Inorg. Chem. **2005**, *44*, 7310–7312

Inorganic Chemistry
Communication

Preference for Nitrogen versus Oxygen Donor Coordination in Uranyl- and Neptunyl(VI) Complexes

Mark J. Sarsfield,*,† Iain May,‡ Stephanie M. Cornet,‡ and Madeleine Helliwell§

Nexia Solutions, Sellafield, Seascale, Cumbria CA20 1PG, U.K., Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Manchester M13 9PL, U.K., and School of Chemistry, The University of Manchester, Manchester M13 9PL, U.K.

Received July 12, 2005

The first actinyl phosphinimine complexes have been synthesized and, in the case of uranium, exhibit strong U–N interactions. Competition reactions clearly demonstrate a surprising preference for $R_3P{=}NH$ ligands over $R_3P{=}O$ in the system $[AnO_2Cl_2(R_3PX)_2]$ (An = U^{VI}, Np^{VI}; R = Ph, Cy; X = O, NH). Spectroscopic evidence for N-donor coordination to $[NpO_2]^{2+}$ in solution indicates chemical similarities to the $[UO_2]^{2+}$ moiety.

Much of the coordination chemistry of the actinyl ion is concerned with the complexation of O-donor ligands to improve our understanding of actinide speciation in the environment[1] and in nuclear fuel reprocessing.[2] Despite relatively few studies concerning the bonding of softer N-donor ligands to the actinyl ion, some new and exciting chemistry is emerging in this area.[3−11]

Recent crystallographic $[UO_2(NCO)_2(\{NMe_2\}_3PO)_2]$[12] and theoretical studies $[UF_4(NCO)_2]$[13] on uranium(VI) complexes with the cyanate/isocyanate ion demonstrate that, of the two possible bonding motifs, U(VI) has a distinct preference for forming U−N rather than U−O bonds.

During our recent studies, we have compared the previously reported monodentate phosphine oxide complexes of the type $[AnO_2Cl_2(R_3PO)_2]$ with the chemistry of new phosphinimine actinyl complexes $[AnO_2Cl_2(R_3PNH)_2]$ to assess the difference in chemistry between O- and N-donor ligands within a similar ligand framework. Here we communicate our preliminary findings of an example of N-donor ligands not only competing with but totally displacing O donors in uranyl- and neptunyl(VI) complexes.

The phosphinimines R_3PNH (R = Ph, Cy) are easily prepared from the corresponding phosphine in high yield.[14] Adding of 2 equiv of R_3PNH to $[UO_2Cl_2(THF)_3]$[15] in THF provides yellow complexes of the type $[UO_2Cl_2(R_3PNH)_2]$ (R = Ph, **1**; Cy, **2**) quantitatively and free of THF.[16] Complex **2**, being the more soluble of the two, is more amenable to solution studies in dichloromethane.

To assess the effects of 5f electrons on equatorial O/N-donor bonding, the neptunyl ion $[NpO_2]^{2+}$ was chosen as the most readily accessible ^{1}f actinyl cation. The target neptunyl complexes $[NpO_2Cl_2(R_3PNH)_2]$ (R = Ph, **3**; Cy, **4**) could not be accessed via the same route as the uranium analogue despite several failed attempts to synthesize the potentially useful starting material $[NpO_2Cl_2(THF)_3]$. However, compounds **3** and **4** could be synthesized in solution by displacing phosphine oxides from $[NpO_2Cl_2(R_3PO)_2]$ (R = Ph, **5**; Cy, **6**).[17] Compound **6** has been reported in the solid state,[19] although no spectroscopic data were presented.

Suitable crystals of **1** were grown from a dichloromethane solution overnight at −15 °C.[18] Structural analysis reveals a linear uranyl dication with two Ph_3PNH and two chloride ligands coordinated in a trans geometry in the equatorial plane (Figure 1). The uranium is in an octahedral site and has a U═O bond length [1.778(1) Å] in the normal range

---

* To whom correspondence should be addressed. E-mail: mark.sarsfield@nexiasolutions.com. Tel: +44(0)1946 779342.

† Nexia Solutions.

‡ Centre for Radiochemistry Research, School of Chemistry, The University of Manchester.

§ School of Chemistry, The University of Manchester.

(1) Katz, J. J.; Morss, L. R.; Seaborg, G. T. *Summary and Comparative Aspects of the Actinide Elements*; London, 1986.

