

Hydrothermal Synthesis and Structure of a New One-Dimensional, Mixed-Metal U(VI) Iodate, $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$

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The reaction of the molecular transition metal iodate, $\text{Cs}[\text{CrO}_3(\text{IO}_3)]$, with UO_3 under mild hydrothermal conditions provides access to a new low-dimensional, mixed-metal U(VI) compound, $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ (**1**). The structure of **1** is quite unusual and consists of one-dimensional $[\text{UO}_2(\text{CrO}_4)(\text{IO}_3)_2]^{2-}$ ribbons separated by Cs^+ cations. These ribbons are formed from $[\text{UO}_7]$ pentagonal bipyramids that contain a uranyl core, $[\text{CrO}_4]$ tetrahedra, and both monodentate and bridging iodate anions. Crystallographic data: **1**, monoclinic, space group $P2_1/n$, $a = 7.3929(5)$ Å, $b = 8.1346(6)$ Å, $c = 22.126(2)$ Å, $\beta = 90.647(1)^\circ$, $Z = 4$ ($T = 193$ K).

The preparation of new actinide compounds with unprecedented structures and unusual properties^{1–4} is an area under significant investigation owing to its relevance to nuclear waste disposal,^{5,6} mineralogy,⁷ and catalysis.^{8,9} Some recent studies in this area have focused on the use of hydrothermal synthetic conditions, in both the mild (<250 °C) and supercritical (>374 °C) regimes, for preparing new phases, as well as attempting to reproduce the conditions under which uranium-bearing minerals may form.^{10,11} These efforts have afforded a number of spectacular compounds as illustrated by the porous structures of $[\text{C}_6\text{H}_{14}\text{N}_2][(\text{UO}_2)_2\text{F}_6]^{12}$ and $[\text{C}_4\text{H}_{12}\text{N}_2][(\text{UO}_2)_2(\text{PO}_3\text{H})_2\{\text{PO}_2(\text{OH})\text{H}\}_2]^{13}$.

Our current research efforts in the solid-state chemistry of uranium are devoted to developing an understanding of the reaction and structural chemistry of compounds containing uranyl, UO_2^{2+} , units, and C_{3v} anions, such as iodate and selenite. This investigation has afforded a series of low-dimensional alkali metal and alkaline-earth metal uranyl iodates including $\text{A}_2[(\text{UO}_2)_3(\text{IO}_3)_4\text{O}_2]$ ($\text{A} = \text{K}, \text{Rb}, \text{TI}$)^{14,15} and $\text{AE}[(\text{UO}_2)_2(\text{IO}_3)_2\text{O}_2] \cdot \text{H}_2\text{O}$ ($\text{AE} = \text{Sr}, \text{Ba}, \text{Pb}$).^{14,15} An additional goal of this work is to incorporate transition metals into these syntheses as a method for developing a group of compounds that not only possess interesting structures but also display unusual electronic properties. While our initial efforts in this area resulted in the serendipitous discovery of the tetraoxoiodate anion, IO_4^{3-} , in $\text{Ag}_4(\text{UO}_2)_4(\text{IO}_3)_2(\text{IO}_4)_2$,¹⁶ our efforts at preparing other compounds that incorporate both the iodate anion and a transition metal have been continually thwarted by the formation of transition metal iodates and $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ ¹⁷ in these reactions.

The solution to this problem has proven to be the use of soluble molecular precursors that contain both a transition metal and the iodate anion, in this case the chromyl iodate anion, $[\text{CrO}_3(\text{IO}_3)]^-$.¹⁸ The hydrothermal reaction of $\text{Cs}[\text{CrO}_3(\text{IO}_3)]$ with UO_3 for 16 h at 180 °C results in the formation of $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ (**1**) in the form of golden prisms.¹⁹ $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, a ubiquitous byproduct of hydrothermal reactions of U(VI) with IO_3^- , and $\text{Cs}_2[(\text{UO}_2)_2(\text{CrO}_4)_3]$ are also observed in these reactions. The latter compound is also new and has the $\text{Cs}_2[(\text{UO}_2)_2(\text{SO}_4)_3]$ anionic sheet topology.^{7,20}

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- $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ (**1**) was prepared by loading $\text{Cs}[\text{CrO}_3(\text{IO}_3)]$ (196 mg, 0.482 mmol), CsCl (81 mg, 0.482 mmol), UO_3 (138 mg, 0.482 mmol), HIO_3 (85 mg, 0.482 mmol), and 0.5 mL of distilled and Millipore filtered water in a 23 mL PTFE-lined autoclave. The autoclave was heated at 180 °C for 16 h and slow cooled at 9 °C/h to 22 °C. The products consisted of pale yellow crystals of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, deep orange tablets of $\text{Cs}_2[(\text{UO}_2)_2(\text{CrO}_4)_3]$, and golden prisms of **1**. Yield for **1**: 300 mg (62% based on U). EDX analysis provided a Cs:U:Cr:I ratio of 2:1:1:2.

