Organometallic Sulfur Complexes. VIII. The Molecular Structure of a Doubly Sulfur-Bridged Dimeric Complex of Molybdenum(V), $[C_5H_5MoO]_2S_2$, Containing a Mo–Mo Interaction[1]

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Abstract: A structural determination of $[C_5H_5MoO]_2S_2$ has revealed the first known example of an organometallic complex which contains doubly bridging sulfur atoms linking two transition metals. Crystals of $[C_5H_5MoO]_2S_2$ are triclinic with reduced cell parameters of a = 6.62 A, b = 8.73 A, c = 10.68 A, α = 95° 40′, β = 92° 56′, and γ = 100° 49′. The space group is $P\bar{1}$; there are two molecules per unit cell with each molecule located on a crystallographic center of symmetry. If each cyclopentadienyl ring is considered to occupy three bonding sites, the idealized dimeric species can be described as two octahedra sharing a common edge bisected by a direct Mo–Mo bond which is proposed to account for the observed diamagnetism of the complex. A detailed comparison of the structural features of $[C_5H_5MoO]_2S_2$ with those of related oxo-bridged molybdenum systems is given.

A variety of organosulfur complexes has been synthesized from the reactions of cyclopentadienylmolybdenum tricarbonyl dimer with various sulfur-containing compounds.[3-6] From the air oxidation of the crude products obtained by the reaction of $[C_5H_5Mo(CO)_3]_2$ with cyclohexene sulfide, Treichel and Wilkes[6] isolated an orange crystalline compound stable to both air and moisture. The chemical analysis and molecular weight determination[7] of this compound indicated that its molecular formula is $[C_5H_5MoOS]_2$. Its diamagnetic character was established from a proton nmr spectrum which showed only a single sharp peak due to the cyclopentadienyl hydrogens. An infrared spectrum of $[C_5H_5MoOS]_2$ revealed absorption bands characteristic of a terminal Mo=O group similar to that found in the possibly isosteric complex $[C_5H_5MoO_2]_2$ reported by Cousins and Green.[8] For this latter complex these workers proposed two possible structural models, one having only a metal–metal bond connecting the two halves of the dimeric species and the other possessing bridging oxygen atoms as well as a metal–metal bond. Since no structural precedent exists for an organometallic complex containing either a terminal Mo=S group or doubly bridging sulfur atoms linking two transition metals,[9] a structural determination of $[C_5H_5MoOS]_2$ was undertaken.[11]

Experimental Section

Crystals of $[C_5H_5MoOS]_2$ were kindly supplied to us by Professor Paul Treichel and Dr. Glenn Wilkes of the University of Wisconsin. A preliminary X-ray examination of a number of crystals mounted in thin-walled Lindemann glass capillaries was made; a well-formed crystal of dimensions 0.2 × 0.2 × 0.15 mm with the 0.15-mm direction as the rotation axis was utilized for the collection of intensity data. Lattice lengths and angles were measured from $hk0$ and $h0l$ precession photographs which were calibrated by the superimposing of a zero-layer reciprocal net from a NaCl crystal on the same films.

Multiple-film equiinclination Weissenberg photographs of reciprocal layers $0kl$ through $\bar{8}kl$ were taken with Zr-filtered Mo Kα radiation. Two sets of Weissenberg photographs, each of which covered a rotation range of approximately 220°, were taken at spindle settings 180° apart for all reciprocal levels except the zero level. This procedure which places all accessible reflections on the upper half of the film eliminates the problem of spot compaction[14] (but not that of spot extension). In addition to the Weissenberg photographs, timed sets of precession photographs of reciprocal levels $hk0$, $h0l$, $h1l$, and $h2l$ were taken. The intensities of all reflections were estimated by comparison with a timed set of standard intensities prepared from the same crystal. Only reflections which were judged at least twice were utilized in the structural analysis. These reflections were corrected for Lorentz-polarization effects and spot extension,[15] but absorption corrections were ignored since $\mu R_{\max} \leqslant 0.35$.

The Weissenberg and precession data were then merged *via* least squares[16] on the basis of common reflections to place all data on a single scale. The weighted reliability index for this least-squares merging, which resulted in a total of 2177 independent reflections, was 4.6%. This low value indicates that the merging process introduced no serious systematic error into the data.

Each structural amplitude was assigned a standard deviation according to the following equations:[17] if $I_0(hkl) \geqslant \sqrt{10}I_{\min}$, $\sigma[F_o(hkl)] = F_o(hkl)/20$; if $I_0(hkl) < \sqrt{10}I_{\min}$, $\sigma[F_o(hkl)] = [F_o(hkl)/20][\sqrt{10}I_{\min}/I_0(hkl)]^2$.

The atomic scattering factors used for all atoms were those of Hanson, *et al.*[18] The real and imaginary anomalous contributions

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(1) For paper VII, see J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

(2) This article is based in part on a dissertation submitted by D. L. Stevenson to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1967.