(2) Wilson, P. D. In *The Nuclear Fuel Cycle*; Wilson, P. D., Ed.; Oxford University Press: Oxford, U.K., 1996.

(3) Sarsfield, M. J.; Helliwell, M. *J. Am. Chem. Soc.* **2004**, *126*, 1036.

(4) Sarsfield, M. J.; Helliwell, M.; Raftery, J. *Inorg. Chem.* **2004**, *43*, 3170.

(5) Sarsfield, M. J.; Helliwell, M.; Steele, H.; Tate, S. *J. Chem. Soc., Dalton Trans.* **2003**, 3443.

(6) Sarsfield, M. J.; Helliwell, M.; Collison, D. *J. Chem. Soc., Chem. Commun.* **2002**, 2264.

(7) Sessler, J. L.; Seidel, D.; Vivian, A. E.; Lynch, V.; Scott, B. L.; Keogh, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 591.

(8) Duval, P. B.; Burns, C. J.; Buschmann, W. E.; Clark, D. L.; Morris, D. E.; Scott, B. L. *Inorg. Chem.* **2001**, *40*, 5491.

(9) Burns, C. J.; Clark, D. L.; Donohoe, R. J.; Duval, P. B.; Scott, B. L.; Tait, C. D. *Inorg. Chem.* **2000**, *39*, 5464.

(10) Berthet, J.-C.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **2003**, 1660.

(11) Brown, D. R.; Denning, R. G. *Inorg. Chem.* **1996**, *35*, 6158.

(12) Crawford, M.-J.; Mayer, P.; Nöth, H.; Suter, M. *Inorg. Chem.* **2004**, *43*, 6860.

(13) Straka, M.; Patzschke, M.; Pyykkö, P. *Theor. Chem. Acc.* **2003**, *109*, 332.

(14) Dehnicke, K.; Weller, F. *Coord. Chem. Rev.* **1997**, *158*, 103.

(15) Wilkerson, M. P.; Burns, C. J.; Paine, R. T.; Scott, B. L. *Inorg. Chem.* **1999**, *38*, 4156.

10.1021/ic051161c CCC: $30.25

(1.75−1.79 Å) for six-coordinate uranyl complexes,[20] while the U−Cl bond [2.671(1) Å] is slightly longer than that in $UO_2Cl_2(Ph_3PO)_2$ [2.645(5) Å].[21] The significance of the U−N bond distance [2.370(1) Å] is difficult to assess because, to our knowledge, there are no other six-coordinate uranyl complexes containing neutral N-donor ligands. The U−N bond appears relatively short considering that the only comparative complexes $[UO_2(NCO)_2(\{NMe_2\}_3PO)_2]$ (U−N, 2.336(5) Å)[12] and $[UO_2(NCS)_2(Ph_3PO)_2]$ (U−N, 2.44(2) Å)[22] contain linear anionic N ligands with less steric bulk *at the metal center* from P═O ligands compared to the chlorides in **1**. Considering the reactivity of **1** and **2** (see later), it is interesting to note that the U−N distance in **1** is longer than the U−*O*═P bond in $UO_2Cl_2(Ph_3PO)_2$ [2.300(8) Å].[21]

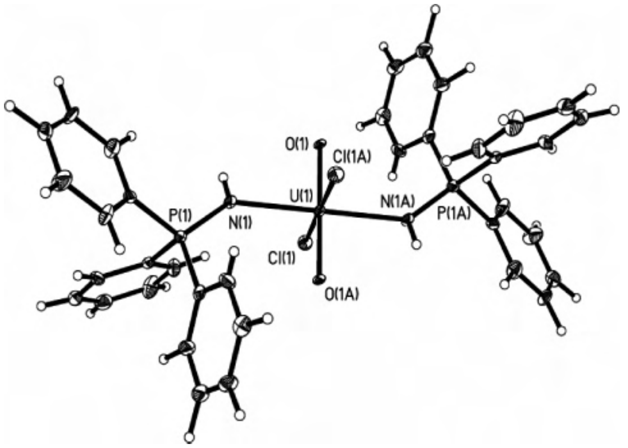


Figure 1. ORTEP representation of $[UO_2Cl_2(Ph_3PNH)_2]$ (**1**) (50% ellipsoids). Selected bond lengths (Å): U(1)−O(1), 1.778(1); U(1)−N(1), 2.370(1); U(1)−Cl(1), 2.6713(4); P(1)−N(1), 1.605(1). Selected bond angles (deg): O(1)−U(1)−N(1), 92.55(5); O(1)−U(1)−Cl(1), 90.00(4), P(1)−N(1)−U(1), 139.19(8); P(1)−N(1)−H(1)N, 110.5(2); U(1)−N(1)−H(1)N, 110.0(2).

