Coordination of pertechnetate [TcO₄]⁻ to actinides†

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The ability of [TcO₄]⁻ to coordinate directly to tetra- and hexa-valent actinides in the presence of organic P=O ligands is confirmed in the crystallographically characterised complexes [UO₂(TcO₄)₂(Ph₃PO)₃] (**1**) and [Th(TcO₄)₄(ⁿBu₃PO)₄] (**2**).

During the PUREX process (*P*lutonium and *U*ranium *R*ecovery by *EX*traction), the pertechnetate anion can co-extract with tetra-valent and hexa-valent actinides, An(VI/IV) and Zr(IV) impinging on the efficient separation and recycling of U and Pu.[1] The extracting media are a nitric acid (∼ 3 M) aqueous phase and a tri-*n*-butyl phosphate (TBP)–odourless kerosene (OK) organic phase. Despite previous exploration of An⁴⁺ and {AnO₂}²⁺ solution speciation in [NO₃]⁻–[TcO₄]⁻–R₃PO systems,[2–4] it is not known whether the pertechnetate anion co-extracts as a ligand directly bonded to an actinide or as a non-coordinated counter anion.

A timely report, containing the structurally characterised [(NpO₂)₂(TcO₄)₂.3H₂O)], presents direct evidence of [TcO₄]⁻ acting as a coordinating ligand, to either a d- or f-block transition metal, for the first time.[5] There are no examples of [TcO₄]⁻ coordinating directly to an actinide in the presence of competing P=O ligands. In contrast, [ReO₄]⁻ coordination chemistry has been studied extensively for d-transition metals and lanthanides.[6] We have recently extended this chemistry to U(VI)[7] and U(IV)[8] with both coordinating perrhenate and P=O donor ligands, including [UO₂(ReO₄)₂(Ph₃PO)₃].[7] The comparative dearth of related pertechnetate chemistry is almost certainly due to the radioactivity of Tc isotopes§ and the scarcity of Tc-containing starting reagents.[9]

Our synthetic entry into actinide/pertechnetate chemistry involves the metathesis reaction of AgTcO₄, prepared from commercially available [NH₄][TcO₄] and AgNO₃,[10] with an actinide chloride (Scheme 1). An organic P=O ligand {Ph₃PO (TPPO) or ⁿBu₃PO (TBPO)} can be added before or after reaction with AgTcO₄ (Scheme 1). We have concentrated on actinides in their highest oxidation states ({UO₂}²⁺ and Th⁴⁺) because of the

redox activity of [TcO₄]⁻.[11] This methodology has provided a high yield route to the complexes [UO₂(TcO₄)₂(TPPO)₃] (**1**) and [Th(TcO₄)₄(TBPO)₄] (**2**). (For experimental details see ESI.¶)

An ORTEP representation of the structure of **1** is shown in Fig. 1.‖ The uranium atom lies at the centre of a pentagonal bipyramidal structure; the oxo-ligands occupy the axial positions, with three TPPO and two monodentate pertechnetate ligands bonded in the equatorial plane through U–O bonds. The U=O bond lengths (1.765(2) and 1.768(2) Å) are typical for equatorially five-coordinate uranyl complexes.[12] The U–O$_{TPPO}$ bond lengths (2.379(2) to 2.397(2) Å) are significantly longer than other complexes of the type [UO₂X₂(TPPO)$_n$] (X = monoanionic, U–O$_{TPPO}$, 2.334(16) to 2.297(2) Å)[13–18] but are comparable to the isomorphous perrhenate complex [UO₂(ReO₄)₂(TPPO)₃] (U–TPPO, 2.374(4) to 2.399(4) Å).[7] The U–O$_{pertechnetate}$ bond lengths (2.382(2) Å) are comparable to the only other structurally characterised example of pertechnetate coordinating to an actinide [(NpO₂)₂(TcO₄)₂·3H₂O)] (Np–O$_{pertechnetate}$, 2.325(6) to 2.396(6) Å).[5]

