modifier k in kF_o^2 being 0.0001. The final Fourier difference map gave no unaccountable electron

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic parameters for $[NH_3(C_6H_{11})]_2Cl[AlCl_4]$ **2**

Atom	*x*	*y*	*z*
Al	0.311 74(16)	0.378 55(23)	0.194 52(12)
Cl(1)	0.352 44(24)	0.473 0(3)	0.105 46(15)
Cl(2)	0.161 85(17)	0.276 7(3)	0.148 31(16)
Cl(3)	0.312 61(18)	0.526 8(3)	0.280 83(13)
Cl(4)	0.430 82(18)	0.219 1(3)	0.247 48(13)
Cl(5)	0.508 25(14)	0.252 43(19)	0.505 76(12)
N(1)	0.425 0(6)	0.500 6(10)	0.588 6(4)
C(1)	0.306 0(6)	0.511 7(9)	0.567 7(4)
C(2)	0.284 7(6)	0.634 8(9)	0.612 3(4)
C(3)	0.165 7(7)	0.653 1(10)	0.592 8(6)
C(4)	0.110 4(7)	0.676 1(12)	0.506 0(8)
C(5)	0.131 0(8)	0.553 1(13)	0.461 4(5)
C(6)	0.253 2(6)	0.527 9(9)	0.480 6(4)
N(2)	0.381 6(7)	1.013 9(10)	0.390 3(5)
C(11)	0.265 8(7)	0.998 2(11)	0.380 4(6)
C(12)	0.214 0(8)	1.130 8(11)	0.383 7(5)
C(13)	0.095 4(10)	1.115 1(14)	0.370 0(7)
C(14)	0.038 2(9)	1.032 4(17)	0.298 8(9)
C(15)	0.090 5(12)	0.900 5(15)	0.295 5(7)
C(16)	0.210 0(8)	0.912 7(10)	0.309 3(5)
H(N1a)	0.440(5)	0.435(6)	0.574(3)
H(N1b)	0.454(6)	0.575(8)	0.570(5)
H(N2a)	0.408(5)	1.068(7)	0.425(3)
H(N2b)	0.420(7)	0.936(8)	0.408(5)
H(1)	0.281(4)	0.421(6)	0.588(3)
H(2)	0.279(7)	0.960(10)	0.436(5)

Estimated standard deviations (e.s.d.s).

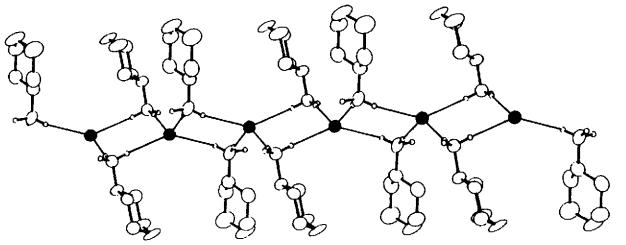

Fig. 1 Perspective view of $\{[NH_3(C_6H_{11})]_2Cl\}_n^{n+}$. Thermal ellipsoids are drawn at the 50% probability level. Solid ellipsoids represent chloride anions, Cl(5), which are hydrogen bonded to H(N1a), H(N1b), H(N2a) and H(N2b) as detailed in Table 2

Table 2 Interatomic distances (Å) and angles (°) for $[NH_3(C_6H_{11})]_2Cl[AlCl_4]$ **2**

(*a*) Intraionic

Al–Cl(1)	2.096(3)	Al–Cl(3)	2.108(3)
Al–Cl(2)	2.102(3)	Al–Cl(4)	2.146(3)
N(1)–C(1)	1.497(10)	N(2)–C(11)	1.494(13)
C(1)–C(2)	1.500(11)	C(11)–C(12)	1.434(14)
C(1)–C(6)	1.512(10)	C(11)–C(16)	1.489(12)
C(2)–C(3)	1.506(11)	C(12)–C(13)	1.515(16)
C(3)–C(4)	1.518(16)	C(13)–C(14)	1.480(22)
C(4)–C(5)	1.496(19)	C(14)–C(15)	1.431(24)
C(5)–C(6)	1.557(13)	C(15)–C(16)	1.525(18)
N(1)–H(N1a)	0.73(5)	N(2)–H(N2a)	0.80(6)
N(1)–H(N1b)	0.92(8)	N(2)–H(N2b)	0.88(8)
N(1)–H(N1c)	1.00(8)	N(2)–H(N2c)	1.03(8)
C(1)–H(1)	1.02(5)	C(11)–H(11)	1.04(9)

