Organometallic Chalcogen Complexes. XV. The Molecular Structure of a Molybdenum (π-CH_2SCH_3) Complex: $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$[1]

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Abstract: A structural determination of the King–Bisnette complex $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ has shown that the CH_2SCH_3 ligand does not at all behave as a olefinic-like unidentate ligand but instead effectively simulates an allylic group in its functioning as a bidentate ligand. The formulation of this ligand in the metal complex as a π-bonding, three-electron neutral donor (with two spin-paired electrons in the π orbital and one unpaired electron in the π^* orbital) is conceptually preferred even though the observed H_2C–S bond length value of 1.78 ± 0.01 Å is not indicative of any significant degree of multiple bond character. A comparison of its structural features with those of $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ and other related $Mo(\pi\text{-}C_5H_5)(CO)_2XY$ complexes is given. The relatively similar orientations of the (CH_2SCH_3) ligand and the allylic part of the $(p\text{-}CH_3C_6H_4CH_2)$ ligand with respect to the common $Mo(\pi\text{-}C_5H_5)(CO)_2$ fragment are found to be in accord with the stereochemical equivalence of the sulfur atom with two of the allylic carbon atoms. Crystals of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ are monoclinic with four monomeric molecules in a unit cell of symmetry $P2_1/n$ and dimensions $a = 13.57 \pm 0.02$ Å, $b = 7.97 \pm 0.01$ Å, $c = 9.70 \pm 0.01$ Å, $\gamma = 97° \pm 20'$. A full-matrix anisotropic–isotropic least-squares refinement with three-dimensional photographic data resulted in discrepancy factors of $R_1 = 8.3\%$ and $R_2 = 9.9\%$.

Several metal carbonyl complexes containing the new ligand (CH_2SCH_3) recently have been prepared by King and Bisnette[3] from the reactions between chloromethyl methyl sulfides and various metal carbonyl anions. From the reaction of $NaMo(\pi\text{-}C_5H_5)(CO)_3$ with $ClCH_2SCH_3$ in tetrahydrofuran at 25°, these workers isolated a yellow crystalline tricarbonyl complex $Mo(\pi\text{-}C_5H_5)(CO)_3(\sigma\text{-}CH_2SCH_3)$ which decarbonylates either by pyrolysis at 70° or by ultraviolet irradiation to give a stable yellow solid. The chemical analyses and osmometric molecular weight determination[4] of this latter compound established its molecular formula as $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$. The corresponding $W(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ and yellow liquid $Mn(CO)_4(\pi\text{-}CH_2SCH_3)$ were also synthesized.[3]

King and Bisnette[3] provided convincing evidence that the (CH_2SCH_3) ligand in the diamagnetic molybdenum tricarbonyl complex is σ-bonded through the methylene group to the molybdenum atom (*i.e.*, without any Mo–S linkage) on the basis of the compound's infrared, ultraviolet, and nmr spectra[5] and their similarities with those of the corresponding σ-bonded alkyl and phenyl derivatives, $Mo(\pi\text{-}C_5H_5)(CO)_3R$ (R = CH_3, C_2H_5, C_6H_5). The close analogies in method of preparation, stoichiometry, and physical properties[6-8] to the allylic complex $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}C_3H_5)$ led King and Bisnette[3] to propose a molecular structure for the dicarbonyl complex with the (CH_2SCH_3) ligand coordinated to the molybdenum atom both by metal–carbon and metal–sulfur bonds. Consistent with the nonequivalence of the two CH_2 protons in the compound's nmr spectrum, they further postulated two possible "limiting" modes of bonding of the neutral three-electron donating (CH_2SCH_3) ligand with the metal atom—one involving a carbon–sulfur double bond π-bonded to the molybdenum atom and the other containing a three-membered molybdenum–carbon–sulfur ring.

In order to gain more definite structural information concerning the nature of the carbon–sulfur interaction of this unusual organosulfur ligand with a transition metal, an X-ray analysis of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ was undertaken. A particular incentive for this investigation was the desire to determine from the detailed molecular parameters whether the (CH_2SCH_3) ligand can be best described in this metal complex as being stereochemically similar to many π-bonding simple olefins in effectively occupying only *one* coordination site of the metal atom (*e.g.*, analogous to the unidentate ethylene group in Zeise's salt, $K[(C_2H_4)PtCl_3]\cdot H_2O$[9]) or whether it instead behaves as a chelating bidentate ligand in an analogous fashion to a metal-coordinated allylic group by the formal occupation of *two* metal coordination sites.

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(1) Previous paper in this series: H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *J. Am. Chem. Soc.*, 90, 3272 (1968). The title of this series has been revised from "Sulfur" to "Chalcogen" in order to include preparative and structural work on oxygen, selenium, and tellurium complexes.

(2) This manuscript is based in part on a dissertation submitted by E. R. de Gil to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Aug 1968.

(3) R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964); *Inorg. Chem.*, 4, 486 (1965).

