Selenate and tellurate complexes of pentavalent uranium†

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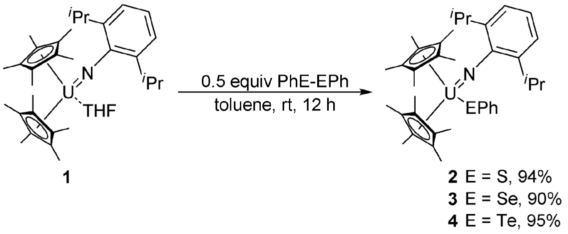
Oxidation of $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(THF)$ with PhE–EPh yields the corresponding U^V-chalcogenate complexes $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(EPh)$ (E = S, Se, Te) in excellent (>90%) isolated yields.

Heavy chalcogen (Se/Te) soft donor ligands have traditionally been exploited to investigate trivalent actinide/lanthanide separation technologies[1] and to address questions regarding covalency in hard–soft interactions.[2,3] Such studies have generated the existing handful of structurally characterized trivalent[1,4] and tetravalent[5,6] uranium–Se/Te complexes and a sole hexavalent U–Se structure,[7] with no corresponding pentavalent examples. The absence of these high-valent uranium chalcogenate complexes limits our understanding of bonding at the extremes of the hard–soft continuum. Recent work by our group[8] and others[9,10] has shown that with appropriate supporting ligands uranium(V) compounds are stable. Herein, we show that pentavalent uranium thiolate, selenate, and tellurate complexes can be easily prepared using readily available PhE–EPh (E = S, Se, Te) reagents.



(1)

As shown in eqn (1), reaction of $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)$-(THF) (**1**) with 0.5 equiv. of PhS–SPh overnight in toluene solution provided the known[8a] U^V-imido thiolate complex $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(SPh)$ (**2**) in 94% yield after work-up. This protocol was conveniently extended to the synthesis of the selenium and tellurium derivatives $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(SePh)$ (**3**) and $(C_5Me_5)_2(=N–2,6-{}^iPr_2–C_6H_3)(TePh)$ (**4**), which were also isolated in excellent yields (90% and 95%, respectively).‡ Although RE–ER reagents have been used as oxidants for low-valent uranium,[5,11] the synthesis of **2–4** represents new chemistry for uranium imido complexes and the first examples of using dichalcogenide reagents to access the U^V/U^{IV} couple.

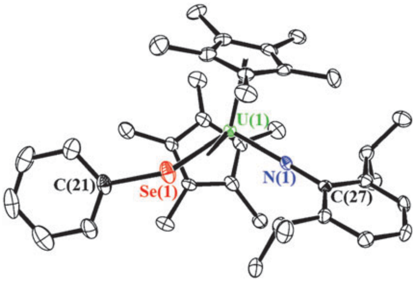


Fig. 1 Molecular structure of **3** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity.

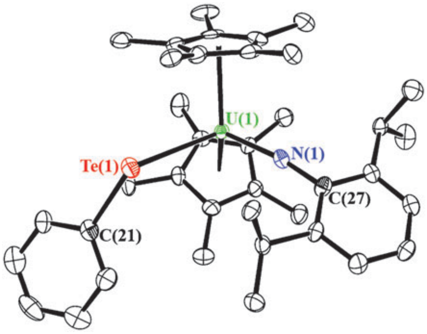


Fig. 2 Molecular structure of **4** with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Single crystals of complexes **3** and **4** suitable for X-ray diffraction‡ were obtained from concentrated hexane solutions at −30 °C. Fig. 1 and 2 show the molecular structures of complexes **3** and **4**, respectively, with select metrical parameters provided in Table 1. Both complexes feature a bent-metallocene framework with the imido and EPh ligand contained within the metallocene wedge, similar in constitution to the related pentavalent $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(X/Y)$ (X = Cl, Br, I; Y = OTf, SPh, NPh_2, $N{=}CPh_2$)[8] complexes. As noted for other high-valent uranium imido complexes,[8b,d] all three complexes **2–4** have short U=N bond distances (1.960(6)–1.984(4) Å) and nearly linear $U{=}N–C_{ipso}$ bond angles (170.6(6)–171.6(3)°), with no obvious trends present on the basis of donating ability of the specific chalcogenide. However, there is a systematic difference in the U–E bond distances in the order U–S (2.7230(13) Å) < U–Se (2.8639(6) Å) < U–Te (3.0845(9) Å) and the $U–E–C_{ipso}$ angles $U–S–C_{ipso}$ (131.08(17)°) > $U–Se–C_{ipso}$ (126.41(15)°) > $U–Te–C_{ipso}$ (121.5(2)°), which both track with increasing size of the chalcogenide ion going down the group.[12] Publication quality X-ray data could not be obtained for the aryloxide complex **5**; however, the aryloxide ligand metrical parameters for the $(C_5Me_5)_2U–OAr$ moiety are quite insensitive to uranium metal

