Homoleptic uranium(III) imidodiphosphinochalcogenides including the first structurally characterised molecular trivalent actinide–Se bond†

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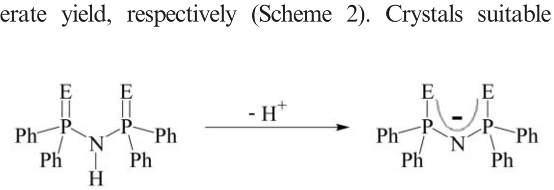
Preparation of U[N(EPPh$_2$)$_2$]$_3$ (E = S or Se) by treating U[N(SiMe$_3$)$_2$]$_3$ with three equivalents of NH(EPPh$_2$)$_2$ is described together with presentation of a hitherto unreported molecular crystal structure containing An(III)–Se bonds (An = actinide).

Traditionally, actinide coordination chemistry has been dominated by the study of relatively hard donor ligands, in particular oxygen, or metal–ligand bonds aided by the stabilising presence of sterically demanding Cp/Cp* type spectator ligands.[1] The utility of bulky substituents as a route to lanthanide chalcogen compounds of low nuclearity has been documented.[2] Current understanding of fundamental bonding involving 5*f*-elements still trails behind that of the corresponding transition metal and lanthanide chemistry and is hindered, in part, by a small number of well characterised molecular complexes of less traditional donor atoms. Recently, there has been increasing interest in the interaction of hard Lewis acidic 5*f* ions with ligands of softer donor atoms, such as nitrogen and sulfur,[3] motivated both by the need for essential elementary knowledge, and the potential for subtle differences between 6*d*5*f* and 5*d*4*f* type metal bonding to be exploited in industrially important actinide/lanthanide separations.[4] The chemistry of lower valent actinides with anionic ligands of the type [N(EPPh$_2$)$_2$]$^-$, in which the negative charge is delocalised over the [EPNPE] moiety (Scheme 1), is surprisingly unexplored, given that they offer an attractive entry route into syntheses of actinide complexes with the heavier chalcogens as donor atoms. Here we report the first examples of actinide complexes with the ligands [N(SPPh$_2$)$_2$]$^-$ and [N(SePPh$_2$)$_2$]$^-$.

Treatment of a red/purple thf solution of U[N(SiMe$_3$)$_2$]$_3$[5] with three equivalents of NH(SPPh$_2$)$_2$[6] or NH(SePPh$_2$)$_2$[7] results in deprotonation of the ligand and gives brown/grey solutions, which after concentration and addition of hexanes, harvests analytically pure U[N(SPPh$_2$)$_2$]$_3$ **1** and U[N(SePPh$_2$)$_2$]$_3$ **2**, in good and moderate yield, respectively (Scheme 2). Crystals suitable for single-crystal X-ray diffraction were crystallised from thf/toluene (**1**) or benzene-d$_6$ (**2**).‡

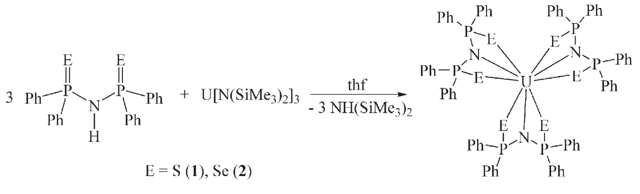


Scheme 1 Deprotonation of NH(EPPh$_2$)$_2$, resulting in delocalisation of the negative charge over the [EPNPE] linkage. E = S or Se.

Compound **1** is insoluble in benzene, toluene and acetonitrile, but moderately soluble in thf. Compound **2** is soluble in thf, moderately soluble in benzene and acetonitrile, but insoluble in toluene. The electronic absorption spectra of benzene solutions of **1** and **2** display distinctive U(III) Laporte-forbidden 5*f*–5*f* transitions[5] with multiple weak absorption bands (750–1300 nm) in the near-IR region and more intense bands (550–700 nm) in the visible region, assigned as Laporte-allowed 5*f*–6*d* transitions.[5a] There is also an intense charge-transfer band below 400 nm.

