

Self-Assembly of a Polar Open-Framework Uranyl Vanadyl Hexaaxioiodate(VII) Constructed Entirely from Distorted Octahedral Building Units in the First Uranium Hexaaxioiodate: $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$

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The reaction of UO_3 with V_2O_5 and KIO_4 under mild hydrothermal conditions produces $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ (**1**) in the form of orange acicular crystals. The structure of **1** consists of UO_6 , VO_6 , and IO_6 distorted octahedra that are assembled into a polar, open-framework structure. The distorted VO_6 and IO_6 octahedra edge-share to form chains that run down the *c*-axis. Each VO_6 octahedron also shares a vertex with an adjacent vanadium atom to link the chains together into a ribbon. The IO_6 units also partake in corner-sharing with the UO_6 units to create interconnected elliptical tubes. The major channels in **1** are filled with K^+ cations and water molecules. The polarity of this compound is caused by alignment of distorted vanadyl hexaaxioiodate ribbons and UO_6 trapezoidal bipyramids resulting in a large second-harmonic generation response of 300 times that of α -quartz. Crystallographic data: **1**, orthorhombic, space group *Pba2*, $a = 9.984(2)$ Å, $b = 16.763(3)$ Å, $c = 4.977(1)$ Å, $Z = 4$ ($T = 193$ K).

Oxoanions containing main group elements in their highest possible oxidation states play an important role in stabilizing transition metals in atypically high oxidation states. Hexaaxioiodate(VII), IO_6^{5-} , and hexaaxotellurate(VI), TeO_6^{6-} , are well noted in this regard, and they have been used to prepare rare examples of Cu(III),¹ Ag(III),² and Ni(IV).³ Despite the importance of these anions in transition metal chemistry, a survey of known compounds reveals that well-characterized examples of actinide compounds containing either the IO_6^{5-} or TeO_6^{6-} anions are absent.⁴ Attempts to prepare these compounds with the former anion by aqueous metathesis reactions under both ambient and hydrothermal conditions have been largely unsuccessful owing to the reduction of I(VII) to I(V).^{5,6} However, it was recently demonstrated that

$Ba_3[(MoO_2)_2(IO_6)_2] \cdot 2H_2O$ could be synthesized from the hydrothermal reaction of BaH_3IO_6 with MoO_3 ,⁷ and given the ostensible similarities between the conditions needed to prepare compounds containing molybdenyl, MoO_2^{2+} , and uranyl, UO_2^{2+} , a program was undertaken to prepare actinide hexaaxioiodate(VII) compounds by hydrothermal methods.

Straightforward hydrothermal reactions of a variety of sources of U(VI) with IO_4^- or IO_6^{5-} result in the reduction of the I(VII) to I(V) and the subsequent isolation of $UO_2 \cdot (IO_3)_2(H_2O)$ or $UO_2(IO_3)_2$.⁵ However, when V_2O_5 was added to these reactions in order to maintain a strongly oxidizing environment, bright orange needles were isolated in high yield.⁸ These crystals were shown to contain K, V, U, and I in a 1:1:1:1 ratio as determined from semiquantitative EDX measurements. Ensuing single-crystal X-ray diffraction experiments revealed the true formula of this compound to be $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ (**1**), and hence the first actinide compound of hexaaxioiodate(VII) was identified.⁹ Powder XRD measurements confirm that the pattern from the bulk sample is the same as the calculated pattern. Evidence for this compound containing V(V) and U(VI) was

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 (8) $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ (**1**) was prepared by loading KIO_4 (275 mg, 1.20 mmol), UO_3 (171 mg, 0.60 mmol), V_2O_5 (54 mg, 0.30 mmol), and 0.5 mL of a 1.7 M KOH aqueous solution in a 23 mL PTFE-lined autoclave. The autoclave was heated at 180 °C for 74 h, and slow cooled at 9 °C/h to 22 °C. Orange needles of **1** were isolated in 94% yield based on uranium (347 mg).
 (9) Crystallographic data: $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ (**1**), orange acicular crystal, dimensions 0.240 × 0.016 × 0.008 mm, orthorhombic, *Pba2*, $Z = 4$, $a = 9.984(2)$ Å, $b = 16.763(3)$ Å, $c = 4.977(1)$ Å, $V = 833.0(3)$ Å³ ($T = 193$ K), $\mu = 247.79$ cm⁻¹, $R1 = 0.0380$, $wR2 = 0.0851$.¹⁹ Bruker APEX CCD diffractometer: $\theta_{max} = 56.64^\circ$, $Mo K\alpha$, $\lambda = 0.71073$ Å, $0.3^\circ \omega$ scans, 8213 reflections measured, 2076 independent reflections all of which were included in the refinement. The data was corrected for Lorentz–polarization effects and for absorption (analytical and SADABS), and the structure was solved by direct methods, followed by a refinement of F^2 by full-matrix least-squares with 129 parameters.¹⁹ Anisotropic displacement parameters were included for all atoms.

