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η^2-Sulfenamido complexes of uranium†

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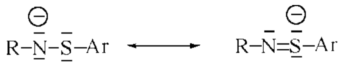
Thermally stable η^2-sulfenamido complexes of uranium, U(η^2-Bu^{t}NSPh)$_4$ **1** and UCp*$_2$(η^2-Bu^{t}NSPh)X, X = Cl **2a** or Br **2b**, have been prepared by metathetical reactions of LiN(Bu^t)SPh with UCl$_4$/PMe$_3$ and UCp*$_2$Cl$_2$, respectively; **2** resists further substitution. Structure determination by X-ray diffraction shows that the bonding of the sulfenamido ligand is analogous to that found in its complexes with the early transition metals Ti, Zr, Mo and W. Indeed **1** is closely isostructural with the homoleptic zirconium complex, and **2a**, **2b** are effectively isostructural with ZrCp$_2$(η^2-Bu^{t}NSPh)X.

Introduction

The sulfenamido complexes exhibit interesting structural features and reactivity across the transition metal[1] and main group[2] elements. In all structurally characterised examples of transition metal complexes the sulfenamido ligand (RNSAr)$^-$, R = Bu^t or 2-Pr^{i}C$_6$H$_4$, Ar = Ph or mes (2,4,6-Me$_3$C$_6$H$_2$), adopts η^2 co-ordination even with electropositive early transition metals such as Ti^{IV} and Zr^{IV}. However, there is strong NMR spectroscopic evidence that in solution interconversion between η^1 and η^2 modes takes place. The bonding of η^2 sulfenamide can be described by the two limiting resonance forms **A**



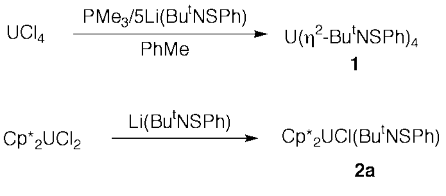
A **B**

(sulfenamide) and **B** (iminosulfide, *N*-alkylsulfilimino). The observed metrical data point to a substantial contribution of **B** to bonding. For example in the homoleptic Zr(η^2-Bu^{t}NSPh)$_4$ the Zr–N distances are 2.12–2.14, the N–S are 1.68–1.69 and the Zr–S 2.77–2.81 Å.

In this paper we describe the first sulfenamido complexes of the actinides, including the homoleptic U(η^2-Bu^{t}NSPh)$_4$.

Results and discussion

Interaction of an excess of Li(Bu^{t}NSPh) with UCl$_4$ in the presence of PMe$_3$ in toluene at room temperature for 48 h results in complete conversion of the *in situ* formed UCl$_4$(PMe$_3$)$_3$ into **1** (see Scheme 1). The choice of starting material and solvent are crucial for the success of the reaction. In general, ethereal solvents (*e.g.* thf, diethyl ether, dme = solv) suppress completely the formation of **1** possibly due to the unfavourable displacement of the hard oxygen ligands in UCl$_4$(solv)$_3$ by the soft sulfur atoms of the sulfenamide. No other products could be observed by varying the ratio of UCl$_4$: Li(Bu^{t}NSPh) or by attempted comproportionation of **1** with UCl$_4$. Compound **1** forms extremely air sensitive yellow-brown crystals. Its ^{1}H NMR spectrum in C$_6$D$_6$ consists of paramagnetically shifted and broadened peaks possibly due to a non-rigid structure in solution. Further insight into the structure of **1** was gained by an X-ray diffraction study. A diagram of the molecule is shown in Fig. 1; important bond lengths and angles are in Table 1. Compound **1** is the first example of a homoleptic actinide complex containing three membered rings. Rare examples of analogous transition metal and lanthanide complexes have recently been described.[3] This complex is structurally and geometrically similar to the isostoichiometric zirconium compound previously reported.[1] Superimposition of the uranium and zirconium structures shows only minor discrepancies in the geometries of the two compounds, which can be attributed to the difference in size of the central metal atoms (RMS deviation 0.1816 Å). A table of numerical fitting data has been included in the supplementary material. The low precision in the light atom positions in these complexes make more detailed comparisons of bond lengths and angles impossible.


