$(Ph_2PCH_2PPh_2)_2$[26] and $Ru_3(CO)_{10}(Ph_2PCH_2PPh_2)$[27] as well. At the other extreme, long-chain diphosphines $R_2P(CH_2)_nPR_2$ ($n > 6$) with bulky substituents on phosphorus form binuclear, macrocyclic metal complexes with trans phosphine ligands on each metal and very long separations between the metals.[28] In these molecules the long span between the metals precludes metal–metal bonding. For intermediate-length diphosphines not only is the stability of bridge vs. chelate structure difficult to estimate, but there is little well-established structural information available. For metal–metal-bonded systems complexes of the type $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$(diphosphine), where diphosphine may be $Ph_2P(CH_2)_nPPh_2$ ($n = 2$–4) or *cis*-$Ph_2PCH{=}CHPPh_2$, diphosphine-bridged structures exist.[29] Bis(diphenylphosphino)ethane acts as a bridging ligand in $Re_2(Ph_2PCH_2CH_2PPh_2)_2Cl_4$[30] and may behave similarly in $Mo_2(Ph_2PCH_2CH_2PPh_2)_2Cl_4$.[31] For systems which do not contain metal–metal bonds, diphosphine-bridged compounds of d^8 metal ions are known for the two diphosphines Ph_2P-$(CH_2)_nPPh_2$ ($n = 3$, 4).[32,33]

For the triphosphine ligand, adoption of the chelating and bridging structure of Figure 5 is not surprising. Meek and co-workers have noted that, for this triphosphine to coordinate all three phosphorus atoms to a single metal atom, the constraints of the bridging methylene groups would limit the trans P–M–P angle (involving the terminal phosphino groups) to no greater than 166°.[34] In the case of the bridging structure this constraint is eliminated. Since there is, presumably, no great barrier to rotation about the Pd–Pd bond, the dihedral angle between the P–Pd–Pd–P group is free to adopt a strain-free orientation. Inspection of space-filling Corey–Pauling–Koltum molecular models indicates that structure D is strain free. A similar geometry for this triphosphine ligand has been proposed for the rhodium polymer [Rh_4(triphosphine)$_3Cl_4]_n$.[34]

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Synthesis and Structure of Tris[μ-(ethanethiolato)]-bis[dichloro(dimethyl sulfide)tungsten(III,IV)]. A Mixed Oxidation State Dimeric Tungsten Compound

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The title compound was prepared by the reaction of $WCl_4(Me_2S)_2$ with 2 mole equiv of Me_3SiSEt in CH_2Cl_2 solution. A single-crystal X-ray diffraction study has shown that $(Me_2S)Cl_2W(SEt)_3WCl_2(SMe_2)$ possesses a confacial bioctahedral molecular structure with three symmetrical bridging thiolate ligands. The W–W bond length is 2.505 (1) Å, and an unusually short nonbonded contact (3.054 (6) Å) between two of the bridging sulfur atoms is observed. An ESR signal ($g = 2.00$) was observed for the solid compound at −183 °C. Crystal data are $a = 15.678$ (5) Å, $b = 15.122$ (6) Å, $c = 15.751$ (5) Å, $\beta = 140.69$ (1)°, $P2_1/c$, and $Z = 4$.

Introduction

The synthesis of polynuclear compounds of tungsten and molybdenum has attracted considerable attention.[1–4] Although there are now several well-demonstrated methods for synthesizing compounds with metal–metal bonds,[5] the synthesis and characterization of dimeric μ-thiolato tungsten clusters have not been previously reported. We have been interested in possible routes to such tungsten clusters involving the stepwise introduction of thiolate groups in lieu of chloride ligands. The subsequent reductive elimination of R_2S_2 which

