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Nanoscale Hemispheres in Novel Mixed-Valent Uranyl Chromate(V,VI), $(C_3NH_{10})_{10}[(UO_2)_{13}(Cr_{12}{}^{5+}O_{42})(Cr^{6+}O_4)_6(H_2O)_6](H_2O)_6$

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Supporting Information

ABSTRACT: The structure of a novel mixed-valent chromium uranyl compound, $(C_3NH_{10})_{10}[(UO_2)_{13}(Cr_{12}{}^{5+}O_{42})(Cr^{6+}O_4)_6(H_2O)_6](H_2O)_6$ (**1**), obtained by the combination of a hydrothermal method and evaporation from aqueous solutions with isopropylammonium, contains uranyl chromate hemispheres with lateral dimensions of 18.9 × 18.5 Å^2 and a height of about 8 Å. The hemispheres are centered by a UO_8 hexagonal bipyramid surrounded by six dimers of $Cr^{5+}O_5$ square pyramids, UO_7 pentagonal bipyramids, and $Cr^{6+}O_4$ tetrahedra. The hemispheres are linked into two-dimensional layers so that two adjacent hemispheres are oriented in opposite directions relative to the plane of the layer. From a topological point of view, the hemispheres have the formula $U_{21}Cr_{23}$ and can be considered as derivatives of nanospherical cluster $U_{26}Cr_{36}$ composed of three-, four-, and five-membered rings.

Within the recent decade, considerable advances have been achieved in the field of actinide nanoparticles.[1] Of particular interest are structures in which nanoscale clusters and units are assembled into periodic three-dimensional (3D) arrays accessible for X-ray diffraction (XRD) studies. Burns and co-workers reported a whole series of novel uranyl peroxide nanospheres with a rich diversity of topologies[2] and demonstrated that they may also exist in aqueous solutions as independent complex ions.[3] Krivovichev et al.[4] reported the formation of uranyl selenate nanotubules; however, despite considerable efforts,[5] only two topological types of tubules have been observed. Nanotubular units have also been found in uranyl diphosphonates.[6] The formation of nanoscale units in uranyl chemistry is associated with the ability of uranyl-based structures to form curved topologies,[7] which is especially favored by the preference of uranyl ions to polymerize in a two-dimensional (2D) mode.[8] Here we report on the synthesis, structure, and properties of the new compound $(C_3NH_{10})_{10}[(UO_2)_{13}(Cr_{12}{}^{5+}O_{42})(Cr^{6+}O_4)_6(H_2O)_6](H_2O)_6$ (**1**), the low-temperature phase in the $(CH_3)_2CHNH_2$−CrO_3−$(UO_2)(NO_3)_2$−H_2O system obtained by evaporation from aqueous solutions.

Uranyl chromates belong to the large group of uranyl compounds containing oxyanions formed by hexavalent elements T^{6+} (T = Mo, S, Cr, Se). The group shows remarkable structural and topological diversity,[4c] and numerous studies revealed specific structural trends associated with the chemical nature of the T^{6+} ion. Most of the structures observed in the group have layered or chain topologies with the remarkable tendency for uranyl molybdates to form 3D frameworks. The majority of uranyl chromates known to date are chromates(VI), i.e., contain Cr^{6+} ions in tetrahedral coordination.[9] There are only four pure uranyl chromates containing Cr^{5+} ions, and all are based on $[(UO_2)_2Cr_2O_8]^{2-}$ sheets typical of the well-known carnotite group compounds.[10,11] Very recently, Unruh et al.[12] reported a series of mixed-valent chromium uranyl compounds with Cr^{5+} ions in square-pyramidal coordination and Cr^{6+} in tetrahedral coordination.

Single crystals of **1** were obtained by the combination of a hydrothermal method and evaporation from aqueous solutions from a mixture of 0.3 g of CrO_3, 0.2 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$, 1.7 mL of $(CH_3)_2CHNH_2$, and 10 mL of distilled water. Other initial ratios between isopropylamine and inorganic components of the synthesis mixture result in the formation of a number of different compounds as described earlier.[13] The reactants were placed in a 23 mL Teflon-lined steel autoclave, heated to 100 °C for 8 days, and then cooled to 25 °C with a cooling rate of 8 °C/h. The resulting red-brown transparent solution was recovered and allowed to slowly evaporate in air for 21 days. Dark-red prismatic crystals of **1** up to 0.4 mm were recovered after this period. The products were filtered and washed with ultrapure water. The yield of the synthesis of **1** is 21% on the basis of uranium.

