The Crystal Structure of Di-μ-ethanethiolato-μ-sulphido-bis[dichloro-(tetrahydrothiophen)tungsten(IV)(*W–W*)]: A Confacial Bioctahedral Complex with a Tungsten-to-tungsten Bond

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The complex $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$ has been prepared by reaction of $[WCl_4(C_4H_8S)_2]$ with one mole equivalent of $SiMe_3(SEt)$ in CH_2Cl_2 solution. A single-crystal *X*-ray diffraction study shows that the molecule has a confacial bioctahedral structure with a W–W bond length of 2.524(1) Å. The structure has been solved by heavy-atom methods from automated diffractometer data, and refined to *R* 0.025 (*R'* 0.037) for 1 593 reflections. The complex crystallizes in the orthorhombic system, space group *Pnam*, with *a* = 10.592(3), *b* = 12.618(4), *c* = 17.430(6) Å, and *Z* = 4.

In spite of the growing interest in compounds with metal-to-metal bonds,[1] there remain several categories of such compounds with few or no known examples. Cotton and co-workers,[2] recently drew attention to the dearth of examples of compounds with metal-to-metal double bonds, whereas single, triple, and quadruple bonds have proven much easier to synthesize, particularly for molybdenum. Tungsten-to-tungsten triple bonds are relatively common, but the scarcity of quadruple bonds was recently highlighted by the successful synthesis and characterization of a new class of W≡W dimers.[3,4]

We have been exploring possible synthetic routes to tungsten clusters, in which the replacement of Cl^- by RS^- in the co-ordination sphere is followed by reductive elimination of R_2S_2.[5,6] This produces co-ordinatively unsaturated tungsten centres of reduced oxidation state which are likely to dimerize or oligomerize. By starting with complexes of general formula $[WCl_4(SR_2)_2]$ the labile nature of the R_2S group[7] assists in the generation of a co-ordinatively unsaturated ' cluster precursor '.

By reaction of $[WCl_4(SMe_2)_2]$ with two mol equivalents of EtS^-, introduced *via* the reagent $SiMe_3(SEt)$, we were able to synthesize, and carry out a structural determination of, $[\{WCl_2(SMe_2)\}_2(\mu\text{-}SEt)_3]$. This is a mixed oxidation state (W^{III}/W^{IV}) confacial bioctahedral molecule with tungsten-to-tungsten bonding.[8]

On the other hand, 1 : 1 reactions between $[WCl_4(SR'_2)_2]$ and $SiMe_3(SR)$ yield quite different results from the 1 : 2 reactions. The initial reaction produces $[WCl_3(SR)(SR'_2)_2]$ which cannot be isolated, and subsequent degradative reactions yield three products, as described in a preliminary communication[6] of this work: (*i*) a sulphonium salt $[SRR'_2][WCl_6]$ (*ca.* 15% yield), (*ii*) an intractable tarry residue of approximate composition $(WSCl_2)_n$, and (*iii*) a red crystalline solid which we previously formulated as $[(R'_2S)Cl_2W(SR)_2WCl_2(SR'_2)]$ (*ca.* 50% yield).

We have now carried out an *X*-ray crystallographic structural determination on the compound (1), previously described as $[(C_4H_8S)Cl_2W(SEt)_2WCl_2(SC_4H_8)]$. We find that instead of being a dibridged structure involving W^{III}, it is in fact a triply bridged tungsten(IV) compound, with an additional μ-sulphido-ion. It should therefore be formulated as $[(C_4H_8S)Cl_2W(\mu\text{-}SEt)_2(\mu\text{-}S)WCl_2(SC_4H_8)]$.

This compound, therefore, belongs to one of the rarer types of metal–metal bonded structure, as it contains a formal W=W bond. Indeed we can find no other examples of confacial bioctahedral tungsten(IV) complexes in the literature.

In this paper we examine the structure of (1), and compare it with similar structures in the literature. We conclude by postulating a mechanism whereby the intermediate, $[WCl_3(SEt)(SC_4H_8)_2]$, can yield the three products observed.

