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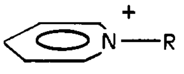
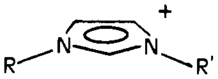
Communications

Complex Hydrogen-Bonded Cations. X-ray Crystal Structure of $[((C_6H_5CH_2)NH_3)_4Cl][AlCl_4]_3$ and Its Relevance to the Structure of Basic Chloroaluminate Room-Temperature Melts

The phenomenon of chloroaluminate-based room-temperature melts continues to be a subject of interest, with activity having tended to focus upon two classes of cation: (i) alkylpyridiniums (1^+),[1] which include the prototypal 1-ethylpyridinium melts;[2,3]



1^+



2^+

(ii) 1,3-dialkylimidazoliums (2^+), which tend to possess a wider electrochemical window and are liquid over a wider range of composition.[4] A topic of particular current interest concerns to what degree, if any, ordering exists in the liquid phase of room-temperature melts. Spectroscopic[5,6] and theoretical[7] evidence has been invoked to suggest some degree of ordering in melts based upon 2^+, and a recent NMR study of 1-butylpyridinium chloroaluminate melts suggests that basic (mole fraction of $AlCl_3 < 0.5$) melts contain cation–anion interactions that affect the alkyl chain.[8] Unfortunately direct crystallographic evidence has not been forthcoming, the only crystallographic study of relevance being the room-temperature study conducted upon the model salt 2^+I^-, which yielded evidence of ion pairing via weak C–H···I⁻ hydrogen bonding.[9]

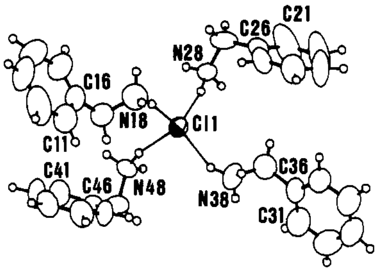
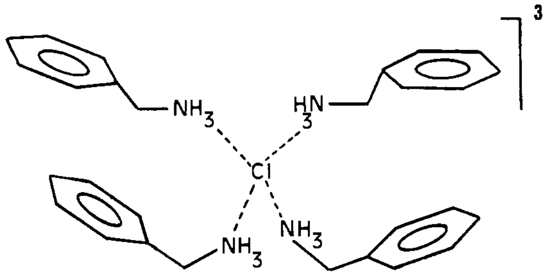


Figure 1. Perspective view of the $[((C_6H_5CH_2)NH_3)_4Cl]^{3+}$ complex cation (3^{3+}). Thermal ellipsoids are drawn at 50% probability level. N···Cl contacts range from 3.14 to 3.28 Å: Cl(4)–N(18), 3.142 (7) Å; Cl(4)–N(28), 3.284 (6) Å; Cl(4)–N(38), 3.141 (7) Å; Cl(4)–N(48), 3.189 (6) Å.

A feature of room-temperature melts that they have in common with a wide range of organic cation chloroaluminate salts is their high hydrocarbon solubility.[2,3,5,10,11] This is a property we have recently utilized to crystallize and crystallographically characterize a range of tetrachloroaluminate salts, including the prototypal salt [1-ethylpyridinium]$[AlCl_4]$.[12,13] These studies indicate that the tetrachloroaluminate anion is at best a very weak hydrogen bond acceptor. The implication is therefore that ordering via hydrogen bonding is unlikely in room-temperature melts, at least in the acidic variety (i.e. $AlCl_3$ mole fraction > 0.5). There has been no solid-state investigation of models for the basic melts, however, and this report concerns such a study in that we have isolated in the solid state and for the first time crystallographically characterized a mixed chloride/tetrachloroaluminate salt, the title compound $[((C_6H_5CH_2)NH_3)_4Cl][AlCl_4]_3$, $3[AlCl_4]_3$.



3^{3+}

Synthesis. A 0.82-mL (7.5-mmol) aliquot of benzylamine (Aldrich) was dissolved in freshly distilled toluene and converted to the corresponding hydrochloride via slow bubbling of dry HCl (Matheson) for 15 min. To the resulting suspension was added 1.00 g (7.50 mmol) of $AlCl_3$ (Johnson Matthey, Aesar), which dissolved within 5 min to generate a liquid–liquid layering effect characteristic of "liquid clathrates".[14] The lower phase was

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(14) A wide variety of complex alkyl aluminate salts has been shown to exhibit ambient temperature liquid–liquid layering when contacted with benzene or similar hydrocarbon compounds. Typically a nonstoichiometric yet fixed amount of hydrocarbon is found in the denser salt-rich or "liquid clathrate" phase: Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Academic Press: New York 1980; Vol. 1, Chapter 9.

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salt-rich and was shown via ^{1}H NMR spectroscopy to contain 3.2 mol of toluene/mol of benzylammonium cation. Rectangular block, colorless crystals of the title compound suitable for crystallographic analysis[15] were obtained by storing the "liquid clathrate" at 0 °C for 2 days. The reaction may also be conducted in benzene or mesitylene, which form "liquid clathrates" with compositions of 5.72 and 1.23 mol of aromatic/mol of cation, respectively.

