

Geometrical features of two novel layered uranium selenite-selenates

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During the last decade, oxygen compounds of uranium have become the objects of numerous studies related to the search for mineral-like matrices for immobilization of long-lived radionuclides. Selenium-containing uranium complexes are of special interest due to their geochemical and mineralogical abundance. The ⁷⁹Se isotope is known to be a long-lived radionuclide with a half-life of 1.1×10^6 years. The stable oxygen-containing selenium complexes include selenate $[\text{Se}^{6+}\text{O}_4]^{2-}$ and selenite $[\text{Se}^{4+}\text{O}_3]^{2-}$ groups. The investigations of mixed uranium selenite-selenates are rather rare. Here, we report on the structural characterization of two novel compounds of this type.

Single crystals of $[\text{C}_2\text{H}_8\text{N}]_3[\text{C}_2\text{H}_7\text{N}][(\text{UO}_2)_3(\text{SeO}_4)_4(\text{HSeO}_3)(\text{H}_2\text{O})]$ (**I**) and $[\text{C}_2\text{H}_8\text{N}]_3[\text{H}_3\text{O}][(\text{UO}_2)_3(\text{SeO}_4)_4(\text{SeO}_3)(\text{H}_2\text{O})](\text{H}_2\text{O})$ (**II**) were prepared by evaporation from aqueous solutions of uranyl nitrate, dimethylamine, selenic acid and distilled water. Crystals of **I** and **II** selected for data collection were mounted on STOE IPDS II diffractometer, and Bruker SMART APEX II CCD diffractometer, respectively. Data were collected using monochromated $\text{MoK}\alpha$ X-radiation.

The structures of **I** and **II** have been solved by direct methods and refined using least-squares techniques. The compound **I** is orthorhombic, space group $Pnma$, $a = 11.6591(11)$ Å, $b = 14.9556(17)$ Å, $c = 22.194(2)$ Å, $V = 3870.0(7)$ Å³, $R_1 = 0.0609$ ($wR_2 = 0.1094$) for 1221 unique reflections with $|F_o| \geq 4\sigma_F$. The compound **II** is monoclinic, space group $P2_1/m$, $a = 8.312(2)$ Å, $b = 18.636(4)$ Å, $c = 11.562(2)$ Å, $\beta = 97.582(1)^\circ$, $V = 3870.0(7)$ Å³, $R_1 = 0.0389$ ($wR_2 = 0.1150$) for 3949 unique reflections with $|F_o| \geq 4\sigma_F$.

The uranium pentagonal bipyramids, selenate tetrahedra and selenite trigonal pyramids share corners to form the $[(\text{UO}_2)_3(\text{SeO}_4)_4(\text{HSeO}_3)(\text{H}_2\text{O})]^{3-}$ layers (in **I**) and $[(\text{UO}_2)_3(\text{SeO}_4)_4(\text{SeO}_3)(\text{H}_2\text{O})]^{4-}$ layers (in **II**). In the crystal structure of **I** the layers are parallel to (001) and are strongly undulated along the c axis. The undulations in the adjacent layers have an anti-phase character which means that large elliptical channels are created along the a axis. The layers in **II** are parallel to (100). The charge of the inorganic layers is compensated by protonated dimethylamine molecules $[\text{C}_2\text{H}_8\text{N}]^+$ and hydronium cation $[\text{H}_3\text{O}]^+$ located in the interlayer space and connected by hydrogen bonds with apical O atoms of inorganic two-dimensional complexes.

The analysis of the layers topology in **I** and **II** by means of the graph theory shows that black-and-white graph corresponds to the same topology type **13/5c**, where the selenate tetrahedra coordinate in the tridentate fashion, and the selenite trigonal pyramids — in the bidentate fashion. The tridentate and bidentate character of the Se^{6+} and Se^{4+} polyhedra gives possibility to the formation of orientational geometrical isomers that differ from each other by 'up' and 'down' orientations of the Se–O bonds relative to the plane of the layer. In spite of the same topology type, the crystal structures of **I** and **II** have the different system of polyhedral orientations. It may be written as (ududud)(ud□du□) and (duuudd)(ud□du□), in **I** and **II** respectively.

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