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Structural and Spectroscopic Trends in Actinyl Iodates of Uranium, Neptunium, and Plutonium

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Two neptunyl(VI) iodates, $NpO_2(IO_3)_2(H_2O)$ (**1**) and $NpO_2(IO_3)_2\cdot H_2O$ (**2**), have been prepared from the aqueous reactions of Np(V) in HCl with KIO_4 or H_5IO_6 at 180 °C and have been characterized by single crystal X-ray diffraction and Raman spectroscopy. Both compounds consist of two-dimensional arrangements of pentagonal bipyramidal $[NpO_7]$ polyhedra with axial neptunyl, NpO_2^{2+}, dioxocations. In **1**, the neptunium centers are bound in the equatorial plane by four bridging iodate anions and one terminal water molecule. The iodate anions link the $[NpO_7]$ units into corrugated sheets that interact with one another through intermolecular $IO_3^-\cdots IO_3^-$ interactions as also observed in $UO_2(IO_3)_2(H_2O)$. Compound **2** is isostructural with the recently reported $PuO_2(IO_3)_2\cdot H_2O$, where oxygen atoms from bridging iodate anions occupy the five equatorial sites around the neptunyl moieties. The iodate anions occur as both μ_2- and μ_3-units and link the neptunyl polyhedra into sheets. Both types of iodate anions have their stereochemically active lone-pair of electrons aligned on one side of each layer creating a polar structure. Raman spectra of **1**, $UO_2(IO_3)_2(H_2O)$, and $PuO_2(IO_3)_2\cdot H_2O$ show a sequential shift of the $\nu_1(AnO_2^{2+})$ stretch to lower wavenumber as the atomic number of the actinide is increased. Crystallographic data: **1**, orthorhombic, space group *Pcan*, $a = 7.684(2)$ Å, $b = 8.450(2)$ Å, $c = 12.493(3)$ Å, $Z = 4$; **2**, orthorhombic, space group $Pna2_1$, $a = 7.314(1)$ Å, $b = 11.631(2)$ Å, $c = 9.449(2)$ Å, $Z = 4$.

Introduction

The solid state chemistry of transuranium compounds has received considerably less attention than that of their uranium analogues owing to decreased availability and the highly specialized facilities needed to safely study long-lived α-emitters. However, understanding the behavior of the early transuranium elements is critical for assessing their environmental impact as long-term contributors to the radioactive dose in nuclear waste repositories.[1,2] Of particular interest is how these elements might react with fission-product radionuclides, such as ^{129}I, or their derivatives.[3,4] In fact, iodine can exist in solution in both oxidized and reduced forms, i.e., IO_3^- and I^-, and studies on the nature of ^{129}I in nuclear waste suggested the existence of iodate, IO_3^-.[2]

Although the potential importance of low-soluble transuranium iodates for lanthanide/actinide separation was recognized about 50 years ago, we still lack a thorough understanding of their structural and spectroscopic properties. Few Np(V) and Np(VI) iodates, such as $NpO_2IO_3\cdot 0.5KIO_3\cdot 2H_2O$ and $[Co(NH_3)_6][(NpO_2)_2(IO_3)_7]\cdot 7H_2O$, have been reported; however, these compounds were characterized only by elemental analyses and IR spectroscopy.[5,6] A brownish-yellow dense crystalline compound, stated as being $NpO_2(IO_3)_2\cdot 2H_2O$, was reported to form upon evaporation.[5] In the past, the constitution of plutonium iodates was even more ambiguous with solubility data reported for a suggested $Pu(IO_3)_4$.[7] More recent efforts lead to the synthesis and structural characterization of $PuO_2(IO_3)_2\cdot H_2O$.[8]

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The structural differences of reported binary U(VI) and Pu(VI) iodates raises the question of which structure type Np(VI) would prefer to adopt. Herein we report the single crystal structures and Raman spectra of two hydrothermally synthesized neptunium(VI) iodates, $NpO_2(IO_3)_2(H_2O)$ (**1**) and $NpO_2(IO_3)_2{\cdot}H_2O$ (**2**). Comparisons will be made with the structure and spectroscopic properties of the chemical analogues, $UO_2(IO_3)_2(H_2O)$ (**3**)[9] and $PuO_2(IO_3)_2{\cdot}H_2O$ (**4**).