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is likely to occur[6] would leave coordinatively unsaturated metal centers which would then be likely to dimerize or to oligomerize. The method of introducing RS^- which we have found to be effective for these air- and moisture-sensitive tungsten chloride starting materials is metathesis with an (alkylthio)trimethylsilane:[6]

$$>\!\!\overset{|}{\underset{|}{W}}\!\!<^{Cl} + Me_3SiSR \longrightarrow >\!\!\overset{|}{\underset{|}{W}}\!\!<^{SR} + Me_3SiCl \quad (1)$$
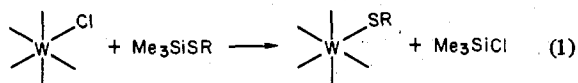
In this paper we report the crystal and molecular structure of $W_2Cl_4(SEt)_3(Me_2S)_2$ which was synthesized by reaction of $WCl_4(Me_2S)_2$ with 2 mol of Me_3SiSEt, in dichloromethane solution. The labile nature of the Me_2S ligands in WCl_4-$(Me_2S)_2$[7] made this an attractive starting material for reactions aimed at the synthesis of polynuclear complexes. The product has been shown to be binuclear, $(Me_2S)Cl_2W(SEt)_3WCl_2$-(SMe_2) with a relatively short metal–metal bond. The most interesting feature is perhaps the mixed oxidation states of the metals (III, IV).

Experimental Section

Materials. Tungsten carbonyl was purchased from Alfa Inorganics, as was tungsten hexachloride. The latter compound was twice resublimed before use. Tungsten tetrachloride was synthesized by the method of McCarley and Schaefer King.[8] Dimethyl sulfide and dichloromethane were obtained from Aldrich Chemicals and were dried over CaH_2 and P_4O_{10}, respectively, distilled, and degassed before use. Chlorotrimethylsilane was purchased from Aldrich Chemicals, as was ethanethiol. (Ethylthio)trimethylsilane was synthesized via the lead salt of EtSH by the published procedure.[9] The adduct $WCl_4(Me_2S)_2$ was prepared as previously described.[7,8] All handling procedures of this compound and derived products were carried out in an atmosphere of purified, dry nitrogen.

Synthesis. $W_2Cl_4(SEt)_3(Me_2S)_2$ was prepared by the following procedure. $WCl_4(Me_2S)_2$ (ca. 2 g) was dissolved in CH_2Cl_2 (ca. 30 mL), and to this stirred solution was added the calculated amount of a solution of (ethylthio)trimethylsilane in CH_2Cl_2 (4 g of Me_3SiSEt in 25 mL of CH_2Cl_2). An exact ratio of 1:2 $WCl_4(Me_2S)_2$:Me_3SiSEt was used. An instantaneous color change occurred, from light to dark red. Over a period of 12-h stirring at room temperature, the solution became brown-red. Addition of hexane (30 mL) caused separation of some oily material, but after the filtered supernatant solution had stood for 3 days at –20 °C, red-brown crystals of the product formed (yield 26%, on the basis of $WCl_4(Me_2S)_2$). Although the reaction has been repeated several times and conditions of crystallization have been varied, only on one occasion were we able to obtain crystals suitable for X-ray study. Usually a microcrystalline product was obtained with spectroscopic properties identical with those of the X-ray sample. Analyses were performed on the X-ray sample batch of crystals. Anal. Calcd for $W_2Cl_4(SEt)_3(Me_2S)_2$: C, 14.68; H, 3.43; Cl, 17.35; W, 44.98. Found: C, 14.48; H, 3.56; Cl, 17.7; W, 45.3.

Collection and Reduction of X-ray Data

The compound $W_2Cl_4(SEt)_3(Me_2S)_2$ was isolated from CH_2Cl_2 reaction solutions as red-brown needles as described above. A sample of suitable size for analysis ($0.20 \times 0.18 \times 0.18$ mm) was obtained by cutting a larger crystal transverse to the needle axis. It was coated in epoxy resin to prevent aerial degradation and/or loss of Me_2S during data collection.

