Oxoneptunium(V) as part of the framework of a polyoxometalate

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$(NH_4)_{14}Na_4[(Np_3W_4O_{15})(H_2O)_3(BiW_9O_{33})_3]\cdot 62H_2O$ (1) and $(NH_4)_{14.5}Na_{3.5}[(Np_3W_4O_{15})(H_2O)_3(SbW_9O_{33})_3]\cdot 40.5H_2O$ (2) each contain three neptunyl(V) moieties encapsulated within heteropolyoxotungstate frameworks in which axial $\{NpO_2\}^+$ oxygens form one face of a WO_6 octahedron.

The linear, di-oxo, actinyl moieties (AnO_2^+/AnO_2^{2+}) dominate the +V and +VI chemistry of the mid-actinide elements (U, Np, Pu and Am) and an increased understanding of the chemistry of these species is required for the development of novel nuclear waste processing technologies and for reliable chemical speciation in any future nuclear waste repositories.[1] One of the most significant areas of current actinyl chemical research is in the synthesis of novel actinide containing materials.[2] Recent discoveries have included the formation of uranyl and neptunyl peroxide nanospheres,[3] and the synthesis of an organic capped U_6O_{13} cluster based on the Lindqvist-type polyoxoanion.[4] Both discoveries have provided a link between the chemistry of the Group 6 d-transition elements and the high oxidation state early actinides.

Tri- (and di-) lacunary heteropolytungstates have become established as effective *ligands* for coordination in the equatorial plane of the early actinyl cations. In 1999 Pope *et al.* reported the first uranyl heteropolytungstate complex, $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$, where two $\{UO_2\}^{2+}$ cations are sandwiched between two trivacant lacunary $[PW_9O_{34}]^{9-}$ anions.[5] Since then many uranyl–heteropolyoxotungstate complexes have been prepared, with both the type of lacunary anion and reaction conditions able to direct structure.[6–10] These complexes have also been proposed as precursors to waste immobilisation matrices, *via* the high temperature formation of tungsten bronze materials.[11] In addition, we have reported the structural and spectroscopic characterisation of the neptunyl(V) analogue of the $\{UO_2\}^{2+}$–'PW_9' complex *i.e.* $[Na_2(NpO_2)_2(PW_9O_{34})_2]^{14-}$.[12] The significant shift in the main Np^V *f–f* transition from 980 to 1004 nm on complexation was indicative of strong coordination in the equatorial plane and/or a strong neptunyl oxygen interaction with incorporated Na cations.

We have previously shown that the uranyl cation can coordinate to both $[SbW_9O_{33}]^{9-}$ and $[TeW_9O_{33}]^{8-}$ (B-type[13] trilacunary anions) to yield analogous open sandwich type complexes, $[(UO_2)_2(H_2O)_2(Sb/TeW_9O_{33})_2]^{14-/12-}$.[9] While $[AsW_9O_{33}]^{9-}$ can form a structurally quite different complex with $\{UO_2\}^{2+}$, $[(UO_2)_3(H_2O)_4As_3W_{26}O_{94}]^{17-}$,[7] we have recently shown that an analogous isostructural open sandwich complex can also be formed with this anion.[14] Addition of $[SbW_9O_{33}]^{9-}$, $[BiW_9O_{33}]^{9-}$ or $[TeW_9O_{33}]^{8-}$, prepared as hydrated sodium salts,[9,15,16] to acidified solutions of $\{NpO_2\}^+$ (4.8 mmol dm^{-3}, generated electrochemically in nitric acid) followed by a gradual increase in pH yields similar results in all three cases.† Typically 2 molar equivalents of ligand were required to keep $\{NpO_2^+\}$ in solution at higher pH values (approaching neutral pH) and a solution colour change from light green to a straw yellow was observed. Again, for all three ligand systems ($[SbW_9O_{33}]^{9-}$, $[TeW_9O_{33}]^{8-}$ and $[BiW_9O_{33}]^{9-}$) similar features were observed in the near IR spectra where the major neptunyl(V) *f–f* transition ($^3H_{2g}\rightarrow^3\Pi_{2g}$) is the dominant band.[17] On raising the pH the band at 980 nm, attributed to $[NpO_2(H_2O)_5]^+$, was replaced by a broad lower energy transition which could be resolved into two bands, one centred at *ca.* 1002 nm and the other at *ca.* 1022 nm. The lowest energy band dominates the spectra at higher pH values (see Fig. 1). In comparison with the spectrum observed for $[Na_2(NpO_2)_2(PW_9O_{34})_2]^{14-}$, we believe that the transition at *ca.* 1002 nm is associated with a 2 : 2 complex, with in this case two $\{NpO_2\}^+$ moieties complexed by two B-type trilacunary anions in the open sandwich type structure previously described for uranyl.[9] However, the transitions at *ca.* 1022 nm represent an extremely large shift in the major $\{NpO_2\}^+$ band and it would appear that there is a major perturbation of the $\{O=Np=O\}$ unit in the complex formed.

