

Actinyl chemistry at the Centre for Radiochemistry Research

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Abstract

Increasing our basic chemical knowledge of the actinyl cations ($\{\text{AnO}_2\}^{2+/+}$, where An=U, Np, Pu or Am) is vital for underpinning the development of novel nuclear waste management and nuclear fuel processing technologies, as well as increasing our understanding of actinide behaviour in the environment. Over recent years there have been significant advances made in uranyl, neptunyl and plutonyl chemistry, with the main focus on uranyl. At the Centre for Radiochemistry Research (CRR), University of Manchester, there are ongoing projects investigating the coordination chemistry of the actinyl cations. These projects are undertaken at the CRR and at higher specific activity alpha facilities accessed through Nexia Solutions and the EU ACTINET programme, as well as concomitant computational chemistry projects at University College London. Recent discoveries have included the complexation of transuranic actinyl cations with tri-lacunary heteropolytungstate ligands and spectroscopic and structural evidence for the direct coordination of the pertechnetate anion to $\{\text{UO}_2\}^{2+}$.

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1. Introduction

The linear dioxo actinyl cations, $\{\text{AnO}_2\}^{x+}$ ($x = 1$ or 2), dominate the +V and +VI chemistry of the mid actinide elements (U, Np, Pu and Am). Usually, 4–6 additional ligands coordinate in the equatorial plane yielding bipyramidal geometry [1]. An increased understanding of actinyl chemistry will underpin a range of nuclear applications, from novel fuel processing technologies through to environmental waste remediation. Of particular relevance are $\{\text{U}^{\text{VI}}\text{O}_2\}^{2+}$ and $\{\text{Np}^{\text{V}}\text{O}_2\}^+$, the dominant forms of U and Np, respectively. In addition, $\{\text{PuO}_2\}^+$ is thought to have environmental significance [2].

By far the most commonly studied actinyl cation is $\{\text{UO}_2\}^{2+}$, primarily due to its chemical stability and the comparatively low radiological hazard associated with uranium based research.

There has been a significant increase in the amount of uranium chemistry undertaken since 2000 [3], particularly with reference to novel uranyl containing materials [4]. Recent advances have include the incorporation of the uranyl moiety into liquid crystals [5], the preparation of uranyl selenate nanotubules [6] and structural evidence for $\{\text{UO}_2\}^{2+}$ cation–cation interactions [7]. Although prone to disproportionation, there are still ongoing investigations into $\{\text{UO}_2\}^+$ chemistry, both generated electrochemically in solution [8] and the solid state structural characterisation of both $[\text{UO}_2(\text{OPPh}_3)_4](\text{OTf})$ [9] and $\{[\text{UO}_2\text{Py}_5][\text{KI}_2\text{Py}_2]\}_n$ [10]. Finally, bis-imido analogues of the uranyl(VI) cation, $\{\text{U}(\text{NR})_2\}^{2+}$, have recently been synthesised and used to probe the role of the 5f and 5d U orbitals in bonding [11].

The higher specific activity of the transuranium elements restricts experimental chemistry to specialist facilities, but significant advances in coordination chemistry are still feasible. A combined structural and spectroscopic study on a neptunyl(V) diamide system has yielded the first experimental evidence in

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support of theoretical calculations on the main $\{\text{NpO}_2\}^+$ f-f transition which is forbidden in high symmetry species [12]. There have been quite a few neptunyl structural studies, particularly with relevance to $\{\text{NpO}_2\}^+$ ‘cation–cation’ interactions [13]. In contrast, the first structural characterisation of $\{\text{PuO}_2\}^{2+}$ [14], and indeed $\{\text{PuO}_2\}^+$ [15], complexes have only recently been reported. This lack of basic knowledge is also reflected in solution chemistry, with a recent study on $\{\text{PuO}_2\}^{2+}$ hydrolysis providing valuable new understanding [16]. Perhaps the most interesting recent development in neptunyl chemistry has been the synthesis of $\{\text{NpO}_2\}^+$ (and indeed $\{\text{UO}_2\}^{2+}$) peroxide nanoclusters from alkaline peroxide solution [17]. Finally, while there is no spectroscopic or structural evidence for $\{\text{PaO}_2\}^+$ a recent EXAFS study points to the existence of a Pa(V) single oxo species, $\{\text{PaO}\}^{3+}$ [18].

