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Intercalation of Iodic Acid into the Layered Uranyl Iodate, $UO_2(IO_3)_2(H_2O)$

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The direct intercalation of iodic acid into the layered uranyl iodate, $UO_2(IO_3)_2(H_2O)$, has been observed to yield $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ in crystalline form. This is the first example of this type of reaction with iodic acid.

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 ($t_{1/2} = 1.7 \times 10^7$ year), 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 $UO_2(IO_3)_2$,[2] $UO_2(IO_3)_2(H_2O)$,[2] and $K[UO_2(IO_3)_3]$.[3] $UO_2(IO_3)_2$ and $UO_2(IO_3)_2(H_2O)$ have been shown to interconvert in supercritical water, and their thermal properties are well understood.[2] $K[UO_2(IO_3)_3]$ 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 $K_3Am_3(IO_3)_{12}\cdot HIO_3$[4] and $3La(IO_3)_3\cdot HIO_3\cdot 7H_2O$.[5] Given that these solids typically contain heavy atoms, resolution of the H atom positions is challenging. 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 preexisting structure. However, it is likely that the iodic acid cocrystallizes 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 $UO_2(IO_3)_2(H_2O)$.

When $UO_2(NO_3)_2\cdot 6H_2O$ is reacted with a 2−5-fold excess of iodic acid under mild hydrothermal conditions, the only compound that results is $UO_2(IO_3)_2(H_2O)$. When the amount of iodic acid is increased 10-fold, a mixture of $UO_2(IO_3)_2(H_2O)$ and $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ is found. When the amount of iodic acid is increased 30-fold, pure samples of $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ can be prepared.[6] More importantly, if $UO_2(IO_3)_2(H_2O)$ is reacted with large excesses of iodic acid, $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ is also found to form. There has historically been controversy over the formula and density of uranyl iodates. We have noted that crystals of $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ are morphologically identical with those of $UO_2(IO_3)_2(H_2O)$, which may have created confusion.

The structure[7] of $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ consists of neutral $UO_2(IO_3)_2(H_2O)$ layers that are interconnected by iodic acid molecules, as is shown in Figure 1. The individual $UO_2(IO_3)_2(H_2O)$ layers found in $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ are nearly identical with those found for the parent compound, $UO_2(IO_3)_2(H_2O)$, and consist of a UO_2^{2+} cation bound by four bridging iodate anions and a water molecule to form a UO_7 pentagonal bipyramid. The terminal U═O bond distances of 1.778(5) Å (×2) and bridging U−O bond distances of 2.335(4) (×2) and 2.349(4) Å (×2) deviate only slightly from that of $UO_2(IO_3)_2(H_2O)$, as does the longest bond

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(6) $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ was prepared by loading $UO_2(NO_3)_2\cdot 6H_2O$ (0.056 g, 0.112 mmol), HIO_3 (0.585 g, 3.321mmol), and 0.5 mL of distilled and Millipore-filtered water in a 23-mL poly(tetrafluoroethylene)-lined autoclave. The autoclave was heated at 200 °C for 3 days and then cooled at a rate of 9 °C/h to room temperature. Clusters of yellow block crystals of $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ were isolated, washed with methanol, and allowed to dry. Yield: 59 mg (53% yield based on U). EDX analysis provided a U/I ratio of 1:4 mmol.

(7) (a) X-ray structural analyses: $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$, yellow block, crystal dimensions 0.086 × 0.071 × 0.054 mm, orthorhombic, *Pbcn*, $Z = 4$, $a = 8.3347(7)$ Å, $b = 7.6594(6)$ Å, $c = 20.899(2)$ Å, $V = 1334.15(19)$ Å^3 ($T = 193$ K), $\mu = 214.99$ cm^{-1}, R1 = 0.0245, wR2 = 0.0627. Bruker APEX CCD diffractometer: $\theta_{max} = 56.60°$, Mo Kα, $\lambda = 0.71073$ Å, 0.3° ω scans, 11929 reflections measured, 1579 independent reflections, all of which were included in the refinement. The data were corrected for Lorentz and polarization effects and for absorption; the solution was solved by direct methods, anisotropic refinement of F^2 was by full-matrix least squares, 92 parameters. (b) Sheldrick, G. M. *SHELXTL PC, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, version 6.12; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 2001.

