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A Room-Temperature Molten Salt Prepared from $AuCl_3$ and 1-Ethyl-3-methylimidazolium Chloride

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Introduction

Room-temperature molten salts, also known as ionic liquids, have been studied for a number of years but have recently begun to receive greater attention because of their possible uses, especially with respect to green chemistry.[1] One of the primary families of room-temperature molten salts (RTMS) is based on mixtures of aluminum chloride and dialkylimidazolium chloride, with the most widely studied mixture using 1-ethyl-3-methylimidazolium chloride (EMIC).[2] These mixtures have a wide range of compositions over which they are liquid at room temperature. By variation of the ratio of EMIC to $AlCl_3$, the relative Lewis acidity and the viscosity of the melt may be altered. In systems where the ratio of EMIC to $AlCl_3$ is greater than 1, the primary anions are Cl^- and $AlCl_4^-$ and these are basic melts in the Lewis sense. Where this ratio is less than 1, there is an excess of $AlCl_3$, the primary anions are $AlCl_4^-$ and $Al_2Cl_7^-$, and these are acidic melts. These systems have been characterized extensively by NMR,[3−7] Raman scattering,[8] and electrochemical[9−12] means. In addition, molecular modeling has been used to help predict the structures of the components in the melt.[13−15] To expand our knowledge of RTMS chemistry, and because R.G.F. has a previous interest in the chemistry of gold, we decided to determine whether similar salts could be prepared by replacing $AlCl_3$ with $AuCl_3$. There are a limited number of reports of ionic liquids based on metals other than aluminum.[16,17] In this note, we report that such ionic liquids have been prepared by directly mixing $AuCl_3$ and 1-ethyl-3-methylimidazolium chloride (EMIC) under an inert atmosphere. Raman spectra indicate that the primary gold species is $AuCl_4^-$, and while ab initio calculations predict that $[(AuCl_3)_2(\mu\text{-}Cl)]$ should be stable, we have no experimental evidence for its formation in a room-temperature melt.

Experimental Section

Materials. $AuCl_3$ was obtained from Aldrich and used without further purification. 1-Ethyl-3-methylimidazolium chloride was purchased from Aldrich and purified as previously reported.[18] NMR solvents were purchased from Cambridge Isotope Laboratories.

$AuCl_3$/EMIC mixtures, over a range compositions and with total mass between 300 and 600 mg, were prepared in a nitrogen atmosphere glovebox. For most samples used, $AuCl_3$ was added slowly, with stirring, to a small glass vial containing EMIC. Samples that were not liquid at room temperature were heated with stirring until they liquified and allowed to cool to room temperature.

Raman Scattering. Laser excitation was provided by a HeNe laser (Research ElectroOptics) and passed through a line filter and a cylindrical lens and was focused onto an NMR tube containing the sample. The laser power at the sample was approximately 15 mW. Scattered light was collected at about 30° from the excitation beam, collimated, passed through a superholographic notch filter (Kaiser HSNF-633-1.0), and focused onto a Spex270M monochromator. The light was dispersed via an 1800 line/mm grating and detected via a liquid nitrogen cooled CCD. Spectral positions were calibrated by reference to spectra of $CDCl_3$ that were collected either immediately before or immediately after the molten salt sample.

NMR. NMR spectra of the neat melts were collected on a Varian XL-200 spectrometer. Lock signals were obtained by inserting a 1-mm-i.d. sealed tube containing deuterated benzene into the NMR tube containing our samples. All proton and carbon shifts are referenced to benzene-d_6.

Computational Method. Ab initio Hartree−Fock calculations were performed to predict the structures, energies, and vibrational (Raman) frequencies of gold(III) chloride complexes. For gold atoms, the calculations implemented the Los Alamos Hay−Wadt [Kr]4d104f14 relativistic effective core potential (ECP) and associated double-ζ basis set.[19] The Los Alamos Hay−Wadt nonrelativistic neon core ECP and associated double-ζ basis set[20] were assigned to each chlorine atom.

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For comparison, the analogous Al species were computed using the same type of basis sets as used for the Au computations. All computations employed either the Gaussian 94D[21] or Gaussian 98W[22] electronic structure packages.