2. Actinyl chemistry at the Centre for Radiochemistry Research

The Centre for Radiochemistry Research (CRR), created in 1999, has followed on from a proud tradition of radiochemical research at the University of Manchester. A major facility refurbishment in 2001 has equipped the laboratories to the extent that $^{238/235}\text{U}$, ^{232}Th , ^{237}Np and ^{99}Tc coordination chemistry research can be conducted safely. In addition, the laboratory has access to specialist alpha active facilities, both in the UK and the EU, with collaborative links through Nexia Solutions and the ACTINET programme, respectively. Collaborative research programmes have also recently been initiated with the computational actinide chemistry research group at University College London, led by Nik Kaltsoyannis.

Actinyl chemical research has been a major component of studies undertaken at the CRR over the past 7 years. Bonding in the uranyl moiety has been probed by coordination to various N-donor ligands (e.g. benzaminate and bis-iminophosphorane). This chemistry has led to the formation of a complex with a U-methylene bond, coordination of an activated Lewis basic uranyl oxygen to a Lewis acid and direct displacement of phosphine for phosphinimine ligands, the latter also studied in the analogous $\{\text{NpO}_2\}^{2+}$ system [19–23]. XAS has been used to prove that the bioreduction of $\{\text{UO}_2\}^{2+}$ to U(IV) can occur via a $\{\text{UO}_2\}^+$ intermediate [24] and that $\{\text{UO}_2\}^{2+}$ can form oligomeric chloride complexes in certain high temperature alkali metal chloride molten salt systems [25–26]. Finally, there have been detailed investigations into the coordination chemistry of polyoxometalates with actinyl cations and weakly coordinating anions with uranyl.

3. Actinyl coordination by tri-lacunary heteropolyoxotungstate ligands

In 1999, Pope et al. showed that the tri-lacunary heteropolyoxotungstate anion $[\text{A-PW}_9\text{O}_{34}]^{9-}$, will react with the uranyl cation to form the sandwich complex $[\text{M}_2(\text{UO}_2)_2(\text{PW}_9\text{O}_{34})_2]^{12-}$, where $\text{M} = \text{Na}^+$, K^+ or NH_4^+ [27]. Analogous closed sandwich type complexes can be prepared

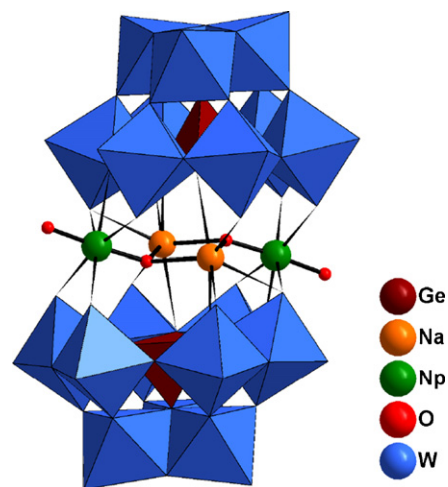


Fig. 1. Polyhedra representation of $[\text{Na}_2(\text{Np}^{\text{V}}\text{O}_2)_2(\text{GeW}_9\text{O}_{34})_2]^{16-}$.

with other A-type ligands, e.g. $[\text{SiW}_9\text{O}_{34}]^{10-}$ [28] whereas B type tri-lacunary ligands form open sandwich type complexes with two uranyl cations, which are also coordinated to one water molecule each, e.g. $[(\text{UO}_2)(\text{H}_2\text{O})_2(\text{TeW}_9\text{O}_{33})_2]^{12-}$ [29]. However, different structural types can also be formed by turning to different ligand systems, for instance the reaction of $[\text{P}_2\text{W}_{15}\text{O}_{59}]^{12-}$ with $\{\text{UO}_2\}^{2+}$ results in the encapsulation of polyoxo-uranium clusters within $[(\text{UO}_2)_{12}(\mu_3\text{-O})_4(\mu_2\text{-H}_2\text{O})_{12}(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{32-}$ [30].

