



Syntheses, structures, characterizations and charge-density matching of novel amino-templated uranyl selenates

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ABSTRACT

Five hybrid organic–inorganic uranyl selenates have been synthesized, characterized and their structures have been determined. The structure of $(C_2H_8N)_2[(UO_2)_2(SeO_4)_3(H_2O)]$ (EthylAUSe) is monoclinic, $P2_1$, $a = 8.290(1)$, $b = 12.349(2)$, $c = 11.038(2)$ Å, $\beta = 104.439(4)^\circ$, $V = 1094.3(3)$ Å³, $Z = 2$, $R_1 = 0.0425$. The structure of $(C_7H_{10}N)_2[(UO_2)(SeO_4)_2(H_2O)]H_2O$ (BenzylAUSe) is orthorhombic, $Pna2_1$, $a = 24.221(2)$, $b = 11.917(1)$, $c = 7.4528(7)$ Å, $V = 2151.1(3)$ Å³, $Z = 4$, $R_1 = 0.0307$. The structure of $(C_2H_{10}N)_2[(UO_2)(SeO_4)_2(H_2O)](H_2O)_2$ (EDAUSe) is monoclinic, $P2_1/c$, $a = 11.677(2)$, $b = 7.908(1)$, $c = 15.698(2)$ Å, $\beta = 98.813(3)^\circ$, $V = 1432.4(3)$ Å³, $Z = 4$, $R_1 = 0.0371$. The structure of $(C_6H_{22}N_4)[(UO_2)(SeO_4)_2(H_2O)](H_2O)$ (TETAUSe) is monoclinic, $P2_1/n$, $a = 13.002(2)$, $b = 7.962(1)$, $c = 14.754(2)$ Å, $\beta = 114.077(2)^\circ$, $V = 1394.5(3)$ Å³, $Z = 4$, $R_1 = 0.0323$. The structure of $(C_6H_{21}N_4)[(UO_2)(SeO_4)_2(HSeO_4)]$ (TAEUSe) is monoclinic, $P2_1/m$, $a = 9.2218(6)$, $b = 12.2768(9)$, $c = 9.4464(7)$ Å, $\beta = 116.1650(10)^\circ$, $V = 959.88(12)$ Å³, $Z = 2$, $R_1 = 0.0322$. The inorganic structural units in these compounds are composed of uranyl pentagonal bipyramids and selenate tetrahedra. In each case, tetrahedra link bipyramids through vertex-sharing, resulting in chain or sheet topologies. The charge-density matching principle is discussed relative to the orientations of the organic molecules between the inorganic structural units.

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1. Introduction

Hexavalent uranium compounds usually contain approximately linear $(UO_2)^{2+}$ uranyl ions that are further coordinated by four, five or six ligands, forming uranyl square, pentagonal and hexagonal bipyramids that are capped by the O atoms of the uranyl ions [1,2]. These polyhedra regularly link to other polyhedra containing higher valence cations through shared equatorial vertices and edges, resulting in structural units with a large number of chain and sheet topologies [1]. Uranyl compounds containing XO_4 tetrahedra, where X is hexavalent Mo, Te, Se and S, often exhibit complex sheet or framework topologies that are dominated by the sharing of vertices between the tetrahedra and uranyl pentagonal bipyramids [3–17]. Although two-dimensional sheets of polyhedra dominate uranyl structures in general, the synthesis of nanotubules [18] and hollow spherical clusters constructed from as many as 50 uranyl polyhedra have been reported [19,20].

Mixed organic–inorganic hybrid materials are currently receiving considerable attention, including a variety of compounds that contain uranyl-based inorganic units [15–17,21–38]. Recently, Krivovichev et al. [17] examined application of the charge-density matching principle to uranyl selenate organic–inorganic hybrids.

This study revealed that although the charge per surface area of uranyl selenate sheets is significantly smaller than those of compounds such as aluminophosphates, the charge-density matching principle can be satisfied by combinations of interdigitiation of monoamine cations, incorporation of inorganic constituents within the interlayer that also contains the organic molecules, and the details of the packing of the organic molecules, especially their angles of inclination relative to the inorganic sheet. Interestingly, uranyl selenate topologies found in inorganic–organic hybrid structures often have not been found in purely inorganic compounds, although the precise role of the organic components of the structure in templating the inorganic topologies is unclear. Similarly, studies of organically template uranyl sulfate structural units have revealed several novel topologies [22–25,30–33,39]. Here we report the structures of five organic–inorganic uranyl selenate hybrid structures that present new inorganic component topologies, as well as known topologies crystallized using different organic structural components.

2. Experimental

2.1. Syntheses

$UO_2(NO_3)_2 \cdot 6H_2O$ (MV Laboratories, Lot no. P705UA1), H_2SeO_4 (40%, Aldrich), ethylamine (C_2H_7N , 70%, Sigma), benzylamine

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Table 1
Crystallographic data for EthylAUSe, BenzylAUSe, EDASe, TETAUSe, and TAEAUSe^a.

