Structural Relationships, Interconversion, and Optical Properties of the Uranyl Iodates, $UO_2(IO_3)_2$ and $UO_2(IO_3)_2(H_2O)$: A Comparison of Reactions under Mild and Supercritical Conditions

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The uranyl iodates, $UO_2(IO_3)_2$ (**AU1−8**) and $UO_2(IO_3)_2(H_2O)$ (**AU2−8**) have been prepared from the reaction of UO_3 with I_2O_5 under hydrothermal conditions. Equilibrium between **AU1−8** and **AU2−8** is established after 3 days at 400 °C, resulting in the isolation of an equimolar ratio of these compounds. Lowering of the reaction temperature to 180 °C or shortening of the reaction duration to 1 day allows for the isolation of **AU2−8** in pure form. At 327 °C, **AU2−8** undergoes dehydration and structural rearrangement to **AU1−8**, which is a reversible process. Single-crystal X-ray diffraction, bond valence sum calculations, EDX, DSC, TGA, and vibrational and fluorescence spectroscopy have been used to characterize these compounds. Crystallographic data are as follows: **AU1−8**, monoclinic, space group $P2_1/n$, $a = 4.2454(8)$ Å, $b = 16.636(5)$ Å, $c = 5.284(1)$ Å, $\beta = 107.57(2)°$, and $Z = 2$; **AU2−8**, orthorhombic, space group $Pbcn$, $a = 8.452(2)$ Å, $b = 7.707(2)$ Å, $c = 12.271(3)$, and $Z = 4$. The structure of **AU1−8** is pseudo-three-dimensional with one-dimensional uranyl iodate chains forming close I···O interchain contacts. Each one-dimensional chain consists of edge-sharing UO_8 hexagonal bipyramids and chelating iodate anions that also bridge the $UO_2{}^{2+}$ units through μ_3-O atoms. **AU2−8** has a corrugated layered structure containing pentagonal bipyramidal UO_7 units that are formed from the binding of four oxygen atoms from four bridging iodates and the coordination of a water molecule to the $UO_2{}^{2+}$ moiety. Both of these compounds fluoresce when irradiated with UV light (365 nm), yielding emission spectra characteristic of the uranyl dication.

Introduction

The continued development of actinide chemistry is of critical importance as it relates to the long-term storage of nuclear reactor waste, especially if seepage into groundwater occurs.[1−4] To gain a thorough understanding of both solution and solid-state actinide chemistry, it is crucial that the stability of actinyl ($AcO_2{}^{n+}$) compounds be explored. Concomitant with these studies is the need to develop the numerous potential uses of actinide-containing materials. Actinide compounds display a wide range of physiochemical properties that will allow the development of new materials for optical,[5,6] magnetic,[7−12] and catalytic applications.[13−15] For example, UO_3-based catalysts show very high efficiency for the decomposition of chlorocarbons to relatively benign products at moderate temperatures.[15] Catalysts currently being employed for this process have a propensity for forming byproducts that have even greater toxicities than the initial pollutants.[15]

The chemistry of uranium under oxidizing conditions is dominated by U(VI), which generally occurs in the form of the uranyl, $UO_2{}^{2+}$, cation.[16−18] The uranyl cation can be incorporated into a wide variety of coordination environments ranging from six-coordinate $[UO_2X_4]^{n-}$

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octahedra, to seven-coordinate $[UO_2X_5]^{n-}$ pentagonal bipyramids, to eight-coordinate $[UO_2X_6]^{n-}$ hexagonal bipyramids.[3,17] In these compounds the uranyl cation is typically complexed with halides, especially fluoride, to form both extended structures and molecular species where $[UO_2F_5]^{3-}$ is the most common building block among synthetic U(VI) compounds.[5,6,9,13,14,19] While the majority of U(VI) compounds possess two-dimensional layered structures based upon the condensation of uranyl-containing polyhedra, a plethora of inorganic architectures including molecular, cluster, one-dimensional, and three-dimensional open-framework structures are known.[3,17]

Contemporary studies on uranium-containing compounds have focused primarily on the hydrothermal preparation of inorganic/organic hybrids. These investigations have afforded a large series of low-dimensional and open-framework fluorides and oxyfluorides,[5−11,13,14,19] phosphates,[20] and molybdates.[21] As has been demonstrated with V,[22−30] Fe,[31−38] Co,[39−42] Nb,[43−46] and U,[5−14,19−21] subtle changes in a number of factors, including choice of template (if any), temperature, and pH have substantial effects on the coordination environments of the metals and the dimensionality of the structures. High-valent early transition metals, lanthanides, and actinides are logical choices for building structural flexibility in hydrothermal syntheses, as these metals show considerable variation in coordination number, geometry, and in some cases, oxidation state. Furthermore, the complexity of these compounds and hence their physiochemical properties can be greatly expanded through the employment of multidentate ligands with variable binding modes such as tellurites,[47−51] germanates,[52−57] and silicates.[3,17]

