



Full paper/Mémoire

## The unusual stability of $[\text{NpO}_2\text{Cl}_4]^{2-}$ : Synthesis and characterisation of $[\text{NpO}_2(\text{DPPMO}_2)_2\text{Cl}]_2[\text{NpO}_2\text{Cl}_4]$ and $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4]$

Stéphanie M. Cornet<sup>a,\*</sup>, Michael P. Redmond<sup>a</sup>, David Collison<sup>b</sup>, Clint A. Sharrad<sup>a</sup>,  
Madeleine Helliwell<sup>b</sup>, John Warren<sup>c</sup>

<sup>a</sup> Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

<sup>b</sup> School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

<sup>c</sup> Department of Chemistry, University of Bath, Bath BA2 7AY, UK

## ARTICLE INFO

## Article history:

Received 5 February 2010

Accepted after revision 14 April 2010

Available online 3 June 2010

Dedicated to Philip Day.

## Keywords:

Neptunium

Bis(diphenylphosphino)methane dioxide

Neptunyl tetrachloride

Single crystal X-Ray diffraction

## Mots clés :

Neptunium

Bis(diphenylphosphino)methane dioxide

Neptunyl tetrachloride

Diffraction rayon X

## ABSTRACT

The  $[\text{NpO}_2(\text{DPPMO}_2)_2\text{Cl}][\text{NpO}_2\text{Cl}_4]$  complex (where  $\text{DPPMO}_2 = \text{bis}(\text{diphenylphosphino})\text{-methanedioxide}$ ) contains the linear neptunyl group,  $\{\text{NpO}_2\}^{2+}$ , with two bidentate P=O donor ligands. Coordinating anion  $\text{Cl}^-$  fills the fifth equatorial coordination site yielding a complex of general formula  $[\text{NpO}_2(\text{DPPMO}_2)_2\text{X}]_2[\text{Y}]$  (**1**) (where  $\text{X} = \text{Cl}^-$  and  $\text{Y} = [\text{NpO}_2\text{Cl}_4]^{2-}$ ). Reaction between our newly prepared neptunium starting material  $[\text{NpO}_2\text{Cl}_2(\text{thf})]_n$  and phosphinimine ligand produced crystals of  $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4]$  (**2**). Compounds **1** and **2** have been structurally characterised.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## R É S U M É

Le complexe  $[\text{NpO}_2(\text{DPPMO}_2)_2\text{Cl}][\text{NpO}_2\text{Cl}_4]$  (où  $\text{DPPMO}_2 = \text{bis}(\text{diphenylphosphino})\text{-methanedioxide}$ ), contient le groupement linéaire  $\{\text{NpO}_2\}^{2+}$ , avec deux ligands bidentés P=O. L'anion  $\text{Cl}^-$  occupe le cinquième site de coordination dans le plan équatorial pour former le complexe de formule générale  $[\text{NpO}_2(\text{DPPMO}_2)_2\text{X}]_2[\text{Y}]$  (**1**) (ou  $\text{X} = \text{Cl}^-$  et  $\text{Y} = [\text{NpO}_2\text{Cl}_4]^{2-}$ ). La réaction de notre récent précurseur  $[\text{NpO}_2\text{Cl}_2(\text{thf})]_n$  avec le ligand phosphinimine a produit des cristaux  $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4]$  (**2**). Les structures cristallines de **1** et **2** ont été déterminées.

© 2010 Académie des sciences. Publié par Elsevier Masson SAS. Tous droits réservés.

## 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.

\* Corresponding author.

E-mail address: [Stephanie.Cornet@manchester.ac.uk](mailto:Stephanie.Cornet@manchester.ac.uk) (S.M. Cornet).

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<sub>2</sub>) 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<sub>4</sub>]<sup>−</sup> and [TcO<sub>4</sub>]<sup>−</sup> (as well as Cl<sup>−</sup>) will fill a fifth coordination site yielding complexes of general formula [UO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>X][X] (where X = [ReO<sub>4</sub>]<sup>−</sup>, [TcO<sub>4</sub>]<sup>−</sup> and Cl<sup>−</sup>), with the X<sup>−</sup> 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<sub>2</sub> ligand as [NpO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>Cl]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] (**1**).

Further investigations to test the reactivity and stability of our recently prepared anhydrous precursor [NpO<sub>2</sub>Cl<sub>2</sub>(thf)]<sub>n</sub> under different experimental conditions have been carried out to compare with the reactivity of [UO<sub>2</sub>Cl<sub>2</sub>(thf)<sub>2</sub>]<sub>2</sub>. Unlike the synthesis of [UO<sub>2</sub>Cl<sub>2</sub>(thf)<sub>2</sub>]<sub>2</sub>, the preparation of [NpO<sub>2</sub>Cl<sub>2</sub>(thf)]<sub>n</sub> 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<sub>2</sub>Cl<sub>2</sub>(thf)<sub>2</sub>]<sub>2</sub> with phosphorus containing ligands R<sub>3</sub>PX (R=Cy, Ph and X=O, NH) [6] so we were particularly interested in comparing the reactivity of phosphinimine ligands with [NpO<sub>2</sub>Cl<sub>2</sub>(thf)]<sub>n</sub>. Reaction of [NpO<sub>2</sub>Cl<sub>2</sub>(thf)]<sub>n</sub> with Ph<sub>3</sub>PNH led to the characterisation of [Ph<sub>3</sub>PNH]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] (**2**).

Both crystals structures of **1** and **2** indicated that the anion [NpO<sub>2</sub>Cl<sub>4</sub>]<sup>2−</sup> seems to be unusually stable in aprotic solvents. We comment here on the relative the stability of [AnO<sub>2</sub>Cl<sub>4</sub>]<sup>2−</sup> along the actinides series and identify the conditions in which this anion is chemically stable.