(*b*) Interionic hydrogen-bond contacts

Cl(5) ··· H(N1b$^{\mathrm{I}}$)	2.31(8)	Cl(5) ··· H(N2a$^{\mathrm{II}}$)	2.36(6)
Cl(5) ··· H(N1a)	2.47(8)	Cl(5) ··· H(N2b$^{\mathrm{I}}$)	2.34(8)
Cl(5) ··· N(1)	3.189(9)	Cl(5) ··· N(2$^{\mathrm{I}}$)	3.171(9)
Cl(5) ··· N(1$^{\mathrm{I}}$)	3.203(9)	Cl(5) ··· N(2$^{\mathrm{II}}$)	3.134(10)

(*a*) Intraionic

Cl(1)–Al–Cl(2)	110.35(14)	Cl(2)–Al–Cl(3)	110.82(13)
Cl(1)–Al–Cl(3)	112.09(14)	Cl(2)–Al–Cl(4)	108.07(14)
Cl(1)–Al–Cl(4)	107.17(14)	Cl(3)–Al–Cl(4)	108.16(12)
N(1)–C(1)–C(2)	107.5(7)	N(2)–C(11)–C(12)	113.7(9)
N(1)–C(1)–C(6)	109.3(6)	N(2)–C(11)–C(16)	109.4(9)
C(2)–C(1)–C(6)	113.3(7)	C(12)–C(11)–C(16)	114.0(8)
C(1)–C(2)–C(3)	110.1(7)	C(11)–C(12)–C(13)	113.5(9)
C(2)–C(3)–C(4)	110.1(7)	C(12)–C(13)–C(14)	112.2(10)
C(3)–C(4)–C(5)	110.6(8)	C(13)–C(14)–C(15)	112.6(10)
C(4)–C(5)–C(6)	112.0(7)	C(14)–C(15)–C(16)	115.0(9)
C(1)–C(6)–C(5)	108.1(6)	C(11)–C(16)–C(15)	110.7(9)
C(1)–N(1)–H(N1a)	111(5)	C(11)–N(2)–H(N2a)	107(5)
C(1)–N(1)–H(N1b)	113(5)	C(11)–N(2)–H(N2b)	113(5)
C(1)–N(1)–H(N1c)	105(5)	C(11)–N(2)–H(N2c)	99(5)
H(N1a)–N(1)–H(N1b)	106(7)	H(N2a)–N(2)–H(N2b)	102(7)
H(N1a)–N(1)–H(N1c)	107(6)	H(N2a)–N(2)–H(N2c)	114(6)
H(N1b)–N(1)–H(N1c)	112(7)	H(N2b)–N(2)–H(N2c)	119(7)
N(1)–C(1)–H(1)	107(3)	N(2)–C(11)–H(11)	95(5)
C(2)–C(1)–H(1)	107(3)	C(12)–C(11)–H(11)	99(5)
C(6)–C(1)–H(1)	112(3)	C(16)–C(11)–H(11)	122(5)