EXPERIMENTAL

Syntheses.—The compound $[WCl_4(SC_4H_8)_2]$ was prepared as previously described.[7,9] All handling procedures of air- and moisture-sensitive compounds were carried out in an atmosphere of dry deoxygenated nitrogen. Ethylthiotrimethylsilane was prepared by the published method.[10]

Tungsten was analysed in our laboratory by ignition to the oxide, and chloride potentiometrically. Other analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tennessee.

The Reaction between $SiMe_3(SEt)$ *and* $[WCl_4(SC_4H_8)_2]$.—The general reaction employed in this investigation is represented by equations (1) and (2). For the specific

$$[WCl_4L_2] + SiMe_3(SR) \xrightarrow{CH_2Cl_2} [WCl_3(SR)L_2] + SiMe_3Cl \quad (1)$$

$$[WCl_3(SR)L_2] \longrightarrow \text{products} \quad (2)$$

synthesis of compound (1), the following procedure was followed. The compound $[WCl_4(SC_4H_8)_2]$ (*ca.* 2 g) was dissolved in CH_2Cl_2 (35 cm^3) and to this stirred solution was added the exact, calculated one mol equivalent of $SiMe_3(SEt)$ dissolved in CH_2Cl_2. Hydrogen-1 n.m.r. studies showed immediate conversion of $SiMe_3(SEt)$ into $SiMe_3Cl$, and there is also an instantaneous colour change of the solution from orange-red to a darker red. A brown precipitate was observed within 2 h, and after stirring overnight at room temperature the solution was filtered to remove this precipitate. Analytical and various spectroscopic data confirmed that this precipitate was a sulphonium salt of the WCl_6^{2-} anion [equation (3)], as previously published.[6] A

possible mechanism for the formation of this salt is considered in the Discussion section below.

After removal of the sulphonium salt the red-coloured

$$[WCl_4(SC_4H_8)_2] + SiMe_3(SEt) \longrightarrow [C_4H_8SEt]_2[WCl_6] \quad (3)$$

filtrate was diluted to *ca.* 100 cm³ with CH_2Cl_2, and hexane (40—50 cm³) was added to deposit a brown oil. The ill defined composition of this material was $(WSCl_2)_n$ although it contained traces of organic material. It was not further investigated. The remaining solution contained the product of interest, and slow evaporation of solvent yielded compound (1) as a red microcrystalline material, in *ca.* 50% yield. The sample of compound (1) utilized in *X*-ray studies was obtained as large, opaque, dark red crystals by placing the filtrate (left after removal of the sulphonium salt, $[C_4H_8SEt]_2[WCl_6]$, and the oily residue) in a refrigerator for 48 h. These crystals were washed with hexane and dried under vacuum. The spectroscopic and analytical properties of this sample were identical with those of the microcrystalline sample obtained by precipitation with hexane.

