purities in every solvent we have used. This suggests that complexation of $[(TPP)Fe]_2N$ with a variety of Lewis bases can be used to probe the coordination chemistry of Fe(IV). We also have evidence for interaction of a second ligand with the dimer at very high concentrations of pyridine. The attachment of a second ligand should reestablish symmetry in the system, giving access to other features of the molecular orbital ordering in these binuclear systems.

In summary, this work has unequivocally demonstrated that $[(TPP)Fe]_2N$ has an A_1 ground state with two equivalent, low-spin iron centers. Complexation by pyridine or other Lewis bases yields an unsymmetrically substituted dimer, which is further distorted below axial symmetry. The adduct remains low spin with the unpaired electron assigned to the Fe(III) center in a $d_{x^2-y^2}$ orbital.

Registry No. $[(TPP)Fe]_2N$, 59114-43-1; pyridine, 110-86-1.

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Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis

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Fused salts that are liquid at room temperature are an unconventional but interesting class of aprotic solvents for studying the chemistry of inorganic, organometallic, and organic solutes. In addition, these ionic liquids are potentially useful as electrolytes in batteries, photoelectrochemical cells, and electroplating. In recent years some mixtures of aluminum chloride and 1-alkylpyridinium chlorides have been reported to be molten at or near room temperature. Melts of this type may be prepared easily,[1] and one example (aluminum chloride/1-butylpyridinium chloride) has been extensively studied.[2-4] One very attractive feature of this system is the wide range of Lewis acidity attainable, as expressed by chloride concentration.[5]

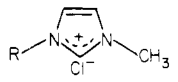
Gale and Osteryoung pointed out that potential measurements at an aluminum electrode in basic mixtures of $AlCl_3$ and 1-butylpyridinium chloride (i.e., less than 1:1 mole ratio) were unreliable due to apparent reaction of aluminum with the melt.[5] They later showed that the 1-butylpyridinium cation was reduced by aluminum in that melt.[6] This reduction of the cation foreshortens the electrochemical window of the basic chloroaluminate melts. The term electrochemical window is used here as the difference between the anodic and cathodic decomposition potentials, in volts, for the melt. Also, none of the 1-alkylpyridinium chloroaluminate melts are liquid at room temperature over the entire available acidity range. We report here the preparation and properties of a new chloroaluminate molten salt that is also liquid at room temperature but has improved electrochemical and physical properties.

While many organic cations would probably have sufficient size to produce low melting chloroaluminate salts, the cations must also have reduction potentials more negative than Al(III) in the melts in order to be unreactive toward Al and to improve the electrochemical window. Using Dewar's MNDO technique,[7] we calculated the electron affinities of a variety of organic cations as a screen for species that would be less easily reduced than 1-alkylpyridinium ions. The 1,3-dialkylimidazolium salts were revealed as attractive candidates since their reduction potentials were predicted to be about 0.8 V lower than the 1-alkylpyridinium salts, and they could be prepared readily from commercially available starting materials. A homologous series of 1,3-dialkylimidazolium chlorides (compounds I–V) were prepared and properties of mixtures of these salts with aluminum chloride were studied.[8] The chloroaluminate melt prepared from one of the chlorides, 1-methyl-3-ethylimidazolium chloride (MeEtImCl), had the most favorable physical and electrochemical properties and was one of the easiest to prepare. The properties that we report here for the melt indicate that it is superior to previous melts in terms of liquidus temperatures, electrochemical window, and reactivity with aluminum. It is similar to the earlier alkylpyridinium chloroaluminates in its conductivity, viscosity, wide range of Lewis acidity, and its ability to solvate both organic, organometallic, and inorganic compounds. For example, thianthrene, ferrocene, $CuCl_2$, and $TiCl_4$ are all soluble. The methylethylimidazolium chloroaluminate melts are miscible with benzene and toluene to about 50% (v/v) and miscible in all proportions with acetonitrile. The new melts and mixtures of them with benzene are suitable solvents for spectroscopic measurements. The 66 mol % melt and melt diluted with benzene (50% v/v) are both useful to ca. 320 nm. The 40 mol % $AlCl_3$ composition and that diluted with similar amounts of benzene are suitable for use to about 280 nm. The $MeEtImCl/AlCl_3$ mixtures are liquid at 25 °C over the range of composition from 40 to 67 mol % $AlCl_3$. The liquidus temperatures for 50 and 67 mol % melts were 8 and −98 °C, respectively, although the lower temperature may be a glass transition of a super-cooled liquid. The low melting point of

Table I. Conductivities of Methylethylimidazolium Chloroaluminate Melts

compn, mol % $AlCl_3$	κ,[a] Ω^{-1} cm^{-1}	temp, °C	compn, mol % $AlCl_3$	κ,[a] Ω^{-1} cm^{-1}	temp, °C
44	0.0117	29.7	67	0.0154	32.2
50	0.0227	30.9			

[a] Specific conductivity.



