Inorganic Chemistry

ARTICLE

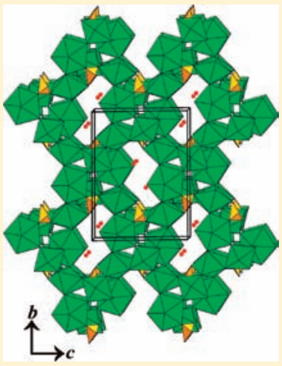
pubs.acs.org/IC

Two New Neptunyl(V) Selenites: A Novel Cation−Cation Interaction Framework in $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ and a Uranophane-Type Sheet in $Na(NpO_2)(SeO_3)(H_2O)$

Geng Bang Jin, S. Skanthakumar, and L. Soderholm*

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

S *Supporting Information*



ABSTRACT: Dark green crystals of $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (**1**) have been prepared by a hydrothermal reaction of neptunyl(V) and Na_2SeO_4 in an aqueous solution at 150 °C, while green plates of $Na(NpO_2)(SeO_3)(H_2O)$ (**2**) have been synthesized by evaporation of a solution of neptunyl(V), H_2SeO_4, and NaOH at room temperature. Both compounds have been characterized by single-crystal X-ray diffraction. The structure of compound contains three crystallographically unique Np atoms that are bonded to two O atoms to form a nearly linear O═Np═O NpO_2^+ cation. Neighboring Np^{5+} ions connect to each other through a bridging oxo ion from the neptunyl unit, a configuration known as cation−cation interactions (CCIs), to build a complex three-dimensional network. More specifically, each $Np(1)O_2^+$, $Np(2)O_2^+$, and $Np(3)O_2^+$ cation is involved in three, five, and four CCIs with other units, respectively. The framework of neptunyl(V) pentagonal bipyramids is decorated by selenite trigonal pyramids with one-dimensional open channels where uncoordinated waters are trapped via hydrogen bonding interactions. Compound adopts uranophane-type $[(NpO_2)(SeO_3)]^-$ layers, which are separated by Na^+ cations and water molecules. Within each layer, neptunyl(V) pentagonal bipyramids share equatorial edges with each other to form a single chain that is further connected by both monodentate and bidentate selenite trigonal pyramids. Crystallographic data: compound, monoclinic, $P2_1/c$, $Z = 4$, $a = 6.6363(8)$ Å, $b = 15.440(2)$ Å, $c = 11.583(1)$ Å, $\beta = 103.549(1)°$, $V = 1153.8(2)$ Å^3, $R(F) = 0.0387$ for $I > 2\sigma(I)$; compound (**2**), monoclinic, $C2/m$, $Z = 4$, $a = 14.874(4)$ Å, $b = 7.271(2)$ Å, $c = 6.758(2)$ Å, $\beta = 112.005(4)°$, $V = 677.7(3)$ Å^3, $R(F) = 0.0477$ for $I > 2\sigma(I)$.

INTRODUCTION

Neptunium, the first transuranic element, shows a rich chemistry that includes relatively stable compounds with Np valence states ranging from +3 to +7.[1] Similar to the chemistry established for uranium, the higher oxidation states of neptunium have a propensity to form the nearly linear dioxo cation NpO_2^{n+} (n = 1, 2).[2] Unlike U chemistry, the most common oxidation state of Np in aqueous solution is pentavalent, with the neptunyl(V) ion being very soluble in aqueous solutions under a wide variety of conditions.[1] Similar to the well-known UO_2^{2+} cation, NpO_2^+ is further coordinated by four, five, or six ligands in the equatorial plane, forming tetragonal, pentagonal, or hexagonal bipyramids, respectively.[2,3] The Np(V)═O axial bonds are weaker than those within the UO_2^{2+} cation due to the lower charge on the metal. To fulfill the bonding requirement of the neptunyl oxygen atoms, the oxo ion from one neptunyl(V) unit tends to bind to an adjacent NpO_2^+ unit as an equatorial ligand, a configuration referred to as a cation−cation interaction (CCI).[4,5] CCIs are known in approximately half of neptunyl(V) inorganic compounds, although, similar to uranyl(VI), these interactions do not appear to be significant in neptunyl(VI) materials.[2,5] The intrinsic nature of this preference is borne out by a study probing neptunyl correlations in aqueous solution, in which CCIs were observed for NpO_2^+ but not NpO_2^{2+}.[6] As demonstrated by uranyl(VI) structural chemistry, actinyl bipyramids generally connect to other metal polyhedra by sharing equatorial vertices to form low-dimensional crystal structures with chain or sheet type topologies.[3] The CCIs connecting adjacent NpO_2^+ cations add extra interactions between neptunyl polyhedra, resulting in more three-dimensional structures.[2] CCIs also provide potential superexchange pathways that can enhance magnetic interactions between Np(V) ($5f^2$) ions.[7] In fact, to the best of our knowledge, all neptunyl(V) compounds reported to exhibit magnetic ordering include CCIs.[7−15]

To further explore the role of lattice dimensionality, as promoted through CCIs, on the magnetic properties exhibited by neptunyl(V) compounds, we are interested in materials containing tetrahedral oxo anions of the hexavalent group VI elements (T = S, Se, Cr, and Mo), in which TO_4^{2-} ligands provide further structural variety owing to the high flexibility of the Np−O−T bonds.[16] Recently, we reported the syntheses and characterizations of three neptunyl(V) selenate hydrates, $(NpO_2)_2(SeO_4)(H_2O)_n$ (n = 1, 2, and 4).[15] The structure of the monohydrate adopts a three-dimensional CCI network of neptunyl(V) pentagonal bipyramids, while the structures of the

Received: April 5, 2011
Published: June 07, 2011

Table 1. Crystal Data and Structure Refinements for $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ and $Na(NpO_2)(SeO_3)(H_2O)$[a]

