Table IV. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

	Bond Lengths		
Zn(1)-Cl(1)	2.233 (3)	Zn(1)-N(1)	2.165 (7)
Zn(1)-N(2)	2.158 (10)	Zn(1)-N(3)	2.200 (8)
Zn(2)-Cl(2)	2.236 (4)	Zn(2)-N(4)	2.203 (10)
Zn(2)-N(5)	2.147 (7)	Zn(2)-N(6)	2.144 (9)
Zn(2)-N(7)	2.246 (7)	N(1)-C(1)	1.461 (18)
N(1)-C(16)	1.462 (14)	C(1)-C(2)	1.535 (17)
C(2)-N(2)	1.468 (12)	N(2)-C(3)	1.498 (14)
C(3)-C(4)	1.524 (14)	C(4)-N(3)	1.481 (17)
N(3)-C(5)	1.488 (13)	C(5)-C(6)	1.517 (19)
C(6)-N(4)	1.460 (11)	N(4)-C(7)	1.474 (11)
C(7)-C(8)	1.499 (16)	C(8)-N(5)	1.478 (19)
N(5)-C(9)	1.467 (14)	C(9)-C(10)	1.519 (15)
C(10)-N(6)	1.442 (12)	N(6)-C(11)	1.502 (13)
C(11)-C(12)	1.543 (19)	C(12)-N(7)	1.472 (13)
N(7)-C(13)	1.460 (11)	C(13)-C(14)	1.492 (14)
C(14)-N(8)	1.488 (16)	N(8)-C(15)	1.487 (11)
C(15)-C(16)	1.518 (12)		
	Angles		
Cl(1)-Zn(1)-N(1)	105.0 (2)	Zn(1)-N(3)-C(5)	115.7 (6)
Cl(1)-Zn(1)-N(3)	110.0 (3)	Cl(1)-Zn(1)-N(8)	111.4 (3)
N(1)-Zn(1)-N(2)	79.5 (4)	N(1)-Zn(1)-N(3)	144.4 (3)
N(1)-Zn(1)-N(8)	81.8 (4)	N(2)-Zn(1)-N(3)	81.4 (3)
N(2)-Zn(1)-N(8)	136.0 (4)	N(3)-Zn(1)-N(8)	91.7 (3)
Cl(2)-Zn(2)-N(4)	104.7 (3)	Cl(2)-Zn(2)-N(5)	113.4 (3)
Cl(2)-Zn(2)-N(6)	106.1 (3)	Cl(2)-Zn(2)-N(7)	113.2 (2)
N(4)-Zn(2)-N(5)	80.7 (3)	N(4)-Zn(2)-N(6)	147.8 (3)
N(4)-Zn(2)-N(7)	95.1 (4)	N(5)-Zn(2)-N(6)	78.9 (4)
N(5)-Zn(2)-N(7)	132.7 (4)	N(6)-Zn(2)-N(7)	81.0 (4)
Zn(2)-N(7)-C(12)	106.8 (7)	Zn(2)-N(7)-C(13)	114.9 (7)
C(12)-N(7)-C(13)	113.2 (8)	N(7)-C(13)-C(14)	114.0 (8)
C(13)-C(14)-N(8)	115.3 (9)	Zn(1)-N(8)-C(14)	112.3 (7)
Zn(1)-N(8)-C(15)	106.2 (7)	C(14)-N(8)-C(15)	112.5 (8)
N(8)-C(15)-C(16)	110.4 (9)	C(15)-C(16)-N(1)	111.1 (9)
Zn(1)-N(1)-C(1)	107.8 (7)	Zn(1)-N(1)-C(16)	108.8 (7)
C(1)-N(1)-C(16)	114.8 (9)	N(1)-C(1)-C(2)	108.1 (9)
C(1)-C(2)-N(2)	108.8 (9)	Zn(1)-N(2)-C(2)	111.4 (7)
Zn(1)-N(2)-C(3)	103.9 (7)	C(2)-N(2)-C(3)	116.0 (9)
N(2)-C(3)-C(4)	107.7 (9)	C(3)-C(4)-N(3)	110.7 (9)
Zn(1)-N(3)-C(4)	107.8 (6)	C(4)-N(3)-C(5)	110.0 (8)
N(3)-C(5)-C(6)	111.9 (9)	C(5)-C(6)-N(4)	114.5 (9)
Zn(2)-N(4)-C(6)	112.3 (6)	Zn(2)-N(4)-C(7)	107.4 (7)
C(6)-N(4)-C(7)	114.9 (9)	N(4)-C(7)-C(8)	111.9 (9)
C(7)-C(8)-N(5)	107.9 (9)	Zn(2)-N(5)-C(8)	104.5 (7)
Zn(2)-N(5)-C(9)	111.8 (7)	C(8)-N(5)-C(9)	114.1 (9)
N(5)-C(9)-C(10)	110.0 (9)	C(9)-C(10)-N(6)	108.0 (9)
Zn(2)-N(6)-C(10)	108.2 (7)	Zn(2)-N(6)-C(11)	109.4 (7)
C(10)-N(6)-C(11)	113.6 (9)	N(6)-C(11)-C(12)	108.7 (9)
C(11)-C(12)-N(7)	110.3 (9)		

