Synthesis and Crystal Structure of Homoleptic Uranium Hexathiolates: $[NEt_2H_2]_2[U(SPh)_6]$ and $[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]$†

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Treatment of $U(NEt_2)_4$ with PhSH gave $[NEt_2H_2]_2[U(SPh)_6]$ **1**. Reaction of UCl_4 with NaSPh in the presence of CuSPh and PPh_3 afforded $[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]$ **2**. The geometrical parameters of the octahedral US_6 core are quite similar in the crystal structures of **1**, **2**·6thf and $[(thf)_3Na(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Na(thf)_3]$ (thf = tetrahydrofuran). The U–Cu distance of 3.05(1) Å supports the presence of a direct metal–metal interaction.

We recently described the synthesis and crystal structure of the uranium compounds $[(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3]$ (thf = tetrahydrofuran, R = Bu^t or Ph)[1] which represent, after $U(SR)_4$ (R = Et, Bu^n or Pr^i),[2,3] $[Li(MeOCH_2CH_2OMe)]_4[U(SCH_2CH_2S)_4]$[4] and $[Li(Me_2NCH_2CH_2NMe_2)]_3[M(SBu^t)_6]$ (M = Yb or Sm),[5] new examples of homoleptic thiolates of an f element. Six-co-ordinate, homoleptic, transition-metal complexes with monodentate thiolate ligands are rare, being limited to $[PPh_4]_2[Nb(SPh)_6]$, $[(thf)_3Na(\mu\text{-}SC_6H_4Me\text{-}p)_3Nb(SC_6H_4Me\text{-}p)_3]$, $[Na(C_{10}H_{20}O_5)][Ta(SPh)_6]$[6] and $[(Ph_3P)Cu(\mu\text{-}SC_6H_4Me\text{-}p)_3M(\mu\text{-}SC_6H_4Me\text{-}p)_3Cu(PPh_3)]$ (M = Mo or W).[7] In order to obtain a better insight into the geometry of the $U(SPh)_6$ entity and to make valid comparisons with the other transition-metal analogues, we have studied the complexes $[NEt_2H_2]_2[U(SPh)_6]$ **1** and $[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]$ **2**. Therefore we present herein the synthesis and crystal structure of **1** and of a thf solvate of **2**.

Results and Discussion

Synthesis.—In contrast to the previously reported reactions of $U(NEt_2)_4$ with thiols which afforded the tetrathiolates $U(SR)_4$ (R = Et, Bu^n or Pr^i)[2,3] or the cluster $[U_3(S)(SBu^t)_{10}]$,[3] treatment of the uranium amide complex with an excess of PhSH in thf immediately gave a red solution which deposited, upon cooling, light red crystals of $[NEt_2H_2]_2[U(SPh)_6]$ **1** (73% yield). This distinct reaction course is obviously due to the greater acidity of the thiophenol, which is deprotonated by the liberated amine NEt_2H. Complex **1** was characterized by elemental analyses and X-ray crystallography (see later).

The trinuclear compound $[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]$ **2**, which is the first heterobimetallic complex containing a 5f element and a copper atom in close proximity, was prepared in thf by mixing UCl_4, NaSPh, CuSPh and PPh_3 in the relative molar proportions 1:4:2:2. A red powder precipitated immediately and after filtration, extraction in thf and crystallization from this solvent, dark red crystals of **2**·6thf were isolated in 60% yield. These crystals were suitable for an X-ray diffraction analysis (see later); by drying under vacuum, they were transformed into a powder of unsolvated **2**, which gave satisfactory elemental analyses. The ^1H NMR spectrum exhibited two similar sets of three signals, in a 2:2:1 ratio, corresponding to the C_6H_5 groups of the triphenylphosphine and benzenethiolate ligands. These two series of resonances were visible in the opposite regions of the spectrum, in agreement with the theoretical expression for the pseudo-contact shifts in axial symmetry,[8] and by analogy with the spectra of the complexes $[(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3]$,[1] the low-field signals would be attributed to the SPh ligands.

