Synthesis and Crystal Structure of $[\{W(SEt)O(PMe_2Ph)\}_2(\mu\text{-}S)(\mu\text{-}SEt)_2]$ *

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Reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with EtSH in air leads to the formation of the diamagnetic complex $[\{W(SEt)O(PMe_2Ph)\}_2(\mu\text{-}S)(\mu\text{-}SEt)_2]$ which is shown by *X*-ray analysis to have a confacial bioctahedral structure with *cis*-oxo-ligands.

As part of our investigation of the reactions of dinitrogen complexes of the transition metals[1] we are studying their interaction with thiolate sources because of the relevance of thiolate ligands to the metal centres in nitrogenase.[2] When treated with thiols the compounds $[M(N_2)_2(L_2)_2]$ (M = Mo or W, L_2 = two tertiary phosphines or one chelating ditertiary phosphine) give different products depending upon the nature of M and L. Thus, *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ gives a series of dithiolato-complexes of molybdenum(II), *trans*-$[Mo(SR)_2(Ph_2PCH_2CH_2PPh_2)_2]$,[3] but *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ gives dimeric, sulphido-bridged compounds derived by loss of tertiary phosphine from the metal and dealkylation of the thiol, *e.g.* $[\{M(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]$.[4] Here we describe the formation and structure of a related dimeric complex $[\{W(SEt)O(PMe_2Ph)\}_2(\mu\text{-}S)(\mu\text{-}SEt)_2]$ (1) from the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and EtSH. The terminal oxo-ligands arise from ingress of air to the reaction system in a similar manner to the formation[5] of the analogous cation $[(WOCl_2)_2(\mu\text{-}Cl)(\mu\text{-}SBu^t)_2]^+$.

Results and Discussion

Treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with an excess of EtSH leads to loss of the dinitrogen ligands as the gas together with the formation of dihydrogen. Exposure of the resulting solution to air then produces complex (1) the structure of which is shown in the Figure. Like its analogue[5] $[(WOCl_2)_2(\mu\text{-}Cl)(\mu\text{-}SBu^t)_2]^+$, complex (1) can be described as a confacial bioctahedron, with the two SEt ligands and the S ligand occupying the bridging positions. The two oxo-groups show the typical[5,6] *trans*-labilising effect of these ligands in that the bridging W–SEt bonds *trans* to oxide [W(1)–S(5) and W(2)–S(5)] are some 0.2—0.3 Å longer than those *trans* to the terminal S–Et groups [W(1)–S(3) and W(2)–S(3)] (Table 1).

The W–W distance of 2.801(1) Å is in the range (2.6—2.85 Å) observed[5,6] for a range of triply bridged dioxo-complexes of molybdenum and tungsten. Although this relatively short W–W distance and the diamagnetism of complex (1) could be taken to indicate a W–W bond, the angle extended at the bridging sulphide [73.5(1)°] indicates an almost pure bioctahedron[5,7] and there is no compelling reason to suggest such a W–W interaction. Other features of the structure such as the W–O, W–S, and W–P distances are very similar to those observed in a range of analogues.[4-6]

