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Precipitation of a Dioxouranium(VI) Species from a Room Temperature Ionic Liquid Medium

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The novel complex 1-butyl-3-methylimidazolium μ_4-(*O*,*O*,*O′*,*O′*-ethane-1,2-dioato)-bis[bis(nitrato-*O*,*O*)dioxouranate(VI)] (**1**) has been precipitated from a room-temperature ionic liquid medium containing 1-butyl-3-methylimidazolium nitrate, nitric acid, and acetone. X-ray analysis of complex **1** shows the unit cell contains four $[C_4mim]^+$ cations and two independent $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties, both of which are located about inversion centers. The $[C_4mim]^+$ cations are arranged such that they produce large channels in which the anions are located. This arrangement of $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ groups is unique to this compound. Crystal data for compound **1**: $M = 1154.56$, monoclinic, space group $P2_1/c$, $a = 15.452(2)$ Å, $b = 20.354(3)$ Å, $c = 10.822(4)$ Å, $\beta = 106.84(2)°$, $U = 3258(1)$ Å^{-3}, $Z = 4$, $\mu = 10.023$ mm^{-1}, $R_{int} = 0.0788$.

There is considerable current interest in room-temperature ionic liquid technologies,[1] with a number of recent publications also pointing to the growing interest in their use by the nuclear industries. Beginning with the work of Hitchcock et al.,[2a] the electrochemical and spectrochemical behavior of dioxouranium(VI) species in chloroaluminate room-temperature ionic liquids has been investigated.[2] Costa et al.[2e] recently compared the dioxouranium(VI) and dioxoplutonium(VI) chemical and electrochemical systems in acidic chloroaluminate ionic liquids and presented arguments for the potential use of ionic liquids throughout the nuclear industry. It has been demonstrated that room-temperature ionic liquids can be used for solvent extraction of metal species from aqueous media;[3] this is an area of great significance to the nuclear industry which currently uses solvent extraction in the PUREX process for reprocessing spent nuclear fuel.[4] Recent work from our laboratories has led to the publication of a series of patents concerned with using ionic liquids in nuclear fuel reprocessing and molten salt waste treatment.[5]

The nuclear industry's interest in the oxalate anion, $[C_2O_4]^{2-}$, centers on its use as a thermally labile ligand and/or a precipitating agent.[6] In this Communication, we report the preparation of a novel dimeric dioxouranium(VI) salt, containing both coordinated nitrate and oxalate ligands, in an ionic liquid. This is the first report of the precipitation of a uranium complex from a room-temperature ionic liquid.

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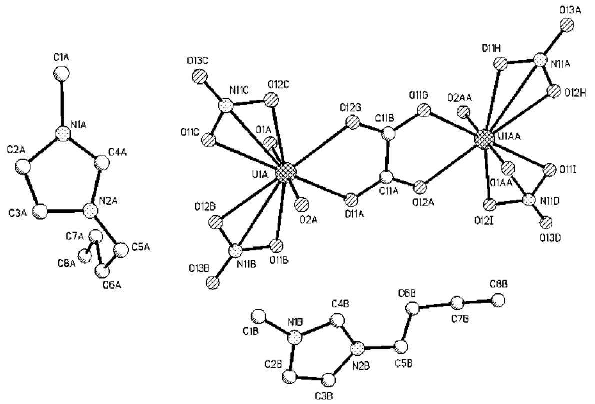

Figure 1. Structure of complex **1** as determined by single-crystal X-ray crystallography. Hydrogen atoms have been removed for clarity.

In a typical synthesis of the dimeric dioxouranium(VI) salt, uranium(IV) dioxide (1 g, *ex* BNFL) was oxidatively dissolved in the ionic liquid 1-butyl-3-methylimidazolium nitrate ([C_4mim][NO_3], 10 g) with concentrated nitric acid (1 g, approximately 10% of the reaction volume) at 70 °C.[5e] This led to the formation of bright yellow solutions of dioxouranium(VI) nitrate. A structured absorbance band at 435 nm in the UV−vis spectrum of the solution confirmed the presence of a dioxouranium(VI) species.[6] Upon cooling, it was not uncommon for a yellow powder to precipitate from the reaction medium.[5c] The amount of precipitate varied even under similar reaction conditions. The yellow powder was then recrystallized from ethanenitrile and identified as 1-butyl-3-methylimidazolium μ_4-(*O*,*O*,*O*′,*O*′-ethane-1,2-dioato)-bis[bis(nitrato-*O*,*O*)dioxouranate(VI)] (**1**) (Figure 1) by single-crystal X-ray diffraction.[7] Comparison of the X-ray powder diffraction pattern of the powder sample with the theoretical pattern generated from the crystal structures shows them to be identical. A manuscript comparing the structure of the solid-state and the solution species is currently being prepared.

It was suspected that the source of the bridging oxalate moiety was an organic species inadvertently coming into contact with the reaction mixture. As acetone is a common organic solvent used in the preparation of ionic liquids and the cleaning of glassware and may be oxidized by nitric acid, it was suggested that this might be the oxalate source. Indeed, studies in the nineteenth century showed that acetone[8] and other aliphatic ketones and aldehydes[9] could be oxidized by nitric acid to give oxalic acid. In fact, it was found that in the complete absence of acetone in the ionic liquid precipitation does not occur.