Experimental Section

Syntheses. KIO_4 (99.9%, Fisher) and H_5IO_6 (98%, Alfa-Aesar) were used as received. A ^{237}Np(V) stock solution (0.1 M) was prepared by dissolution of $^{237}NpO_2$ in 3 M HCl, followed by a subsequent precipitation with 1 M NaOH and dissolution of the washed precipitate in 0.5 M HCl. Distilled and Millipore filtered water with a resistance of 17.2 MΩ was used in all reactions. The Raman spectra were collected on a Nicolet Magna 560 FT-IR/Raman spectrometer. Approximately 5 mg crystalline samples in doubly contained NMR tubes were used for Raman spectroscopy studies. Crystals of **1** and **2** appeared to be produced in high yield (estimated 90% by neptunium) from evidence of a clear solution over pure product.

$NpO_2(IO_3)_2(H_2O)$ (1). KIO_4 (82.7 mg, 0.36 mmol) and 800 μL of water were loaded in a 10-mL PTFE-lined autoclave followed by the addition of 300 μL of ^{237}Np(V) stock solution. The autoclave was sealed, doubly contained in two heat-sealed Teflon bags, and placed in a box furnace previously heated to 180 °C. After 24 h, the furnace was cooled at 13 °C/h to 25 °C. The product consisted of a clear solution of pH 4−5 over large green multifaceted single crystals of **1**. The crystals were placed in a small vial where the majority of the mother liquor was removed to enable clear viewing under a microscope. Raman (cm^{-1}): $\nu_1(NpO_2^{2+})$ 872 (s); ν(I−O) 789 (s), 760 (s), 750 (w, sh), 727 (s).

$NpO_2(IO_3)_2{\cdot}H_2O$ (2). H_5IO_6 (63.1 mg, 0.30 mmol) and 500 μL of water were loaded in a 10-mL PTFE-lined autoclave followed by the addition of 200 μL of ^{237}Np(V) solution. The autoclave was tightened, doubly contained in two heat-sealed Teflon bags, and placed in a box furnace preheated to 180 °C. After 24 h, the furnace was cooled at 13 °C/h to 25 °C. The product consisted of a clear acidic solution over brown blocks of **2**. The crystals were placed in a small vial where the majority of the mother liquor was removed to enable clear viewing under a microscope.

Crystallographic Studies. Crystals of **1** and **2** were mounted in glass capillaries after coating with epoxy. The capillaries were then coated with clear nail polish as a third form of containment. The crystals were placed on a Bruker P4/CCD/PC X-ray diffractometer and cooled to 203 K using a Bruker LT-2 low-temperature device. The data were collected using a sealed, graphite monochromatic Mo Kα X-ray source. A hemisphere of data was collected using a combination of φ and ω scans, with 30-s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.[10] Frame integration and final cell parameter calculations were carried out using SAINT software.[10] The data were corrected for absorption using SADABS because the geometry of this instrument prevents complete face-indexing.[10] The program suite SHELXTL was used for space group determination (XPREP), structure solution (XS), and refinement (XL).[11] The final refinement included anisotropic displacement parameters for all atoms, excluding O(3) in **2**, and a secondary extinction parameter. Some crystallographic details are listed in Table 1; additional details can be found in the Supporting Information.

Table 1. Crystallographic Data for $NpO_2(IO_3)_2(H_2O)$ (**1**) and $NpO_2(IO_3)_2{\cdot}H_2O$ (**2**)

	$NpO_2(IO_3)_2(H_2O)$ (**1**)	$NpO_2(IO_3)_2{\cdot}H_2O$ (**2**)
formula mass (amu)	636.82	636.82
space group	*Pcan*	$Pna2_1$
a (Å)	7.684(2)	7.314(1)
b (Å)	8.450(2)	11.631(2)
c (Å)	12.493(3)	9.4490(16)
V (Å^3)	811.2(4)	803.8(2)
Z	4	4
T (°C)	−70	−70
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	5.214	5.262
μ(Mo Kα) (cm^{-1})	204.40	206.29
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0297	0.0289
$R_w(F_o^2)^b$	0.0700	0.0604

