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The unusual stability of $[NpO_2Cl_4]^{2-}$: Synthesis and characterisation of $[NpO_2(DPPMO_2)_2Cl]_2[NpO_2Cl_4]$ and $[Ph_3PNH_2]_2[NpO_2Cl_4]$

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ABSTRACT

The $[NpO_2(DPPMO_2)_2Cl][NpO_2Cl_4]$ complex (where $DPPMO_2$ = bis(diphenylphosphino)-methanedioxide) contains the linear neptunyl group, $\{NpO_2\}^{2+}$, with two bidentate P=O donor ligands. Coordinating anion Cl^- fills the fifth equatorial coordination site yielding a complex of general formula $[NpO_2(DPPMO_2)_2X]_2[Y]$ (**1**) (where $X = Cl^-$ and $Y = [NpO_2Cl_4]^{2-}$. Reaction between our newly prepared neptunium starting material $[NpO_2Cl_2(thf)]_n$ and phosphinimine ligand produced crystals of $[Ph_3PNH_2]_2[NpO_2Cl_4]$ (**2**). Compounds **1** and **2** have been structurally characterised.

RÉSUMÉ

Le complexe $[NpO_2(DPPMO_2)_2Cl][NpO_2Cl_4]$ (où $DPPMO_2$ = bis(diphenylphosphino)methanedioxide), contient le groupement linéaire $\{NpO_2\}^{2+}$, avec deux ligands bidentés P=O. L'anion Cl^- occupe le cinquième site de coordination dans le plan équatorial pour former le complexe de formule générale $[NpO_2(DPPMO_2)_2X]_2[Y]$ (1) (ou $X = Cl^-$ et $Y = [NpO_2Cl_4]^{2-}$). La réaction de notre récent précurseur $[NpO_2Cl_2(thf)]_n$ avec le ligand phosphinimine a produit des cristaux $[Ph_3PNH_2]_2[NpO_2Cl_4]$ (**2**). Les structures cristallines de **1** et **2** ont été déterminées.

1. Introduction

Interest in transuranic coordination chemistry is driven not only by scientific curiosity to understand the fundamentals of all of the accessible elements in the Periodic Table, but also through a recognition that a comprehensive grasp of the basic electronic structure, bonding, and reactivity of the early to middle actinides (Th-Cm) is vital to support the development of advanced nuclear fuel cycles, and novel separation and waste remediation processes that are crucial to allow nuclear power to continue to play a significant role in meeting global energy demands [1].

Although investigations on aqueous and non-aqueous uranium chemistry remain dominant [2], research on transuranium chemistry is witnessing some great developments, but our current understanding of the electronic structure and bonding interaction of these elements is from aqueous systems for which the choice of ligands are limited to water-stable "hard" donors that will displace the water/hydroxy ligands and coordinate to the metal centre [3]. However, despite the synthesis of promising precursors [4], anhydrous chemistry of Np and Pu is still in the early stages of development.

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Phosphine oxides have been used in the nuclear industry as extraction agents for waste reprocessing (e.g., PUREX process). Hence, academic research into the coordination chemistry of f-elements with P═O donor ligands has been particularly intense. Many research groups have turned their attention to the bidentate bis(diphenylphosphino)methane dioxide ($DPPMO_2$) ligand and its coordination with uranium [5], but no transuranic complexes have been reported so far. Previously, we have shown that the weakly coordinating oxoanions $[ReO_4]^-$ and $[TcO_4]^-$ (as well as Cl^-) will fill a fifth coordination site yielding complexes of general formula $[UO_2(DPPMO_2)_2X][X]$ (where $X = [ReO_4]^-$, $[TcO_4]^-$ and Cl^-), with the X^- anion acting in both monodentate coordinated and uncoordinated modes [5b,f]. As part as our investigations into transuranic phosphine oxide complexes, we prepared a neptunyl complex with the $DPPMO_2$ ligand as $[NpO_2(DPPMO_2)_2Cl]_2[NpO_2Cl_4]$ (**1**).

Further investigations to test the reactivity and stability of our recently prepared anhydrous precursor $[NpO_2Cl_2(thf)]_n$ under different experimental conditions have been carried out to compare with the reactivity of $[UO_2Cl_2(thf)_2]_2$. Unlike the synthesis of $[UO_2Cl_2(thf)_2]_2$, the preparation of $[NpO_2Cl_2(thf)]_n$ remains challenging because of the rapid reduction of Np(VI) to Np(V) in organic solvents. Solid-state characterisation of both compounds showed differences between both complexes with the neptunyl compound crystallising as a polymer compared to a dimer for the uranyl species [4b,4c]. Our group has extensively studied the reactivity of $[UO_2Cl_2(thf)_2]_2$ with phosphorus containing ligands R_3PX (R═Cy, Ph and X═O, NH) [6] so we were particularly interested in comparing the reactivity of phosphinimine ligands with $[NpO_2Cl_2(thf)]_n$. Reaction of $[NpO_2Cl_2(thf)]_n$ with Ph_3PNH led to the characterisation of $[Ph_3PNH]_2[NpO_2Cl_4]$ (**2**).