Because the crystal was mounted about the ac diagonal, the only symmetry element recognized in Weissenberg and precession photographs was the screw axis. As a consequence the data were collected, and the structure was solved in space group $P2_1$ ($a = 29.598$ (9) Å, $b = 10.572$ (3) Å, $c = 15.122$ (5) Å, $\beta = 90.40$ (1)°). Examination
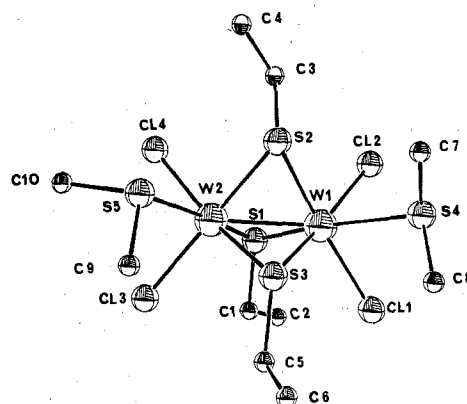
Figure 1. ORTEP view of the $W_2Cl_4(SEt)_3(Me_2S)_2$ molecule, showing the numbering scheme. Arbitrary-sized spheroids have been used for the sake of clarity.

of the structure showed that the space group was $P2_1/c$. The new unit cell dimensions were refined from the angular parameters of 12 high-angle reflections. The data were reindexed, and the refinement was carried out in the correct space group. All the discussion that follows refers to space group $P2_1/c$.

The intensity data were collected on a Picker FACS-1 diffractometer with Mo Kα radiation and a graphite monochromator. The data were collected in the θ–2θ scan mode at a rate of 1°/min, with a scan width $\Delta 2\theta = (1.5 + 0.692 \tan \theta)°$. Background counts were measured for 20 s at either end of the scan. Of the 4380 unique reflections measured in the range $2\theta \leq 50.2°$, 2756 had intensities greater than $3\sigma(I)$, where $\sigma(I) = [T + B + (0.02I)^2]^{1/2}$, T is the total count, and B is the total background count normalized to the interval of the scan. Three standard reflections ($5,0,4$; $12,0,\overline{12}$; $1,\overline{12},1$) were measured every 50 reflections. The data were normalized by a scaling procedure to compensate for a small systematic decrease in intensity ($\sim$10% overall). Standard Lorentz and polarization corrections and also an analytical absorption correction ($\mu = 111.2$ cm^{-1}) were applied. The minimum and maximum values of the correction were 4.618 and 7.224.

Solution and Refinement of the Structure

The metal atoms were located from sharpened Patterson functions, and the remaining atoms were located from successive difference Fourier calculations, on the basis of heavy-atom phasing. The scattering factors and anomalous dispersion terms were taken from ref 10.

Crystal data for $W_2Cl_4S_5C_{10}H_{27}$: $M_r = 817.1$; a 15.678 (5), $b = 15.122$ (6), $c = 15.751$ (5) Å; $\beta = 140.69$ (1)°; $V = 2365.7$ Å^3; $D_m = 2.20$ (5) g cm^{-3} (flotation), $D_c = 2.29$ g cm^{-3} ($Z = 4$); $F_{000} = 1508$; λ(Mo Kα) = 0.7107 Å; space group $P2_1/c$, monoclinic.

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. Reflections with $I < 3\sigma(I)$ were included in the refinement if $F_c > F_o$. The refined value of the secondary extinction parameter, g, is 8 (4) × 10^{-5}. A final electron density difference map revealed no peaks higher than 0.47 e Å^{-3}, and these were located within 1 Å of the tungsten atoms. The final R values are $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.048$, for 3561 contributing reflections, and $R' = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.063$. The weighting scheme used was $w = [\sigma^2(F) + 0.0007F^2]^{-1}$, where $\sigma(F)$ was derived from counting statistics. The standard deviation of an observation of unit weight was 0.868, and the average shift to error ratio for the final cycle was 0.006. The final positions of the nonhydrogen atoms are given in Table I, with the atoms labeled according to Figure 1. A listing of observed and calculated structure factor amplitudes with weights is available as supplementary material.