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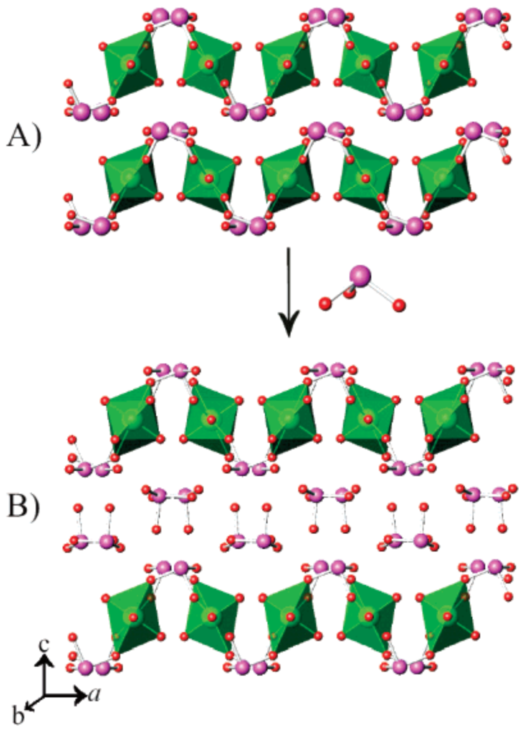

Figure 1. Depiction of the intercalation of iodic acid into $UO_2(IO_3)_2(H_2O)$ (A) to yield $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ (B). UO_7 pentagonal bipyramids are shown in green, I atoms in purple, and O atoms in red.

distance to the terminal water molecule of 2.464(6) Å. The similarities between the layers found in $UO_2(IO_3)_2(H_2O)$ and $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ can also be expressed in terms of the dimensions of the unit cells in the [*ab*] plane. For the parent compound, these dimensions are 8.452(2) × 7.707(2) Å, whereas those for the intercalated product are 8.3347(7) × 7.6594(6) Å. Both compounds crystallize in the orthorhombic space group *Pbcn*, and the differences in the units cells are primarily found in the *c* direction, where $UO_2(IO_3)_2(H_2O)$ is 12.271(3) Å and $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ is 20.899(2) Å. Taken together, these metrics indicate that $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ differs from $UO_2(IO_3)_2(H_2O)$ 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 28 high-resolution iodate crystal structures to arrive at a value of 1.792(5) Å for terminal I−O bonds (see the Supporting Information). In contrast, I−O bond distances for bridging or μ_2-O bonds from 32 different structures show an average distance of 1.831(5) Å. Fortunately, during the course of other studies, we were able to prepare $K_2SeO_4\cdot 2HIO_3$,[8] which contains a single protonated I−OH moiety. Here the bond distance is 1.912(2) Å. On the basis of 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 O atoms within the layers. In addition to hydrogen bonds, iodate•••iodate interactions play a critical role in stabilizing many iodate compounds.[9] In $UO_2(IO_3)_2(H_2O)$, these interactions interconnect the layers and are probably the origin of the crystallinity and low solubility of this phase. These interactions also exist in $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$. The intermolecular I•••O interactions range from 2.611(5) to 2.802(5) Å.

The IR spectrum of $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ is particularly rich in that it shows a characteristic I−OH stretch at 1138 cm^{-1}.[10] In 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] and an iodate bending mode (δ) is found 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 $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ 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 $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ than for $UO_2(IO_3)_2(H_2O)$. The new feature in the thermogram of $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ 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 O atom from an iodic acid molecule in the interlayer space, yielding $UO_2(IO_3)_2(HIO_3)\cdot HIO_3$. Attempts are ongoing to isolate this compound from higher temperature reactions.

In addition to the intercalation of iodic acid, there are other protonated oxoanions, which are of interest from the perspective of the oxidation of spent nuclear fuel, that might intercalate into $UO_2(IO_3)_2(H_2O)$. Selenous acid is a high priority in this regard.[12] Future publications will detail ongoing efforts to explore the intercalation of neutral molecules into $UO_2(IO_3)_2(H_2O)$.

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Supporting Information Available: X-ray crystallographic files (CIF) for $UO_2(IO_3)_2(H_2O)\cdot 2HIO_3$ and $K_2SeO_4\cdot 2HIO_3$ and a reference list used to generate average I−O bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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