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ARTICLE

Effects of ionic liquid media on the cation selectivity of uranyl structural units in five new compounds produced using the ionothermal technique

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Ionothermal reactions of uranyl salts in several ionic liquids containing cyclic cations produced single crystals of five new uranyl compounds. $(C_4H_7N_2)[(UO_2)(AsO_4)]$ (**1**), $(C_8H_{15}N_2)_2[(UO_2)_4(SeO_3)_5]$ (**2**), $(C_6H_{11}N_2)_2[(UO_2)_3(C_2H_5PO_4)_4]$ (**3**), and $(C_5H_5N)_2[(UO_2)_2(SeO_4)_3]$ (**4**) are each comprised of two-dimensional structural units. $(C_4H_7N_2)[(UO_2)_5(PO_4)_3(HPO_4)(H_2O)_2].3H_2O$ (**5**) is composed of a three-dimensional network. While the uranyl structural units in all five compounds are directly related to ones found in either uranyl minerals or compounds produced in aqueous media, each contain cyclic ionic liquid constituents as charge-balancing agents. These results suggest that the cation selectivity of these structural units is low, even under various solvation conditions and templating effects from cyclic cations donated from ionic liquid media.

Introduction

The chemical diversity of hexavalent uranium compounds has expanded significantly over the last few decades due in part to the remarkable ability for uranyl structural units to accommodate a wide range of charge-balancing ions. These units range from isolated uranyl polyhedra to extended frameworks, though sheets of polyhedra are the most dominant.¹ The majority of the routes used to synthesize new uranyl compounds involve the use of aqueous media due to the relatively high solubility of hexavalent uranium salts in water. However, several techniques have been reported that utilize non-aqueous solvents or solid-state methods to isolate uranyl compounds with unique chemical and/or structural properties.²⁻⁵

The use of ionic liquid media for the design of novel compounds suited for unique structural, physical, or chemical studies has been described for several broad chemical families including molecular sieves,⁶⁻⁸ metal-organic frameworks,^{9,10} and polyoxometallates.¹¹⁻¹³ The use of room-temperature ionic liquids is advantageous due to their ability to behave both as a solvent and as a templating agent, their low vapor pressure, and

their exceptional tunability for a desired set of solvation properties through systematic variation of cation and anion pairing.¹⁴

In addition to the design perspective, fundamental research is underway to study the use of task-specific ionic liquids in nuclear fuel cycle applications, primarily liquid-liquid extraction processes.^{15,16} Though the spectroscopic properties of the uranyl ion are well-documented in common ionic liquids,^{17,18} and some simple salts have been isolated from solution,¹⁹⁻²¹ more work is needed to establish systematic relationships in a range of complex matrices. The study of the crystal chemical behavior of the uranyl ion in ionic liquid media will contribute to these efforts and ultimately improve the modeling of future applications.

We are interested in examining the effects of the organic cation contributed from room temperature ionic liquids on the selectivity of common uranyl structural units. In this context, selectivity is defined as the range of cations that these structural units can accommodate. To this end, we report the ionothermal synthesis and characterization of five new uranyl compounds: $(C_4H_7N_2)[(UO_2)(AsO_4)]$ (**1**), $(C_8H_{15}N_2)_2[(UO_2)_4(SeO_3)_5]$ (**2**), $(C_6H_{11}N_2)_2[(UO_2)_3(C_2H_5PO_4)_4]$ (**3**), $(C_5H_5N)_2[(UO_2)_2(SeO_4)_3]$

(4), and $(C_4H_7N_2)[(UO_2)_5(PO_4)_3(HPO_4)(H_2O)_2] \cdot 3H_2O$ (5). These were synthesized in the methylimidazolium- and pyridinium-based ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM Tf₂N), 1-ethyl-3-methylimidazolium diethyl phosphate (EMIM DetPO₄), and pyridinium *p*-toluenesulfonate (PPTS), respectively. These ionic liquids were chosen as reactive media due to their diverse properties, thermal stability, and commercial availability. Together, the reported compounds provide insight into the selectivity of uranyl structural units in chemically and structurally diverse, room-temperature ionic liquid media.

Experimental

Synthetic procedure

$UO_2(NO_3)_2 \cdot 6H_2O$ (MV Laboratories, Lot #s P705UA1, IBI55963), $MgSO_4 \cdot 7H_2O$ (Fisher Scientific 99.9%), H_3PO_4 (Fisher Scientific 85%), As_2O_5 (Aldrich 90%), $LiNO_3 \cdot H_2O$ (Alfa Aesar 99%), H_2SeO_4 (Aldrich 40%), H_3BO_3 (Fisher Scientific 99%), 1-butyl-3-methylimidazolium $C_2F_6NO_4S_2$ (BASF 98%), pyridinium $CH_3C_6H_4SO_3$ (Alfa Aesar 98%), and 1-ethyl-3-methylimidazolium $C_4H_6PO_4$ (BASF > 95%) were used as received. All reactions were performed in 23 mL Teflon-lined stainless steel reaction vessels heated in mechanical convection ovens. All solids were combined with the reaction solutions using gentle stirring over the course of several minutes resulting in heterogeneous mixtures. Each reaction reported yielded the largest ratio of crystals relative to total uranium. Approximate yields are averaged over several reactions. When reaction salts that are not incorporated into the reported compounds were removed, crystalline products were not observed or yields were reduced. *While isotopically depleted U was used in these experiments, precautions for handling radioactive materials should be followed.*

$(C_4H_7N_2)[(UO_2)(AsO_4)]$ (1) was obtained by mixing solid uranyl nitrate (100 mg), arsenic pentoxide (79.9 mg), and lithium nitrate (39.3 mg) into 1 mL of BMIM Tf₂N and heating the mixture for four days at 130 °C. The reaction vessel was then removed from the oven and allowed to cool to room temperature. The products, consisting of a yellow, amorphous material containing U and As and yellow plates of 1, were recovered by filtration and allowed to dry. Crystals of 1, with an estimated yield of 50% on the basis of U, were separated for further study.

