Structural Studies of Binuclear Sulphido-bridged Complexes of Tungsten. Preparation and *X*-Ray Crystal Structures of $[S_2W(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ and $[\{W(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]\cdot CH_2Cl_2$ †

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The reaction of $[NBu^n{}_4]_2[WS_4]$ with $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ yields the asymmetric binuclear complex $[S_2W(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ (1). Complex (1) crystallizes in space group *Cc*, with a = 15.389(2), b = 10.292(4), c = 18.406(2) Å, β = 90.43(1)°, and Z = 4; final R = 0.061 based on 4 091 reflections collected, 2 116 used. One tungsten is trigonally pyramidally co-ordinated with two $NNMe_2$ groups in the equatorial plane and one axial and one equatorial bridging sulphide with a W–W separation of 3.024(1) Å. The reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with Bu^tSH gives the symmetric binuclear complex $[\{W(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]$ (2). Complex (2) crystallises in space group $P\bar{1}$, with a = 9.654(4), b = 10.331(4), c = 13.288(5) Å, α = 78.09(1), β = 69.36(1), γ = 82.49(1)°, and Z = 1; final R = 0.071 based on 4 732 reflections collected, 2 310 used. The centre of symmetry imposes planarity on the W_2S_2 system with a W–W distance of 2.736(2) Å. Each tungsten has distorted trigonal-bipyramidal geometry with bridging sulphide and phosphorus in the apical sites.

The chemistry of thiometallates of molybdenum is a subject of continuing extensive investigation because of their key role in biological processes, including nitrogen fixation,[1] and also because of their unusual spectroscopic and structural properties.[2]

Whereas the structural chemistry of sulphido-bridged binuclear complexes of molybdenum has received considerable investigation, that of analogous tungsten compounds remains largely unexplored. Here we report the synthesis and structural characterisation of $[S_2W(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ (1) and $[\{W(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]$ (2), species which incorporate the W_2S_2-bridging moiety. Complex (1) is prepared in 60% yield by reaction of $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ with one equivalent of $[NBu^n{}_4]_2[WS_4]$ in acetonitrile at room temperature. The complex crystallises from the reaction mixture as analytically pure reddish brown plates. The related complex $[S_2Mo(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ can be prepared in an analogous fashion using $[NBu^n{}_4]_2[MoS_4]$.

Complex (2) is produced in relatively low yield (28%) from the reaction of Bu^tSH with *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ in tetrahydrofuran (thf), a reaction which involves dealkylation of the thiol. This latter phenomenon has already been observed in the preparation of the molybdenum analogue of (2) [3] from $[Mo(SBu^t)_4]$ and PMe_2Ph and in the preparation of $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$ from $[WCl_4(SC_4H_8)_2]$ and $SiMe_3(SEt)$.[4]

Treatment of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with Bu^tSH gives the molybdenum analogue of (2), $[\{Mo(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]$ (3) in high yield. This reaction therefore provides an alternative route to (3), but, however, the only route so far available to (2) is that above, because the $[W(SBu^t)_4]$ required has not yet been prepared.

The preparation of (2) and (3) contrasts with the formation of simple monomeric thiolato-complexes $[Mo(SR)_2(dppe)_2]$ (R = Me, Et, Bu^n, or Ph *etc*; dppe = $Ph_2PCH_2CH_2PPh_2$) by the analogous reaction of RSH with *trans*-$[Mo(N_2)_2(dppe)_2]$.[5] Further investigations of the reactions of thiols with dinitrogen complexes which give a variety of thiolate products will be reported at a later date.

Experimental

All reactions involving air-sensitive materials were carried out under dinitrogen or in a vacuum using conventional high vacuum or Schlenk techniques. Solvents were dried and distilled under dinitrogen before use. Infrared spectra were obtained using Pye Unicam SP2000 or SP3-200 instruments and n.m.r. spectra using a JEOL FX90Q instrument. The compounds *cis*-$[M(N_2)_2(PMe_2Ph)_4]$,[6] $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ [7] and $[NBu^n{}_4][MS_4]$ [8] (M = Mo or W) were prepared by published methods. Analyses were by Mrs. G. Olney of the University of Sussex.