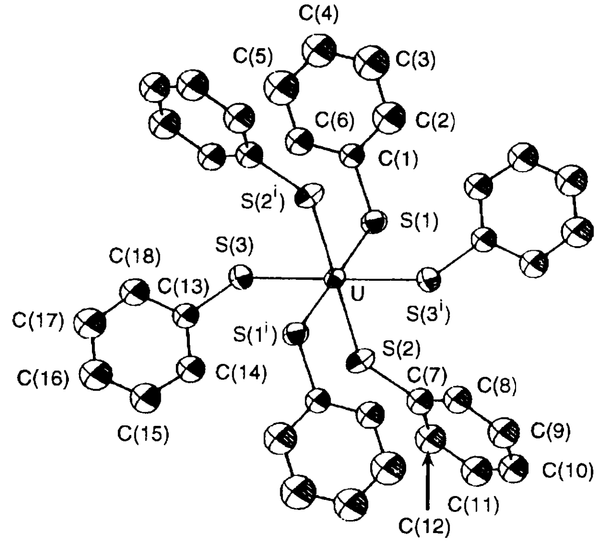

Fig. 1 Perspective view of $[NEt_2H_2]_2[U(SPh)_6]$; atoms labelled i are related by a centre of symmetry

Crystal Structures.—The crystals of compound **1** are composed of discrete cation–anion pairs. The ORTEP drawing[9] of the $[U(SPh)_6]^{2-}$ dianion is shown in Fig. 1; selected bond distances and angles are listed in Table 1. The uranium atom, which lies on an inversion centre, is surrounded by six sulfur atoms in a slightly distorted octahedral environment. The U–S

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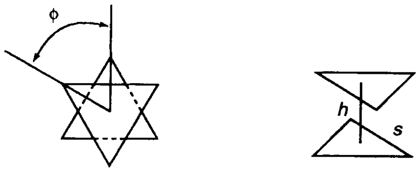
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

bond distances vary from 2.705(3) to 2.759(3) Å and the *cis* S–U–S angles range from 81.2(1) to 83.0 (1)°.

Following the proposal of Stiefel and Brown,[10] the six-coordinate polyhedron of D_3 symmetry can be defined by the two parameters Φ and *s*/*h*, *i.e.* the twist angle between two triangular faces of the polyhedron and the ratio of the side of the triangle to the distance between the triangles (see below).



In **1**, Φ is equal to 60°, as in the undistorted octahedron, but *s*/*h* is equal to 1.01 [s = 3.58(2) Å and h = 3.55(2) Å] instead of 1.22 in the regular octahedron, indicating that the structure is elongated along one of the pseudo C_3 axes. This trigonal elongation can also be measured either by the *cis* S–U–S angles which deviate by 8° from the ideal value in the octahedron (90°) or the polar angle θ between the C_3 axis and the U–S direction, which is equal to 49.5° instead of 54.44° for the perfect octahedron. The geometry of the US_6 core in **1** is very similar to that found in the centrosymmetric anions $[Nb(SPh)_6]^{2-}$ and $[Ta(SPh)_6]^-$ where the *cis* S–M–S angles average 87 and 85° respectively.[6] The octahedral co-ordination of these homoleptic complexes with monodentate thiolate ligands differs markedly from that encountered in the series of tris(dithiolene) or tris(dithiolate) compounds which prefer to adopt a trigonal-prismatic stereochemistry (Φ = 0 and s/h = 1 in many cases).[11] These distortions away from the octahedron toward the trigonal prism, which are more important than would be expected from simple repulsion–energy calculations,[12] have been explained by interligand bonding interactions within the S_3 triangles and by optimum overlap between the sulfur π orbitals and the metal d orbitals.[13] It is noteworthy that the geometrical parameters of the $U(SPh)_6$ fragment are quite identical in **1** and in the trinuclear complex $[(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3]$ (Table 2),[1] showing that in the latter the elongation along the C_3 axis cannot be attributed to the presence of the capping sodium atom. In contrast, the structure of the $M(SR)_6$ unit, which is octahedral in $[PPh_4]_2[Nb(SPh)_6]$ and $[Na(C_{10}H_{20}O_5)][Ta(SPh)_6]$, is nearly trigonal-prismatic in $[(thf)_3Na(\mu\text{-}SC_6H_4Me\text{-}p)_3Nb(SC_6H_4Me\text{-}p)_3]$.[6]

The geometry of the tetrahedral cation $[NEt_2H_2]^+$ is unexceptional, with the C–N–C angle and the N–C distance 111.7(9)° and 1.50(2) Å respectively.

