the present one. Thus, we have the Mo_3O_{13} unit in $Zn_2Mo_3O_8$, for which the Mo–Mo distance is 2.524 Å[11] and the structurally similar $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion[12] where the distance is 2.486 Å. In these Mo^{IV} compounds there are equilateral triangles of molybdenum atoms, and it is reasonable to believe that each molybdenum atom forms single bonds to its neighbors, but in any case there are not enough electrons available to form bonds of any greater order than 1. It can certainly be argued that the different arrangement of bridging oxygen atoms in the trinuclear species, particularly the presence of one oxygen atom that is symmetrically bound to all three metal atoms, causes a close approach of the metal atoms to one another. However, a consideration of these compounds drives home the point that no conclusion can be drawn about the bond order simply from the distance.

We are, however, inclined to believe that there is actually a direct double bond. The concept of only one Mo–Mo single bond with the remaining two electrons coupled through the bridging system is disfavored by the fact that the configurations at the bridging oxygen atoms are distinctly pyramidal, whereas good spin coupling would presumably be possible only with a planar configuration. The nature of such a double bond is dependent upon the structural properties of this molecule. It is instructive to analyze this aspect of the problem by contrasting the $Mo_2(O\text{-}i\text{-}Pr)_8$ molecule with the $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ molecule, since there is a trigonal-bipyramidal arrangement of ligands about the metal atoms in both compounds.

A trigonal-bipyramidal field splits the metal d orbitals into three sets $e'(d_{x^2-y^2},d_{xy})$, $e''(d_{xz},d_{yz})$, and $a'(d_{z^2})$ with the d_{xz}, d_{yz} degenerate pair lying lowest in energy. In the nitrosyl, each Mo atom may be assumed, formally, to have four 4d electrons after the formation of σ bonds to each of the five ligands, provided we also use the conventional though purely formal description of the linear Mo–N–O moiety as Mo^-–(NO^+). These four electrons should then fill up the $e''(d_{xz},d_{yz})$ orbitals, where they can participate very effectively in back-bonding to the NO, thus explaining the very low (1632 cm^{-1}) value of ν_{NO} and the absence of an Mo–Mo bond. In $Mo_2(O\text{-}i\text{-}Pr)_8$, where the formal oxidation number of Mo is +2, each Mo atom has two 4d electrons. It is possible to envision the formation of a double bond as the result of d_{xz}–d_{xz} and d_{yz}–d_{yz} overlaps. This could be construed as a combination of one π bond and one δ bond, but whether the lower symmetry that actually exists will materially alter such a formal description is problematic. In any event, in both compounds the molybdenum atoms have 14-electron valence shell configurations. If the double bond in $Mo_2(O\text{-}i\text{-}Pr)_8$ does consist of this rather unusual combination of a π and a δ combination instead of the conventional $\sigma + \pi$ pair, this might explain why it is relatively long since, in general, δ components of multiple bonds are always much less effective than σ ones.

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Registry No. $Mo_2(OCHMe_2)_8$, 66526-46-3.

Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Di-μ-sulfido Binuclear Compounds of W(IV) and W(V). Unambiguous Examples of Formal Single and Double Bonds between Tungsten Atoms

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The preparation and structural characterization of two compounds containing tungsten–tungsten bonds of orders 1 and 2 in very similar environments are reported. In **1**, $W_2(\mu\text{-}S)_2(Et_2NCS_2)_2(\mu\text{-}Et_2NCS_2)$, the W–W distance, 2.530 (2) Å, corresponds to a double bond, while in **2**, $W_2(\mu\text{-}S_2)(Et_2NCS_2)_2(CH_3O)_4$, the W–W distance of 2.791 (1) Å is consistent with a single bond. While the assignment of M–M bond order in any one molecule with bridging ligands is frequently ambiguous, the totality of the data for this pair of structurally analogous molecules makes these two bond order assignments very secure. Both compounds are easy to prepare and can be handled in the air. Crystallographic data are as follows. **1**: space group $C2/c$, $a = 21.37$ (2) Å, $b = 9.211$ (5) Å, $c = 18.367$ (8) Å, $\beta = 108.31$ (4)°, $Z = 4$. The structure was refined to final residuals of $R_1 = 0.047$ and $R_2 = 0.057$. For **2**: space group $P2_1/c$, $a = 9.028$ (4) Å, $b = 12.776$ (8) Å, $c = 12.126$ (4) Å, $\beta = 112.29$ (3)°, $Z = 2$; final residuals were 0.041 and 0.053.

