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Crystallization of Uranyl Salts from Dialkylimidazolium Ionic Liquids or Their Precursors

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The interaction of uranyl nitrate hexahydrate with three ionic liquids and one ionic liquid precursor with minimal solvent addition led to the isolation and crystallographic characterization of four new uranyl salts: bis(1,3-dimethylimidazolium) bis-μ-hydroxo-bis[bis(nitrato-*O*,*O*)dioxouranate(VI)], bis(1-ethyl-3-methylimidazolium) bis-μ-hydroxo-bis[bis(nitrato-*O*,*O*)dioxouranate(VI)], bis(1,2,3-trimethylimidazolium) bis-μ-hydroxo-bis[bis(nitrato-*O*,*O*)dioxouranate(VI)], and bis(1-ethyl-3-methylimidazolium) trichlorobis(nitrato-*O*,*O*)dioxouranate(VI). Each ion in the four isolated salts has precedence in the crystallographic literature, although the exact combinations of ions we observe in these salts are new. Some interesting differences in the packing of the ions can be related to the lack of an acidic C2-H ring hydrogen atom in the 1,2,3-trimethylimidazolium cation. It is suggested that future studies of these reactions be carried out under more strictly anhydrous conditions.

Introduction

Recently, there has been a growing interest in investigating the potential use of Ionic Liquids (ILs, typically defined as salts which melt below 100 °C)[1] in many new applications. The older focus on the solvent properties of ILs has led to the development of an extensive and diverse range of ions (ranging from simple, mononuclear to complex) which can form ILs, and to the exploration of materials applications utilizing the novel physical, chemical, and biological properties of the newly reported ILs.[2] While we also continue to be interested in such applications of ILs as materials, the rapidly growing numbers of ions being shown to form ILs might still lead to some unique solvent applications.

In this context, we and others have been particularly interested in study of the behavior of f-element salts dissolved in or comprising ILs or solutions and many high quality experimental and theoretical studies have appeared.[3] Recently, however, our attention has been drawn to what *solid state phases* might be crystallized from these unique, totally ionic solutions at ambient temperatures which ILs provide, and if these phases might be related to their high temperature molten salt analogs. We believe that such totally ionic solutions will allow the isolation of novel metal coordination geometries and coordination numbers, thus far not observed when crystallizing from molecular solvents. We also believe that the large, asymmetric ions typical of many ILs will provide unique packing frustration which must be overcome and this too should lead to unique structures. However, without any guidelines or rules-of-thumb to guide this work, we also expect that a number of routine crystalline materials will also be isolated and indeed some of these have also appeared.[4]

Here we will focus on our early work studying the crystallization of uranyl complexes from dialkylimidazolium ILs or by reaction with IL precursors, including the use of molecular solvents to help solubilize the uranyl salts. Only a few uranyl salts have been crystallized from ILs and crystallographically characterized. These typically consist of complex uranyl anions charged balanced with dialkylimidazolium cations. Examples include a series of salts of 1-alkyl-3-methylimidazolium cations and either oxalate-bridged uranyl anion dimers of the formula $[(UO_2)_2(NO_3)_4(C_2O_4)]^{2-}$ or uranyl tetranitrate anions $[UO_2(NO_3)_4]^{2-}$ reported by Bradley et al.,[5,6] and a uranyl tetrabromide reported by Nockemann et al.[7]

There are of course other examples of crystallographically characterized uranyl salts of imidazole-based cations or neutral imidazoles. The early uranyl-imidazolium structures reported were obtained from combination of neutral imidazoles and uranyl salts leading to the protonation of imidazole to imidazolium. The solid state compounds isolated typically consist of negatively charged uranium species (mononuclear or dinuclear) charge balanced by imidazolium cations. For example, salts of $[UO_2Cl_4]^{2-}$ with pro-

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tonated imidazolium cations ([HIm]$^+$) reported by Perry et al., were obtained in the reaction of $UO_2Cl_2{\cdot}3H_2O$ with neutral imidazole in an acidic environment.[8,9] Norquist et al.,[10] reacted UO_2SO_4(propylamine)$_2$ with neutral imidazole which resulted in the formation of an anionic uranyl sulfate coordination polymer, $[(UO_2)(SO_4)_3]_n[HIm]_{2n}$ where the protonated imidazolium cations charge balance the anion. Also a few other examples of neutral uranyl complexes crystallized with neutral imidazoles have been reported.[11–13]

Some of the more interesting isolated structures have actually been a result of IL impurities (e.g., the notoriously hard to remove alkylimidazole and the ubiquitous water). The first reported structure of an imidazole coordinating to a uranium atom was crystallized from ionic liquid and recently reported by our group.[14] Although it was later prepared reproducibly by reacting uranyl acetate and 1-methylimidazole in [C$_4$mim]Cl as solvent, it was originally isolated as an unintended product in the mixture of uranyl acetate and [C$_4$mim]Cl, where 1-methylimidazole was present as an impurity.

Here we present our initial results attempting to dissolve and crystallize uranyl salts from ILs. In these examples, we included the use of a molecular solvent to assist in getting the salts to completely dissolve or in one case react appropriately; however, none of the molecular solvents appeared in the crystal structures. The overall results, while not earth shattering, are but our first step on the road to understanding the complexity of these systems, the role of impurities in directing the results, and the subtlety of multiple weak interactions which dictate the final structural results.