	$(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$	$Na(NpO_2)(SeO_3)(H_2O)$
fw	1005.02	436.97
color and habit	dark green polyhedron	pale green plate
space group	$P2_1/c$	$C2/m$
a (Å)	6.6363(8)	14.874(4)
b (Å)	15.440(2)	7.271(2)
c (Å)	11.583(1)	6.758(2)
β (deg)	103.549(1)	112.005(4)
V (Å^3)	1153.8(2)	677.7(3)
ρ_c (g/cm^3)	5.786	4.283
μ (cm^{-1})	300.36	207.31
$R(F)$[b]	0.0387	0.0477
$R_w(F_o^2)$[c]	0.0906	0.1173

[a] For both structures, crystal system: monoclinic, $Z = 4$, $\lambda = 0.71073$ Å, and $T = 100(2)$ K. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$.

dihydrate and the tetrahydrate consist of two-dimensional "cationic square nets" of neptunyl(V) units. Consistent with other reports of Np(V) compounds containing cationic square nets, the tetrahydrate was found to undergo a ferromagnetic transition below 8(1) K.[15] In further attempts to explore a variety of $NpO_2^{2+}-SeO_4$ systems, we observed the reduction of selenate anions during solution syntheses, which resulted in the preparation of neptunyl(V) selenite crystals.

The selenite anion, SeO_3^{2-} has a stereochemically active lone pair of electrons, the presence of which can favor the formation of polar structures. For example, $Pb(UO_2)(SeO_3)_2$ crystallizes in a noncentrosymmetric space group,[17] although the only two reported neptunyl(V) selenites, $Ag(NpO_2)(SeO_3)$[18] and $Np(NpO_2)_2(SeO_3)_3$,[19] do not. Interesting and technologically important physical properties associated with noncentric space groups include optical activity, enantiomorphism, piezoelectricity, and pyroelectricity.[20] Herein, we present the single-crystal structures of two new neptunyl(V) selenites produced as reduced byproducts during studies of the neptunyl(V) selenate system: $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (**1**) and $Na(NpO_2)(SeO_3)(H_2O)$ (**2**). Compound **1** adopts a novel three-dimensional CCI network of neptunyl(V) pentagonal bipyramids with one-dimensional open channels. Compound **2** is the first actinyl selenite containing uranophane-type $[(NpO_2)(SeO_3)]^-$ layers.[3]

■ EXPERIMENTAL SECTION

Caution! *^{237}Np is an α- and γ-emitting radioisotope and as such is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials.*

Synthesis of $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (1). A total of 0.215 mL of a 0.116 M Np(V) stock solution (in 1 M HCl), 102 mg (0.276 mmol) of $Na_2SeO_4 \cdot 10H_2O$ (Aldrich, 99.999%), and 0.785 mL of distilled H_2O were added to a 7 mL Teflon cup with a tightly closed screw-top lid. The pH of the resulting solution was adjusted to 3.5 using a 2 M NaOH (Fisher, 98.5%) solution. Two such Teflon cups were placed in a 125 mL Teflon-lined Parr reaction vessel with 30 mL of counter-pressure water and heated in a convection oven at 150 °C for a week; then the oven was turned off. The reaction product consisted of a pale green solution, indicating dissolved NpO_2^+ and several dark green polyhedral crystals of compound **1** (0.2−0.5 mm in length).

Synthesis of $Na(NpO_2)(SeO_3)(H_2O)$ (2). A total of 0.215 mL of a 0.116 M Np(V) stock solution (in 1 M HCl), 0.102 mL of a 3.88 M H_2SeO_4 acid (Aldrich, 99.95%), and 0.785 mL of distilled H_2O were added to a 7 mL Teflon cup. The pH of the resulting solution was adjusted to 3.4 using a 2 M NaOH (Fisher, 98.5%) solution. The Teflon cup was left open inside of a fume hood, allowing evaporation of most of the water, and then was closed tightly with a screw-top lid. After three months, the solution was completely dry, resulting in a white salt matrix, a green aggregate, and a large number of green plates of compound **2**. The yield of compound **2** is about 10% based on Np from a visual inspection.

Structure Determinations. Single-crystal X-ray diffraction data for $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (**1**) and $Na(NpO_2)(SeO_3)(H_2O)$ (**2**) were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K on a Bruker APEX2 diffractometer.[21] The crystal-to-detector distance was 5.106 cm. Data were collected by a scan of 0.3° in ω in groups of 600 frames at φ settings of 0°, 90°, 180°, and 270°. The exposure time was 20 s/frame for compound **1** and 50 s/frame for compound **2**. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2.[21] Face-indexed absorption corrections as well as incident beam and decay corrections were performed with the use of the program SADABS.[22] The structures were solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL.[23] Hydrogen atoms could not be identified from the difference Fourier maps with high confidence. Each final refinement included anisotropic displacement parameters for all non-hydrogen atoms. In the structural refinements of compound **2**, two large residual peaks (~12 electrons each) were found that are approximately 0.8 Å from the Np atom. Face-indexed absorption corrections did not help. Numerous crystals have been tried, and all of them have various degrees of twinning problems, which is a possible reason for the presence of these two residual peaks. For example, multiple orientation matrices for the current data sets were detected utilizing the program CELLNOW,[24] with 70% of the reflections belonging to the first domain and less than 10% for each of the remaining domains. Separation of component reflections was not attempted.

The program STRUCTURE TIDY[25] was used to standardize the positional parameters. Additional experimental details are given in Table 1 and in the Supporting Information.

