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Structural Variability in Neptunium(V) Oxalate Compounds: Synthesis and Structural Characterization of $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$

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Reaction of a ^{237}Np(V) stock solution in the presence of oxalic acid, calcium chloride, and sodium hydroxide under hydrothermal conditions produces single crystals of a neptunium(V) oxalate, $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$. The structure consists of one-dimensional chains running down the *a* axis and is the first example of a neptunium(V) oxalate compound containing hydroxide anions.

The oxalate ligand is widely used in process and separation schemes for recovery of radioactive elements by oxalate precipitation because of their low solubility in acidic solutions.[1] Whereas much of the focus has been on plutonium reprocessing, studies of the effect of the presence of neptunium have been limited. It has been shown that, because neptunium is a long-lived radionuclide, its existence in radioactive liquid waste can affect the efficiency of the precipitation by oxalate of certain elements in this high-level liquid waste.[2] The existence of neptunium in nuclear waste can lead to concerns of neptunium's environmental impact when interacting with various carboxylic acids, e.g., oxalate.[3,4] Few studies have been conducted to study the complexation species of neptunium and oxalate in the solid state.

The hydrothermal reaction[5] of a ^{237}Np(V) stock solution with $H_2C_2O_4$ and $CaCl_2{\cdot}2H_2O$, using NaOH and HCl to adjust to pH ≈ 12, produces brilliant green hexagonal-shaped crystals. Originally, calcium chloride was added as a reactant because of its presence in oxalate precipitation conditions for reprocessing of plutonium solutions in actual plant conditions. However, neither calcium nor chlorine atoms were found to be incorporated at these reaction conditions. Of the Np(V) oxalate structures known, $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$ is the first compound to incorporate the hydroxide ligand. In synthetic procedures, the actual pH does not have much bearing on the final structural product. For example, there are three compounds containing hydroxide, all produced at different pHs: $Cs[(UO_2)_3Cl_2(IO_3)(OH)O_2]{\cdot}2H_2O$ ($pH \approx 2-3$),[6] $(PuO_2)_2(IO_3)(\mu_2\text{-}OH)_3$ ($pH = 5$),[7] and $Na_4(UO_2)_2(OH)_4(C_2O_4)_2$ ($pH = 8$).[8]

The structure of $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$, characterized by X-ray diffraction,[9] consists of one-dimensional chains of $[NpO_2(C_2O_4)OH]^{2-}$, separated by Na^+ atoms and water molecules, that run down the *a* axis, as shown in Figure 1. The chains are made up of $[NpO_7]$ units, which share edges through hydroxyl oxygen atoms, forming pseudo-dimeric components. This is the first evidence of hydroxide bonding in the neptunium(V) oxalate system. Bridging oxalate

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(5) $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$: $H_2C_2O_4$ (97.0 mg, 0.77 mmol), $CaCl_2{\cdot}2H_2O$ (67.0 mg, 0.46 mmol), 1 mL of NaOH (2.1 M), and 0.7 mL of HCl (0.5 M) were loaded in a 10-mL PTFE-lined autoclave, followed by 100 μL of ^{237}Np(V) stock solution. The autoclave was sealed, doubly contained in two heat-sealed Teflon bags, and placed in box furnace preheated to 100 °C. After 20 h, the furnace was cooled at 13 °C/h to 25 °C. The product consisted of colorless solution of pH 12 over green hexagonal single crystals. CAUTION: Neptunium-237 is a highly radioactive element and standard precautions for handling radioactive materials should be followed.

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(9) Crystal data for $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$: $M = 438.02$, $P2_1/c$, $a = 6.147(5)$ Å, $b = 18.83(1)$ Å, $c = 6.688(5)$ Å, $\beta = 93.00(1)°$, $V = 773.1(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.737$ g/cm^3, μ(Mo Kα) = 135.64 cm^{-1}, $T = -70$ °C, R1 = 0.0500, wR2 = 0.1196. Crystals of $Na_2NpO_2(C_2O_4)OH{\cdot}H_2O$ were mounted in glass capillaries after being coated with epoxy. The capillaries were then coated with clear nail polish as a third form of containment. Triple containment is necessitated by the associated health hazards of working with neptunium. Data were collected on a Bruker P4/CCD/PC X-ray diffractometer using a Bruker LT-2 low-temperature device. 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, initial indexing, and cell refinement were handled using SMART software. Frame integration and final cell parameter calculations were carried out using SAINT software. The data were corrected for absorption using SADABS. The program suite SHELXTL was used for space group determination (XPREP), structure solution (XS), and refinement (XL). The final refinement included anisotropic displacement parameters for all nonhydrogen atoms and a secondary extinction parameter.

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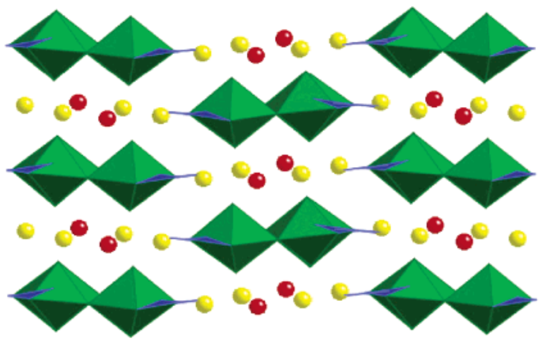

Figure 1. Polyhedral representation of the packing of $Na_2NpO_2(C_2O_4)$-$OH\cdot H_2O$ viewed along the *a* axis. The Na^+ cations (yellow) and water molecules (red) separate the neptunium oxalate chains, shown in green and blue, respectively.