Results and Discussion

Synthesis and Crystallization

Figure 1 provides an overview of the crystallization experiments discussed in this report. Our overall strategy in this study was to compare the solubility and crystallization of uranyl nitrate hexahydrate from a) two ILs whose anions possessed quite different coordinating abilities, and b) by combination in solution with two IL precursors where in situ generation of IL-like systems might be observed. For the first strategy, we chose the highly coordinating chloride (Cl^-) anion and the much lower coordinating 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide ([TSAC]$^-$) anion paired with 1-ethyl-3-methylimidazolium (C_2mim^+) cations. The second strategy involved co-dissolution of uranyl nitrate hexahydrate with the zwitterionic 1,3-dimethylimidazolium-2-carboxylate[15] or the salt 1,2,3-trimethylimidazolium methyl carbonate[16] ([C$_1$mmim][MeCO$_3$]), both being previously shown as suitable IL precursors. In every case it was found necessary to include a molecular solvent to assist in dissolution of the salts or substrates.

[C$_1$mim]$_2$[(UO$_2$)$_2$(μ-OH)$_2$(NO$_3$)$_4$] (4). Compound **4** was formed after reacting 0.1 mmol each of $UO_2(NO_3)_2{\cdot}6H_2O$ and 1,3-dimethylimidazolium-2-carboxylate under reflux conditions in 10 mL of acetonitrile (Figure 1, a). The reaction mixture was filtered, while hot, to remove any unreacted starting material and the solvent was slowly evaporated leading to the formation of yellow, needle-like single crystals which were used for the X-ray diffraction analysis.

Based on results of our previous work with zwitterionic 1,3-dimethylimidazolium-2-carboxylates (1,3-dimim-2-COO), we believe that the reaction proceeds via decarboxylation of the 1,3-dimim-2-COO zwitterion and the formation of 1,3-dimethylimidazolium cation. For this reaction to proceed, the presence of an acidic proton is required.[15] Here, such an acidic proton could only come from uranyl dinitrate hexahydrate as it forms bridged bis-μ-hydroxo-bis[bis-(nitrato-*O*,*O*)dioxouranate(VI)] through hydrolysis of water molecules.

It is interesting to note that literature examples exist where 4,5-dicarboxylic acid-substituted neutral imidazole was treated with uranyl dinitrate hexahydrate without decarboxylation and the resulting crystal structures show the –COO$^-$ groups are coordinated to the uranyl center.[12] Such major differences in the reactivity of the 2-carboxylate group in our study most likely arise from the much lower stability of the protonated 2-carboxylic acid in comparison to the known greater stability of the 4-COOH adduct.[15]

The acidic nature of the uranyl dinitrate hexahydrate can also explain the formation of bridged bis-μ-hydroxo-bis[bis-(nitrato-*O*,*O*)dioxouranate(VI)] species upon reaction with ILs or IL precursors. As shown by Choppin,[17] uranyl ions have a negative reduction potential and at pH levels below neutral, the formation of $UO_2(OH)_2$ species is expected. In the crystallization of **4**, the acidic proton undergoes further reaction with the zwitterionic 1,3-dimethyl-2-carboxylate as discussed above.

[C$_2$mim]$_2$[(UO$_2$)$_2$(μ-OH)$_2$(NO$_3$)$_4$] (5). Compound **5** was isolated after the dissolution of 0.099 mmol of $UO_2(NO_3)_2{\cdot}6H_2O$ in 0.12 mmol of [C$_2$mim][TSAC] at room temperature in the minimum amount of dichloromethane (2 mL) needed for dissolution (Figure 1, b). After two days of slow evaporation at room temperature, yellow needle-like crystals were selected and analyzed by X-ray diffraction. The hydroxide bridged dianion in **5** is the same as observed for **4**. In the formation of crystalline **5**, the $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]^{2-}$ anion preferentially crystallizes with the ILs $[C_2mim]^+$ cation.

[C$_1$mmim]$_2$[(UO$_2$)$_2$(μ-OH)$_2$(NO$_3$)$_4$] (6). Compound **6**, was prepared by reacting 0.096 mmol $UO_2(NO_3)_2{\cdot}6H_2O$ with 0.084 mmol [C$_1$mmim][MeCO$_3$] in 10 mL of dichloromethane at 70 °C for 6 h (Figure 1, c). The unreacted material was filtered while the solution was hot, and the remaining solution was allowed to slowly evaporate under ambient conditions. Yellow crystals formed after a few days. Once again, we note the formation of the $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]^{2-}$ anion which preferentially crystallizes with the ILs $[C_1mmim]^+$ cation. In this case, we believe, but have not yet proven, that the acidic proton will protonate the methyl carbonate anion leading to the decomposition reaction which forms MeOH, CO_2, and H_2O, as shown in one of our recent publications.[16]

