

Crystal chemistry and ion-exchange properties of the layered uranyl iodate $\text{K}[\text{UO}_2(\text{IO}_3)_3]$

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Abstract

Single crystals of the potassium uranyl iodate, $\text{K}[\text{UO}_2(\text{IO}_3)_3]$ (**1**), have been grown under mild hydrothermal conditions. The structure of **1** contains two-dimensional $[\text{UO}_2(\text{IO}_3)_3]^{1-}$ sheets extending in the $[ab]$ plane that consist of approximately linear UO_2^{2+} cations bound by iodate anions to yield UO_7 pentagonal bipyramids. There are three crystallographically unique iodate anions, two of which bridge between uranyl cations to create sheets, and one that is monodentate and protrudes in between the layers in cavities. K^+ cations form long ionic contacts with oxygen atoms from the layers forming an eight-coordinate distorted dodecahedral geometry. These cations join the $[\text{UO}_2(\text{IO}_3)_3]^{1-}$ sheets together. Ion-exchange reactions have been carried out that indicate the selective uptake of Cs^+ over Na^+ or K^+ by **1**. Crystallographic data (193 K, $\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$): **1**, orthorhombic, $Pbca$, $a = 11.495(1) \text{ \AA}$, $b = 7.2293(7) \text{ \AA}$, $c = 25.394(2) \text{ \AA}$, $Z = 8$, $R(F) = 1.95\%$ for 146 parameters with 2619 reflections with $I > 2\sigma(I)$. Published by Elsevier Inc.

Keywords: Hydrothermal synthesis; Layered structure; Uranyl compound; Ion exchange

1. Introduction

Uranyl iodates have been known since at least the early 1900s with the correct composition of $\text{UO}_2(\text{IO}_3)_2 \cdot (\text{H}_2\text{O})$ being reported in 1913 [1]. The precipitation of uranyl iodate as its hydrate has been used as a method of quantifying uranium for almost 50 years [2,3]. The speciation of uranyl iodates in solution and subsequent precipitation has also been implicated in the fate of ^{129}I ($t_{1/2} = 1.7 \times 10^7 \text{ yr}$), a key fission product in spent nuclear fuel [4]. $\text{UO}_2(\text{IO}_3)_2 \cdot (\text{H}_2\text{O})$ was also used as an early probe of the effects of radiation damage on uranium-bearing materials [5]. Despite the importance of iodate in uranyl chemistry, the solid-state structure of a uranyl iodate was not known until Weigel and Engelhardt reported that $\text{UO}_2(\text{IO}_3)_2 \cdot (\text{H}_2\text{O})$ was isostructural with $\text{UO}_2(\text{BrO}_3)_2 \cdot (\text{H}_2\text{O})$, the latter structure being identified from X-ray powder diffraction methods [6].

In recent years uranyl iodates have been a rapidly expanding group of compounds prepared via hydrothermal conditions whose structures are dominated by the formation of one-dimensional topologies. These one-dimensional structures are known for relatively simple compounds such as $\text{UO}_2(\text{IO}_3)_2$ [7], as well as for materials that incorporate a diverse set of ligands, e.g., $\text{Cs}_2[(\text{UO}_2)_3\text{Cl}_2(\text{IO}_3)(\text{OH})\text{O}_2] \cdot 2\text{H}_2\text{O}$ [8], $\text{Rb}[(\text{UO}_2)(\text{CrO}_4)(\text{IO}_3)(\text{H}_2\text{O})]$ [9], and $A_2[(\text{UO}_2)(\text{MO}_4)(\text{IO}_3)_2]$ ($A = \text{K, Rb, Cs}$; $M = \text{Cr, Mo}$) [9,10]. Unidimensional features also occur in additional uranyl iodates that incorporate μ_3 -oxo atoms such as $A_2[(\text{UO}_2)_3(\text{IO}_3)_4\text{O}_2]$ ($A = \text{K, Rb, Tl}$) and $AE[(\text{UO}_2)_2(\text{IO}_3)_2\text{O}_2]$ ($AE = \text{Sr, Ba, Pb}$) [11,12], and in complex low-symmetry compounds like $\text{K}_3[(\text{UO}_2)_2(\text{IO}_3)_6](\text{IO}_3) \cdot \text{H}_2\text{O}$ [13]. Two-dimensional structures are less common, but are known for $\text{UO}_2(\text{IO}_3)_2 \cdot (\text{H}_2\text{O})$ [6,7] and $\text{Ag}_4(\text{UO}_2)_4(\text{IO}_3)_2(\text{IO}_4)_2\text{O}_2$ [14]. All of these compounds incorporate the classical approximately linear uranyl dioxo cation, UO_2^{2+} [15–17] bound by iodate anions and other groups to form extended structures. The ligation of the uranyl cations

