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# $K(NpO_2)_3(H_2O)Cl_4$: A Channel Structure Assembled by Two- and Three-Center Cation−Cation Interactions of Neptunyl Cations

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Supporting Information

**ABSTRACT:** A Np(V) compound containing three-center cation−cation interations, $K(NpO_2)_3(H_2O)Cl_4$, has been prepared by reacting Np(V) with KCl in molten boric acid. This compound forms a three-dimensional channel structure that is constructed from both two- and three-center cation−cation interactions. Three new bonding modes for cation−cation interactions are added to the summary of all known Np(V) compounds.

Cation−cation interactions (CCIs) in actinide compounds describe the scenario where the oxo atom of an actinyl unit can further bond to another actinide center in its equatorial plane. More generally, these would be called bridging oxo atoms. CCIs between $UO_2^{2+}$ and $NpO_2^+$ were first observed in solution studies by Sullivan et al. in 1961 and have subsequently been detected using a variety of techniques including absorption, vibrational, and Mossbauer spectroscopy as well as X-ray scattering.[1] CCIs in the solid state were first described from the crystal structure of $Na(NpO_2)_2(C_{12}O_{12})(H_2O)_8$, which contains a slipped dimer of $NpO_2^+$ connected through CCIs.[2] It is now known that 53% of Np(V) compounds contain these interactions in the solid state.[3] This bonding motif also exists in other An(V) compounds such as U(V),[4] Pu(V),[5] and Am(V).[6] This linkage plays an important role both in the disproportionation of An(V)[7] and in the magnetic ordering in some Np(V) compounds.[8] Although it is very rare, CCIs can also be found in U(VI) compounds.[9]

The most common CCI bonds involve two actinide centers, where the oxo atoms of an actinyl unit bond to only one secondary actinide atom. This is called a two-center CCI. However, CCI bonds can also involve three actinide centers, where the oxo atoms of an actinyl unit coordinate to two adjacent actinide centers, i.e., a $\mu_3$-oxo. Although CCIs are rare in U(VI) compounds, a three-center CCI was first reported in a uranium(VI) hydroxide compound, $Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$, in which only one oxo atom is involved in the three-center CCI, and the corresponding U≡O distance is very long at 1.967(9) Å compared to the normal length of 1.79(3) Å for an oxo atom not involved in further bonding.[10] Three-center CCIs were further detected in the structures of $(K,Na)Na_3[(UO_2)_5O_6(SO_4)]$[11] and $Li_4[(UO_2)_{10}O_{10}(Mo_2O_8)]$.[12] These four compounds are the only examples of U(VI) compounds that contain three-center CCIs. Despite the fact that CCIs are much more common in Np(V) compounds than in U(VI) materials, there is only one example of the three-center CCIs for Np(V) in the solid state, and these are found in the structure of $Np_2O_5$.[13] These interactions in $Np_2O_5$ result in a relatively complex magnetic structure at low temperatures.[13] Herein, we report the crystal structure and the optical spectrum of the second example of Np(V) compounds containing three-center CCIs: $K(NpO_2)_3(H_2O)Cl_4$.

$K(NpO_2)_3(H_2O)Cl_4$ was synthesized by reacting neptunium(V) chloride in a molten boric acid flux with an excess of KCl at 220 °C.[14] The product was washed by boiling water, and acicular crystals with bright-green coloration were isolated. Surprisingly, $K(NpO_2)_3(H_2O)Cl_4$ is not soluble in water.[15]

Single-crystal X-ray diffraction studies[16] revealed that $K(NpO_2)_3(H_2O)Cl_4$ crystallizes in the polar orthorhombic space group $Pna2_1$. The structure of $K(NpO_2)_3(H_2O)Cl_4$ contains three crystallographically unique Np(V) sites. All of these Np(V) sites are found to have a pentagonal-bipyramidal coordination environment containing $Cl^-$ in their equatorial planes. One of the Np(V) sites is also bound by an additional water molecule in the equatorial plane. These Np(V) pentagonal bipyramids are connected through CCIs and bridging chloride to form a remarkable three-dimensional channel structure with potassium cations in the channels, as shown in Figure 1.