(4) *Anal.* Calcd for $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$: C, 38.8; H, 3.6; S, 11.5; Mo, 34.5; O, 11.5; mol wt, 278. Found: C, 38.9, 38.3; H, 3.6, 3.7; S, 11.2, 11.6; Mo, 33.5, 34.5; O, 11.1, 11.6; mol wt, 262.[3]

(5) The reported infrared spectrum[3] of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ taken in halocarbon oil mulls shows two strong absorption bands in the metal carbonyl region at 1838 and 1922 cm^{-1}. Other reported bands are at 3060 (vw), 1415 (m), 1305 (w), 1055 (w), 1003 (w), 963 (w), 807 (m), 778 (w), 715 (vw), and 686 (vw) cm^{-1}. The reported nmr proton spectrum[3] displays a characteristic AX pattern for the π-CH_2SCH_3 ligand with two nonequivalent but coupled CH_2 protons exhibiting two doublets at τ 7.33 and 8.11, $J = 6.0$ cps. Typical sharp singlet resonances at τ 4.85 and 8.12 are due to the cyclopentadienyl and methyl hydrogen atoms, respectively.

(6) The observance of four strong infrared metal carbonyl stretching frequencies in solutions of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}C_3H_5)$ and related species[7] (in contrast to only two infrared carbonyl solution bands in $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$) has been interpreted by Davison and Rode[8] from an nmr temperature-dependence study to result from a configurational equilibrium in solution between two π-allyl isomers which probably interconvert by internal rotation.

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Experimental Section

Unit Cell and Collection of Intensity Data. Orange crystals of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ were generously supplied to us by Dr. R. B. King of Mellon Institute (now at the University of Georgia). Precession and Weissenberg photographs, taken at room temperature with Mo Kα radiation, showed the crystals to be monoclinic with C_{2h}-2/m Laue symmetry. The lattice parameters[10] a = 13.57 ± 0.02 Å, b = 7.97 ± 0.01 Å, c = 9.70 ± 0.01 Å, γ = 97° ± 20′ were determined from $0kl$ and $hk0$ precession photographs taken on a camera whose settings were calibrated with a NaCl crystal; volume of the unit cell = 1041.3 Å^3. The calculated density of 1.77 g/cm^3 for four molecules per unit cell is consistent with the experimental value of 1.76 g/cm^3 determined by the flotation method in solutions of ethyl iodide and 2-iodopropane.

A crystal of approximate dimensions 0.15 × 0.10 × 0.20 mm was used for the gathering of intensity data. This crystal was mounted in a thin-walled glass capillary with the 0.20-mm direction (which approximately corresponds to the b axis) oriented along the spindle axis. Multiple-film equiinclination Weissenberg data for reciprocal levels $h0l$ through $h8l$ and timed-exposure precession data for $0kl$, $1kl$, $hk0$, and $hk1$ were taken with Zr-filtered Mo Kα radiation. The intensities of all reflections were visually estimated with a series of timed exposures of a selected reflection from the same crystal. Corrections were made for spot extension[11] and Lorentz-polarization effects, but no extinction or absorption corrections were applied. For Mo Kα radiation (λ 0.7107 Å) the linear absorption coefficient (μ) of 13.9 cm^{-1} results in a μR_{max} value of only 0.1 for which the variation of absorption correction factors with θ is negligible.[12] The Weissenberg and precession intensity data were placed on a single relative scale by a least-squares method[13] to give a total of 1761 independent reflections. The weighted disagreement factor for the least-squares merging was 5.7%.

The observed systematic absences, which are $\{hk0\}$ with $h + k$ odd and $\{00l\}$ with l odd, uniquely define $P2_1/n$ [nonstandard setting of $P2_1/b$ (C_{2h}^5, no. 14)][10] as the probable space group. Since all atoms were found to be in fourfold sets of general positions $\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z)$, the structural analysis required the location of one molybdenum, one sulfur, nine carbon, two oxygen, and ideally ten hydrogen atoms corresponding to one molecule as the crystallographically asymmetric unit.

Determination and Refinement of the Structure. A three-dimensional Patterson function[14] led to a self-consistent set of coordinates for the independent molybdenum and sulfur atoms. A first approximation to an electron density map[14] phased on the molybdenum and sulfur atoms was calculated, and an interpretation of this map yielded initial coordinates for the 11 remaining nonhydrogen atoms. Four cycles of isotropic least-squares rigid-body refinement[15] with the restriction of the cyclopentadienyl ring to a regular D_{5h} pentagon of bond length 1.41 Å gave discrepancy values of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ = 10.2% and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$ = 12.2%. One additional cycle of least squares with individual isotropic thermal parameters for all atoms but with no rigid-body constraints imposed on the cyclopentadienyl ring yielded the same discrepancy values but gave significant changes (greater than 3σ) in the corresponding coordinates of the carbon atoms in the cyclopentadienyl ring. Since a three-dimensional Fourier difference map[14] indicated some anisotropic electron density around the molybdenum and sulfur atoms, additional cycles of least-squares refinement without rigid-body constraints on the cyclopentadienyl ring were carried out with anisotropic thermal parameters for the molybdenum and sulfur atoms and isotropic ones for the carbon and oxygen atoms.[16] The discrepancy factors were reduced to R_1 = 8.3% and R_2 = 9.9%. During the last cycle no parameter changed by more than 0.05σ. The final positional parameters agreed within 1σ with the corresponding values from the isotropic nonrigid-body least-squares refinement. A final three-dimensional Fourier difference map based on the anisotropic–isotropic refinement showed no residual density greater than +1.8 e/Å^3 or less than −0.9 e/Å^3.