$(C_8H_{15}N_2)_2[(UO_2)_4(SeO_4)_5]$ (2) was obtained by mixing solid uranyl nitrate (101 mg) into a solution of 200 μL H_2SeO_4 (40%) and 500 μL of BMIM Tf₂N and heating the mixture for five 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 2 with an estimated yield of >95% on the basis of U. After they were allowed to dry, crystals of 2 were separated for further analysis.

$(C_6H_{11}N_2)_2[(UO_2)_3(C_2H_5PO_4)_4]$ (3) was obtained by mixing solid uranyl nitrate (202 mg) and boric acid (52.0 mg) into 500 μL of EMIM DetPO₄ for three 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 prismatic crystals 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.

$(C_5H_5N)_2[(UO_2)_2(SeO_4)_3]$ (4) was obtained by mixing uranyl nitrate (509 mg), magnesium sulfate (8.2 mg), and PPTS (531 mg) into a solution of 250 μL of QH_2O and 20 μL of H_2SeO_4 . The mixture was heated for four days at 120 °C after which the reaction vessel was removed from the oven and allowed to cool to room temperature. The products were recovered by filtration and consisted of small clear crystals of PPTS and large yellow pseudocubes of 4 with an estimated yield of 10% on the basis of U. After they were allowed to dry, crystals of 4 were separated for further analysis. Several experiments were performed to improve the yield of 4 but rapid recrystallization of PPTS near room temperature consistently resulted in the low reported yield.

$(C_4H_7N_2)[(UO_2)_5(PO_4)_3(HPO_4)(H_2O)_2] \cdot 3H_2O$ (5) was obtained by mixing solid uranyl nitrate (500 mg) into a solution of 250 μL H_3PO_4 (85%) and 500 μL of BMIM Tf₂N and heating the solution for three days at 130 °C. The reaction vessel was then removed from the oven and allowed to cool to room temperature. After 24 hours, the products were recovered by filtration and consisted of pale-yellow plates of 5 with an estimated yield of >95% on the basis of U. After they were allowed to dry, crystals of 5 were separated for further analysis. These crystals repeatedly transitioned into an amorphous powder material over the course of 12-24 hours after they were separated from the product material.

Crystallographic Studies

Single crystals of each compound were selected under polarized light and mounted on a cryoloop. A sphere of diffraction data with frame widths of 0.5° in ω and count times of 10 s per frame was collected for each compound at 175 K using a Bruker three-circle X-ray diffractometer equipped with an APEX II CCD detector and Mo $K\alpha$ radiation. APEX II software²² was used to refine the unit-cell parameters using least squares techniques and for data integration and correction for background, Lorentz, and polarization effects. SADABS²³ was used to correct for absorption. Structures were solved and refined using SHELXTL. Selected data collection parameters and crystallographic information are listed in Table 1. Complete details are provided in the Supporting Information.

The U, As, P, and Se atoms in each respective compound were refined anisotropically. When possible, O atoms were refined anisotropically. The C and N atoms comprising the organic cations in each compound were refined isotropically. Due to the disorder between carbon atoms comprising one of the ethyl groups coordinated to the phosphate tetrahedra in compound 3, a DFIX command was added to restrain the distance between the two atoms to 1.53 Å. This distance is similar to the carbon atoms in the ethyl group coordinated to the other phosphate tetrahedron. Refinement without the second carbon atom results in significant R-value increases, and

without the DFIX command the bond distance between the carbon atoms refines to an unreasonable value of 0.83 Å.

Spectroscopic Studies

Absorption data were acquired from single crystals placed on a glass slide using a Craic Technologies UV-vis-near-IR (NIR) microspectrophotometer. The absorption data were collected in the range of 250–1200 nm at room temperature.

X-ray fluorescence spectra for each compound were obtained using an EDAX Orbis microXRF. Single crystals of each compound were mounted on double-sided carbon tape and spectra were collected under vacuum at room temperature at 20 kV for 60 s.

Infrared spectra were obtained for single crystals using a SensIR Technology IlluminatIR FT-IR microspectrometer. A single crystal of each compound was placed on a glass slide, and the spectrum was collected using a diamond ATR objective. The spectra were taken from 650 to 4000 cm^{-1} with a beam aperture of 100 μm .

Raman spectra were collected for each compound using a Bruker Sentinel system equipped with a TE-cooled 1024 x 255 CCD array linked via fiber optics to a video-assisted Raman probe in a microscope mount. The laser wavelength was 785 nm with a power of 400 mW. Crystals were placed on a glass slide for analysis.