Introduction

Although compounds with single,[2] triple,[3,4] and quadruple bonds are well-known for both molybdenum[4,5] and tungsten,[5–7] there has been a dearth of compounds with double bonds between pairs of these atoms. There are, in fact, relatively few compounds containing M=M bonds of any kind[4a] and, consequently, there is little systematic chemistry of M=M bonds with the conspicuous exception of the chemistry of the trinuclear trirhenium compounds[8] such as Re_3Cl_9, $Re_3Cl_{12}^{3-}$, etc.

Very recently this situation has begun to change. To the only two previously known cases in which Mo=Mo bonds have

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2S_2(Et_2NCS_2)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.04720 (4)	−0.0010 (2)	0.05770 (4)	2.56 (3)	3.11 (3)	2.63 (4)	−0.18 (9)	0.79 (3)	0.2 (1)
S(1)	−0.0758 (3)	0.0850 (6)	0.0370 (3)	2.8 (3)	3.6 (3)	3.3 (3)	0.4 (3)	1.5 (2)	0.2 (3)
S(2)	0.1807 (3)	−0.0707 (7)	0.1280 (3)	2.9 (3)	4.8 (3)	3.0 (3)	0.1 (3)	0.9 (2)	0.1 (3)
S(3)	0.0643 (3)	0.0568 (6)	0.1753 (3)	3.6 (3)	4.7 (4)	3.3 (4)	−0.1 (3)	1.1 (3)	−0.3 (3)
S(5)	0.0189 (3)	−0.2502 (6)	0.0822 (3)	3.8 (3)	3.2 (3)	4.1 (4)	−0.4 (3)	0.5 (3)	0.3 (3)
S(6)	−0.1095 (3)	−0.2280 (6)	−0.0466 (3)	3.3 (3)	4.1 (4)	4.2 (4)	−0.6 (3)	0.7 (3)	0.4 (4)
N(2)	0.2010 (8)	−0.043 (1)	0.2598 (8)	2.9 (4)					
N(5)	−0.0816 (9)	−0.453 (2)	0.0337 (8)	3.6 (4)					
C(2)	0.157 (1)	−0.025 (2)	0.197 (1)	4.4 (5)					
C(5)	−0.058 (1)	−0.317 (2)	0.025 (1)	3.5 (5)					
C(21)	0.171 (1)	0.011 (3)	0.313 (1)	5.1 (5)					
C(22)	0.137 (1)	−0.142 (3)	0.333 (1)	6.7 (7)					
C(23)	0.277 (1)	−0.112 (3)	0.272 (1)	4.9 (6)					
C(24)	0.339 (1)	0.007 (4)	0.280 (1)	7.2 (6)					
C(51)	−0.148 (1)	−0.523 (3)	−0.015 (1)	5.5 (6)					
C(52)	−0.219 (2)	−0.496 (4)	0.006 (1)	8.8 (8)					
C(53)	−0.040 (1)	−0.544 (2)	0.092 (1)	5.7 (7)					
C(54)	−0.069 (1)	−0.539 (3)	0.148 (1)	6.4 (7)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

been proposed, viz., MoO_2[2,9] and $Mo_2S_2(S_2CN(C_3H_7)_2)_2(S-CN(C_3H_7)_2)_2$,[10] have been added $Mo_2(OCMe_3)_6(\mu\text{-}CO)$[11] and $Mo_2(OCHMe_2)_6(\mu\text{-}OCHMe_2)_2$.[12] For tungsten, it would appear that only in the case of WO_2[13] (which is isostructural with MoO_2) is there any prior instance of the probable existence of a double bond.