■ RESULTS

Syntheses. Single crystals of $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (**1**) and $Na(NpO_2)(SeO_3)(H_2O)$ (**2**) were obtained as a result of the reduction of selenate to selenite in acidic aqueous solutions. Similar behavior has been observed in several other reported reactions, including the syntheses of $Th(SeO_3)_2$[26] and $Ag_4(Mo_2O_5)(SeO_4)_2(SeO_3)$[27] from H_2SeO_4.[28−30] Selenic acid is known to be less stable than sulfuric acid, and it evolves oxygen when heated above ~200 °C. Thermal decomposition of selenate salts has been used to prepare selenite compounds.[31,32] Selenate might slowly decompose to selenite during the reaction that forms compound **1** at 150 °C. However, this is not likely to occur during the synthesis of compound **2**, as the reaction took place at room temperature. Alternatively, selenic acid is a strong oxidizing agent with $E° = 1.15$ V, which is comparable to the value of water, $E° = 1.229$ V. Under these acidic conditions, selenic acid might be able to oxidize water to yield selenite anions. In any case, because metal selenites are much less soluble

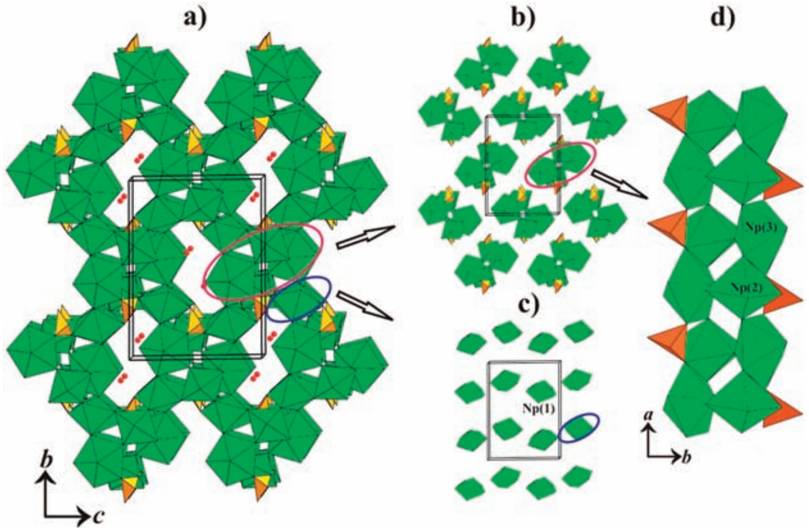


Figure 1. (a) A view of the three-dimensional channel structure of $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ down the [100] direction with a double chain of neptunyl(V) and selenite polydedra in a red circle and isolated neptunyl(V) polydedra in a blue circle. Red balls are oxygen atoms of water molecules. (b) A separated view of double chains of neptunyl(V) and selenite polydedra. (c) A separated view of isolated neptunyl(V) pentagonal bipyramids. (d) A depiction of one double chain of neptunyl(V) pentagonal bipyramids (green) decorated by selenite trigonal pyramids (orange).

than selenates, their formation would act to drive any solution equilibrium to crystallize the selenites.

Structures. $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (**1**) crystallizes in the monoclinic space group $P2_1/c$. As shown in Figure 1a, compound **1** adopts a complex three-dimensional framework of neptunyl(V) pentagonal bipyramids decorated by selenite trigonal pyramids with one-dimensional open channels along the [100] direction. Uncoordinated water molecules are trapped inside these channels through hydrogen bonding interactions. There are certainly several different ways to describe the network of neptunyl and selenite polyhedra in compound **1**. In order to better compare to a related architecture found in $(NpO_2)_2(SeO_4)(H_2O)$[15] (see below), its structure can be divided into two components, double chains of $Np(2)O_7$, $Np(3)O_7$, and SeO_3 polyhedra (Figure 1b) and isolated $Np(1)O_7$ pentagonal bipyramids (Figure 1c). An individual double chain along the [100] direction is shown in Figure 1d, which is further connected by those isolated $Np(1)O_7$ polyhedra in the *bc* planes to form the channel structure (Figure 1a). The local coordination environments for Np(1), Np(2), Np(3), and Se(1) atoms are shown in Figure 2. All Np atoms are bonded to two O atoms in a nearly linear fashion to form neptunyl (NpO_2^+) cations. The $Np-O_N$ distances and O_N-Np-O_N angles (O_N = neptunyl oxygen) range from 1.855(6) to 1.880(6) Å and 177.3(3) to 178.5(3)°, respectively (Table 2). Each NpO_2^+ unit is further coordinated by five O atoms in the equatorial plane to form a pentagonal bipyramid: for $Np(1)O_2^+$, as shown in Figure 2a, they are $O_N(7)$ ($Np(3)O_2^+$), O(12) (OH^-), O(2) and O(6) (SeO_3^{2-}), and O(8) (H_2O) atoms; for $Np(2)O_2^+$ (Figure 2b), they are $O_N(4)$ and $O_N(5)$ ($Np(1)O_2^+$), $O_N(11)$ ($Np(3)O_2^+$), O(9) (SeO_3^{2-}), and O(1) (H_2O) atoms; for $Np(3)O_2^+$ (Figure 2c), they are $O_N(3)$ and $O_N(10)$ ($Np(2)O_2^+$), O(12) (OH^-), and O(2) and O(9) (SeO_3^{2-}) atoms. The $Np-O_E$ (O_E = equatorial oxygen) distances are in the range of 2.317(6)−2.595(8) Å. Each SeO_3^{2-} trigonal pyramid is bound to two $Np(1)O_2^+$, one $Np(2)O_2^+$, and two $Np(3)O_2^+$ cations (Figure 2d). Se−O distances within the SeO_3^{2-} anion are 1.699(6), 1.704(6), and 1.717(6) Å with O−Se−O angles of 100.0(3), 101.9(3), and 102.3(3)°. As stated earlier, all hydrogen atoms for the hydroxide anion and water molecules could not be determined from X-ray diffraction experiments. $O(12)H^-$ anion bridges a $Np(1)O_2^+$ and a $Np(3)O_2^+$ cation with Np(1)−O(12) and Np(3)−O(12) distances of 2.317(6) and 2.328(6) Å, respectively. All three water molecules reside in the channels created by neptunyl cations. $H_2O(1)$ coordinates to a $Np(2)O_2^+$ cation, and $H_2O(8)$ coordinates to a $Np(1)O_2^+$ cation with Np(2)−O(1) and Np(1)−O(8) distances of 2.519(6) and 2.595(8) Å, respectively. Uncoordinated $H_2O(13)$ possesses several potential hydrogen bonding interactions with neighboring oxygen atoms with O(13)···O distances of 2.80(1) for O(1), 2.95(1) for O(8), 2.96(1) for $O_N(10)$, and 2.85(1) Å for O(12), respectively.