Results

When $AuCl_3$ and EMIC were mixed in a 1/2 (mole/mole) ratio, a liquid formed that was deep orange. Besides color, the first obvious difference between the salts prepared from $AuCl_3$ and those prepared from $AlCl_3$ is the limited, and different, composition range over which the mixture is a liquid at room temperature. While the $AlCl_3$/EMIC system is liquid at room temperature over the range 2/1 to 1/2 $AlCl_3$/EMIC, the $AuCl_3$/EMIC system is only a room-temperature liquid from 1/2 to nearly 1/3 $AuCl_3$/EMIC (this mixture is a cloudy suspension). The melting points for the 1/1, 1/1.5, and 1/1.75 $AuCl_3$/EMIC were 70, 55, and 50 °C, respectively. That is, we were only able to produce ionic liquids with Lewis basic character. Those samples that contained less than 1 part of $AuCl_3$ to 2 parts of EMIC were not homogeneous liquids at room temperature. We have not been able to prepare any homogeneous samples with an excess of $AuCl_3$ under conditions where we were confident in the integrity of the sample.

A Hartree−Fock geometry optimization of $AuCl_4^-$ found the most stable structure to be a square planar complex with Au−Cl bond lengths of 2.402 Å. This is in good agreement with the structure optimized by Schwerdtfeger.[23] The Hartree−Fock optimization of $AuCl_3$ found an essentially T-shaped C_{2v} structure. Table 1 lists both calculated and experimental Raman frequencies for Au- and Al-containing species. For $AuCl_4^-$, calculations give three Raman-active modes: the totally symmetric a_{1g} mode at 321 cm^{-1}, a b_{1g} mode at 305 cm^{-1}, and a b_{2g} mode at 154 cm^{-1}. The calculated intensity of the a_{1g} mode is approximately twice the intensity of the b_{1g} mode. The experimentally determined Raman spectrum of the low-wavenumber range of the ionic liquid with 1 part of $AuCl_3$ to 2 parts of imidazolium is shown in Figure 1. The primary features are two overlapping bands with maxima at 328 and 352 cm^{-1}, respectively, and a feature at 170 cm^{-1}. The first two are the b_{1g} and a_{1g} vibrations for this species, respectively, while the 170 cm^{-1} feature is the b_{2g} vibration. These features are identical to those seen in our solution spectrum of $HAuCl_4$ and within experimental error of those previously reported.[24] The calculated values are consistently lower in energy than those observed experimentally. However, using the Los Alamos basis sets appears to underestimate the Raman frequencies for the Al species both by comparison with experiment and with calculations done at the 6-31G* level. Thus, our calculations for $AuCl_4^-$ and $Au_2Cl_7^-$ do not appear unreasonable. This and, more importantly, the agreement with experimental data from the literature indicate that the primary gold-containing species present in the melt is $AuCl_4^-$.

Table 1. Experimental and Calculated Raman Frequencies for Chloroaurates and Chloroaluminates[a]

	calcd features		
species	freq (intens)[b]	freq[b]	measd
$AlCl_4^-$	110.0 (5.5)	121.1	
	175 (12.3)	187.6	180[c]
	326 (9.1)	353.1	347
	496 (1.5)	511.4	504
$Al_2Cl_7^-$	2.3 (0.03)	15.5	
	11.8 (0.00)	17.3	
	24.0 (0.13)	39.9	
	80.7 (2.3)	90.4	
	81.1 (2.9)	90.6	
	89.1 (2.1)	98.0	
	112.5 (0.5)	125.0	
	130.9 (1.3)	151.3	
	151.2 (6.6)	162.9	157[c]
	153.4 (6.6)	168.2	
	173.1 (1.7)	182.9	
	180.5 (1.6)	196.2	
	183.5 (1.1)	206.8	
	278.1 (11.8)	310.5	310
	333.0 (1.8)	332.7	
	375.3 (0.1)	393.2	
	411.3 (8.4)	441.6	432
	532.7 (2.3)	553.4	
	533.8 (2.4)	557.7	566
	543.6 (0.3)	572.4	
	544.3 (0.9)	572.7	
$AuCl_4^-$	154[a] (28.6)		170
	305 (64.9)		328
	321 (134.8)		352
$Au_2Cl_7^-$	14.6 (2.7)		
	27.4 (3.4)		
	38.4 (12.3)		
	65.1 (1.7)		
	68.3 (4.3)		
	81.7 (6.4)		
	108.2 (1.0)		
	117.5 (1.3)		
	140.2 (0.6)		
	144.9 (1.1)		
	148.6 (8.2)		
	149.7 (25.8)		
	151.1 (10.2)		
	253.1 (25.5)		
	282.9 (2.7)		
	318.4 (124.2)		
	320.1 (74.0)		
	356.0 (42.8)		
	357.9 (5.8)		
	358.6 (1.4)		
	362.1 (127.8)		