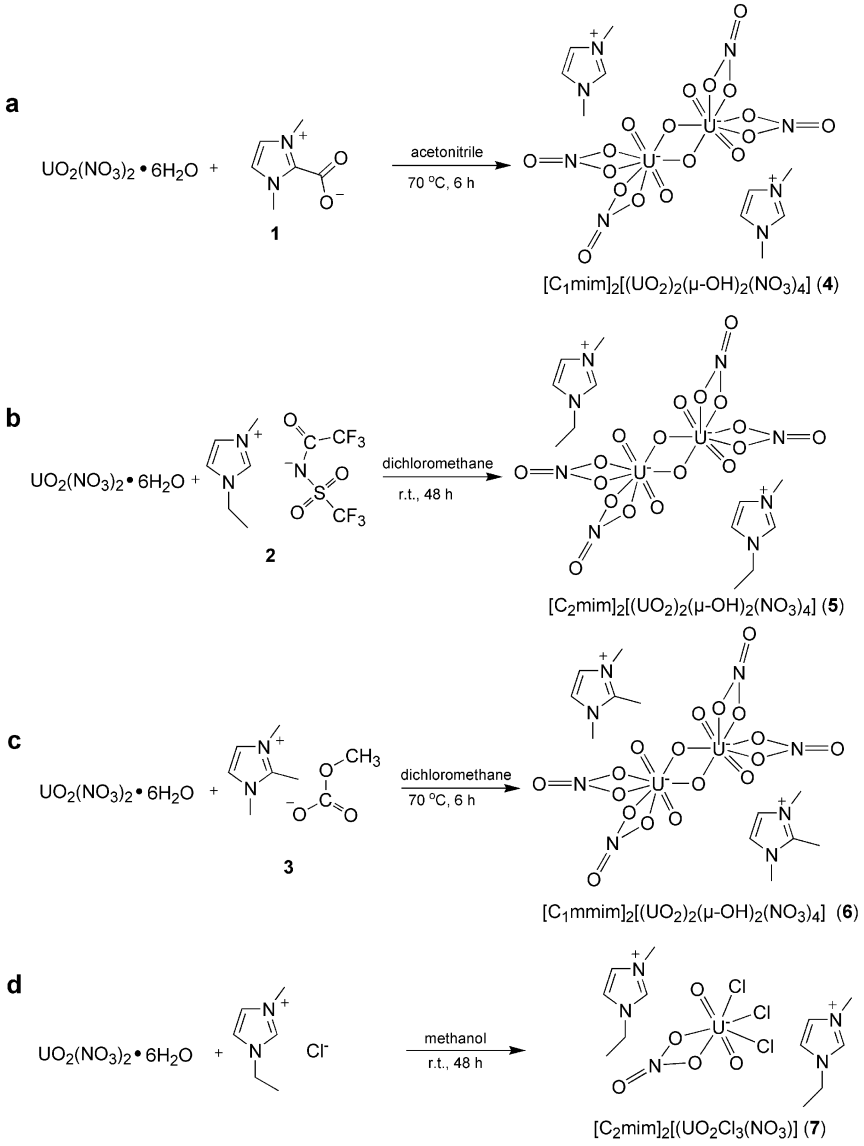

Figure 1. Crystallization of uranyl salts via molecular solvent-assisted dissolution in dialkylimidazolium ILs or reaction with IL precursors. Other reaction products are not shown.

$[C_2mim]_2[UO_2Cl_3(NO_3)]$ (7). Compound **7** was formed after reacting 0.4 mmol of $UO_2(NO_3)_2{\cdot}6H_2O$ and 0.09 mmol $[C_2mim]Cl$ in 2 mL of methanol at room temperature. Slow evaporation of the solvent resulted in the formation of yellow crystals of **7** which were used for X-ray data collection. In contrast to **4**, **5**, and **6**, the reaction of $UO_2(NO_3)_2{\cdot}6H_2O$ and $[C_2mim]Cl$ did not result in hydrolysis. The lack of hydrolysis of uranyl species in the presence of chloride ions was recently investigated and supported by the spectroscopic analysis of chloride complexes of Np^{IV} and Pu^{IV} in $[C_4mim][NTf_2]$,[18] where it was reported that the presence of water did not influence the absorption spectra of $[NpCl_6]^{2-}$ and $[PuCl_6]^{2-}$ species in this IL.

Crystallographic Results

Each ion in the four isolated salts has precedence in the crystallographic literature, although the exact combinations of ions we observe in these salts are new. The ions themselves do not exhibit widely different structural parameters than previously observed examples, therefore here we will briefly review any subtle differences in the ions themselves and any unique packing effects which result from the different cations.

Along these lines, it is interesting to note the similarity in the packing of **4** and **5** which contain dialkylimidazolium cations containing the acidic C2 (between the nitrogen atoms) ring hydrogen atom and their differences with the packing in **6** where this position is blocked with a methyl substituent. To review this, let us first describe the structures of each salt individually.

Salts **4**–**6** all crystallize in the monoclinic space group $P2_1/n$ and consists of a uranyl dimer dianion $\{[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]^{2-}\}$ residing around a crystallographic center of inversion and charged balanced by two organic cations (Figure 2). A search of the Cambridge

Crystallographic Database[19] found only 10 other examples of this dimer[20] such as the representative example reported by Perry obtained at low pH from a mixture of imidazole and uranyl nitrate.[5] In all literature reported cases the counter cation is relatively large, for example imidazolium,[5] tetrabutylammonium,[21] or 4,4′-dipyridinium.[22] This makes sense given that the small charge to size ratio found for these and many IL cations can reduce the electrostatic interaction between the large uranyl dimers and effectively pack in space. Given the relative ease with which these have been isolated here, we expect many more examples will be forthcoming as ILs are further explored for crystallization of uranyl species.

