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## Structures of the Tetrachloroaluminate Salts of the *N*-Ethylpyridinium, 2-Ethylpyridinium, Pyridinium and 1-Chloromethyl-1,2,3,4,5,6-hexamethylbenzenium Cations

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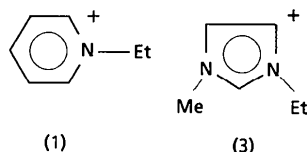
**Abstract.** The crystal structures of four organic-cation tetrachloroaluminate salts have been determined: *N*-ethylpyridinium tetrachloroaluminate, [C<sub>7</sub>H<sub>10</sub>N][AlCl<sub>4</sub>],  $M_r = 277.0$ , monoclinic,  $C2/c$ ,  $a = 14.112$  (3),  $b = 12.893$  (5),  $c = 14.949$  (3) Å,  $\beta = 110.63$  (2)°,  $V = 2545.6$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.445$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70926$  Å,  $\mu = 0.952$  mm<sup>-1</sup>,  $F(000) = 1120$ ,  $T = 295$  K,  $R = 0.053$  for 589 unique observed reflections; pyridinium tetrachloroaluminate, [C<sub>5</sub>H<sub>6</sub>N][AlCl<sub>4</sub>],  $M_r = 248.9$ , orthorhombic,  $Cmcm$ ,  $a = 9.204$  (3),  $b = 8.314$  (2),  $c = 14.001$  (5) Å,  $V = 1071.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.543$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70926$  Å,  $\mu = 1.12$  mm<sup>-1</sup>,  $F(000) = 496$ ,  $T = 295$  K,  $R = 0.041$  for 356 unique observed reflections; 2-ethylpyridinium tetrachloroaluminate, [C<sub>7</sub>H<sub>10</sub>N][AlCl<sub>4</sub>],  $M_r = 277.0$ , monoclinic,  $P2_1/c$ ,  $a = 7.674$  (2),  $b = 13.322$  (3),  $c = 12.641$  (3) Å,  $\beta = 96.18$  (2)°,  $V = 1284.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.432$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70926$  Å,  $\mu = 0.944$  mm<sup>-1</sup>,  $F(000) = 560$ ,  $T = 295$  K,  $R = 0.064$  for

1134 unique observed reflections; 1-chloromethyl-1,2,3,4,5,6-hexamethylbenzenium tetrachloroaluminate, [C<sub>13</sub>H<sub>20</sub>Cl][AlCl<sub>4</sub>],  $M_r = 380.6$ , monoclinic,  $P2_1/n$ ,  $a = 8.951$  (2),  $b = 12.322$  (2),  $c = 16.763$  (4) Å,  $\beta = 98.43$  (2)°,  $V = 1828.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.38$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70926$  Å,  $\mu = 0.823$  mm<sup>-1</sup>,  $F(000) = 784$ ,  $T = 295$  K,  $R = 0.057$  for 1354 unique observed reflections. The structures reveal little or no interaction between the tetrachloroaluminate anions and the cations. The significance of this observation is discussed in the context of tetrachloroaluminate sustained room-temperature melts.

**Introduction.** That halogenoaluminate salts may exist as liquids under ambient conditions was first realized by Hurley and Wier in 1951 when they reported the properties of the prototypal melts, *N*-ethylpyridinium [(1)] halogenoaluminates (Hurley & Wier, 1951*a,b*). Activity in this field has steadily increased since 1951, with the related methylpyridinium salts having likewise been investigated (Newman, Tillack, Morgan & Wan,

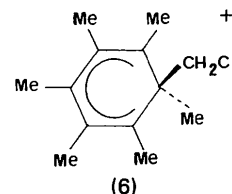
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1977). Recent efforts, however, have tended to focus upon two other bulky organic cations, *N*-butylpyridinium [(2)] (Tait & Osteryoung, 1984; Takahashi, Koura, Murase & Ohno, 1986; Zawodzinski, Kurland & Osteryoung, 1987) and 1-ethyl-3-methylimidazolium [(3)] (Wilkes, Levisky, Wilson & Hussey, 1982; Fannin, King, Levisky & Wilkes, 1984; Abdul-Sala, Greenway, Hitchcock, Mohammed, Seddon & Zora, 1986; Abdul-Sala, Avent, Parkington, Ryan, Seddon & Welton, 1987; Sun, Ward, Hussey, Seddon & Turp, 1987; Zawodzinski & Osteryoung, 1987; Dieter, Dymek, Heimer, Rovang & Wilkes, 1988).



