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# Unprecedented layer topology in the crystal structure of a new organically templated uranyl selenite-selenate

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**The crystal structure of the new organically templated uranyl selenite-selenate $[C_2H_8N][(H_5O_2)(H_2O)][(UO_2)_2(SeO_4)_3(H_2SeO_3)](H_2O)$ is based upon complex layers with a unique topology, which was not observed previously in inorganic compounds.**

The oxo salt compounds of uranyl have been intensively studied owing to their importance in radioactive waste management, uranium mineralogy, catalysis, ion-exchange, *etc*.[1] Special attention was attracted to organically templated uranyl compounds as promising materials for separation and extraction technologies. A variety of compounds of this class, including organically templated uranium sulfates,[2–6] selenites,[7] molybdates,[8–12] vanadates[13,14] and silicates,[15] have been prepared recently. Uranyl selenates,[16–21] which can form nanotubular structures[22–24] that have no analogues among well-known inorganic oxo salts, are of special interest. Here, we report on the synthesis[†] and structural characterization of a new uranyl selenite-selenate, $[C_2H_8N][(H_5O_2)(H_2O)][(UO_2)_2(SeO_4)_3(H_2SeO_3)](H_2O)$ **1**, with an unprecedented layer topology.

The crystal structure of **1**[‡] contains two independent U atoms that form the linear uranyl cation $[O{=}U{=}O]^{2+}$. The U=O bond lengths are 1.751(5)–1.765(4) Å. Both uranyl cations formed by the U(1) and U(2) atoms are surrounded in the equatorial plane by five $O_{eq}$ atoms to form the pentagonal bipyramids $[UO_7]^{8-}$. In the crystal structure of **1**, the U–$O_{eq}$ bond lengths vary from 2.378(4) to 2.414(5) Å. In the structure of **1**, three sites [Se(1), Se(2) and Se(3)] of four independent Se positions correspond to $Se^{VI}$, whereas the Se(4) site is occupied by $Se^{IV}$. The $Se^{VI}$ positions are surrounded by four O atoms each with the average ⟨Se–O⟩ bond lengths of 1.638, 1.636 and 1.642 Å for Se(1), Se(2) and Se(3), respectively. The Se(4) site has a trigonal pyramidal coordination with an apex occupied by the $Se^{IV}$ atom. This coordination is typical of the $Se^{IV}$ atom with a stereoactive lone electron pair. The $Se(4)O_3$ trigonal pyramid is strongly distorted with one short Se(4)–O(17) bond [1.661(4) Å], and the Se(4)–O(18) and Se(4)–O(19) bonds being appreciably longer [1.713(5) and 1.735(5) Å, respectively]. Such a distorted coordination geometry is typical of biprotonated selenite groups ($H_2SeO_3$); in particular, it was observed in the structure of $[C_5H_{14}N]_4(UO_2)_3(SeO_4)_4(HSeO_3)(H_2O)(H_2SeO_3)(HSeO_4)$.[27]

The crystal structure of **1** is based upon $[(UO_2)_2(SeO_4)_3(H_2SeO_3)]^{2-}$ layers formed as a result of the condensation of $[UO_7]^{8-}$, $[SeO_4]^{2-}$ and ($H_2SeO_3$) coordination units by sharing common oxygen atoms. The $[(UO_2)_2(SeO_4)_3(H_2SeO_3)]^{2-}$ layers are parallel to (101) (Figure 1). Protonated dimethylamine molecules, $[C_2H_8N]^+$, and $[H_5O_2]^+$ hydroxonium complexes are located in the interlayer space and form hydrogen bonds to the O atoms of uranyl groups and selenium oxo complexes.

Figure 2(*a*) shows the structure of the $[(UO_2)_2(SeO_4)_3(H_2SeO_3)]^{2-}$ layer in more detail. The selenate tetrahedra and ($H_2SeO_3$) trigonal pyramids coordinate uranyl ions in a mono-

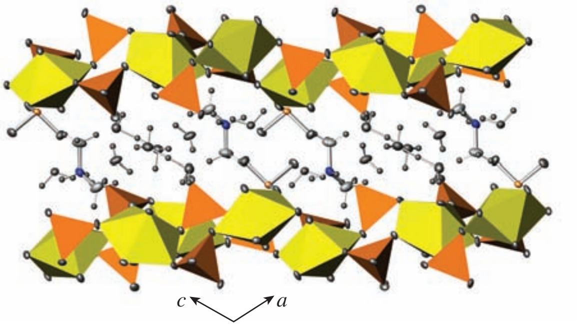

**Figure 1** Crystal structure of **1** projected along the *b* axis. Displacement ellipsoids are drawn at a 50% probability level.