In this report we describe the preparation and structures of two dinuclear tungsten compounds in which two tungsten atoms are bridged by sulfur atoms. In one it seems likely that the tungsten atoms are connected by a double bond. In the other one, which is a di-μ-sulfido binuclear compound of W(V), there appears to be a formal single bond between the two tungsten atoms.

Experimental Section

Preparation of $W_2S_2(Et_2NCS_2)_4$, 1. Tris(acetonitrile)tricarbonyltungsten,[14] 0.50 g, was dissolved in 100 mL of dry acetone under nitrogen. Tetraethyldithiuram disulfide, $Et_2NC(S)SSC(S)NEt_2$, 0.37 g, was added to this solution and the reaction mixture was stirred 12 h at ca. 20 °C. A green precipitate was collected by filtration and recrystallized from hot chloroform. Anal.[15] Calcd for $C_{20}H_{40}N_4S_{10}W_2$: C, 23.48; H, 3.91; N, 5.47. Found: C, 23.7; H, 3.86; N, 5.52. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in approximately 1:1 CCl_3H/CH_3CN.

Preparation of $W_2S_2(Et_2NCS_2)_2(CH_3O)_4$, 2. Tris(acetonitrile)-tricarbonyltungsten, 0.5 g, was dissolved under N_2 in 100 mL of methanol. Tetraethyldithiuram disulfide, 0.37 g, was added and the reaction mixture was stirred overnight at room temperature. The green precipitate, $W_2S_2(Et_2DTC)_4$, which formed was filtered, and the clear red solution was allowed to evaporate slowly in the air, yielding a mixture of green and orange crystals. A few of the orange crystals were separated mechanically and were used for the structure determination.

X-ray Crystallography of 1. A crystal was coated with epoxy resin, attached to the end of a glass fiber, and mounted on a Syntex $P\bar{1}$ four-circle diffractometer. General procedures for data collection have been reported elsewhere.[16] Rotation photographs and ω scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the monoclinic system with C centering. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $20° < 2\theta < 30°$ giving $a = 21.37$ (2) Å, $b = 9.211$ (5) Å, $c = 18.367$ (8) Å, $\beta = 108.31$ (4)°, and $V = 3432$ (7) Å^3. The assumption that $Z = 4$ gives a reasonable calculated density of 1.984 g cm^{-3}.

Intensity data were collected at 22 ± 2 °C using Mo Kα radiation, monochromated by a graphite crystal in the incident beam. The θ–2θ scan technique was employed with a variable scan rate (4.0–24.0° min^{-1}). A total of 4163 reflections in the range $0° < 2\theta < 45°$ were collected of which 1528 had $I > 3\sigma(I)$. Three standard reflections were measured every 97 reflections and did not show any significant decay. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 76.98 cm^{-1}.

The structure was solved[17] by conventional heavy-atom methods and refined in space group $C2/c$ to convergence using anisotropic thermal parameters for W and S and isotropic thermal parameters for C and N. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where $p = 0.07$ as defined previously.[16,17] The discrepancy indices used were

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

The final residuals are $R_1 = 0.047$ and $R_2 = 0.057$ with an error in an observation of unit weight equal to 1.10. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

X-ray Crystallography of 2. All crystallographic operations and solution and refinement of the structure were similar to those described above for $W_2S_2(Et_2NCS_2)_4$ with the exception that the heavy-atom positions were obtained by direct methods using the MULTAN program. In the last three cycles of refinement all nonhydrogen atoms were refined with anisotropic temperature factors. Systematic absences uniquely suggested the space group $P2_1/c$, and unit cell dimensions were found to be $a = 9.028$ (4) Å, $b = 12.776$ (8) Å, $c = 12.126$ (4) Å, $\beta = 112.29$ (3)°, $V = 1294$ (3) Å, $Z = 2$, and $d_x = 2.188$ g cm^{-3}. A crystal approximately 0.1 × 0.1 × 0.1 mm ($\mu = 98.95$ cm^{-1}) was used to collect 1908 unique data of which 1261 with $I > 3\sigma(I)$ were used to solve and refine the structure to final reliability indices of $R_1 = 0.041$ and $R_2 = 0.053$. The esd of an observation of unit weight was 1.17. A table of structure factors is available as supplementary material.