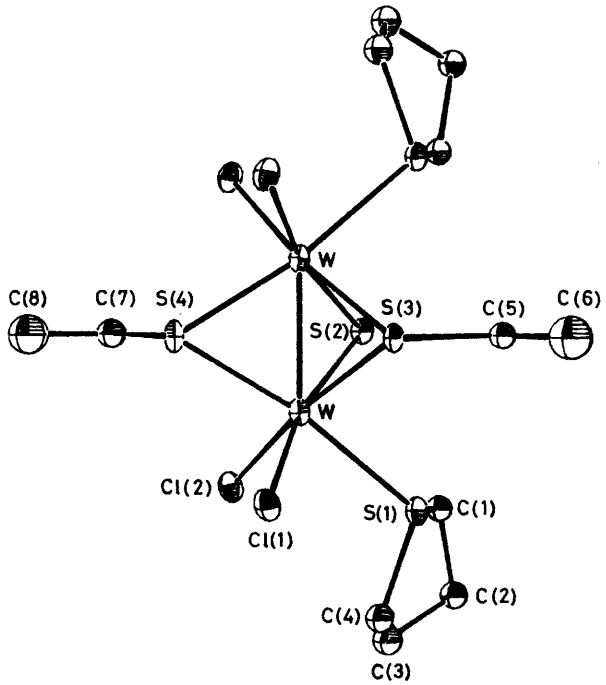
Collection and Reduction of the X-*Ray Data.*—Compound (1) was isolated from CH_2Cl_2 solution as dark red prisms, as described above. The space group was determined to be either *Pnam* or $Pna2_1$ from Weissenberg and precession photographs. Systematic absences were observed for: $0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. A sample of suitable size for data collection (0.30 × 0.12 × 0.16 mm) was mounted on a glass fibre and coated with epoxy-resin to protect it from aerial degradation and the possible loss of tetrahydrothiophen ligand. The intensity data were collected on a Picker FACS-1 diffractometer with Mo-K_α radiation and a graphite monochromator. The data were collected in the θ—2θ scan mode at a rate of 1° min⁻¹, with a scan width $\Delta 2\theta = (1.4 + 0.692 \tan\theta)°$. Background counts were measured for 20 s at either end of the scan. Of the 2 760 unique reflections measured in the range $2 < 2\theta < 55°$, 1 593 had intensities greater than $3\sigma(I)$ where $\sigma(I) = (T + B)^{\frac{1}{2}}$; T is the total peak count and B is the background count normalized to the interval of the scan. Three standard reflections (008, 400, 381) were measured every 50 reflections. No significant loss of intensity was observed. Standard Lorentz and polarization corrections were applied and also absorption corrections, using the program ABSORB [μ(Mo-K_α) = 113.0 cm⁻¹]. This program integrates the path length within the crystal by Gaussian quadrature. 240 Grid points were included in the calculation. The minimum and maximum values of the correction were 2.181 4 and 3.162 7 respectively.

Solution and Refinement of the Structure.—The metal atoms were located from sharpened Patterson functions and the remaining non-hydrogen atoms were located from successive difference-Fourier calculations, based on heavy-atom phasing. The scattering factors were taken from Cromer and Mann,[11] and the anomalous dispersion corrections from ref. 12.

In order to resolve the space group ambiguity, use was made of the second and third moments of the intensities (Foster and Hargreaves [13]). For a model with three sulphurs and two ethyl groups on the mirror plane, the theoretical values of the second and third moments are 2.10 and 6.53 for the acentric case ($Pna2_1$) and 3.15 and 18.93 for the centric case (*Pnam*). The experimental values are 3.23 and 16.08, providing a very strong indication that the true space group is *Pnam*. No significant differences in intensities of Friedel pairs could be detected, although more than 60 pairs of these were recorded. In addition, we solved and refined the structure in both space groups, and found that no significant structural differences occur between the two refinements. We therefore concluded the refinement in *Pnam* and present all our data for this space group.

Crystal Data. $C_{12}H_{26}Cl_4S_5W_2$, $M = 840.2$, Orthorhombic, $a = 10.592(3)$, $b = 12.618(4)$, $c = 17.430(6)$ Å, $U = 2\,329.5$ Å³, $D_m = 2.38$ g cm⁻³ (flotation), $Z = 4$, $D_c = 2.39$ g cm⁻³, $F(000) = 1\,576$, $\lambda = 0.710\,7$ Å, space group *Pnam*.

Refinement of the atomic positions by a full-matrix least-squares procedure was successfully concluded, with anisotropic thermal parameters for the heavy atoms, and isotropic thermal parameters for the carbon atoms. Hydrogen atoms were not included in the model, and no attempt was made to locate them. The refined value of the secondary extinction parameter, g, is $1.8(4) \times 10^{-3}$. A final electron-density difference map revealed no peaks higher than 1.44 e Å⁻³; the two highest of these peaks were located



Structure of $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$ (thermal ellipsoids drawn to enclose 20% probabilities)

ca. 1.5 Å from C(5) and C(7) respectively, but displaced from the mirror plane by *ca.* 0.75 Å. These are an artefact of the isotropic refinement of the C(6) and C(8) atoms, whose electron density would doubtless be smeared out on either side of the mirror plane by the vibration of the ethyl group. Other peaks (*ca.* 0.5 e Å⁻³) occur within 1 Å of the tungsten atoms.