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

Results and Discussion

Syntheses. The reactions of KIO_4 or H_5IO_6 with Np(V) at 180 °C for 24 h in aqueous media produce either dark green crystals of $NpO_2(IO_3)_2(H_2O)$ (**1**) or brown blocks of $NpO_2(IO_3)_2{\cdot}H_2O$ (**2**), respectively. As expected, the metaperiodate anion ($E°$ (IO_4^-/IO_3^-) = 1.65 V)[12] oxidizes Np(V) in acid completely to the +6 oxidation state ($E°$ (NpO_2^+/NpO_2^{2+}) = 1.16 V).[13] The reduction of the I(VII) to I(V) can also occur by oxidizing water under hydrothermal conditions, which has been noted in the preparation of both uranyl and lanthanide iodates.[9,14−17] Although other iodate starting materials, such as KIO_3 or I_2O_5, precipitate Np(V) instantly, only microcrystalline or powdered materials were obtained.

Structures. $NpO_2(IO_3)_2(H_2O)$ (1). Compound **1** is isostructural with its two-dimensional uranyl iodate analogue, $UO_2(IO_3)_2(H_2O)$ (**3**).[9] The layers are built up by pentagonal-bipyramidal [NpO_7] polyhedra, which are linked by μ_2-[IO_3] pyramids, as shown in Figure 2. In the [NpO_7] polyhedra, the neptunium atoms are coordinated by two axial *trans*-

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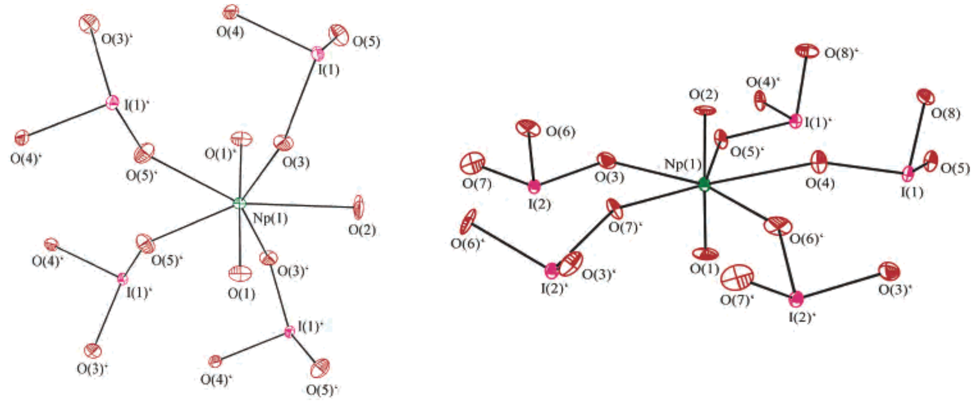

1 **2**

Figure 1. Pentagonal bipyramidal coordination environment of the neptunium atoms in $NpO_2(IO_3)_2(H_2O)$ (**1**) and $NpO_2(IO_3)_2{\cdot}H_2O$ (**2**), respectively. 50% displacement ellipsoids are shown.

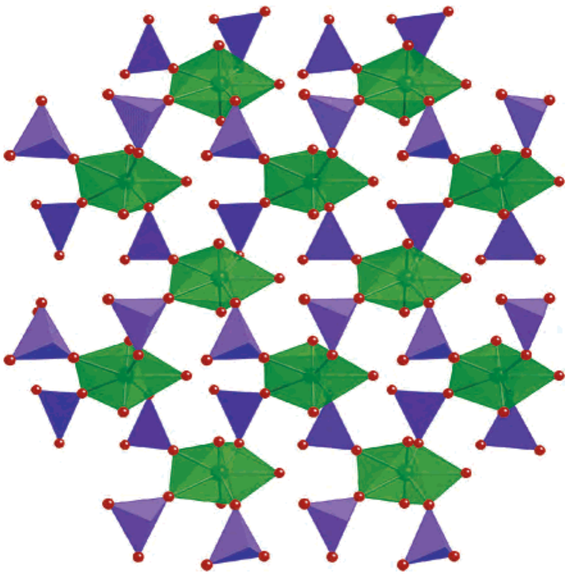

Figure 2. Depiction of the ${}^{2}_{\infty}[NpO_2(IO_3)_2(H_2O)]$ layers in $NpO_2(IO_3)_2(H_2O)$ (**1**) that formed from the coordination of NpO_2^{2+} cations by bridging iodate anions and water molecules.