The addition of TBPO to a solution of Th(TcO₄)₄ (4 : 1 ratio) in methanol gives [Th(TcO₄)₄(Bu₃PO)₄] (**2**) as a white solid that recrystallises from dichloromethane solution providing single crystals suitable for X-ray diffraction.‖ Compound **2** is the first example of a tetra-valent actinide coordinated to pertechnetate. The crystallographic study revealed two reversible transitions to different space groups, as the temperature is reduced from 293 to 100 K. At 293 K, the crystal is cubic, space group *I*4̄3*m*, but the refined structure shows considerable disorder. At 230 K, the symmetry reduces to C-centred orthorhombic, space group *Cmc*2₁; when the temperature is reduced still further, to 205 K and below, the symmetry reduces to the primitive orthorhombic space group, *Pbc*2₁, which is the structure reported here (Fig. 2). The structure of **2** can be described as a distorted triangular dodecahedron
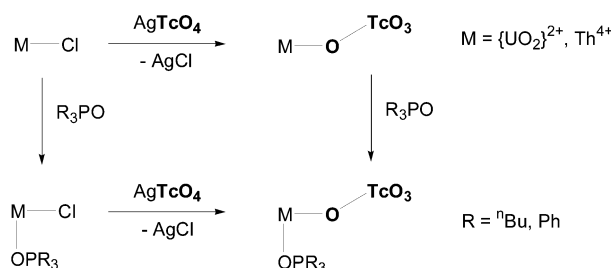
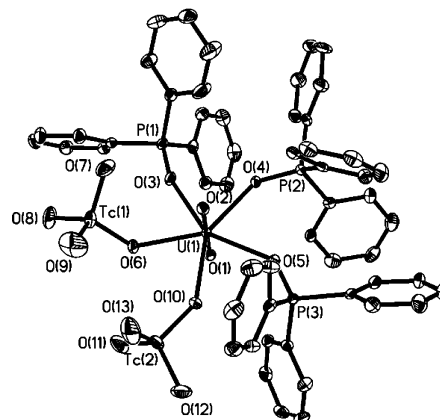**Scheme 1** Synthetic strategy for the formation of actinide–R₃PO–pertechnetate complexes.

Fig. 1 ORTEP representation of [UO₂(TcO₄)₂(TPPO)₃] (**1**) with H atoms omitted (50% probability ellipsoids). Selected bond lengths (Å): U(1)–O(1) 1.765(2), U(1)–O(2) 1.768(2), U(1)–O(3) 2.397(2), U(1)–O(6) 2.381(2), Tc(1)–O(6) 1.755(2), Tc(1)–O(7) 1.696(3), P(1)–O(3) 1.501(2). Selected bond angles (deg): O(1)–U(1)–O(2) 179.32(11), O(1)–U(1)–O(3) 86.87(10), O(1)–U(1)–O(6) 94.35(10), O(6)–Tc(1)–O(7) 109.54(13).

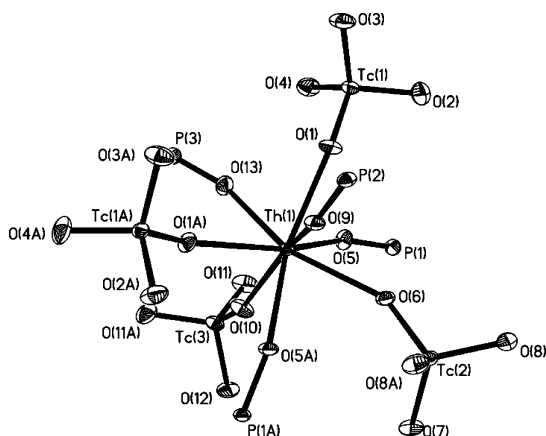**Fig. 2** ORTEP representation of [Th(TcO$_4$)$_4$(TBPO)$_4$] (**2**) with H and C atoms omitted for clarity (30% probability ellipsoids). Selected bond lengths (Å): Th(1)–O(1) 2.465(8), Tc(1)–O(1) 1.758(8), Th(1)–O(9) 2.347(8), P(2)–O(9) 1.519(8), Tc(1)–O(3) 1.702(9). Selected bond angles (deg): O(1)–Tc(1)–O(3) 107.9(5), Th(1)–O(9)–P(2) 156.1(5), Th(1)–O(1)–Tc(1) 146.8(5).