The final R values are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.025$ for 1 593 contributing reflections, and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.037$. The weighting scheme used was $w = [5.0 + \sigma(F) + 0.000\,1\,F^2]^{-1}$, where $\sigma(F)$ was derived from counting statistics. The standard deviation of an observation of unit weight was 1.00, and the average shift-to-error in the final cycle was 0.07. Final positions of the

non-hydrogen atoms are given in Table 1, with atoms labelled according to the Figure. Observed and calculated structure factor amplitudes and thermal parameters are available as Supplementary Publication No. SUP 22926 (13 pp.).* The *X*-RAY '76 programs † were used for all calculations.

TABLE 1

Fractional co-ordinates for the non-hydrogen atoms of $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
W	0.131 39(3)	0.048 24(2)	0.177 60(2)
S(1)	0.241 6(2)	0.172 0(2)	0.081 5(1)
S(2)	0.315 3(3)	0.057 4(2)	0.250
S(3)	0.078 0(3)	0.209 4(2)	0.250
S(4)	0.004 7(3)	−0.075 7(2)	0.250
Cl(1)	−0.048 4(2)	0.089 3(2)	0.102 3(2)
Cl(2)	0.200 3(2)	−0.092 4(2)	0.097 5(2)
C(1)	0.409 1(9)	0.134 8(8)	0.072 1(5)
C(2)	0.432(1)	0.146 5(8)	−0.015 9(6)
C(3)	0.318(1)	0.094 4(9)	−0.053 4(6)
C(4)	0.196(1)	0.137 3(8)	−0.018 6(6)
C(5)	0.211(1)	0.306(1)	0.250
C(6)	0.175(2)	0.412(2)	0.250
C(7)	0.069(1)	−0.210(1)	0.250
C(8)	−0.026(2)	−0.287(2)	0.250

RESULTS AND DISCUSSION

The Structure of $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$.—The molecular structure of (1) as shown in the Figure consists of a confacial bioctahedral framework, in which the bridging ligands are a μ-sulphido and two μ-ethanethiolato-groups. The point group symmetry is C_s with the only plane of symmetry lying normal to the W–W bond, and containing the bridging atoms. The W–W bond length (Table 2) is 2.524(1) Å, which we interpret as being consistent with a formal double bond between the two metal atoms, as predicted for a tungsten(IV) (d^2) dimer. The structure of the tungsten(IV) complex $[W_2S_2(S_2CNEt_2)_4]$ reported by Cotton and co-workers [2] is an important benchmark for such systems. It contains a $\overline{WSWS}$ entity in which the W–W bond length is 2.530(2) Å, and is thus very similar to that

TABLE 2

Bond distances (Å) and estimated standard deviations in parentheses

W–W	2.524(1)	S(1)–C(1)	1.84(1)
W–Cl(1)	2.370(2)	S(1)–C(4)	1.86(1)
W–Cl(2)	2.373(3)	C(1)–C(2)	1.56(1)
W–S(1)	2.571(2)	C(2)–C(3)	1.52(1)
W–S(2)	2.324(3)	C(3)–C(4)	1.53(1)
W–S(3)	2.460(3)	C(5)–C(6)	1.39(3)
W–S(4)	2.416(3)	C(7)–C(8)	1.40(3)
S(3)–C(5)	1.86(1)		
S(4)–C(7)	1.83(2)		

observed in (1). It differs from (1), however, in possessing only two bridging groups instead of three.

