

Intercalation of Iodic Acid into the Layered Uranyl

Iodate, $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$

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Uranyl iodates are known primarily for their ability to form novel one-dimensional topologies.¹ However, the importance of these compounds is equally well addressed by their potential formation during the oxidative dissolution of spent nuclear fuel where it is expected that some of the long-lived β -emitter, ^{129}I ($t_{1/2} = 1.7 \times 10^7$), will be converted to iodate, which can then bind solubilized uranium in the form of UO_2^{2+} to form uranyl iodates. While the structural chemistry of uranyl iodates is relatively mature, little is known about the physicochemical properties of these compounds, with the exceptions of $\text{UO}_2(\text{IO}_3)_2$,² $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$,² and $\text{K}[\text{UO}_2(\text{IO}_3)_3]$.³ $\text{UO}_2(\text{IO}_3)_2$ and $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ have been shown to interconvert in supercritical water, and their thermal properties are well understood.² $\text{K}[\text{UO}_2(\text{IO}_3)_3]$ exhibits selective ion-exchange of its K^+ cations for Cs^+ cations.³

Among iodate compounds in general, there are a small number of acidic solids that are thought to possess iodate in its protonated form, i.e. as HIO_3 . Examples of these compounds include $\text{K}_3\text{Am}_3(\text{IO}_3)_{12} \cdot \text{HIO}_3$ ⁴ and $3\text{La}(\text{IO}_3)_3 \cdot \text{HIO}_3 \cdot 7\text{H}_2\text{O}$.⁵ Given that these solids typically contain heavy atoms, resolution of the hydrogen atom positions is generally not possible or even advisable. Iodic acid is a neutral molecule, and it is therefore possible that some of these compounds are the result of the intercalation of iodic acid into a pre-existing structure. However, it is likely that the iodic acid co-crystallizes along with the other components of the system because these iodic acid molecules are typically part of hydrogen bonding and iodate...iodate networks that are integral parts of the overall structures. Herein we demonstrate the direct intercalation of iodic acid into the layered structure of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$.

When $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is reacted with a two to fivefold excess of iodic acid under mild hydrothermal conditions, the only compound that results is $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$. When the amount iodic acid is increased to tenfold, a mixture of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ and $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ is found. By

increasing the amount of iodic acid to 30-fold, pure samples of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ can be prepared.⁶ More importantly, if $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ is reacted with large excesses of iodic acid, $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ is also found to form. There has historically been controversy over the formula and density of uranyl iodates. We have noted that crystals of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ are morphologically identical with $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, which may have created confusion.

The structure⁷ of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ consists of neutral $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ layers that are interconnected by iodic acid molecules as is shown in Figure 1. The individual $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ layers found in $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ are nearly identical to those found for the parent compound, $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, and consist of UO_7^{2+} cation bound by four bridging iodate anions and a water molecule to form a UO_7 pentagonal bipyramid. The terminal $\text{U}=\text{O}$ bond distances of 1.778(5) Å ($\times 2$), and bridging $\text{U}-\text{O}$ bond distances of 2.335(4) ($\times 2$) and 2.349(4) Å ($\times 2$) deviate only slightly from that of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, as does the longest bond distance to the terminal water molecule of 2.464(6) Å. The similarities between the layers found in $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ and $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ can also be expressed in terms of dimensions of unit cells in the $[\text{ab}]$ plane. For the parent compound these dimensions are $8.452(2) \times 7.707(2)$ Å. Whereas those for the intercalated product are $8.3347(7) \times 7.6594(6)$ Å. Both compounds crystallize in the orthorhombic space group $Pbcn$, and the differences in the

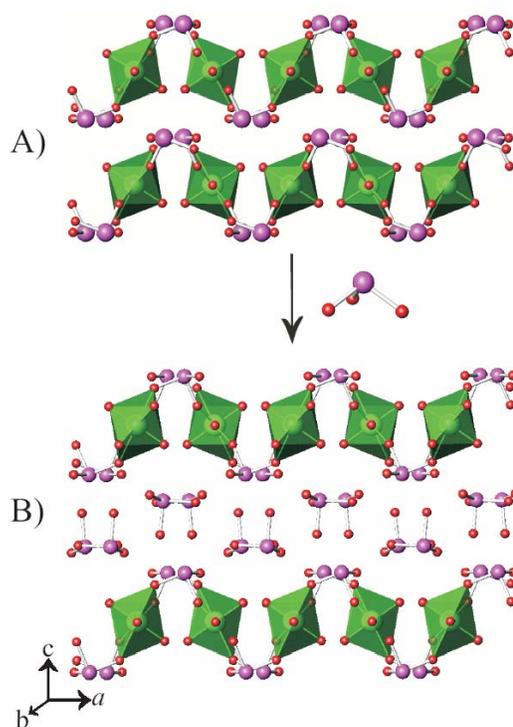


Figure 1. A depiction of the intercalation of iodic acid into $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ (A) to yield $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ (B). UO_7 pentagonal bipyramids are shown in green, iodine in purple, and oxygen in red.