In the ^{13}C NMR spectra of **1**, there are eight peaks arising from the eight carbon atoms in the [C_4mim]$^+$ cation plus a singlet peak at 177 ppm arising from the oxalate carbon atom. However, when the oxidation of uranium(IV) oxide by nitric acid in [C_4mim][NO_3] was carried out in the presence of either $(CH_3)_2{}^{13}CO$ or $(^{13}CH_3)_2CO$ (*ex* Aldrich), then in both cases, the peak at 177 ppm in the ^{13}C NMR spectra showed a significant increased magnitude relative to the other peaks in the ^{13}C NMR spectra with respect to samples of complex **1** prepared using unlabeled acetone. Further experiments showed that the oxalate source, acetone, can be added either prior to or after oxidative dissolution of UO_2 has occurred. In both cases, the ^{13}C NMR spectra again have a peak at 177 nm.

A search of the Cambridge Structural Database for uranyl oxalate complexes revealed 36 structures. Of these, 26 are polymeric, 6 are dimers with bridging oxalate moieties, and 4 are momomeric. Examination of the six dimeric complexes[10−12] showed that there are two main bridging modes for oxalate anions in conjunction with dioxouranium(VI), namely μ_2-[*O*,*O*′] and μ_4-[*O*,*O*,*O*′,*O*′] coordination. Of the six dimers, three show μ_2-[*O*,*O*′] coordination, whereas the other three, namely $[(H_5O_2)((NO_2)_2\text{benzo-15-crown-5})_2]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ (**2**) and $[(H_3O)(18\text{-crown-6})]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ (**3**) reported by Rogers et al.,[11] and $[(C_2N_2H_{10})_2][(UO_2)_2(\mu_4\text{-}C_2O_4)_3\cdot(i\text{-}Me_2CHNHO)_2]\cdot H_2O$ (**4**) reported by Shchelokov et al.,[12] are, like compound **1**, μ_4-[*O*,*O*,*O*′,*O*′] coordinated.

X-ray analysis of complex **1** shows the unit cell contains four [C_4mim]$^+$ cations and two independent $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties, both of which are located about inversion centers. The [C_4mim]$^+$ cations are arranged such that they produce large channels in which the anions are located (Figure 2). This arrangement of $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ groups is unique to this compound. In complexes **2** and **3**, the lattice is dominated by the presence of the large crown ether molecules, and consequently, the $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties are oriented at 78.7° and 47.2° to one another, respectively.[11] In complex **4**, the anions still contain the bridging oxalate, but there are also two terminal oxalate moieties and two hydroxylamine ligands.[12] The anionic components of complexes **2** and **3** are the same as those found in complex **1**, and the origin of the bridging oxalate moiety is attributed to the presence of impurities in the nitric acid.[11] The preceding ^{13}C NMR experiments indicate that adventitious acetone is the most likely source of the bridging oxalate moiety in these salts, but other organic impurities cannot be ruled out.[8,9]

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(7) Crystallography: Data were collected on a Siemens P4 diffractometer using the XSCANS software with ω scans. A crystal was mounted on the diffractometer at low temperature under dinitrogen at ∼120 K. The structure was solved using direct methods with the SHELXTL program package. Crystal data for compound **1**: $M = 1154.56$, monoclinic, space group $P2_1/c$, $a = 15.452(2)$ Å, $b = 20.354(3)$ Å, $c = 10.822(4)$ Å, $\beta = 106.84(2)°$, $U = 3258(1)$ Å^{-3}, $Z = 4$, $\mu = 10.023$ mm^{-1}, $R_{\text{int}} = 0.0788$. A total of 5100 reflections were measured for the angle range $4° < 2\theta < 45°$, and 4033 independent reflections were used in the refinement. The final parameters were wR2 = 0.1459 and R1 = 0.0584 [$I > 2\sigma$I]. Powder diffraction measurements were performed on a Siemens D5000 powder diffractometer in continuous mode with step size of 0.02° and step time of 1 s.

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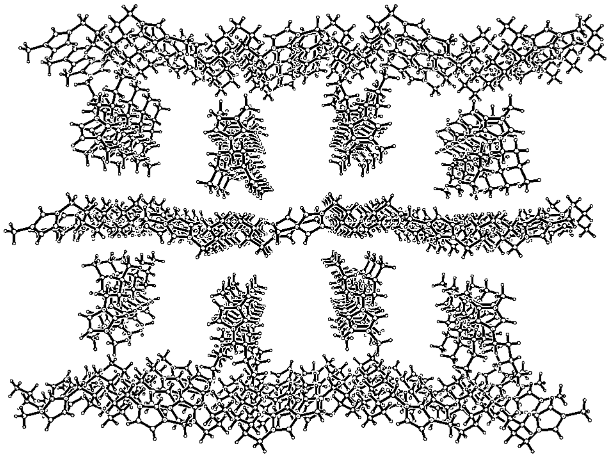

Figure 2. Arrangement of $[C_4mim]^+$ cations in the crystal of complex **1** as determined by single-crystal X-ray crystallography. The $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties are located inside the rectangular holes formed by the $[C_4mim]^+$ cations and have been left out for clarity.

An attempt to adapt this precipitation technique to other metal nitrates, such as Ce^{3+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, and Ni^{2+} and oxides of Fe^{2+}, Mo^{4+}, Re^{2+}, Ru^{2+}, and Zr^{4+}, proved unsuccessful. It is significant that a precipitate is only generated in the presence of Cu^{2+} and Ni^{2+}, and these, probably polymeric, oxalato-containing precipitates are only soluble in ammonia solutions. The initial results from these experiments suggest that the use of acetone as a reagent for producing oxalate ions could be an effective method for separating dioxouranium(VI) from metallic contaminants by selective precipitation of complex **1**, followed by removal from the polymeric compounds with an aqueous or organic wash. The concept is very similar to that proposed by Varga et al.,[13] wherein they precipitated a dioxouranium(VI) nitrate complex of *N*-cyclohexyl-2-pyrrolidone from aqueous solution of 7 mol L^{-1} nitric acid.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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