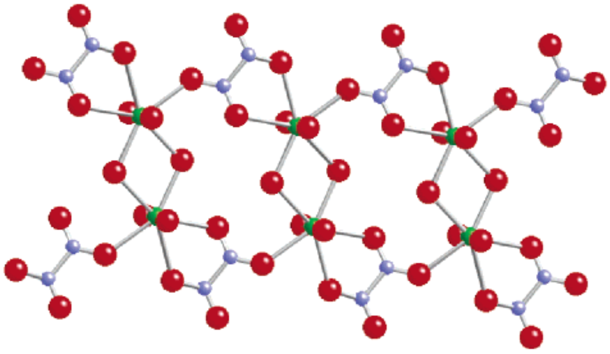

Figure 2. Infinite one-dimensional $[NpO_2(C_2O_4)OH]^{2-}$ chains of $Na_2NpO_2(C_2O_4)OH\cdot H_2O$ made up of edge-sharing neptunium centers through a hydroxide ligand. The pseudo-dimers are bridged by mono- and bidentate oxalate ligands.

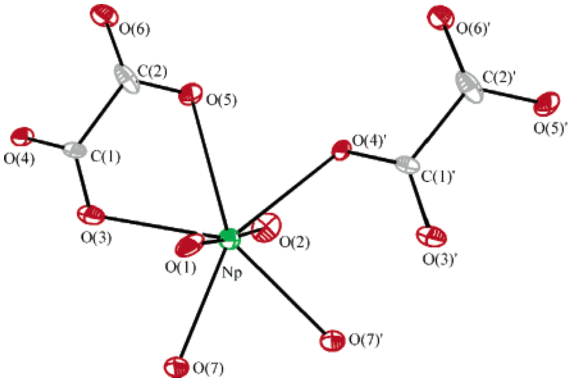

Figure 3. ORTEP depiction (50% ellipsoids) of the pentagonal bipyramidal coordination of the Np center in $Na_2NpO_2(C_2O_4)OH\cdot H_2O$. The *trans*-dioxo cation terminates the coordination down the *c* axis, and oxygen atoms from oxalate and hydroxide complete the equatorial plane.

ligands, demonstrated in Figure 2, connect these dimeric components further. The pentagonal bipyramidal $[NpO_7]$ unit, depicted in Figure 3, is composed of the *trans*-dioxo monocation ($[O{=}Np{=}O]^+$), which sits perpendicular to the five equatorial oxygen atoms. Three of the five oxygen atoms participate as mondodentate and bidentate bridging oxalate anions, while the remaining two oxygen atoms edge-share neptunium polyhedra, completing the equatorial plane.

The *trans*-dioxo monocation bond lengths are 1.85(1) and1.86(1) Å, with a bond angle of 176.6(5)°. These values are in good agreement with other Np(V) compounds[10−12] and are indicative of the oxidation state, +5, for neptunium. The five oxygen atoms surrounding the neptunium center range in bond distance from 2.40(1) to 2.54(1) Å and show a nice trend from decreasing to increasing distance, as the shortest distances belong to the edge-sharing hydroxyl oxygen atoms [O(7)], whereas the longest distances are attributed to the bidentate bridging oxalate anion. The equatorial oxygen bond distances are in good agreement with other neptunium(V) oxalate compounds[10,11,13,14] There are two crystallographically unique carbon atoms, C(1) and C(2), and four oxygen atoms that make up the oxalate ligands. The distance between C(1) and C(2) is 1.58(2) Å, and the distances between the C and O atoms in the oxalate ligand range from 1.23(2) to 1.29(2) Å, all of which agree well with other lanthanide and uranium oxalate compounds.[15−18] The charge balance is attained by two crystallographic unique sodium atoms, Na(1) and Na(2), that separate the chains. Each forms long ionic contacts with neighboring oxygen atoms to generate varying coordination environments. Na(1) is five-coordinate with bond distances ranging from 2.41(1)−2.51(1) Å, whereas Na(2) is five-coordinate with bond distances varying from 2.34(1) to 2.48(1) Å and with a sixth longer distance of 2.76(1) Å, all distances being in good agreement with those of other Na···O-bearing structures.[19−21] The Np···Np interatomic bond distance found in $Na_2NpO_2(C_2O_4)OH\cdot H_2O$ is 3.960(3) Å; the Np···Np distances for neptunium(V) oxalate compounds vary from 4.08 to 6.27 Å.[10,11,13,14] Bond valence sum calculations provide a value of 5.10 for Np in $Na_2NpO_2(C_2O_4)OH\cdot H_2O$.[22−24]