Both crystals structures of **1** and **2** indicated that the anion $[NpO_2Cl_4]^{2-}$ seems to be unusually stable in aprotic solvents. We comment here on the relative the stability of $[AnO_2Cl_4]^{2-}$ along the actinides series and identify the conditions in which this anion is chemically stable.

2. Results and discussions

2.1. $[NpO_2(DPPMO_2)_2Cl]_2[NpO_2Cl_4]$

A MeOH solution of $DPPMO_2$ (2 eq.) was added to a solution of Np(VI) in HCl yielding a pale yellow solution. Crystals of $[NpO_2(DPPMO_2)_2Cl]_2[NpO_2Cl_4]$ (Fig. 1) were obtained by slow evaporation of the solvent at room temperature. To our knowledge, this complex is the first neptunium compound containing another Np(VI) counterion. The structure of **1** revealed a neptunium(VI) mixed salt comprising a dianionic complex $[NpO_2Cl_4]^{2-}$ (**1a**) and two monocationic pentagonal bipyramidal $[NpO_2(DPPMO_2)_2Cl]^+$ (**1b**) (Fig. 1). Selected bond distances and angles are given in Table 1.

The Np atom in **1a** is located on an inversion centre, with half the molecule contained in the unit cell, exhibiting identical Np═O distances (1.751(7) Å), which are within the range expected for Np–O$_{yl}$ bond lengths [7]. Np–Cl distances are different with Np(2)–Cl(2) (2.652(3) Å) being slightly shorter than Np(2)–Cl(3) (2.666(3) Å). The structure of neptunyl tetrachloride complex **1a** has previously been reported in the mixed valence species $Cs_7[Np^VO_2][Np^{VI}O_2]_2Cl_{12}$, [8], $Cs_2[NpO_2Cl_4]$ [9] and $[NBu_4]_2[NpO_2Cl_4]$ [10]. Comparison of the bond lengths in **1a** with those found in $Cs_7[Np^VO_2][Np^{VI}O_2]_2Cl_{12}$ is precluded due to the extensive disorder present in the structure in the mixed valence compound. In contrast with **1a**, in $[NBu_4]_2[NpO_2Cl_4]$, the Np–O bonds are inequivalent by symmetry but the Np–O distances (1.733(5) and 1.740(6) Å) are indistinguishable and the O═Np═O angle is close to linearity (178.6(3)°) as in **1a** (180°).

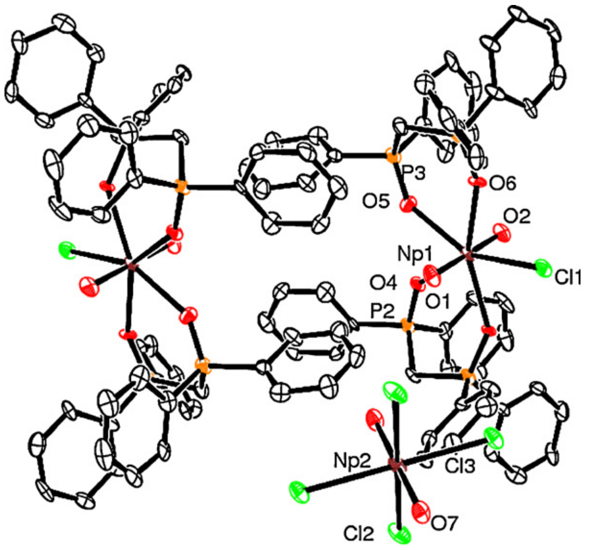

Fig. 1. ORTEP representation of $[NpO_2(DPPMO_2)_2Cl]_2[NpO_2Cl_4]$ (**1**).

To the best of our knowledge, $[NpO_2(DPPMO_2)_2Cl]^+$ (**1b**) is the first seven-coordinated neptunium(VI) complex reported so far. In **1b**, the Np–O$_{yl}$ distances (average 1.769(8) Å) are statistically similar to the one found in **1a** and other structurally characterised neptunyl complexes (1.767(10) Å for $[NpO_2Cl_2(thf)]_n$ [4b], 1.739(10) Å and 1.751(18) Å for $[NpO_2Cl_2(TPPO)(NO_3)]$ and $[NpO_2Cl_2(TPPO)_2]$ [11] respectively). An═O distances are statistically the same as the one observed in seven coordinated uranyl-DPPMO complexes that have U═O bond distances of average 1.7555(12) Å [5a,5e]. The O═Np═O unit is linear (179.4(4)°). The Np–Cl bond distance of 2.670(3) Å is

Table 1
Selected bond lengths [Å] and angles [°] for **1.**

Bond length (Å)		Bond angle (°)	
1b			
Np(1)-O(1)	1.766(8)	O(1)-Np(1)-O(2)	179.4(4)
Np(1)-O(2)	1.773(8)		
Np(1)-Cl(1)	2.670(3)		
Np(1)-O(3)	2.388(7)		
Np(1)-O(4)	2.415(7)		
Np(1)-O(5)	2.373(8)		
Np(1)-O(6)	2.381(7)		
1a			
Np(2)-O(7)	1.751(7)	O(7)-Np(2)-O(7)	180.0(5)
Np(2)-Cl(2)	2.652(3)	Cl(3)-Np(2)-Cl(3)	180
Np(2)-Cl(3)	2.666(3)		