In these least-squares refinements the function minimized was $\Sigma w||F_o| - |F_c||^2$ where individual weights were assigned to the observed structure factors according to the function $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o(\text{min})$ and $\sqrt{w} = 1.25I_o^2/F_oI_o^2(\text{min})$ if $I_o < 4I_o(\text{min})$. The scattering factors reported by Thomas and Umeda[17] were utilized for molybdenum; for sulfur the scattering factors were those of Dawson,[18] while for carbon and oxygen the values used were those of Berghuis, *et al.*[19] Although no anomalous dispersion corrections of the scattering factors were made, the real and imaginary dispersion corrections for Mo Kα radiation are sufficiently small (*i.e.*, $\Delta f'$ = −1.7 and $\Delta f''$ = 0.9 for molybdenum; $\Delta f'$ = 0.1 and $\Delta f''$ = 0.2 for sulfur)[20] that their estimated net effect on the atomic coordinates of this centrosymmetric crystal was considered to be negligible.[21]

The positional and thermal parameters obtained from the output of the last cycle of the anisotropic–isotropic least-squares refinement are presented in Table I.[22] Intramolecular distances and bond angles together with estimated standard deviations, calculated with the Busing-Martin-Levy program[23] from the full inverse matrix (containing estimated lattice parameter uncertainties), are listed in Table II. Least-squares calculations[24] of "best" molecular planes formed by certain atoms and the perpendicular distances of these and other atoms from these planes are given in Table III.

Table I. Final Atomic Parameters with Estimated Standard Deviations of Last Significant Figures Given in Parentheses

Atom	x	y	z	B
Mo	0.0118 (0.5)	0.2415 (0.8)	0.2200 (1)	a
S	−0.0552 (1)	0.2784 (3)	0.4507 (3)	a
C_1	0.1861 (8)	0.2507 (14)	0.2230 (13)	4.4 (2)
C_2	0.1529 (8)	0.2576 (14)	0.0831 (13)	4.5 (2)
C_3	0.1108 (7)	0.4072 (13)	0.0639 (12)	4.1 (2)
C_4	0.1171 (8)	0.4973 (14)	0.1867 (13)	4.4 (2)
C_5	0.1622 (9)	0.4055 (15)	0.2867 (14)	5.1 (2)
C_6	−0.1505 (8)	0.1011 (14)	0.4954 (13)	4.4 (2)
C_7	−0.1065 (7)	0.3819 (13)	0.3114 (12)	4.1 (2)
C_8	−0.0945 (6)	0.1860 (11)	0.0939 (11)	3.0 (1)
C_9	−0.0140 (7)	0.0005 (13)	0.2382 (10)	3.9 (1)
O_8	−0.1593 (5)	0.1524 (9)	0.0134 (9)	4.7 (1)
O_9	−0.0334 (6)	−0.1508 (11)	0.2455 (8)	4.7 (1)

[a] 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 the molybdenum and sulfur atoms. The resulting thermal coefficients (×10^5) with esd of the last significant figure given in parentheses are

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	414 (4)	1004 (12)	974 (11)	24 (4)	−28 (6)	129 (10)
S	521 (14)	1395 (45)	901 (37)	−97 (18)	−14 (18)	75 (28)

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(10) The lattice dimensions and space group symmetry are based on the c direction (rather than the b direction) as the unique symmetry axis in the monoclinic system.

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Table II

A. Intramolecular Distances (Å) with Estimated Standard Deviations

Mo–S	2.442 (3)	Mo–C_1	2.35 (1)
Mo–C_7	2.24 (1)	Mo–C_2	2.32 (1)
Mo–M_{sc}[a]	2.18	Mo–C_3	2.32 (1)
Mo–N_{sc}[b]	2.16	Mo–C_4	2.36 (1)
		Mo–C_5	2.37 (1)
S–C_7	1.78 (1)		2.34 (av)
S–C_6	1.82 (1)	Mo–C_{cp}[c]	2.018
$C_6 \cdots C_7$	2.86 (1)		
Mo–C_8	1.903 (9)	C_1–C_2	1.43 (1)
Mo–C_9	1.918 (10)	C_1–C_5	1.39 (1)
		C_2–C_3	1.38 (1)
	1.910 (av)	C_3–C_4	1.40 (1)
		C_4–C_5	1.45 (1)
C_8–O_8	1.18 (1)		
C_9–O_9	1.20 (1)		1.41 (av)
	1.19 (av)		