Over the past 4 years we have also started to investigate the coordination chemistry of transuranic actinyl cations with tri-lacunary heteropolyoxotungstate ligands. Recently we have obtained structural evidence that $\{\text{NpO}_2\}^{2+}$ forms complexes with A and B type ligands which are analogous to those previously observed for $\{\text{UO}_2\}^{2+}$ [31]. We have also prepared the $\{\text{NpO}_2\}^+$ analogue of the original Pope et al. complex for both $[\text{PW}_9\text{O}_{34}]^{9-}$ [32] and $[\text{GeW}_9\text{O}_{34}]^{10-}$ (see Fig. 1) [31]. In addition, by comparing the near infra-red solution spectra of isoelectronic $\{\text{NpO}_2\}^+$ and $\{\text{PuO}_2\}^{2+}$ systems it seems likely that analogous plutonyl(VI) can also be prepared with A-type ligands [33]. B-type ligand complexation to plutonyl(VI) has also been observed [34]. However, the reaction of the B-type anions $[\text{BiW}_9\text{O}_{33}]^{9-}$ and $[\text{SbW}_9\text{O}_{33}]^{9-}$ with $\{\text{NpO}_2\}^+$ results in the formation of $[(\text{Np}_3\text{W}_4\text{O}_{15})(\text{H}_2\text{O})_3(\text{BiW}_9\text{O}_{33})_3]^{18-}$ and $[(\text{Np}_3\text{W}_4\text{O}_{15})(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})_3]^{18-}$ which both contain three neptunyl(V) moieties actually encapsulated within heteropolyoxotungstate frameworks [35]. One axial oxygen from each $\{\text{NpO}_2\}^+$ forms one face of a WO_6 octahedron, a WO_6 octahedron that is not present in the almost identical uranyl complex $[(\text{UO}_2)_3(\text{H}_2\text{O})_6\text{As}_3\text{W}_{30}\text{O}_{105}]^{15-}$ [36]. The central $[\text{Np}_3\text{W}_4\text{O}_{15}]^{9+}$ core of the Bi containing species is shown in Fig. 2.

There is both structural and spectroscopic (Raman and near infra red absorption) evidence that tri-lacunary heteropolyoxotungstates coordinate very strongly to actinyl cations, in a similar manner to hydroxide. These ligands are thus good candidates to probe bonding in the actinyl moiety across the U, Np and Pu series which is the goal of a current joint experimental (CRR

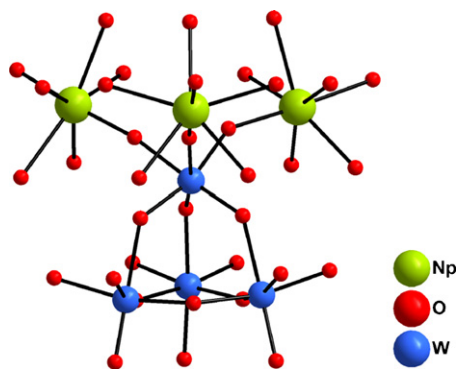


Fig. 2. Ball and stick representation of the central $[\text{Np}_3\text{W}_4\text{O}_{15}]^{9+}$ group in $[(\text{Np}_3\text{W}_4\text{O}_{15})(\text{H}_2\text{O})_3(\text{BiW}_9\text{O}_{33})_3]^{18-}$.

and Nexia Solutions) and computational (University College London) programme.

4. Uranyl coordination with weakly co-ordinating anions

At the opposite extreme from the interaction between actinyl cations and strongly coordinating ligands we have also been studying the interaction between uranyl(VI) and weakly coordinating ligands. This interest first stemmed from our attempts to understand how the pertechnetate anion co-extracts with actinide cations in the PUREX process (Plutonium and Uranium Recovery by Extraction) in the presence of a P=O donor ligand co-extractant (tri-*n*-butyl phosphate). Initial studies focussed on the non-radioactive analogue, perrhenate. A series of uranyl complexes with coordinated perrhenato ligand(s) were prepared with structure dictated by the nature of the additional P=O donor ligand (phosphate or phosphine oxide) [37–39]. The different structural types are outlined in Fig. 3. In addition, we have prepared isostructural pertechnetato complexes where the P=O donor ligand is triphenyl phosphine oxide (TPPO) and bis(diphenylphosphine)methane (DPPMO₂), forming $[\text{UO}_2(\text{TcO}_4)_2(\text{TPPO})_3]$ and $[\text{UO}_2(\text{TcO}_4)(\text{DPPMO}_2)_2][\text{TcO}_4]$, respectively [39–40]. In the case of the latter complex, ⁹⁹Tc and