The P═N [1.605(1) Å] bond distance in **1** is greater than that of the free ligand Ph_3PNH [1.582(2) Å].[23] The only other f element complex containing a Ph_3PNH ligand $[Cp^*_2UCl_2(Ph_3PNH)]$ shows no change upon complexation [P═N, 1.58(1) Å], despite suggestions that the resonance form, $Ph_3P^{+-}HN^-$, is stabilized by multiple U−N bond character.[24]

---

(16) [***Caution!*** *Uranium is an α-emitting radionuclide* (specific activity 1.24 × 10^4 Bq/g). The synthetic procedures for complexes **1**, **2**, and **8** were the same, using the following method. A solution of $UO_2Cl_2(THF)_3$ (0.50 g, 1.03 mmol) in THF (20 cm^3) was treated with 2 equiv of Ph_3PNH (0.57 g, 2.06 mmol) dissolved in THF. The reaction was stirred for 1 h, while a pale yellow precipitate developed. The solution was filtered, and the solid obtained was washed with THF (10 cm^3 × 1) and hexane (10 cm^3 × 2) and dried under vacuum. For $UO_2Cl_2(Ph_3PNH)_2$ (**1**). Yield: 81%. Anal. Calcd for $C_{36}H_{32}Cl_2N_2P_2O_2U$: C, 48.28; H, 3.60; Cl, 7.92; N, 3.13; P, 6.92; U, 26.58. Found: C, 48.49; H, 3.49; Cl, 8.43; N, 3.06; P, 6.73; U, 26.65. Raman (3500−400 cm^{-1}, solid in glass capillary): N−H, 3302(w); O═U═O, 833(s). IR (cm^{-1}, ATR): O═U═O, 904(s). ^1H NMR (400 MHz, CD_2Cl_2, 0 °C; three N*HP*Ph_3 signals due to isomers): δ 6.17 (d, 0.42 H, $^2J_{HP} = 6.1$ Hz), 6.54 (d, 1.54 H, $^2J_{HP} = 7.1$ Hz), 6.78 (d, 0.14 H, $^2J_{HP} = 6.8$ Hz), 7.4−8.2 (m, 30 H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 0 °C): δ 128.6 (d, *i*-Ph, $^1J_{CP} = 100$ Hz), 128.8 (d, *o*-Ph, $^2J_{CP} = 13$ Hz), 132.9 (d, *p*-Ph, $^4J_{CP} = 3$ Hz), 133.5 (d, *m*-Ph, $^3J_{CP} = 10$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 0 °C, 85% H_3PO_4; three isomer signals with relative intensities in parentheses): δ 44.4 (10), 44.7 (40), 45.0 (1). For $UO_2Cl_2(Cy_3PNH)_2 \cdot 2CH_2Cl_2$ (**2**·$2CH_2Cl_2$). Yield: 78%. Anal. Calcd for $C_{38}H_{72}Cl_6N_2P_2O_2U$: C, 41.43; H, 6.59; Cl, 19.31; N, 2.54; P, 5.62; U, 21.61. Found: C, 41.50; H, 6.71; Cl, 18.77; N, 2.49; P, 5.65; U, 21.37. Raman (cm^{-1}, solid in glass capillary): N−H, 3340(w); O═U═O, 817(m). IR (cm^{-1}, ATR): O═U═O, 900(s). ^1H NMR (400 MHz, CD_2Cl_2, 0 °C; two N*HP*Cy_3 signals due to isomers): δ 1.20−2.40 (m, 66 H, Cy), 5.56 (minor isomer; d, 0.1 H, Cy_3PN*H*, $J_{HP} = 8.1$ Hz), 5.82 (major isomer; d, 0.9 H, Cy_3PN*H*, $J_{HP} = 7.8$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 0 °C): δ 26.1 (s, *p*-Cy), 26.8 (d, *m*-Cy, $^3J_{CP} = 2.8$ Hz), 27.3 (d, *o*-Cy, $^2J_{CP} = 7.3$ Hz), 35.3 (d, *i*-Cy, $^1J_{CP} = 54.2$ Hz), $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 0 °C, 85% H_3PO_4; two isomer signals with relative intensities in parentheses): δ 59.4 (9), 59.8 (1). For $UO_2Cl_2(Cy_3PO)_2 \cdot 2CH_2Cl_2$ (**8**·$2CH_2Cl_2$). Yield: 81%. Anal. Calcd for $C_{38}H_{70}Cl_6P_2O_4U$: C, 46.31; H, 7.12; Cl, 7.59; P, 6.65; U, 25.49. Found: C, 47.08; H, 7.52; Cl, 7.84; P, 6.65; U, 24.98. Raman (cm^{-1}, solid in glass capillary): O═U═O, 832(s). IR (cm^{-1}, ATR) O═U═O, 918(s). ^1H NMR (400 MHz, CD_2Cl_2, 0 °C): δ 1.20−2.50 (m, 66 H, Cy). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 0 °C): δ 26.2 (s, m, *p*-Cy), 27.1 (d, *o*-Cy, $^2J_{CP} = 12$ Hz), 35.4 (d, *i*-Cy, $^1J_{CP} = 59$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 0 °C, 85% H_3PO_4; two isomer signals with relative intensities in parentheses): δ 73.4 (90), 73.0 (10).]