(3) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

(4) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

(5) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966).

(6) P. M. Treichel and G. R. Wilkes, *ibid.*, **5**, 1182 (1966).

(7) *Anal.* Calcd for $[C_5H_5MoOS]_2$: C, 28.97; H, 2.41; O, 7.67; mol wt, 418. Found: C, 28.99; H, 2.42; O, 7.61; mol wt, 406.[6]

(8) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1567 (1964).

(9) The inorganic complex Mo_2S_3 has been shown to contain metal-coordinated doubly bridging sulfur atoms.[10]

(10) F. Jellinek, *Nature*, **192**, 1065 (1961).

(11) Another possible structure for $[C_5H_5MoOS]_2$ involving a metal-coordinated disulfide bridging group (similar to that found in $[SFe(CO)_3]_2$[12]) was suggested by Wilkes.[13]

(12) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(13) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965, p 121.

(14) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, pp 227–229.

(15) D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

(16) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1964.

(17) D. L. Smith, "DACOR—A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

(18) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

to the scattering factors of the molybdenum and sulfur atoms were taken from Templeton's tabulation.[19]

Crystal Data

The lattice parameters of the reduced triclinic cell of $[C_5H_5MoOS]_2$ are $a = 6.62 \pm 0.02$ A, $b = 8.73 \pm 0.02$ A, $c = 10.68 \pm 0.02$ A, $\alpha = 95° 40' \pm 10'$, $\beta = 92° 56' \pm 10'$, and $\gamma = 100° 49' \pm 10'$. The calculated density of 2.31 g/cc for two dimeric molecules in the unit cell compares favorably with the experimental density of 2.28 g/cc as measured by the flotation method. The probable space group of the triclinic cell was taken to be $P\bar{1}$; this choice was verified by the successful refinement of the structure. Thus, two molybdenum, two sulfur, two oxygen, ten carbon, and ten hydrogen atoms comprise the asymmetric unit. Since the subsequent structural analysis showed that each molecule possesses a crystallographic center of symmetry, the structurally independent unit of $[C_5H_5MoOS]_2$ consists of two half-molecules.

Solution of the Structure

The positional parameters of the 16 independent nonhydrogen atoms were determined by the usual combination of three-dimensional Patterson and Fourier maps.[20] The atomic parameters were refined with a local version of the Busing–Martin–Levy ORFLS program.[21] Several cycles of full-matrix, least-squares isotropic refinement yielded discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 8.5\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 10.5\%$.

An inspection of the C–C bond lengths in the two independent cyclopentadienyl rings showed that these bond lengths varied from 1.34 to 1.49 A, but no trend in the variations was discernible. Hence, it was decided to continue the refinement of the structure with a rigid-body, least-squares program[22] in order to constrain each of the cyclopentadienyl rings to a regular pentagonal configuration of side 1.41 A. Although no attempt had been made to locate and refine the hydrogen atoms for the unconstrained model, their contribution to the structure factor calculations was included in the rigid-body refinement. In this constrained model each hydrogen atom was required to be 1.08 A from the carbon atom to which it is bonded and to be collinear with that carbon atom and the midpoint of the opposite side of the cyclopentadienyl ring. In the beginning a variable over-all temperature factor was assigned to each cyclopentadienyl ring. After two cycles of least-squares refinement, discrepancy factors of $R_1 = 8.5\%$ and $R_2 = 10.7\%$ were obtained. A comparison of the unconstrained and constrained isotropic least-squares refinements showed the calculated positions of the carbon atoms of the constrained cyclopentadienyl ring to vary by as much as 2.5σ from their corresponding positions in the unconstrained model, but none of the coordinates for the nongroup atoms (*viz.*, the molybdenum, sulfur, and oxygen atoms) changed by more than 0.5σ for the two refinements.

Since a Fourier difference map indicated anisotropic thermal motion for the nongroup atoms, an anisotropic–isotropic rigid-body, least-squares refinement was carried out in which the isotropic constraint imposed on these atoms in previous least-squares cycles was removed. In addition individual isotropic temperature factors were assigned to both the carbon and hydrogen atoms of the constrained cyclopentadienyl rings, but only those of the carbon atoms were allowed to vary. Several cycles resulted in discrepancy factors of $R_1 = 5.9\%$ and $R_2 = 7.8\%$. In the last cycle all positional and thermal parameter shifts were less than 0.4σ. A comparison of the corresponding atomic coordinates for the anisotropic–isotropic rigid-body refinement with those for the completely isotropic rigid-body model showed no deviation greater than 2.0σ.

A final three-dimensional Fourier difference map based on the observed and calculated structure factors obtained from the last refinement cycle showed no residual electron-density peaks greater than 1.4 e/A^3 or less than -1.5 e/A^3 except in the vicinity of the cyclopentadienyl rings where the residual density along the C–C bonds indicates substantial ring libration. This cyclopentadienyl librational motion, which is not without precedent,[5] is more marked for one of the rings, $C_5H_5(2)$, as shown by the greater residual electron density along the bonds of this ring and by the uniformly higher isotropic thermal parameters for the individual carbon atoms in this ring.