A question of topical interest concerns to what degree ordering exists in room-temperature ionic melts. Spectroscopic (Fannin, King, Levisky & Wilkes, 1984; Tait & Osteryoung, 1984) and theoretical (Dieter, Dymek, Heimer, Rovang & Wilkes, 1988) evidence has recently been presented which suggests that at least short-range order might be present in the liquid phase in imidazolium-based melts. The only crystallographic study of direct relevance, however, has been conducted upon a model salt, (3)<sup>+</sup>I<sup>-</sup> (Abdul-Sala, Greenway, Hitchcock, Mohammed, Seddon & Zora, 1986). The result of the investigation indicated that ion pairing *via* C—H...X hydrogen bonding could be a factor influencing the existence of room-temperature ordered melts, at least in the so-called 'basic' melts (*i.e.* mole fraction of AlCl<sub>3</sub> < 0.5). The dearth of X-ray structural investigations conducted upon simple tetrachloroaluminate salts has prompted us to study a range of such salts with a view to determining the propensity of the tetrachloroaluminate anion for being a hydrogen-bond acceptor. Our initial crystallographic investigation, conducted upon piperidinium tetrachloroaluminate and piperidinium chloride, indicated that AlCl<sub>4</sub> is at best a weak hydrogen-bond acceptor (Gaudet, Zaworotko & White, 1989). The salts we have chosen to investigate for this more comprehensive study include that of the prototypal *N*-ethylpyridinium cation [(1)] and are all solids under ambient conditions. The four salts studied nevertheless exhibit another important characteristic of room-temperature melts in that they are all highly soluble in benzene and other liquid aromatic hydrocarbon compounds. The latter property has permitted facile crystallization of the salts under investigation. Two of the remaining three salts, pyridinium tetrachloroaluminate {(4) [AlCl<sub>4</sub>]} and 2-ethylpyridinium tetrachloroaluminate, {(5) [AlCl<sub>4</sub>]}, were chosen as they are similar to (1) [AlCl<sub>4</sub>] yet contain N—H bonds and are therefore more likely to become involved in

hydrogen-bonding interactions with the tetrachloroaluminate anion. The fourth salt investigated, 1-chloromethyl-1,2,3,4,5,6-hexamethylbenzenium tetrachloroaluminate {(6) [AlCl<sub>4</sub>]}, was chosen as it represents another important class of room-temperature ionic liquid, the so-called 'Friedel-Crafts oils' (Olah, 1963, and references therein).



**Experimental. Synthesis.** All four salts were crystallized by cooling toluene 'liquid clathrates' (Atwood, 1984) sustained by the heptachlorodialuminate salts at 258 K overnight. The 'liquid clathrate' phases from which the salts were crystallized were prepared in stoppered Erlenmeyer flasks under ambient conditions. The synthetic details are outlined below.

(1) [AlCl<sub>4</sub>]: 2.00 g (10.6 mmol) of (1)Br was reacted with 2.83 g (21.2 mmol) of AlCl<sub>3</sub> in 25 mL toluene to yield the (1)[Al<sub>2</sub>Cl<sub>6</sub>Br].4.3C<sub>7</sub>H<sub>8</sub> sustained 'liquid clathrate'.

(4) [AlCl<sub>4</sub>]: pyridine (1.00 mL, 12.4 mmol) was dissolved in 25 mL of toluene and contacted with 1 atm (101.3 kPa) of dry HCl for a period of 15 min. The resulting 'liquid clathrate' was reacted with 3.31 g (24.8 mmol) of AlCl<sub>3</sub>, resulting in evolution of HCl gas and formation of the (4)[Al<sub>2</sub>Cl<sub>7</sub>].4.6C<sub>7</sub>H<sub>8</sub> 'liquid clathrate'.

(5) [AlCl<sub>4</sub>]: the (5)[Al<sub>2</sub>Cl<sub>7</sub>].4.7C<sub>7</sub>H<sub>8</sub> sustained 'liquid clathrate' was formed using 1.00 mL (8.74 mmol) of 2-ethylpyridine in a manner similar to that outlined for (4) [AlCl<sub>4</sub>].

(6) [AlCl<sub>4</sub>]: hexamethylbenzene (2.00 g, 12.4 mmol) was reacted with 1.64 g (12.4 mmol) of AlCl<sub>3</sub> in 25 mL of dichloromethane. Slow reaction occurred to give a pale yellow/orange solution of (6) [AlCl<sub>4</sub>]. (6) [AlCl<sub>4</sub>] was subsequently precipitated *via* addition of 50 mL of distilled hexanes. (6) [AlCl<sub>4</sub>] dissolves readily in toluene in the presence of one more equivalents of AlCl<sub>3</sub> to give a 'liquid clathrate' phase containing 6.0 moles of toluene per mole of (6) [AlCl<sub>4</sub>].

A more detailed account of the hydrogen-chloride sustained 'liquid clathrate' phases has been published elsewhere (Gaudet, Peterson & Zaworotko, 1988).