The crystal structure of **2**·6thf revealed that the unit cell

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses*

$[NEt_2H_2]_2[U(SPh)_6]$ **1**					
U–S(1)	2.721(3)	U–S(2)	2.705(3)	U–S(3)	2.759(3)
S(1)–C(1)	1.79(1)	S(2)–C(7)	1.77(1)	S(3)–C(13)	1.78(1)
S(1)–U–S(2)	83.0(1)	S(1)–U–S(3)	81.2(1)	S(2)–U–S(3)	82.4(1)
U–S(1)–C(1)	108.5(4)	U–S(2)–C(7)	127.8(4)	U–S(3)–C(13)	115.1(4)
$[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]\cdot6thf$ **2**·6thf					
(*i*) First molecule [U(1) on an inversion centre]					
U(1)–S(1)	2.75(1)	S(1)–Cu(1)	2.37(1)	Cu(1)–P(1)	2.24(2)
U(1)–Cu(1)	3.05(1)	S(1)–C(1)	1.78(4)		
S(1)–U(1)–S(1^{i})	80.0(3)	U(1)–S(1)–Cu(1)	72.7(3)	S(1)–Cu(1)–P(1)	120.6(3)
S(1)–Cu(1)–S(1^{i})	96.4(4)	U(1)–S(1)–C(1)	102(1)	Cu(1)–S(1)–C(1)	112(1)
(*ii*) Second molecule					
U(2)–S(2)	2.74(1)	U(2)–S(3)	2.76(1)	S(2)–Cu(2)	2.38(1)
S(3)–Cu(3)	2.34(1)	U(2)–Cu(2)	3.05(1)	U(2)–Cu(3)	3.07(1)
Cu(2)–P(2)	2.24(2)	Cu(3)–P(3)	2.25(2)	S(2)–C(19)	1.76(4)
S(3)–C(13)	1.76(4)				
S(2)–U(2)–S(2^{ii})	80.3(3)	S(3)–U(2)–S(3^{ii})	78.7(3)	S(2)–U(2)–S(3^{ii})	96.5(3)
U(2)–S(2)–Cu(2)	72.8(4)	U(2)–S(3)–Cu(3)	73.5(4)	S(2)–Cu(2)–P(2)	120.9(3)
S(3)–Cu(3)–P(3)	120.5(3)	S(2)–Cu(2)–S(2^{ii})	95.9(4)	S(3)–Cu(3)–S(3^{ii})	96.5(4)
U(2)–S(2)–C(19)	98(1)	U(1)–S(3)–C(13)	107(1)	Cu(2)–S(2)–C(19)	112(1)
Cu(3)–S(3)–C(13)	112(1)				

* Symmetry codes: i $-x, -y, -z$; ii $1 - y, 1 + x - y, z$.

Table 2 Geometrical parameters of the $U(SPh)_6$ core in $[NEt_2H_2]_2[U(SPh)_6]$ **1**, $[Na(thf)_3]_2[U(SPh)_6]$ and $[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]\cdot6thf$ **2**·6thf

			2·6thf	
	1	$[Na(thf)_3]_2[U(SPh)_6]$	Molecule 1	Molecule 2
U–S/Å	2.73(3)	2.717(3)	2.75(1)	2.75(1)
S–U–S/°	82(1)	82.18(9)	80.0(3)	79.5(8)
θ/°	49.5(2)	49.4(2)	47.9(2)	47.5(6)
Φ/°	60	60	60	52(1)
s/Å	3.58(2)	3.57(2)	3.54(2)	3.52(2)
h/Å	3.55(2)	3.54(2)	3.68(2)	3.71(2)
s/*h*	1.01	1.01	0.96	0.95