As shown in Figures 1 and 2, three nonequivalent NpO_2^+ cations in compound **1** bind to each other through CCIs within the three-dimensional network, and their connectivities with neighboring units are very different. Each $Np(1)O_2^+$ cation acts as a center coordinated by one $Np(3)O_2^+$ unit and also as a ligand binds to two $Np(2)O_2^+$ centers. Each $Np(2)O_2^+$ cation acts as a center coordinated by two $Np(1)O_2^+$ and one $Np(3)O_2^+$ unit and as a ligand binds to two $Np(3)O_2^+$ centers. Each $Np(3)O_2^+$ cation acts as a center coordinated by two $Np(2)O_2^+$cations and as a ligand binds to one $Np(1)O_2^+$ and one $Np(2)O_2^+$ center. Therefore each $Np(1)O_2^+$, $Np(2)O_2^+$, and $Np(3)O_2^+$ cation is involved in three, five, and four CCIs with other units, respectively. To our knowledge, this is the first example of a neptunyl(V) cation participating in five CCIs with other actinyl cations. In additional to the CC bond between a $Np(2)O_2^+$ and a $Np(3)O_2^+$ cation involving the $O_N(10)$ atom, the two Np atoms also share an equatorial O(9) atom to form a dimer (Figure 2b). Similar pairs of neptunyl moieties have been observed in the structures of $Na_2[(NpO_2)_2(MoO_4)_2(H_2O)] \cdot H_2O$[33] and $(NpO_2)_2(SeO_4)(H_2O)$.[15] The metal distance within the dimer in compound **1** is 3.7430(5) Å, which is between the value of 3.727 and 3.8569(4) Å found in $Na_2[(NpO_2)_2(MoO_4)_2(H_2O)] \cdot H_2O$ and $(NpO_2)_2(SeO_4)(H_2O)$, respectively.[15,33] This progression of bond distances correlates

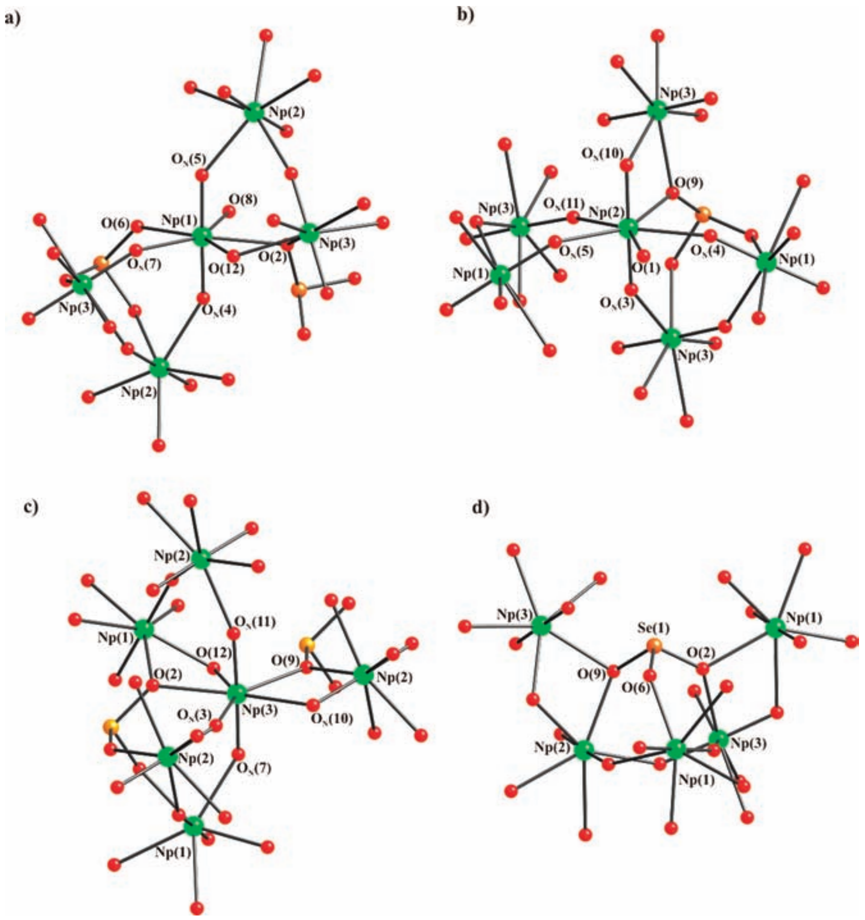


Figure 2. An illustration of the coordination environments for Np(1) (a), Np(2) (b), Np(3) (c), and Se(1) (d) atoms in $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$. O_N = neptunyl oxygen.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$