Using the aforementioned concepts, we have begun the exploration of uranyl halates, for which there are very few well-characterized examples. While uranyl iodates have been reported in the past, the characterization of these compounds has been highly limited.[58] The only thoroughly established uranyl halate is $UO_2(BrO_3)_2(H_2O)$.[59] This compound is apparently isostructural with $UO_2(IO_3)_2(H_2O)$,[59] although few details beyond unit cell comparisons have been reported, and a single-crystal structure of $UO_2(BrO_3)_2(H_2O)$ has yet to be determined. Uranyl halates possess two redox active centers with strong oxidizing abilities and a stereochemically active lone pair, making these compounds potentially useful as selective oxidation catalysts. Herein, we report the hydrothermal syntheses, structural characterization, and optical properties of two low-dimensional uranyl iodates, one-dimensional $UO_2(IO_3)_2$ (**AU1−8**) and two-dimensional $UO_2(IO_3)_2(H_2O)$ (**AU2−8**). We have carried out experiments that strongly suggest that **AU2−8** is the kinetic product of these reactions and that equilibrium between **AU1−8** and **AU2−8** is established in supercritical water. These compounds also help to illustrate the striking differences between mild hydrothermal reaction conditions and those at supercritical temperatures.[60,61]

Experimental Section

Syntheses. UO_3 (99.8%, Alfa-Aesar) and I_2O_5 (98%, Alfa-Aesar) were used as received. Distilled and Millipore filtered water was used in all reactions. The resistance of the water was 18.2 MΩ. *While the UO_3 contains depleted U, standard precautions for handling radioactive materials should be followed.* Extreme care should always be taken when scoring

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and opening sealed tubes from hydrothermal reactions because these are typically under pressure. SEM/EDX analyses were performed using a JEOL 840/Link Isis instrument. Reactions performed at 180 °C were run in Parr 4749 23-mL autoclaves with PTFE liners. Reactions at 425 °C were performed in sealed tubes of quartz or gold placed in a Parr 4740 71-mL autoclave that was counter pressured with 2500 psi of argon prior to heating. *Do not exceed these conditions using this vessel.* A Leco Tem-Press 27-mL autoclave filled with 20 mL of water was employed for reactions above 425 °C. The naming system for these compounds stands for Auburn University, the dimensionality of the structure, and the compound number.[10]

*$UO_2(IO_3)_2$ (**AU1−8**) and $UO_2(IO_3)_2(H_2O)$ (**AU2−8**).* UO_3 (69 mg, 0.24 mmol) and I_2O_5 (81 mg, 0.24 mmol) were loaded in a 7-cm gold tube with an 8.3-mm internal diameter. Water (0.6 mL) was then added to the solids, which represents a fill level of ≈45%. The open end of the tube was crimped, hammered flat, and then welded with a torch while the bottom half of the tube was immersed in water. This procedure prevents the boiling of water within the tube so long as it is sealed rapidly. The tube was then placed in a Parr 4740 71-mL autoclave and counter pressured with 2500 psi of argon. The autoclave was sealed and placed in a vertical tube furnace and heated at 10 °C/min to 425 °C. After 72 h the furnace was cooled at 0.2 °C/min to 23 °C. The gold tube was subsequently removed from the autoclave and pierced with wire cutters to relieve excess pressure. The product consisted of a colorless solution over a mixture of bright yellow truncated tetragonal bipyramids (**AU2−8**), pale columns with both square and hexagonal bases (**AU1−8**), and elemental iodine. The mother liquor was decanted from the crystals, which were then washed with methanol (removing iodine) and allowed to dry; yield (**AU1−8** and **AU2−8**), 100 mg (66% yield based on U). Manual separation of the crystals revealed that **AU1−8** and **AU2−8** are present in a 1:1 ratio; that is, 50 mg of each product was isolated. EDX analysis for **AU1−8**: U, 34.35%; I, 65.65%.