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by these anions creates tetragonal bipyramidal [UO₆], pentagonal bipyramidal [UO₇], and hexagonal bipyramidal [UO₈] geometries around the uranium centers that are typical for uranyl compounds [15–17].

One of the key features of the uranyl iodate system is the presence of a stereochemically active lone pair of electrons on the I(V) center. The nonbonding nature of these electron pairs can cause the loss of a second dimension of connectivity, thereby leading to the formation of one-dimensional topologies that are in some cases seemingly excised from previously known two-dimensional compounds [11,12]. These lone pairs also have the ability to align in the solid state to create polar structures, albeit this is rare in uranyl compounds because the approximately linear uranyl cations often reside on, or are related by, centers of inversion or higher symmetry. In fact, all uranyl iodates known to date are centrosymmetric. If the discussion is expanded to include compounds containing NpO₂⁺, NpO₂²⁺, and PuO₂²⁺, then three actinyl iodates are known to form polar structures, NpO₂(IO₃) [18], NpO₂(IO₃)₂·H₂O [19], and PuO₂(IO₃)₂·H₂O [20], all of which crystallize in the polar space group *Pna*2₁. If the composition is allowed to diverge further by considering all uranyl compounds with anions containing nonbonding electrons, then a few other acentric structures can be identified for PbUO₂(SeO₃)₂ [21] and Na₈(UO₂)₆(TeO₃)₁₀ [22]. Members of the uranyl family of compounds with oxoanions of Sb(III) and Bi(III) are thus far found to be centrosymmetric [23,24]. Channels can also be created to house the lone pair of electrons in these types of compounds, which occurs in β-AgNpO₂(SeO₃) [18]. Herein we report the preparation, crystal structure, and ion-exchange properties of a new layered uranyl iodate, K[UO₂(IO₃)₃] (**1**).

2. Experimental

2.1. Syntheses

UO₃ (99.8%, Alfa-Aesar), H₅IO₆ (99%, Alfa-Aesar), NaOH (97%, Aldrich), NaCl (99.99%, Aldrich), KOH (85.8%, Fisher), KCl (99%, Aldrich), K₂CO₃ (99%, Aldrich), CsCl (99.9%, Aldrich), CsOH (99.9%, Aldrich) and V₂O₅ (99.95%, Alfa-Aesar) were used as received. Distilled and millipore filtered water with a resistance of 18.2 MΩ·cm was used in all reactions. Reactions were run in Parr 4749 23-mL autoclaves with PTFE liners. Accumet Basic AB 15 pH-meter was used for potentiometric measurements. SEM/electron dispersive analysis by X-ray (EDX) analyses were performed using a JEOL 840/Link Isis instrument. K, U, and I percentages were calibrated against standards. Typical results were surprisingly good and are within 1% of ratios determined from single crystal X-ray diffraction.

Warning: While the UO₃ contains depleted U, standard precautions for handling radioactive materials should be followed.