Computer programs used include the XRAY-76 programs (J. M. Stewart, Ed.) and several programs from the Los Alamos Scientific Laboratory System of Programs (A. C. Larson).

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Table I. Positional and Thermal Parameters ($\times 10^2$) and Their Estimated Standard Deviations for $W_2Cl_4(SEt)_3(Me_2S)_2$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	0.86341 (5)	0.22118 (4)	0.11589 (5)	3.38 (3)	5.63 (3)	4.27 (3)	0.00 (2)	2.84 (3)	0.28 (3)
W(2)	0.61684 (5)	0.22089 (4)	−0.04074 (5)	3.35 (3)	6.25 (4)	3.92 (3)	−0.40 (2)	2.78 (3)	−0.28 (2)
S(1)	0.6994 (3)	0.1776 (2)	−0.1143 (3)	4.7 (2)	6.3 (2)	4.2 (2)	0.6 (2)	3.5 (2)	0.4 (2)
S(2)	0.7583 (3)	0.3488 (2)	0.1024 (3)	3.8 (2)	5.4 (2)	4.4 (2)	0.0 (2)	3.0 (2)	−0.1 (2)
S(3)	0.7794 (3)	0.1585 (2)	0.1823 (3)	5.2 (2)	5.8 (2)	4.6 (2)	−0.5 (2)	3.7 (2)	0.5 (2)
S(4)	1.0865 (4)	0.2586 (3)	0.3692 (4)	4.0 (2)	8.4 (3)	5.1 (2)	−1.1 (2)	2.7 (2)	−0.2 (2)
S(5)	0.4895 (4)	0.2664 (3)	−0.0004 (5)	6.6 (3)	9.1 (3)	9.0 (3)	−2.4 (2)	6.8 (3)	−3.0 (2)
Cl(1)	0.9958 (4)	0.0930 (3)	0.1844 (4)	5.6 (2)	7.4 (3)	6.6 (2)	2.1 (2)	4.1 (2)	0.6 (2)
Cl(2)	0.9628 (4)	0.3154 (3)	0.0898 (4)	5.5 (2)	9.1 (3)	8.1 (3)	−0.5 (2)	5.6 (2)	1.1 (2)
Cl(3)	0.4774 (3)	0.0927 (3)	−0.1472 (4)	5.9 (2)	8.0 (3)	6.9 (2)	−2.9 (2)	5.0 (2)	−2.9 (2)
Cl(4)	0.4582 (3)	0.3165 (3)	−0.2299 (3)	4.1 (2)	9.1 (3)	4.4 (2)	1.5 (2)	2.9 (2)	0.9 (2)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
C(1)	0.696 (1)	0.059 (1)	−0.134 (1)	5.6 (3)	C(6)	0.837 (2)	0.007 (1)	0.315 (2)	9.4 (6)
C(2)	0.758 (2)	0.036 (1)	−0.170 (2)	7.9 (5)	C(7)	1.069 (3)	0.353 (2)	0.426 (2)	13.6 (9)
C(3)	0.731 (1)	0.444 (1)	0.008 (1)	6.9 (4)	C(8)	1.121 (2)	0.173 (1)	0.475 (2)	7.8 (5)
C(4)	0.654 (2)	0.516 (1)	−0.006 (2)	8.0 (5)	C(9)	0.498 (2)	0.174 (1)	0.080 (2)	9.0 (5)
C(5)	0.775 (2)	0.035 (1)	0.186 (2)	7.7 (5)	C(10)	0.311 (2)	0.269 (1)	−0.165 (2)	9.0 (5)