$Np(1)-O_N(4)$	1.868(6)	$Np(3)-O_N(10)$	2.567(6)
$Np(1)-O_N(5)$	1.862(6)	$Np(3)-O(12)$	2.328(6)
$Np(1)-O(2)$	2.508(6)	$Se(1)-O(2)$	1.717(6)
$Np(1)-O(6)$	2.375(6)	$Se(1)-O(6)$	1.699(6)
$Np(1)-O_N(7)$	2.452(6)	$Se(1)-O(9)$	1.704(6)
$Np(1)-O(8)$	2.595(8)	$Np(1)-Np(2)$	4.0076(6)
$Np(1)-O(12)$	2.317(6)	$Np(1)-Np(2)$	4.1020(6)
$Np(2)-O_N(3)$	1.859(6)	$Np(1)-Np(3)$	3.8475(6)
$Np(2)-O_N(10)$	1.880(6)	$Np(1)-Np(3)$	4.0645(5)
$Np(2)-O(1)$	2.519(6)	$Np(2)-Np(3)$	3.7430(5)
$Np(2)-O_N(4)$	2.419(6)	$Np(2)-Np(3)$	4.0355(5)
$Np(2)-O_N(5)$	2.402(6)	$Np(2)-Np(3)$	4.1663(5)
$Np(2)-O(9)$	2.380(6)	$O_N(4)-Np(1)-O_N(5)$	178.5(3)
$Np(2)-O_N(11)$	2.386(6)	$O_N(3)-Np(2)-O_N(10)$	177.3(3)
$Np(3)-O_N(7)$	1.857(6)	$O_N(7)-Np(3)-O_N(11)$	177.8(3)
$Np(3)-O_N(11)$	1.855(6)	$O_E(9)-Np(3)-O_N(10)$	78.0(2)
$Np(3)-O(2)$	2.461(6)	$O(2)-Se(1)-O(6)$	102.3(3)
$Np(3)-O_N(3)$	2.423(6)	$O(2)-Se(1)-O(9)$	100.0(3)
$Np(3)-O(9)$	2.459(6)	$O(6)-Se(1)-O(9)$	101.9(3)

directly with the deviation of O_E from the plane formed by the equatorial ligands of one of the Np atoms involved in the CCI, specifically $Na_2[(NpO_2)_2(MoO_4)_2(H_2O)] \cdot H_2O$ < compound **1** < $(NpO_2)_2(SeO_4)(H_2O)$.[15,33] For example, the $O_E(9)-Np(2)-O_N(10)$ angle in compound **1** is only 78.0(2)°, compared to the corresponding values of 80.1 and 70.5(2)° found in $Na_2[(NpO_2)_2(MoO_4)_2(H_2O)] \cdot H_2O$ and $(NpO_2)_2(SeO_4)(H_2O)$, respectively.[15,33] A $Np(1)O_2^+$ and a $Np(3)O_2^+$ cation share an equatorial edge comprised of O(2) and O(12) to form a different type of dimer. These two neptunyl units are further bridged by a $Np(2)O_2^+$ cation through two CCIs (Figure 2a). As a result, the distance between Np(1) and Np(3) within the dimer is only 3.8475(6) Å, considerably shorter than a normal distance of 4.0−4.2 Å for equatorial edge-sharing neptunyl(V) pentagonal pyramids.[2] The Np−Np distances between two corner-sharing neptunyl polyhedra range from 4.0076(6) to 4.1663(5) Å, comparable to other reported Np(V)−Np(V) distances in CCI coordination units.[5]

A similar double chain of neptunyl(V) pentagonal bipyramids in compound **1** has been found in $(NpO_2)_2(SeO_4)(H_2O)$,[15] within which the chain is decorated by selenate tetrahedra. Compared to the $Np(2)O_7$ polyhedron in compound **1**, the corresponding $Np(1)O_7$ pentagonal bipyramid in the structure of $(NpO_2)_2(SeO_4)(H_2O)$ is much more distorted. Each double chain of neptunyl polydedra in $(NpO_2)_2(SeO_4)(H_2O)$ connects to four identical neighbors by corner-sharing to form a three-dimensional structure, while double chains in compound **1** are linked together by additional isolated neptunyl(V) polyhedra to

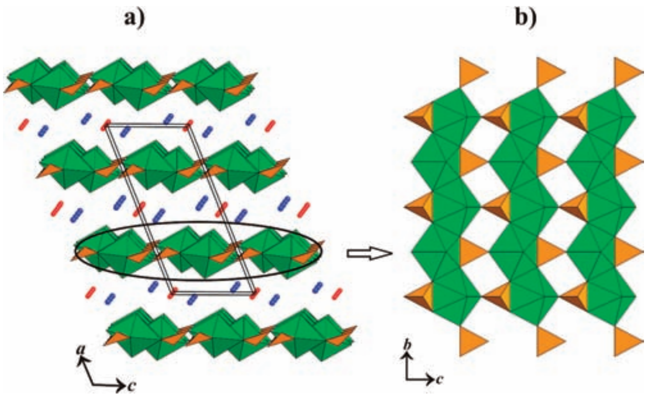


Figure 3. (a) The two-dimensional structure of $Na(NpO_2)(SeO_3)(H_2O)$ down the [010] direction including neptunyl(V) and selenite polydedra layers (circled) and interstitial Na^+ cations (blue ball) and water molecules (red ball). (b) A depiction of a uranophane-type sheet consisting of edge-sharing neptunyl(V) pentagonal bipyramidal chains (green) connected by selenite trigonal pyramids (orange).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $Na(NpO_2)(SeO_3)(H_2O)$

Na(1)−O(3)	2.34(1)	Se(1)−O(1) × 2	1.695(6)
Na(1)−O(4)	2.30(1)	Se(1)−O(3)	1.683(8)
Na(1)−O(4)	2.52(1)	Np(1)−Np(1)	4.103(1)
Na(1)−O(5) × 2	2.355(7)	O(2)−Np(1)−O(4)	176.1(4)
Np(1)−O(2)	1.82(1)	O(1)−Se(1)−O(1)	94.5(4)
Np(1)−O(4)	1.829(9)	O(1)−Se(1)−O(3) × 2	102.7(3)
Np(1)−O(1) × 2	2.412(6)		
Np(1)−O(1) × 2	2.531(6)		
Np(1)−O(3)	2.398(8)		

form a channel structure (Figure 1a). Consequently, the overall structure of $(NpO_2)_2(SeO_4)(H_2O)$ is more condensed than that of compound **1**, as exemplified by their densities at 100(2) K, 6.135 g/cm^3 for the former and 5.786 g/cm^3 for the latter compound.[15] The presence of nonbonding lone-pair electrons on Se(IV) together with waters in compound **1** are partially responsible for the occurrence of open channels.