1,1-Bis[dimethylhydrazido(2−)]-1,2-di-μ-sulphido-2,2-disulphido-1-(triphenylphosphine)ditungsten(VI) $[S_2W(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ (1).—Solutions of $[WCl(NNMe_2)_2(PPh_3)_2]^+$ (0.5 g, 6.2×10^{-4} mol) and $[NBu^n{}_4]_2[WS_4]$ (0.50 g, 6.3×10^{-4} mol) in acetonitrile (30 cm^3 each) were mixed at room temperature to give an instantaneous colour change from yellow to brown-purple and slow crystallisation of the complex (yield 0.36 g, 65%) (Found: C, 29.8; H, 3.4; N, 3.1. $C_{22}H_{27}N_4PS_4W_2$ requires C, 30.2; H, 3.1; N, 3.2%).

The related complex $[S_2Mo(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ was prepared similarly using $[NBu^n{}_4]_2[MoS_4]$ (Found: C, 37.9; H, 4.0; N, 8.1. $C_{22}H_{27}MoN_4PS_4W$ requires C, 37.8; H, 3.8; N, 8.0%).

Di-μ-sulphido-bis[bis(t-butylthiolato)(dimethylphenylphosphine)tungsten(IV)] $[\{W(SBu^t)_2(PMe_2Ph)\}_2(\mu\text{-}S)_2]$ (2).—The compound Bu^tSH (0.59 g, 6.6 mmol) was added to *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.89 g, 1.12 mmol) in thf (20 cm^3) under dinitrogen and the mixture stirred at 20 °C for 48 h. The original yellow solution darkened to green-brown over this period. The solution was then concentrated to approximately one third of its volume in a vacuum, then hexane (*ca.* 30

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† 1,1-Bis[dimethylhydrazido(2−)]-1,2-di-μ-sulphido-2,2-disulphido-1-(triphenylphosphine)ditungsten(VI) and di-μ-sulphido-bis[bis(t-butylthiolato)(dimethylphenylphosphine)-tungsten(IV)]–dichloroethane (1/1) respectively.

Supplementary data available (No. SUP 23578, 35 pp.): structure factors and anisotropic thermal parameters for (1) and (2) and H-atom co-ordinates for (2). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Summary of crystal data and experimental details of the structural study of complexes (1) and (2)

	Complex (1)[a]	Complex (2)[b]
Crystal system	Monoclinic	Triclinic
a/Å	15.389(2)	9.654(4)
b/Å	10.292(4)	10.331(4)
c/Å	18.406(2)	13.288(5)
α/°		78.09(1)
β/°	90.43(1)	69.36(1)
γ/°		82.49(1)
U/Å^3	2 915.12	1 211.0
Space group	Cc	$P\bar{1}$
Z	4	1
D_c/g cm^{-3}	1.99	1.59
D_m/g cm^3 (flotation)	2.01(2)	1.57(2)
F(000)	2 096	557
Crystal dimensions/mm	0.24 × 10.26 × 0.20	0.19 × 0.15 × 0.20
Radiation	Mo-K_α (λ = 0.710 73 Å)	Mo-K_α (λ = 0.710 73 Å)
Monochromator	Graphite	Highly oriented graphite (equatorial mode)
Scan width/°	1.0	1.2
Scan speed/° min^{-1}	Variable 6—30	Variable 6—10
Background measurements	10 s at each end of the 2θ scan range	Stationary crystal–stationary counter at the beginning and end of each 2θ scan, each for half the time taken for the 2θ scan
Standards	3 reflections every 100 data	3 reflections every 147 data
No. of reflections collected	4 091	4 732
Data with $\lvert F_o \rvert > 6.0\sigma\lvert F_o \rvert$	2 116	2 310
Absorption coefficient/ cm^{-1}	96.84	51.91
R	0.061	0.071
R'	0.057	0.065
Goodness of fit[c]	1.37	1.36

[a] At 23 °C. [b] At 21 °C. [c] Goodness of fit = $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\text{n.o.} - \text{n.v.})]^{\frac{1}{2}}$ where n.o. is the number of observations and n.v. is the number of variables. Common to both complexes (1) and (2): Nicolet R3/m automated diffractometer; scan mode, coupled θ(crystal)—2θ(counter); scan range, $0 < 2\theta \leqslant 45°$.