2.2. K[UO₂(IO₃)₃] (**1**)

UO₃ (0.269 g, 0.94 mmol), K₂CO₃ (0.130 g, 0.94 mmol), V₂O₅ (0.171 g, 0.94 mmol), H₅IO₆ (0.429 g, 1.88 mmol), and 1.5 mL of deionized water were loaded into the 23 mL autoclave. The pH of the initial mixture was 1.1. The autoclave was heated to 180 °C in a box furnace for 72 h, and cooled at a rate of 9 °C/h to room temperature. The product mixture consisted of a colorless solution with a pH of 2.9 over a bright yellow precipitate containing tablets of **1**. The product was washed with methanol and allowed to dry. Crystals then were separated from the mixture for further study. Yield, 260 mg (26% yield based on the U). EDX analysis provided K:U:I ratio of 1:1:3 (21%:19%:60%). IR (KBr, cm⁻¹): 902 (ν₃, UO₂²⁺), 857 (ν₁, UO₂²⁺), 832 (ν, IO₃⁻), 817 (ν, IO₃⁻), 808 (ν, IO₃⁻), 786 (ν, IO₃⁻), 763 (ν, IO₃⁻), 733 (ν, IO₃⁻), 525 (δ, IO₃⁻).

2.3. Crystallographic studies

A tablet of K[UO₂(IO₃)₃] (**1**) with dimensions of 0.133 × 0.046 × 0.013 mm³ was mounted on a thin glass fiber with epoxy, secured on a goniometer head, cooled to -80 °C with an Oxford Cryostat, and optically aligned on a Bruker SMART APEX CCD X-ray diffractometer using a digital camera. Intensity measurements were performed using graphite monochromated MoKα radiation from a sealed tube with a monocapillary collimator. SMART was used for preliminary determination of the cell parameters and data collection control. The intensities of reflections of a sphere were collected by a combination of three sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 30 s.

Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. An analytical absorption correction [25] was applied followed by a semi-empirical absorption correction using SADABS [26]. The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), structure solution (XS), and refinement (XL) [25]. The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Additional crystallographic details are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Additional details can be found in the Auxiliary Material.

Table 1
Crystallographic data for $K[UO_2(IO_3)_3]$ (**1**)

Compound	$K[UO_2(IO_3)_3]$ (1)
Formula mass (amu)	833.83
Color and habit	Yellow tablet
Crystal system	Orthorhombic
Space group	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	11.495(1)
<i>b</i> (Å)	7.2293(7)
<i>c</i> (Å)	25.394(2)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	2110.3(3)
<i>Z</i>	8
<i>T</i> (°C)	−80
λ (Å)	0.71073
$2\theta_{\max}$	56.64
ρ_{calcd} (g cm ^{−3})	5.249
μ (MoK α)(cm ^{−1})	246.03
<i>R</i> (<i>F</i>) for $F_o^2 > 2\sigma(F_o^2)^a$	0.0195
$R_w(F_o^2)^b$	0.0458

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum wF_o^4} \right]^{1/2}$$

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $K[UO_2(IO_3)_3]$ (**1**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²) ^a
U(1)	0.0255(1)	0.0351(1)	0.6519(1)	0.009(1)
I(1)	0.0654(1)	0.4563(1)	0.5630(1)	0.013(1)
I(2)	−0.2992(1)	0.1366(1)	0.6557(1)	0.011(1)
I(3)	0.3409(1)	0.0593(1)	0.7031(1)	0.010(1)
K(1)	0.1642(1)	−0.9480(2)	0.4781(1)	0.026(1)
O(1)	0.0605(3)	0.3375(4)	0.6280(1)	0.012(1)
O(2)	−0.0357(3)	0.3232(5)	0.5246(1)	0.018(1)
O(3)	0.1980(3)	0.3599(5)	0.5391(1)	0.021(1)
O(4)	−0.1523(3)	0.2142(5)	0.6423(1)	0.016(1)
O(5)	−0.3464(3)	0.1100(5)	0.5888(1)	0.019(1)
O(6)	−0.3497(3)	0.3740(4)	0.6669(2)	0.017(1)
O(7)	0.2277(3)	0.0367(5)	0.6539(1)	0.014(1)
O(8)	0.2723(3)	0.2224(5)	0.7463(1)	0.016(1)
O(9)	0.4362(3)	0.2138(4)	0.6671(1)	0.014(1)
O(10)	0.0261(3)	0.0927(5)	0.7202(1)	0.015(1)
O(11)	0.0272(3)	−0.0278(4)	0.5842(1)	0.014(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2.4. Ion-exchange studies

