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Ionothermal synthesis of uranyl compounds that incorporate imidazole derivatives

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ABSTRACT

Ionothermal reactions of uranyl nitrate with various salts in methylimidazolium-based ionic liquids have produced single crystals of three uranyl compounds that incorporate imidazole derivatives as charge-balancing cations. $(C_4H_7N_2)[(UO_2)(PO_3F)(F)]$ (**1**) crystallizes in space group *C*2, $a=17.952(1)$ Å, $b=6.9646(6)$ Å, $c=8.5062(7)$ Å, $\beta=112.301(1)^\circ$, $(C_6H_{11}N_2)_2[(UO_2)(SO_4)_2]$ (**2**) crystallizes in space group $C2/c$, $a=31.90(1)$ Å, $b=9.383(5)$ Å, $c=13.770(7)$ Å, $\beta=93.999(7)^\circ$ and $(C_6H_{11}N_2)[(UO_2)_2(PO_4)(HPO_4)]$ (**3**) crystallizes in space group $P2_1/n$, $a=9.307(2)$, $b=18.067(4)$, $c=9.765(2)$, $\beta=93.171(2)$. The U^{6+} cations are present as $(UO_2)^{2+}$ uranyl ions coordinated by three O atoms and two F atoms in **1** and five O atoms in **2** and **3** to give pentagonal bipyramids. The structural unit in **1** is composed of F-sharing dimers of uranyl pentagonal bipyramids linked into sheets through corner-sharing fluorophosphate tetrahedra. The structural unit in **2** is composed of uranyl pentagonal bipyramids with one chelating sulfate tetrahedron linked into chains by three other corner-sharing sulfate tetrahedra. In **3**, the structural unit is composed of chains of uranyl pentagonal bipyramids linked into sheets through edge- and corner-sharing phosphate and hydrogen phosphate tetrahedra. *N*-methylimidazolium cations occupy the interstitial space between the uranyl fluorophosphate sheets in **1**, whereas 1-ethyl-3-methylimidazolium cations link the uranyl sulfate and phosphate units in **2** and **3** into extended structures.

1. Introduction

The structural chemistry of hexavalent uranium is remarkable in its diversity, due in part to the unique coordination environment about the uranyl ion. Structural units ranging from isolated polyhedra to extended frameworks are common in uranyl compounds, although sheets of polyhedra are the most dominant [1]. Solid-state studies of uranyl compounds have focused on synthesis techniques that include evaporation, sol–gel, hydrothermal, and high-temperature flux-based methods, among others. Several studies have provided compounds in which organic molecules and ions are incorporated as templating agents for the synthesis of uranyl compounds with novel structural units [2–15].

A relatively new synthesis technique, the ionothermal method, utilizes the unique solvating properties of room temperature ionic liquids (ILs). ILs are advantageous as a synthesis medium because they can act as both the solvent and a templating agent, they typically have a very low vapor pressure, and they can be tuned for specific applications [16]. These properties have led to their use in the syntheses of several groups of new compounds including molecular sieves [17–23], metal-organic frameworks [24–28], and polyoxometalates [29–36] that typically employ more traditional techniques such as the hydrothermal method.

Although the behavior of the uranyl ion is documented in ILs [37–39], and the structures of some simple compounds crystallized from ILs have been reported [40–44], the potential of the ionothermal method to produce novel uranyl compounds is undeveloped. Here we report the ionothermal synthesis and characterization of three uranyl compounds: $(C_4H_7N_2)[(UO_2)(PO_3F)(F)]$ (**1**), $(C_6H_{11}N_2)_2[(UO_2)(SO_4)_2]$ (**2**), and $(C_6H_{11}N_2)[(UO_2)_2(PO_4)(HPO_4)]$ (**3**). These were synthesized in the imidazolium-based ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6), 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM $EtSO_4$), and 1-ethyl-3-methylimidazolium diethyl phosphate (EMIM DEP), respectively, and contain imidazole derivatives as charge-balancing cations. Together, they provide interesting examples of how the ionothermal synthesis method can be utilized to produce structurally diverse uranyl compounds.