Table II. Bond Distances (A) with Estimated Standard Deviations in Parentheses

W(1)–W(2)	2.505 (1)	W(2)–Cl(3)	2.383 (4)
W(1)–Cl(1)	2.401 (5)	W(2)–Cl(4)	2.385 (4)
W(1)–Cl(2)	2.369 (7)	W(2)–S(1)	2.401 (7)
W(1)–S(1)	2.401 (4)	W(2)–S(2)	2.450 (3)
W(1)–S(2)	2.437 (5)	W(2)–S(3)	2.423 (4)
W(1)–S(3)	2.421 (7)	W(2)–S(5)	2.613 (9)
W(1)–S(4)	2.623 (3)	S(5)–C(9)	1.82 (3)
S(4)–C(7)	1.81 (4)	S(5)–C(10)	1.83 (2)
S(4)–C(8)	1.83 (3)	C(1)–C(2)	1.49 (4)
S(1)–C(1)	1.82 (2)	C(3)–C(4)	1.50 (4)
S(2)–C(3)	1.87 (2)	C(5)–C(6)	1.47 (4)
S(3)–C(5)	1.87 (2)		

Table III. Bond Angles (Deg)

W–Bridge–W Angles

W(1)–S(1)–W(2)	62.9 (2)	W(1)–S(3)–W(2)	62.3 (1)
W(1)–S(2)–W(2)	61.7 (1)		

Bridge–W–Bridge Angles

S(1)–W(1)–S(2)	102.9 (1)	S(1)–W(2)–S(3)	103.8 (2)
S(1)–W(2)–S(2)	102.5 (2)	S(2)–W(1)–S(3)	77.9 (2)
S(1)–W(1)–S(3)	103.9 (2)	S(2)–W(2)–S(3)	77.6 (1)

Bridge–W–Terminal Angles

S(1)–W(1)–S(4)	165.0 (1)	S(1)–W(2)–S(5)	171.0 (1)
S(2)–W(1)–S(4)	88.7 (1)	S(2)–W(2)–S(5)	83.5 (2)
S(3)–W(1)–S(4)	87.6 (2)	S(3)–W(2)–S(5)	83.9 (2)
S(1)–W(1)–Cl(1)	90.0 (2)	S(1)–W(2)–Cl(3)	88.9 (2)
S(2)–W(1)–Cl(1)	165.8 (2)	S(2)–W(2)–Cl(3)	167.0 (2)
S(3)–W(1)–Cl(1)	93.4 (2)	S(3)–W(2)–Cl(3)	93.8 (1)
S(1)–W(1)–Cl(2)	89.0 (2)	S(1)–W(2)–Cl(4)	89.6 (2)
S(2)–W(1)–Cl(2)	90.0 (2)	S(2)–W(2)–Cl(4)	89.9 (1)
S(3)–W(1)–Cl(2)	163.9 (2)	S(3)–W(2)–Cl(4)	163.3 (2)

Terminal–W–Terminal Angles

Cl(1)–W(1)–Cl(2)	96.2 (2)	Cl(3)–W(2)–Cl(4)	96.4 (1)
Cl(1)–W(1)–S(4)	79.5 (2)	Cl(3)–W(2)–S(5)	85.9 (2)
Cl(2)–W(1)–S(4)	81.5 (2)	Cl(4)–W(2)–S(5)	83.6 (2)

Table IV. Nonbonded Distances (A)

S(1)···S(2)	3.785 (7)	S(3)···S(4)	3.494 (7)
S(1)···S(3)	3.796 (9)	S(5)···Cl(3)	3.407 (9)
S(2)···S(3)	3.054 (6)	S(5)···Cl(4)	3.34 (1)
S(4)···Cl(1)	3.218 (7)	Cl(3)···Cl(4)	3.555 (7)
S(4)···Cl(2)	3.264 (9)	S(1)···Cl(3)	3.351 (9)
Cl(1)···Cl(2)	3.551 (7)	S(1)···Cl(4)	3.373 (7)
S(1)···Cl(1)	3.397 (4)	S(2)···Cl(4)	3.415 (4)
S(1)···Cl(2)	3.345 (5)	S(2)···S(5)	3.372 (9)
S(2)···Cl(2)	3.40 (1)	S(3)···Cl(3)	3.510 (4)
S(2)···S(4)	3.541 (5)	S(3)···S(5)	3.371 (7)
S(3)···Cl(1)	3.51 (1)		