B. Bond Angles (Degrees) and Estimated Standard Deviations

C_8–Mo–C_9	77.5 (4)	Mo–C_9–O_9	177.3 (9)
C_8–Mo–C_{cp}[c]	124.5 (7)	Mo–C_8–O_8	178.6 (8)
C_9–Mo–C_{cp}[c]	123.4 (7)		
C_8–Mo–C_7	78.5 (4)		178.0 (av)
C_8–Mo–S	109.3 (3)	Mo–C_7–S	73.5 (3)
C_9–Mo–C_7	114.0 (4)		
C_9–Mo–S	89.9 (3)	C_2–C_1–C_5	105 (1)
C_8–Mo–N_{sc}[b]	90.1 (6)	C_1–C_2–C_3	108 (1)
C_9–Mo–N_{sc}[b]	105.9 (7)	C_2–C_3–C_4	108 (1)
C_8–Mo–M_{sc}[a]	94.9 (6)	C_3–C_4–C_5	109 (1)
C_9–Mo–M_{sc}[a]	102.5 (7)	C_4–C_5–C_1	107 (1)
C_7–Mo–C_{cp}[c]	120.9 (7)		
S-Mo-C_{cp}[b]	119.6 (7)		107 (av)
N_{sc}[b]-Mo-C_{cp}[c]	123.1 (7)		
M_{sc}[a]–Mo–C_{cp}[c]	122.9 (8)		
C_7–Mo–S	44.4 (3)		
C_7–S–C_6	105.0 (5)		
Mo–S–C_6	111.9 (4)		
Mo–S–C_7	61.9 (3)		

[a] M_{sc} designates the midpoint between atoms S and C_7. [b] N_{sc} designates the point on the S–C_7 line such that the dot product between the (Mo–N_{sc}) and (S–C_7) vectors is zero (*i.e.*, the two vectors are perpendicular to each other). [c] C_{cp} is the centroid of C_5H_5.

Table III. Least-Squares Molecular Planes for the Unconstrained Refinement Model of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$

I. Equations of Best Planes[a,b] and Perpendicular Distances from These Planes (Å)

(A) Plane through C_1, C_2, C_3, C_4, and C_5			
$0.845X + 0.462Y - 0.269Z - 2.261 = 0$			
C_1	−0.001	C_8	−3.06
C_2	0.004	O_8	−3.69
C_3	−0.004	C_9	−3.04
C_4	0.004	O_9	−3.71
C_5	−0.002	S	−3.29
C_6	−4.99	Mo	−2.015
C_7	−3.21		
(B) Plane through C_8, O_8, C_9, O_9, and Mo			
$0.682X - 0.108Y - 0.724Z + 1.802 = 0$			
C_8	−0.01	C_7	−1.95
C_9	0.00	C_1	1.58
O_8	0.00	C_2	2.24
O_9	−0.00	C_3	1.76
Mo	0	C_4	0.82
S	−2.29	C_5	0.67
C_8	−3.22		
(C) Plane through S, C_7, C_8, and C_9			
$0.839X + 0.504Y - 0.205Z + 0.651 = 0$			
S	−0.00	C_6	−1.73
C_7	0.03	O_8	−0.70
C_8	−0.02	O_9	−0.70
C_9	0.02	C_{cp}	3.13
Mo	1.11		
(D) Plane through S, C_6, and C_7			
$0.474X - 0.592Y - 0.652Z + 4.620 = 0$			
C_6	0	S	0
C_7	0	Mo	2.06

II. Angles (Degrees) between Normals to Planes

A–B	44	B–C	48
A–C	4	B–D	31
A–D	72	C–D	77

[a] The equations of the planes are given in an orthogonal ångström coordinate system (X, Y, Z) which is related to the fractional unit cell coordinate system (x, y, z) as follows: $X = xa + yb \cos \gamma$, $Y = yb \sin \gamma$, $Z = zc$. [b] Individual weights were assigned to the atoms which form the planes according to the relation $W_k = [a\sigma(x_k)b\sigma(y_k)c\sigma(z_k)]^{-2/3}$ where $\sigma(x_k)$, $\sigma(y_k)$, and $\sigma(z_k)$ are the standard deviations in fractional coordinates of the atomic coordinates x_k, y_k, and z_k, respectively.

Results and Discussion

General Configuration. The $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ complex exists in the solid state as discrete monomeric molecules of point-group symmetry C_1-1. Figure 1 shows two views of the molecular configuration with pertinent molecular parameters; the basic geometry with the $Mo(\pi\text{-}C_5H_5)(CO)_2$ fragment coordinated to both the methylene carbon and sulfur atoms of the CH_2SCH_3 ligand is as predicted by King and Bisnette.[3] The arrangement of the four molecules in the unit cell is given in Figure 2. The closest intermolecular approaches of 3.43 Å for C···O contacts and 3.47 Å for C···C contacts are greater than van der Waals distances and hence indicate that no unusual intermolecular interactions exist in the crystalline state.