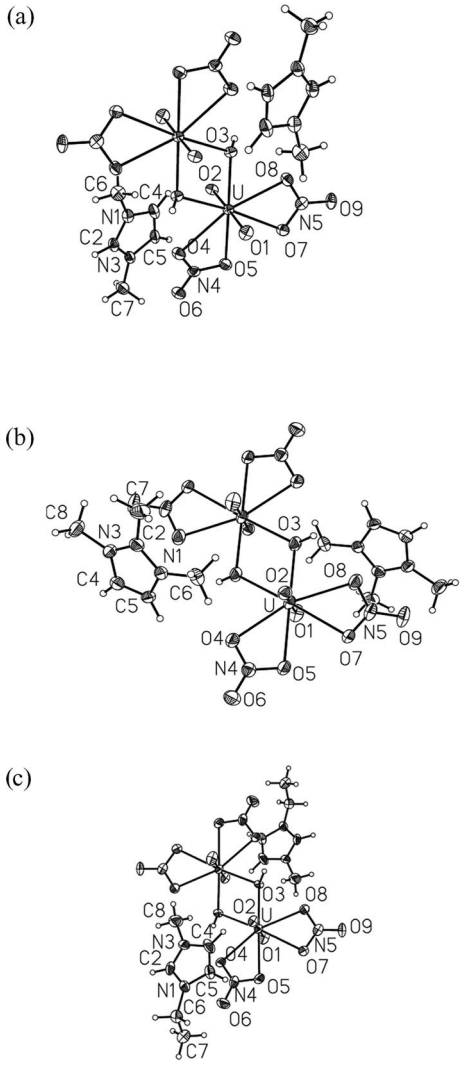

Figure 2. Formula units (ORTEP, 50% probability ellipsoids) for **4** (a), **5** (b), and **6** (c).

In each dianion, the uranium atoms have slightly distorted hexagonal bipyramidal geometry with two bidentate terminal nitrates and two bridging hydroxides in the hexagonal plane and nearly linear O1–U–O2 angles (Table 1). There are some differences, however, between the anions in **4** and **5** vs. **6**. In **4** and **5**, the bidentate nitrate anions are each coordinated in an asymmetric fashion, while in **6** each unique nitrate is symmetrically bound, but the two nitrates have different distances from the uranium. Of the 10 structures containing this anion found using the CSD, only two have inequivalent nitrate groups with symmetric bonds as observed in **6**. The distances and asymmetry in **4** and **5** are more consistent with similar uranyl dimers reported in the literature.[11,23]

Table 1. Selected bond lengths [Å] and angles [°] in the anions of **4**, **5**, and **6**.

Compound	**4**	**5**	**6**
Distances:			
U=O1	1.774(3)	1.775(7)	1.778(3)
U=O2	1.782(3)	1.786(7)	1.775(3)
U–O3	2.322(3)	2.322(7)	2.334(3)
U–O3[a]	2.325(3)	2.323(6)	2.345(3)
U–O4	2.540(3)	2.552(7)	2.536(3)
U–O5	2.559(3)	2.579(7)	2.530(3)
U–O7	2.548(4)	2.543(8)	2.517(3)
U–O8	2.511(3)	2.508(7)	2.517(3)
U···U[a]	3.867(1)	3.871(2)	3.951(9)
Angles:			
O1–U–O2	177.3(1)	177.9(3)	176.3(1)
U–O3–U[a]	112.7(1)	112.9(3)	115.2(1)

[a] Symmetry code: $-x$, $-y$, $-z$.

The O1–U–O2 angle in **6** [176.4(1)°] is further from linearity than either those in **4** [177.3(1)°] or **5** [177.8(3)°] and the overall U···U separation within each dimer is longer in **6** [3.951(9) Å] than in **4** [3.867(1) Å] and **5** [3.871(2) Å]. In the structure of **6**, the bridging U–O_{OH} distances of 2.334(3) Å and 2.345(3) Å are longer and more asymmetric than in the structures **4** and **5**. The difference in the U–O_{OH} distances between structure **6** vs. **4** and **5**, may be related to the lack of hydrogen bonding observed for the hydroxide bridges in **6** resulting in a greater π-donation ability of the oxygen to the uranium atom. This extra electron density on the U atoms, can increase the electrostatic repulsion of the proximal uranium atoms, resulting in the lengthening of the distance between the two U atoms in the dimer as noted earlier.

The small differences between the observed structural parameters of the anions in **4** and **5** vs. **6**, might have their origin in the completely different packing and hydrogen bonding observed for the first two vs. the latter. Compounds **4** and **5** pack as alternating one dimensional cation and anion columns along the crystallographic *a* axis (see parts a, b in Figures 3 and 4) with the $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]^{2-}$ anions hydrogen bonded via donation from the hydroxo bridges to axial uranyl oxygen atoms in neighboring anions [O3–H···O 2.06(7) Å in **4**, and 2.141(7) Å in **5**].