0.01 M NaCl/NaOH, 0.01 M KCl/KOH, and 0.01 M CsCl/CsOH solution pairs were used for the study of the ion-exchange properties of $KUO_2(IO_3)_3$ (**1**) for Na⁺, K⁺, and Cs⁺ ions, respectively. The concentrations of the solutions before and after uptake were measured

with ion-selective electrodes. The volume:mass ratio was 1000:1 (10 mL of the solution for 0.01 g of **1**). Samples were equilibrated for 3 days for all measurements.

3. Results and discussion

3.1. Syntheses

The reaction of UO_3 with KIO_4 and V_2O_5 under mild basic hydrothermal conditions has been previously shown to result in the formation of $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$ in high yield [27]. In an effort to explore both the compositional space of this reaction and the effects of pH on product formation we have continued to investigate this reaction. In acidic conditions $K[UO_2(IO_3)_3]$ (**1**) forms in moderate yield from similar reactants (K_2CO_3 and H_5IO_6 instead of KIO_4) that yielded $K_2[(UO_2)_2(VO)_2(IO_6)_2O] \cdot H_2O$.

3.2. Structures. $K[UO_2(IO_3)_3]$ (**1**)

The structure of **1** consists of an approximately linear UO_2^{2+} cation with U=O distances of 1.777(3) and 1.785(3) Å and an O=U=O angle of 178.39(15)°. This moiety is bound by five iodate anions to form a pentagonal bipyramidal coordination environment around the uranium center as is depicted in Fig. 1. A similar building unit also occurs in one-dimensional $K_3[(UO_2)_2(IO_3)_6](IO_3) \cdot H_2O$ (**13**), although the overall connectivity and dimensionality is different from **1**. The

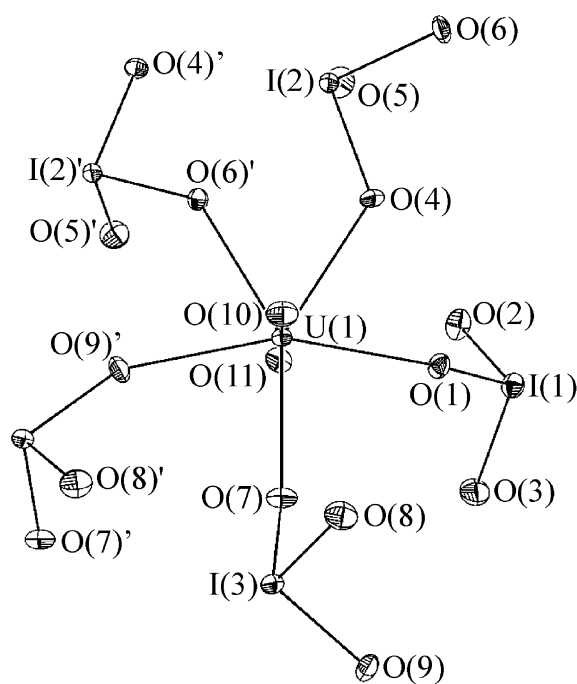


Fig. 1. A view of the $[UO_2(IO_3)_3]^{-}$ fundamental building unit in $K[UO_2(IO_3)_3]$ (**1**). Fifty percent probability ellipsoids are depicted.

