



# Ring opening of azetidine cycle: First examples of 1-azetidinetripropanamine molecules as a template in hybrid organic-inorganic compounds

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## ABSTRACT

Three novel uranyl selenate and sulfate oxysalts templated by protonated azetidine molecules,  $[\text{AzH}]^+$ , and its ring-opened counterpart 1-azetidinetripropanamine,  $[\text{AzH}(\text{CH}_2)_3\text{NH}_3]^{2+}$ , have been prepared and studied by X-ray structural analysis. Conformations of azetidinium cations were analysed by means of infrared vibrational assignments supported by the DFT calculations. Crystallization of  $[\text{AzH}]_2[(\text{UO}_2)_2(\text{SeO}_4)_3(\text{H}_2\text{O})]$  (**I**) from highly acidic solutions suggests that low pH does not necessarily result in the opening of azetidine ring.  $[\text{AzH}(\text{CH}_2)_3\text{NH}_3][(\text{UO}_2)_2(\text{SeO}_4)_3(\text{H}_2\text{O})](\text{H}_2\text{O})$  (**II**) and  $[\text{AzH}(\text{CH}_2)_3\text{NH}_3][(\text{UO}_2)_2(\text{SO}_4)_3(\text{HSO}_4)]$  (**III**) are the first structurally characterized crystalline compounds bearing isolated ring-opened azetidine moiety.

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## 1. Introduction

Mixed organic-inorganic compounds are of interest due to the combination in the same compound of organic and inorganic substructures with their specific structure and properties. The important problem is the nature of synergetic interactions between organic and inorganic components. From this point of view, uranyl compounds are of special interest due to their unique crystal chemistry. Over the past 20 years several hundreds of  $\text{U}^{6+}$ -containing compounds have been reported with structures based upon the complexes of uranyl ions linked via oxygen atoms to high-valent cations such as  $\text{P}^{3+}$ ,  $\text{P}^{5+}$ ,  $\text{V}^{5+}$ ,  $\text{As}^{5+}$ ,  $\text{S}^{6+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Se}^{4+}$ ,  $\text{Se}^{6+}$ ,  $\text{Mo}^{6+}$ , etc., and separated by organic molecules of different shape and charge [1–6]. Careful analysis of structural architectures of these compounds has revealed a number of fundamental principles describing interactions between organic and inorganic substructures. Exploration of novel structures largely confirms the proposed rules, but subtle details can still be found in a particular

chemical system. During investigations of phase formation in the aqueous uranyl selenate and uranyl sulfate systems with various amine molecules, our attention was attracted by a simple heterocyclic ring system, azetidine. Our interest arose mostly because of the very limited information on the behaviour and the role of azetidinium cations in the crystal structures. Only recently several papers have been published on the structural description of metal-organic frameworks with azetidinium cations [7–11]. Herein we report on the synthesis, structural description, IR-spectroscopy characterisation and quantum-chemical calculations on three novel uranyl compounds templated by azetidinium molecules and its derivatives.

## 2. Experimental

### 2.1. Synthesis

Azetidine ( $(\text{CH}_2)_3\text{NH}$ , 98%, Sigma-Aldrich), uranyl nitrate hexahydrate  $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%, Vekton), selenic acid ( $\text{H}_2\text{SeO}_4$ , 40 wt % in  $\text{H}_2\text{O}$ , 99.95%, Sigma-Aldrich), and sulphuric acid (Aldrich, 98%) were used as received. For the synthesis of **I**, a newly

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obtained azetidine reagent have been used, whereas compounds **I** and **III** have been synthesized using azetidine reagent from storage (~1 year). Single crystals of  $(C_3H_8N)_2 [(UO_2)_2(SeO_4)_3(H_2O)]$  (**I**) have been prepared by evaporation from aqueous solution of 0.1 g (0.2 mmol) of uranyl nitrate, 0.2 ml (3.8 mmol) of selenic acid, 0.01 ml (0.15 mmol) of azetidine in 2 ml of deionized water.  $(C_6H_{16}N_2)[(UO_2)_2(SeO_4)_3(H_2O)](H_2O)$  (**II**) have been prepared by evaporation from aqueous solution of 0.1 g (0.2 mmol) of uranyl nitrate, 0.2 ml (3.8 mmol) of selenic acid, 0.01 ml (0.15 mmol) of azetidine in 2 ml of deionized water.  $(C_6H_{16}N_2)(H_5O_2)[(UO_2)_2(SO_4)_3(HSO_4)]$  (**III**) have been prepared by evaporation from aqueous solution containing 0.1 g (0.2 mmol) of uranyl nitrate, 0.2 ml (3.7 mmol) of sulphuric acid, 0.01 ml (0.15 mmol) of azetidine in 2 ml of deionized water. Homogeneous liquid solution was left in a watch glass at room temperature. The yellowish-green flattened crystals formed in one week.