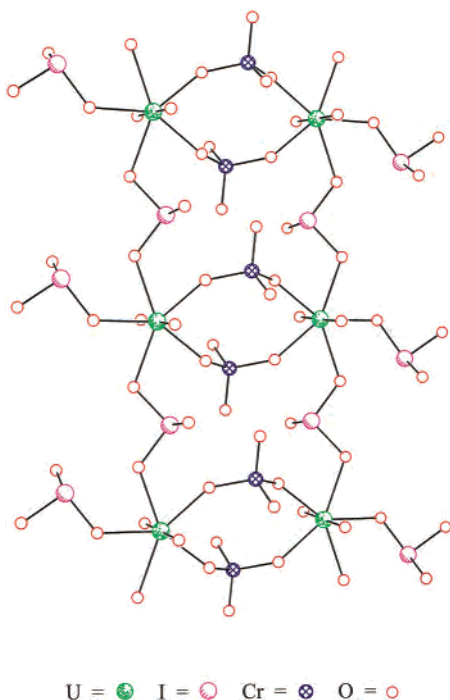


Figure 1. Part of the one-dimensional ${}^1_{\infty}[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]^{2-}$ ribbons in **1**.

Given the dramatic differences between the colors and crystal habits of these three compounds, manual separation is trivial when necessary. We have been able to optimize the yield of **1** to 62% by adding additional Cs^+ and IO_3^- to the reactions, diminishing the need for product separation. This reaction can also be successfully carried out using $\text{K}[\text{CrO}_3(\text{IO}_3)]$ as the source of chromyl iodate. In this case $\text{K}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ is isolated, and while not isostructural with **1**, it contains nearly identical uranyl chromatoiodate structural features.

The structure of **1** is quite unusual and consists of one-dimensional ${}^1_{\infty}[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]^{2-}$ ribbons separated by

Table 1. Selected Bond Distances (Å) for $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ (**1**)^a

U–O and U=O			
U(1)–O(1) (U=O)	1.776(4)	U(1)–O(8)′	2.455(4)
U(1)–O(2) (U=O)	1.791(4)	U(1)–O(9)	2.447(4)
U(1)–O(3)	2.310(4)	U(1)–O(11)	2.315(4)
U(1)–O(6)′	2.310(4)		
Cr–O			
Cr(1)–O(3) (br)	1.703(4)	Cr(1)–O(5) (ter)	1.587(5)
Cr(1)–O(4) (ter)	1.604(5)	Cr(1)–O(6) (br)	1.691(4)
I–O			
I(1)–O(7) (ter)	1.781(4)	I(2)–O(10) (ter)	1.792(5)
I(1)–O(8) (br)	1.835(4)	I(2)–O(11) (br)	1.842(4)
I(1)–O(9) (br)	1.840(4)	I(2)–O(12) (ter)	1.790(4)

^a (U=O) = uranyl, UO_2^{2+} , (br) = bridging, (ter) = terminal.

Cs^+ cations.²¹ The ribbons are formed from $[\text{UO}_7]$ pentagonal bipyramids that contain a uranyl core, $[\text{CrO}_4]$ tetrahedra, and both monodentate and bridging iodate anions. Part of one of these ribbons is depicted in Figure 1. In fact, this compound can be viewed as an intricate Lewis acid–base complex of UO_2^{2+} , CrO_4^{2-} , and IO_3^- as there are no additional oxo or hydroxo ligands present.

The ribbons can be broken down into small units for a more thorough understanding of the structural chemistry. First, each UO_2^{2+} moiety is bound by two CrO_4^{2-} anions and three IO_3^- anions. Both of the chromate anions bridge uranium centers creating a $[(\text{UO}_2)_2(\text{CrO}_4)_2]$ cluster in the form of an eight-membered ring. The clusters are in turn bridged to other clusters by two iodate anions. This pattern repeats along the *a*-axis to create the one-dimensional ribbons. The remaining iodate anion is monodentate and forms long ionic contacts through its two terminal oxo ligands to the Cs^+ cations, which separate the ribbons from one another as depicted in Figure 2. As found in $\text{A}_2[(\text{UO}_2)_3(\text{IO}_3)_4\text{O}_2]$ (A = K, Rb, Tl)^{14,15} and $\text{AE}[(\text{UO}_2)_2(\text{IO}_3)_2\text{O}_2]\cdot\text{H}_2\text{O}$ (AE = Sr, Ba, Pb),^{14,15} the iodate anions terminate the edges of the one-dimensional chains. It is interesting to note that the vast majority of one-dimensional U(VI) compounds are found to contain C_{3v} ligands such as selenite.⁷ Among the