U–O bond distances in the equatorial plane range from 2.304(3) to 2.432(3) Å. These oxygen atoms are approximately planar and deviate from planarity by only approximately 0.08 Å. There are three crystallographically unique iodate anions in **1**. Two of these anions bridge between two uranyl cations and have one terminal oxygen atom. The bridging versus terminal I–O bond distances can be differentiated with bridging distances occurring from 1.811(3) to 1.834(3) Å, whereas the terminal I–O distances are both shorter at 1.793(3) Å. The third iodate anion is monodentate and has a bridging I–O distance of 1.862(3) Å, and two terminal distances of 1.782(3) and 1.796(3) Å (Table 3). Surprisingly, there are no long I–O contacts between iodate anions in different sheets. These types of contacts are common in uranyl iodates [7,11,12] and in iodates in general [28–30]. Bond-valence sum calculations on U [15] and I [31,32] yield values of 6.04 for U and 4.99, 4.98, and 5.08 for I(1), I(2), and I(3), respectively, which are consistent with U(VI) and I(V).

The bridging of the uranyl cations by the iodate anions creates two-dimensional sheets in the *ab* plane as shown in Fig. 2. From this perspective it appears that the monodentate iodate anions reside in cavities within the layers. In fact, a view along the *b*-axis (Fig. 3) shows that these iodate anions protrude in between the layers and provide their terminal oxo atoms for forming interactions with the K⁺ cations. The interactions between the K⁺ cations and iodate anions stitch the structure together. The K⁺ cations form long interactions with the terminal oxo atoms from both the monodentate iodate group as well as with the terminal oxo atoms from one of the bridging iodate anions. These cations also interact with the oxo atoms from the uranyl cations forming a surprisingly short contact of 2.715(3) Å [33–38]. A total of eight K⁺–O contacts are formed, with distances ranging from 2.615(4) to 3.175(4) Å, creating a distorted dodecahedral environment around the potassium centers.

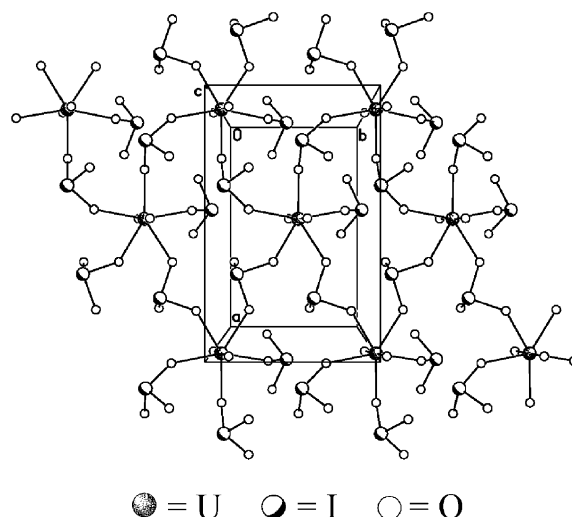


Fig. 2. An illustration of the $\infty [\text{UO}_2(\text{IO}_3)_3]^{1-}$ sheets in $\text{K}[\text{UO}_2(\text{IO}_3)_3]$ (**1**) that extend *ab* plane.

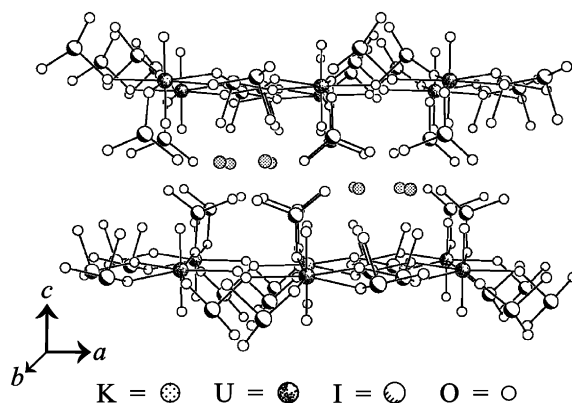


Fig. 3. A view along the *b*-axis of $\text{K}[\text{UO}_2(\text{IO}_3)_3]$ (**1**) showing that the monodentate iodate anion protrudes in between the layers, providing its terminal oxo atoms for forming interactions with the K⁺ cations that reside between the layers.

