



A sulphur and uranium fiesta! Synthesis, structure, and characterization of neutral terminal uranium(VI) monosulphide, uranium(VI) eta-2-disulphide, and uranium(IV) phosphine sulphide complexes

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-07-2018-002932.R1
Article Type:	Paper
Date Submitted by the Author:	25-Sep-2018
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Journal Name

ARTICLE

A sulphur and uranium fiesta! Synthesis, structure, and characterization of neutral terminal uranium(VI) monosulphide, uranium(VI) η^2 -disulphide, and uranium(IV) phosphine sulphide complexes[†]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Three new uranium species $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$, $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$, and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ were synthesized and fully characterized by a combination of NMR, IR, and UV/vis–NIR spectroscopies, elemental analysis, and cyclic voltammetry. The solid state structures of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ were also determined. The compound $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ is the first neutral uranium complex with a terminal sulphido ligand, and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ is the first uranium compound with a coordinated phosphine sulphide ligand. The phosphine sulphide adduct, $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$, can be synthesized either by reaction of the uranium(IV) complex $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ with $S=PMe_3$ or by the reaction of the uranium(VI) terminal sulphido complex $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ with PMe_3 .

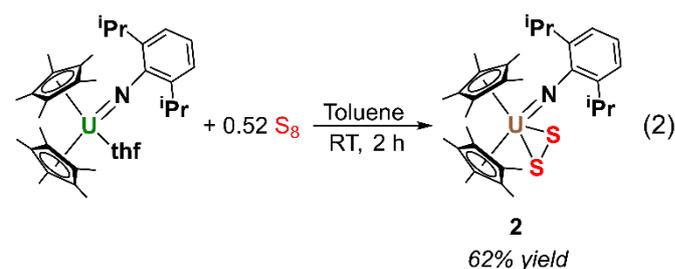
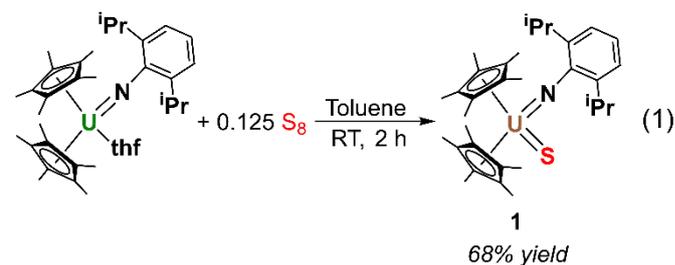
Introduction

Soft-donor atoms such as nitrogen and sulphur are critical in actinide-lanthanide separations, as the “softer” early actinides show a preference for binding to ligands containing soft-donor atoms, which is exploited to perform these difficult processes.^{1–6} As such, it is fundamentally important to develop a comprehensive understanding of dative, single, and multiple bonding interactions between the actinide metals and soft-donor atoms.^{7–10} While there have been several studies of uranium amido ($U-NR_2$),^{11–16} thiolate ($U-SR$),^{17–20} bridging sulphido ($U-S-U$),^{21–29} and terminal uranium imido ($U=NR$) complexes,^{30–46} reports on the synthesis and chemistry of terminal uranium sulphido ($U=S$) complexes have been limited. For example, since Ephritikhine and coworkers synthesized the first uranium sulphido complex $(C_5Me_5)_2U(S^tBu)[S\{Na(18-C-6)\}]$ in 1999,⁴⁷ there have only been four reported examples of terminal sulphido compounds, and these all have been anionic uranium species.^{48–53} To the best of our knowledge, no neutral uranium compounds bearing a terminal sulphido ligand have been synthesized. We have synthesized several high-valent uranium compounds with multiply bonded ligands,^{54–61} and surmised that similar strategies to reach uranium sulphidos may be effective. Herein, we disclose the first neutral uranium species containing a terminal sulphido ligand $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) and the neutral uranium(VI) species with a

terminal η^2 -disulphide ligand $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**), as well as the first uranium phosphine sulphide adduct $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**). Together, these compounds represent a unique opportunity to study the properties of a variety of uranium–sulfur bonding interactions.

Results and Discussion

As shown in equation 1, the reaction of a toluene solution of the known uranium(IV) imido $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ with 0.125 equivalents of S_8 at ambient temperature for two hours cleanly affords the uranium(VI) complex $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) in 68% isolated yield upon workup. Similarly, the reaction of a toluene solution of



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[†]Electronic Supplementary Information (ESI) available: Crystallographic data for compounds **1** and **2** are available from the CCDC: 1857870. See DOI: 10.1039/x0xx00000x

$(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ with 0.52 equivalents of S_8 at ambient temperature for 2 hours gives $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**) in 62% yield (equation 2). The dark red compounds **1** and **2** are thermally stable in solution at 80 °C for at least two days.