*$UO_2(IO_3)_2(H_2O)$ (**AU2−8**).* UO_3 (572 mg, 2 mmol), pyrazole (157 mg, 2.3 mmol), and I_2O_5 (3.460 g, 10.35 mmol) were loaded in a 23-mL PTFE-lined autoclave. Water (3 mL) was then added to the solids. The autoclave was sealed and placed in a box furnace and heated to 180 °C. After 72 h the furnace was cooled at 9 °C/h to 23 °C. The product consisted of a colorless solution over bright yellow truncated tetragonal bipyramids and few crystals of elemental iodine. The mother liquor was decanted from the crystals, which were then washed with water and methanol (removing iodine) and allowed to dry. Yield, 868 mg (68% yield based on U). EDX analysis: U, 34.12%; I, 65.88%. IR (KBr, cm^{-1}): ν (OH) 3346 (b, m); ν (H_2O bending) 1577 (m); ν (U═O) 900; ν (U═O, U−O, and I−O) 872 (s), 816 (s), 769 (s), 743 (s), 718 (s).

Crystallographic Studies. Intensity data were collected from a single crystal of **AU1−8** that had a columnar habit (0.016 × 0.060 × 0.430 mm) with the use of a Nicolet R3M X-ray diffractometer. Data were collected from a truncated tetragonal bipyramid (0.12 × 0.14 × 0.16 mm) of **AU2−8** utilizing a Siemens Platform/CCD SMART diffractometer. Data for each compound were processed and analytical absorption corrections were applied. The structures were solved by direct methods and refined using the SHELXTL-93 package.[62] Uranium and iodine atoms dominate the X-ray scattering in these compounds, making the determination of hydrogen positions for the water molecule in **AU2−8** unreliable, and they were not included in the structural model. The final refinement included displacement parameters for all atoms and a secondary extinction parameter. Some crystallographic details are listed in Table 1 for **AU1−8** and **AU2−8**.

Fluorescence Spectroscopy. Crystals used for spectral measurements were placed onto a microscope slide and rinsed with a drop of methanol. Emission spectra of single crystals were collected using a Nikon Eclipse E400 microscope equipped with an epifluorescence attachment (Southern Micro Instruments) and an imaging spectrometer (Lightform Inc.) coupled to a CCD detector (Electrim Corp.). A 100-W Hg arc lamp was used as the source and a blue filer set was used for detection (Ex. 425−475 nm, DM 480 nm, long pass Em. >495 nm). Spectral image processing was performed on a PC using PARISS Software (v. 3.2 Lightform Inc.). The exposure times used to achieve spectral resolution were 300 ms for **AU1−8** and 350 ms for **AU2−8**. These spectra are an average of 240 individual spectra.

Table 1. Crystallographic Data for $UO_2(IO_3)_2$ (AU1-8) and $UO_2(IO_3)_2(H_2O)$ (AU2-8)

formula	$UO_2(IO_3)_2$	$UO_2(IO_3)_2(H_2O)$
formula mass (amu)	619.83	637.85
space group	$P2_1/n$ (No. 14)	*Pbcn* (No. 60)
a (Å)	4.2454(8)	8.452(2)
b (Å)	16.636(5)	7.707(2)
c (Å)	5.284(1)	12.271(3)
α (deg)	90	90
β (deg)	107.57(2)	90
γ (deg)	90	90
V (Å^3)	355.8(1)	799.3(3)
Z	2	4
T (°C)	22	−80
λ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	5.786	5.300
μ(Mo $K\alpha$) (cm^{-1})	314.91	280.05
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0260	0.0306
$R_w(F_o^2)$ ^{b}	0.0630	0.0536

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$.

Thermal Analysis. Thermal data for **AU1−8** and **AU2−8** were collected using a TA Instruments, model 2920 differential scanning calorimeter (DSC) and a DuPont 951 thermogravimetric analyzer (TGA). Samples (20 mg) were encapsulated in aluminum pans and heated at 10 °C/min from 25 to 600 °C under a nitrogen atmosphere.

Results and Discussion

Syntheses. The reaction of UO_3 with I_2O_5 in aqueous media at 180 °C for 72 h results in the formation of $UO_2(IO_3)_2(H_2O)$ (**AU2−8**) in reasonable yield, reaction (1). When the temperature of this reaction is increased to 425 °C with a reaction duration of 3 days, $UO_2(IO_3)_2$ (**AU1−8**) and $UO_2(IO_3)_2(H_2O)$ (**AU2−8**) are isolated in an approximately equimolar ratio, reaction (2).

$$UO_3 + I_2O_5 \xrightarrow[H_2O]{180\ °C,\ 3\ days} UO_2(IO_3)_2(H_2O) \tag{1}$$

$$UO_3 + I_2O_5 \xrightarrow[H_2O]{425\ °C,\ 3\ days} UO_2(IO_3)_2(H_2O) + UO_2(IO_3)_2 \tag{2}$$