Addition of three equivalents of $Na_9[BiW_9O_{33}]\cdot 18H_2O$ to an acidic solution of 10 mmol $\{NpO_2\}^+$ and elevation of the pH to 7 by addition of NaOH solution led to the formation of the straw yellow coloured solution with a dominant absorption band at 1022 nm. A subsequent addition of NH_4Cl followed by slow
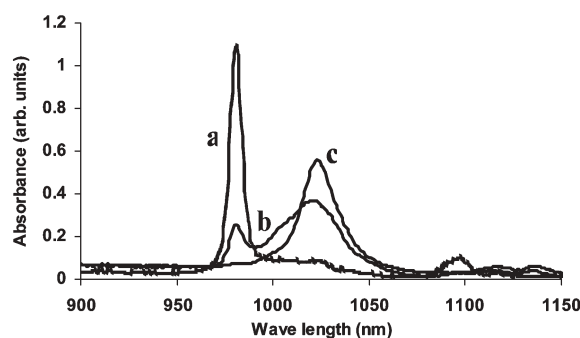

Fig. 1 Near-IR aqueous solution spectra of: **a.** $[NpO_2(H_2O)_5]^+$, **b.** $\{NpO_2\}^+$ and $[BiW_9O_{33}]^{9-}$ at 1 : 1 molar ratio, pH 6.4 and **c.** $\{NpO_2\}^+$ and $[BiW_9O_{33}]^{9-}$ at 1 : 2 molar ratio, pH 7.

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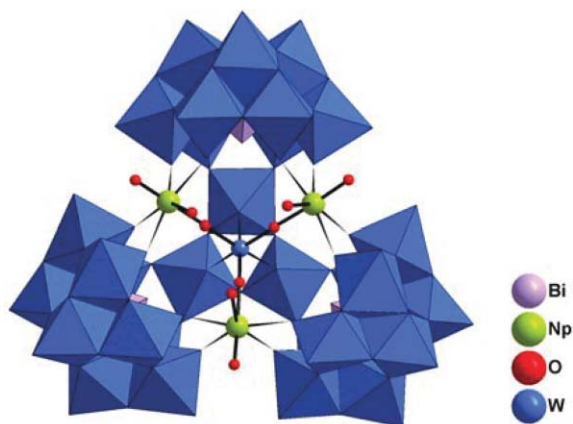[c]Nexia Solutions, Sellafield, Seascale, Cumbria, UK CA20 1PG

Fig. 2 Polyhedral and ball and stick representation of the anion [(Np₃W₄O₁₅)₃(H₂O)₃(BiW₉O₃₃)₃]¹⁸⁻ (**1**).