**X-ray crystallography.** Colourless moisture-sensitive crystals of (1) [AlCl<sub>4</sub>], (4) [AlCl<sub>4</sub>], (5) [AlCl<sub>4</sub>] and (6) [AlCl<sub>4</sub>] were sealed in thin-walled glass capillaries. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated MoK $\alpha$  radiation. Data collection and refinement parameters are summarized in Table 1. Intensities reduced to a standard scale (Cameron & Cordes, 1979), Lorentz and polarization corrections

Table 1. Crystallographic data collection and structure-refinement parameters

	(1) [AlCl <sub>4</sub> ]	(4) [AlCl <sub>4</sub> ]	(5) [AlCl <sub>4</sub> ]	(6) [AlCl <sub>4</sub> ]
Crystal dimensions (mm)	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.4	1.0 × 0.3 × 0.25	0.8 × 0.4 × 0.3
Lattice-parameter reflections	25	25	25	25
θ range (°)	20–28	20–28	24–32	24–28
Range of h	–15 to 15	–1 to 10	–9 to 9	–9 to 9
k	–1 to 14	–1 to 9	–1 to 15	–1 to 30
l	0 to 16	0 to 16	–1 to 15	–1 to 18
No. of standards	3	3	3	3
Crystal decomposition	None	None	None	~50%
Scan type	ω:2θ	ω:2θ	ω:2θ	ω:2θ
ω-scan width (°)	1.1 + tanθ	1.0 + tanθ	1.0 + tanθ	1.0 + tanθ
Scan speed		Variable at 0.7–4.0° min <sup>-1</sup>		
2θ range (°)	4–46	4–50	4–50	4–46
Reflections measured	2142	717	2948	2997
Unique reflections	1773	523	2254	2537
R <sub>int</sub>	0.067	0.038	0.040	0.030
Reflections observed*	589	356	1134	1354
Parameters refined	132	45	132	212
Weight: k, g	0.081, 0.04	0.7188, 0.0005	0.667, 0.005	0.687, 0.0005
Final Δ <sub>max</sub> /σ	0.4	1.3	0.5	0.6
Ratio data/parameter	4.5	7.9	8.6	6.4
R	0.053	0.041	0.064	0.057
wR	0.055	0.041	0.067	0.056
Max. residual peak (e Å <sup>-3</sup> )	0.4	0.35	0.4	0.5

\* I &gt; 2σ(I).

applied, absorption correction (Walker & Stuart, 1983) applied only for (5) [AlCl<sub>4</sub>] (μ ranged from 0.823 to 1.112 mm<sup>-1</sup>), no correction for extinction. Scattering factors for atoms were taken from *International Tables for X-ray Crystallography* (1974) and corrected for the real part of anomalous dispersion. The structures were solved by direct methods, using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for (1) [AlCl<sub>4</sub>], (4) [AlCl<sub>4</sub>] and (5) [AlCl<sub>4</sub>], and *SHELX76* (Sheldrick, 1976) for (6) [AlCl<sub>4</sub>]. Full-matrix least-squares refinements were carried out using the *SHELX76* system and minimizing the function  $\sum w(|F_o| - |F_c|)^2$  where the weight, *w*, is defined as  $k/[\sigma^2(F) + gF^2]$ .

(1) [AlCl<sub>4</sub>]: direct methods revealed the atoms of the anion and the atomic positions within the cation were observed from subsequent Fourier maps. All non-H atoms were refined anisotropically, at which point H atoms appeared in the difference map. The H atoms, however, were placed geometrically and constrained as rigid groups. The final difference map was without significant features. Final fractional coordinates are given in Table 2 and selected inter- and intra-ionic distances and angles are given in Table 3.\* A view of the packing arrangement around the cation is presented in Fig. 1.

(4) [AlCl<sub>4</sub>]: direct methods (*MULTAN80*) revealed atomic positions for the anion. The Al atom was found

Table 2. Final fractional coordinates for (1) [AlCl<sub>4</sub>]

The equivalent isotropic temperature factor (Å<sup>2</sup>) is defined as  $U_{iso} = (U_{11}U_{22}U_{33})^{1/3}$ .

	x	y	z	U <sub>iso</sub>
Al	0.2659 (2)	0.0877 (2)	0.2457 (2)	0.0533
Cl(1)	0.1104 (2)	0.0445 (3)	0.2013 (2)	0.0722
Cl(2)	0.3406 (2)	0.0440 (2)	0.3906 (2)	0.0711
Cl(3)	0.3384 (2)	0.0174 (2)	0.1545 (2)	0.0799
Cl(4)	0.2721 (2)	0.2526 (2)	0.2354 (2)	0.0703
N(1)	0.4934 (7)	0.2734 (8)	0.4775 (6)	0.0569
C(1)	0.5307 (9)	0.1995 (11)	0.5421 (9)	0.0590
C(2)	0.4906 (11)	0.1832 (12)	0.6099 (10)	0.0693
C(3)	0.4084 (12)	0.2418 (12)	0.6127 (9)	0.0775
C(4)	0.3732 (9)	0.3165 (11)	0.5419 (10)	0.0719
C(5)	0.4137 (9)	0.3318 (11)	0.4739 (9)	0.0605
C(6)	0.5391 (10)	0.2892 (11)	0.4038 (9)	0.0786
C(7)	0.6237 (11)	0.3674 (12)	0.4393 (11)	0.1069

