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The First Structural and Spectroscopic Characterization of a Neptunyl Polyoxometalate Complex

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Increasing our understanding of the coordination chemistry of the neptunyl ion (NpO_2^+) is vital if we are to develop novel technologies for the separation and safe disposal of the long-lived Np-237 radioisotope. We report the structural and spectroscopic characterization of the first neptunyl polyoxometalate complex, $[Na_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]^{14-}$. This complex is readily formed in aqueous solution and is as extractable into an organic solvent as the UO_2^{2+} structural analogue, $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$. This contrasts with known actinyl coordination chemistry where UO_2^{2+} forms more stable complexes and is often significantly more extractable than NpO_2^+. This remarkable similarity in coordination chemistry may have great significance in the development of new waste treatment technologies.

Polyoxometalates readily form complexes with the tri- and tetravalent lanthanides and actinides[1] and have been studied as potential sequestering/separation agents for nuclear waste remediation.[2] However, it was thought that polyoxometalates complex only very weakly with the actinyl ions, characteristic of the higher oxidation states of the actinides (AnO_2^+ and AnO_2^{2+}).[1,3] Polyoxometalates are very high denticity ligands, whereas the *trans*-oxo actinyl cations can only coordinate in the equatorial plane and are thus sterically very demanding.

A recent study by Pope et al. has shown that the uranyl ion, UO_2^{2+}, forms sandwich complexes with $A\text{-}PW_9O_{34}^{9-}$ (e.g., $Na_{12}[Na_2(UO_2)_2(PW_9O_{34})_2]$).[4] This group have also synthesized a range of tungstoarsenate(III) uranyl complexes where three uranyl cations bridge three polyoxometalate anions.[5] Therefore, it would appear that polyoxometalates can complex to actinyl ions with the *trans*-oxo groups directing the structures of the complexes formed. In addition, a recent spectrophotometric study into the interaction between NpO_2^{2+} and $[SiW_{11}O_{39}]^{8-}$ indicates the formation of a stable complex at low pH with a log β_1 value comparable with that for An(III).[6]

We have recently started to study the complexation of NpO_2^+ with polyoxometalate anions, including $[PW_9O_{34}]^{9-}$ (PW_9).[7] A stock solution of NpO_2^+ (0.1 M) in 2 M HCl was evaporated to dryness under a heat lamp. Solid $Na_8HPW_9O_{34}$ was then added in a 1:1 PW_9:Np molar ratio, and the mixture was dissolved in 0.2 M NaCl to yield a deep straw colored solution. The UV/vis/nIR electronic absorption spectrum of this solution (Figure 1a) reveals the dominant 5f → 5f transition for NpO_2^+ at 980 nm, the most commonly observed position for this peak in the presence of a range of ligands,[8,9] and a second major absorption peak at 1005 nm, which we attribute to the neptunyl PW_9 complex. From the extinction coefficient of the peak at 980 nm (398 M^{-1} cm^{-1}),[8] we estimate that at least 90% of the NpO_2^+ is complexed by the polyoxometalate anion. An increase of 8−30 nm in wavelength of this major band is often associated with the formation of neptunyl cation−cation bonds in the solid state through the central actinide and -yl oxygens of adjacent neptunyl moieties.[10] Spectra were recorded from 300 to 1250 nm with high-intensity O → W charge-transfer bands observed below 350 nm but no evidence for either Np(IV) or (VI).[9]

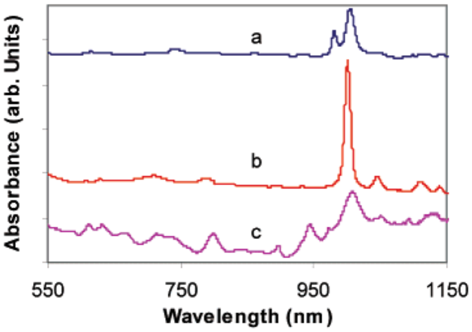

Figure 1. Electronic absorption spectrum of an aqueous solution of $PW_9O_{34}^{9-}$ and NpO_2^+ in a 1:1 ratio (a), the toluene phase after vigorous mixing with this aqueous solution (b), and the diffuse reflectance spectrum of crystals of **1** (c).

