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Gold Compounds as Ionic Liquids. Synthesis, Structures, and Thermal Properties of *N*,*N*′-Dialkylimidazolium Tetrachloroaurate Salts

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The salts $[C_6H_{11}N_2][AuCl_4]$ (**1**) and $[C_8H_{15}N_2][AuCl_4]$ (**2**) ($[C_6H_{11}N_2]^+$ = 1-ethyl-3-methylimidazolium; $[C_8H_{15}N_2]^+$ = 1-butyl-3-methylimidazolium), prepared by a solvent-free method, display similar crystal structures. **1** crystallizes in the monoclinic $P2_1/c$ space group ($a = 11.1915(15)$ Å, $b = 12.380(2)$ Å, $c = 9.2883(13)$ Å; $\beta = 98.810(16)°$; $Z = 4$) and **2** in the triclinic $P\bar{1}$ space group ($a = 7.9354(14)$ Å, $b = 8.3930(15)$ Å, $c = 11.397(2)$ Å; $\alpha = 83.94(2)°$, $\beta = 87.93(2)°$, $\gamma = 78.04(2)°$; $Z = 2$). In both cases, a unique motif is seen consisting of linear chains of alternating corner-to-face arranged $[AuCl_4]^-$ ions at Au···Cl separations of 3.356(3) Å (**1**) and 3.452(3) Å (**2**). Ionic liquid behavior is observed from 58 to 220 °C for **1** and 50 to 250 °C for **2**.

Introduction

The group of molten organic salts comprising mixtures of *N*,*N*′-dialkylimidazolium (e.g., 1-ethyl-3-methylimidazolium, $[EMIM]^+$; 1-(*n*-butyl)-3-methylimidazolium, $[BMIM]^+$) chloride and aluminum chloride was first demonstrated by Wilkes *et al.*[1] to possess tunable Lewis acidity, low vapor pressure, and extended electrochemical and thermal windows. They have been used as alternatives to nonaqueous solvents for spectroscopic studies[2] and as electrolytes for batteries, photoelectrochemical cells, or electroplating.[3] Current research is focused upon the use of ionic liquids as solvents for organic synthesis[4] (with or without added metal complex catalysts) and for solvent extraction.[5] Solution and solid-state studies have examined the influence of the cation and anion structures and interionic interactions on the behavior of the $[EMIM]Cl/AlCl_3$ ionic liquids.[6] Subsequently, other [EMIM]X salts (e.g., $X = NO_2^-$, NO_3^-, SO_4^{2-}, BF_4^-, and PF_6^-) were prepared and structurally characterized.[7] The correlation of melting point with structure for a wide range of $[NR_4]X$ and [RMIM]X salts (R = alkyl, X^- = perfluorinated anions) has been reported recently.[8]

Ionic liquids composed of or containing transition metal ions are of great interest regarding their potential catalytic applica-

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tions.[4] The chemistry of transition metal halide complexes in chloroaluminate ionic liquids was reviewed a decade ago.[2c] There have been a small number of spectrochemical and electrochemical solution studies in these media,[9] but fewer reports of structural characterization in the solid state have appeared.[10,11] Reports on the role of gold in heterogeneous oxidation[12a] and ethyne hydrochlorination[12b] and of gold(I) and gold(III) complexes in the addition of alcohols to alkynes,[12c] alcoholysis of nitriles,[12d] olefin carbonylation,[12e] and sulfide oxidation to sulfoxides[12f] (using [NBu$_4$][AuCl$_4$] in a phase-transfer process) have recently led to a reawakening of interest in its chemistry. From the limited data currently available, the catalytic activity of gold complexes is found to be distinctly different from that of other precious metals.[12g]

In this work, we have investigated the influence of the anion structure and interionic interactions on the behavior of ionic media. More particularly, we have studied the effect of a change in geometry from tetrahedral to square planar around the metal atom of the anions. The square planar tetrachloroaurate(III) anion, which has high symmetry[13] and uniform charge delocalization, was, as a consequence, selected for our studies. Previous studies on transition metal halide complexes in ionic liquids do not appear to have included complexes of gold. In this paper, we report the synthesis, characterization, thermal properties, and single-crystal X-ray structures of two new salts, [EMIM][AuCl$_4$] **(1)** and [BMIM][AuCl$_4$] **(2)**.