Compound	EthylAUSe	BenzylAUSe	EDASe	TETAUSe	TAEAUSe
Formula mass	1061	784.11	655.99	652	827.01
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁</i>	<i>Pna2₁</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/m</i>
<i>a</i> (Å)	8.290 (1)	24.221 (2)	11.677 (2)	13.002 (2)	9.2218 (6)
<i>b</i> (Å)	12.349 (2)	11.917 (1)	7.908 (1)	7.962 (1)	12.2768 (9)
<i>c</i> (Å)	11.038 (2)	7.4528 (7)	15.698 (2)	14.754 (2)	9.4464 (7)
β (°)	104.439 (4)		98.813 (3)	114.077 (2)	116.165 (1)
<i>V</i> (Å ³)	1094.3 (3)	2151.1 (3)	1432.4 (3)	1394.5 (3)	959.88 (12)
<i>Z</i>	2	4	4	4	2
Abs. coeff. (mm ⁻¹)	19.843	10.991	16.478	16.918	14.217
θ (°) range	1.91–34.47	1.68–34.52	1.76–34.50	1.76–34.48	2.40–34.55
ρ_{calcd} (g/cm ³)	3.22	2.421	3.042	3.105	2.861
<i>R</i> (<i>F</i>) for $F_o^2 > 2\sigma(F_o^2)$	0.0425	0.0307	0.0371	0.0323	0.0322
<i>R_w</i> (F_o^2) ^b	0.1053	0.0812	0.0805	0.0830	0.0751

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum wF_o^4} \right]^{1/2}$$

(C₇H₉N, 99%, Fluka), ethylenediamine (C₂H₈N₂, 99%, Sigma), tris(2-aminoethyl)-amine (C₆H₁₈N₄, 96%, Aldrich), and triethylenetetramine (C₆H₁₈N₄, 97%, Fluka), were used as received without further purification. Distilled and Millipore filtered water with a resistance of 18.2 MΩ/cm was used in all reactions. While UO₂(NO₃)₂ · 6H₂O normally contains depleted U, standard precautions for handling radioactive materials should be followed.

EthylAUSe was synthesized by mixing 0.037 g ethylamine (0.57 mmol) with a solution containing 0.086 g UO₂(NO₃)₂ · 6H₂O (0.17 mmol), 0.25 mL H₂SeO₄ (0.97 mmol), and 2 mL distilled water in a 20-mL glass vial. The vial was left to stand at room temperature in air and yellow blocky crystals grew during the evaporation of the aqueous solution. BenzylAUSe, EDASe, TETAUSe, and TAEAUSe were synthesized by replacing ethylamine with 0.065 g benzylamine (0.57 mmol), 0.035 g ethylenediamine (0.57 mmol), 0.086 g triethylenetetramine (0.57 mmol), or 0.086 g tris(2-aminoethyl)-amine (0.57 mmol), respectively.

2.2. Crystallographic studies

Single crystals of EthylAUSe, BenzylAUSe, EDASe, TETAUSe, and TAEAUSe were selected using a polarized stereomicroscope and mounted on tapered glass fibers with epoxy for X-ray diffraction analysis. A sphere of data was collected for each compound at 110 K using a Bruker three-circle X-ray diffractometer equipped with an APEX CCD detector. The data were collected using monochromatic MoK α radiation with a frame width of 0.3 in ω , and a counting time per frame of 10 s. Unit-cell parameters were refined by least-squares techniques using the Bruker SMART software, and the SAINT software was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS. Selected data collection parameters and crystallographic information are listed in Table 1. Selected bond distances in these compounds are listed in Tables 2–6. Atomic coordinates and additional structural information is provided in the supplementary materials.

2.3. Infrared spectroscopy

Infrared spectra were obtained for single crystals of each compound 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 with a diamond ATR objective. Each spectrum was taken from 400 to 4000 cm⁻¹ with a beam aperture of 100 μ m. Infrared spectra are shown in Fig. 1.

Table 2
Selected bond distances (Å) for EthylAUSe.

Distances (Å)			
U (1)–O (1)	1.756 (7)	Se (1)–O (3)	1.646 (6)
U (1)–O (2)	1.768 (7)	Se (1)–O (4)	1.646 (6)
U (1)–O (3)	2.360 (7)	Se (1)–O (10)	1.629 (7)
U (1)–O (4)	2.439 (7)	Se (1)–O (15)	1.603 (7)
U (1)–O (5)	2.361 (7)	Se (2)–O (5)	1.654 (7)
U (1)–O (6)	2.357 (6)	Se (2)–O (11)	1.661 (7)
U (1)–O (7)	2.499 (8)	Se (2)–O (12)	1.646 (7)
U (2)–O (8)	1.782 (7)	Se (2)–O (16)	1.621 (8)
U (2)–O (9)	1.769 (7)	Se (3)–O (6)	1.660 (6)
U (2)–O (10)	2.354 (7)	Se (3)–O (13)	1.639 (6)
U (2)–O (11)	2.406 (7)	Se (3)–O (14)	1.648 (7)
U (2)–O (12)	2.434 (7)	Se (3)–O (17)	1.620 (7)
U (2)–O (13)	2.386 (6)		
U (2)–O (14)	2.373 (6)		

Table 3
Selected bond distances (Å) for BenzylAUSe.

Distances (Å)			
U (1)–O (1)	1.774 (3)	Se (1)–O (3)	1.655 (3)
U (1)–O (2)	1.765 (3)	Se (1)–O (4)	1.654 (3)
U (1)–O (3)	2.342 (3)	Se (1)–O (9)	1.631 (3)
U (1)–O (4)	2.334 (3)	Se (1)–O (10)	1.605 (3)
U (1)–O (5)	2.276 (4)	Se (2)–O (5)	1.652 (3)
U (1)–O (6)	2.495 (4)	Se (2)–O (7)	1.657 (3)
U (1)–O (7)	2.263 (4)	Se (2)–O (11)	1.633 (3)
		Se (2)–O (12)	1.606 (4)

2.4. Thermalgravimetric analysis (TGA)

TGA measurements were conducted using a Netzsch TG209 F1 Iris thermal analyzer. Samples were loaded into an aluminum crucible and heated from 20 to 620 °C at a rate of 5 °C/min under flowing nitrogen gas. Data are in Fig. 2.