$$\mathrm{UCl_4} \xrightarrow[\mathrm{PhMe}]{\mathrm{PMe_3/5Li(Bu^tNSPh)}} \mathrm{U(\eta^2\text{-}Bu^tNSPh)_4}\ \mathbf{1}$$

$$\mathrm{Cp^*_2UCl_2} \xrightarrow{\mathrm{Li(Bu^tNSPh)}} \mathrm{Cp^*_2UCl(Bu^tNSPh)}\ \mathbf{2a}$$

Scheme 1

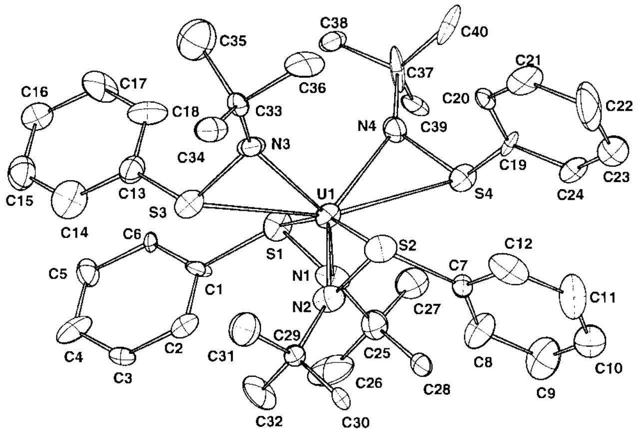


Fig. 1 Structure of U(η^2-Bu^{t}NSPh)$_4$ **1**.

Interaction of UCp*$_2$Cl$_2$ (Cp* = C$_5$Me$_5$) with one or two equivalents of Li(Bu^{t}NSPh) in toluene gives good yields of UCp*$_2$Cl(η^2-Bu^{t}NSPh) **2a** as air sensitive orange-red crystals.

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† Electronic supplementary information (ESI) available: crystallographic superimposition diagrams and numerical fitting data. See http://www.rsc.org/suppdata/dt/b0/b000304m/

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Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

U(1)–N(1)	2.30(2)	S(2)–N(2)	1.73(3)
U(1)–N(2)	2.30(3)	S(2)–C(7)	1.80(2)
U(1)–N(3)	2.28(2)	S(3)–N(3)	1.70(2)
U(1)–N(4)	2.30(2)	S(3)–C(13)	1.77(2)
U(1)–S(1)	2.867(7)	S(4)–N(4)	1.67(2)
U(1)–S(2)	2.840(8)	S(4)–C(19)	1.771(14)
U(1)–S(3)	2.885(8)	N(1)–C(25)	1.53(3)
U(1)–S(4)	2.873(7)	N(2)–C(29)	1.48(4)
S(1)–N(1)	1.69(2)	N(3)–C(33)	1.43(3)
S(1)–C(1)	1.799(13)	N(4)–C(37)	1.57(3)
N(1)–U(1)–N(2)	100.9(8)	N(3)–U(1)–S(1)	101.8(6)
N(1)–U(1)–N(3)	135.5(8)	N(3)–U(1)–S(2)	90.6(6)
N(1)–U(1)–N(4)	96.9(8)	N(3)–U(1)–S(3)	36.0(5)
N(2)–U(1)–N(3)	98.8(9)	N(3)–U(1)–S(4)	124.1(5)
N(2)–U(1)–N(4)	138.7(9)	N(4)–U(1)–S(1)	88.2(7)
N(3)–U(1)–N(4)	93.8(7)	N(4)–U(1)–S(2)	103.7(7)
N(1)–U(1)–S(1)	36.1(6)	N(4)–U(1)–S(3)	125.4(6)
N(1)–U(1)–S(2)	127.8(6)	N(4)–U(1)–S(4)	35.6(6)
N(1)–U(1)–S(3)	108.0(6)	S(1)–U(1)–S(2)	162.4(2)
N(1)–U(1)–S(4)	85.6(5)	S(1)–U(1)–S(3)	85.2(2)
N(2)–U(1)–S(1)	126.7(7)	S(1)–U(1)–S(4)	98.6(2)
N(2)–U(1)–S(2)	37.6(7)	S(2)–U(1)–S(3)	98.0(2)
N(2)–U(1)–S(3)	83.6(7)	S(2)–U(1)–S(4)	84.4(2)
N(2)–U(1)–S(4)	109.2(7)	S(3)–U(1)–S(4)	159.6(2)