The salient feature of the structure of $\mathbf{3}[AlCl_4]_3$ is the manner in which the benzylammonium cations dispose themselves to hydrogen bond to the chloride anion rather than the tetrachloroaluminate anions, thereby forming the complex tricationic species $\mathbf{3}^{3+}$. The chloride anion is therefore demonstrably displaying its ability to act as a stronger Lewis base than the tetrachloroaluminate anion. As can be observed from the ORTEP[18] view of $\mathbf{3}^{3+}$ presented in Figure 1, the benzylammonium cations are hydrogen bonded via one N–H hydrogen atom to the chloride anion. The resulting geometry is approximately tetrahedral with N-Cl(4)-N angles ranging from 97.4 to 118.3° and the N–H···Cl contacts are within the 3.30 Å expected for N–H···Cl hydrogen bonding.[19] The contacts are at the long end of the range previously observed, although most earlier structural characterizations were effected upon systems that contain only one or two hydrogen bonds to each chloride anion.[20] Perhaps the most direct analogy may be drawn with polyammonium macrocycles which are able to coordinate halides in tetrahedral (F^-) or octahedral fashion (Cl^-).[21]

The tetrachloroaluminate anions show no indication of order in the manner they dispose themselves around the complex trication. The interionic contacts to $\mathbf{3}^{3+}$ range from 3.28 Å (N(38)···Cl(32)) upward, with only two other contacts within 3.45 Å, N(28)···Cl(24) and N(18)···Cl(33) at 3.36 and 3.41 Å, respectively. The 3.28-Å contact is close to the longest N···Cl distance within $\mathbf{3}^{3+}$; however the hydrogen atom in $\mathbf{3}^{3+}$, H(28C), is located only 2.35 Å from the chloride anion (N–H···Cl angle = 152°) whereas H(38B) is found 2.52 Å from the tetrachloroaluminate anion (N–H···Cl angle = 136°). The bond distances (Al–Cl = 2.121 Å average) and angles (Cl–Al–Cl = 107.1 (1)–112.7 (2)°) within the tetrachloroaluminate moieties are consistent with the expected values. Bond distances and angles within the benzylammonium moieties are also within expected ranges.

The ability of the chloride ion to dominate as a hydrogen-bond acceptor in the presence of tetrachloroaluminate anions is expected and complements well the spectroscopic studies hitherto conducted upon molten salts containing $\mathbf{1}^+$ and $\mathbf{2}^+$. A surprising feature of the present investigation, however, is that the complex trication is stable even in the presence of a slight excess of aluminum trichloride (the reaction was effected with a 1:1 molar ratio of benzylammonium chloride and aluminum trichloride). Such behavior is atypical as it occurs in neither classical room-temperature melts[22,23] nor any of the other organic cation tetrachloroaluminates[12,13] we have synthesized in a manner similar to that utilized for the title compound. The latter studies were conducted upon tetrachloroaluminate salts that contain sterically accessible N–H bonds, yet they exhibited no tendency to crystallize as complex cations.[12,13] A possible explanation could be related to the observation that benzylammonium chloride does not readily dissolve in aromatic hydrocarbon solvents when contacted with excess HCl. The other cations we studied do however dissolve quickly to produce complex hydrogen halide anion sustained "liquid clathrate" ionic phases that readily dissolve aluminum trichloride.[24] The existence of the complex trication could therefore be a simple manifestation of any or all of the following: (i) the relatively low solubility of aluminum trichloride in toluene versus a "liquid clathrate" phase; (ii) the higher solubility of $Al_2Cl_7^-$ salts in toluene; (iii) kinetic stabilization of the complex cation.[25]

Finally, it is interesting to note that the prototypal melt, 1-ethylpyridinium bromide/$AlCl_3$, exhibits two eutectics as the proportion of $AlCl_3$ is varied.[2] One eutectic corresponds to a 1:2 mol ratio basic melt, and could therefore contain a complex cation with two *N*-ethylpyridinium cations associated with a chloride anion and countered by $AlCl_2Br_2^-$.

Further investigations are currently under way with the title cation and other bulky organic cations in an attempt to further rationalize our observations, in particular the unusual liquid–liquid phase phenomena exhibited by the salts in the presence of aromatic hydrocarbon compounds.

Acknowledgment. We thank the NSERC (operating (M.J.Z.) and infrastructure (P.S.W.) grants) and Imperial Oil Limited (University Research Grant (M.J.Z.)) for financial support of this work.

Supplementary Material Available: Tables SI–SV, listing details of structure solution and refinement, coordinates of non-hydrogen atoms, bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom coordinates and isotropic thermal parameters (7 pages); Table SVI, listing observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

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(15) Enraf-Nonius CAD-4 (graphite-monochromated Mo Kα radiation); $C_{28}H_{40}N_4Al_3Cl_{13}$, $M = 974.14$, triclinic, $P\bar{1}$, $a = 10.1333$ (11) Å, $b = 16.2286$ (18) Å, $c = 16.5847$ (22) Å, $\alpha = 66.018$ (9)°, $\beta = 79.152$ (10)°, $\gamma = 73.671$ (9)°, $V = 2382.87$ Å^3, $D_c = 1.455$ g cm^{-3}, $F(000) = 992$, 22 °C, Mo Kα ($\lambda = 0.709\,30$ Å), $\mu = 8.4$ cm^{-1}. The structure was solved via MULTAN80[16] and refined by using the NRCVAX system.[17] Final values of $R = \sum|F_o| - |F_c|/\sum|F_o| = 0.060$ and $R_w = [\sum(w(F_o - F_c)^2)/\sum wF_o^2]^{1/2} = 0.090$ were obtained for 3869 observed ($I > 2.5\sigma(I)$) reflections. Hydrogen atoms were placed in calculated positions and refined with isotropic temperature factors during the final stages of refinement. Weights based on counting statistics were used, the weight modifier k in kF_o^2 being 0.005. No corrections were made for extinction or absorption. Atomic scattering factors and corrections for anomalous dispersion for Al, Cl, C, and N were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England; 1974; distributor D. Reidel, Dordrecht, The Netherlands.

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(25) As indicated by a reviewer the simple $[(C_6H_5CH_2)NH_3][AlCl_4]$ salt should be thermodynamically favored over the title compound.