

1-Methyl-3-ethylimidazolium Hexachlorouranate(IV) and 1-Methyl-3-ethylimidazolium Tetrachlorodioxouranate(VI): Synthesis, Structure, and Electrochemistry in a Room Temperature Ionic Liquid

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Salts of the hexachlorouranate(IV) and tetrachlorodioxouranate(VI) are well known [1, 2], and the development of molten salt fast reactors has encouraged a significant number of studies of these systems in high temperature fused salt mixtures [3]. To the best of our knowledge, however, there have been only two studies [4, 5] of chlorouranium systems in room temperature molten salts, and these have focussed upon the uranium(IV)/uranium(III) system in the aluminium chloride: *N*-butylpyridinium chloride (AlCl_3 -[*N*-Bupy]Cl) ionic liquids in the acidic regime (*i.e.* where the ionic liquid contains a stoichiometric excess of aluminium chloride over the organic chloride salt [6]). A related study of thorium(IV) has also appeared [7].

The new salt 1-methyl-3-ethylimidazolium hexachlorouranate(IV), $[\text{MeEtim}]_2[\text{UCl}_6]$, was prepared as a lime-green crystalline solid by the conventional route of treating a solution of uranium(IV) chloride in 6 M hydrochloric acid with $[\text{MeEtim}]\text{Cl}$ under strictly dioxygen-free conditions. In addition to routine analytical and spectroscopic characterisation, the crystal and molecular structures of the salt were solved.* As anticipated, the uranium is in a perfectly octahedral, O_h , environment of chloride ions, with a mean uranium–chlorine bond length of 0.2610 nm.

The salt 1-methyl-3-ethylimidazolium tetrachlorodioxouranate(VI), $[\text{MeEtim}]_2[\text{UO}_2\text{Cl}_4]$, was prepared

*Crystal data: $\text{C}_{12}\text{H}_{22}\text{Cl}_6\text{N}_4\text{O}_2\text{U}$, $M = 673.1$, orthorhombic, space group $Pbca$, $a = 1.5499(3)$, $b = 0.9904(3)$, $c = 1.4792(3)$ nm, $U = 2.2700$ nm³, $Z = 4$, $D_c = 1.969$ g cm⁻³, $F(000) = 1264$, $\mu(\text{Mo K}\alpha) = 74.9$ cm⁻¹, $\lambda = 0.071069$ nm, crystal dimensions = $0.20 \times 0.15 \times 0.10$ mm. The data were measured on an Enraf-Nonius CAD4 diffractometer. 915 reflections were used in the refinement, which converged at $R = 0.037$, $R' = 0.042$. See 'Supplementary Material'.

ed by a slow controlled aerial oxidation of a methanolic solution of $[\text{MeEtim}]_2[\text{UCl}_6]$. This yellow crystalline salt was also characterised crystallographically**. The anion exhibits a *trans*, C_{4v} , structure, with $\bar{r}(\text{UCl}) = 0.2664$ nm and $r(\text{U=O}) = 0.1760$ nm, and it is of some interest to compare this structure with that of the related salt, $[\text{imH}]_2[\text{UO}_2\text{Cl}_4]$, in which the anion is significantly distorted by inter-ionic hydrogen bonding [8].

$[\text{MeEtim}]_2[\text{UO}_2\text{Cl}_4]$ dissolves in the 44.4 mol % AlCl_3 - $[\text{MeEtim}]\text{Cl}$ ionic liquid to give a pale yellow solution and exhibits two voltammetric reduction waves at a glassy carbon disc electrode (Fig. 1a).

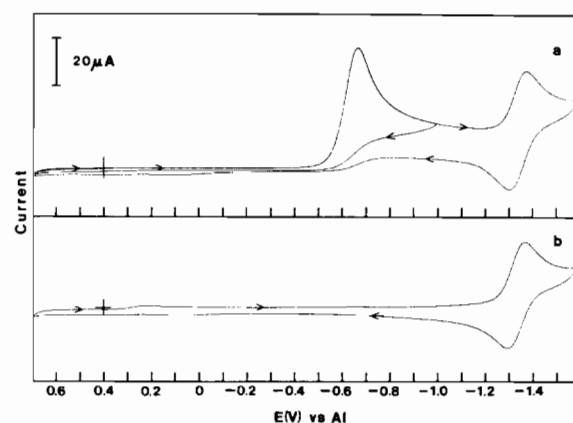


Fig. 1. Cyclic voltammograms at a glassy carbon electrode in the 44.4/55.6 mol % AlCl_3 - $[\text{MeEtim}]\text{Cl}$ ionic liquid at 40.0 °C, (a) 10.8 mM solution of $[\text{MeEtim}]_2[\text{UO}_2\text{Cl}_4]$ and (b) a solution of the product obtained after exhaustive electrolytic reduction of the above solution at -0.66 V. The scan rates were 50 mV s⁻¹, and the initial potentials were 0.40 V.