In neither structure were absorption corrections performed because of the smallness of the crystals, their uniform shapes, and the fact that ψ scans at $\chi = 90°$ for several reflections showed no variation greater than 9%.

Results

$W_2S_2(Et_2NCS_2)_4$. The atomic positional and thermal parameters are listed in Table I, while Figure 1 shows the structure of the molecule and the atomic numbering scheme used in the tables. The bond distances and bond angles are listed in Table II and some mean planes and dihedral angles are described in Table III. There is a crystallographic inversion center midway between the tungsten atoms. Because of this, the $W_2(\mu\text{-}S)_2$ bridge system is strictly planar. The tungsten atoms have roughly octahedral coordination, although there are severe distortions. The bonding to the bridging sulfur atoms is unsymmetrical; the two W–(μ-S) distances differ by 0.07 (1) Å and have a mean value of 2.34 Å.

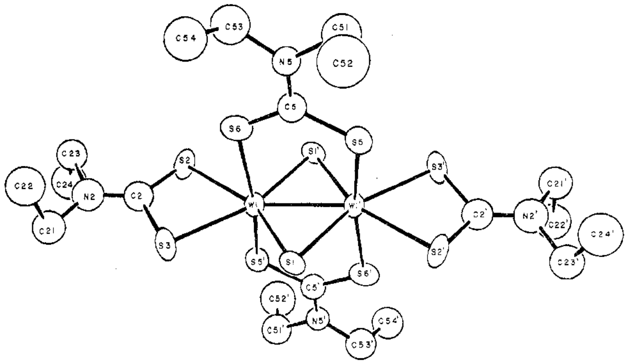

Figure 1. ORTEP drawing of the $W_2S_2(Et_2NCS_2)_4$ molecule, showing the atomic numbering scheme. Atoms are represented by their thermal vibrational spheres or ellipsoids scaled to enclose 30% of the electron density.

Table II

Bond Distances (Å) for $W_2S_2(Et_2NCS_2)_4$

W(1)-W(1)'	2.530 (2)		
W(1)-S(1)	2.302 (5)	W(1)-S(3)	2.490 (6)
W(1)-S(1)'	2.375 (6)	W(1)-S(5)	2.446 (6)
W(1)-S(2)	2.523 (5)	W(1)-S(6)	2.447 (6)
S(2)-C(2)	1.71 (2)	S(5)-C(5)	1.67 (2)
S(3)-C(2)	1.78 (2)	S(6)-C(5)	1.73 (2)
C(2)-N(2)	1.35 (2)	C(5)-N(5)	1.36 (2)
N(2)-C(21)	1.50 (3)	N(5)-C(51)	1.47 (3)
N(2)-C(23)	1.48 (2)	N(5)-C(53)	1.49 (3)
C(21)-C(22)	1.65 (4)	C(51)-C(52)	1.53 (3)
C(23)-C(24)	1.55 (4)	C(53)-C(54)	1.46 (3)