3. Results

The structures of each of the five compounds reported herein are based upon uranyl pentagonal bipyramids and selenate tetrahedra that are linked into inorganic structural units. Each structure contains one or more crystallographically unique U⁶⁺ cations that are present as approximately linear (UO₂)²⁺ uranyl ions, with U=O bond lengths ranging from 1.757(7) to 1.782(7) Å

Table 4
Selected bond distances (Å) for EDAUSe.

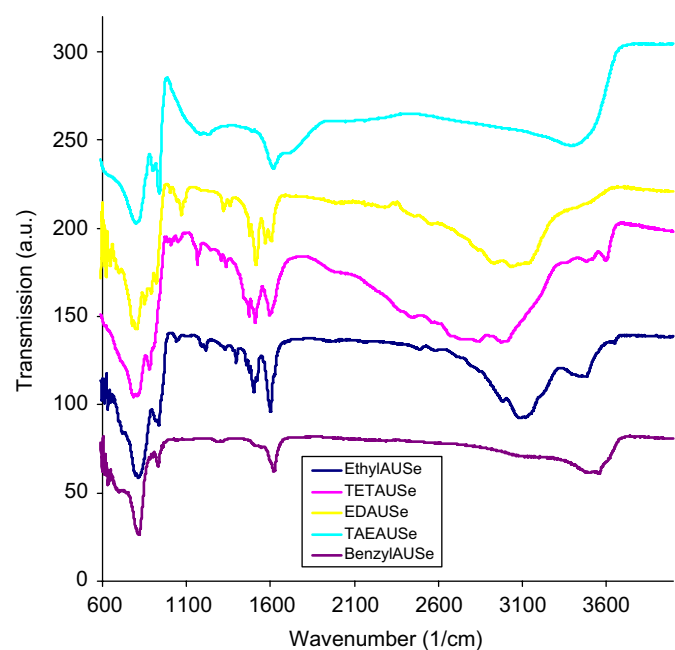
Distances (Å)			
U (1)–O (1)	1.773 (4)	Se (1)–O (3)	1.663 (4)
U (1)–O (2)	1.768 (4)	Se (1)–O (4)	1.658 (4)
U (1)–O (3)	2.362 (4)	Se (1)–O (10)	1.630 (4)
U (1)–O (4)	2.346 (4)	Se (1)–O (11)	1.609 (4)
U (1)–O (5)	2.371 (4)	Se (2)–O (5)	1.648 (4)
U (1)–O (6)	2.248 (4)	Se (2)–O (6)	1.652 (4)
U (1)–O (7)	2.470 (4)	Se (2)–O (8)	1.633 (4)
		Se (2)–O (9)	1.606 (4)

Table 5
Selected bond distances (Å) for TETAUSe.

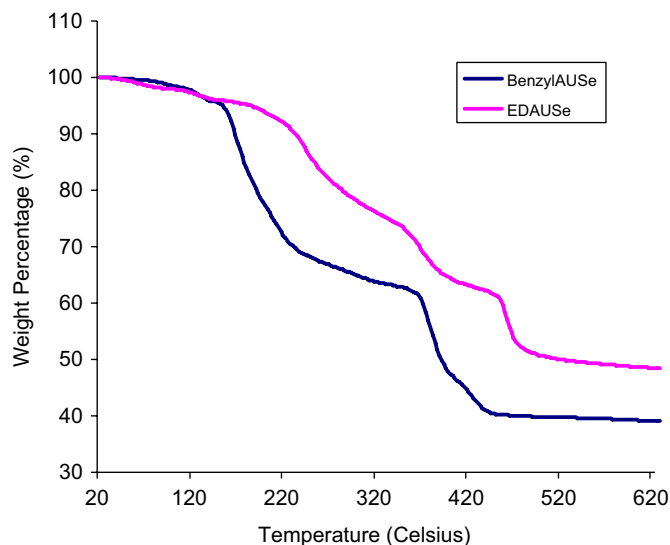
Distances (Å)			
U (1)–O (1)	1.777 (3)	Se (1)–O (3)	1.649 (3)
U (1)–O (2)	1.781 (4)	Se (1)–O (4)	1.643 (3)
U (1)–O (3)	2.450 (3)	Se (1)–O (8)	1.621 (4)
U (1)–O (4)	2.395 (4)	Se (1)–O (9)	1.630 (4)
U (1)–O (5)	2.371 (3)	Se (2)–O (5)	1.644 (3)
U (1)–O (6)	2.234 (3)	Se (2)–O (6)	1.649 (3)
U (1)–O (7)	2.463 (4)	Se (2)–O (10)	1.630 (4)
		Se (2)–O (11)	1.630 (4)

Table 6
Selected bond distances (Å) for TAEAUSe.