The structure of **1**[14] contains five symmetrically independent U^{6+} cations, four Cr^{5+}, and two Cr^{6+} cations. All U atoms are strongly bonded to two O atoms to form a uranyl ion, $UO_2{}^{2+}$. The uranyl ions of the U(1), U(3), U(4), and U(5) atoms are coordinated by five O atoms arranged at the equatorial vertices of UO_7 pentagonal bipyramids. The $U(2)O_2{}^{2+}$ ion is coordinated by six O atoms, thus forming a UO_6 hexagonal bipyramid (Figure 1). The Cr(1), Cr(2), Cr(3), and Cr(4) atoms have square-pyramidal coordination, whereas the Cr(5) and half-occupied Cr(6) sites are tetrahedrally coordinated. Bond valence sums for Cr^{VI} were calculated using the parameters derived by Brese and O'Keefe,[15] and the mean parameter suggested by Locock et al.[10] was used for Cr^{V}. The bond valence sums are 4.93, 4.88, 5.00, 5.1, and 6.2 valence

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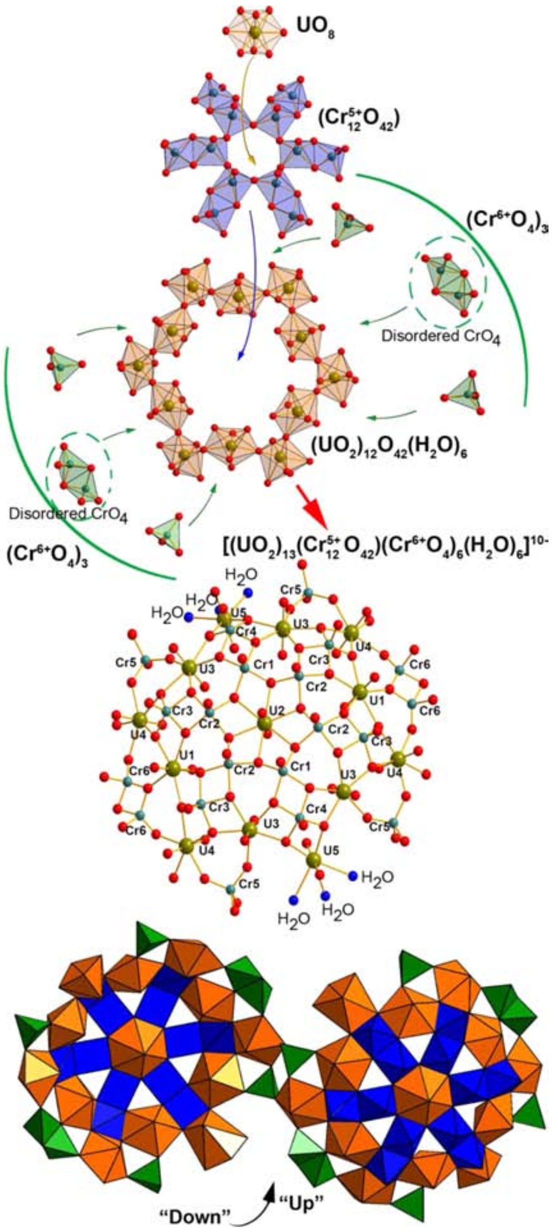

Figure 1. Ball-and-stick uranium and chromium arrangements representing how [(UO$_2$)$_{13}$(Cr$_{12}$$^{5+}O_{42}$)(Cr^{6+}O$_4$)$_6$(H$_2$O)$_6$]$^{10-}$ hemispheres are formed in the structure of **1**. The hemispheres are related by the inversion center (polyhedra legend: UrO$_5$, UrO$_6$ = orange, Cr^{5+}O$_5$ = blue, Cr^{6+}O$_4$ = green).