Both compounds display 1H NMR behavior consistent with other previously characterized uranium(VI) metallocenes, with sharp resonances for all protons observed ($\delta_{C_5Me_5} = 5.23$ ppm (**1**), 5.68 ppm (**2**)). All phenyl and isopropyl resonances in both compounds are inequivalent ($\delta_{Ph} = 9.92, 9.57,$ and -1.24 (**1**), 10.08, 9.78, and -1.59 (**2**); $\delta_{iPr} = 2.51$ and 1.57 (**1**), 1.96 and 1.94 (**2**)). $^{13}C\{^1H\}$ NMR data were also obtained for both compounds, showing inequivalent resonances for all 2,6- $iPr_2-C_6H_3$ carbons. This inequivalency is not observed for the uranium(IV) imido starting material $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)$,³¹ suggesting that the introduction of the terminal sulphido and η^2 -disulphide ligands in **1** and **2** creates a barrier to rotation due to increased steric pressure within the $(C_5Me_5)_2U$ wedge. Similar behaviour has been observed for the structurally analogous uranium(V) systems $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(X)$.^{34, 36, 62}

IR spectroscopy was also carried out to attempt to identify vibrational modes of the U=S linkage of **1**. There has only been one report of an authenticated U=S stretch ($\nu_{U=S} = 395$ cm^{-1})⁴⁹ observed by Raman spectroscopy for $[(C_5Me_5)_2Co][U(=S)(=O)[N(SiMe_3)_2]_3]$. To help assign this stretch by IR spectroscopy, ^{34}S -labeled $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=^{34}S)$ (**341**) was synthesized using $^{34}S_8$. Unfortunately, no shifts in the IR resonances were observed, suggesting that the energy of any U=S vibration is outside of the spectral window (4000–500 cm^{-1}). A S–S vibrational mode was identified at 526 cm^{-1} for $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**), which compares well with previously identified stretches for an $\eta^2-S_2^{2-}$ disulphide ligand on $Tp^*_2U(\eta^2-S_2)$ ($Tp^* =$ hydrotris(3,5-dimethylpyrazolyl)borate) ($\nu_{S-S} = 508$ cm^{-1})⁵⁰ and $[(n-C_3H_7)_2NH_2]_2[(UO_2)[(n-C_3H_7)_2NCOS]_2(\eta^2-S_2)]$ ($\nu_{S-S} = 510$ –530 cm^{-1}).²¹

The electronic spectra of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**) were also collected in

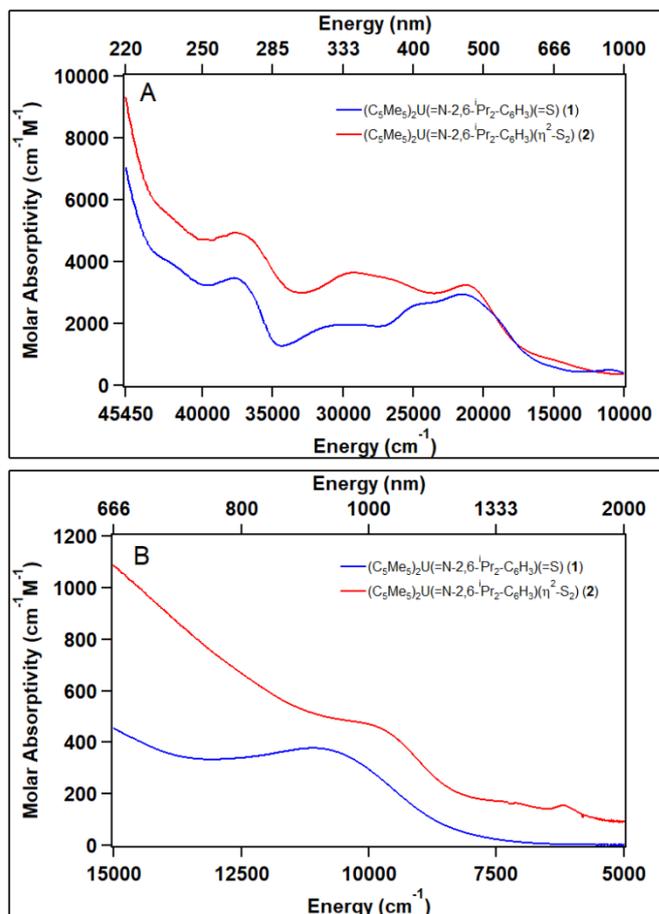


Figure 1: UV/visible (top, Panel A) and NIR (bottom, Panel B) spectra of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**) collected in hexanes at 298 K.

hexanes. As seen in Figure 1, panel A, the UV/visible region of the spectra are dominated by several broad, structured ligand-to-metal charge-transfer (LMCT) transitions that span the entirety of the spectral window. These spectra have a similar structure to the uranium(VI) bis-imido $(C_5Me_5)_2U(=NPh)_2$,⁶³