Experimental Section

Materials. Sodium tetrachloroaurate (98%), aluminum trichloride (99%), 1-ethyl-3-methylimidazolium chloride, *n*-butyl chloride (99.5%) (Aldrich), and tetrachloroauric acid tetrahydrate (Johnson Matthey) were used without purification. Schlenck techniques were applied when necessary to protect the reaction systems from air and moisture. Solvents were dried and distilled under dry nitrogen using standard procedures. 1-Methylimidazole (Aldrich) was dried over calcium hydride and distilled twice under dry N$_2$. The [EMIM][AlCl$_4$] ionic liquid was prepared in a glovebox by slowly adding AlCl$_3$ (9.1 g) to [EMIM]Cl (10.6 g) with mechanical stirring according to a literature method.[1]

Techniques. The melting points measured are uncorrected. A Carlo Erba Instruments Co. elemental analyzer Model 1106 was used for carbon, hydrogen, and nitrogen analysis. IR spectra were obtained on a Perkin-Elmer 883 infrared spectrophotometer: for **1** from Nujol mulls on CsI plates protected by a thin film of polythene; for **2** from KBr disks. ^{1}H NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer; chemical shifts are reported relative to Me$_4$Si. The positive ion FAB mass spectra were obtained on a VG Analytical 7070 E double-focusing magnetic sector mass spectrometer using xenon gas at 1 mA (70 eV). Solid samples were placed in a 3-nitrobenzyl alcohol matrix. The masses of the peaks quoted are based on the most abundant isotope of the elements present in the ion. The thermogravimetric analysis (TGA) of [EMIM][AuCl$_4$] was performed using a Perkin-Elmer TGA 7 analyzer. The carrier gas was air, and the sample (6 mg) was heated from 40 to 700 °C at a heating rate of 20 °C/min. The TGA was calibrated using iron, nickel, and perkalloy curie point. The TGA of [BMIM][AuCl$_4$] was recorded on a Netzsh STA 429 instrument at ICI, Chemical & Polymers, Runcorn. The sample (18 mg) was heated from 30 to 500 °C at 10 °C/min.

Preparation of 1-Butyl-3-methylimidazolium Chloride ([BMIM]-Cl). [BMIM]Cl was prepared by a modification of the literature method.[1a] A 500-mL three-neck round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon-coated magnetic bar was charged under N$_2$ with 1-methylimidazole (82.10 g, 1 mol). Butyl chloride (130 mL) was added into the reaction vessel with continuous magnetic stirring in batches of 20 mL. The reaction mixture was heated under N$_2$ at 80 °C for 72 h. After cooling to room temperature, the reaction vessel was placed in an ice−acetone bath and left overnight to give a pale yellow viscous oil. The oily product was treated with methyl acetate (100 mL) and stirred vigorously for 15 min to give a white sticky solid. The washing was decanted and the process repeated 8 times to give a milky white solid. The product was dried under vacuum at 70 °C for 12 h to yield pure crystalline [BMIM]-Cl (155 g; 88.7% based on 1-methylimidazole). Anal. Calcd for C$_8$H$_{15}$-ClN$_2$: C, 55.00; H, 8.66; N, 16.04%. Found: C, 53.4; H, 9.6; N, 15.7%.