(17) [***Caution!*** *Np-237 is a high specific activity, α-emitting radionuclide* (specific activity 2.61 × 10^7 Bq/g). The possession and use of radioactive materials are subject to statutory controls. The synthetic procedures for complexes **5** and **6** were modified from a previous method.[19] An aliquot (0.43 cm^3) of 0.1 M (23.7 g/L) neptunyl(V) chloride, in 2 M HCl, was evaporated to dryness using a heat lamp. Concentrated perchloric acid (70%, 0.5 cm^3) was then added, and the solution was heated until fuming. The mustard yellow solution turned pink as it was diluted with a few drops of water (~0.3 cm^3). The pH was increased by the addition of 6 M NaOH so that a brown precipitate of neptunyl(VI) hydroxide was produced. The suspension was centrifuged and washed with water twice. The brown solid was suspended in distilled water (0.5 cm^3) and then dissolved in a minimum of 1.2 M HCl. For Ph_3PO, 3 equiv of ligand (0.035 g, 0.126 mmol) in 1 mL of acetone was layered on top of the aqueous solution and placed in a freezer overnight (−15 °C). Yellow crystals of **7** were isolated and dried (21 mg, 56%). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C; two isomer signals with relative intensities in parentheses): 4.83 and 5.09 (3:1; br, 12 H, *o*-Ph), 7.18 and 7.25 (1:3; br, 12 H, *m*-Ph), 7.40 and 7.46 (1:3; br, 6 H, *p*-Ph). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4): δ 15.2. Raman (cm^{-1}, solid): O═Np═O, 810. For Cy_3PO, 3 equiv of ligand (0.035 g, 0.126 mmol) in 1 mL of acetone was added to the aqueous solution, giving a pale yellow precipitate, which was centrifuged; the resulting liquor was removed and the solid dried under vacuum (30 mg, 80%). The solid was dissolved in dichloromethane and placed in a freezer overnight (−15 °C). Yellow crystals of **6** were isolated. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): major isomer δ −0.84 (br s, 3 H, *i*-Cy), −0.12 (b m, 12H, *o*-Cy), 0.71 (m, 6 H, *p*-Cy), 1.62 (m, 12 H, *m*-Cy). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4): δ 49.8. Raman (cm^{-1}, solid): O═Np═O, 802. For NMR reactions of **5** and **6** with R_3PNH (R = Ph, Cy), typically ~10 mg of **5** or **6** was dissolved in a poly(tetrafluoroethylene) NMR tube in CD_2Cl_2 and the spectrum taken. Next, 2 equiv of the required phosphinimine in CD_2Cl_2 was added over an argon atmosphere, then the tubes were resealed, and the spectrum was retaken.]

(18) [Crystal data for **1**·$2CH_2Cl_2$: $C_{38}H_{36}Cl_6N_2O_2P_2U$, $M = 1065.36$, $a = 9.7149(6)$ Å, $b = 11.3826(7)$ Å, $c = 19.0621(11)$ Å, $\beta = 102.7250(1)°$, $V = 4778(2)$ Å^3, monoclinic, space group *P*21/*n*, $Z = 2$, $T = 100(2)$ K, $\mu = 4.450$ mm^{-1}, reflections collected/unique = 17 356/4890, R1 ($I > 2\sigma(I)$) = 0.0149, and wR2 ($I > 2\sigma(I)$) = 0.0358. The structure was solved by direct methods. The non-H atoms were refined anisotropically. The asymmetric unit contains half of the molecule. The U atom lies on a center of symmetry. H atoms were found by difference Fourier techniques and refined with the isotropic thermal parameters of each constrained to 1.2 times that of the atomto which it is bonded.]