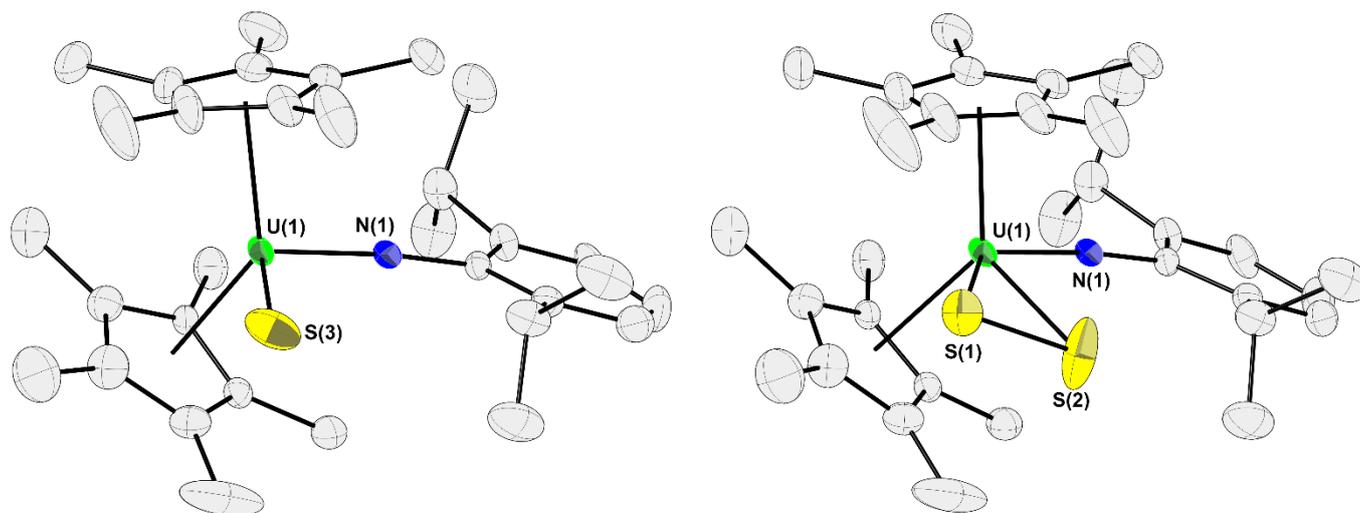
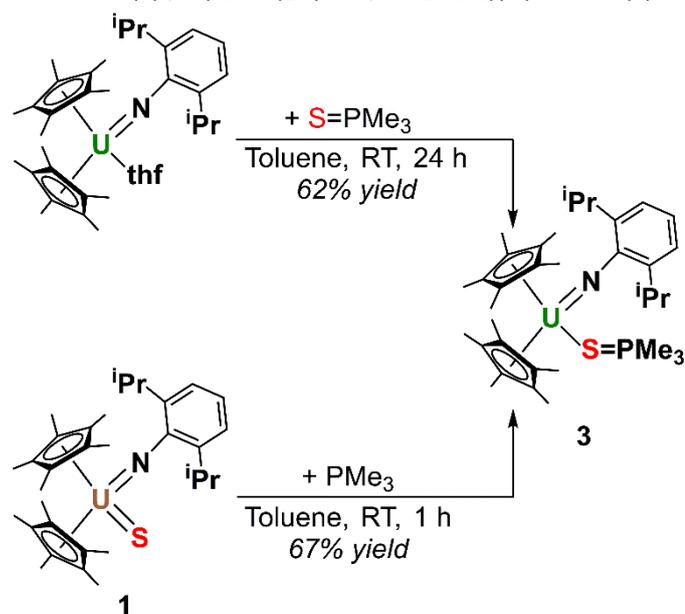


Figure 2: Molecular structure of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**) with thermal ellipsoids displayed at 50% probability. All hydrogen atoms and modelled (C_5Me_5) disorder have been omitted for clarity.

though the intensity of the transitions for **1** and **2** are roughly 50% lower than those of the bis-imido, reflective of a weaker covalent U–S interaction compared to a uranium imido interaction. Also seen in figure 1, panel B, the NIR region of the spectra of **1** and **2** is also dominated by these LMCT bands, and as expected for uranium(VI), $5f^0$ complexes no f-transitions are observed. Cyclic voltammetry of compounds **1** and **2** display a reversible U(VI)/U(V) couple at -1.13 and -1.21 V vs Fc/Fc⁺, respectively, which compare reasonably well to the uranium(VI) bis(imido) $(C_5Me_5)_2U(=NPh)_2$ (-1.70 V).⁶³ Compound **2** also displays a second reversible couple at -1.75 V, similar to that observed for $(C_5Me_5)_2U(=NPh)_2$ (-2.00 V) which we have previously tentatively assigned to a U(V)/U(IV) couple.⁶³