Table I lists the final atomic parameters for the nongroup atoms and the final group parameters. The individual atomic parameters of the group atoms are given in Table II.[23] In order to corroborate the over-all correctness of the molecular determination, structure factors for all reflections not utilized in the X-ray analysis were generated to the edge of the observed reciprocal lattice corresponding to $\sin \theta = 0.6$. Each of these reflections was assigned a value equivalent to the minimum observed intensity for the given reciprocal level and then corrected for Lorentz-polarization and spot-extension effects. A comparison of the derived structure factors for these unobserved but experimentally accessible reflections with the corresponding calculated structure factors revealed no $F_c > 1.7F_o(\text{min})$.

Intramolecular distances and angles are given in Tables III and IV, respectively. Distances and angles together with estimated standard deviations were obtained for the nongroup atoms with the Busing–Martin–Levy ORFFE progam[24a] from the inverse matrix (which included estimated errors of the lattice parameters). Molecular parameters involving group atoms were calculated with a local program.[24b]

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(19) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(20) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS—A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963.

(22) "DBCGHW, A Fortran Crystallographic Least-Squares Rigid-Body Program for the CDC 1604 and 3600 Computers," University of Wisconsin, 1965; *cf.* R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

(23) Calculated and observed structure factors for $[C_5H_5MoO]_2S_2$ are deposited as Document No. 9421 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and remitting \$1.25 for photopirnts or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(24) (a) D. L. Smith, "BLANDA—A Bond Length and Angle Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix III), University of Wisconsin, 1962; extensively modified by S. F. Watkins, University of Wisconsin, 1966; (b) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

Table I. Final Atomic Parameters with Standard Deviations[a]

	x	y	z	B
Mo(1)	0.0526 (1)	0.1696 (1)	0.0173 (1)	b
Mo(2)	−0.1949 (1)	0.4059 (1)	0.4472 (1)	b
S(1)	−0.1407 (4)	0.0082 (4)	−0.1490 (2)	b
S(2)	0.1201 (4)	0.4418 (4)	0.3604 (3)	b
O(1)	−0.1249 (10)	0.2476 (10)	0.0939 (7)	b
O(2)	−0.3344 (10)	0.5053 (11)	0.3604 (8)	b
C$_5$H$_5$(1)[c]	0.3316 (8)	0.3222 (8)	−0.0064 (5)	d
C$_5$H$_5$(2)[c]	−0.3308 (12)	0.1819 (12)	0.4956 (7)	d

	ϕ, deg	θ, deg	ρ, deg
C$_5$H$_5$(1)[c]	−138.1 (4)	167.4 (3)	−74.8 (3)
C$_5$H$_5$(2)[c]	76.2 (6)	155.4 (4)	−95.0 (7)

[a] The standard deviations of the last significant figures are enclosed in parentheses. [b] Anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ were used for all nongroup atoms; the resulting thermal coefficients are as follows.

Atom	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Mo(1)	71 (2)	63 (1)	49 (1)	4 (1)	11 (1)	12 (1)
Mo(2)	95 (2)	70 (1)	47 (1)	10 (1)	10 (1)	11 (1)
S(1)	123 (5)	92 (4)	52 (2)	−3 (4)	−12 (2)	19 (3)
S(2)	132 (5)	103 (4)	56 (2)	5 (4)	32 (3)	−8 (3)
O(1)	140 (15)	84 (12)	85 (8)	15 (11)	22 (9)	5 (9)
O(2)	139 (16)	121 (15)	103 (8)	32 (12)	−5 (9)	32 (10)

[c] The internal orthogonal axial system for the two cyclopentadienyl rings (x', y', z') is defined as follows: the origin of each group is the intersection of the line joining C(2)–C(5) [C(7)–C(10)] with the line joining C(1) [C(6)] and the midpoint of C(3)–C(4) [C(8)–C(9)]. The $+x'$ direction is the C(1)-midpoint of C(3)–C(4) [C(6)-midpoint of C(8)–C(9)] vector; the $+y'$ direction is the C(5)–C(2) [C(10)–C(7)] vector. The z' direction is the vector product of x' and y'. The three angles ϕ, θ, and ρ refer to the orientation of the internal axial system with respect to an external orthogonal system by rotations around y', x', and z', respectively. In our program the orthogonal axes a_0, b_0, and c_0 for a right-handed system are defined relative to the crystal axes as $a_0 = a$, $b_0 = c_0 \times a_0$, $c_0 = a \times b$. [d] Individual isotropic temperature factors were assigned to each atom in the cyclopentadienyl rings. These values, along with the positional parameters for each atom, are given in Table II.