I, R = methyl
II, R = ethyl
III, R = propyl
IV, R = butyl

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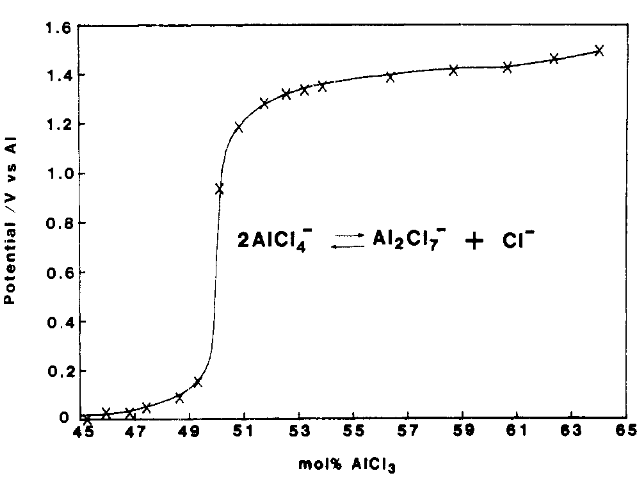

Figure 1. Potentiometric titration of the methylethylimidazolium chloroaluminate melt. Potentials were measured at an Al electrode vs. an Al reference electrode immersed in the 44 mol % melt.

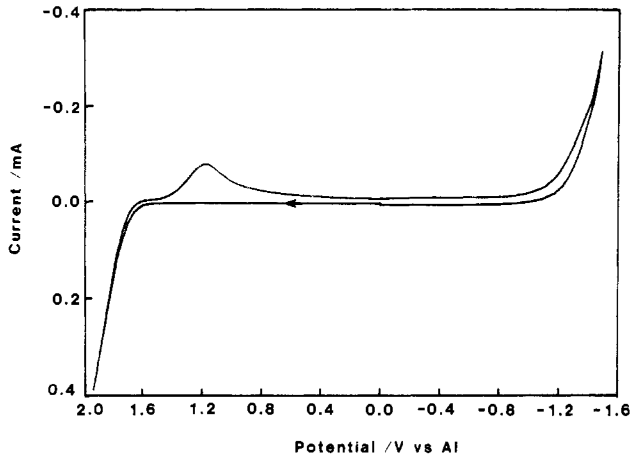

Figure 2. Cyclic voltammetry of 40 mol % methylethylimidazolium chloroaluminate melt.

the $AlCl_3$-rich composition is unprecedented for molten salts. The specific conductivities of several compositions of the $MeEtImCl/AlCl_3$ melt are shown in Table I. The values are similar to those reported for the 1-alkylpyridinium chloride/$AlCl_3$ melts at 30 °C.[2]

The behavior of the basic (MeEtImCl-rich) melt toward reduction by Al is significantly different from the earlier room temperature melts. An Al wire immersed in the 40 mol % melt for several days at 110 °C showed no apparent reaction. Some reaction on the surface of the aluminum probably occurs, since a drift in potential of several millivolts is observed with respect to an inert electrode. No drift is observed at aluminum in acidic compositions. A similar experiment using an alkylpyridinium chloride/$AlCl_3$ melt under milder conditions resulted in immediate visible reduction of the organic cation. The electrochemical window was determined by cyclic voltammetry to be wider than the alkylpyridinium melts, as expected. Surprisingly, the cathodic limit of the basic (chloride rich) melt is not Al(III) reduction but appears to be an irreversible reduction associated with the organic cation. Figure 2 shows a cyclic voltammogram that demonstrates the electrochemical window of a basic melt. In the acidic melts Al is deposited at the cathodic limit.

The Lewis acidity of these melts is determined by chloride activity, as in other chloroaluminate melts[5,9] according to eq 1. A preliminary equilibrium constant of 2.0×10^{-19} was determined from the potentiometric titration data for the $MeEtImCl/AlCl_3$ melt shown in Figure 1. This value implies a range of acidity for the new melt at least as broad as the alkylpyridinium melts and much broader than the alkali halide chloroaluminate melts.