Bond Angles (deg) for $W_2S_2(Et_2NCS_2)_4$

W(1)'-W(1)-S(1)	58.6 (1)	W(1)'-W(1)-S(1)'	55.9 (1)
-S(2)	145.3 (2)	-S(3)	144.3 (1)
-S(5)	95.1 (2)	-S(6)'	95.6 (2)
S(1)-W(1)-S(1)'	114.5 (1)		
-S(2)	156.0 (2)	S(1)'-W(1)-S(2)	89.5 (2)
-S(3)	85.7 (2)	-S(3)	159.8 (2)
-S(5)	95.9 (2)	-S(5)	89.8 (2)
-S(6)'	98.3 (2)	-S(6)'	87.9 (2)
S(2)-W(1)-S(3)	70.3 (2)	S(5)-W(1)-S(6)'	165.3 (2)
-S(5)	82.3 (2)	S(2)-W(1)-S(6)'	83.1 (2)
S(3)-W(1)-S(5)	87.3 (2)	S(3)-W(1)-S(6)'	90.0 (2)
W(1)-S(1)-W(1)'	65.5 (1)		
W(1)-S(2)-C(2)	89.1 (7)	W(1)-S(3)-C(2)	88.5 (7)
W(1)-S(5)-C(5)	112.1 (8)	W(1)-S(6)-C(5)	110.7 (7)
S(2)-C(2)-S(3)	111 (1)	S(5)-C(5)-S(6)	125 (1)
S(2)-C(2)-N(2)	126 (2)	S(5)-C(5)-N(5)	118 (2)
S(3)-C(2)-N(2)	122 (2)	S(6)-C(5)-N(5)	117 (2)
C(2)-N(2)-C(21)	118 (2)	C(5)-N(5)-C(51)	122 (2)
C(12)-N(2)-C(23)	118 (2)	C(5)-N(5)-C(53)	122 (2)
C(21)-N(2)-C(23)	124 (2)	C(51)-N(5)-C(53)	116 (2)
N(2)-C(21)-C(22)	100 (2)	N(5)-C(51)-C(52)	109 (2)
N(2)-C(23)-C(24)	109 (2)	N(5)-C(53)-C(54)	116 (2)

The W–W distance, 2.530 (2) Å, is clearly indicative of a direct bond between the metal atoms, and the presence of such a bond is further indicated by the very small angle, 65.5 (1)°, at the bridging sulfur atom and the very obtuse angle, 114.5 (1)°, subtended by the bridging sulfur atoms at the tungsten atom.

The other features of the structure are unremarkable, except perhaps for the fact that the two ethyl groups on N(5) point in the same direction, whereas, ordinarily, as is the case for N(2) in this same structure and N(1) in compound **2**, they point in opposite directions. This appears to be a consequence of intermolecular forces, as indicated by Figure 2 which shows the arrangement of the molecules in the unit cell.

$W_2S_2(Et_2NCS_2)_2(OCH_3)_4$. The atomic parameters for this structure are listed in Table IV. Figure 3 shows the molecule and defines the atomic numbering scheme. The bond lengths and angles are listed in Table V. Once again, there is a crystallographic inversion center midway between the tungsten atoms which means that the central $W_2(\mu\text{-}S)_2$ unit is strictly planar. Each tungsten atom is coordinated by a roughly octahedral set of six ligand atoms, four essentially coplanar sulfur atoms and two methoxide oxygen atoms lying above and below the WS_4 plane. There is again a small but real asymmetry in the bridging system, with the W–S distances differing by about 0.04 Å, i.e., by only about half as much as in the W^{IV} compound. The mean W–(μ-S) distance, 2.34 Å, is equal, within 0.01 Å, to that in compound **1**.

Table III. Planes and Dihedral Angles for $W_2S_2(Et_2NCS_2)_4$

	atom	dist from plane, Å
plane 1	W(1)	0.000
	S(1)	0.000
	W(1)'	0.000
	S(1)'	0.000
plane 2	W(1)	0.016
	S(1)	−0.008
	S(2)	−0.009
	S(3)	0.003
plane 3	W(1)	−0.106
	S(5)	0.089
	S(6)	−0.089
	W(1)'	0.107

plane	plane	angle, deg
1	2	0.08
2	3	88.9

The W–W distance, 2.791 (1) Å, is much longer than that in **1** but, nonetheless, sufficiently short to indicate that there is a direct bond between the metal atoms. The conclusion is supported strongly by the acute angles (73.2°) at the bridging sulfur atoms and the obtuse angles (106.8°) subtended by the bridging sulfur atoms at the tungsten atoms.

Discussion

The two compounds whose preparation and structures are reported here are of unusual interest, especially when considered together, because they illustrate the structural effects of increasing the order of metal–metal bonds while maintaining the main features in the environment of those bonds essentially unchanged.