(19) Alcock, N. W.; Roberts, M. M.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1982**, 25.

(20) Data were collected from the Cambridge Crystallographic Database. From the 587 hits of uranyl structures with RFAC < 10%, the mean U═O distance is 1.762 Å with a standard deviation of 0.033 Å. This relates to an approximate range of 1.696−1.828 Å within a 95% confidence limit, from 2003.

(21) Bombieri, G.; Forsellini, E.; Day, J. P.; Azeez, W. I. *J. Chem. Soc., Dalton Trans.* **1978**, 677.

(22) Bombieri, G.; Forsellini, E.; Paoli, G. D.; Brown, D.; Tso, T.; Chung, J. *J. Chem. Soc., Dalton Trans.* **1979**, 2042.

(23) Grun, M.; Harms, K.; Kocker, R. M. z.; Dehnicke, K.; Goesmann, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1091.

(24) Cramer, R. E.; Roth, S.; Gilje, J. W. *Organometallics* **1989**, *8*, 2327.

Multinuclear NMR data for compounds **1** and **2** indicate the presence of two major species in solution. For example, for **1** the $^{31}P\{^1H\}$ NMR shows two major signals (in a 4:1 ratio), with two signals of the same relative intensity (4:1) observed for the NH protons in ^1H NMR spectra. Also, variable-temperature ^1H NMR spectra show that each of the signals starts to broaden and merge, reversibly, above 40 °C, indicating a dynamic equilibrium on the NMR time scale (Supporting Information). With this limited evidence, we suspect that cis/trans structural isomerism is occurring in solution. Although isomerism of uranyl complexes has not been reported in solution before, there is structural evidence for the existence of cis/trans isomers in $[UO_2Cl_2(Ph_3PO)_2]$[25] and $[UO_2Br_2(Ph_3AsO)_2]$,[26] with the cis isomer reported to be thermodynamically more stable in the latter.[26] While not central to the theme of this paper, we continue to investigate geometric isomerism in actinyl complexes further.

Consistent with the lengthening of the P═N bond in **1**, compared to the free ligand, there is a dramatic change in the charge distribution around the coordinating P═NH moiety, possibly the consequence of a strong U−N interaction. This is reflected in the large difference in chemical shift ($\Delta\delta$: **1**, 5.53 ppm; **2**, 6.33 ppm) between the N*H* ^1H NMR signal (**1**, 6.54 ppm; **2**, 5.82 ppm) compared to that of the uncomplexed ligand (Ph_3PNH, 1.01 ppm; Cy_3PNH, −0.51 ppm). It is therefore possible that phosphinimines interact more strongly with the uranyl ion than with hard Lewis acids such as Ta and Al, where a much smaller change in δ is observed for $[(C_5Me_5)TaF_4(Ph_3PNH)]$,[27] $[AlMe_2Cl(Cy_3PNH)]$,[28] and $[AlMe_3(Ph_3PNH)]$[25] ($\Delta\delta = 2.59$, 1.01, and 0.81 ppm, respectively). Also, a substantial change in the stretching frequency of the N−H bond in the solid-state Raman spectrum (e.g., free Ph_3PNH, 3353 cm^{-1}; **1**, 3302 cm^{-1}) adds to the evidence for a strong U−N interaction in **1** (Supporting Information).

The addition of R_3PNH to solutions of $[UO_2Cl_2(R_3PO)_2]$ (R = Ph, **7**; Cy, **8**) results in selective displacement of the P═O ligands and the formation of phosphinimine complexes **1** and **2** (Scheme 1). For example, when Cy_3PO is added to dichloromethane solutions of $[UO_2Cl_2(Cy_3PNH)_2]$ (**2**), there is no reaction either at ambient temperature, with heating, or with a 10-fold excess of Cy_3PO. By contrast, adding 1 equiv of Cy_3PNH to a dichloromethane solution of $[UO_2Cl_2(Cy_3PO)_2]$ (**8**) results in the immediate release of 1 equiv of Cy_3PO and the formation of an intermediate complex, presumed to be $[UO_2Cl_2(Cy_3PNH)(Cy_3PO)]$ (**9**). Complex **9** reacts with a further equivalent of Cy_3PNH to give **2** quantitatively and a total of 2 equiv of free Cy_3PO (Supporting Information).