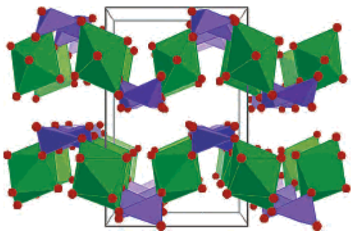

Figure 3. Distorted zigzag layers, ${}^{2}_{\infty}[NpO_2(IO_3)_2(H_2O)]$, in the (010) plane of $NpO_2(IO_3)_2(H_2O)$ (**1**).

Table 2. Selected Bond Distances (Å) for Comparison of $NpO_2(IO_3)_2(H_2O)$ (**1**), $NpO_2(IO_3)_2{\cdot}H_2O$ (**2**), $UO_2(IO_3)_2(H_2O)$ (**3**), and $PuO_2(IO_3)_2{\cdot}H_2O$ (**4**)

	1	**2**	**3**	**4**
$An-O_{ax}$	O(1)×2 1.760(7)	O(1) 1.73(1)	1.782(4) ×2	1.75(1)
		O(2) 1.77(1)		1.757(9)
$An-O_{eq}$	O(3)×2 2.332(7)	O(6) 2.341(7)	2.330(4) ×2	2.332(7)
	O(5)×2 2.375(8)	O(7) 2.360(7)	2.376(4) ×2	2.360(7)
	O(2) 2.48(1)	O(5) 2.394(7)	2.458(5)	2.397(7)
		O(3) 2.404(8)		2.404(7)
		O(4) 2.431(8)		2.418(8)
$I-O_{br}$	O(5) 1.802(7)	I(1)−O(5) 1.811(7)	1.792(4)	1.807(6)
	O(3) 1.821(7)	I(1)−O(4) 1.844(8)	1.815(3)	1.844(7)
$I-O_{ter}$	O(4) 1.821(8)	I(1)−O(8) 1.81(1)	1.816(4)	1.808(8)
$I(\mu_3)-O$		I(2)−O(6) 1.790(9)		1.810(7)
		I(2)−O(7) 1.807(8)		1.810(7)
		I(2)−O(3) 1.812(9)		1.815(8)

oxygen atoms that are perpendicular to four bridging iodate anions and one terminal water molecule in the equatorial plane (Figure 1). Each of the four iodate ligands is linked to another $[NpO_7]$ polyhedron, thus forming corrugated ${}^{2}_{\infty}[NpO_2(IO_3)_2(H_2O)]$ layers, which lie parallel to (010), as displayed in Figure 3.

The neptunyl O═Np═O moiety is nearly linear (178.3(5)°), and the Np═O distances of 1.760(7) Å are slightly shorter than the O═U═O distances (1.782(4) Å) in **3**. The four iodate ligands are bound in the equatorial plane with bond distances of 2.332(7) Å for Np−O(3), 2.375(8) Å for Np−O(5), and 2.48(1) Å for Np−O(2). The longest Np−O distance of 2.48(1) Å belongs to the terminal water group. These distances are very similar to those observed in **3**. The I−O bond distances are within the expected range between 1.802(7) and 1.821(8) Å. Selected bond lengths for **1** are given in Table 2. There are close I···O contacts between iodate anions in parallel layers of 2.816(6) Å. These interactions are thought to stitch low-dimensional features in iodate structures together in much the same way as hydrogen bonds.