(*b*) Interionic hydrogen-bonded atoms

N(1) ··· Cl(5) ··· N(2$^{\mathrm{II}}$)	130.54(23)
N(1) ··· Cl(5) ··· N(1$^{\mathrm{I}}$)	86.65(23)
N(1$^{\mathrm{I}}$) ··· Cl(5) ··· N(2$^{\mathrm{I}}$)	137.56(22)
N(1) ··· Cl(5) ··· N(2$^{\mathrm{I}}$)	116.87(23)
N(1$^{\mathrm{I}}$) ··· Cl(5) ··· N(2$^{\mathrm{II}}$)	109.58(22)
N(2$^{\mathrm{II}}$) ··· Cl(5) ··· N(2$^{\mathrm{I}}$)	82.48(23)
H(N1a) ··· Cl(5) ··· H(N1b$^{\mathrm{I}}$)	91.0(23)
H(N1a) ··· Cl(5) ··· H(N2b$^{\mathrm{I}}$)	108.4(23)
HN(1b$^{\mathrm{I}}$) ··· Cl(5) ··· HN(2b$^{\mathrm{I}}$)	144(3)
H(N1a) ··· Cl(5) ··· H(N2a$^{\mathrm{II}}$)	126.5(20)
H(N1b$^{\mathrm{I}}$) ··· Cl(5) ··· H(N2a$^{\mathrm{II}}$)	109.2(24)
H(N2a$^{\mathrm{II}}$) ··· Cl(5) ··· H(N2b$^{\mathrm{I}}$)	83.1(24)
Cl(5) ··· H(N1a) ··· N(1)	166(6)
Cl(5$^{\mathrm{I}}$) ··· H(N1b) ··· N(1)	164(7)
Cl(5$^{\mathrm{III}}$) ··· H(N2a) ··· N(2)	164(6)
Cl(5$^{\mathrm{I}}$) ··· H(N2b) ··· N(2)	156(7)

Atoms are related to those in Table 1 by the following symmetry operations: I $1 - x, 1 - y, 1 - z$; II $x, -1 + y, z$; III $x, 1 + y, z$.

density, the deepest hole being −0.28 e Å^3 and the highest peak 0.49 e Å^3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Final fractional coordinates for salt **2** are given in Table 1 and selected bond distances and angles in Table 2. The salient features of the structure are manifestations of hydrogen bonding, in particular the relative propensities of chloride and tetrachloroaluminate anions to act as hydrogen-bond acceptors. As revealed by the ORTEP[28] view presented in Fig. 1, the chloride anions act as hydrogen-bond acceptors and complex formation results, affording a cationic polymer. The atom numbering is given in Fig. 2.

This contrasts with salt **1**, for which a discrete cation with approximately tetrahedral N ··· Cl ··· N angles ranging from 97.39(14) to 118.32(18)° and N ··· Cl contacts ranging from 3.142(7) to 3.284(6) Å was observed.[20] The geometry around the chloride anion of **2** is also approximately tetrahedral but the distortions from ideal geometry are more extreme. This is exemplified by the N ··· Cl ··· N angles which range from 82.5(2) to 137.6(2)°. The N ··· Cl and N–H ··· Cl contacts are similar to those observed for **1**, ranging from 3.134(10) to 3.203(9) Å and 2.31(8) to 2.47(8) Å, respectively. It is generally accepted that for A–H ··· B systems a hydrogen bond is present if the A ··· B distance is less than the sum of the van der Waals radii of A and B.[29] The interionic distances are therefore supportive of hydrogen bonding, the N ··· Cl contacts being within the sum of the van der Waals radii for N and Cl,