$Na(NpO_2)(SeO_3)(H_2O)$ (**2**) crystallizes in the monoclinic space group $C2/m$. As shown in Figure 3, the structure of compound **2** consists of uranophane-type layers of $[(NpO_2)(SeO_3)]^-$ in the *bc* plane, which are separated by Na^+ cations and water molecules along the *a* axis.[3,34] A single $[(NpO_2)(SeO_3)]^-$ layer is presented in Figure 3b. The Np atom is bonded to two O atoms in a nearly linear fashion to form a NpO_2^+ cation, which is further coordinated by three monodentate and one bidentate SeO_3^{2-} anions in the equatorial plane in a pentagonal bipyramidal geometry. Each neptunyl polyhedron shares equatorial edges along the *b* axis to form a single chain that is further connected by selenite trigonal pyramids along the *c* axis to form a single layers of $[(NpO_2)(SeO_3)]^-$. The Np−O distances within the NpO_2^+ unit are 1.82(1) and 1.829(9) Å, and the O−Np−O angle is 176.1(4)° (Table 3). The equatorial Np−O distances range from 2.398(8) to 2.531(6) Å. Each SeO_3^{2-} anion is bound to four NpO_2^+ cations with Se−O distances of 1.683(8) and 1.695(6) Å and O−Se−O angles of 94.5(4) and 102.7(3)°. The interstitial Na^+ cation is surrounded by five O atoms from NpO_2^+, SeO_3^{2-}, and H_2O units with Na−O distances ranging from 2.30(1) to 2.52(1) Å. Each $H_2O(5)$ molecule coordinates to two Na^+ cations and is also involved in two potential hydrogen bonding interactions with neighboring O(2) atoms with O(5)···O(2) distances of 2.82(1) Å.

■ DISCUSSION

Both $(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$ (**1**) and $Na(NpO_2)(SeO_3)(H_2O)$ (**2**) adopt centrosymmetric structures despite the presence of a lone pair of electrons on the selenite anions. This is consistent with the observation that actinyl cations tend to sit on, or be related by, inversion centers. In the present two cases, every atom is related by an inversion center. All of the selenite group's electron lone pairs point to the cavities created by neptunyl(V) polyhedra.

As stated earlier, CCIs are more prevalent in actinyl(V) compounds than in actinyl(VI) phases, a result of the enhanced bonding requirements of actinyl(V) oxygen atoms. However as demonstrated by compound **2** not all neptunyl(V) structures contain CCIs, while several uranyl(VI) phases do.[2,3,5] Clearly, synthetic conditions and lattice free energies, both of which can be influenced by the presence of other cations and anions, add to the electronic stabilization afforded by the CCI. It is noteworthy that CCIs occur in all reported inorganic neptunyl(V) phases that include no additional cations, as exemplified by Np_2O_5,[9] $(NpO_2)(IO_3)$,[18] $(NpO_2)Cl(H_2O)$,[35] $(NpO_2)(ClO_4)(H_2O)_4$,[36] $(NpO_2)_2(NO_3)_2(H_2O)_5$,[37] $(NpO_2)_2(QO_4)(H_2O)_n$ (Q = S, Se; n = 1, 2, 4, 6),[15,38−43] and compound **1**. This is clearly not the case for actinyl(VI) compounds. For example, $(NpO_2)(IO_3)_2(H_2O)$[44] and $(NpO_2)_2(SO_4)_2(H_2SO_4)(H_2O)_4$[45] contain no CCIs. These behaviors can be explained through the aforementioned rationale; without other cations, the neptunyl(V) oxo groups turn to neighboring AnO_2^+ units to fulfill their bonding requirements. In addition, most of the compounds with CCIs, including several uranyl(VI) phases, have a relatively low ratio of anion ligands to actinyl cations (≤1:1), such that CCIs are invoked to complete the actinyl cation's coordination environment.[2,3,5] In this regard, actinyl(V) compounds become statistically more favored to have CCIs than actinyl(VI) phases, because a monovalent AnO_2^+ cation requires fewer anions for charge balancing than does a divalent AnO_2^{2+}. These two hypotheses are consistent with the structures reported for the compounds discussed herein. Compound **1** does not contain other cations and has a low anion/cation ratio, while compound **2** contains Na^+ cations and has a relative higher ratio of SeO_3^{2-}/NpO_2^+.