In **6**, however, there are no such hydrogen bonds between the anions, rather the anions form chains via short contacts between the two inequivalent nitrates [Figure 3 (c), O9···N4 2.996(5) Å]. This results in some distortion of the coordination of one of the nitrate groups (the nitrate group with shorter O–U bonds) which is bent out of the uranium's hex-

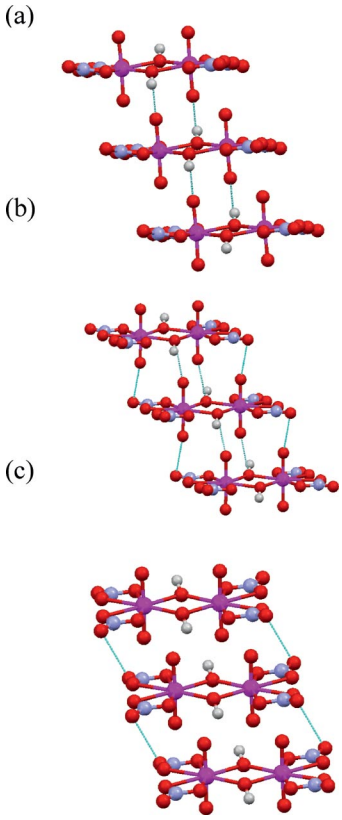

Figure 3. Anion-anion contacts less than the sum of the van der Waals radii in **4** (a), **5** (b), and **6** (c).

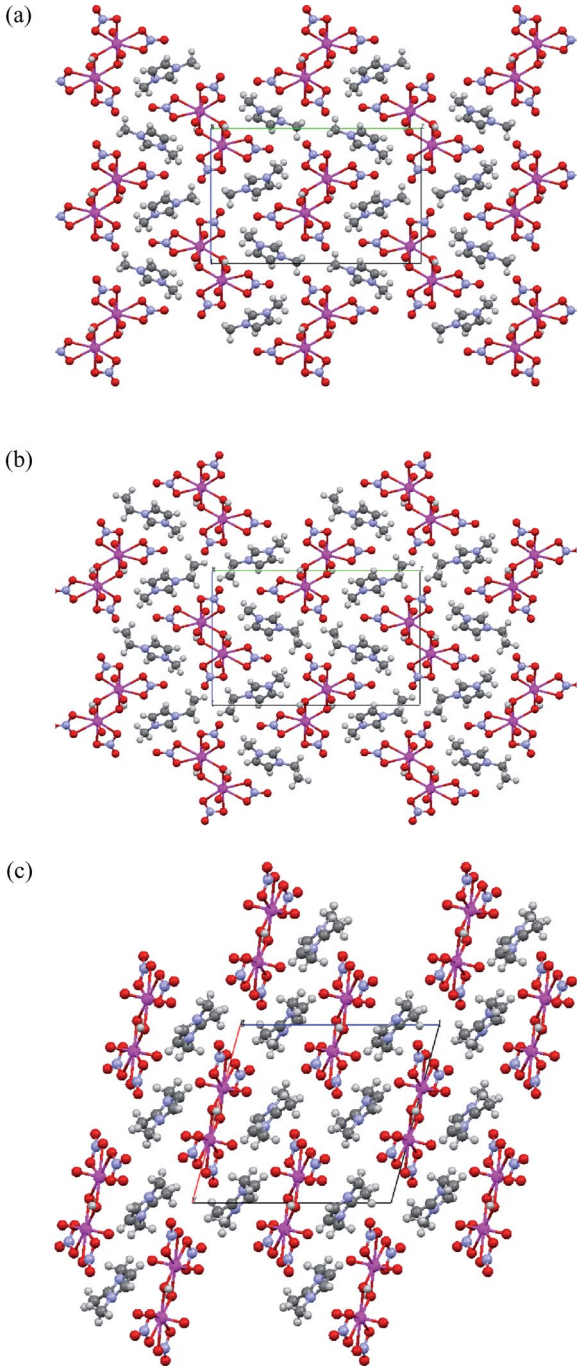

Figure 4. Packing diagrams for **4** (a) and **5** (b) along the *a* axis and **6** (c) along the *b* axis.

agonal coordination plane by 12.55°; the only such distorted nitrate coordination in **4**–**6**. The overall packing in **6** which results consists of alternating 2-dimensional layers of cations and anions (Figure 4, c).

Anion-anion interactions between $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]^{2-}$ anions have been reported to take place through the bridging hydroxo groups and either the terminal oxygen atoms of the nitrate groups (coordinated in a bidentate fashion to the uranyl center)[23] or the axial oxygens.[24] In addition to hydrogen bonding a very short contact is observed in **4** [2.895(5) Å] and **5** [2.83(1) Å] between the axial oxygen atom, O1, and the nitrogen atom, N5, from the nitrate group coordinated to the uranyl center from adjacent anions in the columnar arrangement, probably as a consequence of the geometric constraints resulting from the very strong short contacts between O2 and H1O3 from the adjacent anions. Such interactions are not observed in compound **6**.

In **4** and **5**, the cations are not situated in the same planes as the anionic dimers, but interact through short contacts. The C2–H from the imidazolium rings in compound **4**, form bifurcated short contacts with nitrate oxygen atoms O7 and O5 in an adjacent anion, explaining the asymmetry in the coordination of these nitrates to uranium. Hydrogen atoms H6A and H7A from the methyl groups interact through short contacts with the terminal oxygen atoms from the nitrate groups of the same anion mentioned above (Figure 5, a). The acidic ring hydrogen atom on C5 interacts through short contacts with O4 and O6 from a different neighboring anion (Figure 5, a). The hydroxo bridge in **4** acts not only as a hydrogen-bond donor as described above but also has a potential acceptor interaction with the hydrogen atom, H6B, from one of the methyl groups [O3···H6B 2.573(3) Å]. There are no π-π type stacking interactions between the imidazolium cations, suggesting that the anion-anion and anion-cation interactions play the most important roles in crystal packing.