Table II. Individual Atomic Parameters of the Two Cyclopentadienyl Rings

Atom	x	y	z	B ($10\sigma_B$)
C(1)	0.383	0.334	0.067	3.0 (2)
C(2)	0.246	0.422	0.017	3.0 (2)
C(3)	0.196	0.365	−0.111	3.2 (2)
C(4)	0.302	0.241	−0.140	3.3 (2)
C(5)	0.417	0.222	−0.030	3.2 (2)
H(1)	0.449	0.349	0.163	8.0[a]
H(2)	0.189	0.517	0.068	8.0[a]
H(3)	0.095	0.408	−0.176	8.0[a]
H(4)	0.296	0.173	−0.231	8.0[a]
H(5)	0.515	0.137	−0.021	8.0[a]
C(6)	−0.366	0.209	0.566	6.5 (4)
C(7)	−0.180	0.159	0.540	5.1 (3)
C(8)	−0.181	0.123	0.409	5.0 (3)
C(9)	−0.367	0.152	0.353	6.1 (4)
C(10)	−0.481	0.205	0.451	5.0 (3)
H(6)	−0.412	0.245	0.659	8.0[a]
H(7)	−0.059	0.150	0.609	8.0[a]
H(8)	−0.060	0.082	0.359	8.0[a]
H(9)	−0.413	0.135	0.254	8.0[a]
H(10)	−0.631	0.236	0.439	8.0[a]

[a] Temperature factors of the hydrogen atoms were not varied in this refinement.

Table III. Intramolecular Distances (A) with Standard Deviations[a,b]

	Bonding Distances		
Mo(1)–Mo(1′)	2.894 (7)	Mo(1)–C(1)	2.38[c]
Mo(2)–Mo(2′)	2.894 (8)	Mo(1)–C(2)	2.33[c]
		Mo(1)–C(3)	2.38[c]
	2.894 (5)	Mo(1)–C(4)	2.46[c]
Mo(1)–S(1)	2.319 (6)	Mo(1)–C(5)	2.46[c]
Mo(1)–S(1′)	2.327 (5)	Mo(2)–C(6)	2.39[c]
Mo(2)–S(2)	2.305 (7)	Mo(2)–C(7)	2.48[c]
Mo(2)–S(2′)	2.312 (6)	Mo(2)–C(8)	2.48[c]
		Mo(2)–C(9)	2.39[c]
	2.317 (3)	Mo(2)–C(10)	2.34[c]
Mo(1)–O(1)	1.673 (8)		2.41 (av)
Mo(2)–O(2)	1.685 (8)		
	1.679 (6)		
	Nonbonding Distances		
S(1)···S(1′)	3.635 (9)	S(1)···O(1)	3.152 (11)
S(2)···S(2′)	3.598 (9)	S(1)···O(1′)	3.170 (10)
		S(2)···O(2)	3.160 (12)
	3.616 (av)	S(2)···O(2′)	3.189 (11)
Mo(1)···O(1′)	3.842 (12)		3.168 (5)
Mo(2)···O(2′)	3.877 (13)		
	3.858 (9)		

[a] Standard deviations of the last significant figures are enclosed in parentheses. [b] For each set of intermolecular distances the "best value" $\bar{x}$ and the corresponding standard deviation $\sigma(\bar{x})$ were weighted according to the individual estimated standard deviations. [c] Standard deviations of the Mo–C bonds are estimated to be approximately 0.03 A due to librational motion of the cyclopentadienyl rings.

Discussion

$[C_5H_5MoO]_2S_2$ exists in the solid state as discrete dimeric molecules of crystallographic point-group symmetry C_i-$\bar{1}$. The two halves of each dimer are linked together by two bridging sulfur atoms such that the molybdenum and sulfur atoms form a planar rhombus. Based on the assumption of cylindrical symmetry for each of the two cyclopentadienyl rings, each idealized molecule possesses C_{2h}-2/m symmetry. The idealized mirror plane, which passes through the centroid of each cyclopentadienyl ring and the oxygen atoms and which is perpendicular to the idealized twofold axis passing through the sulfur atoms, intersects the two molybdenum atoms; for each of the two crystallographically independent half-molecules this mirror plane is within 0.7° of being perpendicular to the rhombic $(MoS)_2$ plane. Examination of the molecular parameters shows both independent half-molecules to be identical within the limits of experimental error except for the orientation of the two cyclopentadienyl rings which differ from each other by a rotation of 180° about an axis defined by the molybdenum atom and the centroid of the coordinated cyclopentadienyl ring. A slight but significant deviation of the cyclopentadienyl carbon atoms from the idealized mirror plane is observed in both molecular configurations, one of which is shown in Figure 1. All distances and angles quoted in this discussion are the averages of the two independent half-molecules of $[C_5H_5MoO]_2S_2$, each based on the assumed C_{2h} molecular symmetry.