Synthesis of [EMIM][AuCl$_4$] (1) and [BMIM][AuCl$_4$] (2). A slight excess of [EMIM]Cl (0.11 g, 0.75 mmol) or [BMIM]Cl (0.13 g, 0.74 mmol) was added to tetrachloroauric acid (HAuCl$_4$·4H$_2$O; 0.275 g, 0.67 mmol) to form instantly a soft yellow solid (eq 1). The reaction was completed by gentle heating on a water bath with stirring, just above the melting points of **1** or **2**. Recrystallization from 4:1 benzene/acetonitrile gave **1** (mp 58 °C) or **2** (mp 50 °C) as yellow shiny plates in yields of 84% **(1)** and 80% **(2)** based on HAuCl$_4$, from which crystals suitable for a single-crystal X-ray analysis were selected. Anal. Calcd for **1** (C$_6$H$_{11}$N$_2$Cl$_4$Au): C, 16.02; H, 2.46; N, 6.23%. Found: C, 16.71; H, 2.47; N, 6.45%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.65 (t, $\mathrm{N^2CH_2C}\mathit{H}_3$), 4.06 (s, N^{1}CH$_3$), 4.36 (q, $\mathrm{N^2}\mathit{CH_2}\mathrm{CH_3}$), 7.27 (d, H^4), 7.35 (d, H^5), 8.89 (s, H^2). IR (Nujol): ν(Au−Cl) stretch 355 cm^{-1}.[12d] Anal. Calcd for **2** (C$_8$H$_{15}$N$_2$Cl$_4$Au): C, 20.10; H, 3.16; N, 5.85%. Found: C, 20.49; H, 3.09; N, 5.63%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.00 (t, N^{2}CH$_3$), 1.43 (m, $\mathrm{N^2(CH_2)_2}\mathit{CH_2}\mathrm{CH_3}$), 1.92 (m, $\mathrm{N^2CH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$), 4.06 (s, N^{1}CH$_3$), 4.28 (t, N^{2}CH$_2$), 7.34 (d, H^4), 7.35 (d, H^5), 8.96 (s, H^2). IR (KBr disk): ν(Au−Cl) stretch 355 cm^{-1}.[12d]

Alternatively, **1** was prepared by adding NaAuCl$_4$ (0.250 g, 0.68 mmol) under nitrogen to an excess of liquid [EMIM][AlCl$_4$] (2 mL) with stirring for 30 min at room temperature (eq 2). Excess [EMIM]-[AlCl$_4$] was washed off by the addition of dry benzene (25 mL), giving a yellow oil which was isolated with a separating funnel. **1** was precipitated by the slow addition of fresh benzene and purified as above. The yield was 96%.

1 and **2** are soluble in water, hot ethanol, chloroform, and acetonitrile but insoluble in benzene, hexane, and diethyl ether. The salts remain unaffected by light and are slightly hygroscopic. Prolonged exposure to air or moisture causes **1** and **2** to turn slowly into liquids from which **1** and **2** can, however, be recovered by recrystallization from 4:1 diethyl ether/ethanol.

X-ray Crystallography for 1 and 2. Data were collected on a STOE-IPDS image plate diffractometer at 193(2) K using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The face-indexing routine FACEIT has been applied for absorption corrections.[14] Structure solution and refinement were carried out using the program SHELX97.[15] Structure refinement by full-matrix least squares was based on all data

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using F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated with C−H distances of 0.99 (methylene C−H), 0.98 (methyl C−H), and 0.95 Å (aryl−H), and assigned isotropic thermal parameters of $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for methylene and aryl−H positions and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl−H positions.[16] Carbon positions C6 in **1** and C6 and C7 in **2** showed high anisotropic displacement parameters, indicating disorder. This was resolved by splitting disordered atoms on two positions and applying geometrical and displacement restraints, giving final occupation factors of 0.47/0.53 (**1**) and 0.71/0.29 (**2**), respectively.