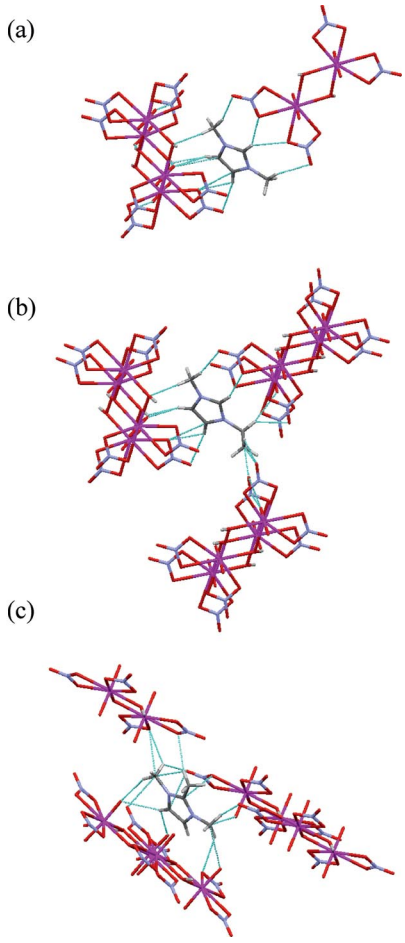

Figure 5. Cation-anion contacts less than the sum of the van der Waals radii in **4** (a), **5** (b), and **6** (c).

The most relevant anion-cation close contacts in **4**–**6** are depicted in Figure 5. Although there are more short contacts in **5** than in **4**, the orientation of the cation with respect to the anions is almost exactly the same, and most of the contacts present in **4** are also observed in **5**. Each of these cations has an acidic hydrogen (C2–H) which forms a relatively short contact with a nitrate oxygen atom from a neighboring anion. The two other less acidic ring hydrogen atoms at C4 and C5 also participate in short contacts with oxygen atoms of other neighboring anions.

The packing of the anions and cations in **6** is quite different as noted above. Here, each cation is surrounded by five anions (Figure 5, c). The acidic C2 position is blocked with a methyl substituent and although the C5–H atom makes close contacts with anion oxygen atoms, the packing is clearly different.

$[C_2mim]_2[UO_2Cl_3(NO_3)]$ (7). **7** crystallizes in the crystallographic space group *C*2/*c* with one-half anion and one cation in the asymmetric unit (Figure 6). The uranium is pentagonal bipyramidal with U, Cl1, N4, and O3 residing on a twofold axis. The axial uranyl oxygen atoms are 1.779(3) Å from uranium and form a O1–U–O1^a bond angle of 175.3(2)°.

The equatorial nitrate oxygen atoms and the chloride atoms complete the coordination to uranium with U–O2 2.531(3) Å and U–Cl1 and U–Cl2 2.673(2) and 2.688(1) Å, respectively. A Cambridge Crystallographic Database search revealed only one compound[25] having a similar anion and the bond lengths and angles are comparable to those found for **7** (Table 2).

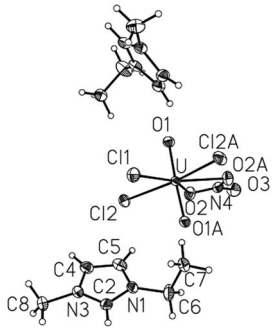

Figure 6. Formula unit (ORTEP, 50% probability ellipsoids) for **7**.

Table 2. Bond lengths [Å] and angles [°] in $UO_2Cl_3(NO_3)$ (**7**) and a related structure.

Compound	**7**	$[C_{14}H_{23}N_2O]_2[UO_2Cl_3(NO_3)]$[25]
Distances:		
U–O1	1.779(3)	1.76(1), 1.75(1)
U–O2	2.531(3)	2.53(1), 2.51(1)
U–Cl1	2.673(2)	2.712(6)
U–Cl2	2.688(1)	2.676(5), 2.705(5)
Angles:		
O1–U–O1[a]	175.2(2)	177.6(5)
O1–U–O2	87.8(1)	88.4(4)
O1–U–Cl1	92.37(8)	94.1(4)
O2–U–O2	50.23(8)	49.8(4)
Cl1–U–Cl2	82.46(4)	83.9(1), 83.0(2)
O2–U–Cl2	72.43(6)	72.7(3), 70.9(3)

[a] Symmetry code: 1 – *x*, *y*, 1.5 – *z*.

Each cation is involved in short contacts with 4 anions (Figure 7). The shortest of these involve the acidic ring protons where C2–H is only 2.943(1) Å from Cl1. The other acidic ring hydrogen atoms, C4–H and C5–H, interact through short contacts with O2 from the nitrate group and O1 from the uranyl, respectively. Other short contacts are noted in Figure 7.

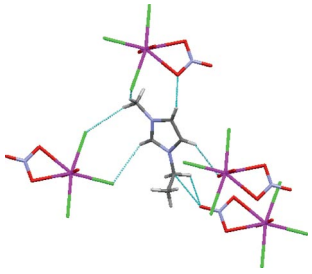

Figure 7. Cation-anion contacts less than sum of the van der Waals radii in **7**.

The overall packing of the ions in **7** is depicted in Figure 8. Alternating layers of anions and cations pack along the crystallographic *a* axis. The short contacts between the equatorial chloride atoms, the axial oxygen atoms, and the

nitrate oxygen atoms to the cation hydrogen atoms above and below the anionic region support the observed packing. The structure reported by Indira et al.[25] crystallizes in a different space group, and this packing Scheme is notably different, where the anions are arranged in columns along the glide planes and surrounded by cations.