Complexes $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) and $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**) crystallized as a single crystal in an approximately 60:40 ratio out of a concentrated Et₂O/hexane solution at -30 °C. The structures were found superimposed. The compounds crystallized in the monoclinic space group C2/c, and their molecular structures are displayed in Figure 2. The U=S bond length for compound **1** is 2.363(1) Å, which is the shortest U=S bond reported to date ($[K(2.2.2-crypt)][U(=S)[OSi(O^tBu)_3]_4] = 2.376(4)$ and $2.397(4)$ Å;⁵³ $(C_5Me_5)_2U(S^tBu)[S[Na(18-C-6)]] = 2.463(1)$ and $2.477(1)$ Å;⁴⁷ $[Ph_3PMe][U(=S)[N(SiMe_3)_2]_3] = 2.446(6)$ and $2.451(7)$ Å;⁴⁸ $[(C_5Me_5)_2Co][U(=S)(=O)[N(SiMe_3)_2]_3] = 2.390(7)$ Å;⁴⁹ $[K(2.2.2-crypt)][U(=S)[N(SiMe_3)_2]_3] = 2.481(6)$ Å.⁵¹). This value is also consistent with the uncapped U=S bond lengths being significantly shorter than the alkali-metal capped sulphido counterparts. The U(1)–N(1) bond length of 1.983(2) Å and the S(3)–U(1)–N(1) angle of 105.30(7)° for compound **1** compares well to other structurally similar mono-imido species ($(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(SePh) = 1.985(4)$ Å and 102.18(3)°;⁶⁴ $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(TePh) = 1.960(7)$ Å and 107.51(3)°;⁶⁴ $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf) = 2.006(5)$ Å and 103.86(3)°;³⁶ $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(Cl) = 1.964(4)$ Å



Scheme 1: Synthesis of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**) through two methods.

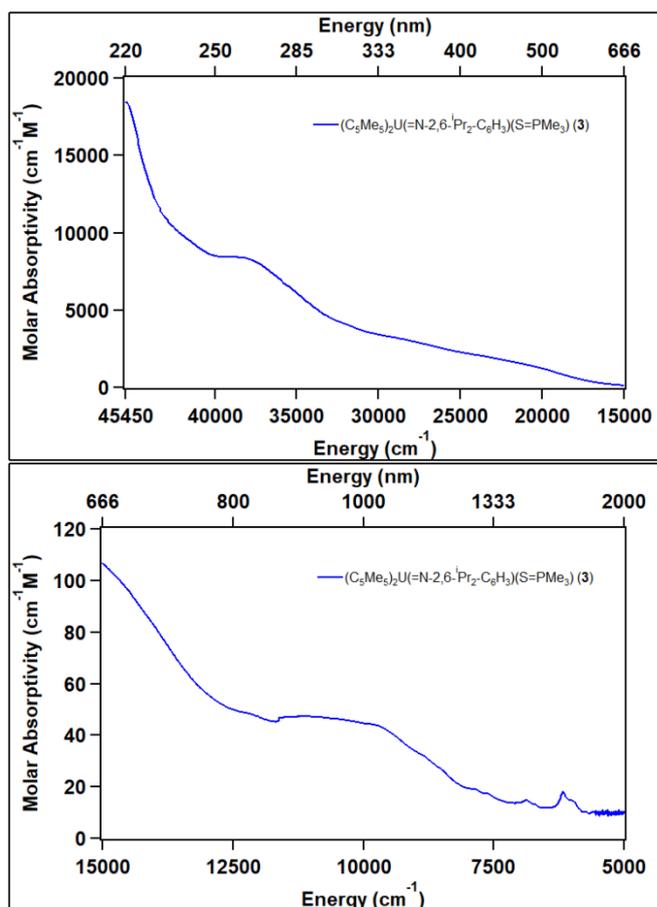


Figure 3: UV/vis (top) and NIR (bottom) spectra of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**) collected in hexanes at 298 K.

and 105.78(4)°;³⁶ $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(Br) = 1.969(7)$ Å and 105.30(3)°.³⁶ $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (**2**) features a terminal disulphide ligand, which is novel for a neutral uranium(VI) system with bond lengths (U(1)–S(1) = 2.679(2) Å, U(1)–S(2) = 2.715(2) Å, S(1)–S(2) = 2.016(3) Å) and angles (S(1)–U(1)–S(2) = 43.90(7)°) that are consistent with other structurally characterized uranium disulphide compounds ($[(n-C_3H_7)_2NH_2]_2[(UO_2)[(n-C_3H_7)_2NCOS]_2(\eta^2-S_2)] = 2.711$ and 2.711 Å, 44.47°;²¹ $Tp^*_2U(\eta^2-S_2) = 2.621(2)$ and $2.629(2)$, 46.56(2)°;⁵⁰ $U[(SiMe_2NPh)_3tacn](\eta^2-S_2) = 2.651(5)$ and $2.642(5)$ Å, 45.09(3)°.⁶⁵ In all, the metrical parameters of both compounds **1** and **2** seem to not be dependent on oxidation state or being neutral/anionic; rather, the coordination sphere and presence of a capping alkali metal seem to affect these parameters the most.

