The Structure of Halogenometallate Complexes dissolved in both Basic and Acidic Room-temperature Halogenoaluminate(III) Ionic Liquids, as determined by EXAFS

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The salts $[MeEtim]_2[MCl_4]$ ($[MeEtim]^+$ = 1-methyl-3-ethylimidazolium; M = Mn, Co, or Ni) are shown by EXAFS to dissolve in basic $[MeEtim]Cl–AlCl_3$ ionic liquids to yield four-co-ordinate $[MCl_4]^{2-}$, and to dissolve in acidic $[MeEtim]Cl–AlCl_3$ ionic liquids to yield six-co-ordinate $[M(AlCl_4)_3]^-$ anions.

Although the structure of the 1-methyl-3-ethylimidazolium chloride–aluminium(III) chloride ionic liquid system is becoming increasingly well understood,[1,2] the detailed structures of solute species remain poorly defined. The chemical and physical properties of the liquids are determined by the percentage of $AlCl_3$; those containing greater than 50 mol% are referred to as acidic and those with less than 50 mol% as basic.[3] The anionic distribution is dominated by the single equilibrium (1). In basic ionic liquids, spectroscopic[4] and electrochemical[5] evidence suggest that dissolved metal chloride species form discrete metal chloride complexes. The situation in acidic ionic liquids is less well defined and several models have been suggested, including unco-ordinated free metal ions[6] and metal complexes with tetrachloroaluminate(III) or heptachlorodialuminate(III) ligands.[7]

$$2[AlCl_4]^- \rightleftharpoons [Al_2Cl_7]^- + Cl^- \qquad (1)$$

A series of 1-methyl-3-ethylimidazolium ($[MeEtim]^+$) salts have been prepared and dissolved in both acidic and basic ionic liquids for examination by EXAFS. The samples were heat-sealed within small poly(ethene) bags under dry dinitrogen, and stored in a desiccator over phosphorus(V) oxide prior to study. *X*-Ray absorption spectra of solutions of $[MeEtim]_2[MCl_4]$ (M = Mn, Co, or Ni), in both basic and acidic ionic liquids, were recorded using the Synchrotron Radiation Source at Daresbury Laboratory on Station 7.1. To avoid problems with the 'thickness effect' due to the high concentration of chlorine in the samples,[8] the data were collected in fluorescence mode, with only a very thin film of liquid exposed to the beam. Transmission EXAFS spectra of solid microcrystalline samples of $[MeEtim]_2[MCl_4]$ (M = Mn, Co, or Ni) and powdered samples of MCl_2 (M = Mn, Co, or Ni) were also measured (as model compounds).

Analyses were performed with *ab initio* phase shifts and backscattering factors, using spherical wave methods with 13 *l* values previously described elsewhere.[9] The model com-