cm^3) was added under dinitrogen to precipitate a brown-green solid. The solid was dissolved in CH_2Cl_2, filtered, and hexane added to give *green platelets* which were filtered off, washed with hexane, and dried in a vacuum (yield 0.15 g, 28%) (Found: C, 36.4; H, 5.7. $C_{32}H_{58}P_2S_6W_2$ requires C, 36.1; H, 5.5%). N.m.r. data ($CDCl_3$ solution): ^{1}H, 6.8—7.8 (Ph, multiplet), 2.85—0.76 p.p.m. [CMe_3 plus PCH_3, complex multiplet] (relative to $SiMe_4$); ^{31}P, −154.6 p.p.m. (singlet) [relative to $P(OMe)_3$]. I.r. (Nujol mull) 1 155 cm^{-1} (δ CMe_3).

Crystals for *X*-ray structure determination were also obtained from CH_2Cl_2–hexane (*ca.* 1 : 8) solution, but as the CH_2Cl_2 solvate.

Di-μ-sulphido-bis[bis(t-butylthiolato)(dimethylphenylphosphine)molybdenum(IV)] [{Mo(SBu^t)$_2$(PMe$_2$Ph)}$_2$(μ-S)$_2$] (3).—The compound Bu^{t}SH (0.25 g, 2.8 mmol) was added to *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] (0.45 g, 0.6 mmol) in thf (40 cm^3) in a vacuum. Dinitrogen and dihydrogen (2.5 mol of total gas per mol Mo) were evolved and the solution changed from yellow to green after stirring for 18 h at 20 °C. The solution was then concentrated to approximately one third of its volume in a vacuum and hexane (30 cm^3) added under dinitrogen to give *lustrous green rhombs* on standing. These were filtered off, washed with a little cold CH_2Cl_2 to remove a small amount of brown impurity, then hexane and dried in a vacuum (yield 0.2 g, 71%) (Found: C, 43.2; H, 6.6. $C_{32}H_{58}Mo_2P_2S_6$ requires C, 43.3; H, 6.5%).

The spectroscopic properties of this compound were similar to those reported by Otsuka and co-workers.[3]

X-Ray Crystal Structure of [S$_2$W(μ-S)$_2$W(NNMe$_2$)$_2$(PPh$_3$)] (1).—A red crystal of (1) suitable for an *X*-ray diffraction study was grown directly from the reaction mixture by using dilute solutions. The crystal data and experimental conditions used for the structure determination are summarised in Table 1.

Reduction of intensity data and structure solution and refinement. Data were corrected for background, attenuators, Lorentz and polarisation effects in the usual fashion. An absorption correction based on ψ scans for five reflections was applied.

The W atoms were located from sharpened Patterson functions and the remaining non-hydrogen atoms from subsequent difference-Fourier maps. The atomic scattering factors for W, S, P, N, and C were taken from ref. 9. The anomalous dispersion corrections were taken from ref. 10 with the scattering factors of W, S, and P being corrected for both real and imaginary components of anomalous scattering.

In an attempt to establish the correct enantiomer for the structures, two models were refined; one with indices as assigned and a second in which *hkl* was changed to $\bar{h}\bar{k}\bar{l}$. They refined to converge at 0.066 and 0.067 respectively and the error individual in an incorrect choice of enantiomer in this space group is negligible.

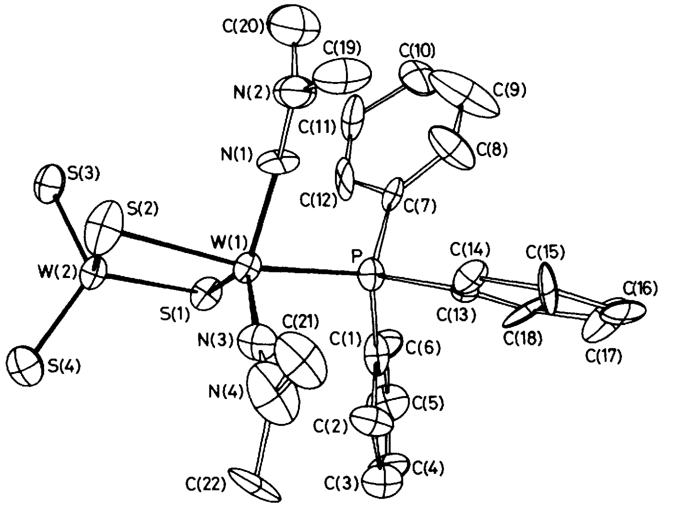

Figure 1. Molecular structure of [S$_2$W(μ-S)$_2$W(NNMe$_2$)$_2$(PPh$_3$)] (1) showing atom-numbering scheme