Table 3. Bond distances (Å) and angles (°) and H–Cl contacts (Å) for (1) [AlCl<sub>4</sub>]

Al–Cl(1)	2.130 (5)	N(1)–C(6)	1.47 (2)
Al–Cl(2)	2.123 (5)	C(1)–C(2)	1.34 (2)
Al–Cl(3)	2.170 (6)	C(2)–C(3)	1.40 (2)
Al–Cl(4)	2.136 (5)	C(3)–C(4)	1.39 (2)
N(1)–C(1)	1.33 (2)	C(4)–C(5)	1.34 (2)
N(1)–C(5)	1.34 (2)	C(6)–C(7)	1.51 (2)
Cl(1)–Al–Cl(2)	109.6 (2)	C(5)–N(1)–C(6)	118.4 (10)
Cl(1)–Al–Cl(3)	110.9 (2)	N(1)–C(1)–C(2)	119.9 (13)
Cl(1)–Al–Cl(4)	107.6 (2)	C(1)–C(2)–C(3)	120.9 (13)
Cl(2)–Al–Cl(3)	110.8 (2)	C(2)–C(3)–C(4)	115.5 (15)
Cl(2)–Al–Cl(4)	108.6 (2)	C(3)–C(4)–C(5)	123.0 (14)
Cl(3)–Al–Cl(4)	109.2 (2)	N(1)–C(5)–C(4)	117.5 (12)
C(1)–N(1)–C(5)	123.1 (13)	N(1)–C(6)–C(7)	109.2 (11)
C(1)–N(1)–C(6)	118.5 (12)		

H(1)···Cl(2 <sup>i</sup> )	2.77	H(5)···Cl(1 <sup>iii</sup> )	2.71
H(4)···Cl(2 <sup>ii</sup> )	2.91	H(8)···Cl(4 <sup>iv</sup> )	2.84

Symmetry code: (i) 1–x, –y, 1–z; (ii) ½–x, ½–y, 1–z; (iii) ½–x, ½+y, ½–z; (iv) 1–x, y, ½–z.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51678 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

to lie at an  $m2m$  position, the Cl atoms on separate mirror planes. Difference Fourier maps subsequently revealed the location of all remaining non-H atoms. The symmetry imposed *via* the choice of space group (attempts to refine in  $Cmc2_1$  were unsuccessful) meant that the cation was disordered. The N atom was found on a twofold axis whereas the C atom directly opposite to it, C(3), was found to lie slightly off the twofold axis in a general position. The remaining C atoms were therefore also disordered. The disorder was further complicated by the fact that the cation was disposed around a mirror plane. The proximity of the disordered atoms to one another did not prevent satisfactory anisotropic refinement of the cation as a rigid group with H atoms placed in calculated positions. The final difference Fourier map was featureless. Final fractional coordinates are given in Table 4 and inter- and intra-ionic distances and angles are presented in Table 5. A view of the packing arrangement around the cation is presented in Fig. 2.

(5)  $[AlCl_4]$ : *MULTAN80* located the atoms of the anion and the atomic positions within the cation were

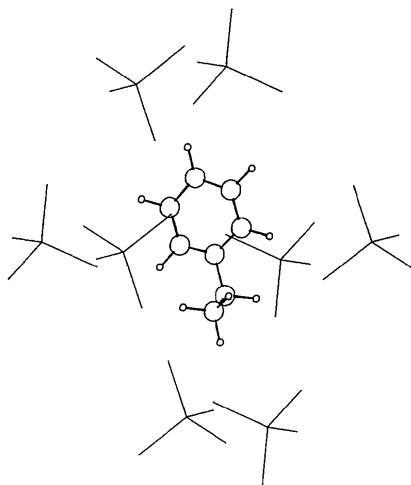


Fig. 1. Packing environment of the cation in (1)  $[AlCl_4]$ .

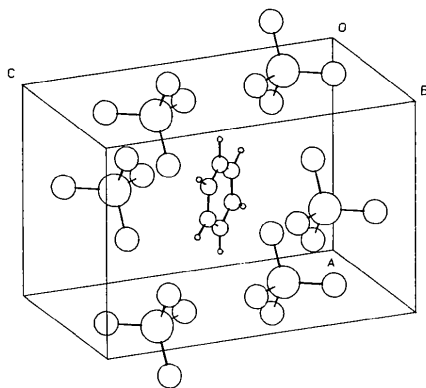


Fig. 2. Packing environment of the cation in (4)  $[AlCl_4]$ .

Table 4. Final fractional coordinates for (4)  $[AlCl_4]$

	<i>x</i>	<i>y</i>	<i>z</i>
Al	0.0	0.3326 (3)	0.25
Cl(1)	0.0	0.4730 (3)	0.1242 (1)
Cl(2)	0.1909 (2)	0.1894 (3)	0.25
N(1)*	0.1389 (16)	0.0	0.5
C(1)*	0.0557 (16)	0.0889	0.5637
C(2)*	-0.0956 (16)	0.0832	0.5589
C(3)*	-0.1636 (16)	-0.0124	0.4897

\* Refined as rigid group with N(1) as pivot atom.