contains three molecules of [$(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)$] (Fig. 2); two of these are different from the other since the uranium atoms occupy two independent positions. Both distinct molecules possess a three-fold axis of symmetry passing through the uranium, the two copper and the two phosphorus atoms, but one has also its uranium [U(1)] on an inversion centre. The two independent molecules can be regarded as rotational conformers about the ternary axis and they differ essentially by the relative orientations of the four parallel equilateral triangles defined by the bridging sulfur atoms and the *ipso* carbons of the PPh_3 ligands. The second molecule, which is shown in Fig. 3, adopts a conformation in which two adjacent triangles are in almost perfectly staggered positions; this conformation would be the best for minimization of the interactions between the thiolate and phosphine ligands. The main deviation from the idealized geometry comes from the sulfur triangle containing S(2) which is rotated by about 8° from the adequate position ($\Phi = 52°$). In the other molecule which has an inversion centre, the sulfur triangles, which are perfectly staggered ($\Phi = 60°$) because of the imposed symmetry, and the carbon triangles are rotated about 15° from eclipsed (or perfectly staggered) orientations. These conformational differences between the two molecules of **2** cannot be easily interpreted, although lattice packing forces could always be invoked. In its two forms, the structure of **2** is built up of an uranium-centred octahedron sharing parallel faces with two copper-centred tetrahedra. The geometry of the $Cu(PPh_3)$ fragment is unexceptional and the hexathiolatouranium(IV) core is very similar to that encountered in **1** and in [$(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3$] (Table 1). The twisting distortion in one molecule has already been mentioned; the other small difference visible in the two conformers of **2** is the slightly more

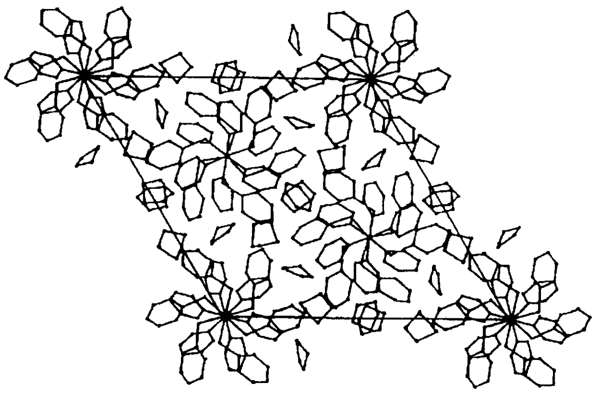


Fig. 2 View of the unit cell of [$(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)$]·6thf along the ternary axis

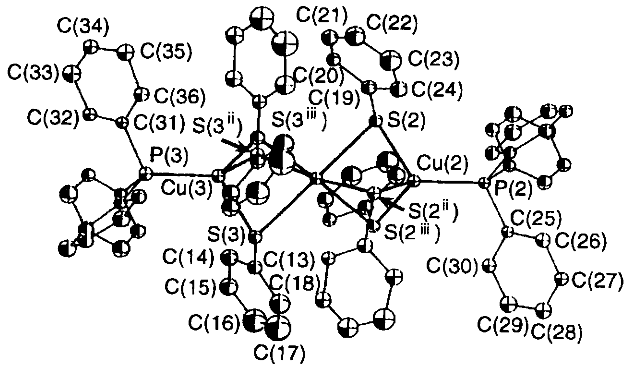


Fig. 3 Perspective view of one of the two independent molecules of [$(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)$]·6thf. Symmetry codes: ii $1 - y, 1 + x - y, z$; iii $-x + y, 1 - x, z$

Table 3 Crystallographic data and experimental details for [$NEt_2H_2]_2[U(SPh)_6$] **1** and [$(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)$]·6thf **2**·6thf

	2·6thf	**1**
Formula	$C_{96}H_{108}Cu_2O_6P_2S_6U$	$C_{44}H_{54}N_2S_6U$
M	1977.37	1041.35
Crystal size/mm	0.5 × 0.4 × 0.2	0.4 × 0.12 × 0.1
Colour	Red	Red
Crystal system	Trigonal	Monoclinic
Space group	$P\text{-}3$	$P2_1/a$
a/Å	20.690(9)	24.311(6)
b/Å	20.690(9)	8.835(5)
c/Å	17.641(4)	11.706(2)
α/°	90	90
β/°	90	117.25(2)
γ/°	120	90
U/Å^3	6539(7)	2235(2)
Z	3	2
D_c/g cm^{-3}	1.506	1.547
μ(Mo-Kα)/cm^{-1}	24.67	37.43
F(000)	3024	1040
T/K	253	295
θ limits/°	2, 20	1, 20
Scan type	ω–2θ	ω–2θ
Scan width	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
Range of absolute transmission	0.873–1.218	0.743–1.403
Range h, k, l	0–19, 0–19, −17 to 17	0–23, −8 to 0, −11 to 11
Reflections collected		
Total	4607	2431
Unique	4068	2080
With $I > 3\sigma(I)$	1326	1299
No. of parameters	235	126
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.066	0.029
$R' = [\Sigma w\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2/\Sigma w(\lvert F_o\rvert)^2]^{\frac{1}{2}}$	0.069	0.035
p in weighting scheme		
$w = 1/(\sigma F)^2 = 4F^2/[\sigma I^2 + (pF^2)^2]^{\frac{1}{2}}$	0.04	$w = 1$
Max. residual electron density/e Å^{-3}	0.72	0.66