This N-donor preference is also demonstrated in neptunyl(VI) chemistry. Although we have yet to crystallographically characterize the products, ^1H and ^{31}P NMR experiments in CD_2Cl_2 show that the addition of R_3PNH to solutions of $[NpO_2Cl_2(R_3PO)_2]$ (Ph, **5**; Cy, **6**) results in the release of free R_3PO, implying the formation of new complexes believed to be $[NpO_2Cl_2(R_3PNH)_2]$ (Ph, **3**; Cy, **4**) (Scheme 1). For example, in Figure 2 (R = Ph), the ^{31}P NMR spectrum clearly shows changes in chemical shift from 15.0 ppm for **5** to a very broad peak (paramagnetic ^1f) at ∼44 ppm (**3**) and the appearance of a very sharp resonance at 27.6 ppm assigned to free Ph_3PO. Changes in the ^1H NMR spectra are consistent with this interpretation (Supporting Information).

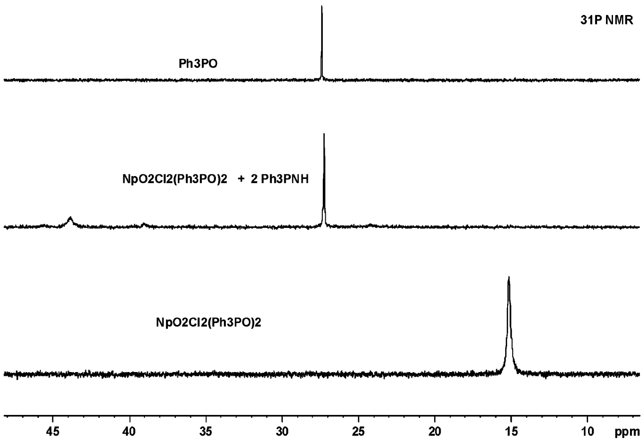
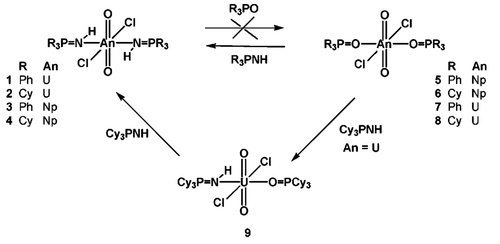


Figure 2. $^{31}P\{^1H\}$ NMR spectra (middle) of the reaction between $[NpO_2Cl_2(Ph_3PO)_2]$ (**6**) (bottom) and Ph_3PNH. The spectrum of free Ph_3PO is shown (top) for comparison. All solutions in CD_2Cl_2.

Scheme 1. Displacement of R_3PO Ligands by R_3PNH in Actinyl Complexes



We have demonstrated that it is possible for the uranyl- and neptunyl(VI) moieties to show a preference for coordination to N-donor ligands in the presence of O-donor ligands. Ongoing computational studies will hopefully provide an answer as to why this is the case, and further experimental investigations are in progress to probe the observed cis/trans isomerization. We are continuing to develop synthetic routes into the preparation of crystalline samples of both neptunyl and plutonyl phosphinimine complexes.

Acknowledgment. We thank Dr. David Collison of The University of Manchester for helpful discussions and Nexia Solutions, the Nuclear Decommissioning Authority (M.J.S.), and the EPSRC (S.M.C.; Grant GR/595152/01) for financial support.

Supporting Information Available: Crystallographic file in CIF format for compound **1**, NMR spectra for compounds **1** and **2**, NMR spectra and table of peak assignments to compliment Scheme 1 for R = Cy and An = U, NMR spectra to compliment Figure 2, NMR spectra of $Cy_3PNH + [NpO_2Cl_2(Cy_3PO)_2]$ (**6**), and Raman spectra of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051161C

---

(25) Akona, S. B.; Fawcett, J.; Holloway, J. H.; Russell, D. R. *Acta Crystallogr., Sect. C* **1991**, *47*, 45.

(26) Arnáiz, F. J.; Miranda, M. J.; Aguado, R.; Mahía, J.; Maestro, M. A. *Polyhedron* **2001**, *20*, 3295.

(27) Schrumpf, F.; Roesky, H. W.; Noltemeyer, M. *Z. Naturforsch., B* **1990**, *45*, 1600.

(28) Ong, C. M.; McKarns, P.; Stephan, D. W. *Organometallics* **1999**, *18*, 4197.