Refinement was by a full-matrix least-squares procedure. The final R values are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.061$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.057$ using the weighting scheme $w = 1/\sigma F^2$.

All calculations were performed on a Data General Nova 3 computer with 32k of 16-bit words using versions of the Nicolet SHELXTL interactive crystallographic software package as described by G. M. Sheldrick.[11]

A perspective drawing of the molecule illustrating the atom numbering scheme is given in Figure 1. Atomic positional parameters and relevant bond lengths and angles are given in Tables 2 and 3 respectively.

The molecule contains two crystallographically and chemically distinct W atoms, bridged through sulphurs S(1) and S(2); the W(1), W(2), S(1), and S(2) atoms being coplanar. The co-ordination about W(2) is distorted tetrahedral with W–(terminal sulphide) distances of 2.158(9) and 2.141(7) Å. These values are very close to those found for other complexes containing ligated tetrathiotungstate. The W(2)–S(1) and W(2)–S(2) distances are not equivalent as W(1) has trigonal-bipyramidal co-ordination and S(1) and S(2) occupy axial and equatorial sites respectively. This is a rare example of a tetrathiometallate ligand spanning axial and equatorial sites in trigonal-bipyramidal geometry and W(1)–S(1) and W(1)–S(2) are significantly different at 2.405(6) and 2.528(8) Å respectively.

When the tetrathiometallates ligate to give a five-co-ordinate metal, the usual geometry is square pyramidal with the tetrathiometallate sulphurs occupying nearly equivalent *cis* sites in the basal plane. However, in this instance the two strongly π-bonded hydrazido(2−) ligands have a preference to occupy equatorial sites in trigonal-bipyramidal geometry thereby minimising competition but maximising overlap with metal orbitals. This strong site preference of the hydrazide ligands dictates the geometry of W(1). The W–N and N–N bond distances for the NNMe$_2$ ligands lie within the range for other hydrazido(2−) complexes,[12] but are not equivalent for the two ligands. These differences in bond distances and angles are ascribable to steric interactions of the hydrazido(2−) alkyl groups with the phosphine phenyls. A similar asymmetry was observed for the NNMe$_2$ ligands in [MoCl(NNMe$_2$)$_2$(PPh$_3$)$_2$]$^+$ [7] and the molybdenum analogue of (1), [S$_2$Mo(μ-S)$_2$Mo(NNMe$_2$)$_2$(PPh$_3$)].[13]

Table 2. Atomic positional parameters for [S$_2$W(μ-S)$_2$W(NNMe$_2$)$_2$(PPh$_3$)] (1)