pronounced trigonal elongation of the US_6 octahedron, as indicated by the parameters listed in Table 2.

The structure of complex **2** bears a strong resemblance to that of the molybdenum and tungsten analogues $[(Ph_3P)Cu(\mu\text{-}SC_6H_4Me\text{-}p)_3M(\mu\text{-}SC_6H_4Me\text{-}p)_3Cu(PPh_3)]$ (M = Mo or W), recently isolated by Boorman and co-workers.[7] In these centrosymmetric molecules, the MS_6 core is quite perfectly octahedral [$\Phi = 60°$, S–Mo–S 88.6(1)°, $\theta = 53.7(1)°$]. The M–S–Cu angles and M–Cu distances led the authors to consider that there was some degree of bonding interaction between the Cu and the Mo or W atoms. Such dative bonds between an early, Lewis acidic and late, electron-rich metal centres have in fact been inferred in a great number of thiolato-bridged heterobimetallics, from the angles at the bridging sulfur atoms and the metal–metal distances.[14] In the trinuclear complex **2**, the U–S–Cu angles which are less than 80° and the U–Cu bond length which is close to the sum of the atomic radii of these metals (3.1 Å),[15] also support the presence of a direct U–Cu interaction. The U–Cu distances in the alloy UCu_5 were found to be equal to 2.92 and 3.05 Å.[16] Similarly closed actinide–transition-metal contacts have been observed in the phosphido-bridged compounds $[(Me_5C_5)_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2]$ [Th–Ni 3.206(2) Å][17] and $[(Me_5C_5)_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)]$ [Th–Pt 2.984(1) Å].[18]

Experimental

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use; $[^2H_8]$thf was dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Engelskirchen (Germany). The ^1H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Benzenethiol (Aldrich) was dried over molecular sieves; NaSPh was obtained as a white powder after the reaction of sodium and a slight excess of PhSH (1.1 equivalent) in thf. The compounds CuSPh (Fluka) and PPh_3 (Aldrich) were dried under vacuum. Both UCl_4[19] and $U(NEt_2)_4$[20] were prepared by published methods.

$[NEtH_2]_2[U(SPh)_6]$ **1**.—A round bottomed flask (100 cm^3) was charged with $U(NEt_2)_4$ (900 mg, 1.7 mmol) in thf (50 cm^3) and PhSH (1900 mg, 17.3 mmol) was added to the green solution which turned red immediately. After stirring for 15 min, the solvent was evaporated and the residue dried under vacuum for 1 h. The solid was dissolved in thf (30 cm^3) and the solution was filtered. Upon cooling at −50 °C, red microcrystals were deposited which were filtered off, washed with pentane (3 × 20 cm^3) and dried under vacuum (1305 mg, 73%) (Found: C, 50.45; H, 5.1; S, 18.25. $C_{44}H_{54}N_2S_6U$ requires C, 50.75; H, 5.25; S, 18.5%). ^1H NMR ($[^2H_8]$thf, 30 °C): δ 7.4 (12 H, *o*-Ph), 6.68 (12 H, *m*-Ph), 4.81 (6 H, *p*-Ph), 2.56 (8 H, q, *J* 6, CH_2), 1.00 (12 H, t, *J* 6 Hz, CH_3).