Figures 2 and 3 show the [100] and [010] views, respectively, of the centrosymmetric triclinic unit cell containing the two dimeric molecules which are centered about 0, 0, 0 and 0, 1/2, 1/2. The closest intermolecular H···H approach of 2.36 A, which is twice the 1.2-A van der Waals radius of hydrogen,[25] indicates that there are no unusual intermolecular interactions.

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(25) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

Table IV. Bond Angles (Degrees)[a]

Mo(1)-S(1)-Mo(1′)	77.0(2)	S(1)-Mo(1)-O(1)	103.1(3)
Mo(2)-S(2)-Mo(2′)	77.6(2)	S(1′)-Mo(1)-O(1)	103.6(3)
	77.3(1)	S(2)-Mo(2)-O(2)	103.6(3)
		S(2′)-Mo(2)-O(2)	104.8(4)
S(1)-Mo(1)-S(1′)	103.0(2)		103.7(2)
S(2)-Mo(2)-S(2′)	102.4(2)		
	102.7(1)	Mo(1′)-Mo(1)-Cent(1)	128.8
		Mo(2′)-Mo(2)-Cent (2)	128.5
Mo(1′)-Mo(1)-S(1)	51.6(2)		128.6(av)
Mo(1′)-Mo(1)-S(1′)	51.4(2)		
Mo(2′)-Mo(2)-S(2)	51.3(2)	S(1)-Mo(1)-Cent (1)	113.1
Mo(2′)-Mo(2)-S(2′)	51.1(2)	S(1′)-Mo(1)-Cent(1)	112.8
	51.4(1)	S(2)-Mo(2)-Cent(2)	112.8
		S(2′)-Mo(2)-Cent(2)	113.2
Mo(1′)-Mo(1)-O(1)	111.7(3)		113.0(av)
Mo(2′)-Mo(2)-O(2)	113.0(3)		
	112.4(2)	O(1)-Mo(1)-Cent(1)	119.5
		O(2)-Mo(2)-Cent(2)	118.4
			119.0(av)

[a] Standard deviations of the last significant figures are given in parentheses for those angles defined by three nongroup atoms. Cent(1) and Cent(2) are the centroids of $C_5H_5(1)$ and $C_5H_5(2)$, respectively. For each set of angles the "best value" $\bar{x}$ and the corresponding standard deviation $\sigma(\bar{x})$ were weighted according to the individual estimated standard deviations.

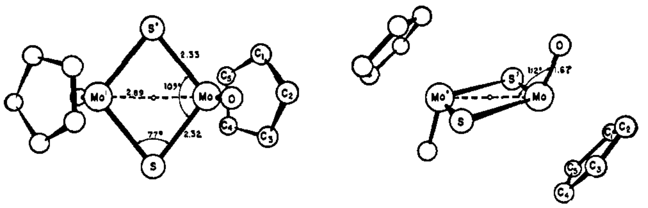

Figure 1. Molecular configuration of one of the two conformers of $[C_5H_5MoO]_2S_2$ with crystallographic symmetry C_i-$\bar{1}$. The other configuration possesses a different orientation of the cyclopentadienyl rings related to the shown conformer by a 180° rotation about an axis defined by the molybdenum atom and the centroid of the coordinated cyclopentadienyl ring.

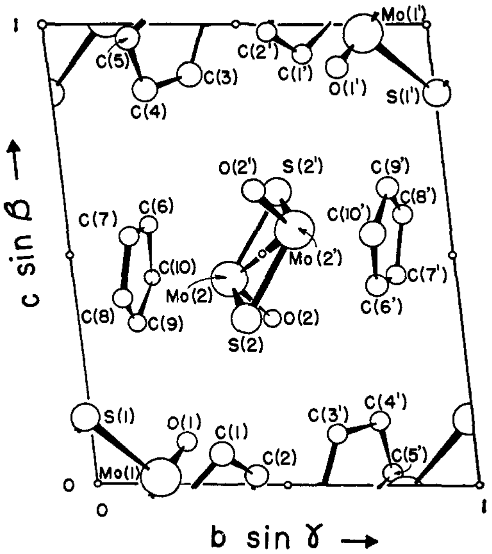

Figure 2. [100] projection of the primitive unit cell of $[C_5H_5MoO]_2S_2$.