Table V. Atom Displacements from Molecular Planes

plane	atoms in plane	σ(plane)	dist of atoms from plane, Å
1	S(1), S(2), S(3)	0.000	1.248 (W(1)), 1.257 (W(2))
2	Cl(1), Cl(2), S(4)	0.000	1.493 (W(1))
3	Cl(3), Cl(4), S(5)	0.000	1.434 (W(2))
4	S(4), W(1), S(1), W(2), S(5)	0.0113	−1.736 (Cl(1)), 1.813 (Cl(2)), −1.773 (Cl(3)), 1.781 (Cl(4))

Results and Discussion

The molecular structure (Figure 1) of (Me$_2$S)Cl$_2$W-(SEt)$_3$WCl$_2$(Me$_2$S) is confacial bioctahedral, with a relatively short tungsten–tungsten distance (2.505 (1) Å). The shared trigonal face exhibits the phenomenon previously noted by McCarley and co-workers,[11] in that two of the sulfur atoms are much closer together than van der Waals contacts (Table IV). The separation of S(2) and S(3) is 3.054 (6) Å, as opposed to the ~3.8 Å which separates S(1) and S(2), and S(1) and S(3). The S(1) atom is trans to the thioethers, whereas S(2) and S(3) are each trans to a terminal chlorine. It is notable that the W–S(1) bond lengths are shorter than those between W and S(2) and W and S(3). The bridging sulfur atoms are all within 3σ values of being equidistant between the two tungstens (Table II), although this is not crystallographically required.

The criteria for tungsten–tungsten bonding as detailed by Cotton and co-workers[12] are met. First, as shown in Table V, the tungsten atoms are significantly closer to the S(1)–S(2)–S(3) plane than to the terminal planes, as defined by Cotton and Ucko.[12] While this is a useful guideline, it cannot be used as the exclusive criterion for this molecule, since strict D_{3h} symmetry is not present. Second, the W–S–W angles subtended at the μ-S atoms (Table III) are more acute (61.7–62.9°) than the 70.53° required for an ideal bioctahedron and are typical of structures in which strong metal–metal attraction exists. This is complemented by the obtuse angles S(1)–W–S(2) and S(1)–W–S(3). The anomalous angles are those involving S(2)–W–S(3), which are much lower than the expected value of 90° for the pure bioctahedron. This is of course a corollary of the short S(2)···S(3) "nonbonded" distance, discussed below. The actual value of the W–W bond length, 2.505 (1) Å, is intermediate between the 2.41 Å found in W$_2$Cl$_9^{3-}$[13] and the 2.60 Å in W$_2$Br$_9^{2-}$.[14] The present compound is isoelectronic with W$_2$Br$_9^{2-}$ and should therefore have five electrons available for metal–metal bonding for which

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a formal metal–metal bond order of 2.5 would be expected. The longer bond in $W_2Br_9{}^{2-}$ may be compared with the situation in $Mo_2Br_9{}^{3-}$ and $Mo_2Cl_9{}^{3-}$ where the Mo–Mo distance in the chloro complex (2.66 Å) is shorter than that in the bromo complex (2.82 Å).[15] We conclude that the W–W distance in $(Me_2S)Cl_2W(SEt)_3WCl_2(Me_2S)$ is certainly within the range that might have been predicted for this species.

