Volume 22
Number 21
October 12, 1983

Inorganic Chemistry

Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80309

# Syntheses and Structures of New Molybdenum Complexes with Dithiobenzoate and Dimercaptotoluene Ligands. Structural Comparisons in a Series of Dithiolate-Bridged Dimers of Molybdenum(III)

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*Received November 9, 1982*

The reaction of $[C_5H_5Mo(CO)_3]_2$ with $Zn(S_3CC_6H_5)_2$ has resulted in the formation of two new molybdenum complexes containing the dithiobenzoate ligand, $C_5H_5Mo(CO)_2S_2CC_6H_5$ (I) and $[C_5H_5Mo(S)S_2CC_6H_5]_2$ (II). Dimer II has been characterized by an X-ray diffraction study. The complex crystallizes in space group $P2_1/n$ with $a$ = 16.708 (4) Å, $b$ = 22.510 (4) Å, $c$ = 6.465 (1) Å, and $\beta$ = 94.88 (1)°. The molecule consists of disulfido-bridged dimers with $\eta^5$-$C_5H_5^-$ and bidentate $S_2CC_6H_5^-$ ligands coordinated to each molybdenum ion. A syn orientation of ligands is observed with the two dithiobenzoate ligands in approximately parallel orientations. The metal–metal distance is 3.073 (1) Å, and in the $Mo_2S_2$ core the dihedral angle between the $Mo(1)S_2$ and $Mo(2)S_2$ planes is 126°. The reaction of $[C_5H_5Mo(CO)_3]_2$ with dimercaptotoluene also results in the formation of two new products. $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$ (III) is proposed to be a single isomer of low symmetry on the basis of spectral data. Irradiation of III produces $[C_5H_5MoS_2C_6H_3(CH_3)]_2$ (IV), which is isostructural with the previously reported dimer $[C_5H_5Mo(SC_2H_2S)]_2$ (V). X-ray diffraction data for IV and V are presented. IV crystallizes in space group $P2_1/c$ with $a$ = 12.065 (2) Å, $b$ = 6.403 (2) Å, $c$ = 16.134 (3) Å, and $\beta$ = 111.53 (1)°. The cell parameters for V in space group *Cmca* are $a$ = 10.440 (1) Å, $b$ = 13.199 (2) Å, and $c$ = 11.015 (2) Å. The structural features of an extensive series of molybdenum(III) dimers of the general formula $[C_5H_5Mo(\mu\text{-}SR)_2]_2$ are compared.

## Introduction

We have observed that dimeric cyclopentadienyl complexes of molybdenum(III) with various bridging 1,2-alkanedithiolate ligands are subject to reactions with alkenes and alkynes in which the hydrocarbon portion of the bridging ligand is exchanged.[2] These systems have been the subjects of synthetic, structural, mechanistic, and theoretical investigations.[2-4] During the course of this work, we became interested in the synthesis of isostructural complexes with other types of chelating sulfur ligands. In this paper we report the syntheses and characterization of four new cyclopentadienylmolybdenum complexes with the anions of 3,4-dimercaptotoluene and 1,1-dithiobenzoic acid as ligands. The complexes have been characterized by spectral methods, and the structures of two dimeric derivatives have been confirmed by X-ray diffraction studies. The bis(dimercaptotoluene) derivative $[C_5H_5MoS_2C_6H_3(CH_3)]_2$ is isostructural with previously reported molybdenum(III) dimers. Several structural parameters in this series of tetrathio-bridged dimers are compared. The dimeric dithiobenzoate derivative $[C_5H_5Mo(S)S_2CC_6H_5]_2$ involves a new structural type for Mo(IV). Structural parameters for this complex have been compared to those of related structures of Mo(V).