$NpO_2(IO_3)_2{\cdot}H_2O$ (2). Compound **2** is isostructural with the previously reported plutonyl(VI) iodate, $PuO_2(IO_3)_2{\cdot}H_2O$ (**4**).[8] As in compound **1**, the layered structure of **2** is characterized by pentagonal bipyramidal $[NpO_7]$ polyhedra that are connected by bridging $[IO_3]$ pyramids. However, in contrast to **1**, all five equatorial oxygen atoms in the equatorial plane of the Np atom derive from five iodate ligands. In this structure type, the water molecules do not coordinate with the neptunium center directly and are rather aligned between the layers (Figure 1). The neptunyl polyhedra are linked by iodate anions forming neutral ${}^{2}_{\infty}[NpO_2(IO_3)_2]$ layers that lie parallel to the *ab* plane (Figure 4). The occluded water molecules located between layers complete the structures as depicted in Figure 5.

The Np═O distances of 1.73(1) and 1.77(1) Å in the $[NpO_7]$ polyhedra compare well with the Pu═O bond lengths

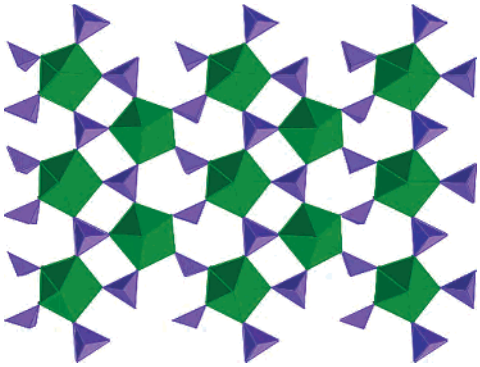

Figure 4. Illustration of the $^2_\infty[NpO_2(IO_3)_2]$ sheets found in $NpO_2(IO_3)_2 \cdot H_2O$ (**2**) that are formed from the coordination of NpO_2^{2+} cations by both doubly and triply bridging iodate anions. These sheets are polar owing to the alignment of the stereochemically active lone-pair of electrons on the I(V) centers along the *c*-axis.

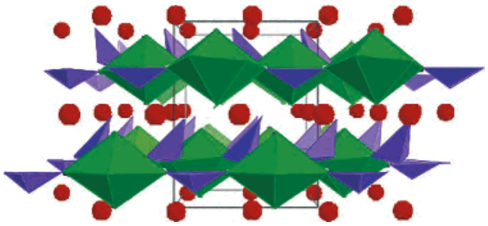

Figure 5. View of the stacking arrangement of the $^2_\infty[NpO_2(IO_3)_2]$ layers in $NpO_2(IO_3)_2 \cdot H_2O$ (**2**).

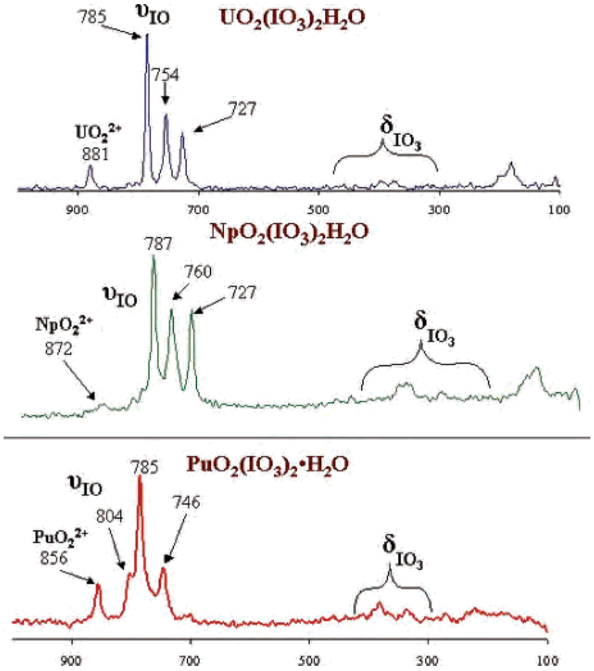

Figure 6. Comparison of the actinyl (O═An═O) and iodate (I═O) stretching frequencies found in $UO_2(IO_3)_2(H_2O)$ (**3**), $NpO_2(IO_3)_2(H_2O)$ (**1**), and $PuO_2(IO_3)_2 \cdot H_2O$ (**4**).

of 1.75(1) and 1.757(9) Å found in **4**. The *trans*-dioxo cations for both **2** and **4** are also nearly linear with bond angles of 178.1(4)° and 178.9(4)°, respectively. The $Np-O_{eq}$ bonds are close to the $Pu-O_{eq}$ (2.332(7)−2.418(8) Å) bond lengths and range from 2.341(7) to 2.431(8) Å.