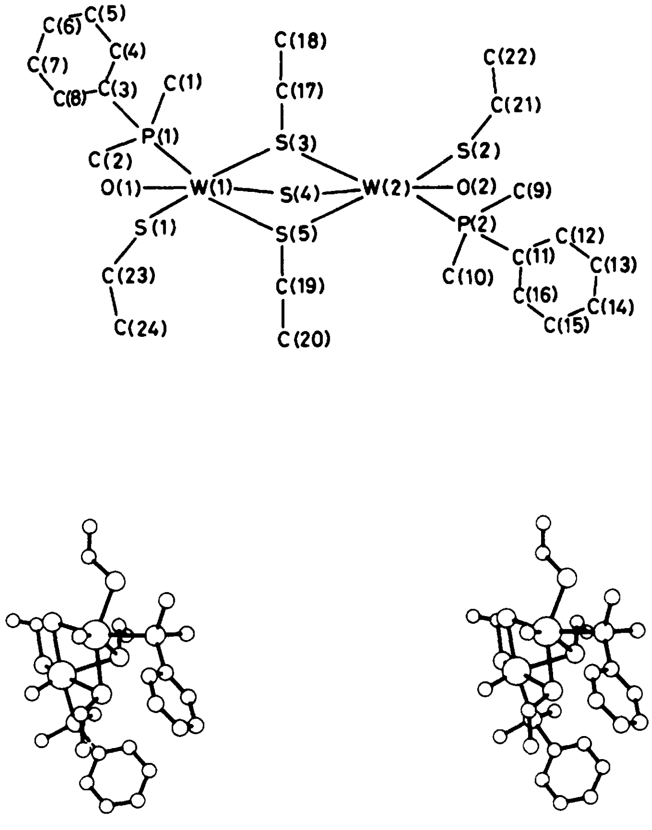

Figure. Atom numbering scheme, structure, and stereoscopic view of $[\{W(SEt)O(PMe_2Ph)\}_2(\mu\text{-}S)(\mu\text{-}SEt)_2]$

The phosphorus atoms of complex (1) are in equivalent structural (Figure) and magnetic (singlet ^{31}P resonance, Experimental section) environments. Because of the overlapping resonances of the PMe_2 and different SEt groups, and the possibility of isomers involving inversion of SEt groups, the ^1H n.m.r. spectrum is complicated and was not analysed in detail.

Experimental

The preparation of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and subsequent manipulation entailed published methods.[4] Spectra were

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* Di-μ-ethanethiolato-μ-sulphido-bis[(dimethylphenylphosphine)(ethanethiolato)oxotungsten(V)].

Supplementary data available (No. SUP 56037, 24 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Bond lengths (Å) and angles (°)

W(1)–W(2)	2.801(1)						
W(1)–S(1)	2.404(5)	W(2)–S(2)	2.400(5)	P(1)–C(1)	1.79(1)	P(2)–C(9)	1.78(1)
W(1)–P(1)	2.604(5)	W(2)–P(2)	2.586(4)	P(1)–C(2)	1.78(1)	P(2)–C(10)	1.80(1)
W(1)–O(1)	1.674(9)	W(2)–O(2)	1.677(9)	P(1)–C(3)	1.84(1)	P(2)–C(11)	1.84(1)
W(1)–S(3)	2.488(4)	W(2)–S(3)	2.465(4)	C(3)–C(4)	1.38(2)	C(11)–C(12)	1.39(2)
W(1)–S(4)	2.338(5)	W(2)–S(4)	2.343(5)	C(4)–C(5)	1.39(2)	C(12)–C(13)	1.35(2)
W(1)–S(5)	2.647(4)	W(2)–S(5)	2.675(4)	C(5)–C(6)	1.36(2)	C(13)–C(14)	1.36(2)
S(1)–C(23)	1.96(3)	S(2)–C(21)	1.82(1)	C(6)–C(7)	1.39(2)	C(14)–C(15)	1.38(2)
C(23)–C(24)	1.01(5)	C(21)–C(22)	1.24(4)	C(7)–C(8)	1.38(2)	C(15)–C(16)	1.40(2)
S(3)–C(17)	1.83(1)	S(5)–C(19)	1.85(1)	C(8)–C(3)	1.36(2)	C(16)–C(11)	1.39(2)
C(17)–C(18)	1.43(2)	C(19)–C(20)	1.41(2)				
O(1)–W(1)–S(1)	105.0(4)	O(2)–W(2)–S(2)	107.7(4)	W(1)–S(3)–C(17)	109.4(6)	W(2)–S(3)–C(17)	108.9(6)
O(1)–W(1)–P(1)	92.4(4)	O(2)–W(2)–P(2)	89.5(4)	W(1)–S(5)–C(19)	109.7(6)	W(2)–S(5)–C(19)	107.1(6)
O(1)–W(1)–S(3)	91.6(4)	O(2)–W(2)–S(3)	91.6(4)				
O(1)–W(1)–S(4)	102.9(4)	O(2)–W(2)–S(4)	104.5(4)	S(3)–C(17)–C(18)	113.2(8)	S(5)–C(19)–C(20)	113.1(8)
O(1)–W(1)–S(5)	157.2(4)	O(2)–W(2)–S(5)	157.1(4)				
P(1)–W(1)–S(1)	75.2(3)	P(2)–W(2)–S(2)	75.8(3)	W(1)–S(1)–C(23)	120.3(5)	W(2)–S(2)–C(21)	116.7(9)
P(1)–W(1)–S(3)	87.3(3)	P(2)–W(2)–S(3)	84.0(3)				
P(1)–W(1)–S(4)	157.9(4)	P(2)–W(2)–S(4)	160.7(4)	S(1)–C(23)–C(24)	108.4(9)	S(2)–C(21)–C(22)	121.2(8)
P(1)–W(1)–S(5)	86.3(4)	P(2)–W(2)–S(5)	87.2(4)				
S(1)–W(1)–S(3)	156.1(2)	S(2)–W(2)–S(3)	151.6(2)	W(1)–P(1)–C(1)	115.4(6)	W(2)–P(2)–C(9)	116.5(6)
S(1)–W(1)–S(4)	85.4(2)	S(2)–W(2)–S(4)	87.1(2)	W(1)–P(1)–C(2)	110.3(6)	W(2)–P(2)–C(10)	114.7(6)
S(1)–W(1)–S(5)	96.6(2)	S(2)–W(2)–S(5)	93.4(2)	W(1)–P(1)–C(3)	117.7(6)	W(2)–P(2)–C(11)	114.0(6)
W(1)–S(3)–W(2)	68.9(1)	W(1)–S(4)–W(2)	73.5(1)	W(1)–S(5)–W(2)	63.5(1)		
P(1)–C(3)–C(4)	117.2(8)	P(2)–C(11)–C(12)	117.2(8)	C(5)–C(6)–C(7)	119.0(9)	C(14)–C(15)–C(16)	118.4(9)
C(3)–C(4)–C(5)	119.4(9)	C(11)–C(12)–C(13)	123.3(8)	C(7)–C(8)–C(3)	119.5(9)	C(15)–C(16)–C(11)	119.7(9)
C(4)–C(5)–C(6)	120.7(9)	C(13)–C(14)–C(15)	122.8(9)	C(8)–C(3)–P(1)	122.3(8)	C(16)–C(11)–P(2)	124.8(8)

