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New uranyl compounds with microporous frameworks

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The first microporous framework structures containing uranium and chromium have been synthesized and characterized. $Rb_2[(UO_2)_2(CrO_4)_3(H_2O)_2](H_2O)_3$ (1) was crystallized from uranyl chromate solution by evaporation. Further evaporation led to increased viscosity of the solution and overgrowing of $Rb_2[(UO_2)_2(CrO_4)_3(H_2O)](H_2O)$ (2) on the crystals of 1. With respect to 1, the framework of 2 is partially dehydrated. Both frameworks differ compositionally by only one water molecule, but this seemingly small difference affects significantly the pore size and overall structural topology of the frameworks, which present very different flexibility of the U-O-Cr links. These are rigid in the pillared framework of 1, in contrast to 2 where the U-O-Cr angles range from 126.3 to 168.2°, reflecting the substantial flexibility of Cr-O-U connections which make them comparable to the corresponding Mo-O-U links in uranyl molybdates.

A templated new organically uranyl sulfate. $(pyrH^{+})_{2}[(UO_{2})_{6}(SO_{4})_{7}(H_{2}O)_{2}]$ (3) was obtained by slow evaporating from the solution containing uranyl nitrate, sulfuric acid and pyridine. The crystals of 3, within two weeks, in the mother liquor gradually disappeared, followed by the simultaneous crystallization of framework $(pyrH^+)(H_3O)[(UO_2)_3(SO_4)_4(H_2O)_2](H_2O)$ (4) and layered $(pyrH^+)_2[(UO_2)_2(SO_4)_3]$ (5). The frameworks, in the structures 3 and 4, contain channel systems with sizes 12.4×10.2 and 12.9×10.8 Å, respectively. Change of frameworks densities and structural complexity after the recrystallization is discussed.

In the crystal structures of $Na_2(SO_3OH)(mfaH^+)[(UO_2)(SO_4)_2]$ (6) and $Na(mfaH^+)[(UO_2)_2(SeO_4)_3(H_2O)](H_2O)_2$ (7) uranyl-sulphate and uranyl-selenate units are interconnected via sodium complexes with mfa into metal-organic frameworks. Both frameworks contain the channels of 10.2×9.8 and 12.8×5.4 Å in 6 and 7, respectively.

Until recently, crystal structures of uranyl compounds containing inorganic nanotubes were known only for uranyl-selenate systems. There are three known topological types of nanotubes with internal diameters of ~7 Å and ~15 Å. Uranyl sulfate Na(phgH⁺)₇[(UO₂)₆(SO₄)₁₀](H₂O)_{3.5} (1) was obtained at room temperature by evaporation from aqueous solution. Its structure contains unique uranyl sulfate $[(UO_2)_6(SO_4)_{10}]^{8-}$ nanotubules templated by protonated N-phenylglycine $(C_6H_5NH_2CH_2COOH)^+$. Their internal diameter is 14 Å.

A comparative crystal chemical analysis of new and previously described micro - and mesoporous framework uranyl compounds will be discussed.

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Keywords: micro - and mesoporous framework uranyl compounds, uranyl nanotubules