A signal was observed in the room temperature ^{31}P NMR spectra at high field chemical shifts of −680.6 ppm for **1** and at −722.6 ppm for **2**, indicating that the complexes are stable in solution, although the possibility of a change in ligand denticity to bidentate and/or solvent coordination to uranium cannot be discounted.§

The resonance is broad, presumably due to the close proximity of paramagnetic U(III) to the phosphorus atoms two bonds away, and displays temperature dependence (varying by *ca.* 250 ppm from 10 to −50 °C, see ESI† for details) as would be expected for a paramagnetically induced shift. Typically in diamagnetic metal complexes with [N(EPPh$_2$)$_2$]$^-$, the ^{31}P NMR signal is observed in the range of 20 to 30 ppm downfield from the protonated free ligand (*ca.* between 50 and 60 ppm).[7,8] In examples of paramagnetic lanthanide complexes, Ibers *et al.* report ^{31}P resonances in the region of 62 to 83 ppm, representing a shift upfield of the protonated ligand (although no signal was found for Cp$_2$Gd[N(SePPh$_2$)$_2$] between −150 and 450 ppm).[8b] The ^{31}P NMR shifts in Sm[N(SePPh$_2$)$_2$]$_2$(SeMes)(thf) were found at 29.8 and 45.8 ppm.[9] A resonance was observed at −459 ppm for the diamagnetic, square planar complex, Ni[N(SPPh$_2$)$_2$]$_2$, but this was interpreted as isomerisation to a paramagnetic tetrahedral complex in solution.[10] The IR spectra show P–E vibrations at 593 cm^{-1} for υ(P–S) in **1** and at 536 cm^{-1} for υ(P–Se) in **2**, and both are at lower energy than the free ligands, consistent with deprotonation and coordination to the uranium centre. The position of the P–Se band in **2** does not differ significantly from the range reported in complexes of [N(SePPh$_2$)$_2$]$^-$ with transition metal ions.[7,8e,8g,11] The assigned P–S vibration in **1** is slightly higher in energy than



Scheme 2 Preparative route for the syntheses of **1** and **2**.

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† Electronic supplementary information (ESI) available: CIF's, NMR (including variable temperature ^{31}P), UV/vis, and IR spectra for compounds **1** and **2**. See http://www.rsc.org/suppdata/cc/b5/b503106k/

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reported P–S bands in many transition metal complexes (up to *ca.* 30 cm^{-1}),[10,11a–d] although some transition metal complexes have comparable υ(P–S) energies, such as in Pt($C_8H_{12}OMe$)[N($SPPh_2$)$_2$] at 587 cm^{-1}.[8e] Therefore, due to the variability of the literature values it is not possible to elucidate the effect of U(III) coordination on weakening the P–S bond compared to 'softer' transition metals. Unfortunately, IR data have not been reported for comparable lanthanide complexes.

The crystal structures of **1** and **2** are homoleptic, isomorphous and comprise of a nine-coordinate U(III) centre, in a geometry best described as distorted tri-capped trigonal prismatic, bonded to three [N($EPPh_2$)$_2$]$^-$ anions.¶ A thermal ellipsoid plot of **2** is shown in Fig. 1. Each triangular face of the trigonal prism is defined by one E atom from each anion and the N atoms occupy the three capping positions (Fig. 2). All three anions in **1** and **2** are tridentate, bonding to uranium through both chalcogen atoms and the nitrogen atom. Both complexes have D_3 symmetry. Compound **1** crystallises with a molecule of benzene and **2** with a toluene molecule. The U–S distance in **1** is 2.9956(5) Å, the U–N distance is 2.632(2) Å, the S–U–S bite angle is 122.82(2)° and the P–N–P angle is 147.43(16)°. In **2** the U–Se distance is 3.0869(4) Å, the U–N distance is 2.701(3) Å, the Se–U–Se bite angle is 124.594(12)° and the P–N–P angle is 144.5(2)°. There are distortions from planarity of the [EPNPE] chain. In **1** the deviations of the S atoms from the plane defined by UP_2 are 0.2415 Å above and 0.2416 Å below the plane and in **2** are 0.2841 Å above and below the plane for the Se atoms. There is no significant displacement of the N atom from the UP_2 plane in either **1** or **2**. The twist from planarity of the UE_2P_2N ring can also be described by the angle between the UP_2 and UE_2 planes of 5.3° in **1** and 6.0° in **2**. The twisting of the ligand is likely due to steric effects and the greater distortion in **2** than **1** is probably caused by the larger size of selenium compared to sulfur.

