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Actinyl chemistry across the U, Np and Pu series

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Abstract

The air stable uranyl and neptunyl phosphine oxide complexes act as good starting material to prepare the air and moisture sensitive phosphinimines species and show a preference for N-donor ligands. Calculations confirmed those observations and proved the U–N bond to be stronger than the U–O bond. To continue our investigations on transuranyl chemistry, the complexes $PuO_2Cl_2(R_3PO)_2$ have been synthesised as well as new amides species of NpO_2^{2+} and PuO_2^{2+} characterised by NMR spectroscopy.

Keywords: Actinyls; Transuranic coordination chemistry; Phosphine oxides; Phosphinimines; Amides

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1. Introduction

The importance of the actinyl species, $\{AnO_2\}^{2+}$ (An: U, Np, Pu, Am), in the nuclear industry and in the natural environment is a particular reason for interest in their chemical properties. The uranyl(VI) cation, $\{UO_2\}^{2+}$, has been the most extensively studied due to its high stability and the comparatively low radiological hazards associated with depleted and natural uranium chemistry. The preparation of the air and moisture sensitive complex $[UO_2Cl_2(thf)_2]_2$ [1] facilitated a significant increase in nonaqueous uranyl chemistry, and is nowadays a widely used precursor to synthesise new uranyl(VI) species such as $[Na(thf)_2][UO_2\{N(SiMe_3)_2\}_3]$ [2], with a coordination number of three in the equatorial plane and the first examples of uranyl-carbon bonds in $[UO_2Cl_2(IMes)_2]$ (IMes = 1,3 dimesitylimidazol-2-ylidene or 1,3, dimesityl-4,5 dichloroimidazol-2-ylidene) [3]. In addition $[UO_2(OTf)_2]$ has also been used in the preparation of uranyl complexes under inert atmosphere [4]. Finally, Duval et al. recently reported a series of air stable uranyl-amide compounds with increased solubility (in comparison with $[UO_2Cl_2(thf)_2]_2$), which could be used as new starting materials to enter air and moisture sensitive chemistry of the uranyl cation [5,6]. Removing moisture eliminates the possibility of hydrolysis and hence competition with strong oxo and hydroxy donor ligands.

Recent studies at The Centre for Radiochemistry Research (CRR) have focused on the reaction between $[UO_2Cl_2(thf)_2]_2$, and softer-N donor ligands (including iminophosphoranes and benzaminates). The complexes formed have shown out of plane coordination, promoted U–C interaction, and enhanced the Lewis basicity of the uranyl oxygen [7–10]. In contrast, due to higher radioactivity of the transuranic elements, the actinyl chemistry of Np, Pu and Am has so far been limited. Although, Np(V) has been studied in depth for cation–cation complexation [11], nonaqueous Np(V) and Np(VI) chemistry remains relatively unexplored due to the current lack of suitable precursor. The same can be said for plutonyl chemistry where only a few research groups have the facilities for classical coordination chemistry research with plutonium. Our current goal is to extend our investigations on O- and N-donor ligands to $\{NpO_2\}^{2+}$ and $\{PuO_2\}^{2+}$, moving towards nonaqueous inert atmosphere systems, where the actinyl bond can be probed by coordination of moisture and air sensitive N-donor ligands.

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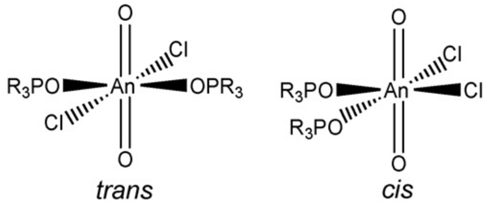

Fig. 1. Structure of *cis* and *trans* $AnO_2Cl_2(R_3PO)_2$ (An = U, Np, Pu and R = Cy, Ph).

2. Phosphine oxide ligands

The coordination of phosphorus compounds to the actinides has often been examined due to their application in several separations processes [12,13]. Many uranium phosphine oxide complexes have been structurally and spectroscopically characterised [14–18]. The triphenyl phosphine oxide ligand (TPPO) has been the subject of numerous investigations with both the uranyl and neptunyl moieties [16,19–22]. At the CRR, we have also used TPPO as a co-ligand for uranyl(VI) and neptunyl(V) in the preparation of several novel complexes [23–25]. Interestingly the air stable $UO_2Cl_2(Ph_3PO)_2$ complex, which exists as *cis* and *trans* isomers, can be used as a starting material to prepare the air and moisture sensitive complexes. Both uranyl(VI) alkoxide, $[UO_2(OR)_2(Ph_3PO)_2]$, and amide $[UO_2(N(SiMe_3)_2)_2(Ph_3O)_2]$ species have been prepared previously from this complex [26].