Let us first consider $W_2S_2(Et_2NCS_2)_2(CH_3O_4)$. Several structural features, of which the W–W distance of 2.791 Å is only one, show that there is a W–W bond. This conclusion is particularly clear when this structure is compared with that recently reported[18] for W_2Cl_{10} where there is no W–W bond, as shown by the pronounced paramagnetism.[19] In W_2Cl_{10}, the W–W distance is 3.814 Å, the angles at bridging Cl atoms are obtuse, and those angles subtended by the bridging atoms at the tungsten atoms are acute. All these are expected features for a nonbonded situation because, if there is no attractive force, there must then be a net repulsive one which causes the $M(\mu\text{-}X)_2M$ system to stretch along the M···M direction.

Since we are dealing in this case with tungsten(V), which has one d electron, the formal W–W bond order cannot exceed unity, and we think it is reasonable to suppose that it is unity, at least as a practical first approximation.

Proceeding then to the tungsten(IV) compound, $W_2S_2(Et_2NCS_2)_4$, we note that the chemical environment of the pair of tungsten atoms is very similar to that found in the W^V compound, particularly insofar as the common, in-plane $Et_2NCS_2W(\mu\text{-}S)_2WS_2CNEt_2$ system is concerned. However, in this case the crucial structural features show that a considerably stronger force exists between the metal atoms. The distance is now shorter by about 0.26 Å, and the angles at the

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2S_2(Et_2NCS_2)_2(OCH_3)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.15142 (7)	0.51551 (4)	0.58851 (5)	2.45 (2)	1.41 (2)	2.70 (2)	0.02 (2)	1.37 (1)	0.01 (2)
S(1)	0.3721 (4)	0.4288 (3)	0.7528 (3)	3.2 (2)	1.8 (1)	3.2 (2)	−0.0 (1)	1.1 (1)	0.5 (1)
S(2)	−0.0059 (5)	0.6390 (3)	0.4481 (4)	3.3 (1)	1.5 (1)	3.9 (1)	−0.1 (1)	1.8 (1)	0.2 (1)
S(3)	0.3782 (5)	0.6449 (3)	0.6849 (4)	3.3 (2)	2.0 (2)	4.0 (2)	−0.1 (1)	1.1 (1)	0.3 (1)
O(1)	0.071 (1)	0.5669 (8)	0.6985 (8)	4.1 (4)	2.9 (4)	2.7 (3)	−0.7 (4)	2.4 (3)	−0.4 (3)
O(2)	0.255 (1)	0.4884 (7)	0.4854 (8)	3.7 (4)	2.1 (4)	2.7 (3)	0.3 (3)	2.2 (3)	0.7 (3)
N(1)	0.608 (1)	0.561 (1)	0.874 (1)	1.8 (4)	3.5 (6)	1.4 (4)	−0.2 (4)	−0.1 (3)	0.0 (4)
C(1)	0.471 (2)	0.548 (1)	0.782 (1)	2.8 (5)	0.9 (5)	4.3 (6)	0.9 (5)	2.0 (4)	0.3 (5)
C(2)	0.685 (2)	0.475 (1)	0.959 (1)	3.4 (7)	2.8 (7)	2.9 (6)	1.0 (6)	0.2 (5)	0.7 (6)
C(3)	0.799 (2)	0.414 (1)	0.919 (2)	5.0 (7)	3.5 (8)	6.7 (9)	0.9 (6)	3.2 (6)	−0.1 (7)
C(4)	0.685 (2)	0.665 (1)	0.902 (1)	1.5 (5)	2.3 (6)	5.1 (7)	−1.5 (5)	0.9 (5)	−0.4 (6)
C(5)	0.626 (2)	0.728 (1)	0.979 (2)	6.4 (9)	1.7 (7)	5.7 (8)	−1.0 (6)	2.7 (6)	−1.6 (6)
C(6)	0.298 (2)	0.535 (2)	0.397 (1)	6.2 (8)	4.7 (9)	5.4 (7)	0.9 (7)	3.8 (5)	2.0 (7)
C(7)	0.029 (2)	0.665 (1)	0.735 (2)	7.1 (8)	3.4 (7)	5.3 (7)	2.4 (6)	3.8 (5)	−0.3 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hkb^*c^*)]$.