The molybdenum atom can be pictured as lying between two planes, one formed by the carbon atoms of the cyclopentadienyl group and the other passing through the two carbonyl carbon atoms and the methylene carbon–sulfur part of the CH_2SCH_3 ligand. As shown in Table III these two planes are within 4° of being parallel. This disposition of the cyclopentadienyl and two carbonyl ligands about the molybdenum atom in $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$ is scarcely different from that in other $Mo(\pi\text{-}C_5H_5)(CO)_2XY$ complexes[25–34] where either (1) X is arbitrarily designated as either a monodentate two-electron σ donor such as CO[25–30] or $P(C_6H_5)_3$,[31] and Y represents a monodentate one-electron σ donor such as CH_2CO_2H[29] or $Sn[Fe(\pi\text{-}C_5H_5)(CO)_2]_2Cl$;[30] or (2) X and Y together represent two coordination sites of a bidentate three-electron donor such as $H[Mo(\pi\text{-}C_5H_5)(CO)_2]P(CH_3)_2$[32] or $p\text{-}CH_3C_6H_4\text{-}CH_2$.[33] From angular considerations the resulting coordination sphere of the molybdenum atom in $Mo(\pi\text{-}$

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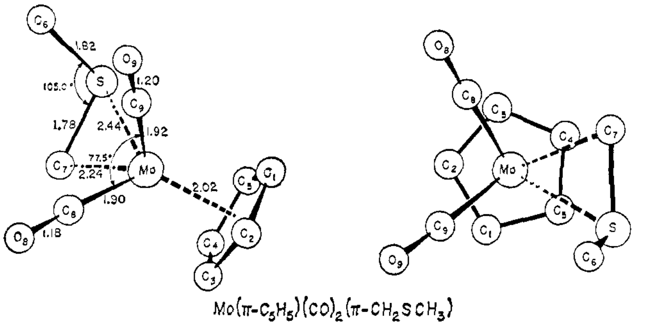

Figure 1. Molecular configuration of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$.

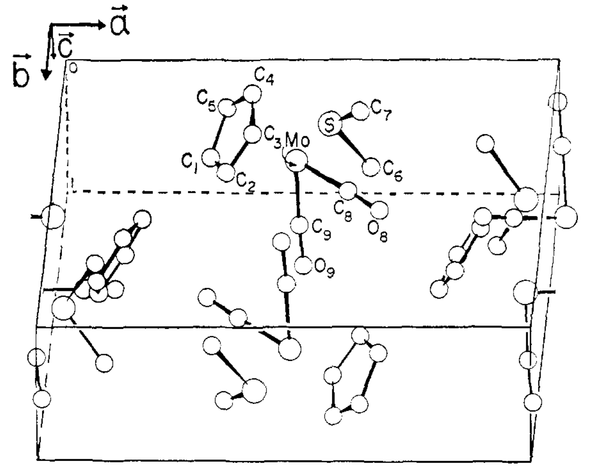

Figure 2. The arrangement of the four $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ molecules in the monoclinic unit cell of symmetry $P2_1/n$ (*c* axis unique).

$C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ approximates the heptacoordinated environment of the molybdenum atoms in the above complexes and of the niobium atom in $Nb(\pi\text{-}C_5H_5)(CO)_4$[34] rather than the hexacoordinated environment in organometallic tricarbonyl systems such as $Mo(CO)_3[NH_2(CH_2)_2NH(CH_2)_2NH_2]$,[35] $Mn(\pi\text{-}C_5H_5)(CO)_3$,[36] $Cr(\pi\text{-}C_6H_6)(CO)_3$,[37] and $Cr(\pi\text{-}C_4H_4S)(CO)_3$.[38] (These metal coordination numbers presume that the cyclopentadienyl, benzene, and thiophene rings in these complexes are stereochemically analogous to diethylenetriamine as tridentate ligands.) Thus, the observed OC–Mo–CO angle of 77.5° in $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ is in the same range as the *cis*-(OC–Mo–CO) angles reported in $[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$ (78.6° (av)),[26] $Mo(\pi\text{-}C_5H_5)(CO)_3C_2H_5$ (78.2° (av)),[27] $Mo(\pi\text{-}C_5H_5)(CO)_3C_3F_7$ (76.4° (av)),[28] $[Mo(\pi\text{-}C_5H_5)(CO)_2]_2(H)[P(CH_3)_2]$ (77.6° (av)),[32] $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ (76.6°),[33] and $Nb(\pi\text{-}C_5H_5)(CO)_4$ (73.9° (av)).[34] In contrast, the OC–metal–CO angles are invariably much larger with values clustered near 90° in *cis*-(diethylenetriamine)molybdenum tricarbonyl (85° (av)),[35] $Mn(\pi\text{-}C_5H_5)(CO)_3$ (92° (av)),[36] $Cr(\pi\text{-}C_6H_6)(CO)_3$ (88°(av)),[37] thiophenechromium tricarbonyl (89°),[38] as well as a large number of other hexacoordinated metal carbonyl complexes. The C_{cp}–metal–CO angles, where C_{cp} designates the centroid of the metal-coordinated $\pi\text{-}C_5H_5$ ring, were calculated to be within the range of 120–126° for both the hexacoordinated and heptacoordinated metal carbonyl complexes containing cyclopentadienyl rings and hence were not utilizable in the stereochemical characterization of the $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$. Nevertheless, it is obvious from the acute OC–Mo–CO angle that the (CH_2SCH_3) ligand in $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ does *not* at all behave as a unidentate ligand but instead effectively functions as a bidentate ligand as does a metal-chelated allylic group.