Distances (Å)			
U (1)–O (1)	1.770 (4)	Se (1)–O (4)	1.651 (3)
U (1)–O (2)	1.793 (4)	Se (1)–O (5)	1.656 (3)
U (1)–O (3)	2.375 (4)	Se (1)–O (6)	1.627 (3)
U (1)–O (4) × 2	2.334 (3)	Se (1)–O (7)	1.621 (3)
U (1)–O (5) × 2	2.396 (3)	Se (2)–O (3)	1.655 (4)
		Se (2)–O (8) × 2	1.637 (3)
		Se (2)–O (9)	1.632 (4)

**Fig. 1.** Infrared spectra of EthylAUSe, BenzylAUSe, EDAUSe, TETAUSe, and TAEAUSe.

in the five structures. These values are consistent with the average uranyl ion bond length of 1.79(3) Å in pentagonal bipyramids contained in 143 structures [1]. Each of the uranyl ions is

**Fig. 2.** TGA thermograms for BenzylAUSe and EDAUSe.

coordinated by five ligands that are arranged at equatorial positions of pentagonal bipyramids that are capped by the O atoms of the uranyl ions. The ligands correspond to either O atoms of selenate or H₂O, and equatorial bond lengths in the five structures are all in the range of 2.33(1) to 2.495(4) Å, with the longer distances being to O atoms of H₂O groups. These are in the normal range of equatorial bond lengths in uranyl pentagonal bipyramids, for which the average is 2.4(1) Å [1]. Bond lengths within the selenate tetrahedra range from 1.60(1) to 1.69(1) Å in the five structures. Bond-valence sums calculated for the U⁶⁺ and Se⁶⁺ sites [2,40] range from 5.97 to 6.13 and 5.87 to 6.14 valence units, respectively.

The structural units of the five compounds differ significantly, despite being constructed from polyhedra with similar geometries. Consider first the structure of TAEAUSe, which is shown in Fig. 3. A single crystallographically unique uranyl pentagonal bipyramid and two unique selenate tetrahedra are linked to form a chain that extends along [010]. The Se(1) tetrahedra are connected to two bipyramids by vertex sharing, and this results in a chain that is one bipyramid wide. Four of the equatorial vertices of each bipyramid are shared with tetrahedra that bridge between bipyramids. The remaining equatorial vertex is shared with the Se(2) tetrahedron, which is only connected to one bipyramid and is not essential to the connectivity of the chain.

The inorganic structural unit in TAEAUSe must possess a formal charge of 3⁻. Therefore, the formula of the structural unit is [(UO₂)(SeO₄)₂(HSeO₄)], although it is not certain which of the selenate tetrahedra contain the proton.

The positions of the C and N atoms of the [C₆H₂₁N₄]³⁺ cations were resolved (Fig. 3b). The organic molecules reside between the uranyl selenate chains and link them into the extended structure.

In the infrared spectrum of TAEAUSe (Fig. 1), a sharp band at 931 cm⁻¹ corresponds to the asymmetric stretches of uranyl ions. A strong band at 1182 cm⁻¹ is assigned as the characteristic Se–OH stretch of HSeO₄. Two bands at 782 and 864 cm⁻¹ are attributed to the stretches of the Se–O bonds. A weak band at 1530 cm⁻¹ is due to the N–H vibrational mode of amine groups. Two sharp bands at 1622 and 1687 cm⁻¹ and a broad band centered at 3376 are due to the absorbed water.

The remaining four structures reported herein contain two-dimensional sheets of uranyl pentagonal bipyramids and selenate tetrahedra. The sheet found in the structure of EthylAUSe (Fig. 4),

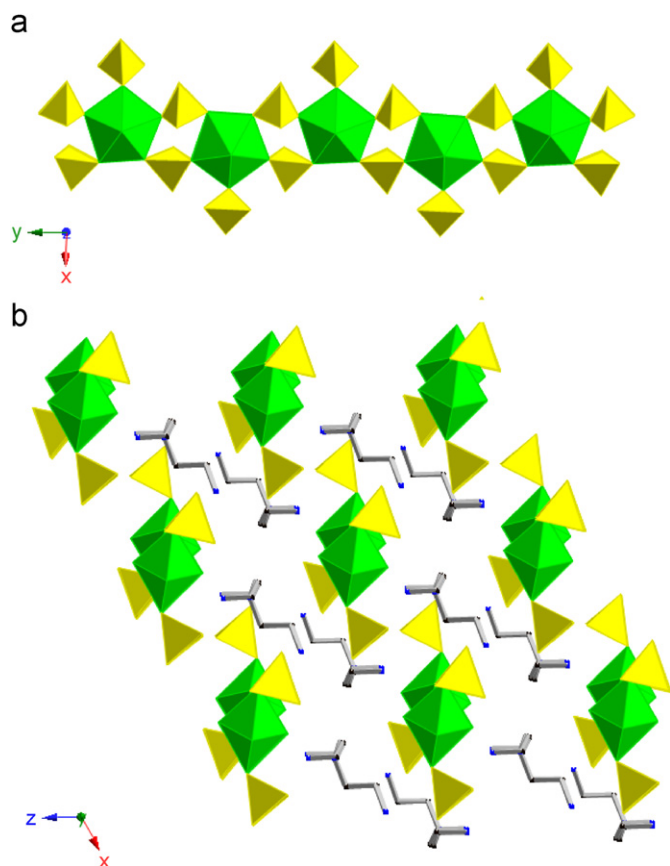


Fig. 3. The structure of TAEAUSe: (a) one-dimensional $[(\text{UO}_2)(\text{SeO}_4)_2(\text{HSeO}_4)]^{3-}$ chain and (b) the stacking mode of the chains. Uranium and selenate polyhedra are in green and yellow. Black and light blue balls represent carbon and nitrogen atoms, respectively.

is closely related to the chain structural unit in TAEAUSe (Fig. 3). Uranyl selenate chains topologically identical to those in TAEAUSe extend along [010] in the sheet, where they are cross-linked into a sheet by additional uranyl pentagonal bipyramids. Each of these additional bipyramids share four of their equatorial vertices with selenate tetrahedra of the chains, and the fifth equatorial position is occupied by H_2O . Thus, each of the selenate tetrahedra shares three of its vertices with uranyl pentagonal bipyramids. The sheets are oriented perpendicular to [100].