than the theoretical ones for sp^3 hybridation (medium value 113.7°). Wide angles are also found between the carbon atoms of the different polyhedra. Bond lengths and angles in the coordination polyhedra are reported in Table IV. The basal planes of the two polyhedra form a dihedral angle of just 20°. If the present structure is compared with that of the analogous binuclear complex[1] $[Zn_2([30]aneN_{10})(NCS)](ClO_4)_3$, it can be seen that in this case the 24-membered macrocycle is much more flattened than the 30-membered macrocycle. This situation reflects the different geometries of both polyhedra: a trigonal bipyramid in the case of $[Zn_2([30]aneN_{10})(NCS)](ClO_4)_3$ and a square pyramid in the present case. The Zn-Zn distance, 5.44 Å, is shorter than that found for the larger macrocycle $[30]aneN_{10}$, 6.40 Å. Several hydrogen bonds are formed between the oxygen atoms of the perchlorate ions and both the hydrogen atoms of the water molecules and the hydrogen atoms linked to the N-H groups. The comparison of the structure of $[Zn_2([24]aneN_8)Cl_2]^{2+}$ with that of the copper(II) complex[7] $[Cu_2([24]aneN_8)Cl_2]^{2+}$ leads to some interesting considerations. In both structures the metal ions are five-coordinated with the same set of donor atoms, four nitrogen atoms and one chloride anion. The coordination polyhedra are in both cases slightly distorted square pyramids. However, besides these similarities, there are also significant differences between the two structures. The larger zinc(II) ions in the $[Zn_2([24]aneN_8)Cl_2]^{2+}$ complex are much more displaced from the least-squares basal plane (0.72 Å) than copper(II) ions (0.34 Å) in the $[Cu_2([24]aneN_8)Cl_2]^{2+}$ complex. As a result, the two complexes have different M-N bond orientations with respect to the basal plane; this situation is also reflected in the different conformations, adopted by the macrocycle in the two complexes and demonstrates the high flexibility of large macrocycle to adapt themselves to metal ion stereochemical requirements.

Acknowledgment. We thank Manuel Castellõ for his contribution to the equilibrium studies.

Registry No. $[Zn_2([24]aneN_8)Cl_2](Cl)ClO_4 \cdot H_2O$, 118977-74-5; $[18]aneN_6$, 296-35-5; $[21]aneN_4$, 296-85-5; $[24]aneN_8$, 297-11-0; $[36]aneN_9$, 24904-24-3.

Supplementary Material Available: Tables of thermal parameters and complete bond lengths and angles and a table containing the initial quantities of reactant, pH range, number of data points for each titration curve, and the computer output of the program SUPERQUAD giving individual data points for emf measurements (52 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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X-ray Crystallographic Characterization of Hydrogen-Bonding Interactions in Piperidinium Chloride and Piperidinium Tetrachloroaluminate: Relevance to the Structure of Room-Temperature Melts

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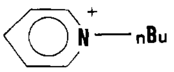
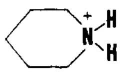
That certain bulky organic cation halides may become room-temperature melts when mixed with aluminum trichloride (in compositions up to 70 mol % $AlCl_3$) has fostered much activity in recent years.[1,2] The prototypal melt, *N*-ethylpyridinium bromide/$AlCl_3$, was first reported in 1951,[3] and the analogous methylpyridinium halides have also been investigated.[4] In more recent years, however, two other bulky organic cations, *N*-butylpyridinium,[1] $Bupy^+$, and 1-methyl-3-ethylimidazolium, Im^+, (and several related alkyl derivatives),[1,2] have been the subject of detailed investigation.