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† Electronic supplementary information (ESI) available: General experimental details, sample protocols, synthetic procedures, a plot of C_5Me_5 ^1H NMR signal versus oxidation potential, and cyclic voltammograms and crystallographic details for **3** and **4**. CCDC numbers for **3** and **4** are 707530 and 707531, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b819097f

Table 1 Selected characterization data for the $(C_5Me_5)_2U({=}N{-}2,6{-}^iPr_2{-}C_6H_3)(EPh)$ complexes **2–5**†

	^1H NMR data for C_5Me_5		Structural data					Electrochemical data[a]	
Compound	δ (ppm)	$\Delta\nu_{1/2}$/Hz	U=N/Å	U=N–C/°	U–E/Å	U–E–C/°	N–U–E/°	$E_{1/2}$ (U^{VI}/U^{V})/V	$E_{1/2}$ (U^{V}/U^{IV})/V
2 (E = S)	4.57	83	1.976(4)	171.6(3)	2.7230(13)	131.08(17)	103.35(12)	0.00	−1.43
3 (E = Se)	4.57	147	1.984(4)	171.4(3)	2.8639(6)	126.41(15)	102.17(11)	0.00	−1.43
4 (E = Te)	4.36	172	1.960(6)	170.6(6)	3.0845(9)	121.5(2)	107.53(18)	−0.07	−1.44
5 (E = O)	3.33	71	—	—	—	—	—	−0.22	−1.75

[a] In ~0.1 M $[Bu_4N][B(3,5-(CF_3)_2-C_6H_3)_4]$–THF at room temperature *vs.* $[(C_5H_5)_2Fe]^{+/0}$ determined from the peak position in a square-wave voltammogram.

oxidation state.[13] For example, the geometric parameters observed for $(C_5Me_5)_2U(-O-2,6-^iPr_2-C_6H_3)(I)$ (U–O = 2.114(6) Å; U–O–C_{ipso} = 166.6(6)°)[13b] are statistically indistinguishable with those obtained for the structurally related U^V complex $(C_5Me_5)_2U(-O-2,6-^iPr_2-C_6H_3)(=O)$ (U–O = 2.135(5) Å; U–O–C_{ipso} = 169.7(5)°).[13a] As such, existing data showing U–O ≪ U–S and U–O–C_{ipso} ≫ U–S–C_{ipso} can be extrapolated for complex **5**, which fits well within the above trends observed for the U^V-chalcogenide complexes.

Although there have been reports of inorganic materials with U^V–Se or U^V–Te interactions,[14] complexes **3** and **4** represent the first structurally characterized pentavalent uranium molecular systems featuring a U–Se or U–Te bond, respectively. At 2.7230(13) Å, the U–Se distance observed in **3** agrees well with analogous parameters observed for structurally characterized U^{IV} metallocene complexes with a U–Se linkage. For example, $(C_5Me_5)_2U(Me)(SePh)$ has a U–Se distance of 2.8432(7) Å,[5d] while $(C_5Me_5)_2U(SePh)_2$ has U–Se distances of 2.8011(7) and 2.7997(7) Å.[5c] Likewise, the U–Te distance observed for **4** (U(1)–Te(1) = 3.0845(9) Å) also compares well with the few structurally characterized U^{IV} metallocene complexes containing a U–Te interaction: $(C_5Me_5)_2U(TePh)_2$ has U–Te distances of 3.0383(6) and 3.0504(6) Å,[5d] while the metallacycle $(C_5Me_5)_2U[\eta^2\text{-}(Te,C)\text{-}(o\text{-}C_6H_4)Te]$ has a U–Te bond length of 2.9648(4) Å.[5d]

