

Actinide Chemistry

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Na₂Li₈[(UO₂)₁₁O₁₂(WO₅)₂]: Three Different Uranyl-Ion Coordination Geometries and Cation–Cation Interactions**

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Synthetic and natural actinide compounds are of great environmental concern^[1] and have also been of interest to materials scientists because of their unique electronic properties.^[2] The structural chemistry of actinides is very diverse because of the possibility of different oxidation states and the large number of coordination geometries. Whereas actinides in low oxidation states sometimes mimic rare-earth elements, actinides in higher oxidation states possess unique coordination chemistry owing to their tendency to form linear actinyl

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ions. The typical coordination geometries of the actinyl ions are octahedral, pentagonal bipyramidal, and hexagonal bipyramidal.^[3] Herein we report the synthesis and structure of $\text{Na}_2\text{Li}_8[(\text{UO}_2)_{11}\text{O}_{12}(\text{WO}_5)_2]$ (**1**), the first actinide compound that contains three different actinyl-ion coordination geometries.

The orange crystals of **1** were obtained by high-temperature solid-state reactions of uranyl acetate, lithium and sodium carbonates, and tungsten(VI) oxide.^[4] The structure solution^[5] revealed elaborate 1.2-nm-thick layers with Na⁺ and Li⁺ ions within and in between these layers (Figure 1).

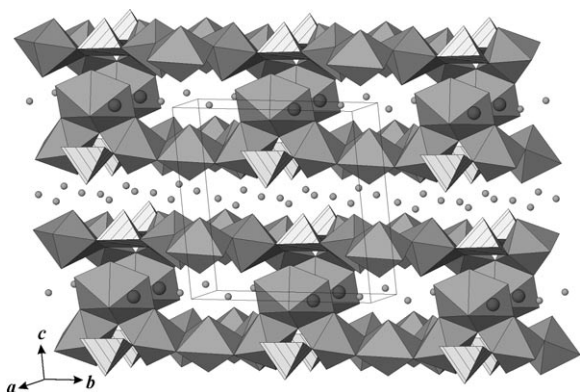


Figure 1. Crystal structure of **1**. U polyhedra gray; W polyhedra lined; Na⁺ large circles; Li⁺ small circles.

The layers have the composition $[(\text{UO}_2)_{11}\text{O}_{12}(\text{WO}_5)_2]^{10-}$ and consist of two equivalent sublayers (Figure 2) that are formed by edge-sharing $[\text{UO}_7]$ pentagonal bipyramids, $[\text{UO}_6]$ octahedra (see below), and $[\text{WO}_6]$ octahedra. The coordination polyhedra are arranged according to the $\beta\text{-U}_3\text{O}_8$ anion topology that has been recognized for many U^{VI} compounds. The sublayers are linked into double layers by the $[\text{UO}_2]^{2+}$ uranyl cations. The interior space of the layers is filled by the Na^+ and Li^+ ions. There are also Li^+ ions that are located in between the layers, thus providing three-dimensional integrity of the structure.

The coordination of the U atoms in **1** is of particular interest. There are six symmetry-independent U^{VI} centers.

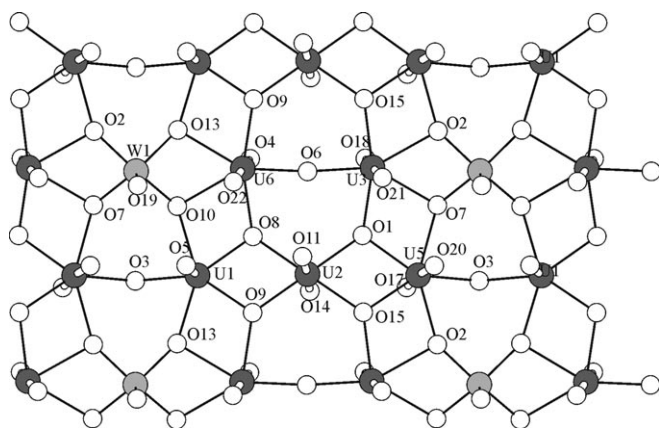


Figure 2. Structure of the uranyl tungstate sublayer in **1**.

Each U^{6+} cation is coordinated by two O atoms, thus forming linear $[\text{O}=\text{U}=\text{O}]^{2+}$ uranyl ions. The $\text{U}=\text{O}$ bond lengths are in the range 1.813–1.868 Å. The uranyl cations of the U1, U3, U5, and U6 centers are coordinated in equatorial planes by five O atoms (O_{eq}) each, which results in the formation of $[\text{UO}_7]$ pentagonal bipyramids. The $\text{U}-\text{O}_{\text{eq}}$ bond lengths in these polyhedra are in the range 2.162–2.518 Å, which indicates a quite high degree of coordinative distortion. The $[\text{O}=\text{U}_2=\text{O}]^{2+}$ ion is coordinated by four O_{eq} atoms with $\text{U}_2-\text{O}_{\text{eq}}$ bond lengths ranging from 2.218 to 2.266 Å. The uranyl cation of the U4 atom is coordinated by six O atoms, which leads to a $[\text{UO}_8]$ hexagonal bipyramid. The $\text{U}_4-\text{O}_{\text{eq}}$ bonds can be clearly separated into two groups: two bonds with lengths of 2.230 Å, and four bonds with lengths of 2.632 to 2.679 Å. Thus, the structure of **1** contains all three coordination geometries of uranyl ions. To our knowledge, this has not been observed previously in uranyl compounds.