Results

Crystal Structure

Compounds **1** and **4** each contain one crystallographically unique U^{6+} cation, compound **3** contains two, compound **2** contains three, and compound **5** contains five. Each occurs as a slightly bent $(\text{UO}_2)^{2+}$ uranyl ion with angles ranging from 175.5(4)° to 179.9(1)°. The U-O_{Ur} (Ur : uranyl) bond lengths range from 1.731(9) to 1.793(5) Å. The uranyl ion in compound **1** is coordinated by four O atoms arranged at the equatorial positions of a square bipyramid capped by the two O atoms of the uranyl ion. The U-O_{eq} (eq : equatorial) bond lengths range from 2.257(5) to 2.294(5) Å. The uranyl ions in compound **2** are coordinated by five or six O atoms arranged at the equatorial positions of pentagonal or hexagonal bipyramids, respectively. The U-O_{eq} bond lengths range from 2.27(1) to 2.472(9) Å in the pentagonal bipyramids and from 2.467(9) to 2.491(9) Å in the hexagonal bipyramid. The uranyl ions in compound **3** are coordinated by four O atoms arranged at the equatorial positions of square bipyramids. The U-O_{eq} bond lengths range from 2.27(1) to 2.308(9) Å. The uranyl ion in compound **4** is coordinated by five O atoms arranged at the equatorial positions of a pentagonal bipyramid. The U-O_{eq} bond lengths range from 2.35(1) to 2.46(1) Å. Four of the uranyl ions in compound **5** are coordinated by five O atoms, and one of the uranyl ions is coordinated by three O atoms and two water molecules, arranged at the equatorial positions of pentagonal bipyramids. The U-O_{eq} bond lengths range from 2.282(8) to 2.524(1) Å and the $\text{U-OH}_{2\text{eq}}$ bond lengths range from 2.48(1) to 2.55(1) Å. One symmetrically distinct As^{5+} cation occurs in

compound **1** that is coordinated by four O atoms in a tetrahedral arrangement. The As-O bond lengths range from 1.663(5) to 1.697(5) Å. Compound **2** contains three symmetrically unique Se^{4+} cations that are each coordinated by three O atoms in a trigonal pyramidal arrangement with Se-O bond lengths ranging from 1.63(1) to 1.740(9) Å. Two symmetrically distinct P^{5+} cations occur in compound **3**. Both are coordinated by four O atoms in a tetrahedral arrangement with P-O bond lengths ranging from 1.49(1) to 1.58(1) Å. Compound **4** contains two symmetrically unique Se^{6+} cations coordinated by four O atoms in a tetrahedral arrangement with Se-O bond lengths ranging from 1.45(2) to 1.58(1) Å. Four symmetrically distinct P^{5+} cations occur in compound **5**. Each is coordinated by four O atoms in a tetrahedral arrangement with P-O bond distances ranging from 1.474(9) to 1.569(9) Å.

The compounds in this study each contain cyclic cations contributed from the ionic liquid as charge-balancing agents. Compounds **1-3** and **5** contain methylimidazolium cations and compound **4** contains pyridinium cations. These cations link the compounds into extended structures through hydrogen bonding networks. The four distinct cations include N-methylimidazolium (NMIM), 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-3-methylimidazolium (BMIM), and pyridinium (PYD) (Fig. 1).

The structural unit of **1** is composed of uranyl square bipyramids that are connected into sheets through corner-sharing with phosphate tetrahedra (Fig. 2A). Each uranyl square bipyramid is coordinated by four monodentate phosphate tetrahedra. These layers are linked through NMIM cations, resulting in an extended structure (Fig. 2B).

Compound **2** contains clusters of uranyl hexagonal and pentagonal bipyramids linked into sheets through selenite trigonal pyramids. The clusters are composed of one uranyl hexagonal bipyramid that shares three edges with three uranyl pentagonal bipyramids and three selenite trigonal pyramids. These groups are linked through corner-sharing selenite trigonal pyramids to form a sheet (Fig. 3A). The sheets are linked through BMIM cations to form an extended structure (Fig. 3B).

The structural unit of **3** is composed of uranyl square bipyramids connected into sheets through edge-sharing ethyl phosphate tetrahedra. Each uranyl square bipyramid is coordinated by four monodentate ethyl phosphate tetrahedra. Each ethyl phosphate tetrahedron shares three corners with uranyl square bipyramids and the ethyl groups extend into the interstitial space (Fig. 4A). The sheets are linked through EMIM cations to form an extended structure (Fig. 4B).

Compound **4** contains uranyl pentagonal bipyramids linked into sheets through monodentate selenate tetrahedra. Each uranyl pentagonal bipyramid shares each of its five corners with selenate tetrahedra (Fig. 5A). The sheets are linked through PYD cations, resulting in an extended structure (Fig. 5B).

The structural unit of compound **5** is composed of sheets of uranyl pentagonal bipyramids with phosphate and hydrogen phosphate tetrahedra linked into a three-dimensional framework

through uranyl ions oriented perpendicular to the sheets. The sheets are composed of chains of edge-sharing uranyl pentagonal bipyramids that are linked into sheets through bi- and monodentate phosphate tetrahedra (Fig. 6A). Three phosphate tetrahedra share an edge with one uranyl pentagonal bipyramid and a corner with another uranyl pentagonal bipyramid. The fourth vertex is shared with the uranyl pentagonal bipyramid of the uranyl ion that is perpendicular to the sheet and that links the sheets into a framework (Fig. 6B). The fourth phosphate group contains a protonated terminal O atom. The pentagonal bipyramid of the uranyl ion that is perpendicular to the sheets shares three equatorial vertices with the phosphate tetrahedra and two vertices are terminal water molecules. NMIM cations and three additional water molecules are located in the channels of the framework.