Including the aryloxide complex $(C_5Me_5)_2U(=N-2,6-^iPr_2-C_6H_3)(OPh)$ (**5**),[8d] the electrochemical and spectroscopic data for this chalcogenide series of U^V-imido complexes (**2–4**) parallel those found for other U^V-imido complexes, in particular those of the corresponding halide series (F, Cl, Br, and I).[8] All the chalcogenide complexes exhibit both U^{VI}/U^V and U^V/U^{IV} redox couples (Table 1). While **1–4** are all stable in neat THF, neither **3** nor **4** is stable in the supporting electrolyte solution. Based on changes in the voltammetric behavior, it appears that the decomposition proceeds to a U^{IV}-imido complex. Potential data cited in Table 1 were collected within ~2 min of preparation of fresh solutions. These early-time voltammograms are included in the ESI.† The correlation noted previously[8d] in the C_5Me_5 ^1H NMR chemical shift *vs.* $E_{1/2}$ (U^{VI}/U^V) is preserved for **3** and **4**, demonstrating that varying electron density at the metal center is the primary influence on both observables. As such, the lesser variability in the $E_{1/2}$ values down the chalcogenide series *versus* the halide series[8a,d] tracks with the smaller change in electronegativity for the chalcogens *versus* the halogens.

Variations in electronic structure down the chalcogenide series are most strongly reflected in the UV-visible-near IR electronic spectral data (Fig. 3). The UV-visible region is dominated by transitions derived from the $(C_5Me_5)_2U{=}N$ core,[8] and the changes that result as the EPh ligand varies from E = O → S → Se → Te are manifest in both a monotonic increase in the intensities of these bands and a notable red-shift in the energy of the lowest energy set of bands ($E < 15\,000$ cm^{-1}) that have been attributed to the two different spin components of the imido-to-metal charge-transfer transition; $^4(\pi_{M=N} \rightarrow nb_{5f})$ and $^2(\pi_{M=N} \rightarrow nb_{5f})$, respectively (nb = non-bonding). As shown in Fig. 3 inset, there are also changes in the f–f spectral region that are most pronounced as EPh changes from E = O → S, but are still discernible for E = S → Se → Te. These spectral changes closely parallel those seen for the halide series,[8b] and indicate that these anionic wedge ligands do influence the electronic energies and transition probabilities associated with both the molecular (*i.e.*, imido-based) and ligand-field states. Presumably, the influence exerted on both classes of electronic states derives from perturbations induced by the chalcogenide ligand on the uranium(V) f-orbital manifold as previously noted for the trivalent uranium and plutonium systems $An[N(EP^iPr_2)_2]_3$ (An = U, Pu; E = S, Se, Te) by Gaunt and co-workers.[3]

In summary, using PhE–EPh reagents we have provided a convenient and high-yielding route for the synthesis of the first pentavalent uranium selenate (U–SePh) and tellurate (U–TePh) complexes. Spectroscopic comparisons of the pentavalent uranium selenate and tellurate complexes with the isostructural aryloxide (U–OPh) and thiolate (U–SPh) derivatives reveal notable variations in electronic structure that can

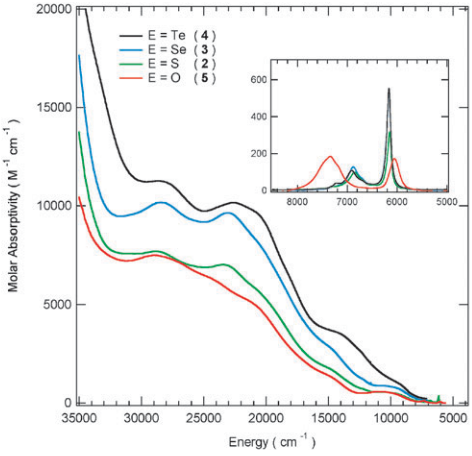

Fig. 3 UV-visible-near IR electronic absorption spectral data for the $(C_5Me_5)_2U(=N-2,6-^iPr_2-C_6H_3)(EPh)$ complexes **2–5** in toluene solution.

be ascribed to differing degrees of perturbation on the U^V f-orbital manifold down the O → S → Se → Te series. This work demonstrates that soft dichalcogenide reagents are not limited to chemistry with soft/low-valent actinide compounds and can be used to access hard uranium complexes in high-valent oxidation states. The understanding of bonding at these hard–soft extremes will promote new separation schemes.