Table 3
Selected bond distances (Å) and angles (°) for $\text{K}[\text{UO}_2(\text{IO}_3)_3]$ (**1**)

Bond lengths (Å)			
U(1)–O(1)	2.304(3)	I(1)–O(1)	1.862(3)
U(1)–O(4)	2.432(3)	I(1)–O(2)	1.796(3)
U(1)–O(6)	2.363(3)	I(1)–O(3)	1.782(3)
U(1)–O(7)	2.325(3)	I(2)–O(4)	1.812(3)
U(1)–O(9)	2.396(3)	I(2)–O(5)	1.793(3)
U(1)–O(10)	1.785(3)	I(2)–O(6)	1.834(3)
U(1)–O(11)	1.777(3)	I(3)–O(7)	1.811(3)
		I(3)–O(8)	1.793(3)
		I(3)–O(9)	1.812(3)
Angles (°)			
O(10)–U(1)–O(11)	178.39(15)		

3.3. Ion-exchange studies

The exchange of interlayer cations has been previously achieved in a number of layered uranyl compounds, most notably in the autunite and meta-autunite group [39]. In addition, certain uranyl compounds such as hydrogen uranyl phosphate (HUP) [40–43] and $\text{Cs}_4[(\text{UO}_2)_2(\text{V}_2\text{O}_7)\text{O}_2]$ [44] have been shown to exhibit high cationic conductivities. In order to evaluate the potential for ion-exchange reactions of alkali metal cations with **1**, samples were equilibrated with 0.01 M solutions of NaCl/NaOH, KCl/KOH, or CsCl/CsOH. The potential ion exchange of K⁺ with Na⁺ or Cs⁺ was measured potentiometrically using ion-selective electrodes. In order to distinguish between absorption and actual ion exchange, the release of K⁺

was also quantified. No measurable exchange was noted with Na^+ . Similarly, there was also no change noted in the concentration of K^+ in solution in K^+ self-exchange reactions, which does not discount the possibility that an equilibrium is established and exchange takes place. However, substantial Cs^+ ion exchange was noted with high uptake values of up to 3.7(1.2) meq/g. The Cs^+ ionophore is 2.53 orders of magnitude more selective for Cs^+ than K^+ . Therefore, the Cs^+ uptake value probably overestimates Cs^+ exchange because some K^+ is simultaneously being detected. In order to address this issue we also measured the release of K^+ back into solution and found a large value of 1.7 meq/g. This determination demonstrates that ion exchange is actually taking place. The resultant solids were examined using EDX, and these measurements demonstrate complete exchange of K^+ for Cs^+ with no measurable amount of K^+ being observed in the ion-exchanged solid. Given that the reaction takes place at room temperature in basic media, and that uranyl iodates are extremely insoluble in water even at low pH, we suggest that dissolution and recrystallization do not occur concomitantly with the exchange process. In order to confirm this, powder X-ray diffraction data were collected before and after ion exchange. The diffraction patterns were superimposable, indicating that there is virtually no structural change that occurs concomitantly with ion exchange.

4. Conclusions

The uranyl iodate system continues to provide remarkable new structure types unparalleled by other types of oxoanions. The formation of $\text{K}[\text{UO}_2(\text{IO}_3)_3]$ (**1**) under less acidic conditions (final pH = 2.9 vs. ca. 1) than have been typically employed in the past to prepare uranyl iodates may point to a new family of compounds that form at higher pH. Studies to address this issue are underway. We note that attempts to prepare $\text{Cs}[\text{UO}_2(\text{IO}_3)_3]$ directly under equivalent conditions used to prepare **1** failed. Instead, a new polycrystalline phase forms with a Cs/U/I ratio of 1:3:1. We have been unable as of yet to determine the structure of this new cesium uranyl iodate. This result suggests that the K^+ cations play a structure-directing role in the formation of **1**.

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Auxiliary Material: Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggen-

stein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdta@fiz-karlsruhe.de) on quoting depository number CSD 413873.

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