$[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]$ **2**.—A round bottomed flask (100 cm^3) was charged with UCl_4 (200 mg, 0.52 mmol), NaSPh (278 mg, 2.1 mmol), CuSPh (180 mg, 1.04 mmol) and PPh_3 (262 mg, 1.0 mmol) and thf (50 cm^3) was condensed into it at −78 °C under vacuum. The red solution was filtered and the red residue extracted in thf (3 × 20 cm^3). After evaporation of the solvent, the red microcrystalline powder was washed with diethyl ether (3 × 10 cm^3) and dried under vacuum (490 mg, 60%) (Found: C, 55.8; H, 3.85; S, 12.25. $C_{72}H_{60}Cu_2P_2S_6U$ requires C, 55.95; H, 3.9; S, 12.45%). ^1H NMR ($[^2H_8]$thf, 30 °C): δ 20.76 (12 H, *o*-SPh), 11.43 (12 H, *m*-SPh), 10.32 (6 H, *p*-SPh), 1.24 (12 H, *m*-PPh_3), 0.82 (6 H, *p*-PPh_3), −5.94 (12 H, *o*-PPh_3).

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses for $[NEt_2H_2]_2[U(SPh)_6]$

Atom	*x*	*y*	*z*
U	0.000	0.000	0.000
S(1)	−0.0065(1)	0.2617(4)	0.1158(3)
S(2)	0.0234(1)	0.1909(4)	−0.1532(3)
S(3)	−0.1209(1)	0.0776(4)	−0.1632(3)
N	0.4066(3)	0.0441(9)	0.8106(7)
C(1)	−0.0436(5)	0.223(1)	0.214(1)
C(2)	−0.0084(6)	0.215(2)	0.346(1)
C(3)	−0.0377(6)	0.183(2)	0.424(1)
C(4)	−0.0993(6)	0.164(2)	0.367(1)
C(5)	−0.1350(6)	0.172(2)	0.237(1)
C(6)	−0.1055(5)	0.203(1)	0.161(1)
C(7)	0.0963(5)	0.239(1)	−0.143(1)
C(8)	0.1501(5)	0.166(1)	−0.066(1)
C(9)	0.2061(5)	0.208(2)	−0.061(1)
C(10)	0.2092(6)	0.326(2)	−0.136(1)
C(11)	0.1564(5)	0.396(2)	−0.214(1)
C(12)	0.1002(5)	0.356(2)	−0.219(1)
C(13)	−0.1582(4)	−0.038(1)	−0.3022(9)
C(14)	−0.1370(5)	−0.048(1)	−0.393(1)
C(15)	−0.1692(5)	−0.136(2)	−0.502(1)
C(16)	−0.2208(5)	−0.212(2)	−0.521(1)
C(17)	−0.2417(6)	−0.207(2)	−0.433(1)
C(18)	−0.2108(5)	−0.122(1)	−0.321(1)
C(19)	0.3729(4)	−0.000(2)	0.6735(9)
C(20)	0.4036(5)	0.062(2)	0.597(1)
C(21)	0.3799(4)	−0.031(2)	0.890(1)
C(22)	0.3149(5)	0.012(2)	0.853(1)