## 2. Results and discussions

### 2.1. [NpO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>Cl]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>]

A MeOH solution of DPPMO<sub>2</sub> (2 eq.) was added to a solution of Np(VI) in HCl yielding a pale yellow solution. Crystals of [NpO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>Cl]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] (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<sub>2</sub>Cl<sub>4</sub>]<sup>2−</sup> (**1a**) and two monocationic pentagonal bipyramidal [NpO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>Cl]<sup>+</sup> (**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<sub>y1</sub> bond lengths [7]. Np–Cl distances are different with Np(2)–Cl(2) (2.652(3) Å) being

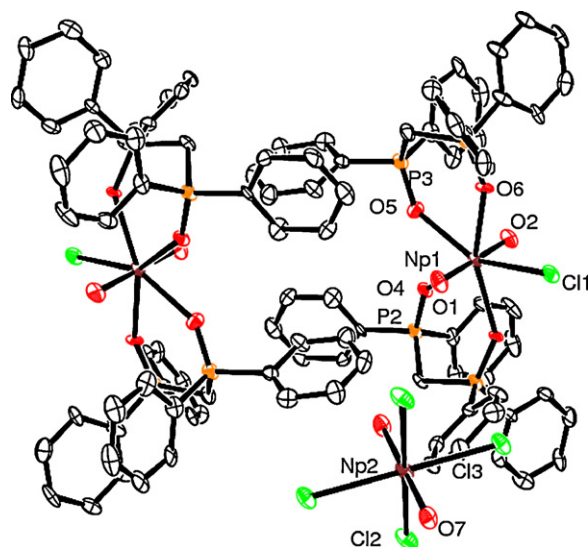


Fig. 1. ORTEP representation of [NpO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>Cl]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] (**1**).

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<sub>7</sub>[Np<sup>V</sup>O<sub>2</sub>][Np<sup>VI</sup>O<sub>2</sub>]<sub>2</sub>Cl<sub>12</sub>, [8], Cs<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] [9] and [NBu<sub>4</sub>]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] [10]. Comparison of the bond lengths in **1a** with those found in Cs<sub>7</sub>[Np<sup>V</sup>O<sub>2</sub>][Np<sup>VI</sup>O<sub>2</sub>]<sub>2</sub>Cl<sub>12</sub> is precluded due to the extensive disorder present in the structure in the mixed valence compound. In contrast with **1a**, in [NBu<sub>4</sub>]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>], 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°).

To the best of our knowledge, [NpO<sub>2</sub>(DPPMO<sub>2</sub>)<sub>2</sub>Cl]<sup>+</sup> (**1b**) is the first seven-coordinated neptunium(VI) complex reported so far. In **1b**, the Np–O<sub>y1</sub> 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<sub>2</sub>Cl<sub>2</sub>(thf)]<sub>n</sub> [4b], 1.739(10) Å and 1.751(18) Å for [NpO<sub>2</sub>Cl<sub>2</sub>(TPPO)(NO<sub>3</sub>)] and [NpO<sub>2</sub>Cl<sub>2</sub>(TPPO)<sub>2</sub>] [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 (°)    |          |
|-----------------|----------|-------------------|----------|
| <b>1b</b>       |          |                   |          |
| 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) |                   |          |
| <b>1a</b>       |          |                   |          |
| 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) |                   |          |

**Table 2**  
Selected bond lengths [Å] and angles [°] for **2**.

| Bond lengths (Å) |            | Bond angles (°) |            |
|------------------|------------|-----------------|------------|
| Np(1)–O(1)       | 1.752(3)   | O(1)–Np–O(2)    | 179.60(14) |
| Np(1)–O(2)       | 1.748(3)   | Cl(1)–Np–Cl(3)  | 176.49(3)  |
| Np(1)–Cl(1)      | 2.6469(11) | Cl(2)–Np–Cl(4)  | 179.70(3)  |
| Np(1)–Cl(3)      | 2.6521(10) |                 |            |
| Np(1)–Cl(2)      | 2.6621(11) |                 |            |
| Np(1)–Cl(4)      | 2.6640(11) |                 |            |
|                  |            |                 |            |
| P(1)–N(1)        | 1.628(4)   |                 |            |
| N(1)–H(1)        | 0.859(19)  |                 |            |
| N(1)–H(2)        | 0.853(19)  |                 |            |

similar to the ones in **1a**, but is longer than the Np–Cl distances found in  $[\text{NpO}_2\text{Cl}_2(\text{TPPO})_2]$  (average of 2.6335(3) Å). As previously observed in the  $[\text{UO}_2(\text{DPPMO}_2)_2\text{X}]^+$  cation, the DPPMO<sub>2</sub> groups are not symmetrical, displaying Np–O<sub>(P=O)</sub> bond lengths in the range between 2.373(8) to 2.415(7) Å. The average Np–O<sub>(P=O)</sub> distance (2.389(7) Å) exhibited by **1b** is longer than that in the Np(VI) tetragonal bipyramidal complex in  $[\text{NpO}_2(\text{TPPO})_4][\text{ClO}_4]_2$  (average of 2.284(6) Å) [11] and is longer than the average Np–O<sub>(P=O)</sub> bond length found in *trans*- $[\text{NpO}_2\text{Cl}_2(\text{TPPO})_2]$  (2.2745(24) Å) [7a]. One of the DPPMO<sub>2</sub> ligands in **1b** has Np–O<sub>(P=O)</sub> bond lengths that are statistically shorter (Np(1)–O(5), 2.373(8) Å; Np(1)–O(6) 2.381(7) Å) than the longest Np–O<sub>(P=O)</sub> distance found in the second chelating DPPMO<sub>2</sub> group (Np(1)–O(4), 2.415(7) Å), whilst the P–O bond lengths are in the range 1.479(8)–1.506(8) Å (Table 2).