An excess of NaCl was then added to the solution, which was clarified by centrifuging, and cooled to 3 °C to yield lime green crystals (hexagonal plates) of $Na_{14}[Na_2(NpO_2)_2(A\text{-}PW_9O_{34})_2].[15H_2O]$ (**1**). A UV/vis/nIR spectrum of the supernatant revealed that over 90% of the Np had crystallized from solution. The crystal structure of **1** (Figure 2)[11] revealed two A-type $\alpha\text{-}PW_9$ anions sandwiching two NpO_2^+ and two Na^+ cations in a complex isostructure with the uranyl analogue,[4] the only major difference being the overall increase in charge on the complex anion from −12 to −14. The two NpO_2^+ and two Na^+ cations sit at opposite corners of a rectangular arrangement with tetrahedral Na and distorted pentagonal bipyramidal Np. An ATR−IR spectrum of the bulk crystalline solid shows a near identical spectrum in the tungsten−oxygen (760−1000 cm^{-1}) and phosphorus−oxygen (1050−1080 cm^{-1}) stretching regions to the uranyl analogue.[4] In other Np(V) complexes,[12] the asymmetric NpO_2^+ stretch comes between 720 and 850 cm^{-1}, which is within the W−O stretching region and is thus obscured.

The Np(V) oxidation state in the bulk solid was confirmed by diffuse reflectance electronic absorption spectroscopy (Figure 1c), which also indicated that the $NpO_2^+{-}PW_9$ solution species is similar to the complex observed in the solid state. We attribute the increased intensity of many of the additional NpO_2^+ transitions relative to the major peak (now centered at 1009 nm) to the low symmetry around the two Np centers in the solid state. From the crystal structure, it would appear that the decrease in energy of the major NpO_2^+ transition is not due to cation−cation interactions,

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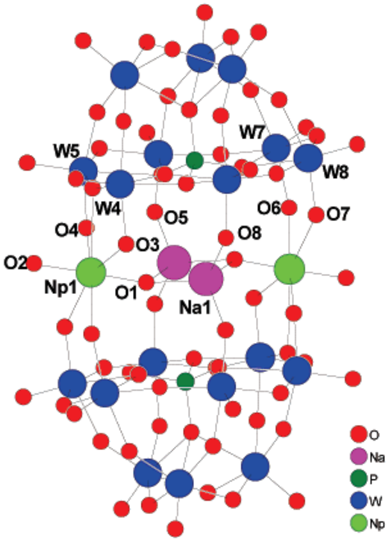

Figure 2. Ball-and-stick representation of the anion structure in **1**. Selected bond distances (Å) and angles (deg) are Np1−O1 1.814(13), Np1−O2 1.863(14), Np1−O3 2.399(15), Np1−O4 2.402(14), Np1−O6 2.336(15), Np1−O7 2.346(17), Np1−O10 2.603(16), W4−O3−Np1 110.8(6), W5−O4−Np1 111.6(6), W7−O6−Np1 140.7(7), W8−O7−Np1 142.7(8), O3−Np1−O6 79.4(5), O6−Np1−O7 77.6(5), O7−Np1−O4 83.4(5), O4−Np1−O10 61.9(5), O10−Np1−O3 62.2(4), O2−Np1−O1 178.6(8).

but may instead be due to interaction between the two internal Na^+ ions and the two NpO_2^+ cations. It cannot therefore be ruled out that the peak at 980 nm observed in solution may also, at least in part, be due to the presence of a NpO_2^+−PW_9 solution species without the inclusion of Na^+ ions. No attempt has yet been made to determine the stability constant for Na^+ (or other cation) inclusion as previously undertaken for the UO_2^{2+} analogue,[4] although we may expect the increased −2 charge on the Np complex to push the equilibrium more toward Na^+ inclusion.