Bond-Valence Analyses

Bond valence sums were calculated for U^{6+} -O, P^{5+} -O, As^{5+} -O, Se^{4+} -O, and Se^{6+} -O interactions.^{24,25} U^{6+} -O sums range from 5.83 to 6.34, P^{5+} -O sums range from 4.81 to 5.02, As^{5+} -O has a sum of 5.06, Se^{4+} -O sums range from 4.01 to 4.58, and Se^{6+} -O sums range from 5.49 to 6.54 valence units, respectively. A compilation of bond valence sums is in the Supporting Information. These sums are in good agreement with the formal valences of U^{6+} , P^{5+} , As^{5+} , Se^{4+} , and Se^{6+} . O^{2-} and OH^- were designated based on valence sums of ~ 2.0 and ~ 1.2 valence units, respectively.

UV-vis-NIR Spectroscopy

The UV-vis-NIR spectrum for each compound is dominated by the vibronically coupled charge transfer band centered near 420 nm due to oxo-to-metal charge transfer between orbitals of the uranyl cation. The spectra of all five compounds also feature a broad, intense band near 300 nm due to ligand-to-metal charge transfer.

X-ray Fluorescence Spectroscopy

X-ray fluorescence spectra collected from each compound confirmed the elemental composition of the uranyl structural units. In each case, uranium was identified. Arsenic, phosphorus, and selenium were identified in compounds **1**, **3** and **5**, and **2** and **4**, respectively.

ATR FT-IR Spectroscopy

The infrared spectra of the compounds under study display several distinct bands in the 700-3500 cm^{-1} region. Compound **1** has a band at 916 cm^{-1} attributed to the ν_3 antisymmetric stretching of $(UO_2)^{2+}$. As -O ν_3 antisymmetric stretching is assigned to a band at 784 cm^{-1} .

The infrared spectrum of compound **2** displays bands at 775, 806, 815, 827, 842, and 868 cm^{-1} that can be attributed to some combination of Se -O ν_3 stretching, Se -O ν_1 stretching, or ν_1 symmetric stretching of $(UO_2)^{2+}$. Bands at 899, 901, and 918 cm^{-1} are attributed to the ν_3 antisymmetric stretching of $(UO_2)^{2+}$.

The spectrum of compound **3** displays bands at 890, 905(sh), 957, and 992 cm^{-1} attributed to the ν_3 antisymmetric

stretching of $(UO_2)^{2+}$. P -O ν_3 antisymmetric stretching is assigned to three bands at 1011, 1037 and 1091(sh) cm^{-1} .

Compound **4** exhibits bands at 925 and 937 cm^{-1} assigned to the ν_3 antisymmetric stretching of $(UO_2)^{2+}$. Se -O ν_3 antisymmetric stretching is assigned to bands at 1022, 1037, and 1097 cm^{-1} . Se -O ν_4 bending is assigned to the peak at 737 cm^{-1} .

The spectrum of compound **5** exhibits bands at 897, 911(sh), 966, and 979(sh) cm^{-1} attributed to the ν_3 antisymmetric stretching of $(UO_2)^{2+}$. P -O ν_3 antisymmetric stretching is assigned to two bands at 1071 and 1127 cm^{-1} . The sharp band at 1602 cm^{-1} is attributed to the δ H_2O bending mode.

All of compounds **1** through **5** display bands in the 1250-1800 cm^{-1} and 2800-3300 cm^{-1} regions indicating carbon-carbon and carbon-nitrogen and hydrogen bonding, respectively.

Raman Spectroscopy

The symmetric "yl" U-O stretch is evident in the spectra of all five compounds. The stretch is attributed to the intense peaks at 825, 803, 823, 837, and 835 cm^{-1} for compounds **1-5**, respectively.

Discussion

The ionothermal technique has been reported to be of value for the ability of ionic liquids to behave both as a solvent and a templating agent during a reaction.¹⁴ This ability is commonly reported for both zeolite frameworks and polyoxometallate cages.^{6-8, 11-15} The ability to tune ionic liquids for desired solution properties results in a great variety of templating agents for use in synthesis reactions.

Our goal is to investigate the templating effects of cyclic cations on uranyl structural units during ionothermal reactions. Several examples of aqueous and solvothermal reactions to produce uranyl compounds have been previously reported that utilize cyclic cations as templating agents.²⁶⁻³⁰ However, there are few studies that examine the use of ionic liquids as both solvent and templating agent for the synthesis of uranyl compounds. Specifically, we are interested in the effects the ionothermal technique may have on the isolation of uranyl structural units that commonly form in aqueous solution. Many layered uranyl compounds form in the presence of a wide variety of templating cations under an equally wide variety of chemical conditions. For example, the zippeite anion topology can be templated by several mono- and divalent cations.³¹ Additionally, it can form in the presence of bridging ligands in the sheet other than sulfate groups.³² This is known to occur in compounds containing the uranophane anion topology as well, with both silicate and phosphate tetrahedra being common constituents of the sheets.¹

Examination of new uranyl compounds synthesized in ionic liquids and their relationship to previously reported structural entities provides new insight into both the templating ability of

cations donated from ionic liquid media, and the ion selectivity of several uranyl structural units.