Results and Discussion

Preparations. Salts **1** and **2** were prepared by a simple one-step solvent-free method, by interacting solid reactants [RMIM]-Cl (R = Et, *n*-Bu) and $\mathrm{HAuCl_4{\cdot}4H_2O}$ (eq 1) at room temperature under aerobic conditions, as yellow shiny plates in 80 to 84% yields. After purification, the water-free products gave satisfactory elemental analyses and no indication of moisture as confirmed by ^{1}H NMR, MS, and TGA. A similar preparative method has been used for the synthesis of liquid organic chloroaluminates under an inert atmosphere.[1a]

$$[\mathrm{RMIM}]\mathrm{Cl} + \mathrm{HAuCl_4} \rightarrow [\mathrm{RMIM}][\mathrm{AuCl_4}] + \mathrm{HCl} \qquad (\mathrm{R} = \mathrm{Et},\ n\text{-Bu}) \quad (1)$$

Salt **1** was also prepared in a very good yield (96%) by an exchange reaction (eq 2) at room temperature under nitrogen. This technique is of general utility, permitting also the synthesis of complexes of platinum(II) and platinum(IV).[17]

$$\mathrm{NaAuCl_4} + [\mathrm{EMIM}][\mathrm{AlCl_4}] \rightarrow [\mathrm{EMIM}][\mathrm{AuCl_4}] + \mathrm{NaAlCl_4} \quad (2)$$

On the other hand, a range of anhydrous quaternary ammonium chlorometalate salts may conventionally be obtained using boiling organic solvents under nitrogen.[18] The synthesis of imidazolium derivatives, $[\mathrm{EMIM}]_2[\mathrm{MCl_4}]$ (M = $\mathrm{Ni^{2+}}$, $\mathrm{Co^{2+}}$)[10b] and $[\mathrm{EMIM}]_2[\mathrm{VOCl_4}]$,[10c] in around 50% yields under vacuum-line conditions has also been described.

Crystal Structures of 1 and 2. The crystal structure data for **1** and **2** are given in Table 1. Both salts show very similar solid-state structures of roughly the CsCl type, with each ion surrounded by eight counterions in a cubic fashion (Figures 1 and 2). However, the situation is more complex because of the nonspherical character of both cations and anions. Both structures contain two crystallographically independent $[\mathrm{AuCl_4}]^-$ anions which are arranged perpendicularly to one another. This results in infinite anionic chains of alternating corner-to-face arranged $[\mathrm{AuCl_4}]^-$ units. This is a unique pattern in salts containing purely tetrachloroaurate(III) anions. The interionic Au···Cl distances amount to 3.356(3) **(1)** and 3.452(3) Å **(2)**. A similar pattern, but with shorter Au···Cl distances (3.160 and 3.005 Å), has only been observed in the mixed-valence compound $\mathrm{Cs_2(AuCl_2)(AuCl_4)}$, which shows linear chains of repeating Cl−Au(I)−Cl···Au(III) units.[19] Au−Cl bond lengths and angles (Table 2) are comparable with those found in other complexes containing $[\mathrm{AuCl_4}]^-$ anions.[20] $[\mathrm{AuCl_4}]^-$ ions are square planar, with Au atoms located on crystallographic inversion centers.

Table 1. Crystal Structure Data for **1** and **2**

	1	2
chem form	$\mathrm{C_6H_{11}AuCl_4N_2}$	$\mathrm{C_8H_{15}AuCl_4N_2}$
fw	449.93	477.05
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a/Å	11.1915(15)	7.9354(14)
b/Å	12.380(2)	8.3930(15)
c/Å	9.2883(13)	11.397(2)
α/°	90	83.94(2)
β/°	98.810(16)	87.93(2)
γ/°	90	78.04(2)
V/Å^3	1271.7(3)	738.4(2)
Z	4	2
ρ_{calc}/g cm^{-3}	2.350	2.146
μ(Mo Kα)/mm^{-1}	12.37	10.19
max/min transm	0.947/0.566	0.927/0.484
data/params	1656/132	2198/158
R1 ($I > 2\sigma(I)$)[a]	0.022	0.038
wR2 (all data)[b]	0.049	0.097

[a] $\mathrm{R1} = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $\mathrm{wR2} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