$Bupy^+$

Im^+



Pip^+

Our interest in this field has evolved as a result of the unusual interaction that another class of low melting point salt, $M[Al_2R_6X]$ (M = a wide variety of cations ranging from alkali-metal cation to tetraalkylammonium;: R = Me, Et, ...; X = halide, azide, thiocyanate, or indeed most anions capable of bridging two aluminum atoms), exhibits when contacted with excess aromatic hydrocarbon. Such mixtures do not form classic solutions but form two liquid phases, the denser of which is salt-rich and has been called a "liquid clathrate" by their original discoverer, J. L. Atwood.[5] That room-temperature melts dissolve in benzene and

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Table I. Crystallographic Data for PipCl and Pip[AlCl$_4$]

compd	PipCl	Pip[AlCl$_4$]
chem formula	$C_5H_{12}NCl$	$C_5H_{12}NAlCl_4$
fw	121.6	254.9
space group	*Pbcm* (No. 57)	$P2_1/c$ (No. 14)
a, Å	9.8480 (10)	6.6036 (8)
b, Å	7.4139 (6)	13.5777 (24)
c, Å	9.765 (9)	13.2367 (12)
β, deg		98.808 (9)
V, Å^3	715.3	1172.8
Z	4	4
T, °C	20	20
λ(Mo Kα), Å	0.070930	0.070930
ρ_{calc}, g cm^{-3}	1.129	1.444
μ, cm^{-1}	4.3	10.4
R	0.052	0.077
R_w	0.066	0.090

other aromatic hydrocarbons has already been noted,[2b,6] and even though the original report on room-temperature melts noted that liquid-liquid binary phases exist in certain regions of the phase diagram of *N*-ethylpyridinium bromide/aluminum chloride/toluene, no correlation has yet been drawn between room-temperature melt and liquid clathrate phenomena. We have recently observed that a wide range of low melting point tetrachloroaluminate salts also form "liquid clathrate" like phase systems when contacted with aromatic hydrocarbon compounds.[7] It therefore appears that the physical properties that favor the existence of room-temperature melts also favor "liquid clathrate" behavior.

The structure of both "liquid clathrates"[5] and room-temperature melts[2b,g] has been suggested as being somewhat ordered, but recent X-ray crystallographic evidence (Im$^+$I$^-$) indicates that ion pairing via C–H···X hydrogen bonds could be a factor in the existence of room-temperature melts, at least in the "basic melts" (i.e. AlCl$_3$ mole fraction < 0.5).[2c] A survey of the literature surprisingly reveals that no X-ray structural studies of simple organic cation salts of the tetrachloroaluminate anion have yet been reported. There has therefore been no direct experimental determination of the propensity that tetrachloroaluminate has for being a hydrogen-bond acceptor. This contribution reports the first such structural determination, and the structures of piperidinium tetrachloroaluminate (Pip[AlCl$_4$]) and its analogous chloride salt (PipCl) are reported.

Experimental Section

Synthesis. X-ray-quality crystals of PipCl (rectangular blocks) were obtained via slow evaporation of HCl from the corresponding Pip[(HCl)$_n$Cl]·C$_6$H$_6$ sustained liquid clathrate phase, which was prepared as described elsewhere.[8] Pip[AlCl$_4$] was prepared by adding 1 molar equiv of AlCl$_3$ (Johnson Matthey-Aesar) to a batch of the analogous toluene-based liquid clathrate. HCl was evolved spontaneously as it was displaced by AlCl$_3$, and the resulting Pip[AlCl$_4$]·CH$_3$C$_6$H$_5$ liquid clathrate was cooled at −15 °C for 2 days to obtain X-ray-quality crystals of Pip[AlCl$_4$] (rectangular blocks).

Table II. Atomic Parameters (*x*, *y*, *z*) and B_{iso} Values for PipCl[a]

	x	*y*	*z*	B_{iso},[b] Å^2
Cl1	0.17437 (10)	0.53728 (13)	$^3/_4$	3.94 (5)
N1	0.1367 (4)	0.9572 (5)	$^3/_4$	4.43 (16)
C1	0.1952 (4)	1.0366 (5)	0.6245 (4)	5.79 (16)
C2	0.3459 (5)	1.0102 (6)	0.6248 (7)	7.6 (2)
C3	0.4095 (6)	1.0903 (9)	$^3/_4$	9.0 (5)