The $Np1O_2^+$ and $Np2O_2^+$ sites are very similar, with average neptunyl bond distances of 1.836(7) and 1.834(7) Å and bond angles of 177.3(3)° and 178.0(3)°, respectively. All of the oxygen atoms on their neptunyl units are further bonded to another Np(V) site to form two-center CCIs. The $Np1O_2^+$ sites have two neptunyl oxo atoms donating to the $Np2O_2^+$ and $Np3O_2^+$ sites, while the $Np2O_2^+$ sites donate two CCIs to the $Np1O_2^+$ and $Np3O_2^+$ sites, respectively. The only difference between the $Np1O_2^+$ and $Np2O_2^+$ sites is that the $Np1O_2^+$ sites are bound by two chlorine atoms and one water molecule besides the oxo atoms from CCIs in the equatorial planes, while the $Np2O_2^+$ sites have three Cl atoms in the equatorial planes (Figure 2).

The most remarkable aspect of the structure of $K(NpO_2)_3(H_2O)Cl_4$ lies at the $Np3O_2^+$ sites. The $Np3O_2^+$ sites contain quite asymmetric neptunyl units with neptunyl bond distances of 1.908(7) (O4) and 1.819(7) (O2) Å and a bond angle of 175.9(3)°. One of the neptunyl oxo atoms, O4, which has the longer Np≡O distance, is further bonded to two other Np(V) sites simultaneously to form a three-center CCI. The bond-valence sum was calculated at 1.93 for O4.[3] The other neptuyl oxygen atom, O2, forms a two-center CCI to another adjacent $Np3O_2^+$ site.

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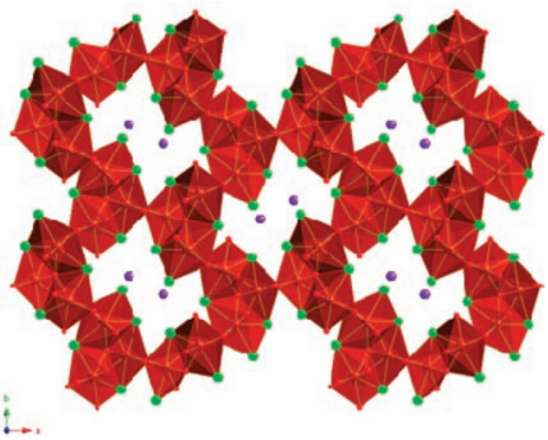

**Figure 1.** View of part of the three-dimensional structure of $K(NpO_2)_3(H_2O)Cl_4$ showing the channels extending along the *c* axis. Np polyhedra are shown in red-brown, chlorine in green, oxygen in red, and potassium in purple.

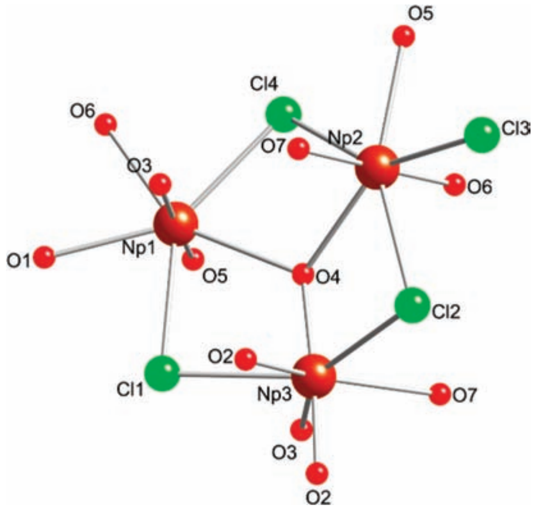

**Figure 2.** Depiction of the coordination environments of the three neptunium sites and the CCIs in $K(NpO_2)_3(H_2O)Cl_4$.