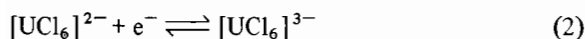
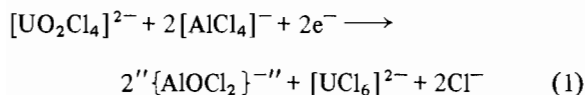
The first wave, with a peak potential of -0.66 V (*vs.* aluminium in the 66.7 mol% ionic liquid at 40 °C), is approximately twice the height of the second reduction wave, which exhibits a peak potential of -1.37 V and a half-wave potential of -1.34 V. No oxidation current was observed when the scan was reversed at -1.00 V following the first reduction wave. The second reduction wave exhibited an oxidation current when the scan was reversed at -1.60 V, and the peak separation for this voltammetric wave was approximately 0.070 V at a

**Crystal data: $\text{C}_{12}\text{H}_{22}\text{Cl}_4\text{N}_4\text{O}_2\text{U}$, $M = 634.1$, monoclinic, space group $P2_1/n$, $a = 1.0086(3)$, $b = 0.9856(3)$, $c = 1.0561(3)$ nm, $\beta = 94.16^\circ$, $U = 1.04707$ nm³, $Z = 2$, $D_c = 2.0$ g cm⁻³, $F(000) = 596$, $\mu(\text{Mo K}\alpha) = 78.7$ cm⁻¹, $\lambda = 0.071069$ nm, crystal dimensions = $0.20 \times 0.15 \times 0.10$ mm. The data were measured on an Enraf-Nonius CAD4 diffractometer. 1251 reflections were used in the refinement, which converged at $R = 0.025$, $R' = 0.028$. See 'Supplementary Material'.

scan rate of 50 mV s⁻¹. This potential separation is close to the theoretical 0.062 V separation expected for a one-electron reversible charge transfer reaction at 40 °C.

Exhaustive controlled potential electrolysis experiments were conducted in a glassy carbon crucible at an applied potential of -1.00 V in order to determine the number of electrons that are associated with the reduction wave at -0.66 V and the product(s) that result. Calculations based on the total charge required gave a value of $n = 2.1$ for the first reduction wave. A cyclic voltammogram of the green electrolysed solution (Fig. 1b) indicated that the sole electroactive product present following reduction is the species which corresponds to the second reduction wave at -1.34 V in Fig. 1a. Furthermore, this wave is identical to that which is obtained at the same electrode in a solution prepared by dissolution of [MeEtim]₂[UCl₆] in an ionic liquid of the same composition.

Taken together, these results suggest that the first reduction wave consumes two electrons per [UO₂Cl₄]²⁻ ion and is accompanied by a very rapid transfer of oxide ion to the melt with the subsequent formation of the uranium(IV) species, [UCl₆]²⁻, according to the overall reaction defined by eqn. (1). The second redox process must therefore correspond to the reversible electrode reaction given in eqn. (2).



The rate of oxide ion transfer accompanying reaction (1) is exceptionally fast, since no reverse current could be detected following the first reduction wave at a scan rate of 100 V s⁻¹. This suggests that the lifetime of the product generated from this reduction process must be less than 10⁻² s. Rapid oxide ion transfer has also been observed during the reduction of transition metal oxochloro species in room temperature chloroaluminate ionic liquids. Both [TiOCl₄]²⁻ [9] and an oxochloromolybdenum(IV) species which is believed to be [MoOCl₄]²⁻ [10] yield the corresponding hexachlorometalate(III) species upon reduction and give no indication for

the formation of a stable reduced oxochloro intermediate in which the metal is in oxidation state +3.

Results similar to those described above also were obtained when these experiments were undertaken in the 49.0 mol% AlCl₃-[MeEtim]Cl melt at 40 °C.

Supplementary Material

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB12 1EW. Any request should be accompanied by the full literature citation for this communication.

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