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Neptunium(VI) Chain and Neptunium(VI/V) Mixed Valence Cluster Complexes

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The synthesis of $[Np^{VI}O_2Cl_2(thf)]_n$ offers the potential for more detailed exploration of neptunyl(VI) chemistry while the synthesis of the mixed valence cluster complex $[\{Np^{VI}O_2Cl_2\}\{Np^{V}O_2Cl(thf)_3\}_2]$ allows neptunyl(V) 'cation-cation' interactions to be probed in a molecular system.

Neptunium has three readily accessible oxidation states, IV, V and VI, which can coexist under certain conditions, with the aqueous soluble neptunyl(V) moiety, $\{NpO_2\}^+$, of most environmental relevance. Careful control of Np chemistry is required during actinide separation processes *e.g.* the PUREX (Plutonium and Uranium Recovery by Extraction) process.[1] In addition, the long half life of the major alpha emitting isotope (^{237}Np, $t_{1/2} = 2.144 \times 10^6$ years) renders Np a major contributor to the radiotoxicity of nuclear waste as a function of time.[2] Significant quantities of neptunium are generated in nuclear reactors and the current surge in interest in nuclear power will lead to an increase in our need to further understand the chemistry of this element.

It is clearly of importance that Np chemistry is well understood and there have been several recent investigations into the structural, spectroscopic and magnetic properties of Np compounds.[3] However, the vast majority of this chemistry has been performed in aqueous solution, prohibiting the use of air and moisture sensitive ligands. This is in stark contrast to uranium and thorium where inert atmosphere chemistry with moisture sensitive donor ligands has flourished, yielding greater insight into the structural and electronic properties of these early actinides.[4] For the uranyl(VI) moiety, $\{UO_2\}^{2+}$, $UO_2Cl_2(thf)_3$ (and the desolvated dimer $[UO_2Cl_2(thf)]_2$) have proven to be excellent moisture-free reagents for inert atmosphere uranyl chemistry.[5] These starting reagents have been used extensively within our group to study soft donor ligand coordination in the uranyl equatorial plane and oxo-activation to Lewis acid coordination.[6] However, until now the absence of such a starting reagent for Np has limited our ability to extend this chemistry any further across the actinide series,[7] which is required if we are to gain a more complete understanding of 5*f* element chemistry.

Our belief that $[NpO_2Cl_2(thf)_3]$ and/or $[NpO_2Cl_2(thf)]_2$ could be prepared appeared to be justified by the recently reported plutonyl(VI) complex $[PuO_2Cl_2(thf)_2]_2$,[8] and we have been able to synthesise and structural characterise the related complex, $[NpO_2Cl_2(thf)]_n$ (**1**). $NpO_2(OH)_2.xH_2O$ was suspended in thf solution and slightly greater than two molar equivalents of HCl in Et_2O solution was added to yield a deep yellow solution, which was evaporated to dryness *in vacuo* to yield $NpO_2Cl_2(thf)_x$. Complex **1**, $[NpO_2Cl_2(thf)]_n$ (Figure 1), could be obtained through crystallizing out of thf by vapour diffusion with hexanes overnight. The structure consists of a one dimensional chain in which each linear neptunyl(VI) moiety is coordinated by two chloride ligands bridged to one additional neptunyl(VI) centre, two chloride ligands bridged to a second neptunyl(VI) centre and one terminally coordinated thf molecule. The axial Np-O$_{yl}$ bond lengths are both 1.767(10) Å and the O=Np=O angle is 178.2(5)°, consistent with known $\{NpO_2\}^{2+}$ structural parameters.[11] The bridging chloride Np-Cl distances are 2.779(3) Å and 2.818(3) Å and are essentially the same as the bridging chloride An-Cl distances in $[PuO_2Cl_2(thf)_2]_2$ (2.810(4) and 2.800(4) Å) and $[UO_2Cl_2(thf)_2]_2$ (2.80(2) and 2.83(2) Å).[5b, 8] The Np-O$_{thf}$ bond distance is 2.396(11) Å, the same, within errors, as the Pu-O$_{thf}$ distance in $[PuO_2Cl_2(thf)_2]_2$ (2.401(10) Å).[8] Complex **1** contains the fewest coordinated thf molecules of all the known actinyl(VI) chloride/thf adducts, and this feature appears to dictate the structure, *viz* $[UO_2Cl_2(thf)_3]$ (monomer), $[UO_2Cl_2(thf)_2]_2$ and $[PuO_2Cl_2(thf)_2]_2$ (dimers) and $[NpO_2Cl_2(thf)]_n$ (chain). We assume that either $[NpO_2Cl_2(thf)_3]$ and/or $[NpO_2Cl_2(thf)_2]_2$ are the dominant species in solution.