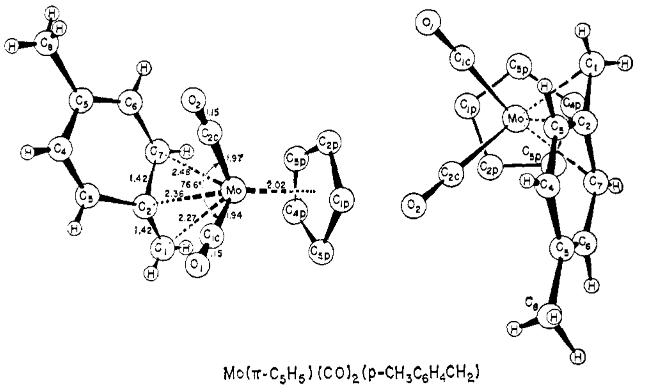

Figure 3. Molecular configuration of $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$.[33]

Stereochemical Relationship of $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ and $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$. It is not surprising then that the $Mo(\pi\text{-}C_5H_5)(CO)_2$ portion of the $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ molecule is closely related to the identical portion in $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$, where the *p*-methylbenzyl ligand is somewhat unsymmetrically attached to the molybdenum atom as an allylic group *via* the methylene carbon atom, the CH_2-bonded ring carbon atom, and one adjacent ring carbon atom. Figure 3 depicts the molecular configuration of $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ along with relevant molecular parameters for comparison with the corresponding ones of $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$. The X-ray investigation of this *p*-methylbenzyl metal complex by Cotton and LaPrade[33] was an outgrowth of the initial preparation by King and Fronzaglia[39] of $Mo(\pi\text{-}C_5H_5)(CO)_2(C_6H_5CH_2)$ as the first known (transition metal)-coordinated benzyl complex and the King-Fronzaglia discovery from nmr that this kind of organometallic molecule possesses fluxional character in solution. It is noteworthy that the formation of this π-allyl metal complex causes a breakdown to some extent in the π-electron delocalization in the phenyl ring as evidenced by a considerable alteration of bond lengths in the remaining four carbon atoms toward those of a *cis*-1,3-butadiene ring; the entire $p\text{-}CH_3C_6H_4CH_2$ ligand remains approximately planar on coordination with the $Mo(\pi\text{-}C_5H_5)(CO)_2$ fragment.[33]

From Figures 1 and 3 it is readily apparent that the methylene carbon atom, C_7, of the CH_2SCH_3 ligand corresponds to the exocyclic methylene carbon atom, C_1, of the allylic group, while the sulfur atom to a first approximation stereochemically occupies the site taken up by the other two allylic carbon atoms, C_2 and C_7, of the *p*-methylbenzyl ligand. This stereochemical equivalence of a divalent sulfur atom with two olefinic-

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like carbon atoms, which was anticipated in this case by King and Bisnette,[3] previously was found[38] in connection with the crystal structures of thiophenechromium tricarbonyl and benzenechromium tricarbonyl being essentially isomorphous with each other; an analogous isomorphous-like relationship between the crystal structures of "free" benzene and "free" thiophene was first suggested by Abrahams and Lipscomb[40] and later confirmed from an analysis of subsequent structural data by Bailey and Dahl.[38]

The relatively similar orientations of the (CH_2SCH_3) ligand and the allylic part of the $(p\text{-}CH_3C_6H_4CH_2)$ ligand with the common $Mo(\pi\text{-}C_5H_5)(CO)_2$ fragment in their respective molecules is made apparent from an examination of the corresponding bond lengths and angles. The approximate angular coincidence of the methylene C_7 atom in the (CH_2SCH_3) ligand and the exocyclic allyl C_1 atom in the $(p\text{-}CH_3C_6H_4CH_2)$ ligand is revealed from the corresponding values of 78.5° for the C_7–Mo–C_8 angle *vs.* 79.9° for the C_1–Mo–C_{1c} angle and 114.0° for the C_7–Mo–C_9 angle *vs.* 120.4° for the C_1–Mo–C_{2c} angle. The molybdenum–(methylene carbon) distance of 2.24 Å in the $(\pi\text{-}CH_2SCH_3)Mo$ complex closely resembles the corresponding distance of 2.27 Å in the $(p\text{-}CH_3C_6H_4CH_2)Mo$ complex but is significantly shorter than the Mo–CH_2 distances of 2.38 Å in $[Mo(C_{10}H_8)(CO)_3CH_3]_2$,[41] 2.40 Å in $Mo(\pi\text{-}C_5H_5)(CO)_3C_2H_5$,[27] and 2.41 Å in $Mo(\pi\text{-}C_5H_5)(CO)_3\text{-}CH_2CO_2H$.[29] This Mo–$CH_2$ bond length of 2.24 Å in $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$ is also 0.24 Å shorter than the Mo–C_7 distance of 2.48 Å from the molybdenum atom to the other terminal allylic carbon atom in $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$. In accord with the stereochemical equivalence of the sulfur atom in the $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$ molecule and the other two allylic carbon atoms (C_2 and C_7) in the $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ molecule, the sulfur atom is constrained by the molecular geometry to an equilibrium position which is oriented relative to those of the C_2 and C_7 atoms such that the S–Mo–C_8 angle of 109.3° is intermediate between the C_2–Mo–C_{1c} angle of 88.1° and the C_7–Mo–C_{1c} angle of 118.8°; the closeness of the S–Mo–C_9 angle of 89.9° with the C_2–Mo–C_{2c} angle of 89.4° and with the C_7–Mo–C_{2c} angle of 83.7° shows that the sulfur atom is similarly situated with respect to both the allyl C_2 and C_7 atoms.

