

Poster Presentations

[MS18-P13] The Effect of Hydrogen Bonding on the Uranyl Selenate and Sulfate Crystal Structures.

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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 perspective 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 uranium, 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. 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., H₅O₂⁺ and H₃O⁺). Thus the organic substructural complexes control the topology formation of massive uranyl containing units.

There are several examples of organic-inorganic uranyl compounds, where the reduction in symmetry proceeds without changes in topological structure of inorganic unit. For instance, recently prepared crystal structures of two novel uranyl compounds, [CH₆N₃]₂[(UO₂)₂(SeO₄)₃] (1) and [CH₃NH₃]₂[(UO₂)₂(SO₄)₃] (2), contain layers with ideal tetragonal symmetry that nevertheless crystallize in low-symmetry space groups. Symmetry reduction is a consequence of weak hydrogen-bond interactions between O atoms of uranyl-based inorganic units and amine headgroups of organic cations. Whereas the topology of the structure is not controlled by organic molecules, interactions between organic complexes and inorganic layers result in significant symmetry reduction.

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