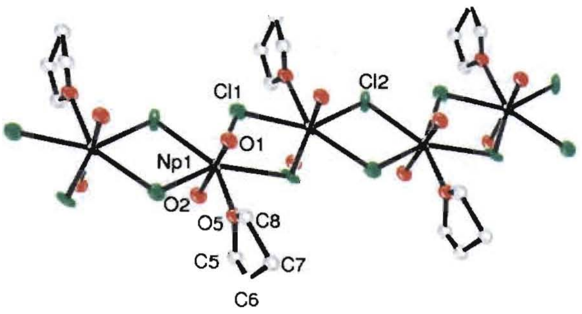

Figure 1. ORTEP representation of part of the chain of **1**, $[NpO_2Cl_2(thf)]_n$

The ^1H NMR spectrum of the thf solvate of $[NpO_2Cl_2]$ in thf-d_8 reveals two broad overlapping peaks in the α-H position of thf (3.61 and 3.64 ppm) and two broad overlapping peaks in the *β*-H position of thf (1.83 and 1.78 ppm) (see ESI). This pattern may correspond to coordinated and uncoordinated thf, as suggested for the comparable Pu^{VI} system.[8] Alternatively, it could correspond to thf and thf-d_7, with Np^{VI} coordinated thf being unobservable due to the paramagnetism of the metal centre (Np^{VI} is an f^1 system). The comparable spectrum for $UO_2Cl_2(thf)_3$ in thf-d_8 reveals only one broad resonance in the α-H region (3.62 ppm) and one broad resonance in the *β*-H region (1.77 ppm).[5a]

The nIR spectrum of $[NpO_2Cl_2]$ in thf exhibited a broad band at 1244 nm, assigned to an *f-f* transition and vibronic coupling below 800 nm, both of which can be attributed to the $\{NpO_2\}^{2+}$ cation.[9] When pure $[NpO_2Cl_2(thf)]_n$ is redissolved in thf some neptunyl(V) can be observed as a contaminant, the major *f-f* transition for this species comes at 1004 nm, a typical energy for this transition when a $\{NpO_2\}^+$ oxygen is coordinating to another metal centre in a 'cation-cation' type interaction (Figure 2).[10]

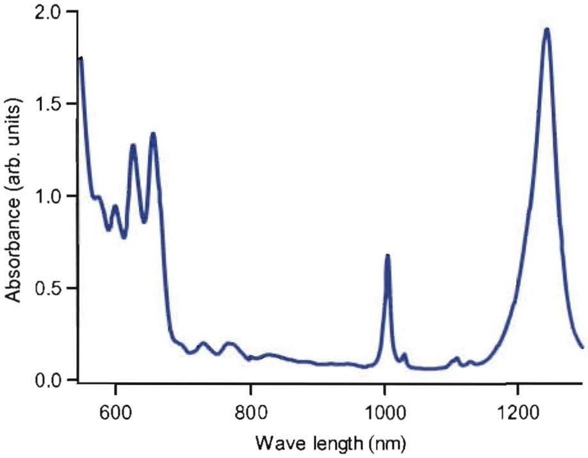

Figure 2. Vis./nIR spectrum of $[NpO_2Cl_2(thf)]_n$ (**1**) dissolved in thf.