units (vu) for Cr(1), Cr(2), Cr(3), Cr(4), and Cr(5) atoms, respectively. These results are consistent with the oxidation states for Cr cations expected from a cation coordination environment. Experimental determination of the average oxidation state of Cr in **1** was performed by the X-ray *K*-line-shift method by means of a crystal diffraction spectrometer installed at the St. Petersburg Nuclear Physics Institute.[16] The following chromium compounds were used as standards: Cr metal (Cr^0), Cr$_2$O$_3$ (Cr^{3+}), NdCrO$_4$ (Cr^{5+}) synthesized in accordance with Saez-Puche et al.,[17] and K$_2$Cr$_2$O$_7$ (Cr^{6+}). The following average oxidation states for Cr in **1** were obtained: 5.38(4), 5.35(4), and 5.31(5) with observed chemical shifts $\Delta E_{K\beta}$ (NdCrO$_4$−K$_2$Cr$_2$O$_7$) = 212 ± 19 meV, $\Delta E_{K\alpha_1}$ (NdCrO$_4$−K$_2$Cr$_2$O$_7$) = 95 ± 11 meV, and $\Delta E_{K\alpha_2}$ (NdCrO$_4$−K$_2$Cr$_2$O$_7$) = 60 ± 9 meV, respectively. The experimental average oxidation states are in good agreement with the value 5.33 determined on the basis of crystal-structure refinement.

Cr(1)O$_5$ and Cr(2)O$_5$ and also Cr(3)O$_5$ and Cr(4)O$_5$ share common edges to form Cr$_2$O$_8$ dimers. Six Cr$_2$O$_8$ dimers share corners to produce [Cr$_{12}$O$_{42}$]$^{24-}$ pseudohexagonal units centered by U(2)O$_8$ hexagonal bipyramids. The units are surrounded by UO$_7$ pentagonal bipyramids and CrO$_4$ tetrahedra to form [(UO$_2$)$_{13}$(Cr$_{12}$$^{5+}O_{42}$)(Cr^{6+}O$_4$)$_6$(H$_2$O)$_6$]$^{10-}$ hemispheres with lateral dimensions of 18.9 × 18.5 Å^2 and a height of about 8 Å. The hemispheres are linked into 2D layers parallel to (001) in such a way that two adjacent hemispheres are oriented in opposite directions relative to the plane of the layer (Figure 2). The organic molecules are poorly resolved and reside in cavities between the uranyl chromate layers, and provide their linkage into a 3D structure (Figure 2).

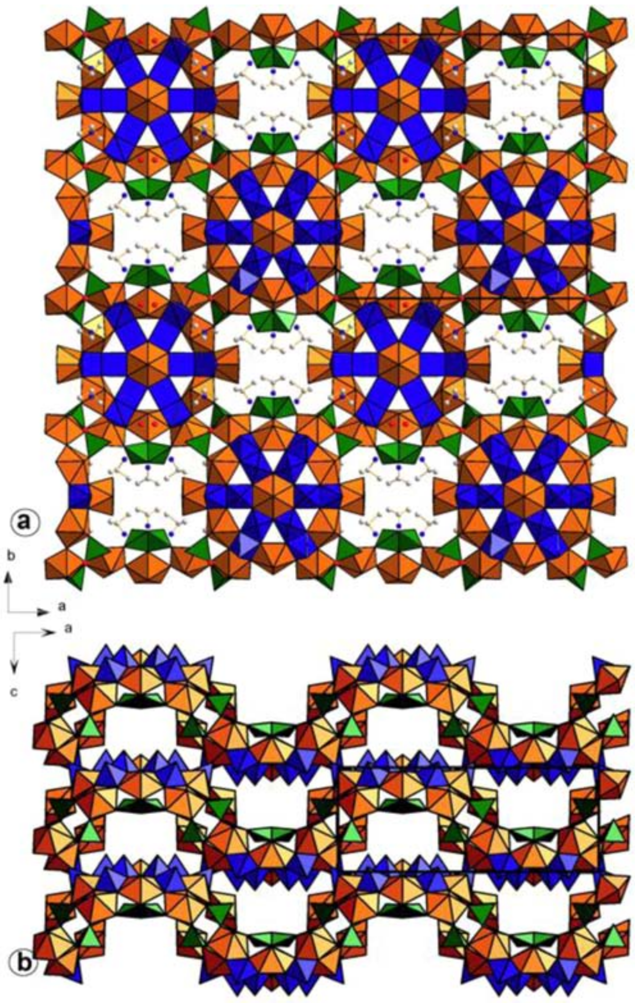

Figure 2. General projection of the crystal structure of **1** along the *c* axis (a). General projection of highly undulated layers along the *b* axis (interlayer amine and water molecules are omitted for clarity) (b).