[a] Esd's refer to the last digit(s) printed. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Atomic Parameters (*x*, *y*, *z*) and B_{iso} Values for Pip[AlCl$_4$][a]

	x	*y*	*z*	B_{iso},[b] Å^2
Al1	0.5564 (3)	0.99622 (16)	0.72131 (14)	4.29 (9)
Cl1	0.3476 (3)	1.04991 (18)	0.59367 (15)	6.66 (11)
Cl2	0.4701 (4)	1.04226 (19)	0.86020 (15)	7.29 (12)
Cl3	0.8576 (3)	1.04671 (20)	0.71225 (17)	7.44 (12)
Cl4	0.5529 (4)	0.83999 (15)	0.71299 (17)	6.86 (11)
N1	0.8195 (12)	0.3167 (5)	0.9993 (5)	6.7 (4)
C1	0.9486 (17)	0.2855 (7)	0.9236 (6)	7.8 (5)
C2	1.1148 (15)	0.2210 (8)	0.9732 (9)	8.4 (6)
C3	1.0385 (15)	0.1369 (7)	1.0254 (9)	7.9 (5)
C4	0.9064 (16)	0.1711 (8)	1.1018 (7)	8.1 (5)
C5	0.7357 (13)	0.2343 (7)	1.0510 (7)	7.1 (5)

[a] Esd's refer to the last digit(s) printed. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

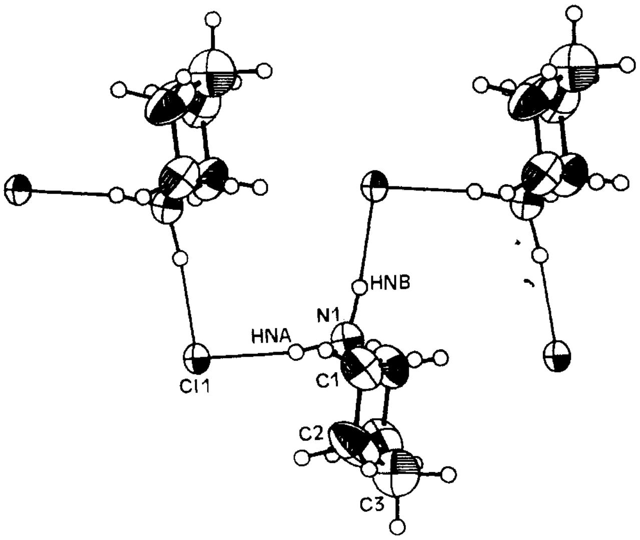

Figure 1. ORTEP plot of PipCl with 50% thermal ellipsoids, showing the polymeric nature of the salt. Important bond distances (Å): Cl1–HNA, 2.067 (10); Cl1–HNB, 2.043 (10); N–C1, 1.480 (4); C1–C2, 1.497 (6); C2–C3, 1.516 (8). Important bond angles (deg): Cl1–HNA–N, 169.9 (2); Cl1–HNB–N, 175.0 (2); HNA–N–HNB, 117.7 (3); all other bond angles are close to expected tetrahedral values.

X-ray Crystallography. Colorless, air-stable but hygroscopic crystals of PipCl and Pip[AlCl$_4$] were mounted and sealed in thin-walled glass capillaries prior to being placed on an Enraf-Nonius CAD-4 diffractometer. Cell dimensions were obtained from 25 reflections with 2θ angles greater than 30° and are found, along with other pertinent data collection parameters, in Table I. The intensities were reduced, and Lorentz and polarization factors were applied. No corrections were made for extinction; however, an empirical absorption correction was applied to Pip[AlCl$_4$] (relative absorption range 0.61–1.22),[9] and a numerical absorption correction was applied to PipCl by utilizing a Gaussian integration method.[10] The structures of PipCl and Pip[AlCl$_4$] were solved

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(1) (a) Tait, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4352 and references therein. (b) Takahashi, S.; Koura, N.; Murase, M.; Ohno, H. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 49. (c) Zawodzinski, T. A.; Kurland, R.; Osteryoung, R. *J. Phys. Chem.* **1987**, *91*, 962.

(2) (a) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263. (b) Fannin, A. A,; King, L. A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem.* **1984**, *88*, 2609. (c) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753. (d) Sun, I.-W.; Ward, E. H.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Inorg. Chem.* **1987**, *26*, 2140. (e) Abdul-Sala, A. K.; Avent, A. G.; Parkington, M. J.; Ryan, T. A.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1643. (f) Zawodzinski, T. A.; Osteryoung, R. A. *Inorg. Chem.* **1987**, *26*, 2920. (g) Dieter, K. M.; Dymek, C. I.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722.