In the past decade, efforts have been made to understand the complexation in the neptunium(V)−oxalate system. There are two previous examples belonging to the 1:1 ($Np/C_2O_4^{2-}$) class, of which our compound, $Na_2NpO_2(C_2O_4)OH\cdot H_2O$, is a member: $NaNpO_2C_2O_4\cdot 3H_2O$[11] and $NH_4NpO_2C_2O_4\cdot nH_2O$.[13] Whereas the latter forms a three-dimensional network, $NaNpO_2C_2O_4\cdot 3H_2O$ forms a one-dimensional chain structure. The neptunium atom is in pentagonal, bipyramidal coordination with four oxygen atoms in the equatorial plane created from two oxalate ligands and a water molecule completing the coordination. In contrast to $Na_2NpO_2(C_2O_4)OH\cdot H_2O$, the

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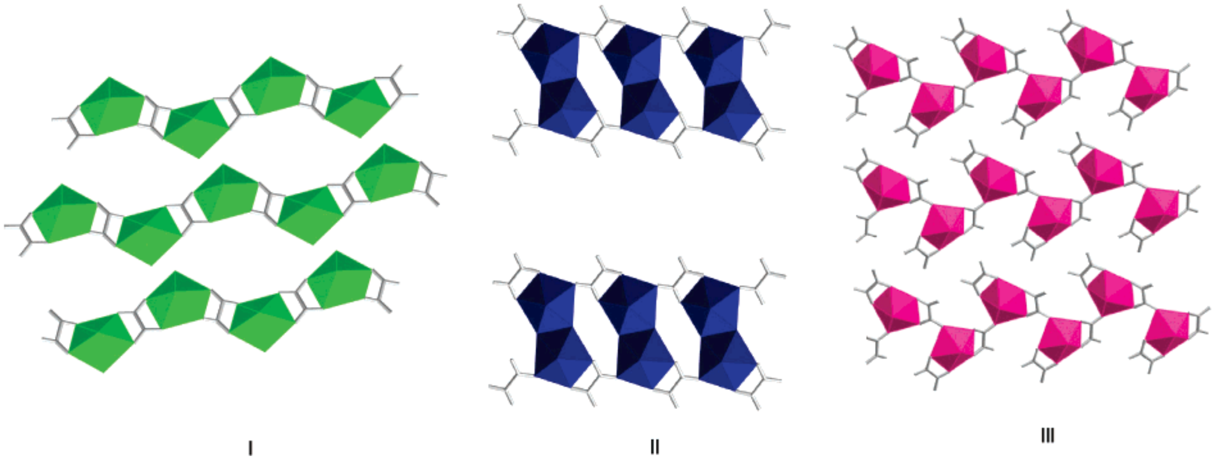

Figure 4. Comparison of three differing one-dimensional structures found in the Np(V)−oxalate system: $NaNpO_2C_2O_4 \cdot 3H_2O$ (**I**), $Na_2NpO_2(C_2O_4)OH \cdot H_2O$ (**II**), and $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot 4H_2O$ (**III**).

neptunium polyhedra are bound only through bridging bidentate oxalate ligands making up the one-dimensional chains. The 1:2 ($Np/C_2O_4^{2-}$) compound, $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot 4H_2O$,[10] is also a chain structure with oxalate coordination more similar to that of our title compound, $Na_2NpO_2(C_2O_4)OH \cdot H_2O$. Although the structure of $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot 4H_2O$ contains two different oxalate anion coordinations, the most important oxalate ligands joining adjacent neptunium atoms are the same bridging motif found in $Na_2NpO_2(C_2O_4)OH \cdot H_2O$, with the oxalate bridging through bidentate and monodentate coordinations from the same oxalate ligand. The inner-sphere coordination of the neptunium atoms in $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot 4H_2O$ is completed by bidentate oxalate anions completing the pentagonal bipyramidal coordination of the neptunium atoms and terminating the chains. Figure 4 provides a comparison of the one-dimensional polyhedral chains found in $NaNpO_2C_2O_4 \cdot 3H_2O$, $Na_2NpO_2(C_2O_4)OH \cdot H_2O$, and $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot 4H_2O$.

Whereas $NaNpO_2C_2O_4 \cdot 3H_2O$ and $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot 4H_2O$ were synthesized from acidic media, $Na_2NpO_2(C_2O_4)OH \cdot H_2O$ is the first neptunium(V) oxalate formed from basic solutions. It is evident that oxalate can precipitate actinide elements in varying pH ranges, and although oxalate has been used in processing liquid, radiological waste for over 50 years, the structural data of the actual products of this process are still unknown.

This work continues to expand the structural knowledge of the transuranic elements and develop a better grasp of the coordination and complexation in the Np(V)−oxalate system. The structure of $Na_2NpO_2(C_2O_4)OH \cdot H_2O$ exposes a new system that could exist by incorporating the hydroxide anion. The binding of hydroxide ligands with neptunium suggests such an affect could play a leading role in environmental and liquid waste speciation. With this first compound in the Np(V)−oxalate system including hydroxide, the wealth of other compounds that could exist in these systems is demonstrated.

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Supporting Information Available: X-ray crystallographic files for $Na_2NpO_2(C_2O_4)OH \cdot H_2O$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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