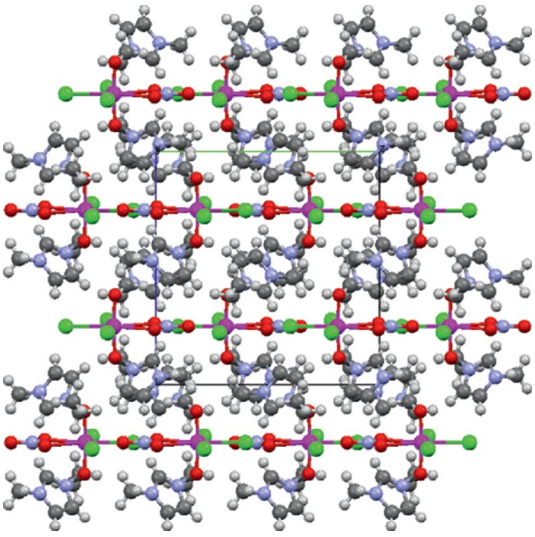

Figure 8. Packing diagram for **7** along the *a* axis.

Conclusions

It is clear from the overall results that this chemistry should in general, be carried out under more carefully controlled conditions. Such conditions should include precise control of moisture, whether from salts, solvents, or the atmosphere, as well as an understanding of any impurities which might contaminate starting salts, ILs, and solvents.

We note, however, that the highly ionic media of many legacy nuclear wastes are rich in water, nitrate, chloride, sulfate, and many organic and inorganic species. As we continue to search for models to these systems, perhaps results such as those presented here can continue to provide useful data which can form a basis for improving our understanding of uranyl speciation in these complex media.

Individually, the crystallographic results presented here are not particularly exciting. Once the chemistry leading to the formation of the complex uranyl ions is rationalized, the resulting crystallized species make sense. Nonetheless, the subtleties which will come to light as we explore numerous additional examples might be important in a future understanding of both how these types of compounds will crystallize, but also in how we might use them to *prevent* crystallization of more complex liquid salts with stoichiometric amounts of uranyl ions. We will thus continue to report both our mundane and novel results as we explore the chemistry of the 5f elements in ionic liquids.

Experimental Section

General: Uranyl nitrate hexahydrate was purchased from Alfa Aesar (Ward Hill, MA). [C_2mim]Cl was supplied as a gift by Solvent Innovation GmbH (Köln, Germany). All chemicals were used as received. All other chemicals were of reagent grade and were purchased from Aldrich Chemicals (Milwaukee, WI) and used without further purification.

1,3-Dimethylimidazolium-2-carboxylate (**1**) was synthesized and purified according to a literature procedure.[26] 1-Ethyl-3-methylimidazolium 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide (**2**) was prepared by a methodology reported by Matsumoto et al.[27] All salts were analyzed by NMR and the data agree with the literature values.

1,2,3-Trimethylimidazolium Methyl Carbonate (3): Dimethyl carbonate (0.05 mol) and 1,2-dimethylimidazole (0.03 mol) were combined and heated in a sealed screw-top pressure tube for 10 d at 77 °C. During the reaction process, the initially clear solution started to change color to light-yellow. After cooling the reaction mixture, a light-yellow powder was formed in a pale yellow supernatant liquid. The product was separated by decantation and washed three times with fresh, cold, dry acetone to remove all byproducts. 1,2,3-Trimethylimidazolium methyl carbonate was separated as a white powder in 80% yield and its purity was confirmed by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.74 (s, 3 H), 3.45 (s, 3 H), 3.94 (s, 6 H), 7.74 (s, 2 H) ppm.

Bis(1,3-dimethylimidazolium) Bis-μ-hydroxobis[bis(nitrato-*O*,*O*)dioxouranate(VI)], [C_1mim]$_2$[$(UO_2)_2$(μ-OH)$_2$(NO_3)$_4$] (4): The synthesis of **4** was carried out in a hood by reacting 0.05 g (0.1 mmol) of $UO_2(NO_3)_2{\cdot}6H_2O$ and 0.014 g (0.1 mmol) of 1,3-dimethylimidazolium-2-carboxylate in 10 mL of acetonitrile with magnetic stirring at about 70 °C for 6 h in a 20 mL borosilicate glass vial. The reaction mixture was filtered, while hot, to remove any unreacted starting material and then left on the bench top at room temperature to slowly evaporate the remaining acetonitrile. After three days, yellow crystals of **4** formed and suitable crystals for X-ray data analysis were selected.

Bis(1-ethyl-3-methylimidazolium) Bis-μ-hydroxobis[bis(nitrato-*O*,*O*)-dioxouranate(VI)], [C_2mim]$_2$[$(UO_2)_2$(μ-OH)$_2$(NO_3)$_4$] (5): The synthesis of **5** was conducted at room temperature by contacting 0.050 g of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.099 mmol) with 0.043 g [C_2mim][TSAC] (0.12 mmol) in a 20 mL borosilicate glass vial whilst stirring in 2 mL of dichloromethane which resulted in a clear yellow solution. The mixture was kept at ambient conditions in order to allow the volatile solvent to evaporate. After two days, yellow crystals of **5** formed and good quality crystals were selected for single X-ray diffraction analysis.