For comparison purposes, we also were interested in synthesizing a compound with a dative uranium–sulphur interaction. A phosphine sulphide coordination complex seemed like an ideal candidate, as phosphine oxide adducts of uranium are known and well studied.⁶⁶ Additionally, phosphine sulphides are easily modified to modulate the steric bulk of the ligand. Surprisingly, there are no reported examples of uranium–phosphine–sulphide complexes, and that the role of phosphine sulphides in uranium chemistry has been limited to sulphur atom transfer to uranium(III) species to form bridging uranium(IV) sulphido complexes.^{22, 23, 29, 65} However, as shown in

Scheme 1, when a toluene solution of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ was reacted with one equivalent of $S=PMe_3$ at ambient temperature for 24 hours, the corresponding phosphine sulphide adduct $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**) was obtained as a dark brown solid in 62% isolated yield following workup. Presumably, due to the less reducing nature of uranium(IV) versus uranium(III), the $S=PMe_3$ was not reduced and therefore did not act as a S-atom transfer agent. Alternatively, complex **3** can be synthesized by the reaction of a toluene solution of the terminal sulphido compound $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) and PMe_3 at ambient temperature to afford $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**) in 67% isolated yield (Scheme 1).

This phosphine sulphide adduct is stable for several days in aliphatic or aromatic solvents, but rapidly decomposes in THF to form $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ and $S=PMe_3$, even at -30 °C. Complex **3** displays 1H NMR behavior typical of a uranium(IV) species, with several sharp resonances paramagnetically shifted across the spectral window ($\delta_{C_5Me_5} = -2.26$; $\delta_{Ph} = 37.11$ and 15.39 ; $\delta_{iPr} = 4.22$; $\delta_{PMe_3} = -9.37$). No $^{13}C\{^1H\}$ or $^{31}P\{^1H\}$ NMR signals were observed for $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**), a common observation for paramagnetic uranium(IV) complexes. The IR spectrum of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**) displays a strong band at 542 cm^{-1} diagnostic of a phosphine sulphide stretching mode and compares favourably to other authenticated P–S vibrational modes of phosphine sulphide adducts ($\nu_{P-S} = 502\text{--}565\text{ cm}^{-1}$).⁶⁷

The electronic spectra of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (**3**) display lower than expected intensity in the $f-f$ bands in the NIR regions of the spectra (Figure 3) for an uranium(IV) imido. Generally, imido complexes have displayed intense electronic transitions, where charge-transfer and ligand localized $\pi-\pi^*$ and $n-\pi^*$ transitions contribute to the spectral envelope. Currently, we cannot reconcile these low $f-f$ intensities and are further investigating the issue. Given the unusual NIR spectrum of **3**, we sought to confirm the uranium(IV) oxidation state through electrochemical study. A reversible voltammetric wave assigned to the U(IV)/U(III) redox couple was observed at -2.60 V (vs. Fc/Fc^+), which is consistent with, but not evidence of, a U(IV) oxidation state.

Table 1: Measured metal-based redox couples for complexes 1–3

Compound	U(VI)/U(V)	U(V)/U(IV)	U(IV)/U(III)
$(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (1)	-1.13	N/A	N/A
$(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(\eta^2-S_2)$ (2)	-1.21 ^a	-1.75 ^a	N/A
$(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(S=PMe_3)$ (3)	N/A	N/A	-2.60

Conditions: 200 mV/s scan rate, 1 mM analyte, $\sim 0.1\text{ M}$ $[NPr_4][B(3,5-(CF_3)_2C_6H_3)_4]$, THF (**1**, **2**) or *o*-difluorobenzene (**3**), Pt disk working electrode. Values given are in V versus Fc/Fc^+ . ^aValue obtained from square wave voltammetry.

Experimental Considerations

General Experimental Procedures

Reactions and manipulations were performed in a recirculating Vacuum Atmospheres NEXUS inert atmosphere (Ar) dry box equipped with a 40CFM Dual Purifier NI-train. NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Chemical shifts for 1H and ^{13}C NMR experiments were referenced to residual benzene-*d*₆ solvent impurities ($\delta = 7.16$ and 128.06 for 1H and ^{13}C experiments, respectively). IR spectra were obtained using a Thermo Scientific Nicolet iS5 FTIR spectrometer using a Golden Gate Diamond ATR (ZnSe lenses) with a reaction anvil. UV–visible–NIR spectra were obtained using a Perkin Elmer Lambda 1050 spectrophotometer in 1 mm path length cells in hexanes at 1–20 mM concentrations. Melting points were measured with a Barnstead Thermolyne MEL-TEMP Capillary Melting Point Apparatus using capillary tubes flame-sealed under inert atmosphere; values are uncorrected. Elemental Analysis was performed by Atlantic Microlabs, Inc. (Norcross, GA). All samples for elemental analysis were dried under reduced pressure for at least 12 h before analysis to ensure the complete removal of solvent.