Table 2. Final fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	−2 348(0)	2 272(0)	2 655(0)	C(8)	446(19)	−316(16)	3 989(11)
W(2)	−943(0)	4 857(0)	2 439(0)	C(9)	2 788(21)	5 696(21)	1 570(11)
S(1)	−4 177(6)	663(5)	1 837(3)	C(10)	2 106(19)	7 856(17)	2 228(11)
S(2)	−1 075(6)	6 057(4)	1 334(3)	C(11)	3 134(16)	6 199(13)	3 199(9)
S(3)	241(4)	3 490(3)	3 225(2)	C(12)	2 872(18)	6 839(16)	3 852(9)
S(4)	−3 497(5)	3 736(5)	2 087(4)	C(13)	3 748(23)	6 967(19)	4 514(11)
S(5)	−286(5)	2 926(4)	1 656(2)	C(14)	4 937(24)	6 429(20)	4 538(12)
P(1)	−1 443(5)	191(4)	2 776(3)	C(15)	5 262(21)	5 754(20)	3 922(12)
P(2)	1 854(5)	6 166(4)	2 339(2)	C(16)	4 340(19)	5 639(17)	3 239(11)
O(1)	−3 035(11)	2 154(12)	3 512(8)	C(17)	144(19)	3 921(15)	4 229(9)
O(2)	−1 022(12)	5 809(10)	3 204(7)	C(18)	762(30)	3 149(23)	4 733(10)
C(1)	−1 210(25)	−592(18)	1 893(12)	C(19)	−1 256(25)	2 808(19)	688(12)
C(2)	−2 829(23)	−1 003(23)	3 200(16)	C(20)	−1 166(33)	1 722(30)	240(14)
C(3)	372(17)	322(14)	3 344(9)	C(21)	−2 929(27)	5 720(24)	784(15)
C(4)	1 690(18)	1 044(15)	3 068(10)	C(22)	−3 315(32)	6 565(29)	429(20)
C(5)	3 097(19)	1 141(17)	3 464(12)	C(23)	−5 454(33)	1 171(30)	1 029(25)
C(6)	3 187(23)	526(20)	4 116(12)	C(24)	−6 521(54)	1 037(53)	1 199(27)
C(7)	1 852(24)	−204(20)	4 381(11)				

obtained using Pye Unicam SP3-200 or JEOL FX90Q instruments. Analyses were by Mr. C. Macdonald of the A.F.R.C. Unit of Nitrogen Fixation.