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Notes and references

‡ All manipulations were performed in a recirculating vacuum atmospheres NEXUS drybox (N_2) with a 40CFM Dual Purifier NI-Train. Complex **5** was prepared as previously reported.[8d]

General synthesis of $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(E–Ph)$: a 125 mL side-arm flask equipped with a stir bar was charged with $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(THF)$ (**1**) (0.50 g, 0.66 mmol) and toluene (100 mL). PhE–EPh (0.33 mmol) was added to the dark brown solution and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered through a Celite-padded coarse frit and volatiles were removed from the filtrate. The residue was extracted into hexane (50 mL) and filtered through a Celite-padded coarse porosity frit. The filtrate was collected and the volatiles were removed under reduced pressure to give **2–4** as brown solids.

Characterization data for $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(SPh)$ (**2**): yield: 0.49 g, 0.62 mmol, 94%. Spectroscopic characterization of **2** matched the literature data:[8a] ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 51.33 (b, 1H, $CH(CH_3)_2$), 29.45 (1H, Ar-H), 24.18 (1H, Ar-H), 11.92 (6H, $CH(CH_3)_2$), 6.31 (2H, Ar-H), 4.57 (30H, (C_5Me_5), 1.42 (1H, Ar-H), 1.24 (1H, Ar-H), 0.89 (1H, Ar-H), −2.47 (6H, $CH(CH_3)_2$), −4.74 (1H, Ar-H), −7.95 (b, 1H, $CH(CH_3)_2$).

Characterization data for $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(SePh)$ (**3**): yield: 0.50 g, 0.60 mmol, 90%. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 49.62 (b, 1H, $CH(CH_3)_2$), 30.20 (1H, Ar-H), 25.44 (1H, Ar-H), 11.60 (6H, $CH(CH_3)_2$), 5.08 (3H, Ar-$H_{Se–Ph}$), 4.57 (30H, (C_5Me_5), 3.74 (2H, Ar-$H_{Se–Ph}$), −1.20 (6H, $CH(CH_3)_2$), −3.52 (1H, Ar-H), −6.78 (b, 1H, $CH(CH_3)_2$). Mp = 212–214 °C. MS (EI, 70 eV): m/z 840 (M^+). Anal. calcd for $C_{38}H_{52}NSeU$ (mol. wt 839.82): C, 54.35; H, 6.24; N, 1.67. Found: C, 54.59; H, 6.20; N, 1.71.

Characterization data for $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(TePh)$ (**4**): yield: 0.55 g, 0.63 mmol, 95%. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 49.69 (b, 1H, $CH(CH_3)_2$), 30.90 (1H, Ar-H), 26.26 (1H, Ar-H), 11.73 (6H, $CH(CH_3)_2$), 4.85 (3H, Ar-$H_{Te–Ph}$), 4.36 (30H, (C_5Me_5), 3.67 (2H, Ar-$H_{Te–Ph}$), −0.76 (6H, $CH(CH_3)_2$), −2.75 (1H, Ar-H), −6.81 (b, 1H, $CH(CH_3)_2$). Mp = 205–207 °C. Anal. calcd for $C_{38}H_{52}NTeU$ (mol. wt 888.46): C, 51.37; H, 5.90; N, 1.58. Found: C, 51.74; H, 5.90; N, 1.58.

Crystal data for $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(SePh)$ (**3**): $C_{38}H_{52}NSeU$, M = 839.80, monoclinic, space group $P2_1/n$, a = 12.0348(10) Å, b = 18.1721(16) Å, c = 15.6860(14) Å, α = 90.00°, β = 99.1150(10)°, γ = 90.00°, V = 3387.2(5) Å^3, Z = 4, D_c = 1.647 mg m^{-3}, μ = 5.893 mm^{-1}, $F(000)$ = 1652, T = 120(1) K, 34 990 measured reflections, 6883 independent (R_{int} = 0.0816), R_1 = 0.0347, wR_2 = 0.0633. for $I > 2\sigma(I)$.

Crystal data for $(C_5Me_5)_2U(=N–2,6-{}^iPr_2–C_6H_3)(TePh)$ (**4**): $C_{38}H_{52}NTeU$, M = 888.44, triclinic, space group $P\bar{1}$, a = 10.078(2) Å, b = 10.161(2) Å, c = 18.643(4) Å, α = 76.745(2)°, β = 78.811(2)°, γ = 70.303(2)°, V = 1735.1(7) Å^3, Z = 2, D_c = 1.701 mg m^{-3}, μ = 5.527 mm^{-1}, $F(000)$ = 862, T = 120(1) K, 16 660 measured reflections, 6280 independent (R_{int} = 0.0572), R_1 = 0.0469, wR_2 = 0.1069 for $I > 2\sigma(I)$.

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