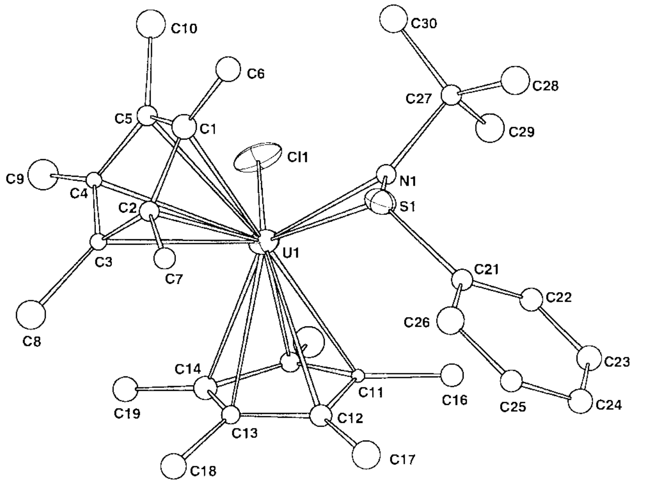

Fig. 2 Structure of UCp*$_2$Cl(η^2-Bu^{t}NSPh) **2a**.

The ^{1}H NMR spectrum of **2a** is broad and isotropically shifted and of low diagnostic value. Attempts to substitute the remaining chloride in **2a** with alkyl or aryl groups were not successful. Lithium, aluminium and zinc alkyls gave intractable mixtures. However, interaction with MeMgBr after prolonged reaction times led, unexpectedly, to the formation of UCp*$_2$Br(η^2-Bu^{t}NSPh) **2b**. The structures of **2a** and **2b** in the solid state have been studied by single crystal X-ray diffraction. The molecules are diagrammatically shown in Figs. 2 and 3; important bond lengths and angles are in Tables 2 and 3. The co-ordination sphere and geometry of **2a** and **2b** are similar to that of the previously reported zirconium complex ZrCp$_2$Cl(η^2-Bu^{t}N-SPh),[1] with only a slight extension and contraction of the bond lengths and angles of the ligands. Superimposition of **2a** and **2b** with the zirconium analogue shows minor differences (RMS deviation 0.0589 and 0.828 Å) in their geometries due to the different size of the central metal ions. Tables of numerical fitting data for both compounds have been included in the supplementary material.

Table 2 Selected bond lengths (Å) and angles (°) for compound **2a**

U(1)–Cl	2.628(7)	S(1)–C(21)	1.80(2)
U(1)–N(1)	2.20(2)	N(1)–C(27)	1.63(3)
U(1)–S(1)	2.825(8)	U(1)–Cp1	2.501
S(1)–N(1)	1.72(2)	U(1)–Cp2	2.487
N(1)–U(1)–Cl	87.5(5)	C(27)–N(1)–U(1)	148.5(15)
N(1)–U(1)–S(1)	37.6(5)	Cp1–U(1)–Cp2	128.42
Cl–U(1)–S(1)	123.4(2)	Cp1–U(1)–Cl	97.92
N(1)–S(1)–U(1)	51.2(7)	Cp1–U(1)–N(1)	114.24
N(1)–S(1)–C(21)	109.4(10)	Cp1–U(1)–S(1)	95.80
C(21)–S(1)–U(1)	117.1(8)	Cp2–U(1)–Cl	99.92
S(1)–N(1)–U(1)	91.2(9)	Cp2–U(1)–N(1)	114.52
C(27)–N(1)–S(1)	115.0(14)	Cp2–U(1)–S(1)	113.02

Cp1 is the centroid of the C$_5$H$_5$ ring C(1)–C(5), Cp2 that of ring C(11)–C(15).