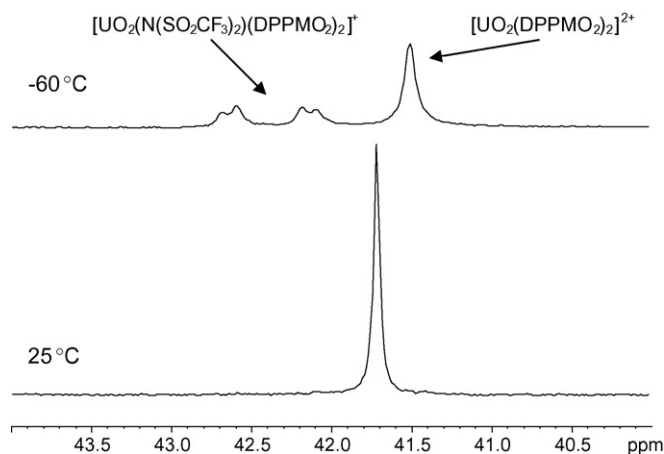


Fig. 4. ^{31}P $\{^1\text{H}\}$ NMR spectrum of $[\text{UO}_2(\text{N}(\text{SO}_2\text{CF}_3)_2)(\text{DPPMO}_2)_2]^+$ ($\text{N}(\text{SO}_2\text{CF}_3)_2$) in CD_2Cl_2 .

^{31}P NMR indicate that $[\text{TcO}_4]^-$ remains coordinated in organic solvent which may give some indication of the mechanism of pertechnetate extraction in the PUREX process.

Attempts to form uranyl complexes with $[\text{BF}_4]^-$ analogous to the $[\text{MO}_4]^-$ ($\text{M} = \text{Re}$ or Tc) species resulted only in fluoride abstraction by fluorophilic uranium [41]. However, considerable success was obtained with the $[\text{UO}_2(\text{X})(\text{DPPMO}_2)_2]\text{X}$ system where two bidentate phosphine oxide ligands and monodentate weakly coordinating anion sit in the uranyl equatorial plane. To date we have been able to coordinate a range of weakly coordinating anions: $\text{X} = [\text{ReO}_4]^-$, $[\text{TcO}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$ and $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ (bistriflimide) as well as Cl^- [40,42]. Perhaps of most interest is the $[\text{UO}_2(\text{N}(\text{SO}_2\text{CF}_3)_2)(\text{DPPMO}_2)_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ complex in which the bistriflimide anion coordinates in a monodentate fashion to the uranium metal centre through a sulphonyl oxygen. Our initial interest in bistriflimide, was as an ionic liquid anion and although it does coordinate to $\{\text{UO}_2\}^{2+}$ in the solid state there is ^{31}P NMR evidence to suggest that $[\text{UO}_2(\text{N}(\text{SO}_2\text{CF}_3)_2)(\text{DPPMO}_2)_2]^+$ is in equilibrium with the dicationic species $[\text{UO}_2(\text{DPPMO}_2)_2]^{2+}$ in solution (Fig. 4).

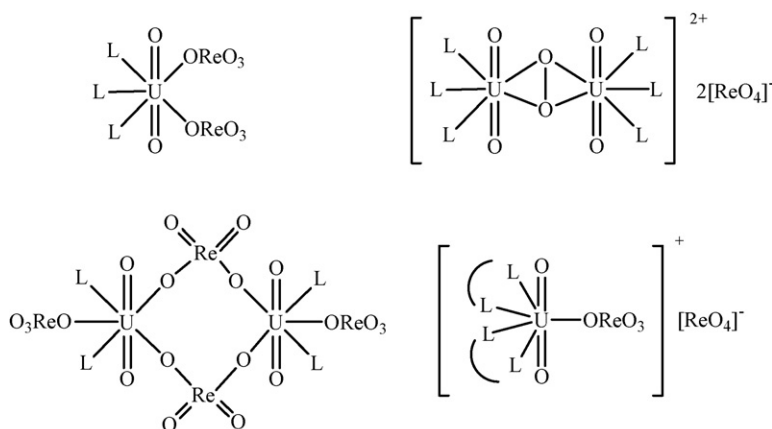


Fig. 3. Different structural types of uranyl/perrhenate complex (where L = phosphate or phosphine oxide).

5. Conclusions

Recent studies have shown that there is still much to learn about the chemistry of the actinyl cations. At the CRR we have the capability to undertake coordination chemistry with uranium and neptunium (as well as technetium) and have developed links to access plutonium chemistry in specialist facilities. We have undertaken several distinctive investigations into actinyl coordination chemistry to gain a better understanding of electronic structure and bonding as well as further insight into radionuclide speciation under environmental and fuel processing conditions.

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