Atom	*x*	*y*	*z*
W(1)	0.994 34(8)	0.836 94(7)	1.069 77(6)
W(2)	0.000 00	0.571 07(8)	0.000 00
S(1)	1.053 2(4)	0.632 9(6)	1.110 7(3)
S(2)	0.935 2(6)	0.745 5(7)	0.951 9(4)
S(3)	0.906 9(6)	0.417 2(8)	1.016 3(5)
S(4)	1.105 9(5)	0.505 3(7)	0.934 9(4)
P	1.033 6(4)	0.900 1(5)	1.195 9(3)
N(1)	0.885 0(11)	0.902 3(16)	1.086 5(12)
N(2)	0.809 9(13)	0.947 7(23)	1.090 3(13)
N(3)	1.065 6(14)	0.940 3(22)	1.026 9(10)
N(4)	1.104 3(20)	1.038 5(20)	0.991 3(15)
C(1)	1.144(2)	0.846(2)	1.227(1)
C(2)	1.212(2)	0.890(2)	1.192(2)
C(3)	1.298(2)	0.866(3)	1.213(1)
C(4)	1.311(2)	0.777(3)	1.271(2)
C(5)	1.242(2)	0.729(3)	1.309(1)
C(6)	1.154(1)	0.766(3)	1.286(1)
C(7)	0.953(1)	0.850(2)	1.263(1)
C(8)	0.903(2)	0.935(3)	1.305(2)
C(9)	0.843(3)	0.888(4)	1.353(3)
C(10)	0.822(2)	0.771(3)	1.359(2)
C(11)	0.869(2)	0.678(3)	1.317(2)
C(12)	0.939(2)	0.714(3)	1.271(1)
C(13)	1.047(1)	1.074(2)	1.216(1)
C(14)	1.015(1)	1.165(2)	1.167(1)
C(15)	1.024(2)	1.295(2)	1.180(1)
C(16)	1.061(1)	1.339(3)	1.248(2)
C(17)	1.089(1)	1.241(2)	1.300(1)
C(18)	1.084(2)	1.111(3)	1.283(2)
C(19)	0.792(1)	1.081(2)	1.072(1)
C(20)	0.742(2)	0.880(5)	1.131(2)
C(21)	1.054(2)	1.154(2)	0.967(1)
C(22)	1.193(2)	1.026(4)	0.972(2)

Table 3. Selected bond lengths (Å) and angles (°) for [S$_2$W(μ-S)$_2$W(NNMe$_2$)$_2$(PPh$_3$)] (1)

W(1) ... W(2)	3.024(1)	S(1)–W(1)–S(2)	94.4(2)
W(1)–S(1)	2.405(6)	S(1)–W(1)–P	81.2(2)
W(1)–S(2)	2.528(8)	S(1)–W(1)–N(1)	127.5(6)
W(1)–P	2.482(6)	S(1)–W(1)–N(3)	116.3(8)
W(1)–N(1)	1.84(2)	S(2)–W(1)–P	169.8(2)
W(1)–N(3)	1.72(2)	S(2)–W(1)–N(1)	87.5(7)
W(2)–S(1)	2.281(6)	S(2)–W(1)–N(3)	93.6(7)
W(2)–S(2)	2.233(8)	P–W(1)–N(1)	88.0(7)
W(2)–S(3)	2.158(9)	P–W(1)–N(3)	96.6(7)
W(2)–S(4)	2.141(7)	N(1)–W(1)–N(3)	115.9(10)
N(1)–N(2)	1.25(3)	S(1)–W(2)–S(2)	106.6(3)
N(2)–C(19)	1.44(4)	S(1)–W(2)–S(3)	108.4(3)
N(2)–C(20)	1.46(4)	S(1)–W(2)–S(4)	108.6(3)
N(3)–N(4)	1.35(4)	S(2)–W(2)–S(3)	110.5(3)
N(4)–C(21)	1.48(4)	S(2)–W(2)–S(4)	111.8(3)
N(4)–C(22)	1.43(5)	S(3)–W(2)–S(4)	110.8(3)
P–C(1)	1.87(3)	W(1)–S(1)–W(2)	80.3(2)
P–C(7)	1.83(2)	W(1)–S(2)–S(2)	78.6(3)
P–C(13)	1.84(2)	W(1)–N(1)–N(2)	173.6(20)
C–C rings	av. 1.40(5)	W(1)–N(3)–N(4)	166.4(20)
		N(1)–N(2)–C(19)	121.1(20)
		N(1)–N(2)–C(20)	121.2(24)
		C(19)–N(2)–C(20)	115.9(28)
		N(3)–N(4)–C(21)	121.1(29)
		N(3)–N(4)–C(22)	118.8(29)
		C(21)–N(4)–C(22)	120.0(31)

X-*Ray Crystal Structure of* [{W(SBu^t)$_2$(PMe$_2$Ph)}$_2$(μ-S)$_2$]·CH$_2$Cl$_2$ (2).—A crystal of (2) suitable for an *X*-ray diffraction study was grown by diffusion of hexane into a solution in