Two crystallographically distinct iodate anions connect the $[NpO_7]$ polyhedra. The μ_2-$[I(1)O_3]$ pyramids show substantial variations in their I(1)−O bond lengths involving bridging or terminal oxygen. The I−O(8) distance for the terminal oxygen is 1.81(1) Å, while the oxygen atoms involved in ligation to the Np(VI) center are 1.811(7) and 1.844(8) Å. The iodate anions containing I(2) utilize all three oxygen atoms to coordinate three neptunium polyhedra. The I(2)−O distances show only small variations and occur from 1.790(9) to 1.812(9) Å. Selected bond lengths for **2** are given in Table 2. When viewed down the *ab* plane (Figure 4), both types of iodate anions in **2** have their stereochemically active lone-pairs of electrons aligned on one side of the layers and induce polarity to the compound.

Raman Spectroscopy. Vibrational data for $UO_2(IO_3)_2(H_2O)$ (**3**), $NpO_2(IO_3)_2(H_2O)$ (**1**), and $PuO_2(IO_3)_2 \cdot H_2O$ (**4**) are shown in Figure 6. Efforts to collect the Raman data for $NpO_2(IO_3)_2 \cdot H_2O$ (**2**) were unsuccessful owing to its decomposition upon the intense laser irradiation. The spectra of **3** and **1** compare very well indicating similar coordination modes of the iodate ligands. The neptunyl and uranyl ν_1-symmetric stretching frequencies are found at 872 and 879 cm^{-1}, respectively, and are clearly separated from the iodate stretching modes. The presence of a single crystallographically unique iodate anion simplifies the interpretation of the iodate stretching modes and single ν_1-symmetric and two ν_3-antisymmetric I−O frequencies were observed at 789, 760, and 727 cm^{-1} for **1** and at 785, 754, and 727 cm^{-1} for **3**. The different coordination of iodate anions in **4** is reflected in its Raman spectrum. The plutonyl(VI) ν_1-symmetric stretch is again well isolated from the iodate stretching modes and is found at 856 cm^{-1}, which follows a trend of increased weakening of the An═O bond across the U/Np/Pu series. The I−O stretching mode region for **4** contains an intense ν_1-symmetric band at 785 cm^{-1} surrounded by weaker ν_3-antisymmetric modes at 803 and 746 cm^{-1}.

Conclusion

Expanding the structural knowledge and spectroscopic characterization of uranium and transuranic compounds is a challenging task due to the difficult nature of handling highly radioactive material. The majority of synthetic studies of transuranium compounds resulted in the formation of rather amorphous or microcrystalline materials. Utilizing mild hydrothermal conditions enables us to approach the formation of crystalline materials and to unravel the largely unknown coordination chemistry of inorganic neptunium and plutonium materials. With the synthesis of $NpO_2(IO_3)_2(H_2O)$ (**1**) and $NpO_2(IO_3)_2 \cdot H_2O$ (**2**), we were able to illustrate the structural diversity and complexity that may occur within the light actinide elements, U, Np, and Pu. The binary plutonyl(VI) iodate is unique in its structure and displays previously unknown actinyl−iodate coordination. Although neptunium can also adopt this structure type, the U-analogue structure type with one coordinated water molecule in the equatorial neptunyl plane is thermodynamically favored. This is the first example of analogous compounds within this series where neptunium can adopt two different structure types exhibited by its element neighbors.

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Supporting Information Available: X-ray crystallographic files for $NpO_2(IO_3)_2(H_2O)$ (**1**) and $NpO_2(IO_3)_2 \cdot H_2O$ (**2**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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