## Results and Discussion

**Syntheses and Characterization of Dithiobenzoate Complexes of Molybdenum.** The perthiobenzoate complex of zinc, $Zn(S_3CC_6H_5)_2$, has been used previously as a source of this sulfur-rich ligand in simple room-temperature metathesis reactions with metal halides.[5] The reaction of this zinc complex with $[C_5H_5Mo(CO)_3]_2$ in refluxing benzene has led to the synthesis of two new products that contain the dithiobenzoate ligand. A monomeric complex has been characterized as $C_5H_5Mo(CO)_2S_2C(C_6H_5)$. Spectral data are reported in Table I. Many other complexes with the general formula $C_5H_5Mo(CO)_2LX$ are known;[6] a sulfur donor analogue with a chelating dithiocarbamate ligand, $C_5H_5Mo(CO)_2(S_2CNR_2)$ ($R = CH_3, C_2H_5$), has been reported previously.[7] The second molybdenum product isolated from the reaction with $Zn(S_3CC_6H_5)_2$ can be formulated as the dimer $[C_5H_5MoS_3CC_6H_5]_2$ on the basis of elemental analyses and mass spectral data. No absorptions characteristic of the S–S stretch of the perthiobenzoate ligand were observed in the infrared spectrum of the complex, and an X-ray diffraction study of a single crystal confirms that the sulfur-rich ligand is not intact. The molecule consists of discrete disulfido-bridged dimers with a $\eta^5$-cyclopentadienyl and a chelating dithiobenzoate ligand coordinated to each molybdenum. No metal–metal interaction is likely.

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[1] Alfred P. Sloan Fellow, 1981–1983; Camille and Henry Dreyfus Teacher-Scholar, 1981–1986.
[2] Rakowski DuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.
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[5] Fackler, J. P.; Coucouvanis, D.; Fetchin, J. A.; Seidel, W. C. *J. Am. Chem. Soc.* **1968**, *90*, 2784.
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0020-1669/83/1322-2973$01.50/0

**Table I.** Spectral Data for Toluenedithiolate and Dithiobenzoate Complexes of Molybdenum

| compd | IR $\nu_{C\equiv O}$,[a] cm$^{-1}$ | $^1$H NMR,[b] ppm | visible,[c] nm | $\epsilon \times 10^{-3}$, M$^{-1}$ cm$^{-1}$ | MS, *m/e* |
|---|---|---|---|---|---|
| $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$ | 1930<br>1980 | 2.36 (s, 6, $-CH_3$)<br>5.50, 4.66 (2s, 10, Cp)[d]<br>6.87, 7.57, 7.65, 7.79 (m, 6, Ar) | 434<br>534 | 5.0<br>9.2 | 630 (P − 2CO)<br>540 (P − $(CO)_2C_7H_6$)<br>476 (P − $(CO)_2S_2C_7H_6$)<br>315 $(P - 2CO)^{2+}$ |
| $[C_5H_5MoS_2C_6H_3(CH_3)]_2$ | | 1.97 (s, 6, $-CH_3$)<br>5.56 (s, 10, Cp)<br>6.25, 6.35, 6.90, 6.97 (m, 6, Ar) | 352<br>602 | 4.8<br>0.7 | 630 (P)<br>540 (P − $C_7H_6$)<br>476 (P − $S_2C_7H_6$)<br>315 ($P^{2+}$) |
| $[C_5H_5Mo(S)S_2CC_6H_5]_2$ | | 5.80 (s, 10, Cp)<br>7.00, 7.10, 7.67, 7.77 (m, 10, Ar) | 347<br>516<br>610<br>694 | 21<br>9.0<br>sh<br>2.8 | 692 (P)<br>571 (P − $SC_7H_5$)<br>450 (P − $2SC_7H_5$) |
| $C_5H_5Mo(CO)_2S_2CC_6H_5$ | 1905<br>1945 | 5.50 (s, 5, Cp)<br>7.46, 8.00 (m, 5, Ar) | 546 | 11 | 370 (P)<br>342 (P − CO)<br>314 (P − 2CO) |
| $C_5H_5Mo(S_2CC_6H_5)[S_2C_6H_3(CH_3)]$ | | 2.52 (s, 3, $-CH_3$)<br>4.90 (s, 5, Cp)<br>7.20–7.70, 8.13, 8.23 (m, 8, Ar) | 486<br>797 | 14<br>0.5 | 468 (P)<br>347 (P − $SC_7H_5$)<br>315 (P − $S_2C_7H_6$) |