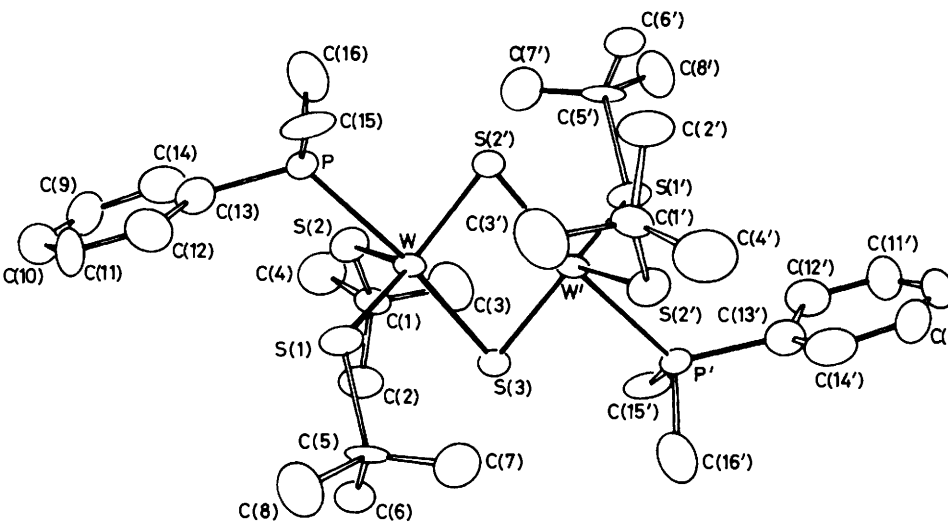

Figure 2. Molecular structure of [{W(SBu^t)$_2$(PMe$_2$Ph)}$_2$(μ-S)$_2$] (2) showing atom-numbering scheme

Table 4. Atomic positional parameters for [{W(SBu^t)$_2$(PMe$_2$Ph)}$_2$(μ-S)$_2$] (2)

Atom	*x*	*y*	*z*
W	0.084 2(1)	−0.001 81(8)	0.393 10(7)
P	0.035 8(6)	−0.047 9(5)	0.225 9(4)
S(1)	0.137 9(8)	0.199 3(5)	0.277 5(4)
S(2)	0.250 8(6)	−0.181 7(5)	0.351 1(4)
S(3)	0.157 7(6)	0.043 7(5)	0.532 0(4)
C(1)	0.223(1)	0.330(1)	0.312(2)
C(2)	0.369(2)	0.278(2)	0.328(1)
C(3)	0.114(2)	0.383(2)	0.413(1)
C(4)	0.246(2)	0.441(2)	0.212(2)
C(5)	0.390(2)	−0.238(2)	0.425(1)
C(6)	0.489(2)	−0.130(2)	0.408(1)
C(7)	0.306(2)	−0.290(2)	0.545(2)
C(8)	0.482(2)	−0.350(2)	0.366(1)
C(9)	0.352(2)	0.073(2)	−0.069(2)
C(10)	0.432(2)	−0.044(2)	−0.095(1)
C(11)	0.391(2)	−0.160(3)	−0.024(2)
C(12)	0.278(3)	−0.163(2)	−0.070(2)
C(13)	0.192(3)	−0.050(2)	0.097(2)
C(14)	0.227(2)	0.071(2)	0.027(2)
C(15)	−0.044(3)	−0.206(2)	0.249(2)
C(16)	−0.103(2)	0.069(2)	0.189(2)
S(061)	−1.020(8)	0.555(5)	0.002(5)
S(062)	0.828(6)	0.494(5)	0.130(3)
S(063)	0.715(7)	0.484(6)	0.112(4)

dichloromethane. The crystal data and experimental conditions employed for the structure determination are shown in Table 1.

Reduction of intensity data and solution structure and refinement. Data were corrected and refined in a manner similar to that for complex (1).

The W atoms were located from a three-dimensional Patterson map and the remaining non-hydrogen atoms by subsequent difference-Fourier techniques. Hydrogen atoms were introduced as fixed contributors in idealized positions in the final refinement. The final *R* factors were $R = 0.071$ and $R' = 0.065$.

A perspective view of the structure showing the atomic numbering scheme is given in Figure 2. Atomic positional parameters and some relevant bond distances and angles are given in Tables 4 and 5 respectively.

