The Effect of Hydrogen Bonding on the Uranyl Selenate and Sulfate Crystal Structures

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Introduction

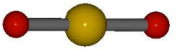
Within the last decade, structural chemistry of uranium oxycompounds and oxysalts in particular attracted considerable attention, due to both problems of storage and disposal of spent nuclear fuel, and the perpspective of fabrication of novel functional materials based on uranium and transuranium elements. By application of a wide range of experimental techniques, synthetic approaches and advanced analytical methods it was possible to identify new classes of actinide-containing compounds, in particular, nanostructures based on uranuim, neptunium and plutonium oxides: nanotubules and nanoclusters.

A separate and, perhaps, another interesting research direction is structural chemistry of uranyl-containing composite compounds, when inorganic blocks alternate with organic molecular assemblies with interactions restricted to weak hydrogen or van-der-Waals bonds only. At present, several hundreds of uranyl selenates, sulfates, chromates and molybdates are known which contain amines and diamines with different C_nH_{2n} carbohydrate fragments ($n = 1 - 12$), cyclic amines and even electroneutral organic molecules.

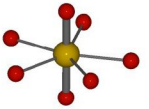
Introduction

These studies helped to understand at least some structural mechanisms that control formation of structural units with different topologies: hydrophobic-hydrophilic interactions, the principle of charge-density matching, and nanoscale models of self-assembly in uranyl selenate systems.

In the crystal structures of amine-templated uranyl selenates, structure formation is regulated by hydrogen bonding systems and by arrangement of hydrophobic and hydrophilic parts of molecules with voids and dense fragments of inorganic complexes. The basic structural principle of organic-inorganic uranyl composites templated by electroneutral molecules (such as crown ethers), is the translation of interactions between organic and inorganic components by means of protonated water molecule complexes (e.g., $H_3O_2^+$ and H_3O^+). Thus the organic substructural complexes control the topology formation of massive uranyl contaning units.



Uranyl ion $[UO_2]^{2+}$ and its equatorial coordination results in formation of bypiramids



Experiment

Single crystals of $[CH_6N_3]_2[(UO_2)_2(SeO_4)_3]$ (**1**) and $[CH_3NH_3]_2[(UO_2)_2(SO_4)_3]$ (**2**) (*Fig.1*) have been prepared by isothermal evaporation from aqueous solutions under room-temperature conditions. The crystal structure of **1** has been solved by direct methods [monoclinic, *P*2, a = 9.9448(15), b = 9.727(2), c = 10.1508(15) Å, β = 90.213(12)°, V = 981.9(3) Å^3, Z = 2] and refined to R_1 = 0.0696 (wR_2 = 0.1611) for 2511 reflections with $|F_o| \geq 4\sigma_F$ using least square techniques. The crystal structure of **2** has been solved by direct methods [triclinic, *P*1, a = 8.4784(6), b = 9.7873(8), c = 9.8121(7) Å, α = 90.170(2), β = 95.744(2), γ = 90.136(2) °, V = 810.12(10) Å^3, Z = 1] and refined to R_1 = 0.0146 (wR_2 = 0.0336) for 5378 reflections with $|F_o| \geq 4\sigma_F$ using least square techniques.

The structures of **1** and **2** are based upon the $[(UO_2)_2(TO_4)_3]^{2-}$ (T = Se, S) two-dimensional uranyl layers formed by linkage of U pentagonal bipyramids and TO_4 tetrahedra via common O atoms.

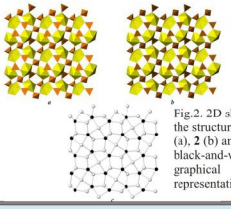


Fig.2. 2D sheets in the structures of **1** (a), **2** (b) and its black-and-white graphical representation (c).

Crystal Structure

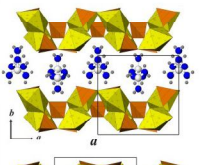


Fig.1. Crystal structures of **1** (a) and **2** (b).