Table 5. Bond distances (Å) and angles (°) and anion-cation contacts (Å) for (4)  $[AlCl_4]$

Al-Cl(1)	2.113 (5)	C(1)-C(2)	1.40*
Al-Cl(2)	2.122 (2)	C(2)-C(3)	1.40*
N(1)-C(1)	1.39*		
Cl(1)-Al-Cl(2)	108.0 (1)		
Cl(1)-Al-Cl(2')	113.0 (2)		
Cl(2)-Al-Cl(2')	111.8 (2)		
Cl(1)...C(3)	3.49	Cl(1)...H(3)	2.54
Cl(1)...C(3)	3.64	Cl(2)...H(4)	2.90
Cl(2)...C(2)	3.61	Cl(2)...H(2)	2.75
Cl(1)...H(1)	2.86		

\* Distances constrained by rigid group.

Table 6. Final fractional coordinates for (5)  $[AlCl_4]$

The equivalent isotropic temperature factor ( $\text{Å}^2$ ) is defined as  $U_{\text{iso}} = (U_{11}U_{22}U_{33})^{1/3}$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}$
Al	0.7921 (2)	0.2393 (1)	0.4412 (1)	0.0603
Cl(1)	0.7869 (2)	0.2365 (1)	0.2725 (1)	0.0836
Cl(2)	0.8203 (4)	0.3890 (1)	0.4928 (1)	0.0934
Cl(3)	1.0020 (3)	0.1513 (2)	0.5132 (2)	0.1067
Cl(4)	0.5514 (3)	0.1785 (2)	0.4836 (2)	0.1012
N	0.3588 (9)	-0.0186 (5)	0.3013 (6)	0.0894
C(1)	0.4897 (9)	-0.0028 (6)	0.2413 (6)	0.0792
C(2)	0.4682 (9)	0.0685 (6)	0.1673 (6)	0.0773
C(3)	0.3190 (11)	0.1217 (6)	0.1521 (7)	0.0872
C(4)	0.1890 (11)	0.1061 (7)	0.2126 (8)	0.0947
C(5)	0.2113 (11)	0.0355 (8)	0.2889 (8)	0.0987
C(6)	0.6492 (15)	-0.0612 (11)	0.2748 (9)	0.1562
C(7)	0.7356 (15)	-0.1084 (10)	0.1854 (9)	0.1548

revealed following difference-Fourier-map inspection. H atoms were placed geometrically and fixed to the appropriate non-H atoms for the final cycles of least-squares refinement. The final difference Fourier map was without significant features. Final fractional coordinates are presented in Table 6 and selected inter- and intra-ionic distances and angles are given in Table 7. A view of the salt is presented in Fig. 3.

(6)  $[AlCl_4]$ : all heavy atoms were found using automatic direct methods (*SHELX76*) and the C atoms were located in subsequent Fourier maps. All non-H atoms were refined anisotropically. H atoms appeared in difference maps but were placed geometrically and constrained as rigid groups. Final H-atom positions by this method were close to those given by the difference

Table 7. Bond distances (Å) and angles (°) and anion-cation contacts (Å) for (5) [AlCl<sub>4</sub>]

Al—Cl(1)	2.129 (5)	C(1)—C(2)	1.330 (12)
Al—Cl(2)	2.102 (3)	C(2)—C(3)	1.343 (12)
Al—Cl(3)	2.116 (3)	C(3)—C(4)	1.336 (14)
Al—Cl(4)	2.137 (3)	C(4)—C(5)	1.345 (15)
N—C(1)	1.339 (12)	C(1)—C(6)	1.473 (15)
N—C(5)	1.337 (12)	C(6)—C(7)	1.508 (18)
Cl(1)—Al—Cl(2)	108.5 (1)	N—C(1)—C(6)	113.8 (8)
Cl(1)—Al—Cl(3)	110.6 (1)	C(2)—C(1)—C(6)	128.0 (9)
Cl(1)—Al—Cl(4)	108.7 (1)	C(1)—C(2)—C(3)	121.1 (8)
Cl(2)—Al—Cl(3)	110.1 (1)	C(2)—C(3)—C(4)	120.9 (9)
Cl(2)—Al—Cl(4)	110.1 (2)	C(3)—C(4)—C(5)	118.3 (8)
Cl(3)—Al—Cl(4)	108.7 (1)	N—C(5)—C(4)	120.1 (9)
C(1)—N—C(5)	121.7 (8)	C(1)—C(6)—C(7)	115.0 (9)
N—C(1)—C(2)	117.8 (7)		
H(1)...Cl(4 <sup>d</sup> )	2.46	C(4)...Cl(1)	3.69
N...Cl(4)	3.46	H(4)...Cl(1)	2.70
C(2)...Cl(1)	3.47	H(2)...Cl(2 <sup>h</sup> )	2.63
H(2)...Cl(1)	3.15		

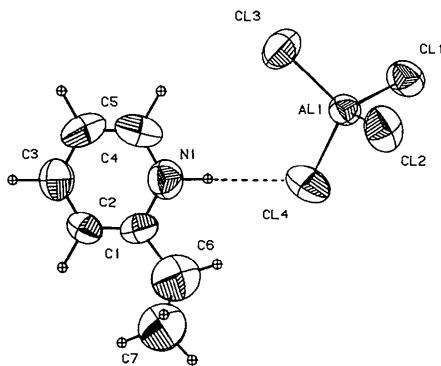
All other C...Cl and N...Cl contacts, 3.70–3.77 Å; all other H...Cl contacts, greater than 2.84 Å.