evaporation led to the crystallisation of $(NH_4)_{14}Na_4[(Np_3W_4O_{15})(H_2O)_3(BiW_9O_{33})_3]\cdot62H_2O$ (**1** – see Fig. 2). A similar procedure, using two equivalents of $Na_9[SbW_9O_{33}]\cdot18H_2O$ followed by vapour diffusion with CH_3CN led to the crystallisation of $(NH_4)_{14.5}Na_{3.5}[(Np_3W_4O_{15})(H_2O)_3(SbW_9O_{33})_3]\cdot40.5H_2O$ (**2** – see Fig. 3). As the reactions were undertaken with only 10 mg Np to minimise radiological hazards, obtaining accurate yields proved difficult. However, it is clear that **1** and **2** were the major products and that some decomposition of both ligand systems must have taken place to yield the $\{W_4O_9\}^{6+}$ fragment in both complex anions. Both structures were crystallographically characterised,‡ revealing isostructural anionic complexes in which the neptunyl moieties are directly incorporated into the polyoxotungstate framework *via* Np–O$_{actinyl}$–W interactions.

The structure of the anion in **1** can be thought of as $[W_4O_9]^{6+}$ fused with three $\{NpO_2\}^+$ moieties to yield $[Np_3W_4O_{15}]^{9+}$ with three $[BiW_9O_{33}]^{9-}$ polyoxoanions also attached. Each $[BiW_9O_{33}]^{9-}$ unit bonds to two neptunyl cations in the equatorial plane *via* four unsaturated oxygen atoms (two to each neptunyl moiety) from the open belt region of the polyoxoanion. The remaining two belt-positioned oxygen atoms link into the framework of the $[Np_3W_4O_{15}]^{9+}$ unit, with three of the W atoms in this unit linked to the three $[BiW_9O_{33}]^{9-}$ anions.§ Each neptunyl cation is five coordinate in the equatorial plane with four of the ligating atoms contributed by the polyoxoanions and a water molecule
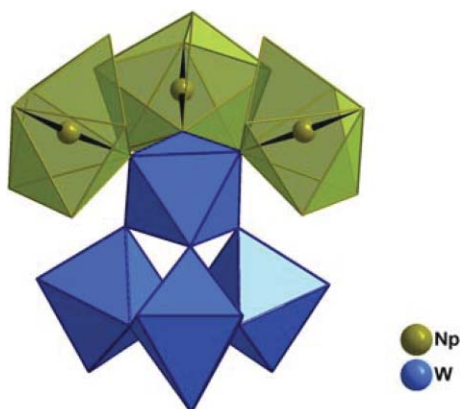

Fig. 3 Polyhedral representation of the central $[Np_3W_4O_{15}]^{9+}$ unit in $[(Np_3W_4O_{15})(H_2O)_3(SbW_9O_{33})_3]^{18-}$ (**2**).

completing the pentagonal bipyramidal geometry. The central $[Np_3W_4O_{15}]^{9+}$ unit is formed through coordination of the three $\{NpO_2\}^+$ moieties *via* axial oxygens to form a face of the central W octahedron. The structural type is very similar to that of the $[(UO_2)_3(H_2O)_6(As_3W_{30}O_{105})]^{15-}$ complex anion characterised by Pope *et al.*[8] This structure, however, does not contain the additional central tungsten addenda atom to which each neptunyl cation is coordinated in **1** and **2**. The difference in behaviour may reflect the poorer donor capacity of the actinyl oxygens in $\{UO_2\}^{2+}$ compared to $\{NpO_2\}^+$, as will be discussed further later in the text.