Table V. Bond Distances and Bond Angles for $W_2S_2(Et_2DTC)_2(CH_3O)_4$

		Bond Distances, A			
W(1)–W(1)′	2.791 (1)	W(1)–S(3)	2.544 (4)	N(1)–C(1)	1.32 (2)
W(1)–S(2)	2.360 (4)	S(1)–C(1)	1.73 (1)	N(1)–C(2)	1.48 (2)
W(1)–S(2)′	2.319 (4)	S(3)–C(1)	1.70 (1)	N(1)–C(4)	1.48 (2)
W(1)–O(1)	1.890 (9)	O(1)–C(7)	1.44 (2)	C(4)–C(5)	1.48 (2)
W(1)–O(2)	1.855 (9)	O(2)–C(6)	1.40 (2)	C(2)–C(3)	1.50 (2)
W(1)–S(1)	2.481 (4)				
		Bond Angles, Deg			
W(1)–S(2)–W(1)′	73.2 (1)	S(2)–W(1)–O(1)	89.4 (3)	S(1)–C(1)–N(1)	121 (1)
W(1)–S(1)–C(1)	88.1 (5)	S(2)′–W(1)–O(1)	95.3 (3)	S(3)–C(1)–N(1)	124 (1)
W(1)–S(3)–C(1)	86.9 (5)	S(2)–W(1)–O(2)	87.5 (3)	C(1)–N(1)–C(2)	123 (1)
W(1)–O(1)–C(7)	139.0 (9)	S(2)′–W(1)–O(2)	96.1 (3)	C(1)–N(1)–C(4)	120 (1)
W(1)–O(2)–C(6)	142.0 (9)	S(1)–W(1)–O(1)	89.6 (3)	C(2)–N(1)–C(4)	117 (1)
S(3)–W(1)–S(1)	70.1 (1)	S(1)–W(1)–O(2)	90.1 (3)	N(1)–C(2)–C(3)	114 (1)
S(3)–W(1)–S(2)	93.2 (1)	S(3)–W(1)–O(1)	84.6 (3)	N(1)–C(4)–C(5)	112 (1)
S(3)–W(1)–S(2)′	160.0 (1)	S(3)–W(1)–O(2)	84.7 (3)	W(1)′–W(1)–O(1)	93.9 (3)
S(1)–W(1)–S(2)	163.3 (1)	O(1)–W(1)–O(2)	168.7 (4)	W(1)′–W(1)–O(2)	93.0 (3)
S(1)–W(1)–S(2)′	89.8 (1)	S(1)–C(1)–S(3)	114.7 (9)	S(2)–W(1)–S(2)′	106.8 (1)

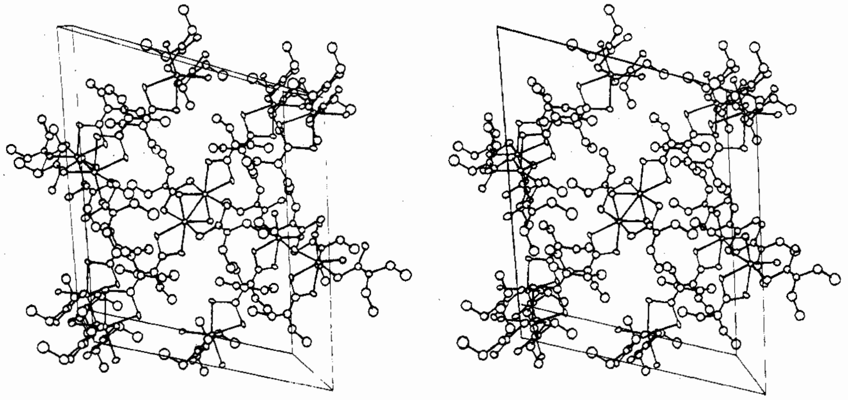

Figure 2. ORTEP stereoview of the contents of the unit cell of $W_2S_2(Et_2NCS_2)_4$.