Symmetry codes: (i) 1-x, -y, 1-z; (ii) x, ½-y, ½+z.

Table 8. Final fractional coordinates for (6) [AlCl<sub>4</sub>]

The equivalent isotropic temperature factor (Å<sup>2</sup>) is defined as  $U_{iso} = (U_{11}U_{22}U_{33})^{1/3}$ .

	x	y	z	U <sub>iso</sub>
Al	0.6075 (2)	0.7405 (2)	0.6501 (1)	0.0495
Cl(1)	0.7919 (2)	0.8208 (2)	0.6091 (1)	0.0817
Cl(2)	0.5552 (2)	0.8240 (2)	0.7531 (1)	0.0737
Cl(3)	0.6686 (3)	0.5791 (2)	0.6834 (2)	0.0915
Cl(4)	0.4199 (2)	0.7434 (2)	0.5566 (1)	0.0681
Cl(5)	0.3218 (2)	0.1749 (2)	0.8090 (1)	0.0709
C(1)	0.2690 (8)	0.3108 (6)	0.5950 (4)	0.0529
C(2)	0.1230 (8)	0.2654 (7)	0.5767 (4)	0.0535
C(3)	0.0864 (7)	0.1601 (6)	0.5973 (4)	0.0493
C(4)	0.1944 (7)	0.0937 (6)	0.6354 (4)	0.0476
C(5)	0.3551 (7)	0.1326 (6)	0.6533 (4)	0.0467
C(6)	0.3814 (7)	0.2461 (6)	0.6342 (4)	0.0501
C(7)	0.2986 (10)	0.4242 (7)	0.5718 (6)	0.0791
C(8)	-0.0003 (9)	0.3346 (8)	0.5324 (6)	0.0836
C(9)	-0.0770 (8)	0.1212 (8)	0.5794 (5)	0.0712
C(10)	0.1621 (9)	-0.0188 (7)	0.6619 (5)	0.0720
C(11)	0.4455 (8)	0.0611 (7)	0.5974 (5)	0.0649
C(12)	0.4227 (8)	0.1045 (6)	0.7413 (4)	0.0551
C(13)	0.5390 (8)	0.2903 (7)	0.6551 (5)	0.0645

Fig. 3. Perspective view of (5) [AlCl<sub>4</sub>].Table 9. Bond distances (Å) and angles (°) and H—Cl contacts (Å) for (6) [AlCl<sub>4</sub>]

Al—Cl(1)	2.123 (3)	C(2)—C(8)	1.50 (1)
Al—Cl(2)	2.121 (3)	C(3)—C(4)	1.35 (1)
Al—Cl(3)	2.115 (4)	C(3)—C(9)	1.53 (1)
Al—Cl(4)	2.122 (3)	C(4)—C(5)	1.50 (1)
Cl(5)—C(12)	1.776 (8)	C(4)—C(10)	1.50 (1)
C(1)—C(2)	1.41 (1)	C(5)—C(6)	1.46 (1)
C(1)—C(6)	1.37 (1)	C(5)—C(11)	1.59 (1)
C(1)—C(7)	1.48 (1)	C(5)—C(12)	1.55 (1)
C(2)—C(3)	1.39 (1)	C(6)—C(13)	1.50 (1)
Cl(1)—Al—Cl(2)	108.2 (1)	C(4)—C(3)—C(9)	120.0 (7)
Cl(1)—Al—Cl(3)	109.9 (1)	C(3)—C(4)—C(5)	119.8 (7)
Cl(1)—Al—Cl(4)	108.8 (1)	C(3)—C(4)—C(10)	123.0 (7)
Cl(2)—Al—Cl(3)	108.7 (2)	C(5)—C(4)—C(10)	117.1 (6)
Cl(2)—Al—Cl(4)	110.4 (1)	C(4)—C(5)—C(6)	116.2 (6)
Cl(3)—Al—Cl(4)	110.9 (2)	C(4)—C(5)—C(11)	105.1 (6)
C(2)—C(1)—C(6)	117.6 (7)	C(4)—C(5)—C(12)	110.3 (6)
C(2)—C(1)—C(7)	120.7 (7)	C(6)—C(5)—C(11)	106.7 (6)
C(6)—C(1)—C(7)	121.7 (7)	C(6)—C(5)—C(12)	111.7 (6)
C(1)—C(2)—C(3)	124.0 (7)	C(11)—C(5)—C(12)	106.0 (6)
C(1)—C(2)—C(8)	118.1 (8)	C(1)—C(6)—C(5)	122.0 (6)
C(3)—C(2)—C(8)	117.9 (7)	C(1)—C(6)—C(13)	119.8 (7)
C(2)—C(3)—C(4)	120.1 (7)	C(5)—C(6)—C(13)	118.1 (6)
C(2)—C(3)—C(9)	119.9 (7)		
H(16)...Cl(2)	2.71		
H(17)...Cl(3 <sup>h</sup> )	2.71		
H(20)...Cl(4 <sup>h</sup> )	2.75		