Crystal-structure Determinations.—Crystals of **1** and **2**·6thf were obtained by recrystallization from thf; they were well shaped, with defined edges and faces, but not of simple geometry. Selected single crystals were introduced into thin-walled Lindeman glass tubes; because the crystals of **2**·6thf readily turned opaque in the glove-box, following desolvation, they were selected from the mother-liquor and immediately placed into the tube together with a droplet of thf. Data were collected (at 20 °C for **1** and −30 °C for **2**·6thf) on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator [λ(Mo-Kα) = 0.710 73 Å]. The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured every hour; a decay was observed (77% in 29 h for **1** and 19% in 27 h for **2**·6thf) and linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[21] The structure was solved by the heavy-atom method and refined by full-matrix least squares on *F* with anisotropic parameters for the uranium and sulfur atoms in **1** and for the uranium atom in **2**·6thf. The hydrogen atoms were introduced at calculated positions (C–H 0.95 Å and $B = 6$ Å^2); they were not refined but constrained to ride on their parent carbon atom. The asymmetric unit of **2**·6thf contains three molecules of thf which were difficult to locate accurately, certainly because of their lability; these solvation molecules show large thermal parameters and some erratic bond distances and angles. All calculations were performed on a Vax 4000-200 computer with the Enraf–Nonius MolEN system.[22] Scattering factors for neutral atoms[23] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3, final positional parameters in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for $[(Ph_3P)Cu(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Cu(PPh_3)]\cdot 6thf$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	0.000	0.000	0.000	C(18)	0.565(2)	0.838(2)	0.599(2)
U(2)	0.333	0.667	0.6570(1)	C(19)	0.164(2)	0.547(2)	0.744(2)
Cu(1)	0.000	0.000	0.1730(3)	C(20)	0.115(1)	0.525(1)	0.683(1)
Cu(2)	0.333	0.667	0.8298(3)	C(21)	0.076(2)	0.450(2)	0.675(2)
Cu(3)	0.333	0.667	0.4829(3)	C(22)	0.071(2)	0.398(2)	0.721(2)
S(1)	0.1112(4)	0.0339(5)	0.1044(4)	C(23)	0.115(2)	0.417(2)	0.786(2)
S(2)	0.2252(4)	0.6432(5)	0.7605(4)	C(24)	0.165(2)	0.490(2)	0.797(2)
S(3)	0.4446(5)	0.7063(5)	0.5505(4)	C(25)	0.272(1)	0.574(1)	1.003(1)
P(1)	0.000	0.000	0.3000(7)	C(26)	0.234(2)	0.561(2)	1.066(1)
P(2)	0.333	0.667	0.9570(7)	C(27)	0.199(1)	0.494(2)	1.099(1)
P(3)	0.333	0.667	0.3554(7)	C(28)	0.202(2)	0.435(2)	1.067(2)
O(1)	0.184(3)	0.352(3)	0.306(4)	C(29)	0.243(1)	0.443(2)	1.005(1)
O(2)	0.025(2)	0.334(2)	0.179(2)	C(30)	0.278(1)	0.511(1)	0.971(2)
O(3)	0.051(3)	0.535(3)	0.037(3)	C(31)	0.384(1)	0.755(1)	0.311(1)
C(1)	0.168(1)	0.132(1)	0.095(1)	C(32)	0.434(1)	0.771(2)	0.254(1)
C(2)	0.162(2)	0.179(1)	0.140(1)	C(33)	0.475(2)	0.849(2)	0.222(2)
C(3)	0.213(2)	0.255(2)	0.134(2)	C(34)	0.462(1)	0.898(1)	0.252(1)
C(4)	0.267(2)	0.281(2)	0.081(1)	C(35)	0.418(2)	0.891(2)	0.312(2)
C(5)	0.273(2)	0.236(2)	0.033(2)	C(36)	0.373(1)	0.812(1)	0.344(1)
C(6)	0.227(2)	0.157(2)	0.044(1)	C(40)	0.217(4)	0.382(4)	0.373(3)
C(7)	−0.025(1)	−0.089(1)	0.343(1)	C(41)	0.152(4)	0.364(4)	0.418(4)
C(8)	0.012(1)	−0.088(1)	0.407(1)	C(42)	0.106(3)	0.310(3)	0.397(3)
C(9)	−0.008(2)	−0.156(2)	0.434(2)	C(43)	0.098(4)	0.298(4)	0.345(3)
C(10)	−0.066(2)	−0.228(2)	0.408(1)	C(44)	−0.030(3)	0.263(3)	0.137(3)
C(11)	−0.099(2)	−0.217(2)	0.346(2)	C(45)	−0.054(3)	0.236(3)	0.187(3)
C(12)	−0.075(1)	−0.151(1)	0.312(1)	C(46)	−0.095(3)	0.285(3)	0.189(3)
C(13)	0.501(2)	0.804(2)	0.552(1)	C(47)	−0.040(3)	0.352(3)	0.191(3)
C(14)	0.483(2)	0.847(2)	0.509(2)	C(48)	0.018(4)	0.454(4)	−0.028(4)
C(15)	0.536(2)	0.930(2)	0.508(2)	C(49)	−0.050(4)	0.436(4)	0.010(3)
C(16)	0.599(2)	0.960(2)	0.557(2)	C(50)	−0.066(4)	0.490(4)	0.030(4)
C(17)	0.616(2)	0.918(2)	0.589(2)	C(51)	−0.014(3)	0.526(3)	0.077(3)

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Received 5th *July* 1994; *Paper* 4/04077E