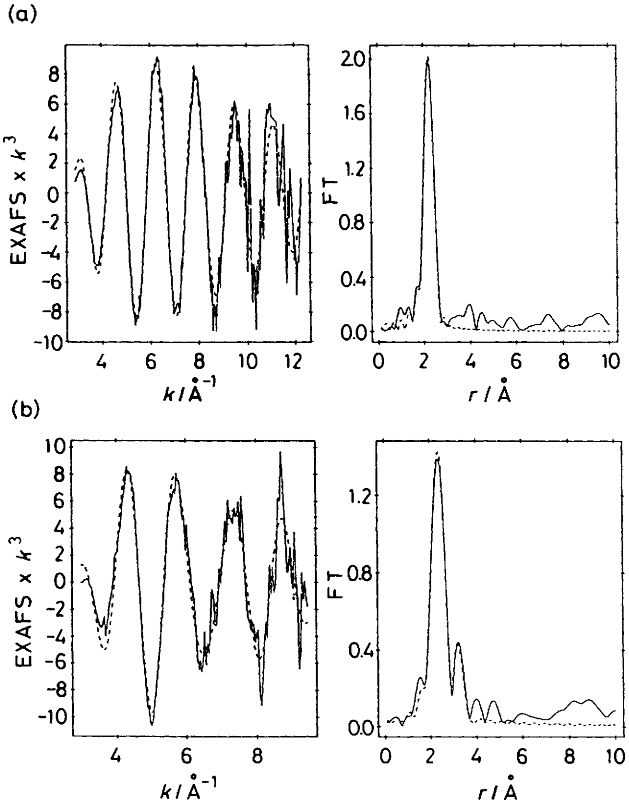

Figure 1. The cobalt k^3-weighted EXAFS (left) and phase-corrected (chlorine) Fourier transform moduli (right) of cobalt(II) in (a) basic and (b) acidic ionic liquids. (——) Experimental data. (----) Calculated curve.

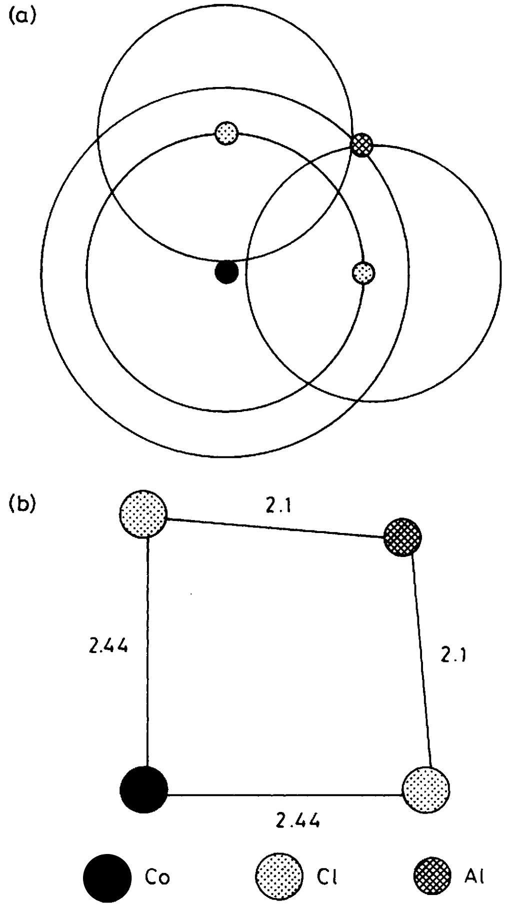

Figure 2. A schematic model of a single $M(\mu\text{-}Cl)_2Al$ unit within $[M(AlCl_4)_3]^-$: (a) the experimental co-ordination spheres and (b) the key structural sub-unit, for M = Co.

Table 1. EXAFS derived structural parameters, including interatomic distances (r/Å), Debye–Waller factors (α/Å^2),[a] and R factors (%).

	X-Ray data	EXAFS data										
	Model	Model			Basic ionic liquid[b]			Acidic ionic liquid[b]				
		4Cl			4Cl			6Cl		3Al		
	r	r	α	R	r	α	R	r_1	α_1	r_2	α_2	R
$[MeEtim]_2[NiCl_4]$	2.254[c]	2.25	0.009	19	2.25	0.008	22	2.38	0.016	3.19	0.023	21
$[MeEtim]_2[CoCl_4]$	2.275[c]	2.27	0.009	19	2.28	0.007	23	2.44	0.018	3.24	0.017	28
$[MeEtim]_2[MnCl_4]$	2.37[d]	2.38	0.010	16	2.38	0.007	27	2.54	0.022	3.33	0.035	32

[a] $\alpha = 2\sigma^2$ (where σ = root mean square deviation in interatomic distance). [b] These are solutions of the model compounds; the basic solutions were prepared *ca.* 0.1 M in 0.35 mol% ionic liquid (based on $AlCl_3$); the acidic solutions were prepared *ca.* 0.05 M in 0.60 mol% ionic liquid (based on $AlCl_3$). [c] Ref. 10. [d] Data collected on $[MeEtim]_2[MnCl_4]$; crystallographic data[11] for $[pyH]_2[MnCl_4]$ (py = pyridine) was used.