The three-dimensional structure of compound **1** is a direct consequence of CCIs between NpO_2^+ cations. Each $Np(1)O_2^+$, $Np(2)O_2^+$, and $Np(3)O_2^+$ cation participates in three, five, and four CCIs, respectively, and they also share additional equatorial vertices with each other. The connectivity pattern between these cations is different from any other reported neptunyl(V) compounds containing CCI networks, where each NpO_2^+ cation forms only one to four or six CC bonds.[2,3,5,9,46]

The structure of compound **2** is constructed by uranophane-type layers, which are the basis for a large number of uranyl(VI) compounds and minerals, and two neptunyl(V) phases, $Ba(NpO_2)(PO_4)(H_2O)$[47] and $Cs(NpO_2)(CrO_4)(H_2O)$.[3,48] A uranophane-type layer consists of edge-sharing actinyl pentagonal bipyramidal chains connected by various oxoanions including silicate, phosphate, arsenate, borate, and chromate, which are charge-balanced by low-valent counter-cations between the layers. Surprisingly, the uranophane-type topology has not been found in any actinyl selenite compounds in spite of their recent prominence.[2,3] Most uranyl(VI) selenites have a selenite anion and uranyl cation ratio of 2:1. As a result, their structures contain less direct connectivities between UO_2^{2+} units compared to those with uranphane layers where the ratio is 1:1, assuming a full occupancy of cation sites by actinides within the layer.[3] $(UO_2)(SeO_3)$ has a suitable ratio; however, its structure contains edge-sharing uranyl hexagonal bipyramidal chains.[49]

Both ^{237}Np and ^{79}Se are long-lived fission products, and their dominant aqueous species NpO_2^+ and SeO_3^{2-} are mobile in oxidizing geological environments.[50,51] Their incorporation into spent fuel (UO_2) alteration products could significantly reduce their mobility and transport from a geological repository.[51−54] Uranophane is the most common uranyl silicate under oxidizing conditions, and it has been identified as one of the alternation products of spent fuel.[52,53] Incorporation of Np(V) into a powder sample of synthetic uranophane ($Ca(UO_2)(SiO_3OH)_2(H_2O)_5$) has been reported without an illustration of the charge-balance mechanism for the substitution of NpO_2^+ for UO_2^{2+}.[54] Possible substitution of SeO_3^{2-} for SiO_3OH^- in α-uranophane has been proposed from the analysis and comparison of known uranyl structures.[51] The current study on compound **2** provides direct structural evidence for the potential coupled substitution of $NpO_2^+ + SeO_3^{2-}$ for $UO_2^{2+} + SiO_3OH^-$ in uranophane phases, which could serve as an optimal mechanism to immobilize both ^{237}Np and ^{79}Se at the same time.

CONCLUSIONS

Two new neptunyl(V) selenites, $(NpO_2)_3(OH)(SeO_3)(H_2O)_2\cdot H_2O$ (**1**) and $Na(NpO_2)(SeO_3)(H_2O)$ (**2**), have been prepared by reactions of neptunyl(V) and selenate in aqueous solutions. Compound **1** crystallizes in a novel three-dimensional channel structure due to the CCIs between NpO_2^+ cations, while compound **2** adopts a well-known two-dimensional uranophane-type layered structure. CCIs play a pivotal role in determining the lattice dimensionality in the titled compounds. The nonbonding, lone-pair electrons on selenite may help to create the cavity in which they can reside, although the structures are not polar in these two cases. Compound **1** contains the first example of a NpO_2^+ cation joining five CC bonds with other neptunyl(V) units, which is very encouraging. More new connectivities involving CCIs await discoveries that will further enrich the structural chemistry of neptunyl(V) compounds. Compound **2** is the first actinyl selenite to adopt a uranophane-type structure, which instills further confidence in the possible incorporation of NpO_2^+ and SeO_3^{2-} into uranophane compounds. Additional experimental studies are required to determine the actual charge-balance mechanism that facilitates their incorporation.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic files in CIF format for $(NpO_2)_3(OH)(SeO_3)(H_2O)_2\cdot H_2O$ and $Na(NpO_2)(SeO_3)(H_2O)$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: +1 630 252 4364. E-mail: ls@anl.gov.

ACKNOWLEDGMENT

This work is supported by the U.S. DOE, OBES, Chemical Sciences, Geosciences, & Biosciences, under contract DE-AC02-06CH11357.

REFERENCES

(1) Yoshida, Z.; Johnson, S. G.; Kimura, T.; Krsul, J. R.; Neptunium. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Katz, J. J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Vol. 2, pp 699−812.

(2) Forbes, T. Z.; Wallace, C.; Burns, P. C. *Can. Mineral.* **2008**, *46*, 1623–1645.

(3) Burns, P. C. *Can. Mineral.* **2005**, *43*, 1839–1894.

(4) Sullivan, J. C.; Hindman, J. C.; Zielen, A. J. *J. Am. Chem. Soc.* **1961**, *83*, 3373–3378.

(5) Krot, N. N.; Grigoriev, M. S. *Russ. Chem. Rev.* **2004**, *73*, 89–100.

(6) Skanthakumar, S.; Antonio, M. R.; Soderholm, L. *Inorg. Chem.* **2008**, *47*, 4591–4595.

(7) Almond, P. M.; Skanthakumar, S.; Soderholm, L.; Burns, P. C. *Chem. Mater.* **2007**, *19*, 280–285.

(8) Forbes, T. Z.; Burns, P. C.; Soderholm, L.; Skanthakumar, S. *Chem. Mater.* **2006**, *18*, 1643–1649.

(9) Forbes, T. Z.; Burns, P. C.; Skanthakumar, S.; Soderholm, L. *J. Am. Chem. Soc.* **2007**, *129*, 2760–2761.

(10) Nakamoto, T.; Nakada, M.; Nakamura, A.; Haga, Y.; Onuki, Y. *Solid State Commun.* **1999**, *109*, 77–81.

(11) Nakamoto, T.; Nakada, M.; Nakamura, A. *J. Nucl. Sci. Technol.* **2002**, No. Suppl. 3, 102–105.

(12) Jobiliong, E.; Oshima, Y.; Brooks, J. S.; Albrecht-Schmitt, T. E. *Solid State Commun.* **2004**, *132*, 337–342.

(13) Nakamura, A.; Nakada, M.; Nakamoto, T.; Kitazawa, T.; Takeda, M. *J. Alloy. Compd.* **2007**, *444*, 621–633.