Another particular feature of the structure of **1** is the presence of strong cation–cation interactions between the uranyl ions. Cation–cation interactions were discovered by Sullivan et al. in 1961^[6] and imply coordination of the actinide center of an actinyl ion $[\text{AnO}_2]^{n+}$ by the O atom of an adjacent actinyl ion. The cation–cation interactions are well-recognized in Np^{V} , Pu^{V} , and Am^{V} chemistry,^[7] but are rather rare for U^{VI} .^[8] In the structure of **1**, the $[\text{U1O}_2]^{2+}$, $[\text{U4O}_2]^{2+}$, and $[\text{U5O}_2]^{2+}$ ions interact with each other to form pentamers as shown in Figure 3. The central group of the pentamer is the

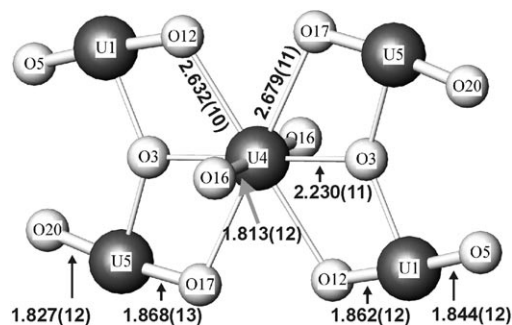


Figure 3. Pentamer of the uranyl ions UO_2^{2+} and cation–cation interactions in **1**.

U4 center, which has hexagonal bipyramidal geometry. The U=O bonds within this uranyl cation are 1.813 Å long. Further, the U4 atom has two short U4–O3 bonds (2.230 Å) and four U–O bonds to the O12 and O17 atoms, which are the parts of the [U1O₂]²⁺ and [U5O₂]²⁺ ions, respectively. These bonds are relatively long (2.632–2.679 Å) in comparison with the usual U–O_{eq} bond length within [UO₈] hexagonal bipyramids (2.47 Å).^[3] The U1=O12 and U5=O17 bonds are rather elongated (1.862 and 1.868 Å, respectively). Thus, the general geometrical configuration of the pentamer is rather unusual. The O16 atom of the [O=U4=O]²⁺ ion also forms a rather long bond to the W atom of the uranyl tungstate sublayer (2.507 Å).

In conclusion, we note that the thickness of the $[(\text{UO}_2)_{11}\text{O}_{12}(\text{WO}_5)_2]^{10-}$ layer in **1** is about 1.2 nm, which, along with reports on similar uranyl compounds, makes it

possible to suggest the occurrence of further uranyl-based layered compounds formed by intercalation of additional uranyl cations in between single sheets of uranium and other high-valent cation polyhedra such as Mo^{VI} and W^{VI} .

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- [4] The synthesis of **1** was carried out using mixture of Li_2CO_3 , Na_2CO_3 , WO_3 , and $\text{UO}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2$ in a ratio of 10:1:10:10. The mixture was heated to 950°C at a rate of 60°C h^{-1} , kept at 950°C for 40 min, and then cooled down to 200°C at a rate of 4°C h^{-1} . Crystals of **1** grew in the melt of $\text{Li}_2(\text{UO}_2)_4(\text{WO}_4)_4$. Powder of **1** can be obtained by keeping a mixture of the same reagents in a ratio of 8:2:2:11 at 800°C for 7 days. In the latter case, the reaction yield can be estimated as 80%. Electron dispersive spectroscopy (EDS) analysis confirmed the presence of Na, U, and W. The infrared spectrum was collected within the range $350\text{--}1000\text{ cm}^{-1}$. The band at 934 cm^{-1} can be assigned to the vibrations of the $\text{W}=\text{O}$ bond; the bands at 808 and $840\text{--}870\text{ cm}^{-1}$ can be attributed to the symmetrical and asymmetrical vibrations of the UO_2^{2+} ion, respectively. The bands at 773, 676, 587, and 448 cm^{-1} can be interpreted as corresponding to the U-O-U and W-O-U bonds.
- [5] Crystallographic data for $\text{Li}_8\text{Na}_2\text{W}_2\text{U}_{11}\text{O}_{44}$: plate-like crystal ($0.13 \times 0.13 \times 0.03\text{ mm}^3$), triclinic, $P\bar{1}$, $a = 6.946(2)$, $b = 11.207(3)$, $c = 12.054(5)\text{ \AA}$, $\alpha = 99.525(17)$, $\beta = 106.21(2)$, $\gamma = 90.223(12)^\circ$, $V = 887.4(5)\text{ \AA}^3$, $Z = 1$, $\rho_{\text{calcd}} = 7.095\text{ g cm}^{-3}$, $2\theta_{\text{max}} = 60^\circ$, $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$, $\omega/2\theta$ scan (STOE STADI-4), 293 K, 10268 measured reflections, 5168 independent reflections, 3891 reflections with $|F_o| = 4\sigma_F$ ($R_{\text{int}} = 0.0542$, $R_\sigma = 0.0645$), structure solution by direct methods, full-matrix least-square refinement (176 parameters) on $|F^2|$, (programs SHELXS-97 (G. M. Sheldrick, program for crystal structure solution, Göttingen, 1997) and SHELXL-97 (G. M. Sheldrick, program for the refinement of crystal structures, Göttingen, 1997)), $R_1 = 0.0567$, $wR_2 = 0.1347$ for observed reflections, $R_1 = 0.0793$, $wR_2 = 0.1427$ for all data, max/min electron density = $6.60\text{--}6.18$. Further details on the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-416364.
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