2. Experimental

2.1. Synthesis

$UO_2(NO_3)_2 \cdot 6H_2O$ (MV Laboratories, Lot no. P705UA1), $In(NO_3)_3 \cdot H_2O$ (Alfa-Aesar 99.5%), Cs_2CO_3 (Sigma Aldrich 99.9%),

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$MgCl_2 \cdot 6H_2O$ (Fisher Scientific 99.9%), $MgSO_4 \cdot 7H_2O$ (Fisher Scientific 99.9%), H_3PO_4 (Fisher Scientific 85%), $RbNO_3$ (Alfa Aesar 99.975%), 1-butyl-3-methylimidazolium PF_6 (Alfa Aesar 98+%), 1-ethyl-3-methylimidazolium $C_2H_5SO_4$ (BASF > 95%), and 1-ethyl-3-methylimidazolium $C_4H_{10}PO_4$ (BASF > 95%) were used as received. For compounds **1** and **2**, reactions were performed in 23 mL Teflon-lined stainless steel reaction vessels. Compound **3** was synthesized in a capped 7 mL Teflon cup added to a 125 mL Teflon-lined reaction vessel with 20 mL of H_2O added for counter pressure. All reactions were heated in mechanical convection ovens. While isotopically depleted U was used in these experiments, precautions for handling radioactive materials should be followed.

$(C_4H_7N_2)[(UO_2)(PO_3F)(F)]$ (**1**) was obtained by dissolving uranyl nitrate (203.6 mg), phosphoric acid (100 μL), indium nitrate (196.6 mg), and caesium carbonate (49.6 mg) into 500 μL of BMIM PF_6 and heating the solution for five days at 180 °C. The reaction vessel was then removed from the oven and allowed to cool to room temperature. The products, consisting of a fine-grained, unidentified green precipitate and yellow, prismatic crystals of **1**, were recovered by filtration and allowed to dry. Crystals of **1** were manually separated from the mixture for further study providing an estimated yield of 50% on the basis of U. While similar reactions of uranyl nitrate, phosphoric acid, and BMIM PF_6 treated with various reagents also produced crystals of **1**, this reaction provided the highest yield.

$(C_6H_{11}N_2)_2[(UO_2)(SO_4)_2]$ (**2**) was obtained by dissolving uranyl nitrate (105.8 mg), magnesium sulfate (11.7 mg), and magnesium chloride (8.9 mg) into 1.0 mL of EMIM $EtSO_4$ and heating the solution for three days at 130 °C. The reaction vessel and oven were then cooled to 25 °C at a rate of 6 °C/h. The products were recovered by filtration and consisted of an unidentified white precipitate and pale-yellow plates of **2**. After they were allowed to dry, crystals of **2** were manually separated from the mixture for further analysis providing an estimated yield of 80% on the basis of U. Crystals of **2** can also be obtained by dissolving uranyl nitrate directly into EMIM $EtSO_4$ though the yield and crystal quality is significantly increased with the addition of divalent cations such as Mg^{2+}.

$(C_6H_{11}N_2)[(UO_2)_2(HPO_4)(PO_4)]$ (**3**) was obtained by heating a solution of 100 mM uranyl nitrate in 1.0 M HCl (125 μL), rubidium nitrate (1.25 mg), phosphoric acid (2.5 μL), and 1.0 mL of EMIM DEP for eight days at 130 °C. The reaction vessel was then removed from the oven and allowed to cool to room temperature. The products were recovered by filtration and consisted of yellow plates of **3** with an estimated yield of > 95% on the basis of U. After they were allowed to dry, crystals of **3** were isolated for further study.