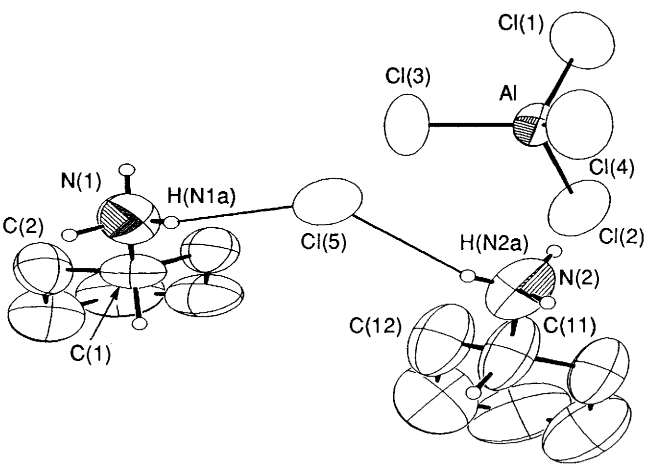

Fig. 2 ORTEP[28] perspective view of the asymmetric unit of **2**

3.30 Å.[30] It has long been recognized that the A–H infrared stretching vibration is very useful for detecting the presence of hydrogen bonds.[31] The infrared spectra obtained for salt **1** in the 'liquid clathrate' medium and as a solid are supportive of hydrogen-bonding but not conclusive as the N–H stretch is not easily resolvable. In the case of the former the N–H stretch appears at 3208 cm^{-1} but is affected by the presence of aromatic solvent, whereas for the latter the peaks are, as one might expect, extremely broad but centred at approximately 3000 cm^{-1}. The tetrachloroaluminate anions exhibit no contacts within hydrogen-bonding distance. All other bond distances and angles are within expected ranges.

That chloride acts as a stronger hydrogen-bond acceptor than tetrachloroaluminate is predictable and has been explored by us recently in the context of simple tetrachloroaluminate and chloride salts.[22] The structures of salts **1** and **2** confirm this assertion. The ultimate significance of the results of this study lie in extrapolating the observations to the pyridinium and imidazolium chloride–chloroaluminate ionic liquids. The complex cations observed in **1** and **2** are clearly models for the type of ordering that could occur in the liquid phase of basic ionic liquids. That they contain N–H bonds, which would be expected to be much stronger hydrogen-bond donors than the C–H bonds present in the pyridinium and imidazolium cations, should not preclude such an extrapolation since spectroscopic and X-ray crystallographic evidence for C–H • • • Cl hydrogen bonding in basic 1-ethyl-3-methylimidazolium melts is quite conclusive.[12–19] It is worth noting that a comparison between 1- and 4-methylpyridinium halide molten salts suggested complex formation in the latter but not in the former.[32] However, no $AlCl_3$ was incorporated into these systems. Indeed, although the prototypal alkylpyridinium systems have not been studied as extensively as 1-ethyl-3-methylimidazolium salts in recent years, evidence for complex formation in the former is found in one of the earliest reports on alkylpyridinium halogenoaluminate melts. In the early report[1a] eutectics corresponding to $C_5H_5NEt^+Br^-$–$AlCl_3$ and $C_5H_5NEt^+$-Br^-–$2AlCl_3$ were found.

A surprising feature of the present study is that salts **1** and **2** are isolable even in the presence of a small amount of $AlCl_3$ (the reactions to form **1** and **2** used an equimolar amount of $AlCl_3$). This feature is presumably a manifestation of the ability of N–H bonds to act as hydrogen-bond donors, particularly when compared to the C–H bonds of alkyl pyridinium and 1-ethyl-3-methylimidazolium. The equilibrium constant of equation (1) could therefore be modified from the value of

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4 \qquad (1)$$

10^{16} observed in 1-ethyl-3-methylimidazolium-based melts. Even so, that the simple tetrachloroaluminate salts were not isolated is surprising from a thermodynamic viewpoint and from the perspective of studies conducted by us on piperidinium and pyridinium tetrachloroaluminate, in which the expected tetrachloroaluminate salts were isolated directly from the 1:1 reaction.[22] However, it is difficult to get an accurate thermodynamic handle on the energy of the N–H • • • Cl hydrogen bonds and the energy associated with the formation of the 'liquid clathrate' phases from which salts **1** and **2** were crystallized.

In summary, mixed chloride–tetrachloroaluminate salts are unexpectedly isolated from the benzene-based 'liquid clathrates' formed from reaction of benzylammonium chloride and cyclohexylammonium chloride with 1 equivalent of $AlCl_3$. The salts exhibit complex formation *via* N–H • • • Cl hydrogen bonding and are particularly relevant in the context of interionic attractions in basic room-temperature chloroaluminate ionic liquids.

