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Mixed-Valent Neptunium(IV/V) Compound with Cation−Cation-Bound Six-Membered Neptunyl Rings

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Ⓢ *Supporting Information*

ABSTRACT: A new mixed-valent neptunium(IV/V) compound has been synthesized by evaporation of a neptunium(V) acidic solution. The structure of the compound features cation−cation-bound six-membered neptunyl(V) rings. These rings are further connected by Np^{IV} ions through cation−cation interactions (CCIs) into a three-dimensional neptunium cationic open framework. This example illustrates the possibility of isolating neptunyl(V) CCI oligomers in inorganic systems using other cations to compete with Np^V in bonding with the neptunyl oxygen.

Higher-valent actinides exhibit a wide-range of coordination environments, reflecting the flexibility in their electronic structures.[1] Common among the bonding motifs is the dioxo moiety seen from penta- and hexavalent lighter actinides, including $An^{V/VI}$ (An = U−Am). Although the oxo ligand is usually seen as chemically inert, there are examples, notably for $Np^VO_2^+$, where it tends bond to other highly charged metal ions to form cation−cation interactions (CCIs).[2]

The most common CCIs are between NpO_2^+ cations, which have been widely observed in solutions and in roughly half of the reported inorganic neptunyl(V) solid compounds.[2b,c] Such CCIs have a significant impact on the neptunium(V) structural chemistry and the resultant electronic properties. For example, by providing additional linkages between metal centers, CCIs have greatly enriched the structural chemistry of neptunium(V) with diverse metal-ion lattice connectivities in various dimensionalities.[2c] CCI also provides a potential superexchange pathway that can enhance magnetic interactions between Np^V ($5f^2$) ions.[3] With a dominating axial crystal field of NpO_2^+ ions, neptunyl(V) CCI compounds provide an ideal system to study the influence of lattice and spin dimensionalities on the overall magnetic properties. However, our knowledge about the existence and formation of different CCI oligomers is very limited, which are key to revealing the formation of CCIs from solutions to solids and to studying the magnetic interactions between metal centers in low dimensionalities. Only discrete dimer species have been unambiguously identified in inorganic systems, even though the extended CCI networks found in most inorganic neptunyl(V) CCI compounds appear to be built by small CCI units.[2b,4] In contrast, various AnO_2^+ (An = U, Np) CCI oligomers including dimeric, trimeric, and tetrameric complexes have been observed in organic solutions and compounds.[5] Isolation of these discrete polynuclear units has been achieved by using bulky organic ligands to compete with the O_{yl} atom in the coordination of the actinyl center and impose the correct constraints around its equatorial plane. Alternatively, it can be realized by using other cations to compete with the NpO_2^+ centers in the binding of the O_{yl} atom. Our previous studies have demonstrated that Na^+ cations can break down the CCI networks by interacting with the O_{yl} atom.[3e,6] This idea is further exemplified in the mixed-valent neptunium compound $Na_xNp^{IV}(Np^VO_2)_6(OH)_{1+x}Cl_9(H_2O)_{8-x}$ $(0 < x \le 1)$ (**1**) reported herein. Compound **1** contains six-membered NpO_2^+ CCI rings that are terminated by Np^{4+} ions through stronger CCIs to form a three-dimensional (3D) neptunium cationic framework (Figure 1).

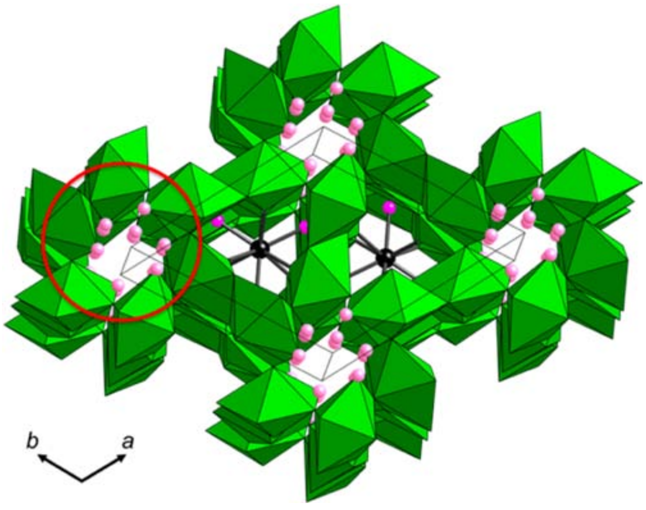

Figure 1. Unit cell of the 3D channel structure of **1** in the [001] direction. Green polyhedra represent $Np^VO_4Cl_3$ pentagonal bipyramids, and black, magenta, and pink balls represent Np^{4+} cations, OH^-/H_2O, and H_2O molecules, respectively. Na^+ ions are omitted for the purpose of clarity. A cation−cation-bound six-membered NpO_2^+ ring is circled in red.