The fact that **AU1−8** and **AU2−8** were isolated in an equimolar ratio from reactions run at 425 °C for 3 days led us to speculate that **AU2−8** is a kinetic product that can slowly be converted to **AU1−8** at temperatures near 425 °C. In addition to thermal analyses (vide infra), reaction durations and temperatures were varied from 1 to 7 days and reaction temperatures increased in 50 °C increments to 575 °C in separate experiments to determine changes in product composition. Reactions run for 1 day at 180−575 °C resulted in the formation of only **AU2−8**. However, as the reaction duration was increased beyond 3 days, the amount of **AU2−8** gradually decreased and the amount of **AU1−8** increased. However, even after 7 days at 400−500 °C, an equimolar ratio of **AU1−8** and **AU2−8** was still isolated. This

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(62) Sheldrick, G. M. *SHELXTL PC, Version 5.0, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI 1994.

evidence suggests that **AU1−8** and **AU2−8** are at equilibrium under supercritical conditions, reaction (3). The heating of pure **AU1−8** in water at 400 °C for 3 days allows for partial conversion to **AU2−8**, providing further support that these compounds are at or near equilibrium in supercritical water.

$$UO_2(IO_3)_2(H_2O) \xrightarrow[H_2O]{425\ ^\circ C} UO_2(IO_3)_2 \qquad (3)$$

I_2O_5 undergoes hydrolysis under hydrothermal conditions to form iodic acid. We have also explored these reactions using iodic acid and H_5IO_6 as sources of iodate. Reactions between UO_3 and I_2O_5, HIO_3, or H_5IO_6 at 425 °C with 3-days durations all produce mixtures of **AU1−8** and **AU2-8**. It is reasonable then to speculate that all of these iodine oxides yield iodate either through hydrolysis or by the oxidation of water in the case of periodate. All of these reactions also produce small amounts of I_2, most likely through thermal disproportionation of IO_3^-. Washing the product mixtures with methanol rapidly removes I_2 so that it does not interfere in subsequent characterization. On a separate note, silver tubing is not suitable for these reactions because it is thoroughly corroded by the reactants and products.

One of the problems faced in these reactions is that crystals of **AU2−8** are typically too small for single-crystal X-ray diffraction studies. However, in a simultaneous effort to prepare organically templated uranyl iodates, we discovered that the templates were completely oxidized in hydrothermal reactions and that **AU2−8** and I_2 were the only insoluble products formed. Fortuitously, the single crystals from these reactions are of the appropriate size (or too large) for single-crystal experiments. Hence, we have reported this preparation in the Experimental Section. A large excess of I_2O_5 is used in these reactions, much of which is used in the complete oxidization of pyrazole. In fact, the pyrazole is completely unnecessary for forming **AU2−8** in yields of approximately 65%. We are still addressing the preparation of organically templated uranyl iodates, but our efforts in this endeavor have been unsuccessful thus far due to the strongly oxidizing nature of I_2O_5.

Structures. *$UO_2(IO_3)_2$ (**AU1−8**).* The structure of **AU1−8** consists of infinite one-dimensional ${}^{1}_{\infty}[UO_2(IO_3)_2]$ chains running down the *a*-axis that are formed from edge-sharing of hexagonal bipyramidal UO_8 units as depicted in Figure 1a. This is the first observation of this coordination environment for U in a one-dimensional structure.[17] This structure is in fact that of a bis-chelate of the uranyl dication with the chain structure forming through the μ_3-O atom of the iodate, joining neighboring U centers. U−O bond lengths range from 1.783(5) Å for U=O bonds of the uranyl unit to 2.404(5)−2.496(5) Å for U−O bonds in the equatorial plane. As O(2) is the μ_3 atom, the I=O bond is lengthened with respect to O(3), which is terminal. The I=O bond lengths are 1.858(5) and 1.788(5) Å for O(2) and O(3), respectively. O(1) bridges solely between U(1) and I(1) with an I=O bond length of 1.825(5) Å, intermediate between I(1)−O(2) and I(1)−O(3) as expected. A view down the chain axis actually shows that this compound is pseudo-three-dimensional, as there are 2.485(6) Å contacts between O(3)′ and I(1) on neighboring chains (Figure 1b). These I···O interactions result in a herringbone arrangement that runs in opposite directions on each side of the chain, making the overall structure centrosymmetric. Selected bond lengths are given in Table 2 for **AU1−8**. Bond valence sum calculations provide values of 6.036 and 5.387 for U(1) and I(1), respectively.[63,64] Parameters for eight-coordinate U(VI) from Burns et al. were used in this calculation.[3]