pounds were used to obtain the proportion of absorption affording EXAFS (0.7) and the magnitude of inelastic effects modelled by an imaginary potential (−2.0 eV). Small corrections were applied to the phase shifts such that the MCl distance was correct to within 0.01 Å. The results of the EXAFS analyses of both the model compounds, and their solutions in both basic and acidic ionic liquids, are summarized in Table 1. The structural parameters presented were calculated with four chlorine atoms in the first co-ordination shell for $[MeEtim]_2[MCl_4]$, both as crystalline solids and in basic ionic liquids; the results in acidic solution were modelled upon six chlorine atoms in the first co-ordination shell, and three aluminium atoms in the second shell. All of the co-ordination numbers came to within ±0.5 of these values, when refined. The error in the first co-ordination shell (MCl) interatomic distances is ±0.01 Å; the error in the MAl distances is ±0.05 Å. Theory–experiment comparisons for the solutions of cobalt(II) in both basic and acidic solution are shown in Figure 1.

In basic ionic liquids, our results (Table 1) indicate that the transition metals are co-ordinated by a single, well defined shell of four chloride ions. This confirms both the interpretation of spectroelectrochemical data[4,5] and that EXAFS is a viable probe for the study of solute structures in ionic liquids. In acidic ionic liquids, the cobalt(II), nickel(II), and manganese(II) data show that the metal ion is co-ordinated by a first shell of six chlorine centres and a second shell of three aluminium centres. These data support a model in which the metal centre is co-ordinated by three bidentate $[AlCl_4]^-$ ligands (see Figure 2), and do not fit any model involving chelating $[Al_2Cl_7]^-$. This is a somewhat surprising result, in view of the expected steric strain within such a complex, but there is some precedent in the solid state structure of $Co(AlCl_4)_2$, which reveals *four* tetrachloroaluminate(III) ions to be co-ordinated to each cobalt(II) centre: two in a bidentate chelating mode, two monodentate but bridging.[12]

Preliminary results on iron(II) indicate that its complexes are isostructural with those detected for cobalt(II) and nickel(II). Data for metal(III) (*e.g.*, V, Cr, Eu, and Tb) and metal(IV) (*e.g.*, Os) salts in ionic liquids have been collected, and are currently being processed.

The results presented here (see Table 1) for solutions of metal(II) chlorides relate to carefully selected ionic liquid compositions. The basic compositions used contain a chloride mole fraction of 0.23 and an $[AlCl_4]^-$ mole fraction of 0.27. Thus, even with a slight excess of $[AlCl_4]^-$ over Cl^- present, there was no evidence detected for it providing significant competition for the chloride ion: a result in complete accord with received wisdom. The acidic compositions correspond to an $[Al_2Cl_7]^-$ mole fraction of 0.23 and an $[AlCl_4]^-$ mole fraction of 0.27: under these conditions, a reading of the current literature would not have allowed prediction of the existence of the $[M(AlCl_4)_3]^-$ anion as the predominant species (or, indeed, as a minor species). However, it must be recognized that the situation in the acidic regime must be a dynamic one, and that EXAFS is a technique which is likely to detect only the predominant species present. The detection of the tetrachloroaluminate(III) complex does not preclude the existence of heptachlorodialuminate(III) complexes in more acidic compositions (or even in very low concentrations in the compositions studied here). Indeed, it would be quite remarkable if such complexes were not present in ionic liquids containing >0.67 mol% $AlCl_3$: experiments are planned to investigate this phenomenon.

We would anticipate, given the similarity in spectral data,[4,13] that similar ions to $[M(AlCl_4)_3]^-$ might also be found in solutions of metal(II) chlorides in high-temperature chloroaluminate(III) ionic liquids (*e.g.*, NaCl–$AlCl_3$).

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