according to Haigh,[19] with four coordinated pertechnetates and four TPPO ligands placed alternately at the vertices; typical of eight coordinate complexes of the type [An(X)$_4$(Y)$_4$]. The Th–O$_{TBPO}$ bond lengths are intermediate (2.336(7) to 2.372(8) Å) between those in [Th(Ph$_2$P(S)O)$_4$(EtOH)$_4$] (2.291(1) Å) and [ThCl$_4$(TPPO)$_3$] (U–O$_{TPPO}$, 2.377 Å).[20] The Th–O$_{pertechnetate}$ bond lengths (2.440(9) to 2.465(8) Å) are longer than those in **1** as expected for the larger ionic radius of Th^{4+}.[21]

Proving that the crystal structures of **1** and **2** were representative of the bulk reaction products was challenging because the radiological hazards of ^{99}Tc prohibited elemental analysis or powder diffraction studies. However, a vibrational spectroscopic analysis was performed. It is possible to assign the symmetric (v_1) and asymmetric (v_3) bands for {UO$_2$}$^{2+}$ and [TcO$_4$]$^-$ of **1** by comparing the Raman and infra-red spectra with [UO$_2$(ReO$_4$)$_2$(TPPO)$_3$] (see ESI).[7] While all the coordinated TPPO and uranyl (v_1, 826; v_3, 920 cm^{-1}) bands are essentially unchanged, those for the tetraoxo-anion shift considerably on going from [UO$_2$(ReO$_4$)$_2$(TPPO)$_3$] (v_1, 979; v_3, 921 and 883 cm^{-1}) to **1** (v_1, 907; v_3, 890 and 857 cm^{-1}). A similar drop in stretching frequency is observed on going from AgReO$_4$ (v_1, 942; v_3, 899 and 862 cm^{-1}) to AgTcO$_4$ (v_1, 880; v_3, 896 and 847 cm^{-1}).[10] In the absence of aromatic and uranyl groups, assignment of the pertechnetate stretches in **2** is more straightforward (v_1, 921; v_3, 911 and 866 cm^{-1}). The variation in stretching energies for [TcO$_4$]$^-$ in **1** *vs.* **2** indicate different M-O$_{TC}$ (M = U, Th) bonding strengths, with the greater probability of stronger coordination in **1** *vs.* **2** due to the higher effective charge density : anionic ligand ratio in the former.[22]

In conclusion, we have shown that AgTcO$_4$ is a very useful reagent for probing the coordination chemistry of pertechnetate in demonstrating that [TcO$_4$]$^-$ will readily coordinate to tetra- and hexa-valent actinide centres. Co-complexation with P=O ligands is significant in terms of the PUREX process; obviously solution speciation is of more direct relevance. Variable temperature ^{31}P and ^{99}Tc NMR spectroscopy (see ESI) are inconclusive, although broadening of the pertechnetate signal could indicate a reduction in symmetry on going from T_d (uncoordinated) to C_{3v} (monodentate coordination) point symmetry because of the quadrupolar ^{99}Tc nucleus (I = 9/2). We expect that the interaction of the oxo-anion will depend on the Lewis basicity of the competing P=O ligand, and thus predict pertechnetate to interact more strongly with actinides in the presence of the less Lewis basic TBP {(^{n}BuO)$_3$PO} ligand, used in the PUREX process. Further solution speciation studies are in progress.

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