The Mo–S bond length of 2.44 ± 0.01 Å is virtually identical with the Mo–S distances of 2.435 and 2.440 Å (indiv esd, 0.006 Å) in $Mo(\pi\text{-}C_5H_5)_2(S_2C_6H_3CH_3)$[42] and is close to the range of 2.46–2.51 Å for the four Mo–S bonds in $[(C_2H_5OCS_2)_2MoO]_2O$[43] which are not *trans* to Mo–O bonds; the mean value of 2.487 ± 0.007 Å for these four particular Mo–S bond lengths in the binuclear oxomolybdenum(V) xanthate complex is presumed by Blake, Cotton, and Wood[43] to represent a normal Mo^V–S bond distance. These Mo–S bond lengths are significantly greater than the Mo–S distances of 2.33 ± 0.02 Å (av) in $Mo(S_2C_2H_2)_3$,[44] which possesses a prismatic structure, and the Mo–S distances of 2.317 ± 0.003 Å (av) in $[C_5H_5MoO]_2S_2$;[45] in this latter molecule considerable π-bonding is proposed[45] to exist in the four-membered Mo_2S_2 ring bridging system.

The inability of this X-ray examination to locate the two methylene hydrogen atoms on C_7 precludes any attempt to determine the extent of deformation of the CH_2SCH_3 ligand from an idealized π-bonding geometry as a result of its coordination with the molybdenum atom. Although this ligand *per se* has not been isolated, if regarded as a π-bonding neutral free radical it necessarily must possess two spin-paired electrons in the π orbital and one unpaired electron in the π* orbital. On metal complexation the ligand thereby becomes a three-electron donor. This ligand no doubt would be more stable in "free" form as a positively charged methyl methylene sulfonium ion (because of the resultant loss of the antibonding electron) which on coordination with a metal would then donate its two remaining π electrons. In metal–(CH_2SCH_3) complexes these two possible formal views of the $(\pi\text{-}CH_2SCH_3)$ group as either a three-electron neutral ligand or a two-electron positively charged one are not distinguishable in terms of the ground-state electronic configuration. The alternative qualitative description of the mode of interaction of the (CH_2SCH_3) group with the molybdenum atom as a neutral three-electron donor involves the formation of electron-pair σ bonds within the three-membered Mo–C–S ring. Our preference for the π-bonding representation is that it conceptually offers a better rationalization for the H_2C–S bond possessing some multiple bond character even though the observed H_2C–S distance given below is not significantly different from the estimated single-bond C–S distance (which in general is subject to some variability with environment). In any event, a bookkeeping of electrons shows that the molybdenum atom in the $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$ molecule achieves a closed-shell electronic configuration in agreement with its diamagnetic character.

The observed H_2C–S bond length of 1.78 ± 0.01 Å in the $(CH_2SCH_3)Mo$ complex, which falls between the estimated double-bond C–S length of 1.61 Å[46] and the presumed single-bond C–S length of 1.82 Å,[46] indicates that no meaningful difference from a C–S single bond exists; the S–CH_3 bond length of 1.82 ± 0.01 Å is the expected single-bond distance. The methyl carbon of the (CH_2SCH_3) ligand is oriented at a perpendicular distance of 1.73 Å out of the mean plane formed by the molybdenum-coordinated C_7, S, C_8, and C_9 atoms in a direction away from the molybdenum atom with a H_2C–S–CH_3 angle of 105° and a Mo–S–CH_3 angle of 112°.

The π-Cyclopentadienyl Carbon Ring. The cyclopentadienyl carbon atoms are planar within 0.005 Å (Table IIIA). The individual carbon–carbon distances vary from 1.38 to 1.45 Å (indiv esd, 0.01 Å); the mean of the individual values is 1.41 Å. The two shortest Mo–C distances of 2.32 Å (indiv esd, 0.01 Å) involve the cyclopentadienyl carbon atoms, C_2 and C_3, which are *trans* to the sulfur atom of the (CH_2SCH_3) ligand; the longest Mo–C distance is from the molybdenum atom to C_5 which lies almost directly below the sulfur atom. These different Mo–C distances reflect the fact that the

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(46) S. C. Abrahams, *Quart Rev.* (London), 10, 407 (1956).