The cause for the short $S(2)\cdots S(3)$ contact is a matter of some interest, since no other abnormally short contacts occur, which might affect these atoms. McCarley and co-workers[11] observed a similar feature in the complexes $(C_4H_8S)Br_2MBr_2(C_4H_8S)MBr_2(C_4H_8S)$ (M = Nb, Ta). These compounds (II) are compared with $(Me_2S)Cl_2W(SEt)_3WCl_2(Me_2S)$ (I):

I

II
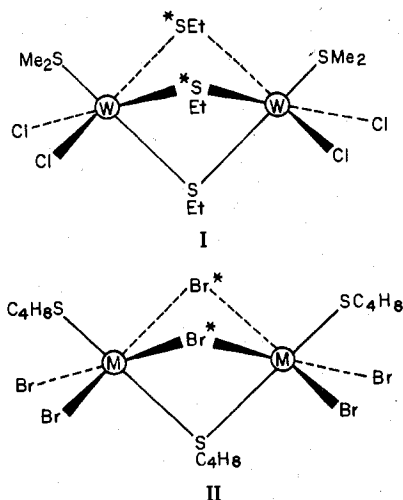
Both molecules exhibit contacts between the bridging atoms marked with an asterisk, which are much shorter than van der Waals contacts. The approximate symmetry of I and II, considering only metals and ligand atoms, is C_{2v}. The compression of the Br* atoms in II was ascribed by McCarley to the direct stereochemical activity of electrons in a b_1 π orbital. This orbital would fill the void between the S and Br* atoms, while the other π orbital, of a_1 symmetry, which would have most density between the Br* atoms, would be vacant.

The electronic structure of I should be very similar to that of II, but one additional electron would have to be contained in the a_1 π-bonding orbital. It might have been anticipated that the compression of the $S^*\cdots S^*$ distance would be small, but it is, under the circumstances, unexpectedly large.

Although we have considered the possibility of a bond between S(2) and S(3), the 3.05-Å separation is at least 0.7 Å too long to entertain this idea seriously. In a recently reported structure of a dialkyl disulfide complex the S–S bond length is 2.111 (13) Å.[16]

It seems likely to us that in both cases, I and II, the distortion from equal separations of the bridging atoms is mainly a function of the lowering in symmetry from D_{3h} (for a pure bioctahedral structure) to the approximate C_{2v} symmetry which is observed. This is caused by the presence of the terminal thioether ligands in both I and II and the μ-SC_4H_8 ligand in II. Thus with loss of the C_3 axial symmetry (passing through the metal–metal vector) there is no constraint on the shared face to exhibit threefold symmetry. This point was discussed by Cotton and Ucko.[12] In another context, desymmetrization arguments of this kind have been presented by Mislow and co-workers in discussing deviations from idealized Newman projections for strained organic molecules.[17] The distortions of the metal–ligand bond angles in I and II can be related to C_{2v} symmetry, in which the C_2 axis passes through the unique bridging atom and is normal to the metal–metal vector. Conforming with this interpretation are the $\sim96°$ angles, Cl(1)–W(1)–Cl(2) and Cl(3)–W(2)–Cl(4), which are larger than expected for a pure bioctahedron. The unique nature of the bridging S(1) atom is further illustrated by its relatively short bonds to both tungsten atoms, and to C(1). Structure I, however, possesses some structural features not consistent with this interpretation. In particular there are crystallographically significant differences between the Cl–W distances. The different orientations of the Me_2S ligands on W(1) and W(2) would be expected to produce different steric interactions, as well as different electrostatic interactions involving the lone pair on S. The orientation of the C_2H_5 groups is also related to the location of CH_3 groups from the terminal Me_2S ligands. Nevertheless the syn configuration of the C_2H_5 groups on S(2) and S(3) is consistent with the approximate C_{2v} symmetry of the molecule. To return to comparisons with other, similar structures, we note that the $W_2Br_9{}^{2-}$ ion reported by McCarley and co-workers[14] retains approximate threefold symmetry, in spite of being isoelectronic with I, since the ligand pattern has not removed D_{3h} symmetry. In this case, however, an angular distortion occurs, ascribed, by the authors, to a Jahn–Teller Effect.

Compound I would be expected to exhibit a doublet ground state and therefore an EPR signal. An EPR experiment[18] on a powdered, crystalline sample at liquid nitrogen temperature showed an isotropic resonance, $g = 2.00$.

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(18) We thank Dr. V. M. Malhotra, Department of Physics, University of Calgary, for making this measurement at Q-band frequency.