The uranyl selenate sheet in EthylAUSe has the composition $[(\text{UO}_2)_2(\text{SeO}_4)_3(\text{H}_2\text{O})]$ and the net charge of 2^- is balanced by the protonated ethylamine $[\text{C}_2\text{H}_5\text{N}]^+$ cations that occur in the interlayer between the sheets (Fig. 4b).

The structure of EthylAUSe contains two crystallographically unique U sites, as well as three Se sites. In the infrared spectrum (Fig. 1), two sharp bands that occur at 935 and 912 cm^{-1} are assigned as asymmetric stretches of uranyl ions. Bands at 813 , 793 , and 728 cm^{-1} are attributed to the stretches of the Se–O bonds. Two broad bands and two weak bands at 3653 , 3458 , 3105 , and 2986 cm^{-1} , respectively, are due to the O–H vibrational modes of the water molecules. Four sharp bands and several weak bands centered at 1500 and 1300 cm^{-1} , respectively, are assigned as the characteristic N–H and C–H vibrational modes of the protonated ethylamine cations.

The structures of BenzylAUSe and EDAAUSe contain topologically and compositionally identical sheets of uranyl pentagonal bipyramids and selenate tetrahedra (Figs. 5 and 6). Each bipyramid shares four of its equatorial vertices with selenate tetrahedra, and the fifth equatorial vertex is occupied by H_2O . The

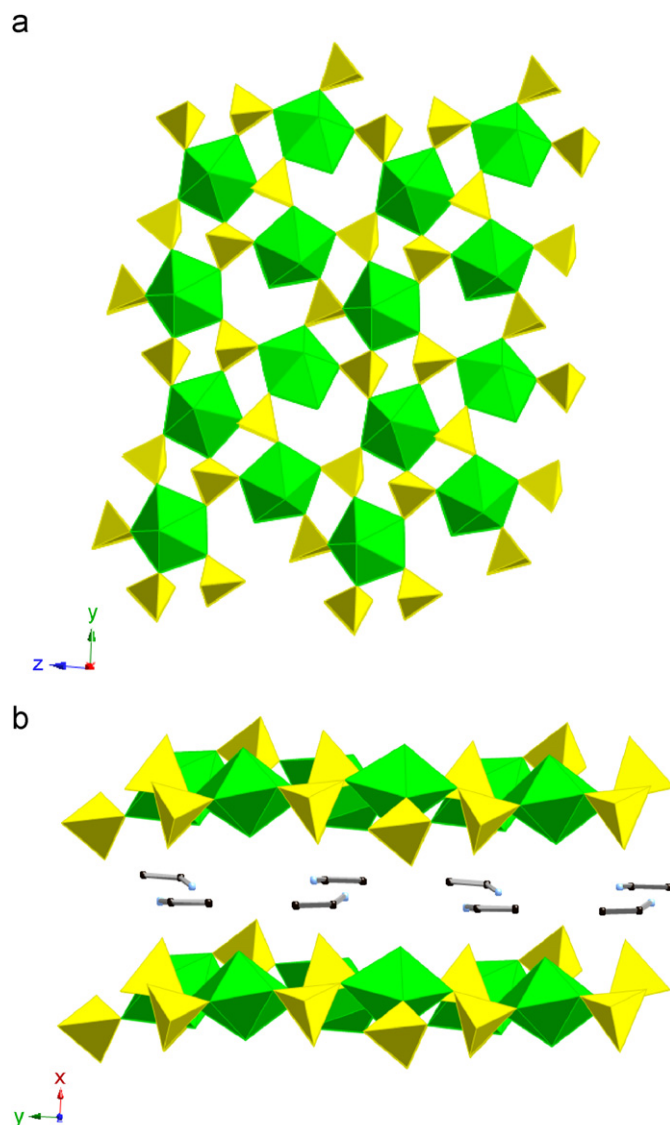


Fig. 4. The structure of EthylAUSe: (a) two-dimensional $[(\text{UO}_2)_2(\text{SeO}_4)_3(\text{H}_2\text{O})]^{2-}$ sheet and (b) the stacking mode of the sheets. Legend as in Fig. 3.

composition of the inorganic sheet in each structure is $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$. Void spaces within the sheet structure are bounded by rings of eight polyhedra, four tetrahedra and four bipyramids that alternate around the ring. The voids are arranged such that each bipyramid bounds four such voids. In this sheet all of the U^{6+} – H_2O bonds extend in the same direction.