As an extension to the TPPO chemistry, we have added Cy_3PO (tricyclohexylphosphine oxide) to $[UO_2Cl_2(thf)_3]$ affording the complex $[UO_2Cl_2(Cy_3PO)_2]$, which presents a greater solubility in organic solvents compared to its TPPO analogue. In addition, reaction of $NpO_2Cl_2{\cdot}xH_2O$ with R_3PO (R = Cy, Ph) yielded the air stable $[NpO_2Cl_2(Ph_3PO)_2]$ [20], and $[NpO_2Cl_2(Cy_3PO)_2]$ as pure crystalline solids in *cis* and *trans* configuration. Access to the laboratories facilities at CEA, Atalante, Marcoule (France) allowed us to extend these investigations to plutonyl(VI) chemistry. Plutonyl chloride was prepared from a Pu(IV) nitrate stock solution. Plutonium(IV) hydroxide was precipitated with NaOH and the resulting solid redissolved in perchloric acid and oxidized to Pu(VI) by addition of silver(II) oxide. Precipitation of $PuO_2(CO_3)$ and re-dissolution in a minimum of HCl afforded PuO_2Cl_2. Treatment of two equivalents of R_3PO ligands to PuO_2Cl_2 yielded yellow precipitates of $[PuO_2Cl_2(R_3PO)_2]$ (R = Cy, Ph). 31P NMR spectra of $PuO_2Cl_2(R_3PO)_2$ exhibited major signals at δ-110.2 and -144.5 ppm for Cy and Ph, respectively. Due to the common stability of the *trans* isomer (versus *cis*) for actinyl species we assigned these two resonances to be *trans* species. This represents a significant shift compared to $\{UO_2\}^{2+}$ ($UO_2Cl_2(Cy_3PO)_2$ δ 73.0 ppm) and $\{NpO_2\}^{2+}$ ($NpO_2Cl_2(Cy_3PO)_2$ δ 49.8 ppm) complexes, and can perhaps be explained by the paramagnetism of the f^2 system although further studies are required (Fig. 1).

3. Phosphinimines ligands

We have recently reported our initial investigations into phosphinimine chemistry with uranyl and neptunyl, and are contunuing to research this area [27]. The reaction with the N-donor phosphinimines (R_3PNH) to solutions of $UO_2Cl_2(R_3PO)_2$ resulted in the selective displacement of the P=O ligands and the formation of the phosphinimine complexes $UO_2Cl_2(R_3PNH)_2$, which have been structurally characterised. Solution NMR experiments suggested that *cis* and *trans* isomers exist in solution, with the *cis* isomer expected to be the minor species due to greater steric repulsion between the bulky phosphinimine ligands. A large difference in chemical shift between the N*H* ^1H NMR signal (R = Ph δ 6.54 ppm, R = Cy, δ 5.82 ppm for *trans* isomers) compared to the uncomplexed ligand (Ph_3PNH δ 1.01ppm, Cy_3PNH δ −0.51 ppm) is observed. Moreover, a short U–N interaction is observed in the crystal structure (2.370(1) Å for R = Ph and 2.350(2) Å for R = Cy) compared to other uranyl containing N donor ligands [20,27–29], suggesting a strong U–N bond. In order to gain further insight into these observations, relavistic, gradient corrected density functional theory has been used to study these compounds. Total bonding energy calculations have been carried out both in gas phase and by inclusion of a solvent model, suggested that the *trans* isomer is the major species. Energy decomposition (using the fragment approach with ADF) and Mayer bond orders demonstrated that the U–N bond of the phosphinimine species is stronger and more covalent compared to the analogous U–O bond in the phosphine oxide complexes (Fig. 2). NMR chemical shifts of the N-*H* ^1H NMR have been calculated for the cyclohexyl complex, in the gas phase or CD_2Cl_2 solution and showed similar chemical shift compared to the experimental results.

This N-donor preference has also been demonstrated for Np(VI) chemistry [27], representing our first foray into inert atmosphere transuranium chemistry. NpO_2Cl_2 $(R_3PNH)_2$ complexes have been characterized by both ^1H and ^{31}P NMR spectroscopy and Raman spectroscopy.

4. Novel starting reagents—neptunyl and plutonyl amide complexation

The synthesis of the uranyl and neptunyl phosphinimines complexes from phosphine oxide complexes shows that the lat-

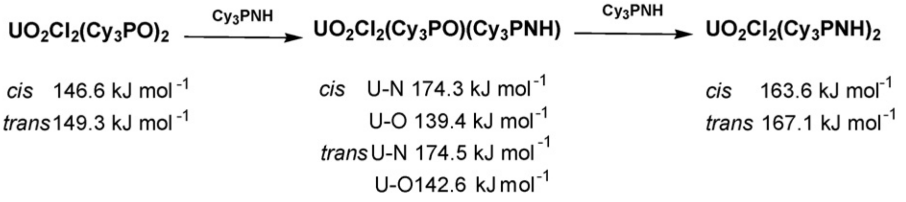

Fig. 2. Comparison in calculated bond strengths (by fragment approach with ADF)) for U–N and U–O in the uranyl phosphinimine and phosphine oxide ligands.