## 2.2. Single crystal X-ray study

Single crystals of **I**–**III** have been selected for data collection under an optical microscope, encased in an oil-based cryoprotectant and mounted on cryoloops. Data for **I** and **II** were collected using a Bruker SMART diffractometer equipped with an APEX II CCD area detector operated with monochromated MoK $\alpha$  radiation ( $\lambda$  [MoK $\alpha$ ] = 0.71073 Å) at 50 kV and 40 mA. Data for **III** were collected using a Bruker Kappa Duo diffractometer equipped with an APEX II CCD area detector operated with monochromated microfocused MoK $\alpha$  radiation at 50 kV and 0.6 mA. Diffraction data were collected at 150 K with frame widths of 0.5° in  $\omega$  and  $\phi$ , and exposition of 80 s (for **I** and **II**) and 30 s (for **III**) spent per each frame. Data were integrated and corrected for background, Lorentz, and polarization effects using an empirical spherical model by means of the Bruker programs *APEX2* and *XPREF*. Absorption correction was applied using the *SADABS* program [12]. The unit-cell parameters (Table 1) were refined by the least-squares techniques. The structures were solved by direct methods and refined using the *SHELX* programs [13] incorporated in the *OLEX2* program package [14]. The final models included coordinates and anisotropic displacement

**Table 2**  
Selected interatomic distances and angles in the structure of **I**.

Bond		Bond	
U1–O1	1.756(7)	Se2–O16	1.599(7)
U1–O2	1.764(7)	Se2–O3	1.649(6)
U1–O4	2.366(7)	Se2–O5	1.651(6)
U1–O3	2.381(7)	Se2–O10	1.661(7)
U1–O7	2.389(6)	<Se2–O>	1.64
U1–O5	2.395(6)		
U1–O6	2.448(7)	Se3–O17	1.605(6)
<U1–O <sub>ur</sub> >	1.76	Se3–O12	1.632(6)
<U1–O <sub>eq</sub> >	2.40	Se3–O14	1.647(7)
		Se3–O6	1.652(7)
U2–O8	1.762(7)	<Se3–O>	1.63
U2–O9	1.768(7)		
		Angle	
U2–O14	2.346(7)	U1–O3–Se2	134.5(4)
U2–O12	2.375(6)	U1–O4–Se1	141.7(4)
U2–O10	2.388(6)	U1–O5–Se2	134.0(4)
U2–O11	2.417(7)	U1–O6–Se3	131.6(3)
U2–H <sub>2</sub> O13	2.489(7)	U1–O7–Se1	141.2(4)
<U2–O <sub>ur</sub> >	1.76	U2–O10–Se2	131.6(3)
<U2–O <sub>eq</sub> >	2.40	U2–O11–Se1	128.1(4)
		U2–O12–Se3	134.5(3)
Se1–O15	1.612(8)	U2–O14–Se3	138.0(4)
Se1–O4	1.643(7)	<U–O <sub>br</sub> –Se>	135.0
Se1–O7	1.646(6)		
Se1–O11	1.655(7)		

parameters for all atoms. The carbon and nitrogen-bound H atoms were placed in calculated positions and were included in the refinement in the ‘riding’ model approximation, with  $U_{iso}(H)$  set to 1.2 $U_{eq}(C)$  and C–H 0.97 Å for CH<sub>2</sub> groups, with  $U_{iso}(H)$  set to 1.2 $U_{eq}(N)$  and N–H 0.98 Å for tertiary NH groups, with  $U_{iso}(H)$  set to 1.2 $U_{eq}(N)$  and N–H 0.97 Å for NH<sub>2</sub> groups, and  $U_{iso}(H)$  set to 1.2 $U_{eq}(N)$  and N–H 0.89 Å for the NH<sub>3</sub> groups. Positions of H atoms of H<sub>2</sub>O molecules, Zundel cations and OH<sup>−</sup> groups were localized from difference Fourier maps and kept fixed during refinement. Selected interatomic distances and angles are listed in Tables 2–4. CCDC files 1518914, 1518912, and 1518913 contain the supplementary crystallographic data for the compounds **I**–**III**,

**Table 1**  
Crystallographic data for **I**, **II** and **III**.

Compound	<b>I</b>	<b>II</b>	<b>III</b>
Formula Mass	1103.16	1121.18	1078.55
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	10.8620 (5)	11.3575 (5)	8.677 (3)
<i>b</i> (Å)	11.1105 (5)	11.0210 (5)	10.294 (3)
<i>c</i> (Å)	17.8815 (8)	17.8038 (8)	26.474 (8)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	90.6080 (10)	97.521 (7)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	2157.98 (17)	2228.39 (17)	2344.4 (12)
Size (mm <sup>3</sup> )	0.19 × 0.12 × 0.05	0.21 × 0.11 × 0.05	0.18 × 0.11 × 0.05
$\mu$ (mm <sup>−1</sup> )	20.130	19.500	14.258
<i>Z</i>	4	4	4
2 $\theta$ range, °	4.32–54.00	3.59–55.00	3.10–55.00
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	3.395	3.342	3.056
Total ref.	23149	24352	21281
Unique ref.	4714	5118	5381
Unique   <i>F</i> <sub>o</sub>   ≥ 4 $\sigma$ <sub><i>F</i></sub>	4536	4475	4953
<i>R</i> <sub>int</sub>	0.0748	0.0758	0.0756
<i>R</i> <sub><math>\sigma</math></sub>	0.0433	0.0455	0.0432
<i>R</i> <sub>1</sub> (  <i>F</i> <sub>o</sub>   ≥ 4 $\sigma$ <sub><i>F</i></sub> )	0.0252	0.0246	0.0241
<i>wR</i> <sub>2</sub> (  <i>F</i> <sub>o</sub>   ≥ 4 $\sigma$ <sub><i>F</i></sub> )	0.0587	0.0545	0.0570
GOF	1.053	1.003	1.041
$\rho$ <sub>min</sub> , $\rho$ <sub>max</sub> , e/Å <sup>3</sup>	−1.764, 1.990	−2.142, 1.749	−1.476, 1.328
CCDC	1518914	1518912	1518913

Note:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2) / 3$ ; GOF =  $\{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$  where *n* is the number of reflections and *p* is the number of refined parameters.

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