Perhaps of most interest in the structural characterisation of **1** is a comparison with the uranyl analogue,  $[\text{UO}_2(\text{DPPMO}_2)_2\text{Cl}]\text{Cl}$  [5b], in order to assess the impact that the identity of the metal ion (U, Np) has upon the structure of the  $[\text{AnO}_2(\text{DPPMO}_2)_2\text{Cl}]^+$  (An=U, Np) complex cation. Of course, this must be approached with caution because the identity of the non-coordinating anion in **1** ( $[\text{NpO}_2\text{Cl}_4]^{2-}$ ) is different to that in  $[\text{UO}_2(\text{DPPMO}_2)_2\text{Cl}]^+$  ( $\text{Cl}^-$ ). Crystal packing forces and unit cell dimensions/space group differences because of the different anion may well have an effect on bond lengths and angles in the first coordination sphere of the metal ion. The U–O<sub>(P=O)</sub> bond distance (average of 2.39(2) Å [5b]), in  $[\text{UO}_2(\text{DPPMO}_2)_2\text{Cl}]^+$  is statistically the same as the Np–O<sub>(P=O)</sub> distance (average of 2.389(7) Å) in **1b**. The average bite angle of the DPPMO<sub>2</sub> groups in **1b** (70.5(4) Å) and  $[\text{UO}_2(\text{DPPMO}_2)_2\text{Cl}]^+$  (70.5(2) Å) [5b] are identical, despite the smaller size of neptunium in comparison to uranium. A comparison of the bond lengths in the O=An=O unit in **1b** (An=Np) (1.766(8) and 1.773(8) Å) and  $[\text{UO}_2(\text{DPPMO}_2)_2\text{Cl}]^+$  (1.762(7) Å) [5b], reveals that the neptunyl(VI) bond distances are statistically the same as the uranyl(VI) bond length. It is intriguing that this structural similarity is present, given the *f* electron located in the  $\{\text{NpO}_2\}^{2+}$  moiety and the smaller size of neptunium. However, the Np–Cl bond distance (2.670(3) Å) in **1b** is shorter than the U–Cl bond length (2.710(2) Å) [5b] in  $[\text{UO}_2(\text{Cl})(\text{DPPMO}_2)_2]^+$ . Neglecting non-bonding ligand–ligand interactions, this difference may in part be explained by the “actinide contraction,” where the chloride ion is drawn closer towards the metal ion as it becomes smaller in passing from U to Np.

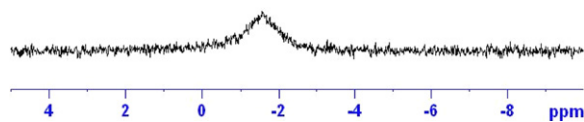


Fig. 2.  $^{31}\text{P}\{^1\text{H}\}$  NMR of crystals of **1** in  $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{OD}$  (50:50).

The room temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{OD}$  is shown in Fig. 2 and displayed a broad signal at  $-1.5$  ppm. Free DPPMO<sub>2</sub> ligand resonates at 25 ppm whilst the bound DPPMO<sub>2</sub> ligand in the  $f^0$  system  $[\text{UO}_2(\text{DPPMO}_2)_2\text{Cl}]\text{Cl}$  exhibits a broad singlet at 43.56 ppm at room temperature [5b]. Both the lineshape and the shift to negative field provide evidence that the DPPMO<sub>2</sub> molecule is bonded to the  $f^1$   $\{\text{NpO}_2\}^{2+}$  ion in solution. Chemical exchange of the  $[\text{X}]^-$  anion in the  $[\text{UO}_2(\text{DPPMO}_2)_2\text{X}]\text{X}$  (X=Br, Cl) compounds is well known and it is highly likely that the bound chloride ion in **1b** is also in chemical exchange in solution on the NMR timescale. It is unclear whether the broad lineshape of the NMR signal of **1** is caused by this phenomenon or by a combination of chemical exchange and/or the line broadening effect an NMR nucleus undergoes when interacting with a paramagnetic metal ion. The possible fluxionality of **1b** in solution was not probed further using low temperature NMR spectroscopy. It was anticipated that the known temperature dependence of isotropic shifts [12] may further complicate the assignment of the peaks in the spectra.

The electronic absorption spectrum crystals of **1** dissolved in  $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$  was recorded and is shown Fig. 3. The UV/vis/nIR spectrum showed the presence of three different oxidation states of neptunium, Np(IV) (bands between 680 and 980 nm), Np(V) (sharp band at 980 nm) and Np(VI) (broad band between 1170 and 1270 nm). Np(VI) readily reduces into Np(IV) and Np(V). In order to understand the behaviour of Np(VI) in organic solvents, absorption spectra of a  $\{\text{NpO}_2^{2+}\}$  stock ( $\text{NpO}_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$ ) solution were recorded in a MeOH or THF solution (Fig. 4a and 4b). As expected, dissolution of the “ $\text{NpO}_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$ ” residue in the reducing solvent MeOH produces Np(V), as evidenced by the characteristic sharp absorption band at 980 nm (Fig. 4a).