Table 3 Selected bond lengths (Å) and angles (°) for compound **2b**

U(1)–Br(1)	2.7935(12)	S(1)–C(21)	1.795(12)
U(1)–S(1)	2.840(4)	N(1)–C(27)	1.494(13)
U(1)–N(1)	2.309(6)	U(1)–Cp1	2.527
S(1)–N(1)	1.696(8)	U(1)–Cp2	2.514
N(1)–U(1)–Br(1)	88.4(2)	C(27)–N(1)–U(1)	146.1(7)
N(1)–U(1)–S(1)	36.6(2)	Cp1–U(1)–Cp2	128.89
Br(1)–U(1)–S(1)	123.65(7)	Cp1–U(1)–Br(1)	99.10
N(1)–S(1)–U(1)	54.5(4)	Cp1–U(1)–N(1)	112.13
N(1)–S(1)–C(21)	110.1(5)	Cp1–U(1)–S(1)	94.44
C(21)–S(1)–U(1)	116.9(5)	Cp2–U(1)–Br(1)	99.73
S(1)–N(1)–U(1)	88.9(4)	Cp2–U(1)–N(1)	115.43
C(27)–N(1)–S(1)	120.4(9)	Cp2–U(1)–S(1)	112.96

Cp1 is the centroid of the C$_5$H$_5$ ring C(1)–C(5), Cp2 that of ring C(11)–C(15).

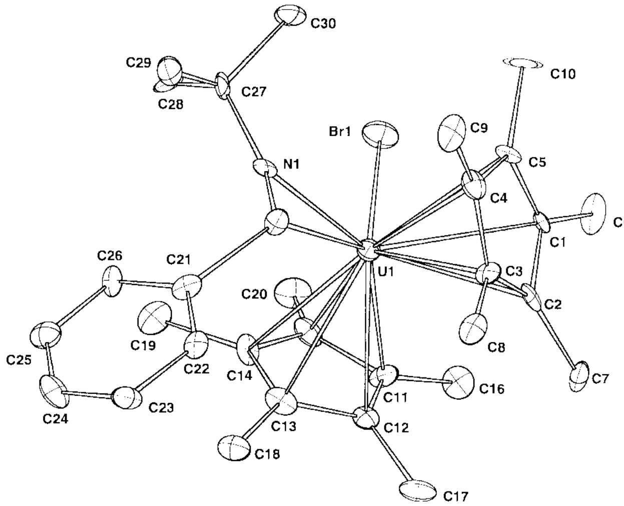

Fig. 3 Structure of UCp*$_2$Br(η^2-Bu^{t}NSPh) **2b**.

Experimental

Analyses were by the University College, London microanalytical laboratory. All operations were carried out under purified N$_2$ or Ar or in Vacuum Atmospheres or Braun glove boxes. Proton NMR data were recorded on a Bruker AMX-300, mass spectra on VG 7070E and Autospec instruments. Commercial chemicals were from Aldrich and Avocado; the light petroleum had bp 40–60 °C. Literature procedures were used for the preparation of UCl$_4$,[4] Bu^{t}NHSPh[1a] and UCp*$_2$-Cl$_2$.[5]

Preparations

Tetrakis(*N*-*tert*-butylbenzenesulfenamido)uranium(IV) 1. To a precooled suspension (−78 °C) of UCl$_4$ (1 g, 2.65 mmol) in toluene (100 cm^3) was added PMe$_3$ (1 cm^3, excess), followed by a suspension of Li(Bu^{t}NSPh) (2.45 g, 13.25 mmol) in the same solvent. The inhomogeneous mixture was allowed to reach room temperature and stirred for 48 h. It gradually changed from green to yellow-brown. Evaporation of the volatiles under

Table 4 Crystal data and structure refinement details for compounds **1**, **2a** and **2b**