Compound **1** contains a familiar anion topology that is adopted by several uranyl minerals and synthetic compounds including autunite, metatorbernite, and threadgoldite, among others.¹ It can be templated by a variety of cations including Ba²⁺, Mg²⁺, Ca²⁺, K⁺, and Cu²⁺ and PO₄³⁻ or AsO₄³⁻ tetrahedra can populate the sheets. Most of the compounds that contain this topology exhibit high symmetry due to the repeating pattern of uranyl square bipyramids and oxoanion tetrahedra.¹ In contrast, compound **1** was resolved in *P* -1 due to the extensive distortion of the sheet relative to four-fold symmetry, presumably due to the hydrogen bonding network imposed by the rather ridged NMIM cations relative to more labile water molecules. Synthesis of this compound under ionothermal conditions suggests that this particular structural unit has very low cation selectivity and can be templated by cyclic cations even in nonaqueous media.

The structural unit that comprises compound **2** has only been reported on three occasions. Each compound contains the same tetrameric group of uranyl polyhedra but contain selenite, phosphite, and phosphonate bridging ligands.³²⁻³⁴ The selenite and phosphite compounds contain Cs⁺ cations and interstitial water molecules, whereas the third compound contains phosphonate rings in the interlayer complex. The large BMIM cations in compound **2** presumably provide enough hydrogen bonding sites to stabilize this structural unit. The selectivity of this unit is likely limited to large cations. As such, the design of compounds containing this structural unit may target large imidazolium cations with long alkyl chains or similar organic entities as templating agents in conjunction with bridging ligands containing lone pairs of electrons that are stereoactive.

Compound **3** contains a structural unit that is topologically similar to that of compound **1**, except that one of four uranyl ions in **1** is omitted in **3**. This is due to the retention of one ethyl group by the diethyl phosphate anions incorporated into the structure during the reaction. These ethyl groups obstruct the four oxygen atoms that would otherwise coordinate the additional uranyl ion as part of a square bipyramid. Similar conditions may permit the retention of both ethyl units in future reactions that would further alter the unit. Additionally, BMIM cations template this compound, strengthening the argument for the low cation selectivity of this structural unit.

The structural unit in compound **4** is only found in a few synthetic uranyl molybdate and uranyl sulfate compounds.¹ These contain Cs⁺ cations as interlayer constituents and the relative size of the PYD cations compared to Cs⁺ may have contributed to the isolation of this structural unit. It may be targeted using a variety of large organic cations in conjunction with hexavalent oxoanion groups.

Compound **5** is the only species in this study that contains a framework structure. Additionally, it is the only compound synthesized here that incorporates water molecules. These are likely present due to the aqueous phosphoric acid that was used in the reaction. The structure is composed of sheets of uranyl pentagonal bipyramids and phosphate as well as hydrogen

phosphate tetrahedra that are linked into a framework by uranyl ions oriented perpendicular to the sheets, and that are part of pentagonal bipyramids. These bipyramids share O atoms with three phosphate tetrahedra, two from one sheet and one from the adjacent sheet. The two other equatorial ligands of the bridging uranyl pentagonal bipyramid are water molecules. The channels that result from this arrangement contain NMIM cations and water molecules. The uranyl phosphate sheets display the uranophane topology that has previously been described from another ionothermal reaction.³⁵ However, the previous compound contains only interlayer NMIM cations without bridging uranyl pentagonal bipyramids and water molecules. A uranyl vanadate compound with this framework unit has also been reported that utilized a templating amine.³⁶

Conclusions

In this study we have reported the synthesis and descriptions of five new uranyl compounds isolated from ionothermal reactions in a variety of ionic liquid media. This work demonstrates the effectiveness of the ionothermal method to produce crystalline material suitable for the examination of crystal-chemical relationships between uranyl compounds. These data provide insight about the cation selectivity of several uranyl structural units and the templating effect that cyclic cations donated from ionic liquid media have on uranyl speciation in the solid state. This work will ultimately contribute to the development of new synthesis strategies to isolate targeted uranyl compounds for applications or structural studies.

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Notes and references

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Electronic Supplementary Information (ESI) available: [UV-vis-NIR, Raman, ATR-FTIR, and XRF EDAX spectra, crystallographic parameters, and bond valence tables]. See DOI: 10.1039/b000000x/C. A.

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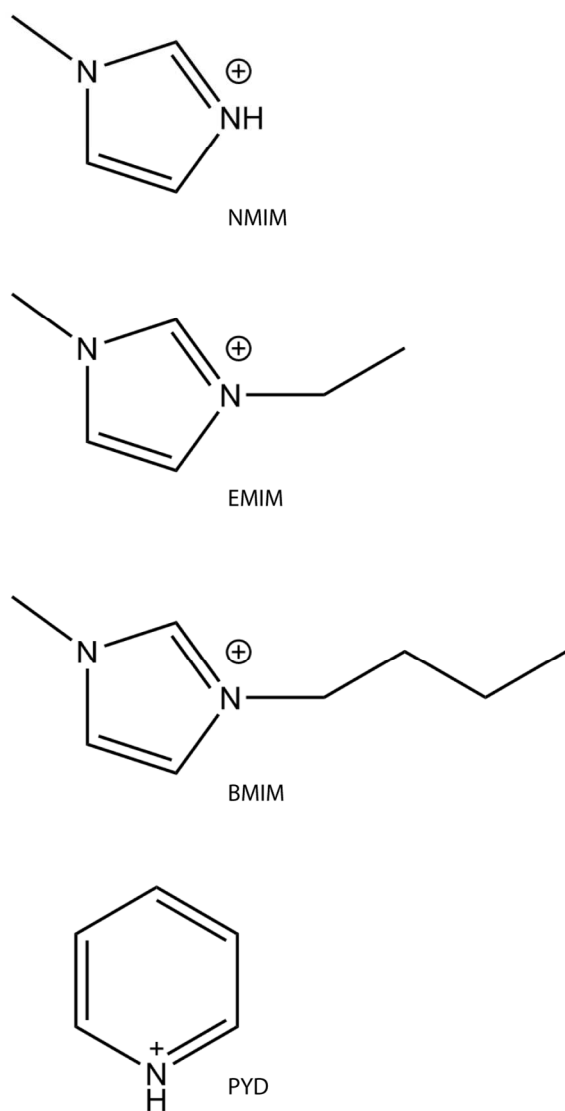