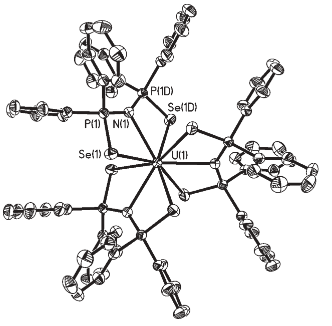

Fig. 1 Thermal ellipsoid plot (at the 50% probability level) of the structure of **2**, with H atoms and lattice solvent omitted. Selected bond lengths (Å): U(1)–Se(1) 3.0869(4), U(1)–N(1) 2.701(3), P(1)–Se(1) 2.1372(8). Selected bond angle (°): Se(1)–U(1)–Se(1D) 124.594(12). Se(1D) and P(1D) are generated by the symmetry operation x − y, −y, 0.5 − z.

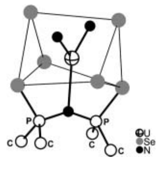

Fig. 2 Ball and stick representation of the distorted tricapped trigonal prismatic coordination sphere of uranium in **2**. For clarity, the outer sphere atoms have been omitted apart from one ligand, which has been truncated at the first C atom of the phenyl rings.

Although there are several examples of extended solid state lattices of uranium selenides,[12] molecular complexes containing uranium and selenium are rare. To our knowledge the only molecular U–Se bonds characterised crystallographically are in the U(VI) uranyl diselenocarbamate, $UO_2[Et_2NCSe_2]_2Ph_3AsO$ (average U–Se distance is 2.98 Å),[13] and a U(IV) polyselenide, containing a discrete [U(Se_2)$_4$]$^{4-}$ anion (average U–Se distance is 2.90 Å), which was prepared through a high temperature solid state reaction under vacuum.[14] There is also a report of a U(IV) selenolate, [U($C_5H_4SiMe_3$)$_3$(SeMe)], which was not structurally characterised.[15] The compound was reduced to U(III) by Na(Hg) and analysed by C, H, N composition and ^1H NMR. Only recently the first structurally characterised U(III)-thiolate bonds were reported. The average U–S bond distance in [Na(18-crown-6)(thf)$_2$][Cp*$_2$U(S^{i}Pr)$_2$] is 2.784 Å,[16] which is shorter than in **1** presumably because the negative charge in the [N($SPPh_2$)$_2$]$^-$ ligand is delocalised. The average U–S bond distance in the U(III) poly(thioimidazolyl)borate (bonds are to thione S atoms) complex, [U{H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_3$][BPh_4], is 2.928(11) Å,[17] which is similar to that in **1**.

