

One-Dimensional Array of Two- and Three-Center Cation–Cation Bonds in the Structure of $\text{Li}_4[(\text{UO}_2)_{10}\text{O}_{10}(\text{Mo}_2\text{O}_8)]$

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Dark-red crystals of the new compound $\text{Li}_4[(\text{UO}_2)_{10}\text{O}_{10}(\text{Mo}_2\text{O}_8)]$ (**1**) have been obtained by high-temperature solid-state reactions. The structure of **1** (monoclinic, $P2_1/c$, $a = 7.9426(4)$ Å, $b = 19.9895(9)$ Å, $c = 10.0796(5)$ Å, $\beta = 90.575(2)^\circ$, $V = 1600.24(13)$ Å³, $Z = 4$) consists of a framework of U and Mo polyhedra with Li^+ cations in the channels. The framework contains seven-polyhedra-wide uranium oxide tapes interlinked by dimers of edge-sharing $[4 + 1]$ -distorted MoO_5 polyhedra. The U–O tapes are parallel to the a axis, and their planes are oriented parallel to (021) and $(02\bar{1})$ so that they are cross-linked within the framework. The core of the tapes consists of unprecedented one-dimensional arrays of cation–cation-bonded uranyl ions. The arrays are constructed from eight-membered cycles with uranyl ions linked through two- and three-center cation–cation interactions.

Synthetic and natural inorganic actinide compounds are of great environmental concern¹ and have also been of interest for materials scientists because of the unique electronic properties of actinides.² The structural chemistry of actinides is very diverse because of the possibility of different oxidation states and the richness of coordination geometries.³ In higher oxidation states, actinides possess unique coordination chemistry, owing to their tendency to

form linear actinyl ions. In 1961, Sullivan et al.⁴ discovered cation–cation interactions between actinide ions that imply coordination of the actinide atom of an actinyl ion, $[\text{AnO}_2]^{n+}$, by the O atom of an adjacent actinyl ion. The cation–cation interactions are well-recognized for Np^{V} , Pu^{V} , and Am^{V} chemistry⁵ but are rather rare for U^{VI} .⁶ In most cases, cation–cation interactions are two-center; i.e., the O atom of an actinyl ion coordinates only one adjacent actinide atom. However, recently several structures have been reported that contain three-center cation–cation interactions;⁷ i.e., the O atom of an actinyl ion coordinates two adjacent actinide atoms. It is remarkable that the bifurcation of cation–cation interactions had been observed for several U^{VI} compounds, whereas only one example of a bifurcated cation–cation bond was reported for Np^{V} ,^{7b} despite the fact that cation–cation interactions are much more common for Np^{V} chemistry.^{5,6} Figure 1 depicts known configurations of the uranyl ions, $[\text{UO}_2]^{2+}$, with respect to the adjacent uranyl ions. In most uranyl compounds,⁸ uranyl ions do not interact with each other (**Ia** and **Ib** configurations). Dimers of cation–cation-bonded uranyl ions (**II**) have been reported in, e.g., $\text{A}[(\text{UO}_2)_3(\text{HIO}_6)_2(\text{OH})(\text{O})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$ ($\text{A} = \text{Li}$ to Cs)^{6a} and $\text{A}(\text{UO}_2)_4(\text{VO}_4)_3$ ($\text{A} = \text{Li}, \text{Na}$).⁹ The presence of the $[\text{O}=\text{U}=\text{O}]-\text{U}-[\text{O}=\text{U}=\text{O}]$ trimers (**III**) is the unique fea-