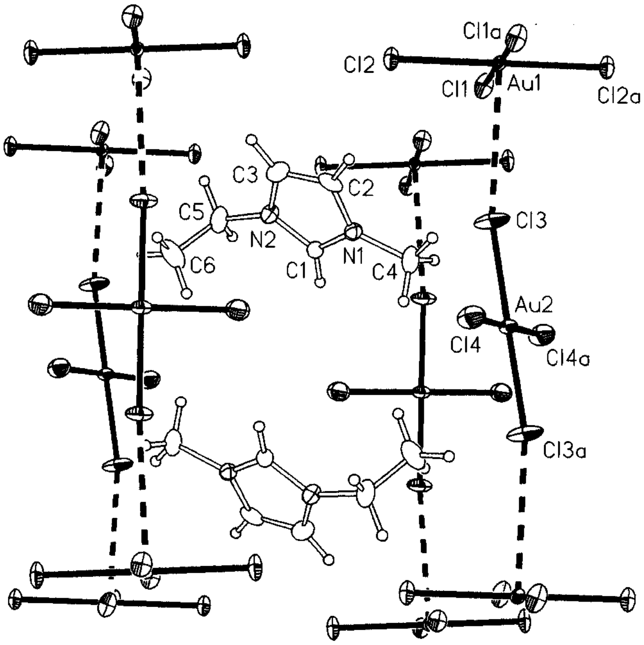

Figure 1. Crystal structure of **1** with thermal ellipsoids at the 30% probability level.

Although exhibiting very similar solid-state structures, both salts exist in different crystal systems. **1** crystallizes in the monoclinic space group $P2_1/c$, whereas **2** adopts the triclinic space group $P\bar{1}$. The fragment of the lattice shown in Figure 2 coincides with the triclinic unit cell of **2**, with Au1 situated at 0,0,0 and Au2 at $^1/_2$,0,0, respectively. On the other hand, the monoclinic unit cell of **1** comprises twice the volume of the related lattice fragment displayed in Figure 1, with Au1 at 0,0,0 and Au2 at 0,0,$^1/_2$, respectively. **1** demands less volume per ion pair (317.9 Å^3) in its solid-state structure than **2** (369.2 Å^3). This is accompanied by a decrease in density from 2.350 (**1**) to 2.146 g cm^{-3} (**2**). This shows that the corner-to-face arrangement

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[16] Applied C−H distances and U(H) values are default settings in SHELX97.[15]

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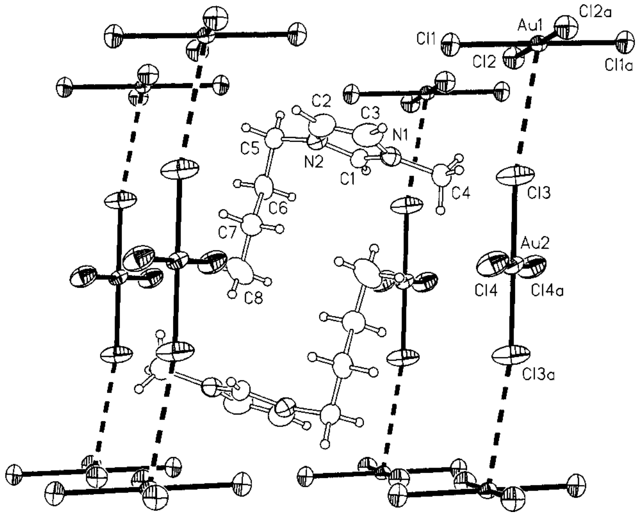

Figure 2. Crystal structure of **2** with thermal ellipsoids at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1	**2**
Au(1)−Cl(1)	2.280(2)	2.286(2)
Au(1)−Cl(2)	2.279(2)	2.280(2)
Au(2)−Cl(3)	2.267(3)	2.267(3)
Au(2)−Cl(4)	2.281(2)	2.271(2)
Au(1)−Cl(3)	3.356(3)	3.452(3)
Cl(1)−Au(1)−Cl(2)	90.95(6)	89.75(7)
Cl(3)−Au(2)-Cl(4)	89.83(9)	89.90(9)
Cl(1)−Au(1)−Cl(3)	91.12(8)	77.30(8)
Cl(2)−Au(1)−Cl(3)	88.99(8)	91.22(7)
Au(1)−Cl(3)−Au(2)	168.4(1)	170.0(1)