An additional structural feature required by strong metal–metal interaction in confacial bioctahedral structures is found in the acute bond angles M–X–M subtended at the bridging atom X (Table 3). Here we observe a W–S(2)–W angle of 65.79(8)°, which compares with the angle of 65.5(1)° reported for $[W_2S_2(S_2CNEt_2)_4]$. The angles at S(3) and S(4) are 61.74(7)° and 62.97(8)° respectively. If there were no metal–metal attraction the angles required for an ideal bioctahedral structure would be 70.53°. Attraction between the metals reduces these angles while repulsive forces would expand them.[14] A corollary of the acute M–X–M angles in M–(μ-X)$_3$–M systems is an expansion of X–M–X angles from the ideal 90°. This we observe for S(2)–W–S(4) [102.36(9)°], and S(3)–W–S(4) [98.01(8)°], but associated with an unusually close contact between S(2) · · · S(3) [3.162(4) Å], the S(2)–W–S(3) angle is only 82.71(9)°.

TABLE 3

Bond angles (°) in $[(C_4H_8S)Cl_2W(\mu\text{-}S)(\mu\text{-}SEt)_2WCl_2(SC_4H_8)]$

(*a*) W–bridge–W angles			
W–S(2)–W	65.79(8)	W–S(4)–W	62.97(8)
W–S(3)–W	61.74(7)		
(*b*) Bridge–W–bridge angles			
S(2)–W–S(3)	82.71(9)	S(3)–W–S(4)	98.01(8)
S(2)–W–S(4)	102.36(9)		
(*c*) Terminal–W–terminal angles			
S(1)–W–Cl(1)	82.59(8)	Cl(1)–W–Cl(2)	94.88(9)
S(1)–W–Cl(2)	86.05(8)		
(*d*) Bridge–W–terminal angles			
S(2)–W–Cl(1)	164.4(1)	S(3)–W–S(1)	86.36(7)
S(2)–W–Cl(2)	95.66(9)	S(4)–W–Cl(1)	89.10(9)
S(2)–W–S(1)	86.75(8)	S(4)–W–Cl(2)	89.68(9)
S(3)–W–Cl(1)	85.33(8)	S(4)–W–S(1)	170.29(7)
S(3)–W–Cl(2)	172.32(8)		

In summary, the structural features necessary to ascribe strong metal–metal bonding are observed. This is also substantiated by the diamagnetic nature of (1).

In searching the literature for compounds comparable with (1), it is surprising to find no examples of tungsten(IV) dimers with a confacial bioctahedral structure. The tungsten(III) species $K_3[W_2Cl_9]$ [15] has a W–W bond length of 2.41 Å and two mixed oxidation state W^{III}/W^{IV} complexes with a confacial bioctahedral structure have been reported.[8,16] The W–W distance in the $W_2Br_9^{2-}$ ion is 2.60 Å,[16] whereas that in $[(Me_2S)Cl_2W(SEt)_3WCl_2(SMe_2)]$ is 2.505(1) Å.[8] The compounds $[M_2Br_6(SC_4H_8)_3]$ (M = Nb or Ta) were recently reported by McCarley and co-workers.[17] These d^2 complexes are isoelectronic with W^{IV}, are confacial bioctahedral, and also have a formal metal–metal double bond.

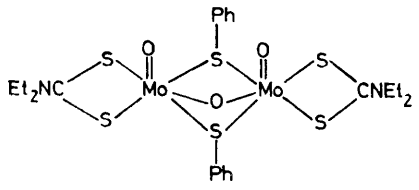
The most extensive and best characterized examples of Group 6 metal compounds with confacial bioctahedral structures involve oxomolybdenum(V).[18,19] The most relevant structure to compare with compound (1) is that of the compound (2).[20] The terminal oxygen causes a significant weakening and lengthening of the Mo–S_{bridge} bond *trans* to it, rendering the –SPh groups inequivalent. The converse effect is seen in the structure of (1) in which the S(4) atom is *trans* to the weakly bonded thioether molecule. Thus the W–S(4) bond is shorter [2.416(3) Å] than the W–S(3) bond [2.460(3) Å]. The W–S(2)–W angle is the largest of those subtended at the bridging sulphurs, and this is associated with shortest W–S_{bridge} bonds. The cause of the short S(2) · · · S(3) contact is

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† Technical Report TR-446, ed. J. M. Stewart Computer Science Center, University of Maryland.