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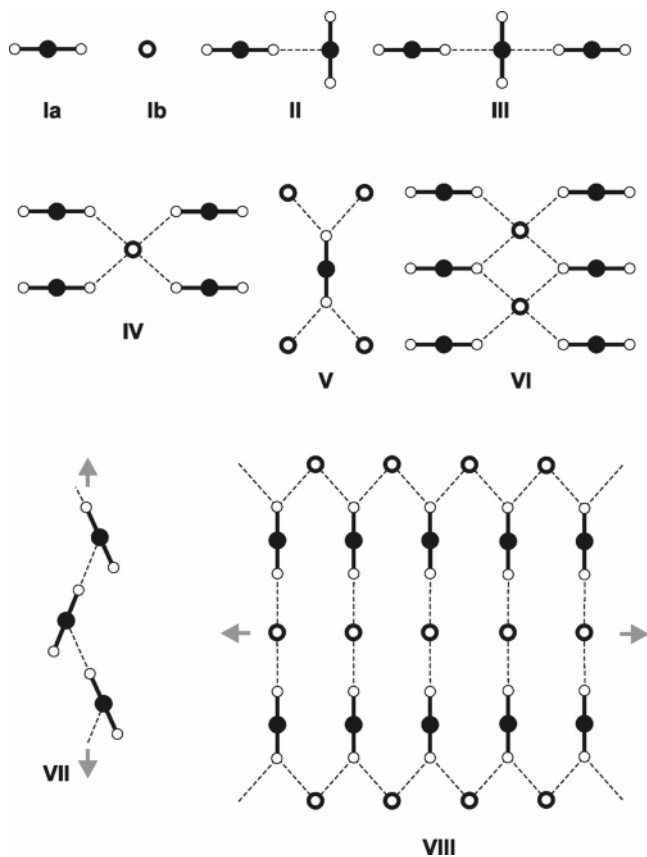


Figure 1. Configurations of uranyl ions with respect to adjacent uranyl ions in inorganic compounds: isolated uranyl ion oriented parallel (**Ia**) or perpendicular (**Ib**) to the plane of the figure; dimer (**II**), trimer (**III**), pentamers (**IV** and **V**), and octamer (**VI**) of cation–cation-bonded uranyl ions; one-dimensional chains (**VII** and **VIII**).

ture of the structure of $\text{Li}_2(\text{UO}_2)_4(\text{WO}_4)_4\text{O}$.¹⁰ There are two different types of pentamers of cation–cation-bonded uranyl ions. Configuration **IV** does not contain bifurcated cation–cation interactions and has been observed in $\text{Na}_2\text{Li}_8[(\text{UO}_2)_{11}\text{O}_{12}(\text{WO}_5)_2]$.¹¹ The pentamer **V** possesses two three-center cation–cation bonds and has been recently reported for $(\text{K},\text{Na})\text{Na}_3[(\text{UO}_2)_5\text{O}_6(\text{SO}_4)]$.³ The structure of $\text{Sr}_5(\text{UO}_2)_{20}(\text{UO}_6)_2\text{O}_{16}(\text{OH})_6(\text{H}_2\text{O})_6$ ^{7a} contains octamers of cation–cation-bonded uranyl ions (**VI**). One-dimensional chains of the type **VII** have been observed in UO_2TO_4 ($T = \text{Se},^{6c} \text{Mo}^{6d}$) and $\text{UO}_2(\text{VO}_3)$.¹² In these compounds, no bifurcated cation–cation bonds are present. Finally, complex one-dimensional tapes of two- and three-center cation–cation interactions (**VIII**) have been found in $\text{Li}_4[(\text{UO}_2)_{10}\text{O}_{10}(\text{Mo}_2\text{O}_8)]$ (**1**), which is the subject of this work.

Dark-red crystals of **1** have been prepared using high-temperature solid-state reactions from the mixture of Li_2CO_3 , UO_3 , and MoO_3 with stoichiometry $\text{Li}:\text{U}:\text{Mo} = 1:2:2$. The reagents were placed into a platinum crucible and

heated to 1143 K with subsequent cooling to room temperature at a cooling rate of 5.5 K/h. The crystals of **1** were found as inclusions in an amorphous yellowish mass quickly absorbing water at ambient conditions. The electron microprobe analysis provided the U/Mo ratio of 5:1, and the phase was also characterized by IR spectroscopy.