Symmetry codes: (i) x, -1+y, z; (ii) ½-x, -½+y, ½-z; (iii) 1-x, 1-y, 1-z.

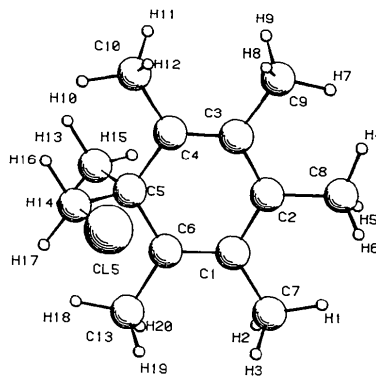


Fig. 4. Perspective view of (6).

maps; however, attempts to refine H atoms were unsatisfactory and led to bond angles in the range 90–120° and C—H bonds down to 0.9 Å. The final difference map was featureless except for one peak of 0.5 e Å<sup>-3</sup> near Cl(2). Final fractional coordinates are given in Table 8 and selected inter- and intra-ionic distances are given in Table 9. A view of the cation is presented in Fig. 4.

**Discussion.** Definition of what constitutes a significant hydrogen bond is obviously of relevance to this study. For the purposes of this discussion we shall use the definition of Joesten & Schaad (1974), *i.e.* that a hydrogen bond exists between X—H...Y moieties if the

distance between  $X$  and  $Y$  is within the sum of the van der Waals radii of  $X$  and  $Y$ . Therefore for  $N-H\cdots Cl$  and  $C-H\cdots Cl$  contacts to be considered manifestations of hydrogen bonding they would have to exhibit  $N\cdots Cl$  or  $C\cdots Cl$  distances within 3.30 and 3.40 Å, respectively. The corresponding  $H\cdots Cl$  contacts would therefore have to be of the order of 2.30 and 2.40 Å, respectively. Relatively large numbers of crystallographic studies have focused upon  $X = N$  and  $Y = Cl^-$  interactions, and many exhibit  $N\cdots Cl$  contacts of less than 3.30 Å (Pimentel & McLellan, 1960). For  $X = N$  and  $Y = ClAlCl_3$ , however, a survey of the literature has revealed that until this work no structural data are available for comparison. It is therefore significant that none of the structures of the salts reported herein exhibit  $N\cdots Cl$  (or  $C\cdots Cl$ ) contacts within the limits expected for hydrogen bonding. The four structures are discussed individually below.

(1)  $[AlCl_4]$ : (1)  $[AlCl_4]$  exhibits no significant interionic contacts, with the closest cation-anion distance being 2.71 Å [ $H(5)-Cl(1)$ ]. The view in Fig. 1 illustrates the cationic environment, which consists of an essentially random disposition of eight tetrachloroaluminate anions around (1). There is therefore no evidence to suggest the existence of  $C-H\cdots ClAlCl_3$  hydrogen bonding. The bond distances and angles within the cation and the anion (mean  $Al-Cl$  2.140 Å) are within expected ranges and the cation is planar to 0.011 Å.

(4)  $[AlCl_4]$ : (4)  $[AlCl_4]$  might be expected to be the salt most likely to exhibit hydrogen bonding (*via*  $N-H\cdots ClAlCl_3$  interactions). Fig. 2 illustrates the environment of the cation and reveals that, in a similar manner to (1)  $[AlCl_4]$ , the cation is randomly surrounded by tetrachloroaluminate anions, with no evidence for ion-pairing or hydrogen bonding. The disorder of the cation further supports the suggestion that the interionic attractions are very weak. Significantly the shortest interionic contact is between a  $Cl$  atom and an  $H$  atom bonded to a  $C$  atom rather than an  $N$  atom [ $H(3)\cdots Cl(1)$  2.54 Å].

(5)  $[AlCl_4]$ : the intra-ionic bond distances and angles within the cation and anion (mean  $Al-Cl$  2.121 Å) are within expected ranges (Table 7). The closest  $N\cdots Cl$  contact exhibited is 3.46 Å [ $N-Cl(4)$ ], which represents the shortest interionic contact observed in any of the four structures presented herein. Interestingly, the  $N-H\cdots ClAlCl_3$  angle is reasonably close to  $180^\circ$ , so it would not be unreasonable to call this contact a weak hydrogen-bonding interaction. The solid state structure could then be interpreted in terms of ion-pairs between (5) and the tetrachloroaluminate counter-ion (Fig. 3). The contact is nevertheless considerably longer than the 3.10 Å typically observed for  $N-H\cdots Cl^-$  hydrogen bonds.