[a] The calculated frequencies for Al are reported as frequency in cm^{-1} (intensity) and 6-31G* frequency in cm^{-1}. The calculated frequencies for Au are reported as frequency in cm^{-1} (intensity). [b] Using Los Alamos basis sets (see Experimental Section). [c] Taken from ref 14.

In the same region of the spectrum, the $AlCl_3$/EMIC melt shows bands at 310 and 347 cm^{-1} when excess $AlCl_3$ is present. The feature at 347 cm^{-1} has been attributed to the a_1 vibration of the tetrahedral $AlCl_4^-$, while the feature at 310 cm^{-1} is due to the presence of $Al_2Cl_7^-$. In the aluminum case, there is an increase in the ratio of the 310/347 bands as the amount of $AlCl_3$ exceeds that of EMIC. In our case, the Hartree−Fock geometry optimization of the analogous dinuclear gold complex finds a structure in which two square planar gold chloride complexes are joined by a bridging chlorine atom (Figure 2). The halves of the molecule are tilted out of the Au−Cl−Au plane, resulting in a propeller-shaped molecule with C_2 symmetry. This geometry is in contrast to that of the aluminum system, which is predicted to consist of two tetrahedra with a shared central, bridging chlorine.

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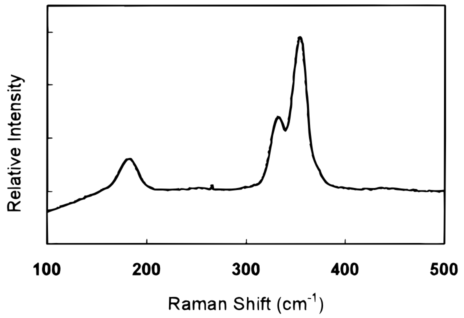

Figure 1. Low-energy Raman spectrum of $AuCl_3$/EMIC ionic liquid. This sample was prepared to have a 1/2 $AuCl_3$/EMIC (mole/mole) ratio.

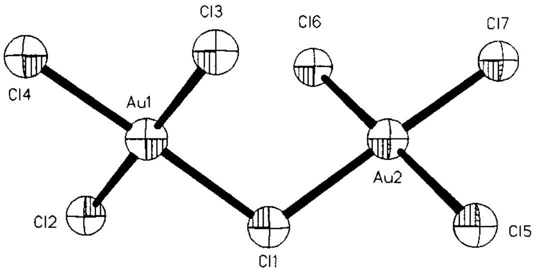

Figure 2. Predicted structure of $[(AuCl_3)_2(\mu\text{-}Cl)]$ optimized with Hartree−Fock calculations implementing Hay−Wadt ECPs and double-ζ basis sets. Graphical output was performed by using SHELXTL/PC.[25]