The ligands in **1** and **2** are all tridentate although a range of bonding motifs are possible for [N(EPR_2)$_2$]$^-$, namely bridging, bidentate or tridentate depending upon the size and preferred geometry of the metal ion, the nature of the R group and the identity of the chalcogen.[8,11,18] Typically, transition metal complexes with [N(EPR_2)$_2$]$^-$ exhibit bidentate coordination through both chalcogen atoms, such as in Co^{II}[N($SPPh_2$)$_2$]$_2$[11a] and Pt^{II}[N($SePPh_2$)$_2$]$_2$·$CHCl_3$.[7] Examples of complexes including bridging anions are [Cu^{I}N(SP^{i}Pr$_2$)$_2$]$_3$[19] and [Ag^{I}N(SeP^{i}Pr$_2$)$_2$]$_3$.[20] Complexes with the larger, relatively hard tetravalent transition metals (*i.e.* Zr^{4+}, Hf^{4+}) have not been reported. There are no isotructural compounds of similarly sized[21] trivalent lanthanide ions (*i.e.* La or Ce), but comparisons with related complexes can be made. Ibers *et al.* found that Y[N($SPPh_2$)$_2$]$_3$ has all three anions coordinated in a tridentate fashion, whereas Y[N($SePPh_2$)$_2$]$_3$ contains two tridentate anions and one that is bidentate. The bidentate ligand is coordinated to yttrium only through the selenium atoms, a feature attributed to the larger size of selenium compared to sulfur.[12d] The larger ionic radius of U(III) allows for tridentate coordination in both **1** and **2**. The closest comparable Ln(III)–Se bond has a distance of 3.1234(4) Å for La–Se in Cp_2La[N($SePPh_2$)$_2$],[12c] slightly longer by 0.0365 Å than the U–Se distance of 3.0869(4) Å in **2**. This difference is consistent with a modest increase in the affinity of An(III) for donor atoms of a 'softer' nature than Ln(III) of similar ionic radii, although it is not known what effect the Cp rings have upon the La–Se bond. Unfortunately, there are no early Ln(III)–S bonds with [N(SPR_2)$_2$]$^-$ ligands to make a similar comparison of U–S in **1**, with the hypothesis that the difference in bond lengths would be smaller because sulfur is more electronegative than selenium. It is also worth noting the preservation of the U(III) oxidation state in the formation of **1** and **2**, in view of the fact that our attempts so far to prepare other homoleptic uranium complexes with chalcogen donor ligands, such as dithio- and diselenophosphinates, invariably leads to U(IV) products with four anions coordinated to the metal centre, whereas in the case of **1** and **2** the steric requirements of the ligands restrict their number, and therefore the valency of the metal, to three. We are currently extending this work to include variations of the ligand substituents, studying An(III) ions of different ionic radii and preparing 4*f* analogs, in order to examine the effect on coordination modes and to consider subtle differences that may be present between An(III) and Ln(III) complexes with soft donor ligand atoms.