Materials

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. All solvents (Aldrich) were purchased anhydrous and were dried over KH for at least 24 h, passed through a column of activated alumina, and were stored over 3Å molecular sieves prior to use. Benzene-*d*₆ (Cambridge Isotope Laboratories) was purified by storage over 3Å molecular sieves for at least 48 h prior to use. Celite was dried by heating to 180 °C under vacuum for 48 h prior to use. Trimethylphosphine sulphide (Alfa Aesar) was crystallized from a saturated THF solution at -30 °C prior to use. $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ was prepared according to a literature procedure.⁵⁴

Caution: Depleted uranium (primary isotope ^{238}U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47×10^9 years; manipulations should be carried out in a monitored fume hood or in an inert atmosphere drybox in a radiation laboratory equipped with α - and β -counting equipment.

Synthesis of $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**):

A 20-mL scintillation vial was charged with a stir bar, $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(thf)$ (0.258 g, 0.341 mmol), S_8 (0.011 g, 0.043 mmol), toluene (5 mL), and a stir bar. The brown-red solution was stirred at ambient temperature for 3 h, after which it was filtered through a Celite-padded coarse-porosity fritted funnel that was washed with toluene (3 x 2 mL) until the washings ran clear. The filtrate was collected and volatiles were removed under reduced pressure to give a sticky red residue, which was washed with cold pentane (2 mL) and dried under reduced pressure to give $(C_5Me_5)_2U(=N-2,6-iPr_2-C_6H_3)(=S)$ (**1**) as an analytically pure red solid (0.166 g, 0.230 mmol, 68%). 1H NMR (benzene-*d*₆, 298 K, 400 MHz) δ 10.39 (sept, $J = 6.8\text{ Hz}$, 1H, $-CH(CH_3)_2$), 9.92 (d, $J = 7.6\text{ Hz}$, 1H, *m*-Ar), 9.57 (d, $J = 7.7\text{ Hz}$, 1H, *m*-Ar), 5.23 (s, 30H, C_5Me_5), 4.50 (sept, $J = 6.0\text{ Hz}$, 1H, $-CH(CH_3)_2$), 2.51 (d, $J = 6.6\text{ Hz}$, 6H, $-CH(CH_3)_2$), 1.57 (d, $J = 6.8\text{ Hz}$, 6H, $-CH(CH_3)_2$), -1.24 (t, $J = 7.6\text{ Hz}$, 1H, *p*-Ar). $^{13}C\{^1H\}$ NMR

(benzene- d_6 , 298 K, 101 MHz) δ 221.51 (C_{ipso}), 200.76 (C_{ortho}), 154.90 (C_{para}), 143.16 ($C_5\text{Me}_5$), 98.43 (C_{meta}), 93.81 (C_{meta}), 38.26 ($-\text{CH}(\text{CH}_3)_2$), 37.44 ($-\text{CH}(\text{CH}_3)_2$), 16.14 ($-\text{CH}(\text{CH}_3)_2$), 13.52 ($-\text{CH}(\text{CH}_3)_2$), 10.57 ($C_5\text{Me}_5$). One carbon (C_{ortho}) resonance is located under the solvent peak. mp: 198–200 °C. Anal. Calcd. for $\text{C}_{32}\text{H}_{47}\text{NSU}$ (mol. wt. 715.82): C, 53.69; H, 6.62; N, 1.96; S, 4.48. Found: C, 53.77; H, 6.22; N, 1.87; S, 4.09.

Synthesis of $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\eta^2\text{-S}_2)$ (**2**):