(3) Hurley, F. H.; Wier, T. P. *J. Electrochem. Soc.* **1951**, *98*, 203, 207.

(4) Newman, D. S.; Tillack, R. T.; Morgan, D. P.; Wan, W.-C. *J. Electrochem. Soc.* **1977**, *124*, 856.

(5) (a) Atwood, J. L. *Recent Dev. Sep. Sci.* **1977**, *3*, 195. (b) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 1, Chapter 9, p 375.

(6) Robinson, J.; Bugle, R. C.; Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3776.

(7) Dubois, R. H.; Sturge, K. C.; Zaworotko, M. J. Unpublished results.

(8) Gaudet, M. V.; Peterson, D. C.; Zaworotko, M. J. *J. Inclusion Phenom.* **1988**, *6*, 425.

(9) DIFABS absorption correction was applied: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

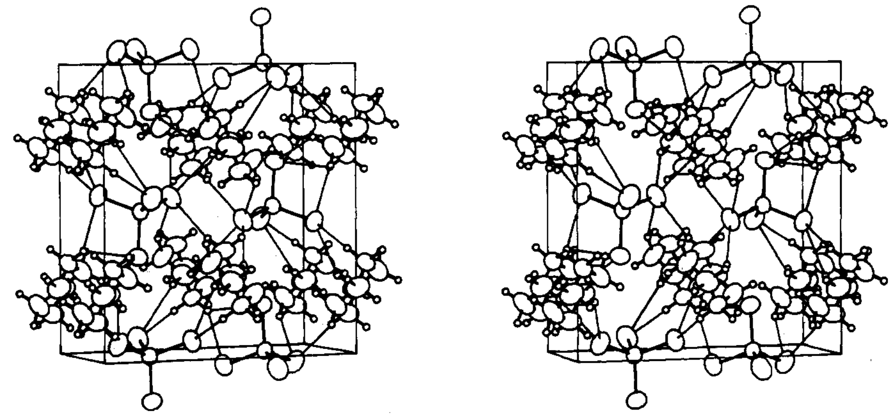

Figure 2. ORTEP stereoscopic cell-packing plot of Pip[$AlCl_4$] with 50% thermal ellipsoids. H···Cl contacts up to 3.15 Å are shown. The closest N···Cl approaches are 3.35 (C3–N1′), 3.43 (C4–N1″), and 3.51 Å (Cl1–N1″). N1′ is related to N1 by the symmetry operation x, $1.5 - y$ $-0.5 + z$; N1″ is related to N1 by the symmetry operation $1 - x$, $0.5 + y$, $1.5 - z$. Important intraionic bond distances are as follows (Å). Cation: N–C1, 1.473 (12); N–C5, 1.463 (12); C1–C2, 1.477 (15); C2–C3, 1.464 (16); C3–C4, 1.507 (17); C4–C5, 1.492 (14). Anion: Al–Cl1, 2.139 (3); Al–Cl2, 2.101 (3); Al–Cl3, 2.125 (3); Al–Cl4, 2.124 (3). Bond angles are close to expected tetrahedral values.

by using the direct methods and structure refinement portions of the NRCVAX Crystal Structure System[10] locally adapted for a Wicat Systems S-1260 computer. For PipCl the atoms N(1), C(3), and Cl(1) were found to lie on a crystallographic mirror plane. Placement and anisotropic refinement of all non-hydrogen atoms enabled location of all hydrogen atoms via difference Fourier map inspection, but hydrogen atoms could not be refined so they were fixed to the appropriate non-hydrogen atom and given arbitrary temperature factors (N–H and C–H distances set to 0.96 Å). No improvement in the R value was obtained via refining the structure in $Pbc2_1$ (hkl and $\bar{h}\bar{k}\bar{l}$ were collected). Weights based on counting statistics were used; the weight modifier, k, in kF_o^2 was 0.001. In the case of Pip[$AlCl_4$] hydrogen atoms were placed in calculated positions with C–H and N–H bond distances also fixed at 0.96 Å and were given temperature factors based upon the value for the appropriate non-hydrogen atom. Weights based on counting statistics were used; the weight modifier, k, in kF_o^2 was 0.0005. In both structures the final values of $R = \sum(F_o - F_c)/\sum F_o$ and $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$ were higher than expected, probably a result of high thermal motion in the cation. Atomic scattering factors were taken from ref 11. Further details of structure refinement parameters are given in Table I.