The structures of BenzylAUSe and EDAAUSe contain protonated $[\text{C}_7\text{H}_{10}\text{N}]^+$ cations and protonated $[\text{C}_2\text{H}_{10}\text{N}_2]^{2+}$ cations in their corresponding interlayer regions (Figs. 5b, 6b). H bonds extending between these cations and O atoms of the inorganic sheets provide linkages between sheets. Each of these structures also has occluded H_2O groups in the interlayers, which provide additional H bonding. The infrared spectrum of BenzylAUSe contains a mode at 930 cm^{-1} that corresponds to the asymmetric stretch of the single crystallographically unique uranyl unit. Modes at 812 , 747 and 712 cm^{-1} are assigned to Se–O stretching. A broad band ranging from 3000 to 3700 cm^{-1} is assigned to the O–H vibrations of water molecules. The sharp band at 1621 cm^{-1} may be a water bending mode, and the two weak bands at 1549 and 1510 cm^{-1} are characteristic N–H vibrational modes of amine groups. Two weak bands at 1310 and 1280 cm^{-1} are thought to correspond to the vibrations of C–H bonds.

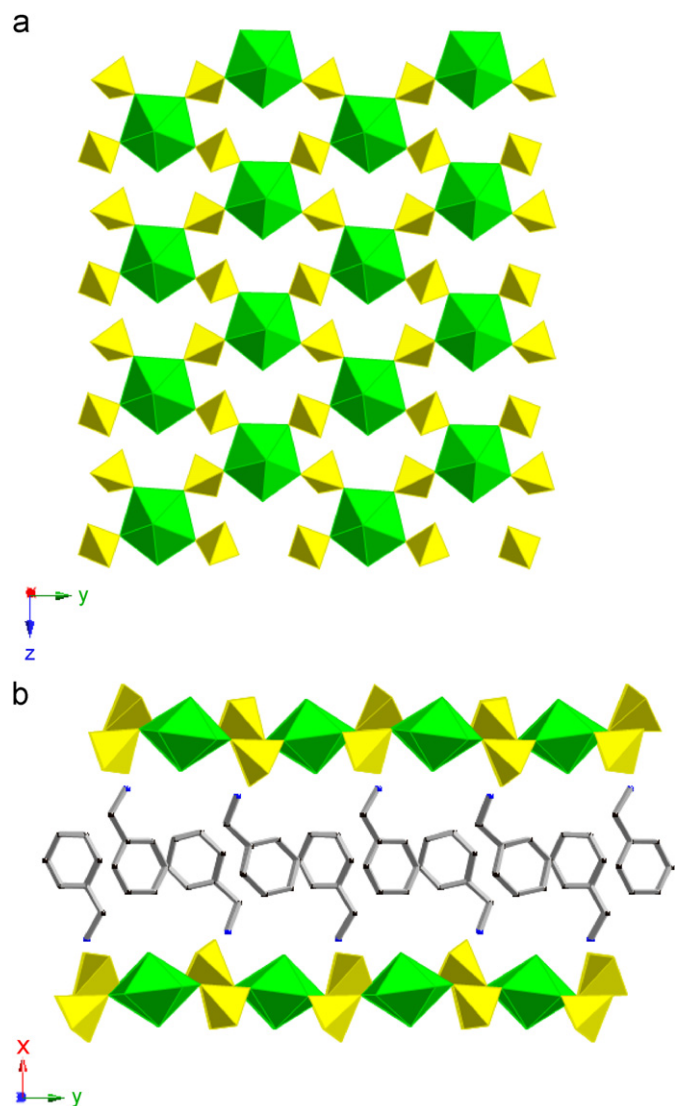


Fig. 5. The structure of BenzylAUSe: (a) two-dimensional $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ sheet and (b) the stacking mode of the sheets. Legend as in Fig. 3.

The infrared spectrum for EDAUSe shows an asymmetric uranyl stretch at 920 cm^{-1} , and Se–O stretching bands at 851, 801, and 774 cm^{-1} . The presence of the organic cation is confirmed by four bands centered at 1520 cm^{-1} and one band located at 1319 cm^{-1} that are assigned as the vibrational modes of N–H and C–H bonds, respectively. A broad band in the range of $3000\text{--}3500\text{ cm}^{-1}$ is due to the O–H vibrations in the water molecules.

Thermal analyses (Fig. 2) of BenzylAUSe and EDAUSe reveal broadly similar behaviors for the two compounds. In the case of BenzylAUSe, the total weight loss by about 150°C is 4.8% and corresponds to the occluded and bound H_2O (4.6% calculated on the basis of the formula). A weight loss of 29.1% over the temperature range from 150 to 360°C corresponds to destruction of the organic component of the structure (29.1% calculated), and the weight loss of 28.1% above 360°C is due to the loss of SeO_2 (28.3% calculated).

In the case of EDAUSe, the 6.6% weight loss between 80 and 200°C corresponds to H_2O groups (6.7% calculated). Decomposition of the organic component occurs over the range of 180 to 320°C and corresponds to 12.9% (12.7% calculated). The final