Figure 1. Cations contributed from the ionic liquids EMIM Tf₂N, BMIM Tf₂N, and PPTS.

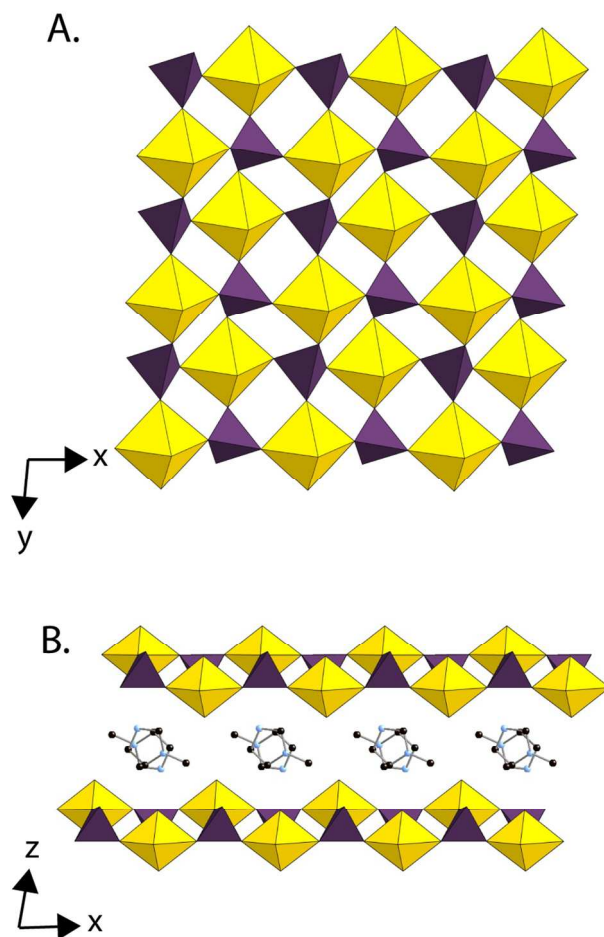


Figure 2. Polyhedral representation of the uranyl (yellow polyhedra) arsenate (purple polyhedra) structural unit (A) and interstitial complex (B) present in compound **1**. Carbon and nitrogen atoms are represented as black and blue spheres, respectively.

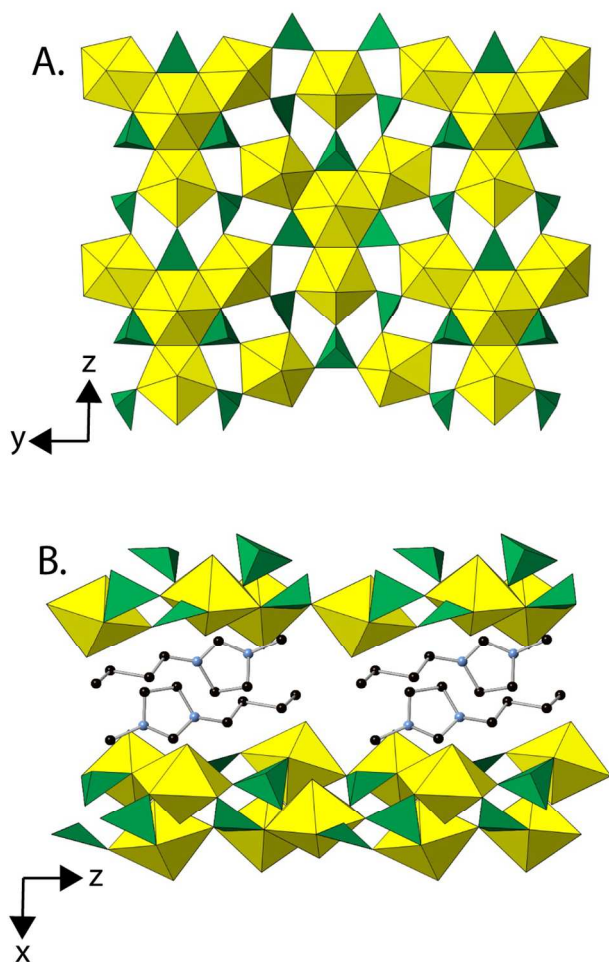


Figure 3. Polyhedral representation of the uranyl (yellow polyhedra) selenite (green polyhedra) structural unit (A) and interstitial complex (B) present in compound **2**. Carbon and nitrogen atoms are represented as black and blue spheres, respectively.