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obtained from its Raman spectrum that revealed vibrational modes at 982 and 862 cm^{-1} , which are consistent with the $\nu(\text{V}=\text{O})$ and $\nu_1(\text{U}=\text{O})$ modes for the vanadyl, VO_3^{3+} , and UO_2^{2+} moieties.¹⁰ Additional strong bands centered around 756 cm^{-1} can be assigned to $\nu(\text{I}-\text{O})$ stretches.¹¹

The structure of **1** is assembled from a combination of UO_6 , VO_6 , and IO_6 distorted octahedra. The distortions of the UO_6 and VO_6 units are caused in part by the presence of a single short terminal $\text{V}=\text{O}$ bond of 1.58(1) Å in the VO_6 polyhedra, and the presence of the nearly linear $(\text{O}=\text{U}=\text{O})^{2+}$ unit with $\text{U}=\text{O}$ bond distances of 1.75(1) and 1.77(1) Å in the UO_6 units. Equatorial $\text{U}-\text{O}$ bond lengths range from 2.25(1) to 2.35(1) Å creating an environment around the central uranium atom that is best described as a tetragonal bipyramid. The $\text{V}-\text{O}$ bond trans to the vanadyl oxygen atom, with a bond length of 2.38(1) Å, shows significant lengthening with respect to the four equatorial $\text{V}-\text{O}$ bonds, which range from 1.774(5) to 2.10(1) Å. While this long bond is a common feature of vanadyl compounds, $\text{V}(\text{V})$ is also highly susceptible to second-order Jahn–Teller distortions,¹² and the asymmetry of the VO_6 octahedra is likely the combination of both of these factors. Finally, the IO_6 octahedra, while less perturbed than the other aforementioned groups, still show substantial variations in $\text{I}-\text{O}$ bond distances and angles, which range from 1.84(1) to 1.93(1) Å and from 79.8(4) $^\circ$ to 97.2(4) $^\circ$. On the basis of the $\text{U}-\text{O}$, $\text{V}-\text{O}$, and $\text{I}-\text{O}$ bond lengths, bond valence sums were calculated for the $\text{U}(\text{VI})$, $\text{V}(\text{V})$, and $\text{I}(\text{VII})$ centers to be 6.2, 5.1, and 7.1, which are consistent with the formula provided for this compound.^{13–15}

The distorted VO_6 and IO_6 octahedra edge-share to form chains that run down the c -axis. Each VO_6 octahedron also shares a vertex with an adjacent vanadium atom to link the chains together into a ribbon. The sixth oxygen around the vanadium center is the terminal oxo atom, and it is not utilized in further covalent interactions. The IO_6 units partake in edge-sharing with the VO_6 octahedra and corner-sharing with the UO_6 tetragonal bipyramids. This fills two of the four positions in the equatorial plane of the UO_6 moieties. The remaining two atoms in this plane are shared with a second crystallographically equivalent IO_6 unit.

This assembly process creates a curving sheet, as shown in Figure 1, that when repeated forms an elliptical tube with interior dimensions of approximately 6.9×8.8 Å. The tubes are in turn fused to create a three-dimensional channel structure depicted in Figure 2a. When viewed along the a -axis (Figure 2b), smaller, perpendicular channels become apparent. These channels run perpendicular to, and intersect with, the larger channels, making **1** an open-framework

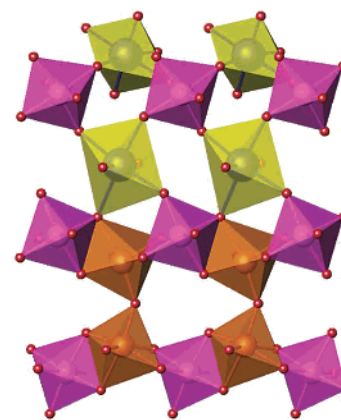


Figure 1. Half of a polar uranyl vanadyl hexaaxioiodate(VII) channel in $\text{K}_2[(\text{UO}_2)_2(\text{VO})_2(\text{IO}_6)_2\text{O}]\cdot\text{H}_2\text{O}$ (**1**). The polarity is induced by the cooperative alignment of the distortions in the vanadyl hexaaxioiodate ribbons and the deformation of the basal plane in the UO_6 trapezoidal bipyramids. The distorted UO_6 , VO_6 , and IO_6 octahedra are shown in yellow, orange, and purple, respectively.