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Notes and references

‡ Synthesis of **1**: a stirred solution of $U[N(SiMe_3)_2]_3$ (0.0900 g, 0.1251 mmol) in thf (7 cm^3) was treated with $NH(SPPh_2)_2$ (0.1740 g, 0.3753 mmol) resulting in a colour change to a grey solution and stirring was continued for 12 h. The solution was filtered and the solvent volume reduced under vacuum by half. Addition of hexanes (8 cm^3) with shaking precipitated a grey powder that was collected, washed with hexanes (5 cm^3) and dried under vacuum. Yield 0.1526 g, 77%. $^{31}P\{^1H\}$ NMR (121.49 MHz, C_4D_8O, 85% H_3PO_4): $\delta = -680.6$. IR (Nujol, KBr plates): (cm^{-1}) = 1311(m), 1204(s), 1180(m), 1158(w, sh), 1100(m), 1070(w), 1028(w), 999(w), 978(w), 970(w), 938(w), 920(w), 756(w), 744(m), 723(s), 714(m,sh), 706(w), 693(s), 626(vw), 618(w), 609(w), 593(s), 512(s) 503(m,sh), 493(m), 468(m). UV/vis/near-IR (C_6H_6 solution prepared *in situ* due to the low solubility of **1**): (nm) = 580, 628, 760, 884, 925, 1028, 1083, 1209, 1225, 1251. Anal. Calc. (%) for $C_{72}H_{60}N_3P_6S_6U$: C, 54.61; H, 3.82; N, 2.65. Found (%): C, 54.92; H, 3.98; N, 2.58. X-ray diffraction quality crystals of **1**. $C_6H_5CH_3$ were grown by layering a toluene solution of $U[N(SiMe_3)_2]_3$ on top of a thf solution of $NH(SPPh_2)_2$ and standing at ambient temperature for several days. Synthesis of **2**: as for **1**, $U[N(SiMe_3)_2]_3$ (0.0500 g, 0.0695 mmol) and $NH(SePPh_2)_2$ (0.1162 g, 0.2086 mmol), except that the reaction solution and product were grey/brown in colour. Yield 0.0895 g, 50%. $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 85% H_3PO_4): $\delta = -722.6$. IR (Nujol, KBr plates): (cm^{-1}) = 1308(m), 1171(w,sh), 1141(m,br), 1101(s), 1027(w), 999(w), 973(m), 936(w), 921(w), 893(w) 848(w), 741(m), 721(s), 690(m), 575(m), 536(m), 511(m), 483(w). UV/vis/near-IR (C_6H_6 solution): (nm) = 597, 640, 761, 884, 921, 1031, 1081, 1205, 1224, 1248. Anal. Calc. (%) for $C_{72}H_{60}N_3P_6Se_6U$: C, 46.37; H, 3.24; N, 2.25. Found (%): C, 46.11; H, 3.52; N, 2.35. X-ray diffraction quality crystals of **2**. C_6D_6 were grown from an NMR sample of **2**, in C_6D_6, standing at ambient temperature, inside a dry-box, for several days.

§ The ^1H NMR spectrum of **2**, dissolved in C_6D_6 shows three signals that integrate for the phenyl *o*-, *m*- and *p*-protons, consistent with the crystal structure. However, **1** is insoluble in C_6D_6 and further variable temperature NMR studies are underway to probe possible ligand exchange and solvent coordination in thf and other solutions.

¶ Crystal data for **1**. $C_6H_5CH_3$: $C_{79}H_{68}N_3P_6S_6U$, $M = 1675.63$, $a = b = 15.0066(9)$, $c = 56.107(4)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $V = 10942.4(12)$ Å^3, trigonal, space group *R*-3*c*, $Z = 6$, $T = 141(2)$ K, $\mu = 2.575$ mm^{-1}, reflections collected/independent = 38545/3129 [R(int) = 0.0579], $R_1(I > 2\sigma(I)) = 0.0234$, and $wR_2(I > 2\sigma(I)) = 0.0564$. Crystal data for **2**. C_6D_6: $C_{78}H_{60}D_6N_3P_6Se_6U$, $M = 1948.99$, $a = b = 15.1699(10)$, $c = 56.846(7)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $V = 11329.1(18)$ Å^3, trigonal, space group *R*-3*c*, $Z = 6$, $T = 203(2)$ K, $\mu = 5.212$ mm^{-1}, reflections collected/independent = 26588/3004 [R(int) = 0.0337], $R_1(I > 2\sigma(I)) = 0.0270$, and $wR_2(I > 2\sigma(I)) = 0.0678$. CCDC deposition numbers are 264688 and 264689. See http://www.rsc.org/suppdata/cc/b5/b503106k/ for crystallographic data in CIF or other electronic format. The structures were solved by direct methods followed by Fourier synthesis, and refined on F^2. The asymmetric units in **1** and **2** contain a sixth of the molecule which has D_3 symmetry. All of the atoms of the uranium containing molecule were refined anisotropically. All of the positions of the hydrogen atoms were calculated. The toluene molecule in **1** was disordered and its electron density accounted for by a PLATON/SQUEEZE calculation.[22] The C atoms of the benzene molecule in **2** were refined isotropically.

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