The structure of **1**¹³ has been solved from a twinned crystal and was found to possess six symmetrically independent U^{VI} atoms each coordinated by two O atoms, thus forming linear $[\text{O}=\text{U}=\text{O}]^{2+}$ uranyl ions. The $\text{U}=\text{O}$ bonds are in the range of 1.78–1.94 Å. The uranyl cations of the U1, U2, U3, and U4 atoms are coordinated in equatorial planes by five O_{eq} atoms, each of which results in the formation of $[\text{UO}_7]$ pentagonal bipyramids. The $\text{U}-\text{O}_{\text{eq}}$ bonds in these polyhedra are in the range of 2.13–2.61 Å, which indicates a quite high degree of coordination distortion. The uranyl cations of the U5 and U6 atoms are coordinated by four O_{eq} atoms with $\text{U}-\text{O}_{\text{eq}}$ bond lengths ranging from 2.08 to 2.39 Å. One symmetrically independent Mo^{VI} atom possesses a $[4 + 1]$ coordination that can be described as a distorted trigonal bipyramid with one apical bond (2.23 Å) essentially elongated compared to the other bond (1.75 Å). In fact, the Mo coordination can be considered as intermediate between tetragonal pyramid and trigonal bipyramid related by a Berry rotation. This type of coordination has been observed previously in uranyl molybdates, e.g., in the structure of $\text{Cs}_4[(\text{UO}_2)_3\text{O}(\text{MoO}_4)_2(\text{MoO}_5)]$.¹⁴ Two adjacent MoO_5 pyramids share the $\text{O}3-\text{O}3$ edge to form dimers Mo_2O_8 . There are two symmetrically independent Li^+ cations. Li1 has a tetrahedral coordination with four $\text{Li}-\text{O}$ bond lengths in the range of 1.89–1.98 Å, whereas Li2 is coordinated by five O atoms with $\text{Li}-\text{O}$ bond lengths of 1.99–2.39 Å. Bond-valence sums for cations¹⁵ are 5.69, 6.09, 5.88, 5.91, 6.23, 5.97, 5.82, 1.17, and 0.97 vu (valence units) for the U1, U2, U3, U4, U5, U6, Mo, Li1, and Li2 sites, respectively. Bond-valence sums for the O atoms are in the range from 1.78 to 2.32 vu.

The structure of **1** is shown in Figure 2. It can be described as consisting of a framework of U and Mo polyhedra with Li^+ cations in the channels. The framework contains seven-polyhedra-wide uranium oxide tapes interlinked by the Mo_2O_8 dimers. The $\text{U}-\text{O}$ tapes are parallel to the a axis,

(13) Crystallographic data for $\text{Li}_4[(\text{UO}_2)_{10}\text{O}_{10}(\text{Mo}_2\text{O}_8)]$: monoclinic, $P2_1/c$, $a = 7.9426(4)$ Å, $b = 19.9895(9)$ Å, $c = 10.0796(5)$ Å, $\beta = 90.575(2)^\circ$, $V = 1600.24(13)$ Å³, $Z = 4$; crystal dimensions $0.18 \times 0.12 \times 0.08$ mm³; crystal twinned on (001); ratio of twin components 0.216:0.784; $\rho_{\text{calcd}} = 6.658$ g/cm³, $\mu = 51.273$ mm⁻¹. Data collection: Nonius Kappa CCD diffractometer, 17 972 total reflections, 3265 unique reflections, 3134 unique reflections $|F_o| \geq 4\sigma(F_o)$. The structure was solved by direct methods and refined to $R1 = 0.043$, $wR2 = 0.117$, $S = 0.936$ (anisotropic displacement parameters for all atoms). The maximum and minimum residual peaks in the difference map are +6.492 and -5.159 e/Å³ and are located within 1 Å to the U sites; their appearance is assigned to problematic absorption effects for a twinned crystal. IR spectrum (cm⁻¹): 970 (Mo=O), 944 (short U=O, asymmetric vibrations), 891, 863 (long U=O, asymmetric vibrations), 796w ($w = \text{weak}$), 785w (U=O symmetric vibrations), 728, 714 (U–O–Mo), 665 (Mo–O–Mo), 605, 544, 503 (U–O–U), 414–372 (Mo–O–Mo).

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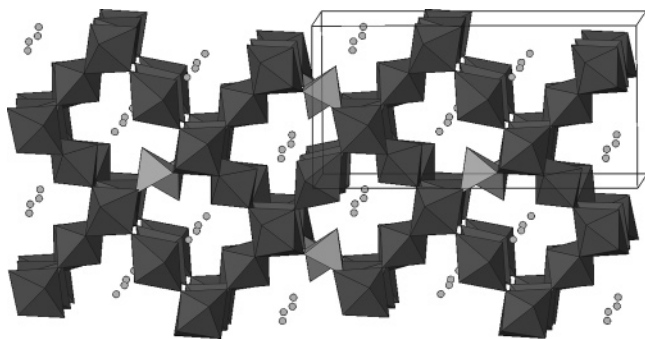


Figure 2. Structure of **1** projected approximately along the *a* axis [U and Mo polyhedra are dark gray and light gray, respectively; Li atoms are shown as small spheres].