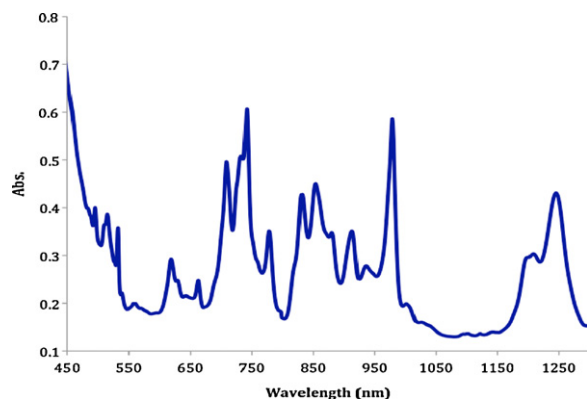


Fig. 3. UV-vis-nIR spectrum of crystals of **1** in  $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{OD}$  (50:50).

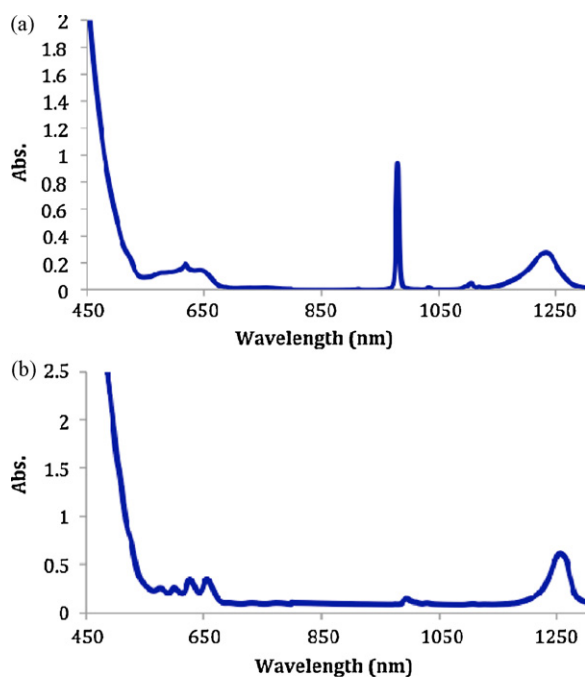


Fig. 4. a: UV-vis-nIR spectrum of  $\text{NpO}_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$  in MeOH. b: UV-vis-nIR spectrum of  $\text{NpO}_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$  in THF.

Crystalline **1** is relatively stable with respect to reduction in THF but is reduced in MeOH. Therefore, this reduction occurs prior to any complexation reaction (for example, with  $\text{DPPMO}_2$ ) if the reducing alcohol is required to dissolve the ligand molecule. The presence of Np(VI) in the spectrum of **1** is confirmed by the two broad bands in the nIR region between 1170 and 1270 nm corresponding to the two Np(VI) chromophores in **1** (Fig. 3).

## 2.2. $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4](2)$

$\text{Ph}_3\text{PNH}$  was added to a  $\text{THF-d}_8$  solution of  $[\text{NpO}_2\text{Cl}_2(\text{thf})]_n$  which had been prepared from dry  $[\text{NpO}_2(\text{OH})_2]$  treated with  $\text{HCl}/\text{Et}_2\text{O}$  and  $\text{SiMe}_3\text{Cl}$  (Scheme 1). Small crystals were formed after a few days from a  $\text{CH}_2\text{Cl}_2$  solution. The structure of  $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4]$  is shown Fig. 5. Selected bond distances and angles are displayed in Table 2. In contrast to **1a**,  $[\text{NpO}_2\text{Cl}_4]^{2-}$  in **2a** does not have a crystallographically imposed inversion centre. The  $\text{Np}=\text{O}$  distances are 1.748(3) and 1.752(3) Å and are within the range expected for Np- $\text{O}_{\text{yl}}$  complexes. Np-Cl (average 2.6600(11) Å) bond lengths are compara-

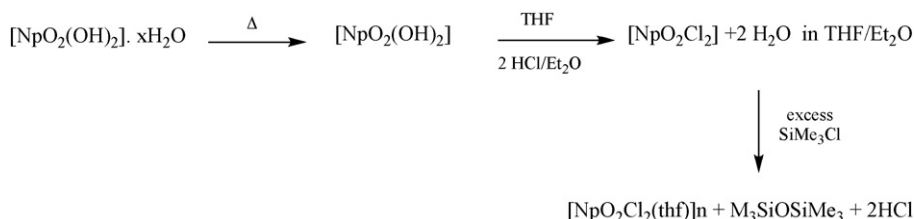
ble to those reported for **1a**. There are two crystallographically distinct  $[\text{Ph}_3\text{PNH}_2]^+$  cations with the P=N bond distances (1.628(4) and 1.614(4) Å) comparable to the values obtained in  $[\text{Ph}_3\text{PNH}_2]_2[\text{OsCl}_6] \cdot 2\text{CH}_3\text{CN}$  [13a],  $[\text{Ph}_3\text{NH}_2]\text{Cl} \cdot \text{CH}_3\text{CN}$ , [13b]  $[\text{Ph}_3\text{PNH}_2]\text{Br} \cdot \text{CH}_2\text{Cl}_2$  [13c],  $[\text{Ph}_3\text{PNH}_2][\text{SCN}]$  [13d]. The phosphonium cations interact with the  $[\text{NpO}_2\text{Cl}_4]^{2-}$  anion through the N-H...Cl hydrogen bonding interactions (Fig. 6).

UV/Vis/nIR spectra of **2** in THF (Fig. 7) exhibit two broad bands at 1193 and 1219 nm characteristic of Np(VI) complexes and may indicate the presence of two Np(VI) compounds in solution. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the crystals dissolved in  $\text{CD}_2\text{Cl}_2$  exhibited a singlet at 36.1 ppm corresponding to the  $[\text{Ph}_3\text{NH}_2]^+$  salt.