Previous studies have indicated the formation of a CCI dimer or even higher order of neptunyl(V) oligomers in acidic aqueous solutions as $[NpO_2^+]$ increases.[4a] Simple evaporation experiments of neptunium(V) stock solutions were set up to mimic the process to prepare neptunyl(V) CCI compounds, which have resulted in dark-green compound **1**, described herein, and green-phase **2** that eluded structural characterization. Compounds **1**

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and **2** can be reproduced by controlled evaporation using heating laser (see the Supporting Information, SI).

The structure of **1** contains two crystallographically unique Np, two Cl, four O, and one Na sites (Figure 2). The Np(1) atom is bonded to O(1) and O(3) atoms in a nearly linear fashion to form a neptunyl cation with Np−O_{yl} distances of 1.824(9) and 1.862(8) Å and a bond angle of 178.8(4)°, respectively. It is further coordinated by one O_{yl}(1), one O(2) (H_2O), and three Cl atoms in the equatorial plane in a pentagonal-bipyramidal geometry, whereas the Np(2) site is coordinated by six O_{yl}(3) and three O(4) $[(OH)_{1+x}(H_2O)_{2-x}]$ atoms in a tricapped trigonal-prismatic arrangement with Np−O distances of 2.353(8) and 2.46(1) Å, respectively. These results strongly support the oxidation state assignments of Np as 5+ for Np(1) and 4+ for Np(2). For example, bond distances within $Np(1)O_4Cl_3$ polyhedra in **1** are comparable with those found for $Np^V(2)O_4Cl_3$ pentagonal bipyramids in $K_4(NpO_2)_3Cl_7(H_2O)_4$ and $K(NpO_2)_3Cl_4(H_2O)$, where both O_{yl} atoms involve CCIs as well.[7] Empirical bond-valence sum calculations indicate a valence of 4.17 for Np(2) in **1**.[8] It is interesting to note that all ion connectivities observed in **1** fall into the hard−soft acid−base concept,[9] which further supports the chemical formula proposed from the structural studies. For example, all softer Cl^- anions coordinate to softer NpO_2^+ and Na^+ cations.

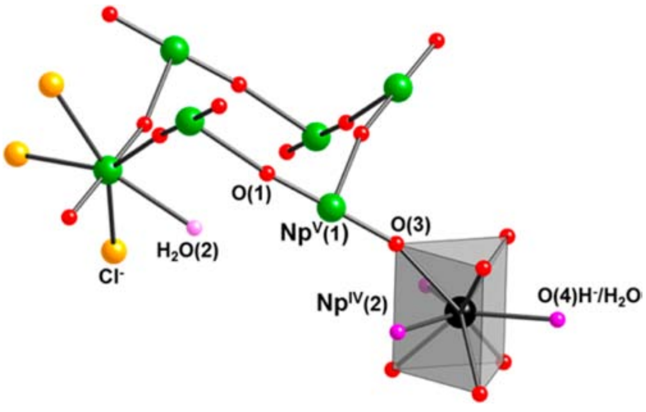

Figure 2. Local coordination environments of $Np^VO_2^+$ and Np^{4+} cations in the structure of **1**.

As shown in Figure 2, each neptunyl cation in **1** involves two CCIs with two identical neighbors acting as a coordinating center and a ligand to form six-membered rings in a chair conformation. They are further bound to Np^{4+} centers through CCIs to build a 3D framework with open channels along the [001] direction in which water resides (Figure 1). The Np(1)−O_{yl}(3) distance [1.862(9) Å] is more elongated than that of Np(1)−O_{yl}(1) [1.824(9) Å], indicating stronger CCIs between $Np(1)O_2^+$ and $Np(2)^{4+}$ cations, which have been observed in two other mixed-valent neptunium(IV/V) compounds.[10] In addition, neptunyl polyhedra are further connected to each other by sharing Cl^- edges or corners between the rings.

Our recent Raman spectroscopy studies have shown that the CCIs can enable both active stretching modes of $O{=}Np^V{=}O_2$ units and shift the stretching bands toward lower frequencies by changing the site symmetry of the neptunyl units and Np−O interactions (see the SI).[3e] These results and previous IR studies have suggested a correlation between the vibrational energies of NpO_2^+ and the character and number of cation−cation bonds involved.[2b] **1** and **2** exhibit several characteristic bands in the Raman spectra within the region attributed to stretching modes of NpO_2^+ units (600−830 cm^{-1}), as presented in Figure 3.

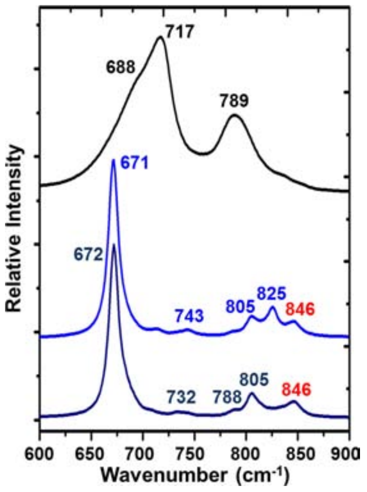

Figure 3. Raman spectra of **1** (black) and **2** (blue and navy).