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References

1 F. H. Hurley and T. P. Wier, *J. Electrochem. Soc.*, 1951, **98**, 203, 207.
2 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263.
3 S. K. D. Strubinger, I.-W. Sun, W. E. Cleland, jun., and C. L. Hussey, *Inorg. Chem.*, 1990, **29**, 993; I.-W. Sun, E. H. Ward, C. L. Hussey, K. R. Seddon and J. E. Turp, *Inorg. Chem.*, 1987, **26**, 2140 and refs. therein.
4 A. J. Dent, K. R. Seddon and T. Welton, *J. Chem. Soc., Chem. Commun.*, 1990, 315.
5 G. P. Smith, A. S. Dworkin, R. M. Pagni and S. P. Zingg, *J. Am. Chem. Soc.*, 1989, **111**, 525.
6 J. Robinson and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1979, **101**, 323; 1980, **102**, 4415.
7 G. D. Luer and D. E. Bartak, *J. Org. Chem.*, 1982, **47**, 1238.
8 V. R. Koch, L. L. Miller and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1976, **98**, 5277.
9 H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1975, **97**, 3264.
10 R. J. Gale, P. Singh and R. Job, *J. Organomet. Chem.*, 1980, **199**, 44.
11 D. W. Slocum, A. L. Edgecombe, J. S. Fowler, H. F. Gibbard and J. Phillips, *J. Organomet. Chem.*, 1989, **363**, 151.
12 A. K. Abdul-Sada, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon and J. A. Zora, *J. Chem. Soc., Chem. Commun.*, 1986, 1753.
13 J. Robinson, R. C. Bugle, H. L. Chum, D. Koran and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1979, **101**, 3776.
14 J. S. Wilkes, J. A. Levisky, J. L. Pflug, C. L. Hussey and T. B. Scheffler, *Anal. Chem.*, 1982, **54**, 2378.
15 A. A. Fannin, jun., L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem.*, 1984, **88**, 2609.
16 T. A. Zawodzinski, jun., R. Kurland and R. A. Osteryoung, *J. Phys. Chem.*, 1987, **91**, 962.
17 R. J. Gale and R. A. Osteryoung, *Inorg. Chem.*, 1980, **19**, 2240.
18 S. Tait and R. A. Osteryoung, *Inorg. Chem.*, 1984, **23**, 4352.
19 K. M. Dieter, C. J. Dymek, jun., N. E. Heimer, J. W. Rovang and J. S. Wilkes, *J. Am. Chem. Soc.*, 1988, **110**, 2722.
20 R. H. Dubois, M. J. Zaworotko and P. S. White, *Inorg. Chem.*, 1989, **28**, 2019.
21 J. L. Atwood, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, New York, 1980, vol. 1, ch. 9.
22 M. V. Gaudet, M. J. Zaworotko and P. S. White, *Inorg. Chem.*, 1989, **28**, 1191; M. J. Zaworotko, K. C. Sturge, A. Linden and T. S. Cameron, *Acta Crystallogr., Sect. C*, 1989, **45**, 996.
23 C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1985, 323.
24 D. R. Bond, G. E. Jackson, H. C. Joao, M. N. Hofmeyr, T. A. Modro and L. G. Nassimbeni, *J. Chem. Soc., Chem. Commun.*, 1989, 1910.

25 M. V. Gaudet, D. C. Peterson and M. J. Zaworotko, *J. Incl. Phenom.*, 1988, **6**, 425.

26 E. J. Gabe, F. L. Lee and Y. LePage, The NRCVAX Crystal Structure System, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Clarendon Press, Oxford, 1985, p. 167.

27 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

28 C. K. Johnson, ORTEP, Report ORNL-3794, revised, Oak Ridge National Laboratory, Tennessee, 1965.

29 M. D. Joesten and L. J. Schaad, in *Hydrogen Bonding*, Marcel Dekker, New York, 1974, p. 35; J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91; W. C. Hamilton and J. A. Ibers, in *Hydrogen Bonding in Solids*, W. A. Benjamin, New York, 1968.

30 L. Pauling, in *The Nature of the Chemical Bond*, 2nd edn., Cornell University Press, Ithaca, New York, 1940, p. 189.

31 G. C. Pimentel and A. L. McLennan, in *The Hydrogen Bond*, W. H. Freeman, San Francisco, 1960, ch. 3.

32 D. S. Newman, R. T. Tillack, D. P. Morgan and W.-C. Wan, *J. Electrochem. Soc.*, 1977, **124**, 856.

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