It might be expected that coordination of the inner neptunyl oxygen atom to W would increase the length of Np–O(axial) bond *versus* the uncoordinated Np–O(axial) bond that points outwards from the cluster. While there is considerable statistical overlap in all six bond lengths it is certainly true that the longest neptunyl bond length (1.99(3) Å) is part of the Np–O–W framework and the shortest neptunyl bond length (1.833(17) Å) belongs to an uncoordinated neptunyl group. In addition, one O(axial)–Np–O(axial) bond angle shows significant distortion from that expected for an isolated neptunyl moiety (172.7(14)°). The equatorial Np–O(terminal) bond distances show a large variation ranging from 2.27(3) Å to 2.54(4) Å, which is comparable to the range in Np^V–O(terminal) bond distances observed in $[Na_2(NpO_2)_2(PW_9O_{34})_2]^{14-}$ (2.336(15)–2.603(16) Å).[12] The three equatorial Np–O(H₂O) bonds have an overall average distance of 2.62(3) Å. The O(axial)–Np–O(equatorial) bond angles range from 82.5(13)° to 94.1(14)° and the adjacent O(equatorial)–Np–O(equatorial) bond angles range from 64.7(11)° to 80.0(11)°, both reflecting significant distortion from ideal pentagonal bipyramidal geometry. The central tungsten atom has W–O bond distances at 2.04(3), 2.03(3) and 2.05(2) Å for the three bonds to oxo neptunyl oxygen atoms and at 1.87(3), 1.77(3) and 1.84(3) Å for the three bonds to oxygen atoms associated with other tungsten addenda atoms, a significant difference. It would appear that the incorporation of $\{NpO_2\}^+$ into the polyoxometalate framework is due to the ability of the neptunyl(V) oxygen to coordinate to other metal cations, *i.e.* 'cation–cation' bonding. Neptunyl(V) axial oxygen coordination to a range of metal cations has been well documented but not, to the best of our knowledge, within a discrete polyoxometalate framework.[18] Bond valence sums for the central W atom (6.0) and the three Np atoms (5.5, 4.6 and 5.4) support the assumption that there have been no changes in oxidation states.[19] Each Np can be considered as an 'addenda type' atom with one terminal oxygen (and additional coordinated H₂O), in a similar fashion to regular addenda atoms in polyoxometalates.

The structure of **2** reveals an asymmetric unit which contains two anionic clusters (**2a** and **2b**) which are both isostructural with **1**, the only major difference being the substitution of Bi with Sb. To a good approximation the bond lengths and angles around the three neptunyl cations in both anions are comparable to those observed for the anion in **1**. However, in **2a** there is no noticeable variation in Np–O(axial) bond lengths on moving from tungsten-bonded to uncoordinated. Nevertheless, there is clear evidence of distortion around the neptunyl(V) centres, with, for example one O(axial)–Np–O(axial) bond angle in **2b** at 169.7(14)°.

The diffuse reflectance spectrum of **1** reveals a broad band centred at 1024 nm and is in good agreement with the solution

spectrum, indicating that the anionic complex structurally characterised is the same as the species originally observed in solution. Higher energy features are also observed, which are more intense than observed in solution, but are still characteristic of a $\{NpO_2\}^+$ complex.[17] The solid state Raman spectrum of **1** reveals a large broad band at 668 cm^{-1}, which we assign to the ν_1 symmetric $\{O=Np=OW\}$ stretch (or stretches), shifted from 767 cm^{-1} for $\{O=Np=O\}^+$ in $[NpO_2(H_2O)_5]^{2+}$.[20] The dramatic decrease in energy of this band on complexation is again indicative of significantly weakened Np=O bonds in the neptunyl(v) moiety on its incorporation into the framework. While the solid state IR spectrum reveals features consistent with the formation of the complex (927 and 850 cm^{-1} for W–O(terminal) and W–O(edge sharing) and 1415 cm^{-1} for NH_4^+) no band could be observed for a ν_3 asymmetric $\{O=Np=OW\}$ stretch (or stretches), probably due to overlapping W–O stretches.

In conclusion we have structurally and spectroscopically characterised a novel class of actinide polyoxotungstate complex in which neptunyl cations form part of the framework of a $\{Np_3W_4O_{15}\}^{9+}$ fragment. These species thus form another group of actinyl oxo-cluster complexes, distinct from equatorially coordinated actinyl heteropolytungstate complexes and recently reported actinyl oxygen clusters. The complete inclusion into a polyoxometalate framework may lead to the exploitation of this class of polyoxotungstate anion (B-type XW_9) in nuclear waste remediation. In addition, there has been a very significant distortion of the neptunyl(v) moiety on incorporation into the cluster, as observed spectroscopically and structurally. We aim to use recent advances in computational polyoxometalate chemistry and open shell actinide chemistry to probe the consequences in regard to neptunyl(v) bonding and electronic structure in collaboration with the Kaltsoyannis group at University College London.

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