If the cyclopentadienyl ring is considered to occupy three coordination sites, each molybdenum atom sits at the center of a distorted octahedron comprised of a cyclopentadienyl ring, two sulfur atoms, and an oxygen

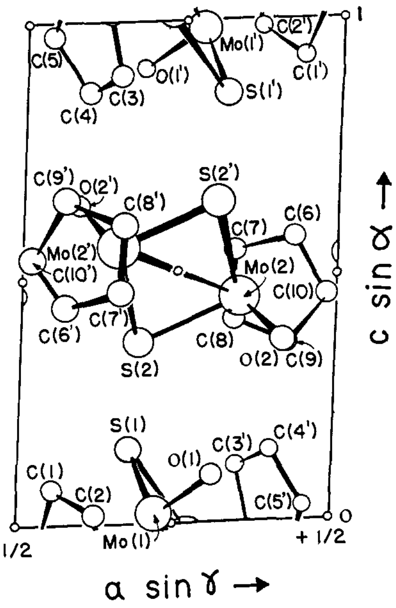

Figure 3. [010] projection of the primitive unit cell of $[C_5H_5MoO]_2S_2$.

atom.[26] The dimeric species then consists of two octahedra sharing a common edge bisected by a direct Mo–Mo bond which is proposed to account for the observed diamagnetism of the compound. Similar seven-coordinated configurations about given metal atoms involving short metal–metal distances, which arise from electron-pair coupling interactions, are found in the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion[27] (see

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(26) The orientation of the crystallographically independent cyclopentadienyl ring in each of the two dimeric molecules is such that the dihedral angle between the rigid-body plane of the cyclopentadienyl ring and the plane of the three monodentate ligands (*viz.*, the oxygen and the two sulfur atoms) coordinated to a given molybdenum atom is 174°. For a regular octahedron the opposite faces are, of course, parallel; the degree of angular deviation from a regular octahedron is indicated from the average observed S–Mo–S and S–Mo–O angles of 103 and 104°, respectively, rather than the 90°.

(27) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965).

Figure 4), $[Mo(OC_6H_5)_3Cl_2]_2$,[28] $[C_5H_5Fe(CO)_2]_2$,[29] and $[C_5H_5CrC_4F_6S_2]_2$.[30] The Mo–Mo bond length of 2.89 A in $[C_5H_5MoO]_2S_2$, which compares favorably to those found in Mo_2S_3 (2.85 A)[10] and $[Mo(OC_6H_5)_3Cl_2]_2$ (2.8 A),[28] is considerably longer than those observed in $[Mo(O_2CCH_3)_2]_2$ (2.11 A),[31] MoO_2 (2.50 and 3.10 A),[32] $Ba\{[MoO(C_2O_4)H_2O]_2O_2\}$ (2.54 A),[27] and in the $[Mo_6Cl_8^{4+}]$ cation (2.63 A),[33] but is substantially shorter than the direct Mo–Mo bond of 3.22 A found in $[C_5H_5Mo(CO)_3]_2$.[34] The average Mo–S bond length of 2.32 A can be compared to the average values of 2.36 and 2.57 A in Mo_2S_3[10] and to the average values of 2.49, 2.54, and 2.70 A in $[(C_2H_5OCS_2)_2MoO]_2O$.[35] The Mo–O bond length of 1.68 A in $[C_5H_5MoO_2]S_2$ is similar to the Mo–O (terminal) bond lengths in $[(C_2H_5OCS_2)_2MoO]_2O$ (1.65 A),[35] $K_2\{[MoO_2(C_2O_4)H_2O]_2O\}$ (1.69 A),[36] $Ba\{[MoO(C_2O_4)H_2O]_2O_2\}$ (1.70 A),[27] $CoMoO_4$ (1.72 A),[37] and (diethylenetriamine)MoO_3 (1.74 A).[38] The mean Mo–C cyclopentadienyl bond distance of 2.41 A in $[C_5H_5MoO]_2S_2$ is not unlike those of 2.38 A in $C_5H_5MoC_2H_5(CO)_3$,[39] 2.36 A in $C_5H_5MoC_3F_7(CO)_3$,[40] 2.34 A in $[C_5H_5Mo(CO)_3]_2$,[34] 2.33 A in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$,[41] 2.33 A in $C_5H_5Mo(\pi\text{-}CH_3SCH_2)(CO)_2$,[42] and 2.29 A in $(C_5H_5)_2MoH_2$.[43]

Attempts have been made to determine the atomic radii of the various formal oxidation states of molybdenum. Bennett and Mason suggested[44] an empirical assignment of radii on the basis of Mo–(cyclopentadienyl carbon) distances with the radius of the cyclopentadienyl carbon atom being taken as 0.77 A. The subtraction of this value from the Mo–C distances cited above leads to the following molybdenum radii: 1.61 A for Mo^{II} in $C_5H_5MoC_2H_5(CO)_3$, 1.59 A for Mo^{II} in $C_5H_5MoC_3F_7(CO)_3$, 1.57 A for Mo^{I} in $[C_5H_5Mo(CO)_3]_2$, 1.56 A for Mo^{II} in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$, 1.56 A for Mo^{II} in $C_5H_5Mo(\pi\text{-}CH_3SCH_2)(CO)_2$, 1.52 A for Mo^{IV} in $(C_5H_5)_2MoH_2$, and 1.64 A for Mo^{V} in $[C_5H_5MoO]_2S_2$. The inclusion of $[C_5H_5MoO]_2S_2$ appears to invalidate any possible systematic variation in molybdenum radii with formal oxidation states. The complex $(C_5H_5)_2MoH_2$ may possess shorter (and therefore stronger) Mo–C bonds due primarily to hydrogen atoms being poorer charge acceptors than carbonyl groups. One difficulty in the comparison of metal–(cyclopentadienyl carbon) distances is the effect on these bond lengths caused by librational motion of the cyclopentadienyl rings which varies considerably in transition metal cyclopentadienyl complexes. A molybdenum radius of approximately 1.6 A is also supported by both the $Mo\text{–}C_2H_5$ distance of 2.38 A (with an sp^3 carbon radius of 0.77 A) in $C_5H_5MoC_2H_5(CO)_3$[39] and by the presumed single-bond Mo–Mo distance of 3.22 A in the metal carbonyl complex $[C_5H_5Mo(CO)_3]_2$.[34,45]