Preparation of $[\{W(SEt)O(PMe_2Ph)\}_2(\mu\text{-}S)(\mu\text{-}SEt)_2]$.—Ethanethiol (0.25 cm³, 5 mol equiv.) was distilled at −196 °C in a vacuum onto *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.45 g) in tetrahydrofuran (35 cm³) and the mixture allowed to warm to 20 °C with stirring. Evolution of N_2 (1.9 mol equiv.) and H_2 (1.8 mol equiv.) occurred during 2 h when the solution changed from yellow to green-brown. Solvent was removed to about 0.25 volume in a vacuum, then hexane (20 cm³) was added under dinitrogen to give a brown amorphous precipitate which was filtered off and discarded. The resulting green-brown solution was allowed to stand in air for 2—3 d when brown *needles* deposited which were filtered off, washed with hexane, and dried (10^{-3} mmHg, *ca.* 0.133 Pa) (0.1 g, 37%) (Found: C, 29.7; H, 4.1. $C_{24}H_{42}O_2P_2S_5W_2$ requires C, 30.3; H, 4.4%). N.m.r. spectra (CD_2Cl_2): ^{31}P [standard $P(OMe)_3$], δ −147.2 (s); ^1H (standard $SiMe_3$), δ 0.61—2.7 (complex multiplet of SEt and PMe_2) and 6.9—8.0 (m, Ph). $\nu_{max.}$(W=O) at 920 cm⁻¹ (Nujol).

Crystallography.—Crystal data. $C_{24}H_{42}O_2P_2S_5W_2$, M = 942.7, triclinic, a = 9.104(2), b = 10.806(2), c = 17.642(3) Å, α = 92.47(2), β = 94.14(2), γ = 105.43(2)°, U = 1 665(2) Å³, space group $P\bar{1}$, Z = 2, D_c = 1.88 Mg m⁻³, $F(000)$ = 460. Brown, air-stable needles, Mo-K_α radiation, graphite monochromator, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 74.7 cm⁻¹.

Data collection and processing. Measurements were made using an Enraf–Nonius CAD4 four-circle diffractometer. A small crystal (0.05 × 0.05 × 0.3 mm) was selected for study. The unit cell was measured by centring 25 independent reflections ($\sin\theta/\lambda > 0.46$), and refining the orientation matrix and unit-cell parameters by least squares. 5 197 Reflections were measured with $(\sin\theta)/\lambda \leqslant 0.56$. These were reduced to 4 809 symmetry-independent reflections of which 3 439 were considered observed applying the criterion $I \geqslant 2.5\sigma(I)$. The intensities were corrected for Lorentz and polarisation effects but not for absorption because facilities for absorption correction were not available at the time; absorption effects were, however, minimised by using a small crystal of regular cross-section.

The structure was solved by the heavy-atom method. The positions of the two tungsten atoms were determined from a three-dimensional Patterson synthesis and a subsequent electron-density map revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement was carried out using first isotropic and then anisotropic thermal parameters. Anomalous dispersion corrections were applied to the tungsten, phosphorus, and sulphur atoms. The positions of the hydrogen atoms were determined from geometric criteria. They were included in the least-squares refinement but were not refined. A weighting scheme $[w^{-1} = \sigma^2(F_o) + 0.01|F_o|^2]$ was applied to the data and refinement was terminated at $R = 0.049$ for all observed reflections.

On the electron-density maps there is evidence to suggest thermal disorder of the carbon atoms in the terminal SEt groups [C(21)—C(24)], the electron-density contours about these atoms being rather diffuse. This is borne out by the high thermal parameters for these atoms. The resulting carbon–carbon bond lengths are short but attempts to constrain them to more acceptable values resulted in a substantial increase in the R factor. They were, therefore, allowed to refine freely and their positions must be regarded as those which produce a minimum in R.

Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. Computations were performed on the University of Surrey Prime 750 network using local programs and the SHELX system of G. M. Sheldrick.[7]

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