Table 3. Positive Ion FAB-MS Spectral Data for **1** and **2**

1		**2**	
ion	*m*/*z*, %	ion	*m*/*z*, %
$[EMIM]^+$	111(100)	$[BMIM]^+$	139(100)
$[(EMIM)_2Cl]^+$	257(5.83)	$[(BMIM)_2Cl]^+$	313(6.06)
$[(EMIM)_3Cl_2]^+$	403(0.16)	$[(BMIM)_3Cl_2]^+$	487(0.04)
$[(EMIM)_2(AuCl_2)]^+$	489(0.72)	$[(BMIM)_2(AuCl_2)]^+$	545(0.60)
$[(EMIM)_2(AuCl_4)]^+$	559(0.25)	$[(BMIM)_2(AuCl_4)]^+$	615(0.49)

of $[AuCl_4]^-$ anions allows a certain degree of flexibility toward the size and shape of the cations.

The closest contacts between anions and cations (≥2.77 Å) exist as the weak C−H···Cl interactions involving imidazolium-bound hydrogen atoms and can be attributed to the interionic Coulomb forces. These interactions, although relatively weak, seem to direct the orientation between ions and might govern the overall assembly. It should be noted that although H positions could not be detected precisely in the difference Fourier syntheses of **1** and **2**, their calculated positions give an adequate model due to the rigid arrangement of the imidazolium C−H units. EMIM chlorometalates containing dianions show shorter C−H···Cl interactions due to the stronger interionic Coulomb forces. Thus $[EMIM]_2[NiCl_4]$ and $[EMIM]_2[CoCl_4]$ show shorter C−H···Cl distances from 2.57 Å, which are accompanied by relatively higher melting points (92−93 and 100−102 °C, respectively).[10b] In addition, the alkyl chains in the crystal structures of both **1** and **2** are disordered, showing freedom of movement that may contribute to the low melting points of these salts (see below).

FAB Mass Measurements. The FAB positive ion mass spectra (Table 3) show peaks previously assigned to $[EMIM]^+$ **(1)** and $[BMIM]^+$ **(2)** cations as the base peaks.[21] Other peaks assigned as $[(RMIM)_2Cl]^+$, $[(RMIM)_3Cl_2]^+$, $[(RMIM)_2(AuCl_2)]^+$, and $[(RMIM)_2(AuCl_4)]^+$ (R = ethyl or *n*-butyl) were also observed at lower intensities from 0.16 to 6%, which is in agreement with FAB-MS spectral data for $[EMIM][AlCl_4]$.[21a,b]

Figure 3. TGA of **1**.

Interestingly, peaks attributable to the species containing two gold ions, such as $[(RMIM)_3(AuCl_4)_2]^+$, were observed at very low intensities (0.002−0.006%). This indicates that some of the Au···Cl interactions between the neighboring $[AuCl_4]^-$ units in the crystal lattice of $[RMIM][AuCl_4]$ remain intact in solution under the conditions of FAB measurements.

Thermogravimetric Analysis. TGA for **1** is shown in Figure 3, and similar data were obtained for **2**. Salts **1** and **2** are stable up to 220 and 250 °C, respectively. Sharp peaks at 292 and 280 °C represent the weight loss accounted for by the $[EMIM]^+$ and $[BMIM]^+$ cations, respectively. The broad shoulders at about 330 **(1)** and 310 °C **(2)** may be attributed to the loss of all four chlorine atoms from $[AuCl_4]^-$. The total weight losses observed (55.4% **(1)** and 56.9% **(2)**) match closely the expected values (56.2% **(1)** and 58.8% **(2)**), assuming a final residue of metallic gold. To further examine thermal stability, bulk samples of **1** and **2** were heated under N_2 at 200 °C for 72 h and then cooled to room temperature. It was found that analytical and spectroscopic purity were retained. Unit cell measurements showed that a single crystal of **2** could be recovered unchanged from the heat-treated melt.