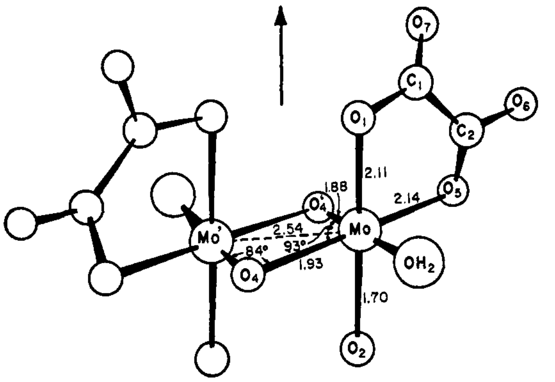

Figure 4. Configuration of the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion of crystallographic symmetry C_2-2.[27]

Yet from several oxygen-coordinated molybdenum complexes a consistent molybdenum radius of approximately 1.45 A can be derived. If the Mo–O bonds in the acetate and oxalate complexes given below are presumed to be single bonds,[31,46] an oxygen radius of 0.66 A[47] leads to atomic radii of 1.44 A for Mo^{II} in $[Mo(O_2CCH_3)_2]_2$,[31] 1.46 A for Mo^{V} in $Ba\{[MoO(C_2O_4)H_2O]_2O_2\}$,[27] and 1.48 A for Mo^{VI} in $K_2\{[MoO_2(C_2O_4)H_2O]_2O\}$.[36] This value of 1.45 A is further supported by the presumed single-bond Mo–S distance of 2.49 A reported for $[(C_2H_5OCS_2)_2MoO]_2O$,[35,48] from which an assumed single-bond sulfur radius of 1.04 A[47] leads to a Mo^{V} radius of 1.45 A. These available data also do not indicate any trend in atomic radii for the various formal oxidation states of molybdenum but rather support the premise that the type of substituent attached to the molybdenum atom is a dominant factor in determining the resulting bond lengths. It is noteworthy that the Mo–N bond lengths in (diethylenetriamine)$Mo(CO)_3$ (Mo^0)[49] and (diethylenetriamine)MoO_3 (Mo^{VI})[38] are not significantly different from each other, which indicates that the terminal oxo ligands and carbonyl groups have similar charge capacities in these complexes.

A detailed comparison of the structural features of $[C_5H_5MoO]_2S_2$ (Figure 1) with those of the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion (Figure 4) is informative. Each of these binuclear transition metal complexes can be considered as two distorted octahedra which are linked to each other along a common edge by a

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(28) Mitchell and Prout, unpublished work; cited by P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).

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(30) S. F. Watkins and L. F. Dahl, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 23-O, to be published.

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(36) F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

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(39) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

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(42) E. Rodulfo de Gil, L. F. Dahl, and R. B. King, to be published.

(43) M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).

(44) M. J. Bennett and R. Mason, *Nature*, **205**, 760 (1965).

(45) It should be noted that the dimeric complex $[C_5H_5Mo(CO)_3]_2$ is stabilized by only a Mo–Mo bond. All of the other molybdenum compounds with Mo–Mo interactions also contain metal-linked doubly or triply bridging ligands which make it difficult to assess accurately the bond orders associated with the Mo–Mo distances.

(46) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).

(47) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 224.

(48) Blake, Cotton, and Wood[35] attribute the lengthening of the other Mo–S bonds in $[(C_2H_5OCS_2)_2MoO]_2O$ to a *trans* effect caused by the oxygen atoms.