*$UO_2(IO_3)_2(H_2O)$ (**AU2−8**).* The structure of **AU2−8** consists of pentagonal bipyramidal UO_7 formed from the coordination of UO_2^{2+} by four oxygen atoms from four bridging iodates and the oxygen atom from a water molecule, Figure 2. The IO_3^- units bridge uranyl moieties to form the corrugated ${}^{2}_{\infty}[UO_2(IO_3)_2(H_2O)]$ layers lying parallel to the (010) plane. The binding of IO_3^- to the uranyl units occurs solely by bridging between uranium centers and no chelation occurs. This is in stark contrast to the binding mode of iodate in **AU1−8**. Part of one of these layers is shown in Figure 3a. Figure 3b depicts the packing of these layers within the structure. As found in **AU1−8**, there are additional long I···O contacts between iodate anions. In this case, these interactions, which range from 2.673(4) to 2.871(4) Å, link adjacent sheets to one another, making the structure of this compound also pseudo-three-dimensional.

The U=O bond length of 1.782(4) Å is typical of uranyl compounds.[3] The equatorial U−O(5), U−O(3), and U−O(2) bond lengths are 2.330(4), 2.376(4), and 2.458(5) Å, respectively, and are in general shorter than those found in the equatorial plane of the UO_8 units in **AU1−8**. The long U−O(2) bond length is actually the U−OH_2 bond. This assignment is based not only on charge balance requirements but also on bond valence sum calculations that yield values of 5.985 for U(1), 5.437 for I(1), and 2.193 for O(2) (with two hydrogen atoms estimated at 1.0 Å), which are consistent with our formula assignment.[63,64] Parameters for seven-coordinate U(VI) from Burns et al. were used in this calculation.[3]

We have considered that this compound may in fact be a hydroxide with the second proton located on an iodate oxygen atom. However, I=O bond lengths of 1.816(4), 1.815(3), and 1.792(4) Å to O(3), O(4), and O(5), respectively, do not support the protonation of iodate. Furthermore, two O(2)···O(3)′ distances of 2.88 Å are consistent with the presence of hydrogen-bonding interactions. Finally, the IR spectrum of **AU2−8** in KBr shows peaks at 3346 and 1577 cm^{-1} corresponding to water stretching and bending modes, respectively.[65] These modes were also observed in fluorolube. All other IR peaks can be assigned to U=O, U−O, and I=O modes.[65,66] Selected bond lengths are given in Table 2 for **AU2−8**.

In general, we expect one-dimensional structures to be less dense than those of two-dimensional networks. However, the densities of **AU1−8** and **AU2−8** are 5.786 and 5.300 g cm^{-3}, respectively, reflecting the three-dimensional nature of **AU1−8**. Therefore, the formation of a denser phase at higher temperatures and pressures is not surprising. The initial formation of **AU2−8** as a