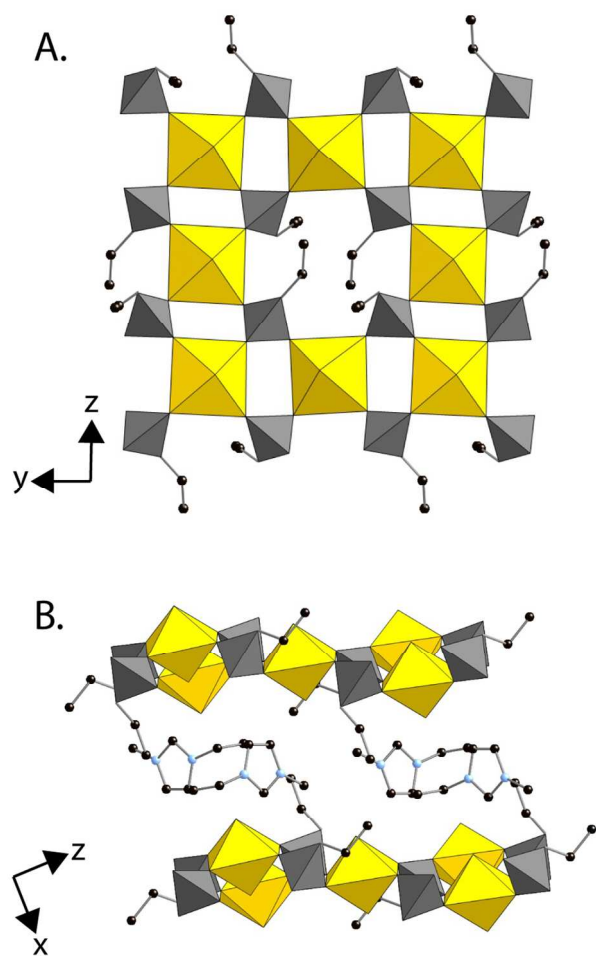


Figure 4. Polyhedral representation of the uranyl (yellow polyhedra) phosphate (grey polyhedra) structural unit (A) and interstitial complex (B) present in compound **3**. Carbon and nitrogen atoms are represented as black and blue spheres, respectively.

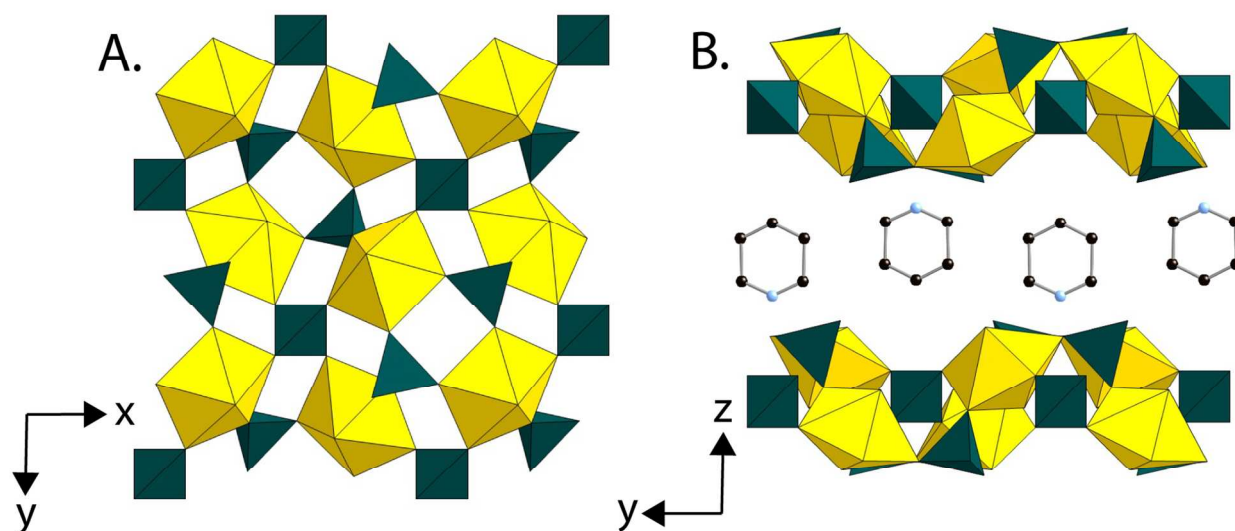


Figure 5. Polyhedral representation of the uranyl (yellow polyhedra) selenate (green polyhedra) structural unit (A) and interstitial complex (B) present in compound 4. Carbon and nitrogen atoms are represented as black and blue spheres, respectively.