not obvious, but unusually short contacts between μ-SR moieties have been previously observed.[8,21]

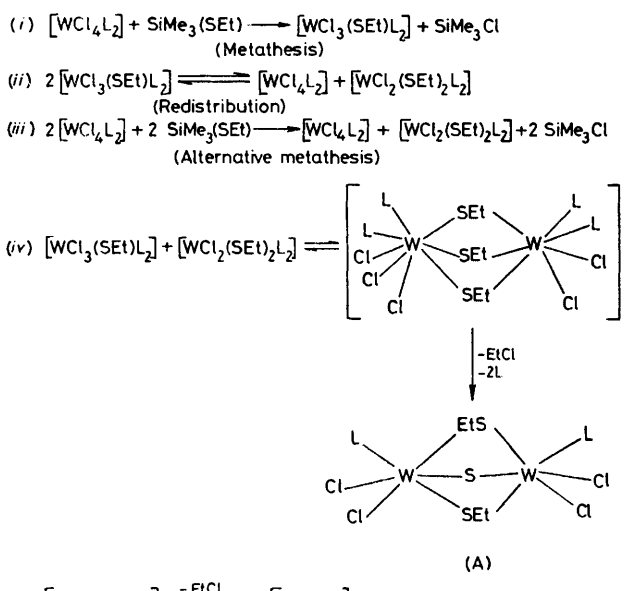
The configurations of S(3) and S(4) both have their ethyl group in an equatorial position. The short tungsten-to-tungsten bond presumably makes any isomers involving axial ethyl groups less stable. The



(2)

^{1}H n.m.r. spectra of this and some related compounds will be described in a later paper, since some interesting fluxional behaviour, similar to that reported by Knox and co-workers,[21] has been observed.

Possible Mechanism of Formation of Products.—One of the main objectives of our work has been to demonstrate how the reactions of co-ordinated organosulphur species can lead to novel inorganic syntheses, and where appropriate, to examine the possible implications of these reactions to industrial and biological chemistry. Thus although the foregoing discussion of compound (1) is the focus of this paper, we believe it is important to comment on how it arises as the major product of the 1 : 1 reactions between $SiMe_3(SEt)$ and $[WCl_4L_2]$ (L = SC_4H_8).



(A)

Scheme Possible reactions ensuing from $SiMe_3(SEt)$ + $[WCl_4L_2]$ (L = SC_4H_8)

In the Scheme is presented a sequence of possible reactions ensuing from the addition of one molar equivalent of $SiMe_3(SEt)$ to $[WCl_4L_2]$.

The initial metathesis, in which W–Cl is converted to W–SR, has been shown to occur,[22] and by following the present reaction using ^{1}H n.m.r. spectroscopy, $SiMe_3Cl$ has been shown to be the exclusive silane product, in 100% yield. Although on average one mole of $SiMe_3(SEt)$ reacts with one mole of $[WCl_4L_2]$ [reaction (*i*)], the alternative metathesis (*iii*) cannot be excluded. Redistribution between two molecules of $[WCl_3(SEt)L_2]$ would have the same effect, and such reactions have been shown to occur for mercury mercaptide complexes.[23] The overall product distribution requires both $[WCl_4L_2]$ and $[WCl_2(SEt)_2L_2]$, in addition to $[WCl_3(SEt)L_2]$. Thus $[WCl_4L_2]$ will lead to the sulphonium salt (B) [reaction (*vii*)], while product (A) could arise from either reaction (*iv*) or reaction (*v*) + (*vi*). Of these two alternatives the work of Fowles *et al.*[24] would favour (*iv*) since the sterically crowded intermediate would be expected to lose EtCl readily. Presumably a number of other side reactions must occur to give the tarry residue as a third product.

The conclusion which can be drawn is that association of tungsten thiolates *via* μ-SEt groups, followed by elimination of EtCl, is a dominant reaction.

The products of the present reaction were unexpected and demonstrate the need for further study of the reactions of organosulphur ligands at heavy metal centres.

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