The $Np3O_2^+$ sites also accept three CCI bonds in the equatorial planes from a $Np1O_2^+$ site, a $Np2O_2^+$ site, and another $Np3O_2^+$ site, respectively. As a result, all oxo atoms coordinating to Np3 are involved in the CCIs. With two other chlorine atoms, a pentagonal-bipyramidal geometry is formed for the $Np3O_2^+$ sites, as shown in Figure 2.

Grigorev et al. summarized all of the bonding modes of CCIs that existed in the all known neptunium compounds as of 2004.[17] However, this review needs to be amended in light of the discovery of the new three-center CCIs. For example, the bonding mode of the $Np3O_2^+$ sites in the title compound can be described as the new type listed in Figure 3, case k. Both of the $Np1O_2^+$ and $Np2O_2^+$ sites still adopt the known CCI bonding type listed as case h. Moreover, in the structure of $Np_2O_5$, two of the three Np sites adopt the new type listed as case i, while the third Np site containing the three-center CCI neptunyl has the type of case j.[13] The two mixed/intermediate-valent neptunium borates, $K_4(Np^{IV}O_2)_{0.73}(Np^{V}O_2)_2(Np^{VI}O_2)_4B_{20}O_{36}(OH)_2$ and $Ba_2(Np^{IV}O_2)_{0.59}(Np^{V}O_2)_2(Np^{VI}O_2)_4B_{20}O_{36}(OH)_2 \cdot H_2O$, contain neptunium tetragonal-bipyramidal sites that are surrounded only by CCIs.[23] As a result, these neptunium sites also adopt a new CCI bonding type listed as case i.

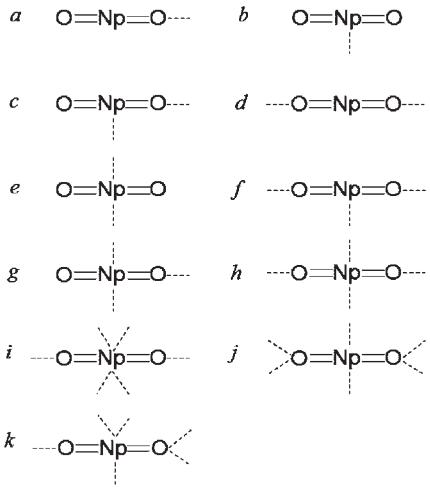

**Figure 3.** New summary of the CCI bonding modes for all known neptunium compounds. The dashed lines represent the CCI bonds.

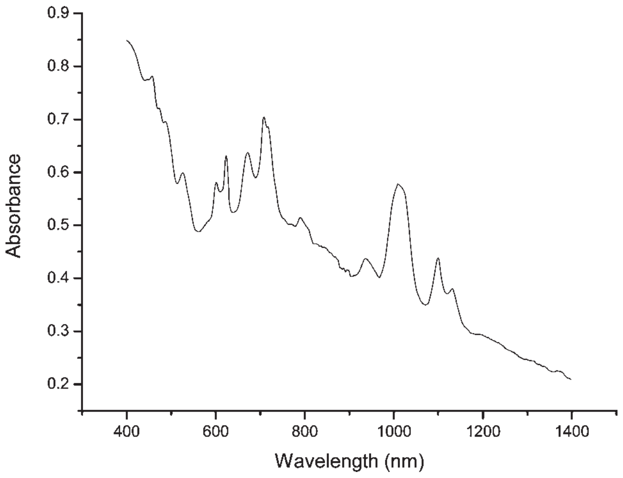

**Figure 4.** UV−vis−near-IR spectrum of $K(NpO_2)_3(H_2O)Cl_4$ obtained from a single crystal. The primary f−f transition for Np(V) is at 1010 nm.