Molecular site group analysis for the $Np(1)O_2^+$ site in **1** indicates that both symmetric (ν_1) and asymmetric (ν_3) stretching should be Raman-active, which can assign two of the three main peaks occurring at 688, 717, and 789 cm^{-1} (see the SI). The origin of the third peak and the small bump around 830 cm^{-1} is not clear. Although two IR absorption peaks at 782 and 850 cm^{-1} for $Np^{IV}(OH)_2(SO_4)$ were assigned as Np−O−H bending modes, which would suggest a Np−O−H vibrational nature for the 789 and 830 cm^{-1} bands in **1**.[11] Similar behavior has been observed in $Na(NpO_2)(OH)_2$,[3b] where three bands at 635, 701, and 752 cm^{-1} were observed for one crystallographically unique NpO_2^+ cation (see the SI). It is worth noting that the Np−O_{yl} distances and the stretching frequencies found in **1** do not fit the trend for other CCI compounds, where the longer distances lead to lower frequencies (see the SI). Depending on the measured samples, **2** displays two similar Raman spectra. Most of the vibrational bands observed in the Raman spectra of **2** agree with those found for other neptunium(V) compounds with CCIs (see the SI), whereas the 846 cm^{-1} band fits into the range 802−863 cm^{-1} observed for ν_1 of the neptunyl(VI) units.[12] For example, the symmetric stretching of the isolated NpO_2^{2+} ion in an aqueous solution by oxidation of the same neptunium(V) stock solution occurs at 855 cm^{-1} (see the SI). Although these peak assignments based on a small database are not conclusive without the structural data, these Raman results suggest that **2** is a mixture of at least two phases containing neptunyl(V) CCI networks or Np^{VI} ions.

Two mixed-valent neptunium(IV/V) compounds have been reported that were obtained by the partial oxidation of Np^{IV} to Np^V.[10] Because the title reaction started with a neptunium(V) solution, the mixed valency found in **1** was generated by a different route. Considering an oxic solution condition, disproportionation of neptunium(V) is a much more probable mechanism than the reduction route. Disproportionation of neptunium(V) was expected to be highly favored during evaporation when the acidity of the solution and $[NpO_2^+]$ increase until saturation. In fact, neptunium(V) disproportionation reactions at high concentrations of various acids have been well documented in the literature.[13] Further evidence lies in the formation of neptunyl(V) CCI dimers during evaporation (see the SI). An^{V} CCI dimers have been considered to be involved in disproportionation.[14] It is generally believed that the disproportionation reaction involves pronation of the O_{yl} atom to a hydroxide under acidic conditions.[14b] The occurrence of the $[Np^{IV}(OH)_{1+x}]$ moiety in compound **1** is consistent with the hypothesis. Stabilizing hydroxides seems to be implausible at first glance during evaporation of 1 M HCl. However, tetravalent actinide hydroxides (An^{IV}), including Np^{IV} synthesized from acidic conditions, have been previously reported mainly because of their high stability constants.[11,15] For example, log β_1^0 = 14.55(0.20) for $NpOH^{3+}$ in the following reaction:[16]

$$Np^{4+} + OH^{-} \rightleftharpoons NpOH^{3+}$$

As a result of the large stability constant, a significant amount of $NpOH^{3+}$ is expected to exist in even highly acidic solutions. For a reference, at pH −0.8, which corresponds to an azeotrope of hydrochloric acid (roughly 20.2% HCl), $[NpOH^{3+}]/[Np^{4+}] \sim 0.6$.

In conclusion, a new mixed-valent neptunium(IV/V) compound prepared via a simple evaporation experiment contains six-membered neptunyl(V) CCI rings. These new CCI oligomers were separated from each other by forming stronger CCIs with Np^{4+} ions. This illustrates an alternative approach to stabilizing neptunyl(V) CCI oligomers in inorganic systems using other cations to compete with Np^{V} in bonding with the O_{yl} atom. With choices of nonmagnetic and magnetic cations, magnetic interactions within and between the neptunyl(V) CCI units can be systematically studied. More bulky and stronger ligands than Cl^{-} such as oxo anions will help to achieve the goal as seen in organic systems. The formation of **1** from a neptunium(V) solution also provides more insight into the disproportionation reaction of Np^{V} ions. In situ studies using a heating laser to control the evaporation of neptunium(V) solutions are underway to further illustrate the underlying chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic file in CIF format for **1**, experimental details including the synthesis, Raman spectroscopy, and structure determination, crystallographic data for **1**, photographs of **1** and **2**, Raman spectra of neptunium(V) compounds, neptunium(V) and -(VI) solutions, and a table of vibrational frequencies and metrical data for neptunium(V) compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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