As with the uranyl analogue, each NpO_2^+ is bound to two terminal oxygens of each of the two PW_9 ligands, with an additional longer bond to a bridging oxygen on only one of the PW_9 ligands. This results in each Np being drawn closer to one of the polyoxometalate anions than the other, giving closer W···Np interactions and tighter W−O−Np and O−Np−O (equatorial) bond angles (again as for the uranyl analogue). The neptunyl bond pointing away from the cluster (1.863(14) Å) is slightly longer than the bond pointing into the center of the cluster (1.814(13) Å), but both are comparable to the normal actinyl oxygen bond length for NpO_2^+ complexes (1.83 Å).[13] The four shorter equatorial bond lengths average to 2.37 Å, with the fifth longer bond at 2.603(16) Å. The average equatorial bond length for NpO_2^+ complexes with five ligands in the equatorial plane is 2.45 Å.[12]

The synthesis was then repeated, but this time instead of adding excess NaCl to crystallize **1**, the aqueous solution was mixed vigorously with an equivolume solution of 0.007 M tetra-*n*-heptylammonium bromide in toluene. After phase separation, the toluene solution was a deep orange color with the aqueous solution now colorless (although with a trace of green precipitate). This indicated essentially complete extraction of the anion of **1**, as confirmed by the electronic absorption spectrum of the toluene solution (Figure 1b). The main peak has shifted slightly to 1001 nm and has increased in intensity, probably due to the change in solvent environment and the close association of the countercations in the solvent phase. This extraction behavior is similar to that previously observed for the UO_2^{2+} analogue, although the extractability of NpO_2^+ complexes is usually much lower than UO_2^{2+} complexes, and the two species are rarely coextractable.[14] Finally, aqueous solutions containing **1** readily form precipitates, making it difficult to record the ^{31}P NMR spectrum in solution. However, no such precipitates form from the toluene solution of the complex, and the ^{31}P NMR spectrum showed a major peak at −21.6 ppm.[15]

In conclusion, we have structurally and spectroscopically characterized the first neptunyl polyoxometalate complex. The comparative ease of formation of this species in near quantitative yield indicates a strong interaction between cation and anion in both solution and the solid state. The fact that the NpO_2^+ complex is as readily prepared and solvent extracted as the UO_2^{2+} structural analogue has clear implications for the development of actinide separation and sequestering technologies. Further structural, spectroscopic, and electrochemical studies of actinyl polyoxometalate complexes are currently in progress.

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Supporting Information Available: X-ray crystallographic files (CIF) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data for $Na_{12}[Na_2(NpO_2)_2(A\text{-}PW_9O_{34})_2]\cdot 19H_2O$, Mw = 5920.43, monoclinic space group, $P2_1/c$, a = 16.6123(10) Å, b = 14.4990(9) Å, c = 21.2765(13) Å, α = 90.00°, β = 111.7610(10)°, γ = 90.00°, V = 4759.5(5) $Å^3$, T = 100 K, Z = 2, Bruker Smart Platform CCD, Mo Kα radiation (λ = 0.71073 Å), μ = 24.04 mm^{-1}, crystal dimensions = 0.18 × 0.2 × 0.01 mm, 33 582 reflections measured, 8369 of which were unique (R_{int} = 0.1946). The structure was solved by direct methods followed by Fourier synthesis, and refined on F^2. All W and Na atoms were refined anisotropically as were the O atoms included in the cluster framework. O atoms belonging to solvent molecules were refined isotropically. Final R ($I > 2\sigma(I)$), R1 = 0.0618, wR2 = 0.1508. Final R (all data), R1 = 0.0829, wR2 = 0.1630.
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(15) This peak was broad (280 Hz line width with 10 Hz line broadening), and we attribute this to the presence of the two paramagnetic Np(V) centers. A second much smaller peak at −9.7 ppm was also observed, but we have, as yet, been unable to assign this peak.

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