CCIs result in changes in the f−f transitions for neptunium(V). The UV−vis−near-IR spectrum acquired from single crystals of $K(NpO_2)_3(H_2O)Cl_4$ is shown in Figure 4. The existence of CCIs in a compound shift the primary transition at 980 nm to longer wavelengths, typically around 1010 nm.[17−19] This transition is, in fact, found at 1010 nm for $K(NpO_2)_3(H_2O)Cl_4$. However, the peak is broader than normal, most likely because $K(NpO_2)_3(H_2O)Cl_4$ contains both two- and three-center CCIs, and there are multiple overlapping transitions. The intensities of Np(V) transitions have been carefully examined by several groups.[20] Krot and co-workers concluded that when the intensity of the ca. 980 nm transition is relatively higher, a pentagonal bipyramidal environment is typically observed.[21] Absorption studies on single crystals are complicated by the potential for an orientational dependence on which transitions are allowed. The acicular nature of the crystals of $K(NpO_2)_3(H_2O)Cl_4$ is not amenable to a detailed study of pleiochroism. However, the spectrum taken from a single crystal, as shown in Figure 4, reveals some important observations. First, the transitions near 616 and 980 nm have been found to obey Beer—Lambert behavior in solution and can be used to calculate the concentration of Np(V). The transitions between 616 and 980 nm are typically too weak to utilize; the same is true for the transitions after 980 nm.

For $K(NpO_2)_3(H_2O)Cl_4$, we find that these typically neglected transitions are of nearly equal intensity to that of the 1010 nm transition, which should be as much as 400× more intense owing to the mixing of 5f $\phi$ and 6d $\delta$ orbitals, which relaxes the selection rules for this transition (f—f transitions are Laporte-forbidden).[22] Given the prevalence of mixed-valent neptunium compounds that result from Np(V) disproportionation,[23] it is becoming increasingly clear that these compounds require very detailed characterization to be confident about oxidation-state assignments. Bond-valence-sum calculations are particularly useful in this regard, and for $K(NpO_2)_3(H_2O)Cl_4$, all of the Np(V) compounds yield sums consistent with Np(V) only.

In conclusion, we have provided an example of a Np(V) compound containing a new type of three-center CCI. The channel structure is built from both two- and three-center CCIs. With the discovery of the three-center CCIs in Np(V) compounds, three new CCI bonding modes can now be added to the summary of known interactions.[17] Moreover, as observed in the actinide borate system,[23,24] the chemistry of actinides in molten boric acid is proving to be substantially different from that observed in aqueous media or high-temperature fluxes. This rare example of a neptunium(V) chloride compound containing three-center CCIs has thus far only been prepared in the molten boric acid.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** X-ray crystallographic file for $K(NpO_2)_3(H_2O)Cl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) **Synthetic details: *Caution!*** *$^{237}Np$ ($t_{1/2}$ = 2.14 × $10^6$ years) represents a serious health risk because of its $\alpha$ and $\gamma$ emission and especially because of its decay to the short-lived isotope $^{233}Pa$ ($t_{1/2}$ = 27.0 days), which is a potent $\beta$ and $\gamma$ emitter.* Neptunium(V) hydroxide was dissolved in a dilute HCl solution. A stock solution of neptunium(V) chloride [containing 10 mg of Np(V)] was transferred to a 10 mL Teflon liner and was reduced to a tiny droplet by heating at 140 °C. Large excesses of boric acid (46.2 mg) and KCl (14.5 mg) were then added directly to the droplet containing Np(V). The mixture was then sealed in an autoclave and heated at 220 °C for 3 days, followed by cooling to room temperature over a 1 day period. The autoclave was opened, and boiling water was added to dissolve the excess boric acid, revealing bright-green crystals with an acicular habit as the major product.

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(16) Crystallographic data for $K(NpO_2)_3(H_2O)Cl_4$: bright-green needles, 0.050 × 0.015 × 0.012 mm, orthorhombic, $Pna2_1$, $Z = 4$, $a$ = 19.49(2) Å, $b$ = 11.295(12) Å, $c$ = 5.654(6) Å, $V$ = 1245(2) $Å^3$ [$T$ = 100(2) K], $\mu$ = 260.56 $cm^{-1}$, R1 = 0.0217, wR2 = 0.0387.

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