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[†] The yellowish green transparent plates of **1** were prepared by evaporation from aqueous solutions. A mixture of 0.0503 g (0.1 mmol) of $UO_2(NO_3)_2{\cdot}6H_2O$, 0.0045 g (0.1 mmol) of dimethylamine, 0.1160 g (0.8 mmol) of 40% $H_2SeO_4$, and 2 ml of distilled water was stirred until complete homogenization, poured onto a watch glass, and kept in a fume hood at room temperature. The crystals of **1** crystallized on the bottom of the vessel after three days.

[‡] *Crystallographic data*. Crystals of **1** ($C_2H_{19}NO_{23}Se_4U_2$, $M = 1217.08$) are monoclinic, space group $P2_1/n$, at 293 K: $a = 14.7979(8)$, $b = 10.0238(6)$ and $c = 16.4176(9)$ Å, $\beta = 111.628(1)°$, $V = 2263.8(2)$ Å$^3$, $Z = 4$, $d_{calc} = 3.571$ g cm$^{-3}$, $\mu(\text{MoK}\alpha) = 20.822$ cm$^{-1}$, $F(000) = 2168$. Intensities of 25431 reflections were measured with a Bruker SMART APEX II CCD diffractometer [$\lambda(\text{MoK}\alpha) = 0.71073$ Å, $2\theta_{max} = 58°$] and 5476 independent reflections ($R_{int} = 0.0734$) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against $F^2$ in the anisotropic-isotropic approximation. Hydrogen atoms of $H_2O$ groups were located from the Fourier synthesis of the electron density. The H(C,N) atom positions were calculated. The refinement converged to $wR_2 = 0.0538$ and GOF = 0.928 for all independent reflections [$R_1 = 0.0265$ was calculated against $F$ for 4285 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.16.

CCDC 824406 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2012.

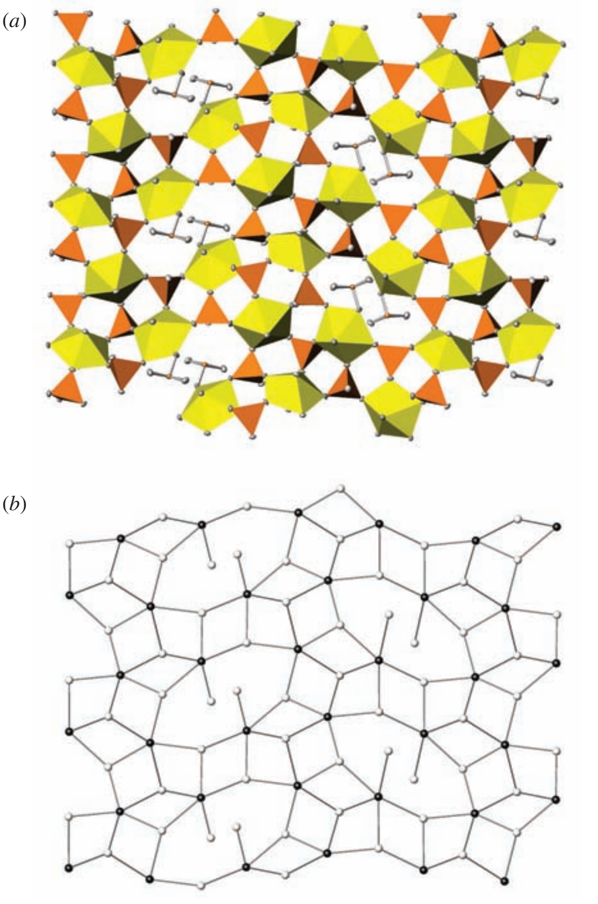

**Figure 2** (*a*) Projection of the uranyl selenite-selenate layer in the crystal structure of **1** (displacement ellipsoids at 50% probability level) and (*b*) its topology shown as a graph (U and Se polyhedra are symbolized by black and white nodes, respectively).

dentate fashion; however, their topological roles are remarkably distinct. The selenate group coordinates three uranyl ions, whereas protonated selenite groups coordinate one uranyl ion each. This is in agreement with the empirical rule formulated previously that, in uranyl selenite-selenate complexes, the connectivity of selenite is lower than that of selenate anions.[28] The linkage topology of the U and Se polyhedra can be described in terms of the graph theory[29] if U and Se atoms are symbolized by black and white nodes. The nodes are linked by a line if the corresponding atoms are bonded to the same bridging O atom. An idealized version of the black-and-white graph for the uranyl selenite-selenate complex in **1** is shown in Figure 2(*b*). This topology is unprecedented for both the chemistry of uranium and the structural chemistry of uranyl oxo salts in general. The topology is remarkable due to the presence of 1-connected branches inside eight-membered rings; this feature has been observed in just two other organically templated uranyl oxo salt compounds[21,30] and has never been observed in other inorganic oxo salts.

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