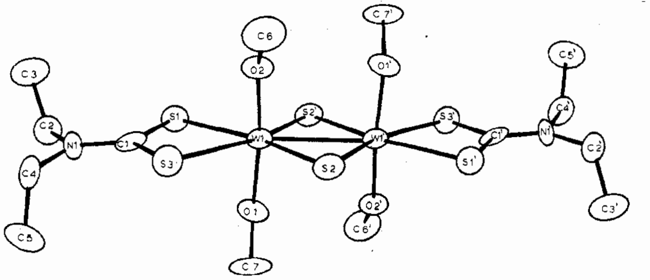

Figure 3. ORTEP drawing of the molecular structure of $W_2S_2(Et_2NCS_2)_2(CH_3O)_4$ showing the atom numbering scheme. Atoms are represented by their thermal vibration spheres or ellipsoids scaled to enclose 30% of the electron density.

bridging sulfur atoms and at the tungsten atoms are now about 8° smaller and larger, respectively, than those in **2**. Since we are now dealing with tungsten(IV) atoms, which have two electrons available, it seems clear that we are now dealing with a W=W double bond.

The problem frequently encountered in dealing with an isolated case in which a double bond *might* be postulated is the following. Arguments for deciding between a double bond, on the one hand, and a single bond together with indirect pairing of the spins of the remaining two electrons through the bridging atoms, on the other, are rarely, if ever, conclusive, because the only data on which to base them are structural in nature. These structural data, for an isolated case, can be used to show that there is a metal–metal bond, but they do not generally allow one to conclude that the bond order *must necessarily* be 2 rather than 1. This problem has been discussed in detail recently with respect to some oxygen-bridged dimolybdenum compounds.[12] The comparing of M–M distances when the compounds used for the comparison involve different bridging atoms and other ligands is risky and sometimes leads to flagrant inconsistencies.

We believe that the two compounds we have compared here have provided a rare, and perhaps even unprecedented, opportunity to develop an unambiguous argument for the existence of a direct double bond between two metal atoms in a situation where there are also bridging atoms.

The reactions used to prepare compounds **1** and **2** merit some comment. The course they take could not readily have been predicted, and yet the results are not entirely unprecedented either. The simplest way in which a dithiuram disulfide, $R_2NC(S)S-SC(S)NR_2$, can react with a metal carbonyl compound is by displacement of CO groups and/or other ligands coupled with oxidative addition of the R_2NCS_2 radicals formed by cleavage of the S–S bond. Reactions of this relatively simple kind have been known since 1964.[20] Even $W(CO)_6$ or $W(CO)_3(CH_3CN)_3$ when refluxed with $Et_2NC(S)SSC(S)NEt_2$ in toluene undergo a simple net reaction and give rise to the eight-coordinate tetrakis(diethyldithiocarbamato)tungsten(IV) complex.[21] However, dithiuram disulfides can also serve as sources of sulfur atoms. It has been shown previously that reduction of $Et_2NC(S)S-SC(S)NEt_2$ under certain conditions can lead to C–S bond cleavage.[22] In our work, abstraction of sulfur must have occurred in order to form the $W(\mu-S)_2W$ bridge groups, but the fate of the remaining fragments of the thiuram disulfide is not known. It is also notable that the dithiocarbamato ion itself can also be a source of sulfur atoms, as in the work of Ricard, Estienne, and Weiss[10] already cited.

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Registry No. **1**, 67426-14-6; **2**, 67426-15-7; tris(acetonitrile)tricarbonyltungsten, 16800-47-8; $Et_2NC(S)SSC(S)NEt_2$, 97-77-8.

Supplementary Material Available: Tables of the observed and calculated structure factors for both structures (13 pages). Ordering information is given on any current masthead page.

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