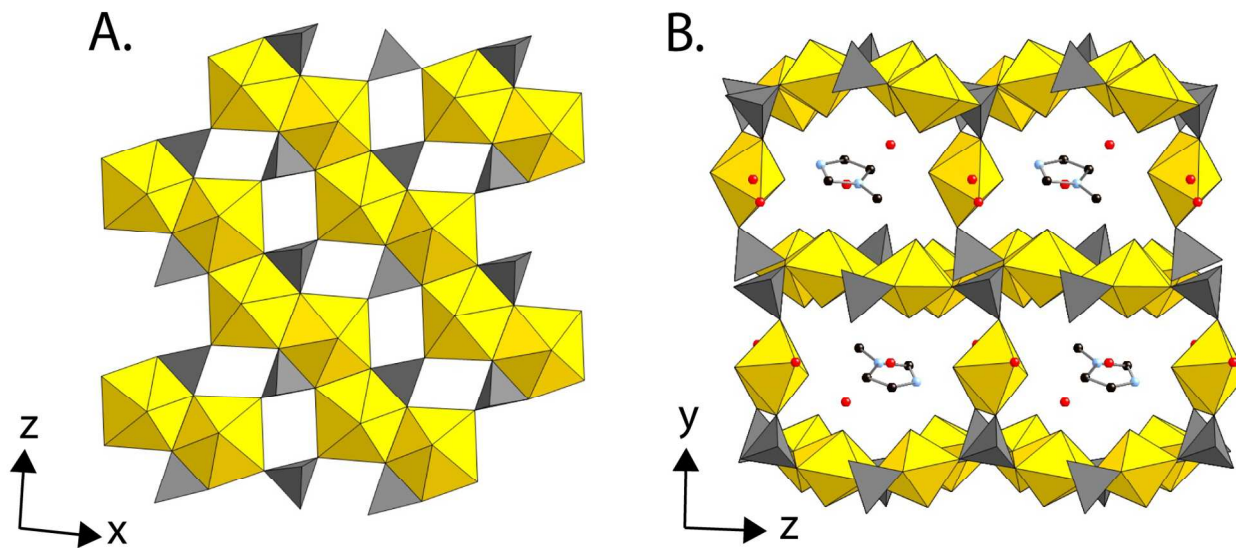


Figure 6. Polyhedral representation of the uranyl (yellow polyhedra) phosphate (grey polyhedra) sheet units (A) and framework (B) present in compound 5. Carbon, nitrogen and oxygen (water) atoms are represented as black, blue, and red spheres, respectively.

Table 1. Crystallographic data and refinement parameters.

	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5
Formula Mass	485.01	1963.12	1486.21	1117.06	1886.09
Crystal System	Triclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space Group	<i>P</i> -1	<i>Pnma</i>	<i>P2₁/n</i>	<i>Pccn</i>	<i>P2₁/n</i>
<i>a</i> (Å)	7.170(3)	18.860(2)	9.954(7)	9.987(7)	9.5152(9)
<i>b</i> (Å)	7.181(3)	18.010(2)	10.264(7)	10.251(7)	33.144(3)
<i>c</i> (Å)	9.831(4)	11.140(1)	19.56(1)	20.95(1)	9.656(1)
α (°)	73.511(4)	90	90	90	90
β (°)	73.892(4)	90	101.75(1)	90	93.211(1)
γ (°)	89.122(4)	90	90	90	90
<i>V</i> (Å ³)	465.2(3)	3784.3(8)	1957(2)	2146(2)	3040.7(5)
<i>Z</i>	2	4	2	4	4
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	20.980	21.960	12.628	20.248	26.866
θ (°) range	2.25 - 27.59	2.12 - 27.54	2.13 - 27.34	1.94 - 27.58	1.23 - 27.53
ρ_{calc} (gm cm ⁻³)	3.463	3.446	2.522	3.458	4.120
<i>S</i>	1.013	1.149	0.979	1.033	1.015
R(F) for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0319	0.0499	0.0497	0.0647	0.0450
R _w (F_o^2) ^b	0.0627	0.1046	0.1014	0.1623	0.1036

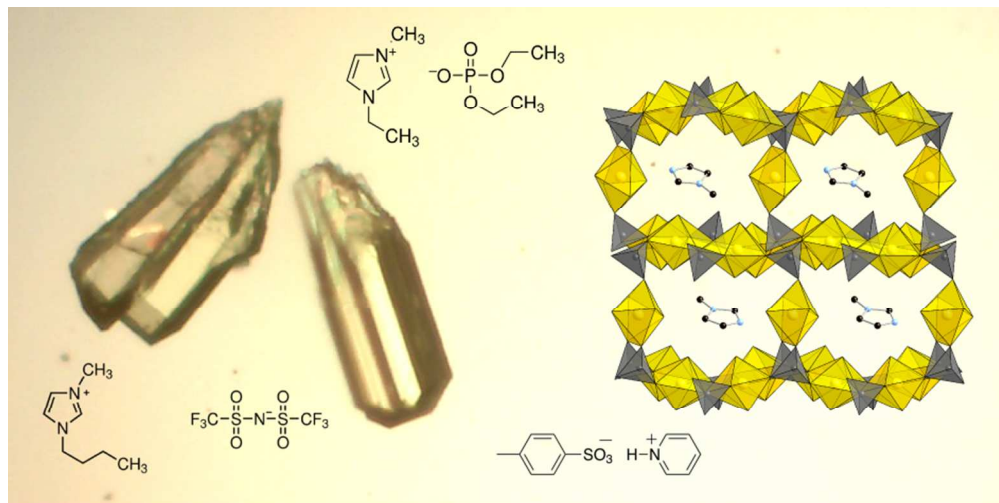
$$R_{int} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum [F_o^2]}$$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$GOOF = S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

$$w = 1 / [\sigma(F_o^2) + (aP)^2 + bP] \text{ where } P \text{ is } [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$$



80x40mm (300 x 300 DPI)

The cation selectivity of several uranyl structural units is examined in the context of five new uranyl compounds produced using the ionothermal synthesis technique.