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

Studies are continuing on the physical and chemical behavior of this promising new electrolyte.

Experimental Section

All experiments involving moisture-sensitive materials were performed in a Vacuum Atmospheres Corp. glovebox containing a dry-argon atmosphere. The moisture sensitivity of the aluminum chloride based melts was not determined quantitatively but was assumed to be similar to $AlCl_3$ itself. The 1-methylimidazole, chloropropane, and chlorobutane were obtained from the Aldrich Chemical Co., and the 1-methylimidazole was distilled before use. The chloromethane and chloroethane were obtained from Linde Specialty Gases. Elemental analyses were performed by Galbraith Laboratories. Melting points are uncorrected. Liquidus temperatures were measured with a Perkin-Elmer Model DSC-2 differential scanning calorimeter. Specific conductivities were obtained with an AC impedance bridge as described previously.[2] UV-vis cutoffs were estimated with quartz cuvettes in a Cary 15 spectrophotometer. Electrochemical experiments were performed in the melts using methods reported in previous studies.[3,4] All potentials are referenced to an aluminum wire immersed in 44 mol % $AlCl_3$ melt and separated from the bulk melt via a fine porosity frit. Reduction half-wave potentials for the imidazolium chloride salts were obtained at a rotating glassy carbon electrode in DMF containing 0.1 M tetra-*n*-butylammonium perchlorate at 25 °C. Calculation of *K* for eq 1 was performed similarly to that described by Gale and Osteryoung.[5]

1,2-Dimethylimidazolium (I) and 1-methyl-3-ethylimidazolium (II) chlorides were prepared by condensing chloromethane or chloroethane (fourfold excess) into a 250-mL glass pressure vessel containing 1-methylimidazole. The mixture was heated at 75 °C for 2 days with magnetic stirring. The excess chloroalkane was allowed to boil off through a drying tube, resulting in a slightly off-white solid product that showed no starting material by NMR spectroscopy. The product was recrystallized from acetonitrile/ethyl acetate. 1,2-Dimethylimidazolium chloride: mp 124.5–128 °C. Anal. Calcd for $C_5H_9N_2Cl{\cdot}0.3H_2O$: C, 43.23; H, 7.04; N, 20.17; Cl, 25.53; O, 3.17. Found: C, 42.82; H, 7.32; N, 20.13; Cl, 26.01; O, 3.72. 1-Methyl-3-ethylimidazolium chloride: mp 82–87 °C. Anal. Calcd for $C_6H_{11}N_2Cl{\cdot}0.2H_2O$: C, 47.97; H, 7.65; N, 18.65; Cl, 23.60; O, 2.13. Found: C, 48.18; H, 7.80; N, 18.66; Cl, 23.52; O, 1.84.

The 3-propyl (III) and 3-butyl (IV) homologues were synthesized by refluxing the 1-methylimidazole with a large excess of the appropriate chloroalkane for 24 h. The excess chloroalkane was removed by evaporation and the crude product recrystallized from acetonitrile/ethyl acetate. 1-Methyl-3-propylimidazolium chloride: mp 58–66 °C. Anal. Calcd for $C_7H_{13}N_2Cl{\cdot}0.3H_2O$: C, 50.63; H, 8.26; N, 16.87; Cl, 21.35; O, 2.89. Found: C, 50.70; H, 8.45; N, 17.08; Cl, 21.55; O, 2.22. 1-Methyl-3-butylimidazolium chloride: mp 65–69 °C. Anal. Calcd for $C_8H_{15}N_2Cl{\cdot}0.1H_2O$: C, 54.45; H, 8.68; N, 15.87; Cl, 20.09; O, 0.91. Found: C, 53.94; H, 8.90; N, 16.03; Cl, 20.52; O, 0.61.

Infrared and NMR spectra and details of the syntheses have been reported separately.[10]

The chloroaluminate melts were prepared by mixing appropriate amounts of aluminum chloride with the 1-methyl-3-alkylimidazolium chloride while stirring under a dry-argon atmosphere. The material obtained was a clear colorless liquid.

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Registry No. I, 79917-88-7; II, 65039-09-0; III, 79917-89-8; IV, 79917-90-1; $AlCl_3$, 7446-70-0.

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