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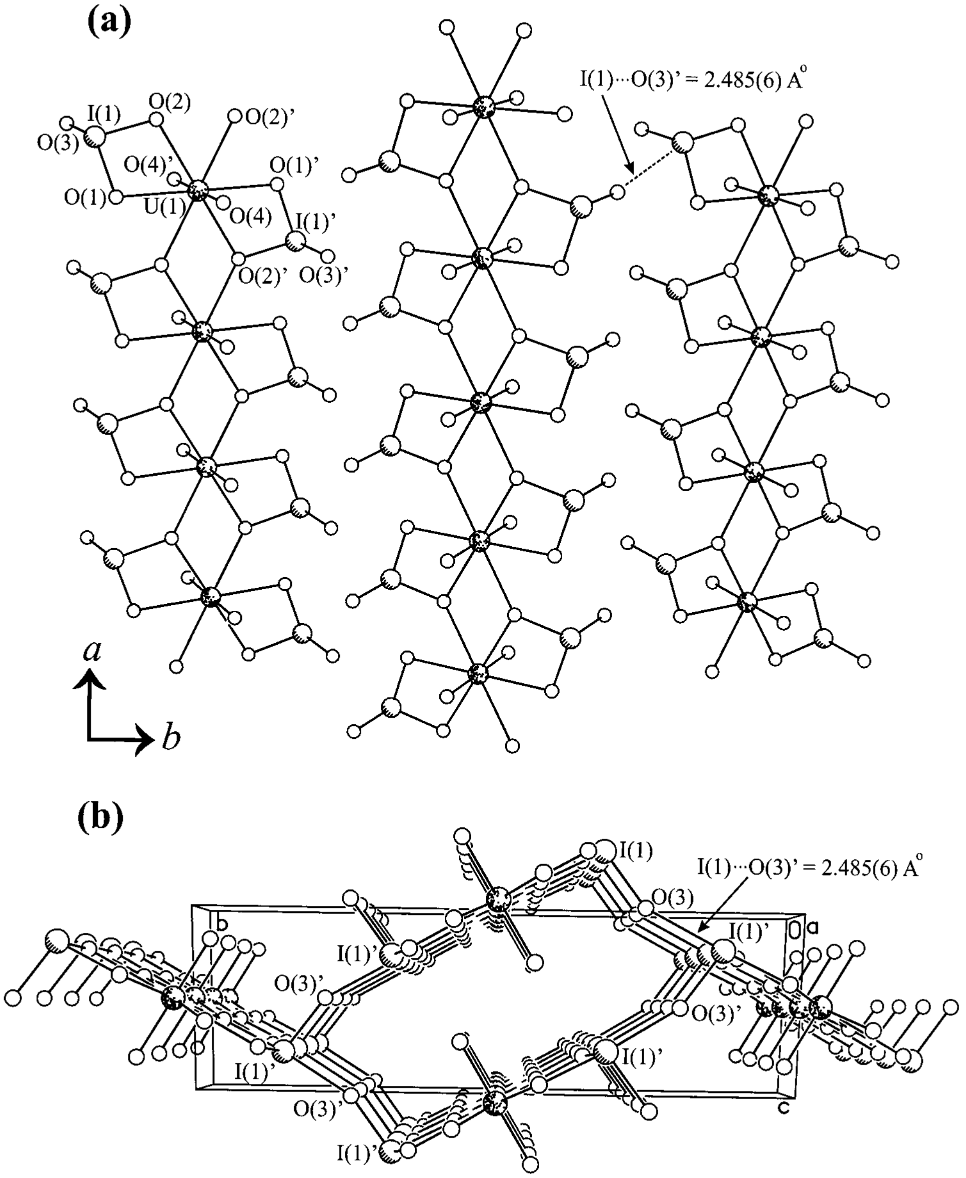

Figure 1. (a) View down the *c*-axis of ${}^{1}_{\infty}[UO_2(IO_3)_2]$ chains running down the *a*-axis in **AU1−8**. (b) Packing of the ${}^{1}_{\infty}[UO_2(IO_3)_2]$ chains viewed down the *a*-axis showing the pseudo-three-dimensional nature of **AU1−8**.

Table 2. Selected Bond Distances (Å) for $UO_2(IO_3)_2$ (AU1-8) and $UO_2(IO_3)_2(H_2O)$ (AU2-8)

	$UO_2(IO_3)_2$ (**AU1−8**)		
U(1)−O(1)	2.496(5) (×2)	I(1)−O(1)	1.825(5)
U(1)−O(2)	2.404(5) (×2)	I(1)−O(2)	1.858(5)
U(1)−O(2)′	2.465(5) (×2)	I(1)−O(3)	1.788(5)
U(1)−O(4)	1.783(5) (×2)		
	$UO_2(IO_3)_2(H_2O)$ (**AU2−8**)		
U(1)−O(1)	1.782(4) (×2)	I(1)−O(3)	1.816(4)
U(1)−O(2)(H₂O)	2.458(5)	I(1)−O(4)	1.815(3)
U(1)−O(3)	2.330(4) (×2)	I(1)−O(5)	1.792(4)
U(1)−O(5)	2.376(4) (×2)		

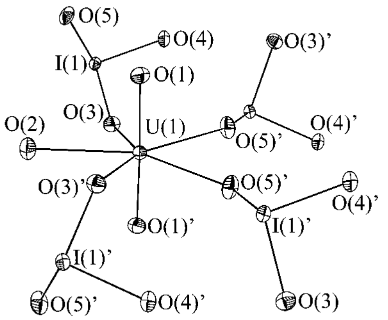

Figure 2. Local pentagonal bipyramidal coordination environment of the uranium centers in **AU2−8**. 50% displacement ellipsoids are shown.

kinetic product demonstrates that water is intimately involved in the initial dissolution processes and remains coordinated during crystallization. Apparently the increased density of **AU1−8** does not impart substantially increased stability over **AU2−8** as these compounds slowly interconvert under hydrothermal conditions.