Results

Final fractional coordinates for non-hydrogen atoms are presented for PipCl and Pip[$AlCl_4$] in Tables II and III, respectively. Examination of the structure of PipCl reveals that strong N–H···Cl hydrogen bonding is exhibited by both nitrogen-bonded hydrogen atoms (H···Cl = 2.043 (10) and 2.067 (10) Å). The N···Cl distances of 3.13 and 3.14 Å are also at the low end of the range expected.[12] The salt adopts a polymeric chain structure (Figure 1). On the other hand, Pip[$AlCl_4$] exhibits minimum N···Cl contacts of >3.35 Å, beyond the 3.30 Å that is considered the upper range for hydrogen bonding to be present in N–H···Cl systems.[13] An ORTEP[14] packing diagram (Figure 2) illustrates the structure of Pip[$AlCl_4$], showing that interionic contacts are weak and random.

Discussion

Pip^+ was chosen for this study, as its low melting tetrachloroaluminate salt also exhibits "liquid clathrate" behavior (Pip^+, as either its tetrachloroaluminate or heptachlorodialuminate salt, dissolves in benzene to give "liquid clathrate" phases[7]). The clear inference of this comparative study is that the tetrachloroaluminate anion is at best a weak hydrogen-bond acceptor, a result that might be expected in the context of the relatively low net charges that have been calculated for the chloride groups in tetrachloroaluminate.[15] It would be natural to assume that the heptachlorodialuminate anion, salts of which typically form liquid clathrates and room-temperature melts even more readily than the tetrachloroaluminate anion, would be even less likely to become involved in hydrogen bonding, as its negative charge would be even more diffusely spread. We are therefore forced to ask if the driving force for the low melting point and high hydrocarbon solubility of chloroaluminate salts is a lack of significant cation–anion interionic attractions. Indeed, if one could even treat such salts as possessing interionic attractions of the low magnitute expected for the intermolecular attractions in nonpolar covalent compounds, then the low melting point of many chloroaluminate salts would become quite predictable (i.e., mass becomes the important factor in predicting the melting point). Basic melts could then be regarded simply as solutions of the appropriate chloride salt in the appropriate tetrachloroaluminate melt, and "liquid clathrates", as saturated solutions of hydrocarbon in melt.

The above rationale does not preclude the existence of ordering in the liquid phase but does suggest that any such ordering would not involve significant cation–anion attractions in acidic melts or "liquid clathrate" phases. Interionic attractions in basic melts would, as already suggested in the literature, therefore involve cation–chloride attractions.

We are currently in the process of structurally characterizing a wider range tetrachloroaluminate salts and finding that absence of significant interionic attractions in the solid state is a common feature of all structures we have so far determined crystallographically.[16]

Acknowledgment. We are indebted to the NSERC (operating and research development grants, M.J.Z.; infrastructure, P.S.W.) for financial support of this work.

Supplementary Material Available: Tables listing full crystallographic data collection and structure refinement parameters, hydrogen atom coordinates, and anisotropic thermal parameters for PipCl and Pip[$AlCl_4$] (4 pages); tables of calculated and observed structure factors for PipCl and Pip[$AlCl_4$] (11 pages). Ordering information is given on any current masthead page.

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(10) Gabe, E. J.; Lee, F. L.; LePage, Y. The NRCVAX Crystal Structure System. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(12) Vincent, B. R. Ph.D. Thesis, Dalhouise University, 1988.

(13) For A–H···B systems a hydrogen bond is assumed to be present if the A···B distance is less than the sum of the van der Waals radii (i.e., 3.30 Å for N and Cl): Joesten, M. D.; Schaad, L. J. In *Hydrogen Bonding*; Marcel Dekker, Inc.: New York, 1974; p 35. Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

(14) Johnson, C. K. "ORTEP"; Report ORNL-3794, revised; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(15) Based upon Al–Cl bond distances of 2.1694 Å, ab initio calculations suggest that each chloride has a net charge of −0.471: Choi, S. C.; Boyd, R. J.; Knop, O. *Can. J. Chem.* **1987**, *65*, 1109. It must also be noted that the distances observed in $Pip^+AlCl_4^-$ (average 2.12 Å) are significantly shorter, implying that Cl···Al π-bonding could be present. This would of course result in even lower net charges on each chloride.

(16) The structures of [pyridinium][$AlCl_4$] and [N-ethylpyridinium][$AlCl_4$], the prototypal melt, reveal that no close cation–anion approaches occur: Zaworotko, M. J.; Sturge, K. C.; Linden, A.; Cameron, T. S. *Acta Crystallogr.*, in press.