A 20-mL scintillation vial was charged with a stir bar, $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\text{thf})$ (0.258 g, 0.341 mmol), S_8 (0.011 g, 0.043 mmol), and toluene (5 mL). The brown-red solution was stirred at ambient temperature for 3 h, after which it was filtered through a Celite-padded coarse-porosity fritted funnel that was washed with toluene (3 x 2 mL) until the washings ran clear. The filtrate was collected and the volatiles were removed under reduced pressure to give a sticky red residue, which was washed with cold pentane (2 mL) and dried under reduced pressure to give $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\eta^2\text{-S}_2)$ (**2**) as an analytically pure red-brown solid (0.158 g, 0.211 mmol, 62%). ^1H NMR (benzene- d_6 , 298 K, 400 MHz): δ 10.06 (d, $J = 7.5$ Hz, 1H, $m\text{-Ar}$), 9.78 (d, $J = 7.4$ Hz, 1H, $m\text{-Ar}$), 8.69 (sept, $J = 6.1$ Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 6.10 (sept, $J = 6.1$ Hz, 1H, $-\text{CH}(\text{CH}_3)_2$), 5.86 (s, 30H, $C_5\text{Me}_5$), 1.96 (d, $J = 7.0$ Hz, 6H, $-\text{CH}(\text{CH}_3)_2$), 1.94 (d, $J = 7.0$ Hz, 6H, $-\text{CH}(\text{CH}_3)_2$), -1.59 (t, $J = 7.4$ Hz, 1H, $p\text{-Ar}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 298 K, 101 MHz): δ 221.50 (C_{ipso}), 200.77 (C_{ortho}), 143.15 (C_{para}), 140.77 ($C_5\text{Me}_5$), 98.41 (C_{meta}), 97.33 (C_{meta}), 38.27 ($-\text{CH}(\text{CH}_3)_2$), 37.44 ($-\text{CH}(\text{CH}_3)_2$), 16.14 ($-\text{CH}(\text{CH}_3)_2$), 13.50 ($-\text{CH}(\text{CH}_3)_2$), 10.57 ($C_5\text{Me}_5$). One carbon (C_{ortho}) resonance is located under the solvent peak. mp: 187–188 °C. Anal. Calcd. for $\text{C}_{32}\text{H}_{47}\text{NS}_2\text{U}$ (mol. wt. 747.88): C, 51.39; H, 6.33; N, 1.87; S, 8.57. Found: C, 51.33; H, 6.01; N, 2.02; S, 8.14.

Synthesis of $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\text{S}=\text{PMe}_3)$ (**3**):

Method A: A 20-mL scintillation vial was charged with a stir bar, $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\text{thf})$ (0.141 g, 0.187 mmol), $\text{S}=\text{PMe}_3$ (0.021 g, 0.190 mmol), and toluene (6 mL). The solution was stirred at ambient temperature for 18 h, at which time it was filtered through a medium-porosity fritted funnel. The filtrate was collected and volatiles were removed under reduced pressure to give $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\text{S}=\text{PMe}_3)$ (**3**) as an analytically pure dark brown solid (0.092 g, 0.116 mmol, 62%). ^1H NMR (benzene- d_6 , 298 K, 400 MHz): δ 37.11 (s, 2H, $m\text{-Ar}$), 15.39 (s, 1H, $p\text{-Ar}$), 4.22 (s, 12H, $-\text{CH}(\text{CH}_3)_2$), -2.26 (s, 30H, $C_5\text{Me}_5$), -9.37 (s, 9H, $\text{S}=\text{PMe}_3$). mp: 167–168 °C. Anal. Calcd. For $\text{C}_{35}\text{H}_{54}\text{NSPU}$ (mol. wt. 791.90): C, 53.09; H, 7.13; N, 1.77; S, 4.05. Found: C, 52.26; H, 7.00; N, 1.98; S, 3.21.

Method B: A 20-mL scintillation vial was charged with a stir bar, $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(=\text{S})$ (**1**) (0.173 g, 0.241 mmol), PMe_3 (24.6 μL , 0.241 mmol), and toluene (4 mL). The solution was stirred at ambient temperature for 1 h, at which time volatiles were removed under reduced pressure to give $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{N}-2,6\text{-iPr}_2\text{-C}_6\text{H}_3)(\text{S}=\text{PMe}_3)$ (**3**) as an analytically pure dark brown solid (0.128 g, 0.161 mmol, 67%).

X-ray Crystallography:

A single crystal containing both compounds **1** and **2** was mounted on a nylon cryoloop using Paratone-N oil under a nitrogen gas flow. The data were collected on a Bruker D8 QUEST diffractometer, with CMOS detector in shutterless mode. The crystals were cooled to 100 K using an Oxford Cryostream liquid nitrogen cryostat. The instrument was equipped with a graphite monochromatized $\text{MoK}\alpha$ X-ray source ($\lambda = 0.71073$ Å) with Triumph™ X-ray source optics. A hemisphere of data was collected using ω scans. Data collection, initial indexing, and cell refinement were handled using APEX III software.⁶⁸ Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.⁶⁹ The data were corrected for absorption using the SADABS program.⁷⁰ Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using direct methods, and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Structure solution, refinement, and creation of publication materials were performed using SHELXTL.⁷¹ The (=S) complex (**1**) and the ($\eta^2\text{-S}_2$) complex (**2**) were superimposed in the crystal structure, and modelled with occupancies of 0.611(1) and 0.389(1), respectively. In addition, one disordered Cp* ligand (C1–C10) was modelled in three positions. A summary of the crystallographic data and details of the structure refinement are provided in table 2.