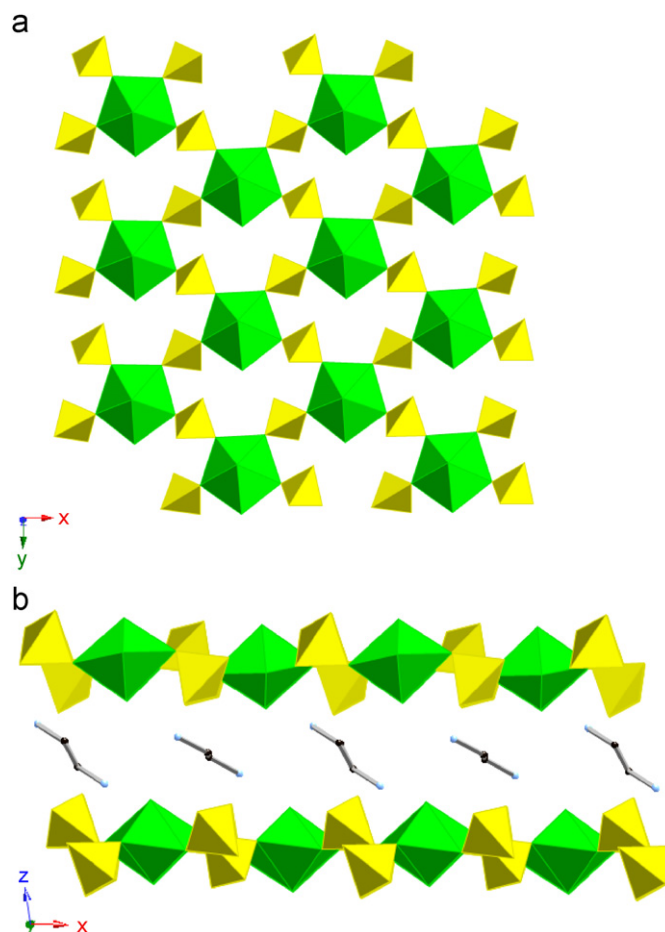


Fig. 6. The structure of EDAUSe: (a) two-dimensional $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ sheet and (b) the stacking mode of the sheets. Legend as in Fig. 3.

weight loss of 31.8% above 320°C corresponds to SeO_2 (32.1% calculated).

The uranyl selenate sheet found in the structure of TETAUSe (Fig. 7) is topologically distinct from that found in BenzylAUSe and EDAUSe. Each of the uranyl pentagonal bipyramids shares four of its equatorial vertices with selenate tetrahedra, and each tetrahedron is linked to two bipyramids, in common with the sheet in BenzylAUSe and EDAUSe. The differences of these sheets are most apparent when considering the lack of alignment of the bonds between the uranyl ions and equatorial H_2O groups, and the shape and size of the void spaces within the sheet. The $\text{U}^{6+}\text{--H}_2\text{O}$ bonds occur in four different orientations within the sheet. The void spaces are contained by rings composed of twelve bipyramids and tetrahedra that alternate along the ring. Thus, this void is larger and more elongated than found in the sheets in BenzylAUSe and EDAUSe.

The sheet in the structure of TETAUSe has the composition $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$. Protonated $[\text{C}_6\text{H}_{22}\text{N}_4]^{4+}$ cations and occluded H_2O groups occur in the interlayer region (Fig. 7b), and provide linkages between the sheets through H bonds.

The infrared spectrum of TETAUSe (Fig. 1) contains a sharp band at 920 cm^{-1} that is assigned to the asymmetric stretch of the uranyl ion. Bands at 881, 809, 789, and 712 cm^{-1} are assigned to Se–O stretches. A broad band in the range of 2500 to 3500 cm^{-1} is due predominantly to the O–H stretching in H_2O groups. The characteristic N–H and C–H vibrations are at 1510 and 1307 cm^{-1} .

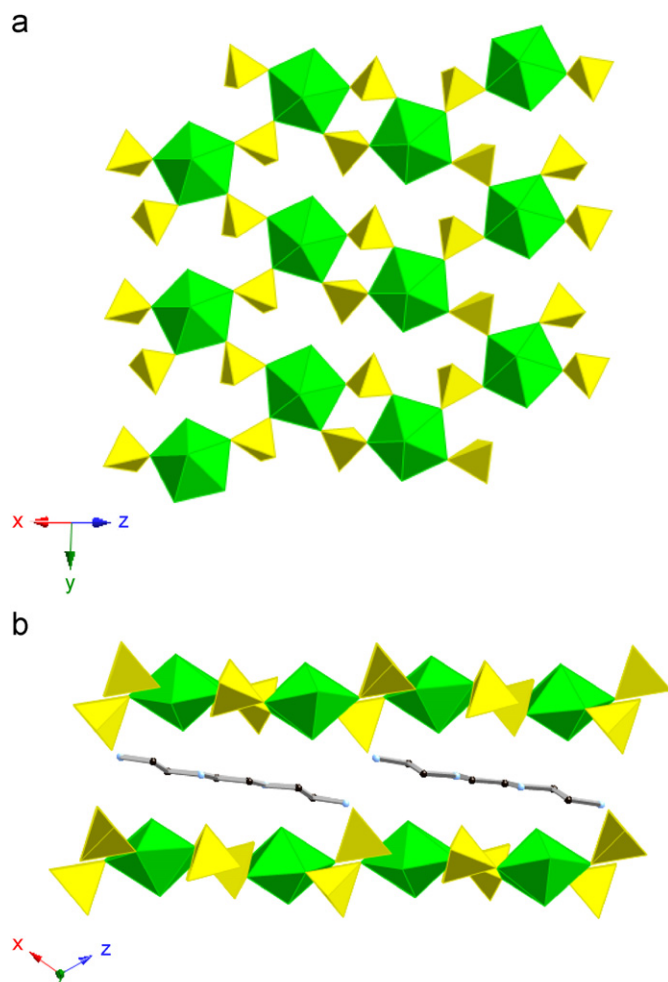


Fig. 7. The structure of TETAUSE: (a) two-dimensional $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ sheet and (b) the stacking mode of the sheets. Legend as in Fig. 3.