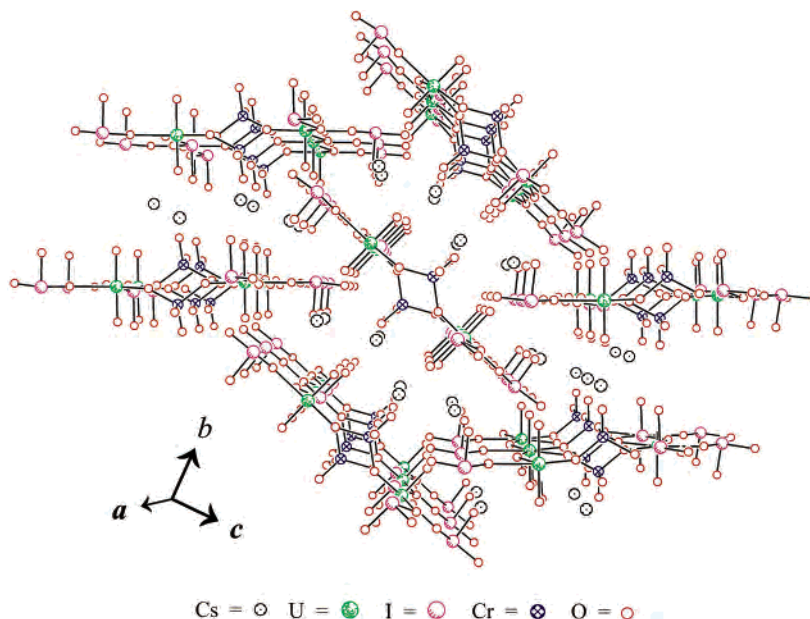


Figure 2. A view down the *a*-axis showing the Cs^+ cations separating the one-dimensional ${}^1_{\infty}[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]^{2-}$ ribbons in **1**.

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new uranyl iodate compounds that we have recently prepared, 10 are one-dimensional, and the remaining two compounds, $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})^{17}$ and $\text{Ag}_4(\text{UO}_2)_4(\text{IO}_3)_2(\text{IO}_4)_2$,¹⁶ both contain two-dimensional uranium oxide topologies. This demonstrates the tendency of compounds that incorporate anions with stereochemically active lone pairs of electrons to adopt low-dimensional architectures.

The Cr–O and I–O bond distances show standard variations based upon whether they are terminal or coordinate to the U(VI) centers, and these are summarized in Table 1. The two terminal and two bridging Cr–O bond lengths are 1.587(5) and 1.604(5), and 1.691(4) and 1.703(4) Å,

respectively. Terminal I–O bond lengths vary from 1.781(4) to 1.792(5) Å, whereas the bridging distances are universally longer and range from 1.835(4) to 1.842(4) Å. The U–O bond distances to the terminal oxo ligands of the uranyl unit are 1.776(4) and 1.791(4) Å, which are normal for a U(VI) compound. Bond valence sums for the U(VI), Cr(VI), and I(V) are 6.02, 6.02, and 5.05 and are consistent with the formula provided for this compound.^{22–24}

In conclusion, we anticipate that the use of molecular transition metal iodates and selenites may be useful precursors for synthesizing mixed-metal uranium compounds. Future reports will detail these ongoing studies.

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Note Added after ASAP. Two formulas in the third paragraph and the reference in footnote 20 were incorrect in the version of this paper posted ASAP on April 2, 2002. The correct information is present in the version posted on April 29, 2002.

Supporting Information Available: X-ray crystallographic files for $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) Crystallographic data for $\text{Cs}_2[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)_2]$ (**1**): golden prisms, crystal dimensions $0.053 \times 0.091 \times 0.260$ mm, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.3929(5)$ Å, $b = 8.1346(6)$ Å, $c = 22.126(2)$ Å, $\beta = 90.647(1)^\circ$, $V = 1330.5(2)$ Å³ ($T = 193$ K); Bruker APEX CCD diffractometer, $\theta_{\text{max}} = 56.72^\circ$, $\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, $0.3^\circ \omega$ scans, 12977 reflections measured, 3308 independent reflections all of which were included in the refinement, data corrected for Lorentz–polarization effects and for absorption (analytical and SADABS), $\mu = 230.55$ cm⁻¹, solution solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 164 parameters, $R1 = 0.0273$, $wR2 = 0.0682$.²⁵
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