Analysis of the topology of the uranyl selenate and uranyl sulfate layers using graphs indicated that the topology of the 2D layers in the structures of **1** and **2** (Fig. 2) is based on the linkage of two types of 4-membered rings. This type of topology (Fig. 2c), cc2-2:3-14, of heteropolyhedral units have been previously observed in the structures of several actynyl compounds ($Cs_2[(UO_2)_2(SO_4)_3]$, $[(NpO_2)_2(SO_4)_2(HSO_4)](H_2O)_4$, β–$Cs_2[(UO_2)_2(MoO_4)_3]$, $[N_2C_3H_5]_2[(UO_2)_2(SO_4)_3]$, $(H_3O)[C_3H_4N_2][(UO_2)_2(SeO_4)_3]$, and recently $(CH_3NH_3)_2[(UO_2)_2(SeO_4)_3]$).

An interesting fact is that all the compounds that possess the topology depicted in Fig. 2c, except for $(CH_3NH_3)_2[(UO_2)_2(SeO_4)_3]$, crystallize in tetragonal or orthorhombic space groups. Crystal structure of $[CH_6N_3]_2[(UO_2)_2(SeO_4)_3]$ is monoclinic, whereas the symmetry of heavy atoms – U and Se – correspond to the $P2_12_12$ space group (it is noteworthy that $[(NpO_2)_2(SO_4)_2(H_2SO_4)](H_2O)_4$ has the same orthorhombic symmetry).

Crystal structure

The guanidinium molecules are arranged in the interlayer space and are highly ordered. The orthorhombic symmetry is violated due to the tilting of selenate tetrahedra (Fig. 3) that correspond to the shift of the O atoms from the ideal location towards protonated amine groups of guanidine molecules, with which they form a moderate hydrogen bond.

Another case was found in the structure of $[CH_3NH_3]_2[(UO_2)_2(SO_4)_3]$. The total structure of **2** has low triclinic symmetry, whereas positions of the U and S atoms could be refined in the higher monoclinic group $P2_1$.

Oxygen atoms of uranyl cations and non-bridging O atoms of sulfate tetrahedra are highly ordered and correspond to the $P2_1$ and $P2/c$ space groups, respectively. In contrast, positions of carbon atoms of the methylammonium molecules obey the Pm symmetry. Reduction of symmetry from monoclinic to triclinic is governed by the mutual shifts of the U-Se bridging O atoms and N atoms of the organic molecules towards each other due to the formation of weak hydrogen bonds (Fig. 4).

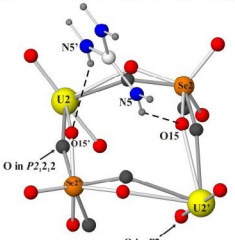


Fig.3. Scheme of the selenate tetrahedra tilting under the hydrogen bonding with guanidinium molecules in the structure of **1**. Flags "O in *P*2" and "O in *P*2,2,2" indicate the position of oxygen atoms at structure refinement in *P*2 and *P*2,2,2 space groups, respectively.

Conclusion

In general, this work shows that even weak hydrogen-bond interactions between O atoms of uranyl-based inorganic units and amine headgroups of organic cations may have a profound influence upon the symmetry of the whole structure. Despite the fact that, in our case, the topology of the structure is not controlled by organic molecules, interactions between organic complexes and inorganic layers result in significant symmetry reduction. The fact that this reduction is not observed in purely inorganic materials (such as $Cs_2[(UO_2)_2(SO_4)_3]$, $[(NpO_2)_2(SO_4)_2(H_2SO_4)](H_2O)_4$, β–$Cs_2[(UO_2)_2(MoO_4)_3]$) provides another evidence supporting our observations. It is very likely that additional H_2O molecules located in the interlayer space may significantly weaken the symmetry-reducing influence of organic molecules due to the formation of shielding hydrogen-bond interactions.

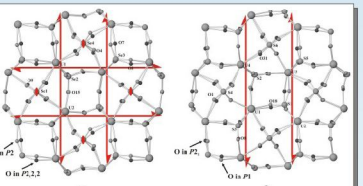


Fig.4. Imposition of uranyl selenate and sulfate layers refined in lower (oxygen atoms are light-grey) and higher (oxygen atoms are dark-grey) space groups in the structures of **1** (a) and **2** (b).

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