Table 5. Selected bond lengths (Å) and angles (°) for [{W(SBu^t)$_2$(PMe$_2$Ph)}$_2$(μ-S)$_2$] (2)

W–P	2.571(7)	S(1)–C(1)	1.88(3)
W–S(1)	2.313(5)	S(2)–C(5)	1.90(2)
W–S(2)	2.317(5)	C(1)–C(2)	1.51(3)
W–S(3)	2.345(7)	C(1)–C(3)	1.54(3)
W–S(3′)	2.254(6)	C(1)–C(4)	1.54(3)
W . . . W′	2.736(2)	C(5)–C(6)	1.49(3)
P–C(9)	1.84(2)	C(5)–C(7)	1.52(3)
P–C(15)	1.82(2)	C(5)–C(8)	1.54(3)
P–C(16)	1.82(2)	C–C ring	av. 1.38(3)
P–W–S(1)	79.7(2)	S(1)–W–W′	117.9(1)
P–W–S(2)	79.1(2)	S(2)–W–W′	118.6(1)
P–W–S(3)	173.2(2)	S(3)–W–W′	52.0(1)
S(1)–W–S(3′)	79.8(2)	W–P–C(9)	118.8(9)
S(1)–W–S(2)	117.6(2)	W–P–C(15)	113.4(8)
S(1)–W–S(3)	97.1(2)	W–P–C(16)	112.4(8)
S(1)–W–S(3′)	116.1(2)	C(9)–P–C(15)	103.5(10)
S(2)–W–S(3)	97.3(2)	C(9)–P–C(16)	104.5(10)
S(2)–W–S(3′)	116.6(2)	C(15)–P–C(16)	102.6(12)
S(3)–W–S(3′)	107.0(2)	W–S(1)–C(1)	121.1(7)
P–W–W′	134.9(1)	W–S(1)–C(5)	120.5(7)
		W–S(3)–W′	73.0(2)

The structure of (2) (Figure 2) is very similar to that of its molybdenum analogue (3) [3] and consists of discrete dimers. The crystallographic centre of symmetry imposes planarity on the W_2S_2 bridge. The geometry about each W atom is distorted trigonal pyramidal, with the thiolate sulphur donors S(1) and S(2) and the sulphido-bridge S(3′) occupying the equatorial plane and the P atom and the second bridging sulphide S(3) located in the axial positions. The significant lengthening of the W–S(3) bond distance [2.345(7) Å] *versus* the W–S(3′) distance [2.254(6) Å] is thus anticipated as a consequence of occupancy of the axial site as well, perhaps, as its position *trans* to PMe$_2$Ph. A similar lengthening of the axial metal–sulphur distance occurs in (1) above and in the analogue of (2), [{Mo(SBu^t)$_2$(NHMe$_2$)}$_2$(μ-S)$_2$].[14]

The W–W distance in (2) is significantly shorter than that observed in (1) [2.736(2) *versus* 3.024(1) Å], thus, as expected, there is considerably more W–W interaction in (2) (a formally d^2–d^2 system) than in (1) (a formally d^0–d^0 system). The d^2–d^2 configuration of (2) allows for the formation of a W=W bond

($\sigma^2\pi^2$), a bonding interaction which is consistent with the diamagnetism of the complex and which has already been proposed for the analogue $[\{Mo(SBu^t)_2(NHMe_2)\}_2(\mu-S)_2]$.[14]

In (1), the electron-withdrawing terminal S and $NNMe_2$ groups reduce availability of electrons for metal–metal interaction. Similarly, the Mo–Mo distances of $[\{Mo(SBu^t)_2(PMe_2Ph)\}_2(\mu-S)_2]$ [2.741(1) Å] and $[\{Mo(SBu^t)_2(NHMe_2)\}_2(\mu-S)_2]$ [2.730(1) Å] are significantly shorter than that observed for the molybdenum analogue of (1), $[S_2MoS_2Mo(NNMe_2)_2(PPh_3)]$ [3.005(2) Å].[13]

Acknowledgements

This research was supported in part by N.I.H. grants. J. R. D. and J. Z. are indebted to N.A.T.O. for award of a travel grant.

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Received 23rd *August* 1982; *Paper* 2/1466