4. Discussion

Although the structural units of uranyl compounds containing XO_4 tetrahedra ($X = \text{hexavalent cation}$) have been fairly extensively studied, the compounds reported here present some interesting new topologies. The uranyl selenate chain in TAEAUSe (Fig. 3) has not been reported previously in a uranyl selenate, but has been documented in uranyl molybdates, phosphates, chromates and sulfates [1]. The U–Se–O linkages are apparently fairly pliable, as the details of their orientations along the chain length appear to respond to steric constraints of the overall structures found to date.

The sheet in EthylAUSe has a U:Se ratio of 2:3, and each uranyl pentagonal bipyramid is either attached to four or five selenate tetrahedra. In those that attach to only four tetrahedra, the fifth equatorial vertex is occupied by H_2O . This exact topology has not been found previously, although one other uranyl selenate sheet is known with the same metal proportions. The structure of $\text{Rb}_2[(\text{UO}_2)_2(\text{SeO}_4)_3(\text{H}_2\text{O})_2](\text{H}_2\text{O})_4$ [13] contains a sheet that has more H_2O , and uranyl pentagonal bipyramids are either linked to five selenate tetrahedra, or to only three, with the remaining two equatorial vertices being H_2O groups. The structure of $\text{K}_2[(\text{UO}_2)_2(\text{CrO}_4)_3(\text{H}_2\text{O})_2](\text{H}_2\text{O})_4$ [7] contains a sheet with a U:Cr ratio of 2:3, but in this case each pentagonal bipyramid is linked to four chromate tetrahedra, with the fifth equatorial position occupied by H_2O .

The uranyl selenate sheets in EDAUSE and BenzylAUSe have a U:Se ratio of 1:2, which is most common in known uranyl selenates. Each uranyl pentagonal bipyramid shares four vertices with selenate tetrahedra, whereas the fifth equatorial vertex is occupied by H_2O . Each selenate tetrahedron is linked to only two bipyramids. Topologically identical uranyl selenate sheets have been reported in the structures of $\text{Rb}_2[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ [13], $[\text{C}_2\text{H}_{10}\text{N}_2][(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ [41] and $[\text{C}_8\text{H}_{20}\text{N}]_2[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ [17], although the interlayer configurations of these three compounds is very different.

Comparing to the uranyl selenate sheets in EDAUSE and BenzylAUSe, the sheet in TETAUSE is unusual in that it contains fairly large voids that are bounded by six tetrahedra and six bipyramids. Topologically identical sheet composed of uranyl and sulfate polyhedra has been reported in the structure of $[\text{N}_2\text{C}_6\text{H}_4][\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)_2]$ [42].

The sheet structures reported herein comply well with the charge-density matching principle discussed by Krivovichev et al. [17]. The surface areas per formula unit for the uranyl selenate sheets in EthylAUSe, BenzylAUSe, EDAUSE, and TETAUSE are 136.307, 88.814, 92.335, and 152.883 \AA^2 and their charge-densities are -0.0147 , -0.0225 , -0.0217 , and $-0.0131 \text{ e}/\text{\AA}^2$, respectively. For BenzylAUSe, the charge-density ($-0.0225 \text{ e}/\text{\AA}^2$) of the $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ sheet is close to that ($-0.0224 \text{ e}/\text{\AA}^2$) of the sheet in $[\text{C}_8\text{H}_{20}\text{N}]_2[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})$ [17]. The protonated monoamine cations, $[\text{C}_7\text{H}_{10}\text{N}]^+$, are stacked such that amine heads alternately point toward overlying or underlying uranyl selenate sheets (Fig. 5b), which is similar to the stacking mode of $[\text{C}_8\text{H}_{20}\text{N}]^+$ cations in $[\text{C}_8\text{H}_{20}\text{N}]_2[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})$. The interdigitation of amine tails enables the charge-density at the surface of the organic templates to be a factor of two lower and match the charge-density of the uranyl selenate sheet. In the structure of EthylAUSe, the charge-density of the $[(\text{UO}_2)_2(\text{SeO}_4)_3(\text{H}_2\text{O})]^{2-}$ sheet is only about 2/3 of that in BenzylAUSe. As can be seen in Fig. 4b, the protonated ethylamine cations, $[\text{C}_2\text{H}_8\text{N}]^+$, are stacked in closer alignment to the uranyl selenate sheet and its surface charge-density is decreased to match the small charge-density of the uranyl selenate sheet. The uranyl selenate sheet in EDAUSE has a similar charge-density to that in BenzylAUSe. If the protonated organic templates stack in the same way as the monoamine molecules in BenzylAUSe, the charge-density would be doubled because the ethylenediamine has amine groups on both ends of the carbon chain. In order to match the charge-density of the uranyl selenate sheet, the ethyleneamine groups are rotated strongly with small inclination angles (30° to 40°) to the uranyl selenate sheet to decrease the charge-density (Fig. 6b). Whilst, in the structure of TETAUSE (Fig. 7b), the longer chain and even smaller inclination angles (in the range of 15° to 20°) decrease the charge-density of the diamine organic templates more and enable it match with the small charge-density ($-0.0131 \text{ e}/\text{\AA}^2$) of the uranyl selenate sheet effectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.11.013.

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