(6)  $[AlCl_4]$ : the cyclohexadienylium cation (6) represents an example of the well studied class of

carbocations that are considered to be  $\sigma$ -complex intermediates in electrophilic substitution. Significantly the first isolated example of such moieties, heptamethylbenzenium tetrachloroaluminate (7)  $[AlCl_4]$ , was observed to dissolve in toluene to form two liquid phases, the denser of which was salt-rich (Doering, Saunders, Boyton, Earhart, Wadley, Edwards & Lober, 1958). The existence of two liquid phases in  $AlCl_3$ -catalyzed Friedel-Crafts alkylation reactions had been noted since the nascent days of such chemistry (Olah, 1963); however it was not until the 1950's that the importance of the salt-rich 'oil' phases was fully realized (Brown & Pearsall, 1952). Cyclohexadienylium cations have subsequently been widely studied and are accepted as the intermediate complexes in Friedel-Crafts alkylation of arenes (Olah, 1973), but (7) remains until this study the only cyclohexadienylium cation that has been crystallographically characterized as its tetrachloroaluminate salt (Baenziger & Nelson, 1968). A view of (6) is presented in Fig. 4. It reveals that (6) has adopted the expected planar geometry, with the five  $sp^2$   $C$  atoms of the  $C_6$  ring retaining planarity (to 0.02 Å) and the  $sp^3$   $C$  atom,  $C(5)$ , lying only 0.075 Å away from the plane. The structure of (6) therefore compares with (7) and other crystallographically characterized cyclohexadienylium cations (Effenberger, Reisinger, Schonwalder, Bauerle, Stezowski, Jogun, Schollkopf & Stohrer, 1987). The bond distances also follow the expected trend with the  $sp^2$   $C$ -atom bond distances gradually lengthening towards  $C(5)$  and a mean  $Al-Cl$  distance of 2.120 Å. The feature of interest in the context of this study is the interionic contacts. The closest interionic contact is 3.54 Å, between an anionic  $Cl$  atom and a ring  $C$  atom of the cation [ $C(3)\cdots Cl(2)$ ]. There is therefore no evidence for the presence of  $C-H\cdots Cl$  hydrogen bonding in the solid state in (6)  $[AlCl_4]$ .

The results of this study indicate that the tetrachloroaluminate anion is not a significant hydrogen-bond acceptor. The implication, therefore, is that room-temperature ionic melts, at least the acidic variety, are unlikely to possess any degree of ordering in the liquid phase, that arises from hydrogen bonding to chloroaluminate anions.

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## Structures of Bis(1,2-diphenylphosphinoethane)nickel(II) Dinitrate and Bis(*cis*-1,2-diphenylphosphinoethene)nickel(II) Diperchlorate

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**Abstract.** [Ni{(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (1), *M<sub>r</sub>* = 979.6, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 10.430 (1), *b* = 16.337 (2), *c* = 13.780 (1) Å, β = 93.29 (1)°, *V* = 2344.3 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.37 (2), *D<sub>x</sub>* = 1.39 Mg m<sup>-3</sup>, Mo *K*α, λ = 0.71069 Å, μ = 0.600 mm<sup>-1</sup>, *F*(000) = 1020, room temperature, *R* = 0.072 for 1611 reflections. [Ni{(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCHCHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2), *M<sub>r</sub>* = 1050.4, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 14.048 (1), *b* = 15.994 (1), *c* = 10.878 (1) Å, β = 97.08 (1)°, *V* = 2424.5 (5) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.43 (2), *D<sub>x</sub>* = 1.44 Mg m<sup>-3</sup>, Mo *K*α, λ = 0.71069 Å, μ = 0.695 mm<sup>-1</sup>, *F*(000) = 1084, room temperature, *R* = 0.054 for 670 reflections. In both compounds the Ni atom lies at a centre of symmetry and is coordinated by two bidentate phosphine ligands in a plane. Slight differences in the structure of the cations arise

from the different conformations of the chelate ring. In both compounds the anions are disordered.

**Introduction.** The two chelating phosphine ligands, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [2-phos, (3)] and the unsaturated analogue *cis*-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCHCHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> [2=phos, (4)] are frequently used in coordination chemistry (McAuliffe & Levason, 1979). The chemistry of (3) and (4) is quite similar, but there are a number of significant differences: with cobalt, for example, octahedral complexes [Co(2=phos)<sub>2</sub>X<sub>2</sub>]<sup>+</sup> are readily formed, whereas the analogous complexes with 2-phos are unstable or may not be prepared (Miskowski, Robbins, Hammond & Gray, 1976). It therefore seemed of interest to study the structures of two closely related complexes of these two ligands in order to investigate