Interestingly, reaction of  $[\text{PuO}_2\text{Cl}_2(\text{thf})_2]_2$  crystals with  $\text{Ph}_3\text{PNH}$  in THF at room temperature yielded  $[\text{Ph}_3\text{PNH}_2]_2[\text{PuO}_2\text{Cl}_4]$  after recrystallisation in  $\text{CH}_2\text{Cl}_2$  [14]. These results indicate the stability of  $[\text{AnO}_2\text{Cl}_4]^{2-}$  compared to  $[\text{AnO}_2\text{Cl}_2(\text{thf})_2]$  for Np or Pu in contrast to the analogous uranium complex, which yielded the  $[\text{UO}_2\text{Cl}_2(\text{Ph}_3\text{PNH})_2]$  complex under air-, moisture- and HCl free conditions [6].

Syntheses of  $[\text{NpO}_2\text{Cl}_4]^{2-}$  and  $[\text{PuO}_2\text{Cl}_4]^{2-}$  have been previously reported by reacting a stock solution of  $\{\text{AnO}_2\}^{2+}$  in HCl with tetrabutylammonium chloride or caesium chloride in HCl solution, respectively [9,10,15]. However, for compound **1**, the only source of chloride available in solution comes from the stock solution of  $\text{NpO}_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$  in conc. HCl. Addition of the  $\text{DPPMO}_2$  ligand in an aprotic solvent yields the complex  $[\text{NpO}_2(\text{DPPMO}_2)_2\text{Cl}]^{2+}$  liberating  $\text{Cl}^-$  to form the stable  $[\text{NpO}_2\text{Cl}_4]^{2-}$  counteranion. This would explain the presence of  $[\text{NpO}_2\text{Cl}_4]^{2-}$  in the solution in the case of **1**. Further investigations will be carried out to prepare  $[\text{NpO}_2(\text{DPPMO}_2)_2\text{Cl}][\text{Cl}]$  by dissolving  $[\text{NpO}_2(\text{OH})_2] \cdot x\text{H}_2\text{O}$  in a dilute HCl solution (1–2 M). Dissolution of  $[\text{NpO}_2(\text{OH})_2] \cdot x\text{H}_2\text{O}$  in conc. HCl might directly form  $[\text{NpO}_2\text{Cl}_4]^{2-}$ . Recent reports on uranyl compounds  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$  showed that when the concentration of  $\text{HNO}_3$  is increased from 9 to 14.5 M then the water molecules are displaced with  $\text{NO}_3^{2-}$  to go from  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$  in 1 M  $\text{HClO}_4$  to  $[\text{UO}_2(\text{H}_2\text{O})(\text{NO}_3)_5]^-$  (9 M  $\text{HNO}_3$ ) and  $[\text{UO}_2(\text{NO}_3)_3]^-$  (14.5 M) [16].

In the case of the synthesis of compound **2**, if moisture was present, coordinated THF in  $[\text{NpO}_2\text{Cl}_2(\text{thf})]_n$  would exchange readily with water and  $\text{Ph}_3\text{NH}$  would be converted to  $\text{Ph}_3\text{PO}$  and  $\text{NH}_3$ . However, there was no evidence for the presence of  $\text{Ph}_3\text{PO}$  in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. It has been observed that, in the presence of chloride ions, the phosphinimine ligand can form  $[\text{Ph}_3\text{NH}_2]^+\text{Cl}^-$  [17], providing a source of chloride for the  $\{\text{NpO}_2\}^{2+}$  cation to form  $[\text{NpO}_2\text{Cl}_4]^{2-}$ . No  $\text{Ph}_3\text{PNH}$  was



Scheme 1. Preparation of a solution of  $[\text{NpO}_2\text{Cl}_2(\text{thf})]_n$ .

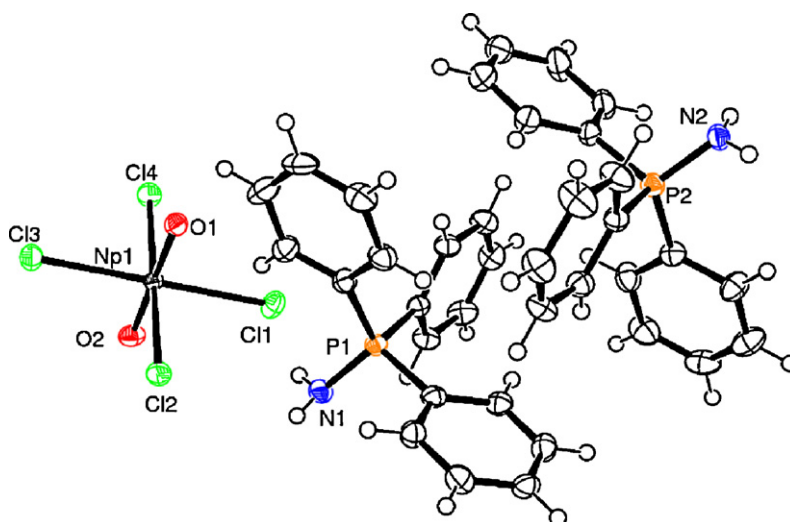


Fig. 5. ORTEP representation of  $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4]$  (**2**).

observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, suggesting that the whole of the ligand has been converted to the  $[\text{Ph}_3\text{NH}_2^+]\text{Cl}^-$ , the chloride ion probably coming from  $\text{SiMe}_3\text{Cl}$  (Scheme 1) still present in the neptunium starting material solution, which then dissociates to form  $[\text{NpO}_2\text{Cl}_4]^{2-}$ .