The partial reduction of Np^{VI} to Np^V for a NpO_2Cl_2 solution in thf resulted in the isolation of product **2**, $[\{Np^{VI}O_2Cl_2\}\{Np^VO_2Cl(thf)_3\}_2]$, which crystallizes from a thf/hexanes solution of neptunyl(VI) chloride after a period of days. Compound **2** is a trimetallic mixed oxidation state neptunyl(VI/V) cluster (Figure 3). Two neptunyl(V) moieties are linked through two bridging chlorides, with their distorted pentagonal bipyramidal inner coordination spheres completed by three coordinated thf molecules per metal centre. One neptunyl oxygen from each of the two neptunyl(V) species coordinates into the equatorial plane of a neptunyl(VI) centre, which has a distorted tetragonal bipyramidal geometry completed by two coordinated chloride ligands.[12] 'Cation–cation' bonding of a neptunyl(V) oxygen to another neptunyl(V) metal centre has been observed on numerous occasions in the solid state, and there are reports of similar interactions with a range of metal cations in solution.[10] In addition, axial oxygen coordination has received recent interest in uranyl(VI/V) chemistry.[6c,13] However, to the best of our knowledge this is the first structurally characterized example of a neptunyl(VI) equatorial coordination shell being occupied by a neptunyl(V) axial oxygen, despite previously structurally characterized examples of mixed neptunyl(VI/V) oxidation state complexes.[14]

The Np^{VI}-O_{yl} bond lengths in **2** are essentially the same (1.771(12) and 1.793(10) Å) and comparable with the analogous bond lengths in **1**. As is typically the case for neptunyl(V) 'cation-cation' bonding,[10] the Np^V-O_{yl} oxygens coordinated to the Np^{VI} centre are significantly longer (1.885(11) and 1.912(11) Å), and hence probably weaker, than the uncoordinated Np^V 'yl' oxygens (1.751(13) and 1.805(12) Å). The Np^{VI}-$O_{Np(V)}$ bond lengths (2.317(11 and 2.303(11) Å) are significantly shorter than the Np-O_{thf} bond length in **1** (2.396(11) Å) which suggests a stronger bonding interaction and at least partially explains why the axial oxygens of two $\{NpO_2\}^+$ moieties out-competes thf for coordination to neptunyl(VI) in **2**.

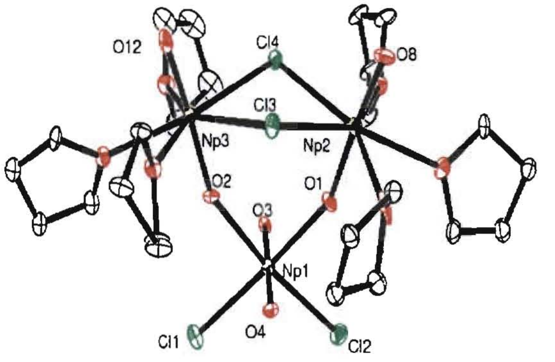

Figure 3. ORTEP Representation of **2**, $[\{Np^{VI}O_2Cl_2\}\{Np^VO_2Cl(thf)_3\}_2]$

In order to gain further insight into the relative strength of the interactions between the Np centres and the coordinated atoms in **1** and **2**, single point density functional calculations were performed at the experimentally determined geometries. For **2** the structure shown in Figure 2 was employed, whereas for **1**, a fragment of the chain containing three neptunyl units was studied in which the outer neptunyl coordination was terminated by one thf molecule and a chloride ligand. We chose to probe the Np–element bonds using Mayer bond orders (MBOs), which are straightforward to calculate and which have been shown to provide useful, if indirect, measures of interaction energies.[6a, 15, 17]

The MBO data are collected in Table 1. Both compounds provide examples of Np–O_{yl} bonds in which the O_{yl} are uncoordinated to other atoms. In all such cases the MBOs are slightly larger than 2.0 (and slightly larger in **1** than **2**). These values are similar to the M–O we found previously in $[MOX_5]^{n-}$ (M = Pa, *n* = 2; M = U, *n* = 1; M = Np, *n* = 0; X = F, Cl or Br); somewhat lower than the formal value of 3.[16] Of more interest are the MBOs of the bridging Np–O bonds in **2**. In **2** the Np2/3–O_{yl}1/2 MBOs (1.54 and 1.58) are significantly reduced from the regular Np–O_{yl} value, reflecting the longer Np–O_{yl} distance in Np2/3–O_{yl}1/2. We also calculated a smaller, but still significant, MBO between Np1 and O1/2 (0.41 and 0.37).

Table 1. Mayer bond orders (MBOs) calculated for **1** and **2**.