Fluorescence Spectroscopy. The fluorescence of compounds containing uranyl units is well-known both in the solid state and in solution and is easily identified from the vibronic fine-structure characteristic of the UO_2^{2+} moiety.[67,68] Hydrothermal syntheses often yield product mixtures until reaction parameters can be refined. Therefore, methods for rapidly determining the presence of multiple products are highly desirable. In our lab, we simply irradiate samples with a hand-held UV lamp emitting 365-nm light. U(VI) compounds typically luminesce with differing intensities, allowing

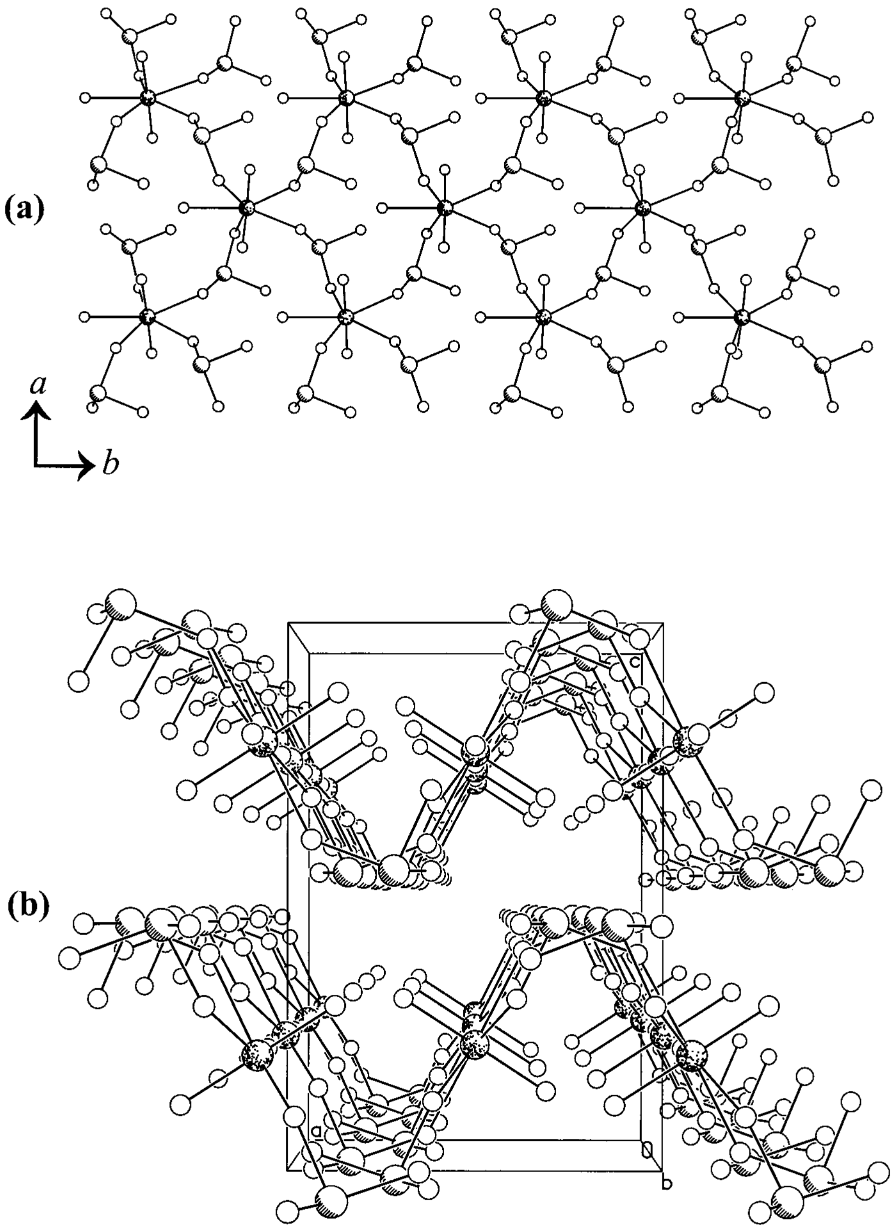

Figure 3. (a) View down the *c*-axis of the $^{2}_{\infty}[UO_2(IO_3)_2(H_2O)]$ layers in **AU2−8**. (b) Packing of the highly corrugated $^{2}_{\infty}[UO_2(IO_3)_2(H_2O)]$ layers in **AU2−8** view down the *b*-axis.

for rapid identification of the presence of multiple products in many cases.[5]

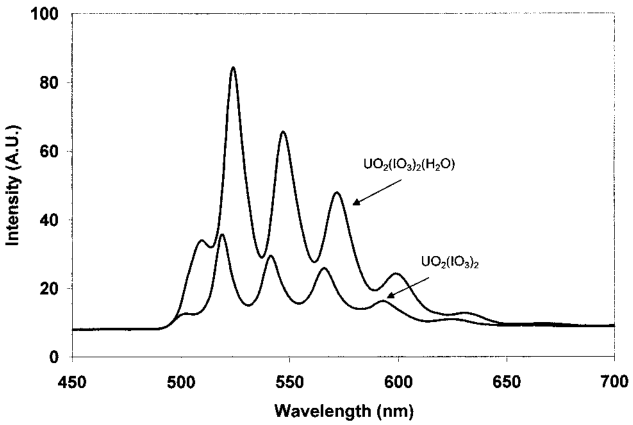

Figure 4. Emission spectra of single crystals of $UO_2(IO_3)_2$ (**AU1−8**) and $UO_2(IO_3)_2(H_2O)$ (**AU2−8**).