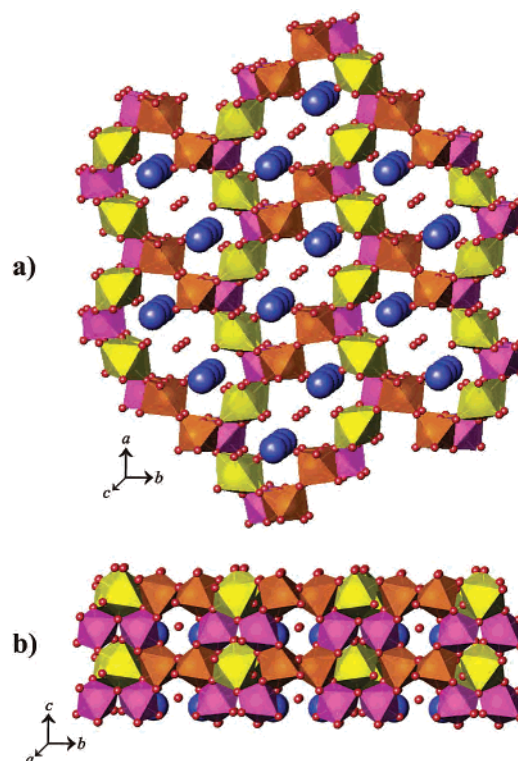


Figure 2. (a) A view down the c -axis showing the three-dimensional structure of $\text{K}_2[(\text{UO}_2)_2(\text{VO})_2(\text{IO}_6)_2\text{O}]\cdot\text{H}_2\text{O}$ (**1**) with elliptical channels with approximate dimensions of 6.9×8.8 Å. The channels are filled with K^+ cations and water molecules. (b) A view along (001) illustrating small channels that are perpendicular to the larger elliptical channels in **1**. The distorted UO_6 , VO_6 , and IO_6 octahedra are shown in yellow, orange, and purple, respectively. The K^+ cations are shown in blue.

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structure. Three-dimensional structures incorporating $\text{U}(\text{VI})$ are generally not expected because the presence of a trans dioxo unit usually eliminates one dimension of linkage, effectively creating layered structures, which the majority of uranyl compounds do indeed adopt.^{16,17}

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The open-framework structure of **1** is anionic in nature, and charge neutrality requirements are satisfied by partially filling the cavities with K^+ cations. One of the most interesting features of the large channels running down (001) is that both the vanadyl and uranyl moieties have their terminal oxo atoms directed into the channels, allowing for long ionic interactions to take place with the K^+ cations. The remaining space is occupied by water molecules that can be gradually removed by heating **1** to 400 °C. The resultant dehydrated compound appears to be stable to 528 °C.

The vanadyl hexaaxoiodate(VII) chains shown in Figure 1 are similar in appearance to the polar one-dimensional $^1[(MoO_2)(IO_6)]^{3-}$ chains found in $Ba_3[(MoO_2)_2(IO_6)_2] \cdot 2H_2O$.⁷ Therefore, the observed polarity of **1**, indicated by its polar space group *Pba2*, can be partially understood in terms of the polarity of the vanadyl hexaaxoiodate(VII) chains. In addition, the tetragonal basal plane of the UO_6 units is in fact distorted into an approximately trapezoidal shape where there is also alignment of this deformation along the polar *c*-axis. The lack of an inversion center in **1** was confirmed by a second-harmonic generation (SHG) measurement of an ungraded powder sample that revealed a large response of approximately 300 times that of α -quartz for the frequency doubling of 1064 nm light from a Nd:YAG laser.¹⁸

In conclusion, we have demonstrated that a hexaaxoiodate-(VII) compound of U(VI) can indeed be prepared under mild hydrothermal conditions through the coinorporation of V(V). The structure of this compound is substantially different from all other uranyl phases, and its polarity in the absence of an oxoanion with a stereochemically active lone pair of electrons indicates the importance of the geometric distortions in U(VI), V(V), and I(VII) octahedra in the formation of this acentric compound. Current studies of **1** are devoted to testing its use as an oxidation catalyst.

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Supporting Information Available: X-ray crystallographic file for $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ (**1**) (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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