Table 2: Summary of crystallographic data for compounds **1** and **2**

Compound	1 and 2
Temperature (K)	100(1)
Wavelength (Å)	0.71073
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	
a (Å)	31.606(2)
b (Å)	10.2542(7)
c (Å)	18.4969(13)
$\alpha = \gamma$ (°)	90
β (°)	92.8494(15)
Volume (Å ³)	5987.3(7)
Z	8
μ (MoK α , mm ⁻¹)	5.511
D _{calc} (mg/m ³)	1.588
F(000)	2832
Crystal Size (mm ³)	0.330 x 0.310 x 0.040
θ range (°)	2.499 to 28.769
2 θ _{max} (°)	57.5
Index Ranges	
	-42 ≤ h ≤ 42
	-13 ≤ k ≤ 13
	-25 ≤ l ≤ 25
Reflections collected/unique	47773/7772
Data/restraints/parameters	7772/181/434
Goodness of fit on F ²	1.092
Final R indices (I > 2 σ)	R ₁ = 0.0343, wR ₂ = 0.0861
R indices (all data)	R ₁ = 0.454, wR ₂ = 0.0922

Conclusions

In summary, we have isolated a new family of complexes that contain a variety of uranium-sulfur bonds supported by the bent metallocene imido framework, (C₅Me₅)₂U(=N-2,6-ⁱPr₂-C₆H₃). All new compounds have been fully characterized by a combination of NMR, IR, and UV/vis-NIR spectroscopies, elemental analysis, cyclic voltammetry, and for compounds **1** and **2**, by single crystal X-ray diffraction.

(C₅Me₅)₂U(=N-2,6-ⁱPr₂-C₆H₃)(=S) (**1**) and (C₅Me₅)₂U(=N-2,6-ⁱPr₂-C₆H₃)(η^2 -S₂) (**2**) represent the first examples of neutral uranium(VI) terminal sulphido and disulphide complexes, respectively. The bulk of the C₅Me₅ and imido ligands prevent the formation of bridging sulphido complexes. Consistent with a U(VI) oxidation state, both complexes display diamagnetic ¹H and ¹³C{¹H} NMR spectra. The UV-visible-NIR spectra for complexes **1** and **2** are similar to the known U(VI) bis-imido complex uranium(VI) bis-imido (C₅Me₅)₂U(=NPh)₂, though the intensity of the transitions for **1** and **2** are roughly 50% weaker than those of (C₅Me₅)₂U(=NPh)₂,⁶³ reflective of a weaker covalent U–S interaction compared to a uranium imido interaction.

Finally, the uranium(VI) terminal sulphido complex reacts with trimethyl phosphine to yield the new uranium(IV) phosphine sulphide adduct (C₅Me₅)₂U(=N-2,6-ⁱPr₂-

C₆H₃)(S=PMe₃) (**3**). This is first example of a uranium compound with a phosphine sulphide ligand. Complex **3** can also be prepared by reacting the known uranium(IV) imido complex, (C₅Me₅)₂U(=N-2,6-ⁱPr₂-C₆H₃) with Me₃P=S. To the best of our knowledge this chemistry is not unique for the actinides, but also the periodic table. Further studies to probe the reactivity of the U=S bond of compound **1** are currently underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Dedicated to Professor Richard Andersen on the occasion of his 75th birthday, in honor of his pioneering work in f-element chemistry. For financial support, we acknowledge the U.S. Department of Energy through the LANL G. T. Seaborg Institute for Transactinium Science (Postdoctoral Fellowship to J.K.P.), the LANL Laboratory Directed Research & Development program (J.L.K.), and the Basic Energy Science, Heavy Element Chemistry Program (C.J.B.). Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy (contract DE-AC52-06NA25396).

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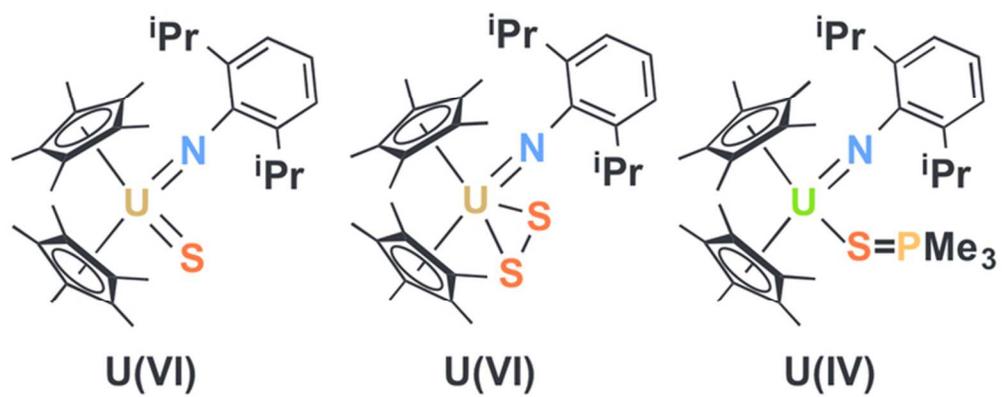
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