(49) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

metal–metal bond as well as by two bridging atoms. The three coordination sites occupied by the cyclopentadienyl ring in $[C_5H_5MoO]_2S_2$ are occupied by a water molecule and a chelating oxalate group in $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$. The short terminal Mo–O bond lengths in $[C_5H_5MoO]_2S_2$ (1.68 A) and in the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion (1.70 A) are equivalent and therefore correspond to a similar degree of multiple bonding in the two complexes; a bond order of 2.4–2.5 has been assigned to the terminal Mo–O bond in the anion.[27,46]

The bond lengths in the bridging systems of both $[C_5H_5MoO]_2S_2$ (2.32 A) and the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion (1.91 A) are also shorter than the corresponding estimated single-bond distances and thereby are characteristic of significant π bonding. A bond order of 1.3 was assigned by Cotton and Morehouse[27] to the bridging Mo–O bonds in the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion. The substantial π bonding in the $(MoS)_2$ bridging system of $[C_5H_5MoO]_2S_2$ is evidenced by the Mo–S bonds being 0.17 A shorter than the presumed single-bond Mo–S distance of 2.49 A in $[(C_2H_5OCS_2)_2MoO]_2O$.[35] However, no established relationship presently exists between Mo–S bond orders and internuclear distances.

A prominent structural difference between the two complexes is that while the $(MoS)_2$ system in $[C_5H_5MoO]_2S_2$ is rigorously planar, the $(MoO)_2$ system in the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion deviates markedly from planarity such that the two planes each formed by the two bridging oxygen atoms and one of the two molybdenum atoms are joined along the $O \cdots O$ line at a dihedral angle of 151°.[50] Cotton and Morehouse[27] rationalized the nonplanarity of the $(MoO)_2$ bridging system as a possible means of shortening the Mo–Mo distance without unduly lengthening the bridging Mo–O bonds or unduly expanding the O–Mo–O bond angles. Yet the observed S–Mo–S angle of 103° in $[C_5H_5MoO]_2S_2$ is 6° greater than the calculated O–Mo–O angle of 97° in a planar rhombic system based on the observed Mo–Mo and Mo–O bond lengths of the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion.

For dinuclear metal complexes with bridging ligand groups, it has been pointed out[51] that the observed diamagnetism may not necessarily be attributable to the formation of a distinct metal–metal bond *per se* but instead may be the consequence of either a superexchange coupling through the bridging ligand groups or a high spin–orbit coupling constant. Cotton and Morehouse[27] concluded that the Mo–Mo distance of only 2.54 A in the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion indicates that a direct metal–metal interaction is the dominant process. The longer Mo–Mo distance of 2.89 A in $[C_5H_5MoO]_2S_2$ suggests a weaker Mo–Mo direct interaction but the inseparability of the combined effects of the bridging atoms and direct metal–metal interaction on the resulting molecular geometry prevents any simple correlations of the metal–metal distance with the bond order (and bond strength) of the metal–metal interaction.

A qualitative representation of the nature of the bonding in these two Mo(V) complexes can be given in terms of simple MO theory based on octahedral-like symmetry. The unshared electron for each molybdenum atom can be placed in a d_{xy} orbital; a direct Mo–Mo interaction can then result from the overlap of these two neighboring orbitals which are directed toward each other. The unoccupied d_{xz} and d_{yz} orbitals of each molybdenum atom are utilized in the extensive π bonding with the filled π-type orbitals of both the terminal oxygen atom and the bridging atoms. This bonding description is consistent with that outlined for the direct metal–metal interaction between pairs of niobium atoms in α-NbI_4.[52,53]

No doubt some of the differences between $[C_5H_5MoO]_2S_2$ and the $\{[MoO(C_2O_4)H_2O]_2O_2\}^{2-}$ anion discussed above are attributable to the dissimilar nonbridging ligands coordinated to the molybdenum atoms in the two complexes. Since the similarity of the infrared spectra[6,8] of $[C_5H_5MoO]_2S_2$ and $[C_5H_5MoO_2]_2$ strongly suggests that the latter complex is the oxygen analog of the former compound, the structural determination of $[C_5H_5MoO_2]_2$ should be carried out to directly compare the $(MoO)_2$ and $(MoS)_2$ systems. Such a comparison would yield significant information concerning the degree of alteration of the molecular geometry of the $(MoX)_2$ system (especially the change in Mo–Mo distance) due to the interchange of first- and second-row congener elements as bridging groups. An additional incentive for this structural determination is the opportunity to determine the effect of the replacement of the bridging sulfur atoms with oxygen atoms on the Mo–(cyclopentadienyl carbon) bond distances.

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(50) The dihedral angles given in this discussion are defined as the angles directly between pairs of planes rather than as the angles between the normals to these planes.

(51) *Cf.* (a) J. Lewis in "Plenary Lectures of the VIIIth International Conference on Coordination Chemistry," Butterworth & Co. Ltd., London, 1965, pp 11–36; (b) W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.*, **86**, 3888 (1964).

(52) L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962); L. F. Dahl and D. L. Wampler, *J. Am. Chem. Soc.*, **81**, 3150 (1959).

(53) The structure of the solid α-NbI_4 and the isomorphous TaI_4 consist of infinite chains formed by MI_6 octahedra sharing two opposite edges; the metal atoms are shifted from the centers of the iodine octahedra toward one another in pairs to give a resulting metal–metal distance of 3.31 A.