2.2. Crystallographic studies

Single crystals of each compound were selected under polarized light and mounted on a tapered glass fiber for compound **1** or a cryoloop for compounds **2** and **3**. A sphere of diffraction data with frame widths of 0.3° in ω and count times of 10 s per frame was collected for compound **1** at 293 K using a Bruker three-circle X-ray diffractometer equipped with an APEX CCD detector and Mo K_α radiation. A sphere of diffraction data with frame widths of 0.5° in ω and count times of 20 s per frame was collected for compound **2** at 147 K and 10 s per frame at 173 K for compound **3** using a Bruker three-circle X-ray diffractometer equipped with an APEX II CCD detector and Mo K_α radiation. For all compounds, APEX II software [45] was used to refine the unit-cell paramenters using least squares techniques and for data integration and correction for background, Lorentz, and polarization effects. SADABS [46] was used to correct for absorption. The SHELXTL version 5 series of programs were used for the solution and refinement of the crystal structures [47]. O atoms in these structures were assigned as O^{2-} or OH^- based on bond valence calculations [48]. Selected data collection parameters and crystallographic information are listed in Table 1. Selected interatomic distances for the compounds are given in Tables 2–4. Complete details are provided in Supporting information.

The structure of compound 1 was refined in space group *C*2, although it is approximately compatible with *C*2/*m*. However, imposing inversion centers in the structure is incompatible with the positions of U-bridging F atoms and the *N*-methylimidazolium cations in the interlayer. Refinement of the structure in *C*2/*m* requires treatment of positional disorder for the F atoms, as well as for the interlayer constituents. Refinement in *C*2, accounting for an inversion twin with a refined BASF factor of 0.49(3), results in a superior model that contains no positional disorder of atomic sites.

2.3. Chemical analyses

Energy dispersive spectra were collected for crystals of each compound using a LEO EVO 50 scanning electron microscope. Elemental atomic ratios for compounds **1**, **2**, and **3** are ~1:1:5:2 (U:P:O:F), ~1:2:10 (U:S:O), and ~1:1:6 (U:P:O). The ratios calculated are in good agreement with the formulae provided by single-crystal X-ray diffraction structure analyses.

Table 1
Crystallographic data and refinement parameters.

Formula	$(C_4H_7N_2)[(UO_2)(PO_3F)(F)]$	$(C_6H_{11}N_2)_2[(UO_2)(SO_4)_2]$	$(C_6H_{11}N_2)[(UO_2)_2(PO_4)(HPO_4)]$
Formula mass	470.11	684.49	842.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2	*C*2/*c*	$P2_1/n$
a (Å)	17.952(1)	31.90(1)	9.307 (2)
b (Å)	6.9646(6)	9.383(5)	18.067(4)
c (Å)	8.5062(7)	13.770(7)	9.765(2)
α (°)	90	90	90
β (°)	112.301(1)	93.999(7)	93.171(2)
γ (°)	90	90	90
V ($Å^3$)	983.9(1)	4112(3)	1639.5(6)
Z	4	8	4
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	16.692	8.153	19.986
θ (°) range	2.45–27.50	1.28–27.61	2.25–27.55
ρ_{calc} ($gm\ cm^{-3}$)	3.126	2.140	3.363
S	1.035	0.989	1.041
$R(F)$ for $F_0^2 > 2\sigma(F_0^2)$ [a]	0.0396	0.0548	0.0489
$R_w(F_0^2)$ [b]	0.0937	0.1331	0.1000

$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$.
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$GOOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2.}$
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2.}$
$w = 1/[\sigma(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

Table 2
Selected interatomic distances for compound **1**.

U1–O2	1.752(8)	P1–F3	1.59(1)
U1–O1	1.780(8)	P1–O4	1.61(2)
U1–O5#2	2.292(7)	N1–C3	1.27(3)
U1–O4#1	2.31(1)	N1–C1	1.29(2)
U1–F2	2.35(1)	N1–C4	1.35(3)
U1–F1	2.35(2)	N2–C2	1.31(2)
U1–O3	2.39(1)	N2–C4	1.31(3)
P1–O3	1.33(2)	C1–C2	1.34(3)
P1–O5	1.485(8)	C3–C4	1.94(3)

#1 *x*, *y*+1, *z*.
#2 −*x*−3/2, *y*+1/2, −*z*−1.