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units cells is primarily found in the *c* direction, where $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ is 12.271(3) Å and $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ is 20.899(2) Å. Taken together, these metrics indicate that $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ differs from $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ only in the intercalation of two molecules of iodic acid per formula unit.

The iodic acid molecules located between the layers show I–O bond distances of 1.787(4), 1.796(5), and 1.866(5) Å. We have surveyed twenty-eight high resolution iodate crystal structures to arrive at a value of 1.792(5) Å for terminal I–O bonds. In contrast, I–O bond distances for bridging or μ_2 -O bonds from thirty-two different structures, show an average distance 1.831(5) Å. Fortunately, during the course of other studies, we were able to prepare $\text{K}_2\text{SeO}_4\cdot 2\text{HIO}_3$,⁸ which contains a single protonated I–OH moiety. Here the bond distance is 1.912(2) Å. Based on these data, it can be concluded that the proton is localized on O(4) with the longest I–O bond. There are several short interactions of appropriate length for a hydrogen bond between O(4) and oxygen atoms within the layers. In addition to hydrogen bonds, iodate...iodate interactions play a critical role in stabilizing many iodate compounds.⁹ In $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, these interactions interconnect the layers, and are probably the origin of the crystallinity and low solubility of this phase. These interactions also exist in $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$. The intermolecular I...O interactions range from 2.611(5) to 2.802(5) Å.

The IR spectrum of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ is particularly rich in that it shows a characteristic I–OH stretch at 1138 cm^{-1} .¹⁰ Addition both asymmetric and symmetric uranyl modes are observed at 902 and 872 cm^{-1} , respectively. Iodate stretches (ν_1 and ν_3) are found at 810, 770, 759, 735, 718, and 671 cm^{-1} .¹¹ As well as an iodate bending mode (δ) at 573 cm^{-1} . The ν and δ modes for the bound water are found at 3410 and 1587 cm^{-1} , respectively.

A calorimetry study of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ reveals two endotherms at 267 and 559 °C. These features are similar to those found for the parent compound, and are ascribed to the loss of water and thermal disproportionation of iodate, respectively. Water loss occurs at a lower temperature for $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ than for $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$. The new feature in the thermogram of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ is an exotherm that immediately follows the loss of water at 299 °C. We suggest that this exothermic feature represents the filling of the open

coordination site previously occupied by water by an oxygen atom from an iodic acid molecule in the interlayer space yielding $\text{UO}_2(\text{IO}_3)_2(\text{HIO}_3)\cdot \text{HIO}_3$. Attempts are ongoing to isolate this compound from supercritical water reactions.

In addition to the intercalation of iodic acid, there are other protonated oxoanions that are of interest from the perspective of the oxidation of spent nuclear fuel that might intercalate into $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$. Selenous acid is a high priority in this regard. Future publications will detail ongoing efforts to explore the intercalation of neutral molecules into $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$.

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Supporting Information Available: X-ray crystallographic files for $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ and $\text{K}_2\text{SeO}_4\cdot 2\text{HIO}_3$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(6) $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ was prepared by loading $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.056 g, 0.112 mmol), HIO_3 (0.585 g, 3.321 mmol), and 0.5 mL of distilled and Millipore filtered water in a 23 mL PTFE-lined autoclave. The autoclave was heated at 200 °C for 3 days and then cooled at a rate of 9 °C/hour to room temperature. Clusters of yellow block crystals of $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$ were isolated, washed with methanol, and allowed to dry. Yield, 59 mg (53% yield based on U). EDX analysis provided U:I ratio of 1:4 mmol.

(7) a) X-ray structural analyses: $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})\cdot 2\text{HIO}_3$: yellow block, crystal dimensions 0.086 x 0.071 x 0.054 mm, orthorhombic, *Pbcn*, *Z* = 4, *a* = 8.3347(7), *b* = 7.6594(6), *c* = 20.899(2) Å, *V* = 1334.15(19) Å³ (*T* = 193 K), μ = 214.99 cm^{-1} , *R*₁ = 0.0245, *wR*₂ = 0.0627. Bruker APEX CCD diffractometer: θ_{max} = 56.60°, MoK α , λ = 0.71073 Å, 0.3° ω scans, 11929 reflections measured, 1579 independent reflections, all of which were included in the refinement. The data was corrected for Lorentz-polarization effects and for absorption, solution was solved by direct methods, anisotropic refinement of *F*² by full-matrix least-squares, 92 parameters. b) Sheldrick, G. M. SHELXTL PC, Version 6.12, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI 2001.

(8) See Supporting Information.

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The direct intercalation of iodic acid into the layered uranyl iodate, $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$, has been observed to yield $\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O}) \cdot 2\text{HIO}_3$ in crystalline form. This is the first example of this type of reaction with iodic acid.