Bis(1,2,3-trimethylimidazolium) Bis-μ-hydroxobis[bis(nitrato-*O*,*O*)-dioxouranate(VI)], [(C_1mmim)$_2$][$(UO_2)_2$(μ-OH)$_2$(NO_3)$_4$] (6): The synthesis of **6** was carried out in the hood by reacting 0.05 g (0.096 mmol) of $UO_2(NO_3)_2{\cdot}6H_2O$ and 0.0156 g (0.084 mmol) of [C_1mmim][$MeCO_3$] in 10 mL of dichloromethane at ca. 70 °C for 6 h in a 20 mL borosilicate glass vial. The unreacted material was filtered while the solution was hot, and the filtered solution was allowed to slowly evaporate under ambient conditions. After a few days, small yellow crystals of **6** formed and suitable crystals for single-crystal X-ray diffraction analysis were isolated.

Bis(1-ethyl-3-methylimidazolium) Trichlorobis(nitrato-*O*,*O*)dioxouranate(VI), [C_2mim][$UO_2C1_3(NO_3)$] (7): **7** was synthesized by reacting 0.060 g (0.4 mmol) of [C_2mim][Cl] and 0.045 g (0.090 mmol) of $UO_2(NO_3){\cdot}6H_2O$ whilst stirring in 2 mL of methanol in a 20 mL borosilicate glass vial. Slow evaporation of methanol led to the formation of yellow crystals of **7** which were isolated and used for X-ray data collection.

Single Crystal X-ray Diffraction: Compounds **4**–**7** were characterized by their single-crystal X-ray structures. Due to the radioac-

tive nature of natural uranium and the need to license its use at The University of Alabama, typical elemental analysis and spectroscopic characterizations are not routinely performed. The X-ray data were collected on a Bruker SMART diffractometer equipped with a CCD area detector using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. For each compound, a single crystal was mounted on a glass fiber and transferred to the goniometer for data collection. The crystals were cooled to –100 °C under a cold nitrogen gas stream. The structures were solved using the SHELXTL software package[28] and the absorption corrections were made with SADABS.[29] The structures were refined by full-matrix least-squares on F^2. All non-hydrogen atoms were readily located and their positions refined anisotropically. Hydrogen atom positions for all the hydrogen atoms except the hydroxo bridges were added at idealized positions. The hydrogen atoms from the hydroxo bridges in compounds **4**–**6** were easily located from the Fourier difference map; that in **4** was allowed to refine isotropically and those in **5** and **6** were refined using the riding model.

Crystal Data for 4: $C_{10}H_{20}N_8O_{18}U_2$, M = 1016.40; monoclinic, space group $P2_1/n$, a = 5.5633(11), b = 18.500(4), c = 11.949(2) Å, β = 92.63(3)°, U = 1228.5(4) Å^3, Z = 2, D_c = 2.748 g/cm^3, μ = 13.263 cm^{-1} (Mo-K_α, λ = 0.71073 Å), T = 173 K, $R(F^2 > 4\sigma)$ = 0.0263, $R_w(F^2$ all data) = 0.0651, goodness-of-fit = 1.020 for all 2976 unique data (8213 measured, R_{int} = 0.0306, $2\theta < 28.21$) and 181 refined parameters.

Crystal Data for 5: $C_{12}H_{24}N_8O_{18}U_2$, M = 1044.45; monoclinic, space group $P2_1/n$, a = 5.573(4), b = 19.386(14), c = 12.669(9) Å, β = 96.053(12)°, U = 1361.0(17) Å^3, Z = 2, D_c = 2.549 g/cm^3, μ = 11.976 cm^{-1} (Mo-K_α, λ = 0.71073 Å), T = 173 K, $R(F^2 > 4\sigma)$ = 0.0343, $R_w(F^2$ all data) = 0.1167, goodness-of-fit: 1.212 for all 1933 unique data (5355 measured, R_{int} = 0.0424, $2\theta < 26.41$) and 183 refined parameters.

Crystal Data for 6: $C_{12}H_{24}N_8O_{18}U_2$, M = 1044.45; monoclinic, space group $P2_1/n$, a = 13.255(3), b = 7.3789(14), c = 14.265(3) Å, β = 105.087(3)°, U = 1347.2(4) Å^3, Z = 2, D_c = 2.575 g/cm^3, μ = 12.099 cm^{-1} (Mo-K_α, λ = 0.71073 Å), T = 173 K, $R(F^2 > 4\sigma)$ = 0.0180, $R_w(F^2$ all data) = 0.0456, goodness-of-fit: 1.059 for all 1940 unique data (5799 measured, R_{int} = 0.0234, $2\theta < 23.27$) and 184 refined parameters.

Crystal Data for 7: $C_{12}H_{22}Cl_3N_3O_5U$, M = 660.73; monoclinic, space group $C2/c$, a = 12.839(4), b = 12.550(4), c = 13.039(4) Å, β = 92.960(5)°, U = 2098(1) Å^3, Z = 4, D_c = 2.092 g/cm^3, μ = 8.149 cm^{-1} (Mo-K_α, λ = 0.71073 Å), T = 173 K, $R(F^2 > 4\sigma)$ = 0.0217, $R_w(F^2$ all data) = 0.0538, goodness-of-fit: 1.056 for all 1510 unique data (4551 measured, R_{int} = 0.0236, $2\theta < 23.30$) and 122 refined parameters.

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