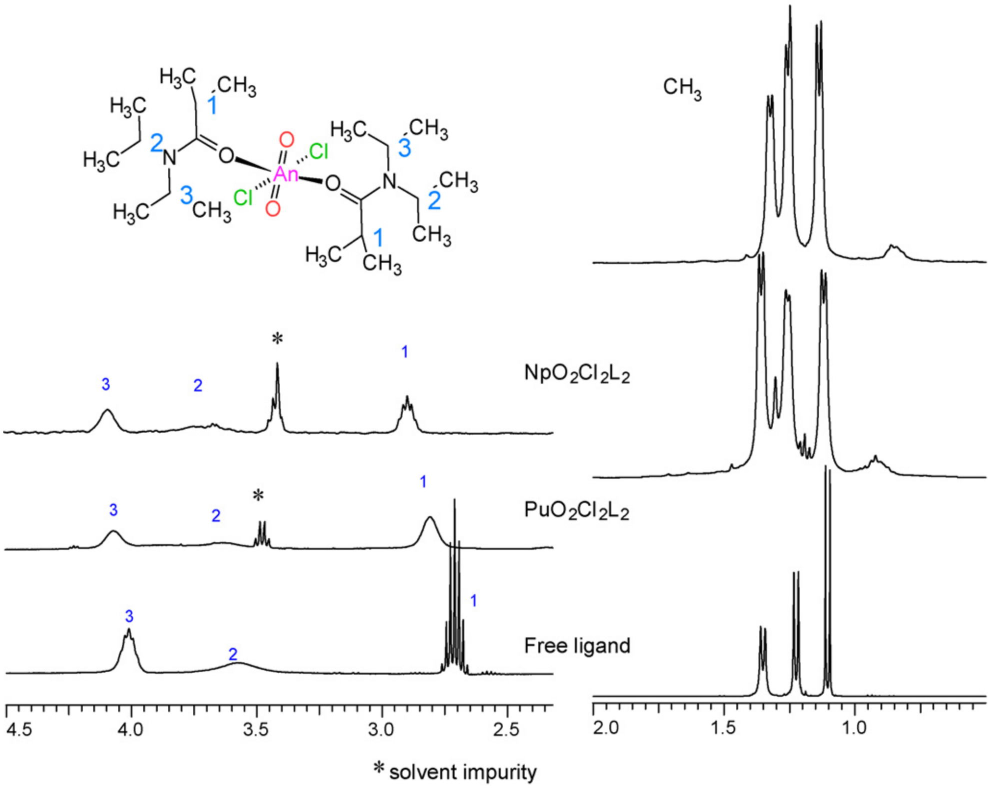

Fig. 3. ^{1}H NMR spectra of $NpO_2Cl_2L_2$ and $PuO_2Cl_2L_2$, where L = diisopropylisobutyramide.

ter can be used as good starting material to enter nonaqueous transuranyl chemistry. However, investigations on new precursors to anhydrous $\{NpO_2\}^{2+}$ and $\{PuO_2\}^{2+}$ chemistry remain necessary. Duval et al. [5] recently described the preparation of some uranyl-amide complexes generated by reaction of UO_2Cl_2 with two equivalents of the organic amides iPrC(O)NR_2 (R = iPr, iBu, sBu). We choose to apply similar reactions between those amide ligands and NpO_2Cl_2, and PuO_2Cl_2. Reaction of a solution of AnO_2Cl_2 in MeOH with a methanol solution of L resulted in a color change from a pale yellow to a deep yellow (An = Np) or orange (An = Pu) solution. ^{1}H NMR spectra in CH_2Cl_2 showed the broad signals assigned to the amides with no significant chemical shift changes with the free ligand (Fig. 3), signal broadening due to complexation to the paramagnetic transuranic metal centres.

5. Conclusion

In recent years, we have used well-characterised moisture free uranyl starting reagents to access coordination chemistry with N-donor ligands that are both air and moisture sensitive. Through both experimental measurement and computational calculations, we have shown that phosphinimine ligands more strongly (and covalently) coordinate to the uranyl(VI) cation. Current research is now focussed on the neptunyl and plutonyl cations, with the synthesis of phosphine oxide and organic amide starting reagents as a mean of accessing inert atmosphere transuranic actinyl chemistry. The initial preparation of neptunyl phosphinimine complexes indicates that this approach should be successful.

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