On a per gram basis, it is obvious to the observer that **AU2−8** fluoresces more intensely than **AU1−8**. To probe this qualitatively, emission spectra for **AU1−8** and **AU2−8** were collected from single crystals of approximately the same size using optical microscopy. These compounds show typical emission features for uranyl compounds with considerable fine structure present, as shown in Figure 4. These spectra are also consistent with those obtained for other uranyl-containing materials.[5] In addition to intensity differences, the peaks in the spectrum of **AU2−8** are red-shifted by 5 nm with respect to **AU1−8**. In the absence of detailed excitation, emission, quantum yield, and lifetime measurements combined with the complete electronic struc-

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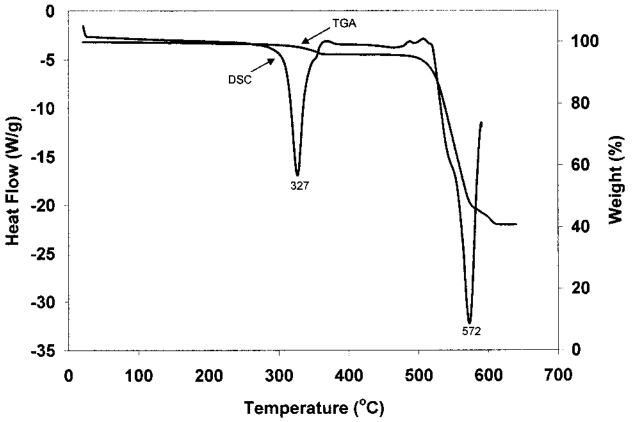

Figure 5. DSC and TGA thermograms of $UO_2(IO_3)_2(H_2O)$ showing the loss of water at 327 °C and decomposition through loss of iodine at 572 °C.

ture of each compound, a more detailed explanation of this difference is not possible.

Thermal Analysis. The thermal behavior of **AU1−8** and **AU2−8** were evaluated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). These measurements were used to determine the dehydration temperature of **AU2−8** and its transformation to **AU1−8**. A DSC thermogram for **AU2−8** was collected over a temperature range of 25−600 °C and is simultaneously depicted with TGA measurements over the same temperature range in Figure 5. These analyses indicate that, at approximately 327 °C, a well-defined endotherm occurs that corresponds to a mass loss of $\approx$2.5%. This value is consistent with the loss of water from **AU2−8**. A large two-step endotherm begins at 572 °C, which is near the temperature limits of these instruments. The first step of this process shows a 40% weight loss that can be attributed to the loss of I_2. Subsequent endotherms are too close to the instrumental limits to be well-defined, but most likely correspond to the loss of oxygen. DSC analysis of **AU1−8** shows only the endotherms at 572 °C.

The surprising feature of these thermal measurements is that integration of the endotherm at 327 °C reveals an enthalpy of reaction of 60(5) kJ/mol. While this value is in the range of values calculated for the loss of water from UO_2^{2+} species,[69] it seems quite small when combined with the observation that the establishment of equilibrium between **AU1−8** and **AU2−8** requires 3 days, even at 525 °C. The sluggishness of this reaction is probably due to two factors. First, as these reactions are hydrothermal, the loss of water from **AU2−8** is not favored from an equilibrium standpoint because the reaction is taking place in a large excess of water. Second, not only does the water need to leave crystals of **AU2−8** to form **AU1−8** but also the whole structure must rearrange and recrystallize, which is probably a slow process. Therefore, establishing equilibrium between these two compounds, even at high temperatures, is slow.

Conclusions

The development of new materials through the combination of ligands with variable binding modes with versatile metal centers represents an important synthetic challenge that has only been touched upon by this work. The demonstration that iodate is a flexible ligand for preparing uranyl compounds with unprecedented structures is a key step toward the development of new oxidation catalysts, a subject that we are currently exploring. On the basis of these studies, we have designed methods for preparing even more complex uranyl iodate systems that will be the subject of reports soon.

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Supporting Information Available: Tables giving structure determinations summaries, positional coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **AU1−8** and **AU2−8** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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