(14) Forbes, T. Z.; Burns, P. C.; Soderholm, L.; Skanthakumar, S. *Mater. Res. Soc. Symp. Proc.* **2006**, *893*, 375–380.

(15) Jin, G. B.; Skanthakumar, S.; Soderholm, L. *Inorg. Chem.* **2011**, *50*, 5203–5214.

(16) Krivovichev, S. V. *Eur. J. Inorg. Chem.* **2010**, 2594–2603.

(17) Almond, P. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2002**, *41*, 1177–1183.

(18) Albrecht-Schmitt, T. E.; Almond, P. M.; Sykora, R. E. *Inorg. Chem.* **2003**, *42*, 3788–3795.

(19) Almond, P. M.; Sykora, R. E.; Skanthakumar, S.; Soderholm, L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2004**, *43*, 958–963.

(20) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10*, 2753–2769.

(21) *APEX2*, version 2009.5-1; *SAINT*, version 7.34a; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2009.

(22) *SMART*, version 5.054; *SAINT-Plus*, version 6.45a; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2003.

(23) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

(24) Sheldrick, G. M. *CELLNOW*, **2008**, University of Gottingen, Germany.

(25) Gelato, L. M.; Parthe, E. *J. Appl. Crystallogr.* **1987**, *20*, 139–143.

(26) Sullens, T. A.; Almond, P. M.; Byrd, J. A.; Beitz, J. V.; Bray, T. H.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2006**, *179*, 1192–1201.

(27) Ling, J.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2007**, *180*, 1601–1607.

(28) Pasha, I.; Choudhury, A.; Rao, C. N. R. *Inorg. Chem.* **2003**, *42*, 409–415.

(29) Almond, P. M.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2003**, *42*, 5693–5698.

(30) Wickleder, M. S.; Buchner, O.; Wickleder, C.; el Sheik, S.; Brunklaus, G.; Eckert, H. *Inorg. Chem.* **2004**, *43*, 5860–5864.

(31) Havlicek, D.; Micka, Z.; Boublikova, R. *Collect. Czech. Chem. Commun.* **1995**, *60*, 969–976.

(32) Krugermann, I.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 147–151.

(33) Grigorev, M. S.; Baturin, N. A.; Fedoseev, A. M.; Budantseva, N. A. *Koord. Khim.* **1994**, *20*, 552–556.

(34) Barinova, A. V.; Rastsvetaeva, R. K.; Sidorenko, G. A.; Pushcharovskii, D. Y. *Dokl. Chem.* **2001**, *378*, 122–124.

(35) Grigorev, M. S.; Bessonov, A. A.; Krot, N. N.; Yanovskii, A. I.; Struchkov, Y. T. *Radiochemistry* **1993**, *35*, 382–387.

(36) Grigorev, M. S.; Baturin, N. A.; Bessonov, A. A.; Krot, N. N. *Radiochemistry* **1995**, *37*, 12–14.

(37) Grigorev, M. S.; Charushnikova, I. A.; Krot, N. N.; Yanovskii, A. I.; Struchkov, Y. T. *Zh. Neorg. Khim.* **1994**, *39*, 179–183.

(38) Budantseva, N. A.; Fedoseev, A. M.; Grigorev, M. S.; Potemkina, T. I.; Afonaseva, T. V.; Krot, N. N. *Sov. Radiochem.* **1988**, *30*, 578–581.

(39) Grigoriev, M. S.; Ianovskii, A. I.; Fedoseev, A. M.; Budantseva, N. A.; Struchkov, I. T.; Krot, N. N.; Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **1988**, *300*, 618–622.

(40) Bessonov, A. A.; Budantseva, N. A.; Fedoseev, A. M.; Perminov, V. P.; Afonaseva, T. V.; Krot, N. N. *Sov. Radiochem.* **1990**, *32*, 447–453.

(41) Grigorev, M. S.; Baturin, N. A.; Budantseva, N. A.; Fedoseev, A. M. *Radiochemistry* **1993**, *35*, 151–156.

(42) Charushnikova, I. A.; Krot, N. N.; Polyakova, I. N. *Crystallogr. Rep.* **2006**, *51*, 201–204.

(43) Forbes, T. Z.; Burns, P. C. *J. Solid State Chem.* **2009**, *182*, 43–48.

(44) Bean, A. C.; Scott, B. L.; Albrecht-Schmitt, T. E.; Runde, W. *Inorg. Chem.* **2003**, *42*, 5632–5636.

(45) Alcock, N. W.; Roberts, M. M.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1982**, 869–873.

(46) Wang, S.; Alekseev, E. V.; Depmeier, W.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2011**, *50*, 4692–4694.

(47) Forbes, T. Z.; Burns, P. C. *Am. Mineral.* **2006**, *91*, 1089–1093.

(48) Grigorev, M. S.; Baturin, N. A.; Fedoseev, A. M.; Budantseva, N. A. *Sov. Radiochem.* **1991**, *33*, 504–511.

(49) Loopstra, B. O.; Brandenburg, N. P. *Acta Crystallogr., Sect. B* **1978**, *34*, 1335–1337.

(50) Kaszuba, J. P.; Runde, W. H. *Environ. Sci. Technol.* **1999**, *33*, 4427–4433.

(51) Chen, F. R.; Burns, P. C.; Ewing, R. C. *J. Nucl. Mater.* **1999**, *275*, 81–94.

(52) Wronkiewicz, D. J.; Bates, J. K.; Wolf, S. F.; Buck, E. C. *J. Nucl. Mater.* **1996**, *238*, 78–95.

(53) Burns, P. C.; Ewing, R. C.; Miller, M. L. *J. Nucl. Mater.* **1997**, *245*, 1–9.

(54) Burns, P. C.; Deely, K. M.; Skanthakumar, S. *Radiochim. Acta* **2004**, *92*, 151–159.