Vibrational calculations predict numerous strong Raman features between 362 and 149 cm^{-1}. While some of these calculated features are as good a match to our experimental spectrum as the features calculated for $AuCl_4^-$ are, there is no experimental band near 253 cm^{-1}. Also, if these calculated frequencies are underestimates, we would expect a strong feature around 380−390 cm^{-1} in the experimental spectrum, which we do not observe. Since we observe no Raman features besides those that may be attributed to $AuCl_4^-$, it is clear that $[(AuCl_3)_2(\mu\text{-}Cl)]$ does not exist in appreciable amounts in our room-temperature melt (for simplicity, we will henceforth use the formula $Au_2Cl_7^-$ instead of $[(AuCl_3)_2(\mu\text{-}Cl)]$). This is not surprising, since this melt has an excess of EMIC. The ab initio calculations indicate that Au_2Cl_7 is 39.3 kcal/mol more stable than separated $AuCl_4^-$ and $AuCl_3$, which is comparable to an unpublished result of Schwerdtfeger noted in ref 23. Analogous calculations on $AlCl_3$, $AlCl_4^-$, and $Al_2Cl_7^-$ indicate that the dialuminate is 32.1 kcal/mol more stable than aluminum chloride and tetrachloroaluminate (the value is 25.5 kcal/mol when the 6-31G* basis set is used). Therefore, the fact that we do not observe room-temperature melts when mixtures are prepared with an excess of $AuCl_3$ does not appear to be due to the inherent instability of the $Au_2Cl_7^-$. Instead, there must be either unfavorable interactions between this putative anion and the imidazolium cation or a kinetic barrier to the formation of $Au_2Cl_7^-$ that is not present in the aluminum case.

^{1}H NMR spectra of the 1/2 $AuCl_3$/EMIC melt show features at 1.1 ($-NCH_2CH_3$), 3.7 ($-NCH_3$), 4.0 ($-NCH_2CH_3$), 7.7 (positions 4 and 5 on the ring), and 9.5 ppm (position 2 on the ring) referenced to C_6D_6. These features are similar to those reported for basic Al melts[7] after accounting for the shift in reference. The most significant difference between our proton NMR data and that reported for the Al systems is that we are unable to resolve the features as well. For example, the triplet that should be observed at 1.1 ppm is a broad peak.

^{13}C NMR spectra of the same ionic liquid show spectral lines very similar to those observed for the aluminum melts. We observe lines at 17, 38, and 46 ppm for the sp^3 carbons and at 124, 125, and 138 ppm for the ring carbons. All frequencies are again referenced to C_6D_6.

Discussion

It appears that there is something special about the 1/2 $AuCl_3$/EMIC ratio that makes this mixture a liquid while those with higher amounts of gold are solids at room temperature. One possible arrangement that would give rise to this ratio is a complex composed of two imidazolium cations with a square planar $AuCl_4^-$ sandwiched between them. Such a sandwich would carry a +1 charge and be associated with the much smaller Cl^- as a counterion. A second possible arrangement would be to have the imidazolium cations interacting through ring proton 2 and through opposing chlorines on the $AuCl_4^-$ in a pseudo-hydrogen-bonding fashion. Evidence for similar structures was recently reported for the case of $[C_3N_2H_3(CH_3)(CH_2CH_3)]_2[PdCl_4]$.[26]

Another way to understand the differences between the $Al_2Cl_7^-$/EMI system and the potential $Au_2Cl_7^-$/EMI system is to examine the different geometries of the two dinuclear metal species. As mentioned above, $Au_2Cl_7^-$ has a calculated structure of square planar halves with a shared, bridging Cl. On the other hand, $Al_2Cl_7^-$ is composed of tetrahedral halves with a shared Cl. At first glance the diaurate species could be formed simply by the approach of the T-shaped $AuCl_3$ to the square planar $AuCl_4^-$. However, if $AuCl_4^-$ is complexed strongly by EMI (as is indicated by the formation of the Pd complex in ref 26) it might not be free to react with $AuCl_3$. Such a complex is less likely to occur with $AlCl_4^-$ because the tetrahedral geometry makes it more difficult for two EMI cations to make a close approach to specific chlorine atoms. In addition, if $Au_2Cl_7^-$ were to form in the presence of EMI, a relatively favorable $Au_2Cl_7^-$/EMI interaction would have to exist. We are beginning a more detailed computational study in an effort to better understand the differences between the Al and Au room-temperature molten salts.

In summary, we have extended the variety of possible room-temperature molten salts by preparing a mixture with $AuCl_3$ and 1-ethyl-3-methylimidazolium chloride. While we have found clear evidence for the formation of $AuCl_4^-$ in mixtures with excess EMIC, we have not yet been able to prepare a sample that clearly contains $Au_2Cl_7^-$, which would be analogous to the $Al_2Cl_7^-$ found in the aluminum-based species.

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Supporting Information Available: An NMR spectrum of the $AuCl_3$/EMIC mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

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