Bond	MBO	Bond	MBO
Np1–Oyl (**1**)	2.12/2.10		
Np1–Oyl (**2**)	2.01/2.01	Np2/3–Oyl1/2 (**2**)	1.54/1.58
Np1–O1/2 (**2**)	0.41/0.37	Np2/3–Oyl8/12 (**2**)	2.08/2.08

Conclusions

We have shown that a neptunyl(VI) chloride thf adduct solution can be prepared and a solid product crystallized from solution, $[NpO_2Cl_2(thf)]_n$. This could provide a convenient entry route into the development of neptunyl(VI) inert atmosphere chemistry, and hence increase our understanding of the chemistry of the $\{NpO_2\}^{2+}$ cation to something approaching that of the chemistry of the $\{UO_2\}^{2+}$ cation. In addition, the structural characterization of a mixed valence neptunyl(VI/V) molecular cluster complex evidences the rich structural and redox neptunium chemistry awaiting discovery in organic solvents. Finally, Mayer bond order data has yielded fundamental insight into the strength of neptunyl(V) 'cation-cation' bonding interactions in the mixed valence complex. This, in turn, should yield fundamental insight into neptunium solvent extraction and redox chemistry in the PUREX process, an area of continuing industrial relevance.[17-18] We are currently studying the synthetic utility of $[Np^{VI}O_2Cl_2(thf)]_n$, undertaking a more detailed study of its stability in organic solvents and seeking to probe the magnetic properties of $[\{Np^{VI}O_2Cl_2\}\{Np^{V}O_2Cl(thf)_3\}_2]$. In addition, it would be interesting to see if a pure neptunyl(V)chloride complex could be crystallised from thf solution, and if 'cation-cation interactions would result in the formation of infinite chains or sheets – as observed in the analogous aqueous systems.[19]

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental and computational details]. See DOI: 10.1039/b000000x/

‡*Caution!* ^{237}Np is a high specific activity radionuclide and all manipulations with this radioisotope should be undertaken in a properly regulated and controlled radiochemical laboratory.

Single crystal X-ray diffraction data was obtained on a Bruker AXS SMART diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 100(2) K. Data collection and structure refinements were achieved using standard Bruker AXS control and integration software and SHELXTL for all compounds. Selected crystallographic data for **1**: $C_4H_8Cl_2NpO_3$, M = 412.00, yellow plate 0.20 × 0.10 × 0.05 mm, monoclinic, space group C2/c, $a = 10.925(3)$, $b = 10.137(2)$, $c = 8.675(2)$ Å, $\alpha = \gamma = 90$, $\beta = 109.519(5)°$, $V = 905.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.022$ g cm^{-3}, $\mu = 12.018$ mm^{-1}. Intensity data of 2575 reflections were collected in the range $-12 \leq h \geq 7$, $-12 \leq k \geq 12$, $-9 \leq l \geq 10$, 791 unique reflections ($R_{int} = 0.042$) $R_1 = 0.043$ (for 727 reflections with $I \geq 2\sigma I$), $wR_2 = 0.102$ (all data), GOF = 1.058, max/min residual electron density = +4.304/-1.693 e Å^{-3}. Selected crystallographic data for **2**: $C_{28}H_{56}Cl_4Np_3O_{13}$, M = 1453.53, yellow prism 0.10 × 0.10 × 0.10 mm, triclinic, space group P-1, $a = 12.384(3)$, $b = 13.733(3)$, $c = 13.829(3)$ Å, $\alpha = 61.578(4)$, $\beta = 89.393(4)$, $\gamma = 86.284(4)°$, $V = 2063.4(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.339$ g cm^{-3}, $\mu = 7.811$ mm^{-1}. Intensity data of 14379 reflections were collected in the range $-14 \leq h \geq +14$, $-16 \leq k \geq 16$, $-16 \leq l \geq 16$, 7189 unique reflections ($R_{int} = 0.096$) $R_1 = 0.061$ (for 3971 reflections with $I \geq 2\sigma I$), $wR_2 = 0.134$ (all data), GOF = 0.974, max/min residual electron density = +2.361/-2.116 e Å^{-3}.

CCDC-679581 and CCDC-679580 contain the supplementary crystallographic data for compounds **1** and **2** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.ca.ac.uk/data_request/cif.

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