	1	**2a**	**2b**
Formula	$C_{40}H_{56}N_4S_4U$	$C_{30}H_{44}ClNSU$	$C_{30}H_{44}BrNSU$
M_r	959.16	724.20	768.66
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a/Å	11.287(4)	9.680(6)	9.724(4)
b/Å	18.28(4)	17.226(10)	17.377(15)
c/Å	20.61(2)	18.166(5)	18.196(7)
β/°		104.23(7)	103.7(4)
U/Å^3	4251(9)	2936(3)	2987(3)
Z	4	4	4
μ(Mo-Kα)/mm^{-1}	3.887	5.708	6.860
Collection temperature/K	150	150	150
Reflections collected	12265	10605	8557
Independent reflections (R_{int})	6162 (0.1704)	4078 (0.2626)	4050 (0.0860)
Data, restraints, parameters	6162, 114, 406	4078, 0, 165	4050, 6, 320
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0497, 0.084	0.0740, 0.1471	0.0405, 0.0679
(all data)	0.1827, 0.1343	0.2035, 0.1893	0.0924, 0.0777

vacuum, extraction of the residue in light petroleum (3 × 40 cm^3), filtration, concentration of the combined filtrates to *ca.* 20 cm^3 and cooling (−20 °C) gave yellow-brown air sensitive crystals. Yield: 0.97 g, 40%. mp 129 °C (decomp.). Found (calc.)%: C 49.8 (50.1), H 6.0 (5.9), N 5.8 (5.8). ^{1}H NMR (C_6D_6): δ 7.5 (20 H, aromatic) and 17 (36 H, broad, Bu^t). X-Ray quality crystals were obtained by slow cooling of petroleum solutions.

(*N-tert*-Butylbenzenesulfenamido)chlorobis(pentamethylcyclopentadienyl)uranium(IV) 2a. To a solution of UCp*$_2$Cl$_2$ (0.29 g, 0.5 mmol) in toluene (30 cm^3) at −78 °C was added dropwise a suspension of Li(Bu^{t}NSPh) (0.10 g, 0.55 mmol) in toluene (30 cm^3). The mixture was allowed to warm up and stirred for 12 h. Removal of the volatiles under vacuum, extraction of the residue with light petroleum (2 × 30 cm^3) followed by filtration, concentration and cooling to −20 °C gave red crystals. Yield: 0.24 g, 67%. mp 134–137 °C. Found (calc.)%: C 49.0 (49.8), H 6.2 (6.1), N 2.0 (1.9), Cl 6.1 (5.9). Mass spectrum (EI): *m*/*z* 723 (M$^+$), 614 (M − PhS), 588 (M − Cp*) and 543 (M − BuNSPh). ^{1}H NMR (C_6D_6): δ 5.2 (s, 9 H, Bu^t), 7.1 (s, 30 H, Cp*) and 8.3 (s, 5 H, Ph).

Bromo(*N-tert*-butylbenzenesulfenamido)bis(pentamethylcyclopentadienyl)uranium(IV) 2b. To a solution of compound **2a** (0.3 g, 0.4 mmol) in diethyl ether (20 cm^3) was added a solution of MeMgBr in ether (1 cm^3 of 1 M solution, excess). The mixture was refluxed for 12 h. Work-up as above afforded orange-red crystals. Yield: 0.12 g, 31.5%. Found (calc.)%: C 46.2 (46.9), H 5.7 (5.7), N 1.8 (1.8). ^{1}H NMR (C_6D_6): δ 5.0 (s, 9 H, Bu^t), 7.1 (s, 30 H, Cp*) and 8.2 (s, 5 H, Ph).

X-Ray crystallography

X-Ray data for compounds **1**, **2a** and **2b** were collected at low temperature using a FAST TV area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71069$ Å), as previously described.[6] Crystal data and other experimental details are given in Table 4. The structures were solved using direct methods in the program SHELXS 97[7] and refined by full matrix least squares on a F_o^2 using SHELXL 97.[7] Corrections for absorption were applied using the DIFABS[8] program. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were fixed in idealised positions using the riding model. Owing to the small and sensitive nature of compounds **1** and **2a** the crystal quality and resulting data quality was not good; as a result isotropic restraints had to be applied to several atoms in each structure. Crystals of compound **2b** were also small and the diffraction was weak, limiting the treatment of the majority of atoms to an isotropic model.

CCDC reference number 186/1915.

See http://www.rsc.org/suppdata/dt/b0/b000304m/ for crystallographic files in .cif format.

Acknowledgements

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