Ionic Liquid Behavior. **1** and **2** melt at 58 and 50 °C, respectively, which is considerably lower compared to a range of reported tetrachloroaurate(III) complexes with ammonium cations (e.g., $[Et_4N]^+$, mp 215−218 °C; $[Bu_4N]^+$, mp 157−169 °C,[22] and $[EtC(OR)NH_2]^+$ (R = Me, mp 88−90 °C; R = Et, mp 93−95 °C)[12d]).

The nonmetallic salts, [EMIM]X, melt in the temperature ranges

X	BF_4^-	NO_3^-	NO_2^-	PF_6^-	SO_4^{2-} (monohydrate)
mp, °C[7a,b]	15	38	55	58−60	70

With regard to EMIM chlorometalates for which data are available, only $[EMIM][AlCl_4]$ stands out from the rest, being an ionic liquid below room temperature (mp 6 °C).[1] A few reported transition metal derivatives, e.g., $[EMIM]_2[NiCl_4]$ (mp 92−93 °C) and $[EMIM]_2[CoCl_4]$ (mp 100−102 °C),[10b] have

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(21) (a) Abdul-Sada, A. K.; Greenway, A. M.; Seddon, K. R.; Welton, T. *Org. Mass Spectrom.* **1993**, *28*, 759. (b) Dyson, P. J.; Grossel, M. C.; Srinivasan, N.; Welton, T.; Williams, D. J.; White, A. J. P.; Zigras, T. *J. Chem. Soc., Dalton Trans.* **1997**, 3465.

(22) Braunstein, P.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845.

higher melting points than **1** and **2**. The relatively low melting points of **1** and **2** can be explained by the loose assembly of singly charged ions in their crystal lattices and their nonrigid interionic interactions. Based on the properties discussed above, therefore, **1** and **2** are the first[23] structurally characterized RMIM chlorotransition metalates (with a 1:1 stoichiometry) that may be classified as low-temperature ionic liquids. Ionic liquid behavior is observed from 58 to 220 °C for **1** and 50 to 250 °C for **2**.

Conclusions

The salts [EMIM][$AuCl_4$] (**1**) and [BMIM][$AuCl_4$] (**2**) are unique among the chlorometalate *N*,*N*′-dialkylimidazolium complexes so far as structure characterization is concerned. Although existing in different crystal systems—monoclinic space group $P2_1/c$ (**1**) and triclinic $P\bar{1}$ (**2**)—both salts exhibit very similar solid-state structures, with overall assembly governed by weak interionic interactions. These structures consist of linear chains of alternating corner-to-face arranged square planar $[AuCl_4]^-$ anions at a relatively large Au···Cl separation of 3.356(3) (**1**) and 3.452(3) Å (**2**) and also include long (≥2.77 Å) contacts between the $[AuCl_4]^-$ anions and *N*,*N*′-dialkylimidazolium cations, with the alkyl groups disordered and showing freedom of movement. Due to the loose assembly of ions and weak interionic interactions, **1** and **2** have relatively low melting points. Based on these properties, **1** and **2** are the first RMIM chlorotransition metalates that may be classified as low-temperature ionic liquids, with ionic liquid behavior from 58 to 220 °C for **1** and 50 to 250 °C for **2**. Given the ease of preparation, extended thermal stability, and high solubilities in both protic and aprotic solvents which is central to catalysis in homogeneous media, **1** and **2** and related Au(III) compounds can find applications in catalysis and electrochemical technologies. Studies on catalysis by these systems are underway in this laboratory.

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Supporting Information Available: A listing of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) After our submission of the manuscript, a report on room-temperature ionic liquid prepared from $AuCl_3$ and 1-ethyl-3-methylimidazolium chloride with various stoichiometries appeared. Schreiter, E. R.; Stevens, J. E.; Ortwerth, M. F.; Freeman, R. G. *Inorg. Chem*. **1999**, 38, 3935.