cyclopentadienyl carbon ring is tilted such that a line from the molybdenum atom to the centroid of the ring is not parallel with the normal to the ring at the centroid but instead forms an angle of 1.7°. A similar trend in the molybdenum to cyclopentadienyl carbon distances was observed[33] in $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ where the cyclopentadienyl ring is significantly tipped away from the allylic carbon atoms. Examination of the intramolecular bonding distances indicates that "steric compression" effects can satisfactorily account for the cyclopentadienyl ring tipping in both molecules; in the $(\pi\text{-}CH_2SCH_3)$-molybdenum complex the $S \cdots C_5$ and $H_2C \cdots C_4$ contacts are 3.40 and 3.29 Å, respectively. A similar "tilting" of the π-cyclopentadienyl ring as a general structural feature in the $Mo(\pi\text{-}C_5H_5)(CO)_2XY$ class of compounds was previously noted from a survey by Churchill and Fennessey.[28,31] Since the shortest Mo–C distances were usually observed for the cyclopentadienyl carbon atoms *trans* to the carbonyl groups, Churchill and Fennessey[28,31] attributed the systematic Mo–C variations to steric repulsion and/or a *trans* effect due to the greater π character in the molybdenum–carbonyl bonds. The average Mo–C distance of 2.34 Å and the perpendicular distance from the molybdenum to cyclopentadienyl ring of 2.02 Å in $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$ are identical with the corresponding values in $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ and are close to the corresponding values reported in the other $Mo(\pi\text{-}C_5H_5)(CO)_2XY$ molecules.[28,31]

A view of the environment of the molybdenum atom perpendicular to the cyclopentadienyl ring in $Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)$ (Figure 1) and in $Mo(\pi\text{-}C_5H_5)(CO)_2(p\text{-}CH_3C_6H_4CH_2)$ (Figure 3) shows almost the same relative orientation of the cyclopentadienyl ring with respect to the two carbonyls; a similar orientation of the cyclopentadienyl ligand relative to two carbonyl groups is observed in $[Mo(\pi\text{-}C_5H_5)(CO)_2]_2(H)[P(CH_3)_2]$[32] and in $Nb(\pi\text{-}C_5H_5)(CO)_4$.[34]

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Organometallic Chalcogen Complexes. XVI. Preparation and Structural Characterization of $Co_4(\pi\text{-}C_5H_5)_4S_6$. A New Mode of Transition Metal Bonding for a Disulfide Group[1]

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Abstract: The reaction of elemental sulfur with $Co(\pi\text{-}C_5H_5)(CO)_2$ has resulted in the synthesis of a new kind of organometallic sulfur complex, $Co_4(\pi\text{-}C_5H_5)_4S_6$. This air-stable, relatively insoluble compound was shown to be diamagnetic from its nmr spectrum which revealed four separate, equivalent resonances characteristic of four nonequivalent cyclopentadienyl rings. Its stereochemical characterization as a tetranuclear cobalt complex was ascertained from a three-dimensional X-ray diffraction study carried out on a crystal of stoichiometry $Co_4(\pi\text{-}C_5H_5)_4S_6 \cdot {}^1/_2CHCl_3$. This solvated crystal contains eight formula species in a monoclinic unit cell of symmetry $P2_1/c$ and dimensions $a = 25.618 \pm 0.010$ Å, $b = 10.604 \pm 0.004$ Å, $c = 19.295 \pm 0.008$ Å, $\beta = 105°\,43' \pm 04'$. The structure, determined by the application of the Hauptman–Karle symbolic addition method, was refined by rigid-body isotropic least squares of the automatically collected diffractometry data to an unweighted R_1 discrepancy index of 11.7%. The molecular structure consists of a distorted tetrahedral array of C_5H_5Co units interconnected by two triply bridging disulfide S_2 groups and two triply bridging sulfur atoms located above the four triangular faces of the distorted tetrahedron of nonbonding cobalt atoms. This molecular complex supplies a heretofore "missing link" in organometallic chemistry in its exemplification of an S_2 ligand covalently coordinated as a four-electron donor with three metal atoms. The one crystallographically independent chloroform molecule is closely associated by presumed hydrogen bonding with only one of the two crystallographically independent $Co_4(\pi\text{-}C_5H_5)_4S_6$ molecules. The detailed molecular features are compared with those of related molecular complexes.

Although a wide assortment of cobalt–sulfur atom carbonyl clusters synthesized by Markó, Bor, and coworkers[3–9] have been crystallographically characterized (*e.g.*, $Co_3(CO)_9S$,[10] $[Co_3(CO)_7S]_2S_2$,[11] Co_2Fe-

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(1) (a) Previous paper in this series: E. R. de Gil and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3751 (1969); (b) presented in part at the First International Symposium of Inorganica Chimica Acta on "New Aspects of the Chemistry of Metal Carbonyls and Derivatives," Venice, Italy, Sept 2–4, 1968; see *Proc. Inorg. Chim. Acta*, B1 (1969).

(2) This manuscript is based in part on a dissertation submitted by V. A. Uchtman to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, July 1968.

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