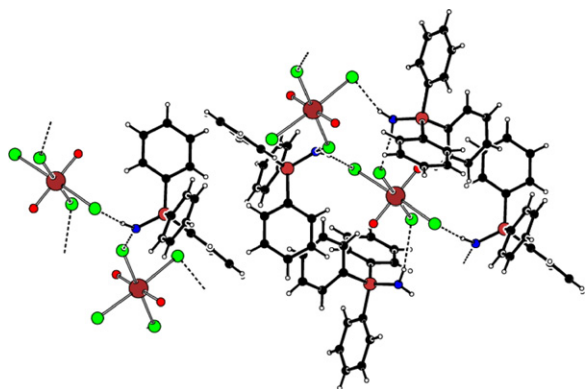


Fig. 6. View of  $[\text{Ph}_3\text{PNH}_2]_2[\text{NpO}_2\text{Cl}_4]$  showing the hydrogen bonding between the N-H protons of the  $[\text{Ph}_3\text{PNH}_2]^+$  cations and the Cl atoms on  $[\text{NpO}_2\text{Cl}_4]^{2-}$ .

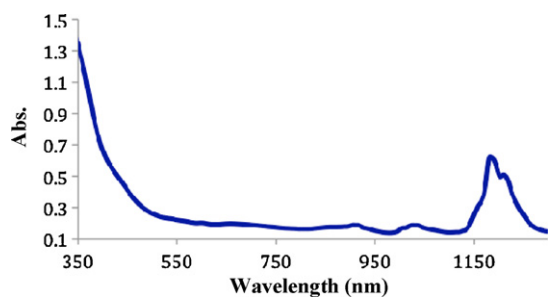


Fig. 7. UV-vis-nIR spectrum of **2** in THF.

### 3. Conclusion

In summary, we have prepared and characterized two neptunyl complexes containing the  $[\text{NpO}_2\text{Cl}_4]^{2-}$  moiety as a counteranion.

Only a few examples of the analogous mixed cations-anions uranium compounds containing the  $[\text{UO}_2\text{Cl}_4]^{2-}$  [18] anion have been reported presumably because, as a Lewis acid, it usually readily reacts with additional organic ligands to form single uranyl complexes [19,20]. In most cases, when  $[\text{UO}_2\text{Cl}_4]^{2-}$  has been isolated it has been in reactions with soft donor ligands where the coordination does not occur.

The solid state comparison of the  $[\text{AnO}_2\text{Cl}_4]^{2-}$  anions does not show any evidence of the actinyl contraction since the bond length and angle along the actinides series are statistically the same (Table 3). However, we believe that the solution chemistry differs from one another since uranium reacts easily with both ligands studied in this report to form uranyl complexes.

Complex **1** exhibited a shorter Np–Cl bond length compared to the uranium compound and the production of  $[\text{AnO}_2\text{Cl}_4]^{2-}$ , where An = Np or Pu, seems to be facilitated. This could be explained by a softening of the metal along the transuranium series.

### 4. Experimental

#### 4.1. General experimental

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

Experiments were carried out either in a radiological fume hood, under an argon atmosphere using standard Schlenk line techniques and apparatus when necessary, or in an inert atmosphere argon glovebox. All solvents

**Table 3**  
Comparison of bond lengths [Å] and angles [°] in [AnO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> ions.

|                        | [UO <sub>2</sub> Cl <sub>4</sub> ] <sup>2-</sup>                                                     | [NpO <sub>2</sub> Cl <sub>4</sub> ] <sup>2-</sup> | [PuO <sub>2</sub> Cl <sub>4</sub> ] <sup>2-</sup>                      |
|------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------------|------------------------------------------------------------------------|
|                        | [UO <sub>2</sub> Cl <sub>4</sub> ] <sub>3</sub> [U <sup>IV</sup> Cl(dmf) <sub>7</sub> ] <sub>2</sub> | Cs <sub>2</sub> NpO <sub>2</sub> Cl <sub>4</sub>  | [Ph <sub>3</sub> PNH] <sub>2</sub> [PuO <sub>2</sub> Cl <sub>4</sub> ] |
| An–O <sub>yl</sub> (Å) | 1.77(1)                                                                                              | 1.775(17)                                         | 1.752(3)                                                               |
| An–Cl (Å)              | 2.669(5)– 2.672(5)                                                                                   | 2.653(3)                                          | 2.6646(8)                                                              |
| O=An=O (°)             | 180                                                                                                  | 180.0(8)                                          | 180.0(3)                                                               |
| Ionic radii (Å)        | {UO <sub>2</sub> } <sup>2+</sup> 0.83                                                                | {NpO <sub>2</sub> } <sup>2+</sup> 0.82            | {PuO <sub>2</sub> } <sup>2+</sup> 0.81                                 |
| Reference              | 20                                                                                                   | 9                                                 | 14                                                                     |

employed were reagent grade and dried by refluxing over appropriate drying agents.

#### 4.2. Instrumentation

<sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance Ultrashield 400 instrument at 161.91 MHz. UV/vis/nIR spectra were measured on a Varian Cary 500.

Single crystal X-ray diffraction data of **1** were obtained on a Bruker AXS SMART diffractometer (MoK $\alpha$  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.

Diffraction data for **2** were collected at 100 K using synchrotron radiation at Daresbury SRS, UK (Station 9.8) with a Bruker-Nonius APEX11 CCD diffractometer ( $\lambda = 0.6934$  Å). Crystals of **2** were surrounded by oil (Fomblin, perfluoro polyether) and mounted inside a polyimide capillaries coated by varnish providing triple containment. The structure was solved by direct methods using SIR92 and refined using SHELXL97 [21,22]. All non-hydrogen atoms not exhibiting disorder were refined anisotropically, while hydrogen atoms were included in calculated positions. All presented ORTEP plots show probability ellipsoids of 50% [23].