The topology of the hemispheres is remarkable and can be analyzed by emphasizing the arrangement of U and Cr atoms linked through oxygen ligands, similar to the approach usually used for the description of complex spherical clusters and complexes.[18] A topological model of the uranyl chromate hemisphere is shown in Figure 3. Its central part contains a Cr$_6$ hexagonal ring centered by the U(2) atom. The ring is

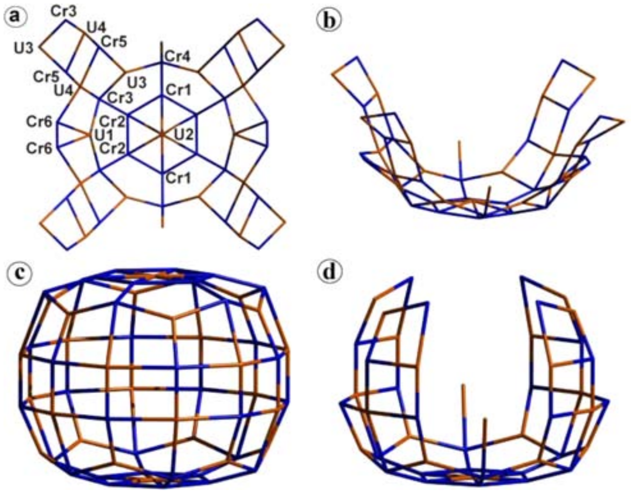

Figure 3. Topology of uranyl chromate hemisphere in the structure of **1**: top (a) and side (b) views. The U and Cr centers are shown as orange and blue nodes, respectively. Ideal imaginary spherical cluster $U_{23}Cr_{36}$ (c) and its $U_{21}Cr_{23}$ (d) hemispherical subcluster with topology identical with that of the uranyl chromate hemisphere in **1**. The U and Cr centers are shown as orange and blue nodes, respectively.

surrounded by six pentagonal rings, which are further linked to four-membered smaller rings (note that the Cr(6)−Cr(6) edge in the topological diagram should be merged into a single vertex because the corresponding Cr site is half-populated). The resulting hemisphere consists of 21 U and 23 Cr atoms and can be viewed as a part of a spherical nanocomplex with topology depicted in Figure 3c. This imaginary complex has the composition $U_{26}Cr_{36}$ and is composed of three-, four-, and five-membered rings. From the topological point of view, the $U_{21}Cr_{23}$ hemisphere in **1** can be obtained from the $U_{26}Cr_{36}$ sphere by the removal of 5 U and 13 Cr atoms. The structure obtained by this operation is topologically identical with the unit observed in **1**.

The results reported herein demonstrate that, in uranyl compounds, curvature is not restricted to specific peroxide units or uranyl selenates with relatively flexible interpolyhedral corner linkage but can also be functional in compounds with nontetrahedrally coordinated ions such as Cr^{5+}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, powder XRD data, and an IR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Crystal data of **1**: A total of 40175 reflections of a dark-red block crystal with dimensions of 0.14 × 0.12 × 0.09 mm^3, orthorhombic, *Pmmn* (No. 59), $a = 25.65(3)$ Å, $b = 26.98(3)$ Å, $c = 10.280(12)$ Å, $V = 7112(14)$ Å^3, $Z = 2$, $\rho_{calc} = 2.893$ g/cm^3, and $\mu(\text{MoK}\alpha) = 16.148$ mm^{-1} were measured on a Bruker Apex II diffractometer at 100 K. An empirical absorption correction based on the symmetry equivalent was applied. The structure was solved by direct methods using the *SHELXTL* suite of programs. The final cycles of refinement converged at R1 = 0.0816, wR2 = 0.2196, and GOF = 0.964 with 301 parameters, $\rho_{max,min} = +1.750/-3.480$ e/Å^3. A total of 10 crystals of **1** from two different syntheses were measured. The results reported are for the best one. Qualitative electron microprobe analysis (LINK AN-10000 EDS system) revealed no other elements, except U and Cr, with the atomic number greater than 11 (Na). Powder XRD analysis of **1** was performed at room temperature in the angular range of 2θ 1−40° with a scan step width of 0.01° using a Stoe IPDS II X-ray diffractometer utilizing Mo Kα radiation. The IR spectrum of **1** was recorded in the 5000−800 cm^{-1} range with a Bruker Vertex 70 spectrometer using a sample pressed in spectroscopically pure KBr pellets.

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