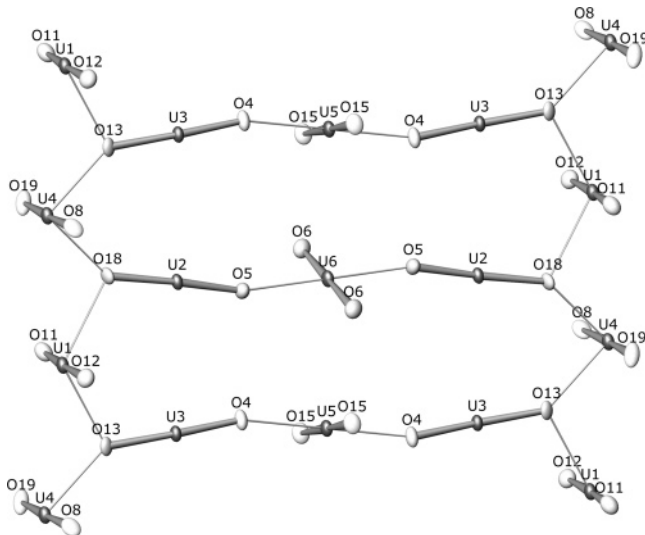


Figure 3. One-dimensional array of cation–cation-bonded uranyl ions in the structure of **1**. U and O atoms are dark and light gray, respectively; U=O and U–O bonds are shown by thick and thin lines, respectively. See the text for details.

and their planes are oriented parallel to (021) and (0 $\bar{2}$ 1) so that they are cross-linked within the framework. The core of the tapes consists of chains of five cation–cation-bonded uranyl ions (Figure 3). The U1O_2^{2+} , U4O_2^{2+} , U5O_2^{2+} , and U6O_2^{2+} ions are oriented perpendicular, whereas the U2O_2^{2+} and U3O_2^{2+} are parallel to the plane of the tape. Altogether, the uranyl ions interact to form one-dimensional arrays constructed from eight-membered cycles with two subsequent ions in the cycle linked through cation–cation interactions. The U5O_2^{2+} and U6O_2^{2+} ions accept two cation–cation bonds each, being central ions for trimers of the type **III** (Figure 1). The U2O_2^{2+} and U3O_2^{2+} ions donate three cation–cation bonds each so that one cation–cation bond is single (two-center) and another is bifurcated (three-center). Finally, the U1O_2^{2+} and U4O_2^{2+} ions accept two cation–cation bonds each. Thus, it is the U2O_2^{2+} and U3O_2^{2+} ions that act as donors for all of the cation–cation interactions in the structure. As a result, their U=O bonds are essentially

elongated. The U2=O5 and U3=O4 bonds (1.88 and 1.86 Å, respectively) participate in the two-center cation–cation interactions, whereas the U2=O18 and U3=O13 bonds (1.94 and 1.93 Å, respectively) are involved in the three-center cation–cation bonding. Therefore, the U=O bonds involved in single cation–cation bonds are shorter than those involved in bifurcated cation–cation bonds, which is in agreement with the expectation. For comparison, the U=O bond lengths not involved in cation–cation bonds are in the range of 1.78–1.86 Å.

In conclusion, it is of interest to identify some observations about cation–cation interactions in actinide chemistry that are awaiting structural and chemical explanations. First, cation–cation interactions are more characteristic for Np^{V} rather than for U^{VI} chemistry because of the higher bonding abilities of the O atoms of neptunyl ions. However, only one example of bifurcated Np–Np cation–cation interactions is known so far, whereas several examples of bifurcated U–U bonds are known. It is tempting to suggest that this difference is due to the magnetism of the Np^{V} centers. Whereas two-center cation–cation bonds allow antiferromagnetic behavior, the three-center bonds may favor the formation of magnetically frustrated systems and therefore are avoided. Second, only zero- and one-dimensional arrays of cation–cation-bonded uranyl ions are known so far, whereas in Np^{V} chemistry, all dimensional possibilities are realized.^{5a} It is very probable that two- and three-dimensional arrays of cation–cation-interacting uranyl ions are still to be discovered. Finally, there is at least a purely structural analogy between cation–cation interactions and hydrogen bonding (HB). In both cases, there is a donor–acceptor interaction mediated by hydrogen for HBs and by oxygen for cation–cation interactions. Recent observations and this work demonstrate that, by analogy to HB, cation–cation interactions may also have two- and three-center character. For HBs, water molecules may form highly sophisticated arrangements, including cages and clathrates. Does this possibility for cation–cation-bonded actinyl ions exist as well?

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Supporting Information Available: X-ray crystallographic data in CIF format and an IR spectrum. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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