#### 4.3. Syntheses

##### 4.3.1. Synthesis of [NpO<sub>2</sub>Cl<sub>2</sub>] in conc. HCl

2.4 mL of an HNO<sub>3</sub> stock solution of {Np<sup>V</sup>O<sub>2</sub>}<sup>+</sup> (50 mg, 0.21 mmol of <sup>237</sup>Np purchased from CERCA LEA- France-) was evaporated to dryness under a heat lamp. An aqueous {Np<sup>VI</sup>O<sub>2</sub>}<sup>2+</sup> solution was generated by dissolving the Np(V) solid in conc. HClO<sub>4</sub> (70%, 5 ml) and heating until fuming. Dilution of this yellow acidic solution with 0.5 mL H<sub>2</sub>O yielded a pink solution. UV/vis/nIR spectroscopy was used to confirm the presence of {Np<sup>VI</sup>O<sub>2</sub>}<sup>2+</sup> (major *f–f* transition at 1223 nm) and the absence of {Np<sup>VO</sup>O<sub>2</sub>}<sup>+</sup> (major *f–f* transition at 980 nm). Brown solid neptunyl hydroxide, [NpO<sub>2</sub>(OH)<sub>2</sub>].xH<sub>2</sub>O, was precipitated from solution through the addition of NaOH (6 M). This brown precipitate of [NpO<sub>2</sub>(OH)<sub>2</sub>].xH<sub>2</sub>O was washed twice with H<sub>2</sub>O, and dissolved in 37% HCl (< 1 ml).

##### 4.3.2. Synthesis of [NpO<sub>2</sub>Cl(DPPMO)<sub>2</sub>]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] (**1**)

A MeOH solution of DPPMO<sub>2</sub> (22 mg, 0.052 mmol) was added to an aliquot of the stock solution of NpO<sub>2</sub>Cl<sub>2</sub> in 37% HCl (6.32 mg, 0.026 mmol of <sup>237</sup>Np). A white precipitate formed immediately and MeOH was added until the

precipitate dissolved yielding a pale yellow solution. The vial containing the solution was left to stand at room temperature for 5 days. Slow evaporation of the solvent afforded yellow crystals of **1**. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>:CD<sub>3</sub>OD):  $\delta$  –1.5 ppm (broad s, w<sub>1/2</sub> 93.55 Hz)

##### 4.3.3. Synthesis of [Ph<sub>3</sub>PNH<sub>2</sub>]<sub>2</sub>[NpO<sub>2</sub>Cl<sub>4</sub>] (**2**)

The synthesis of [NpO<sub>2</sub>(OH)<sub>2</sub>].xH<sub>2</sub>O has been described above. The brown precipitate of [NpO<sub>2</sub>(OH)<sub>2</sub>].xH<sub>2</sub>O was washed twice with H<sub>2</sub>O, once with acetone and then dried *in vacuo*. Under an argon atmosphere, the brown residue was suspended in thf (5 mL). A solution of HCl in Et<sub>2</sub>O (2 mol L<sup>-1</sup> < 1 mL) was added until the brown residue dissolved to yield a yellow solution. A few drops of SiMe<sub>3</sub>Cl were then added to remove any trace of H<sub>2</sub>O [**4c**] and the resulting mixture was stirred for 15 minutes to give [NpO<sub>2</sub>Cl<sub>2</sub>(thf)<sub>n</sub>] which was used immediately. A solution of Ph<sub>3</sub>PNH in THF (29 mg, 0.1 mmol) was added to a solution of [NpO<sub>2</sub>Cl<sub>2</sub>] in THF (12.63 mg, 0.053 mmol of <sup>237</sup>Np). A yellow precipitate formed upon addition. The solid was left to precipitate and the supernatant was removed. The solid was dried and redissolved in CD<sub>2</sub>Cl<sub>2</sub> and left to stand at room temperature; yellow crystals formed after a few days. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  36.1 ppm (s).

#### Acknowledgments

We acknowledge the Engineering and Physical Sciences Research Council (EPSRC), the School of Chemistry, University of Manchester and ACTINET for funding. In particular, S.M. Cornet was funded from the EPSRC grant no. GR/S95152/01.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.crci.2010.04.013.

#### References

- [1] (a) M.P. Jensen, A.H. Bond, J. Am. Chem. Soc. 124 (2002) 9870; (b) A.E.V. Gorden, J. Xu, G. Szigethy, A. Oliver, D.K. Shuh, K.N. Raymond, J. Am. Chem. Soc. 129 (2007) 6674.
- [2] M. Ephritikhine, Dalton Trans. (2006) 2501.
- [3] C.J. Burns, M.P. Neu, H. Boukhalfa, K.E. Gutowski, N.J. Bridges, R.D. Rogers, in: Comprehensive Coordination Chemistry II, McCleverty, J.A., Meyer, T.J. (Eds.), Elsevier Pergamon: Amsterdam, The Netherlands, 2004, Vol. 3, p. 189.
- [4] (a) A.J. Gaunt, S.D. Reilly, T.W. Hayton, B.L. Scott, M.P. Neu, Chem. Commun. 16 (2007) 1659;

- (b) S.M. Cornet, L.J.L. Häller, M.J. Sarsfield, D. Collison, M. Helliwell, I. May, N. Kaltsoyannis, *Chem. Commun.* (2009) 917;  
(c) M.P. Wilkerson, C.J. Burns, R.T. Paine, B.L. Scott, *Inorg. Chem.* 38 (1999) 4156.
- [5] (a) S. Kannan, M.A. Moody, C.L. Barnes, P.B. Duval, *Inorg. Chem.* 45 (2006) 9206;  
(b) A.D. Sutton, G.H. John, M.J. Sarsfield, J.C. Renshaw, I. May, L.R. Martin, A.J. Selvage, D. Collison, M. Helliwell, *Inorg. Chem.* 43 (2004) 5480;  
(c) S. Kannan, N. Rajalakshmi, K.V. Chetty, V. Venugopal, M.G.B. Drew, *Polyhedron* 23 (2004) 1527;  
(d) T.W. Hayton, G. Wu, *J. Am. Chem. Soc.* 130 (2008) 2005;  
(e) G.H. John, I. May, D. Collison, M. Helliwell, *Polyhedron* 23 (2004) 3097;  
(f) S.M. Cornet, I. May, M.P. Redmond, A.J. Selvage, C.A. Sharrad, O. Rosnel, *Polyhedron* 28 (2009) 363.
- [6] (a) G. Bombieri, E. Forsellini, J.P. Day, W.I. Azeez, *J. Chem. Soc., Dalton Trans.* (1978) 677;  
(b) M.J. Sarsfield, I. May, S.M. Cornet, M. Helliwell, *Inorg. Chem.* 44 (2005) 7310.
- [7] (a) N.W. Alcock, M.M. Roberts, D. Brown, *J. Chem. Soc., Dalton Trans.* (1982) 25;  
(b) M.S. Grigoriev, A.M. Fedoseev, N.A. Budantseva, A.A. Bessonov, J.-C. Krupa, *Crystallogr. Rep.* 49 (2004) 598;  
(c) M.P. Wilkerson, C.A. Arrington, J.M. Berg, B.L. Scott, *J. Alloys Compds.* (2007) 444;  
(d) N.W. Alcock, M.M. Roberts, D. Brown, *J. Chem. Soc., Dalton Trans.* (1982) 869;  
(e) C. Talbot-Eeckelaers, S.A.J. Pope, A.J. Hynes, R. Copping, C.J. Jones, R.J. Taylor, S. Faulkner, D. Sykes, F.R. Livens, I. May, *J. Am. Chem. Soc.* 129 (2007) 2442.
- [8] N.W. Alcock, D.J. Flanders, D. Brown, *J. Chem. Soc., Dalton Trans.* (1986) 1403.
- [9] M.P. Wilkerson, C.A. Arrington, J.M. Berg, B.L. Scott, *J. Alloys Compds.* 444–445 (2007) 634–639.
- [10] M.P. Wilkerson, H.J. Dewey, P.L. Gordon, B.L. Scott, *J. Chem. Crystallogr.* 34 (2004) 807.
- [11] I.A. Charushnikova, N.N. Krot, Z.A. Starikova, I.N. Polyakova, *Radiochimia* 49 (2007) 464.
- [12] G.N. La Mar, W. DeW. Horrocks, Jr, R.H. Holm, *NMR of Paramagnetic Molecules, Principles and Applications*, 1973, Academic Press, Inc. Ltd, London.
- [13] (a) B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* 633 (2007) 841;  
(b) D. Nußhär, F. Weller, K. Netmieke, *Z. Anorg. Allg. Chem.* 619 (1993) 1121;  
(c) J.-S. Li, F. Weller, F. Schmock, K. Dehnicke, *Z. Anorg. Allg. Chem.* 621 (1995) 2097;  
(d) A. Dietrich, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* 626 (2000) 1837.
- [14] C. Berthon, N. Boubals, I. A. Charushnikova, D. Collison, S. M. Cornet, C. Den Auwer, A. J. Gaunt, L. J. L. Häller, N. Kaltsoyannis, I. May, S. Petit, M. P. Redmond, Sean D. Reilly, and B.L. Scott, [in preparation].
- [15] M.P. Wilkerson, B.L. Scott, *Acta Cryst. Sect. E64* (2008) i5.
- [16] A. Ikeda-Ohno, C. Hennig, S. Tsushima, A.C. Scheinost, G. Bernhard, T. Yaita, *Inorg. Chem.* 48 (2009) 7201.
- [17] (a) E.W. Abel, S.A. Mucklejone, *Phosphorus Sulfur* 9 (1981) 235;  
(b) M.B. Hursthouse, N.P.C. Walker, C.P. Warrens, J.D. Woollins, *J. Chem. Soc., Dalton Trans.* (1985) 1043 and refs. therein.
- [18] (a) O. Pons y Moll, T. Le Borgne, P. Thuéry, M. Ephritikhine, *Acta Cryst. C57* (2001) 392;  
(b) D.R. Brown, A.M. Chippindale, R.G. Denning, *Acta Cryst. C52* (1996) 1164.
- [19] (a) C.C. Gatto, E. Schulz Lang, A. Jagst, U. Abram, *Inorg. Chimica Acta* 357 (2004) 4405;  
(b) P.C. Leverd, D. Rinaldo, M. Nierlich, *J. Chem. Soc., Dalton Trans.* (2002) 829;  
(c) V.P. Markov, V.V. Tsapkin, *Russ. J. Inorg. Chem.* 6 (1961) 1052.
- [20] D.L. Kepert, J.M. Patrick, A.H. White, *J. Chem. Soc., Dalton Trans.* (1983) 381 and refs. therein.
- [21] A. Altomare, G. Cascorano, C. Giacovazzo, A. Gualardi, *J. Appl. Crystallogr.* 26 (1993) 343.
- [22] G.M. Sheldrick, *SHELXL-97*, A program for crystal structure determination, Release 97-2; University of Göttingen, Germany, 1997.
- [23] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.