[a] In $CCl_4$ solution. [b] In $CDCl_3$. [c] In $CH_2Cl_2$. [d] The Cp resonances maintain equal intensities in the following solvents: $CS_2$, $C_6D_6$, $CDCl_3$.

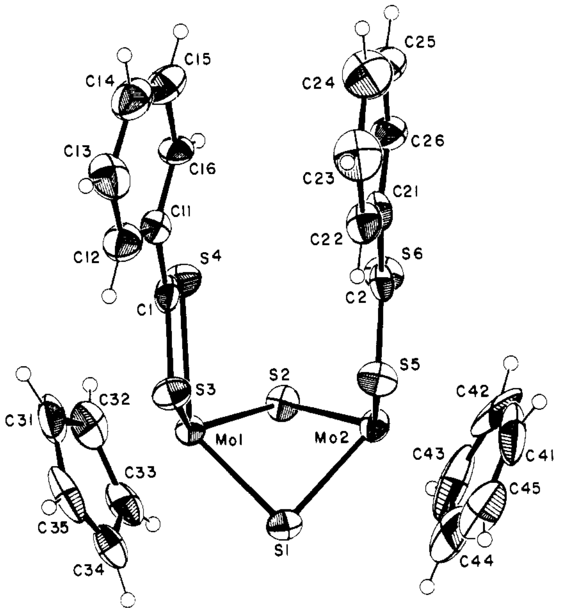

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**Figure 1.** Perspective drawing and numbering scheme for $[C_5H_5Mo(S)S_2CC_6H_5]_2$. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

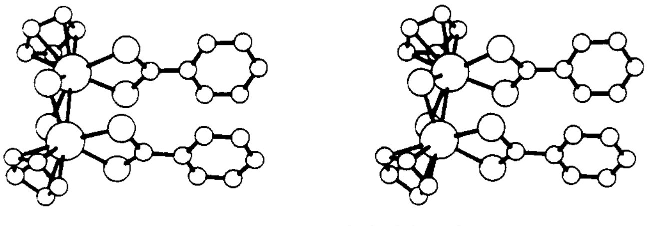

**Figure 2.** Stereoview of $[C_5H_5Mo(S)S_2CC_6H_5]_2$.

The structural details for this unusual Mo(IV) dimer are discussed below.

The monomeric complex seems a likely intermediate in the dimer formation. However, attempts to synthesize the dimer by refluxing $C_5H_5Mo(CO)_2S_2CC_6H_5$ with elemental sulfur were unsuccessful. Photolysis of the monomer with ultraviolet light in the presence of excess ligand was a useful approach to the synthesis of oxidized carbonyl-free complexes. For example, irradiation in the presence of elemental sulfur led to the formation of the dimer discussed above, $[C_5H_5Mo^{IV}S_3CC_5H_6]_2$, and the photosubstitution reaction with dimercaptotoluene has led to the synthesis of $C_5H_5Mo^{IV}(S_2CC_6H_5)(S_2C_6H_3(CH_3))$, which has been characterized spectrally (Table I). The latter monomeric complex is an analogue of each molybdenum coordination sphere in the dimer.

**Table II.** Selected Bond Distances and Angles for $[C_5H_5Mo(S)S_2CC_6H_5]_2$[a]

| | | | |
|---|---|---|---|
| Distances, Å | | | |
| $Mo_1$–$S_1$ | 2.319 (2) | $C_{11}$–$C_1$ | 1.460 (11) |
| $Mo_1$–$S_2$ | 2.331 (2) | C–$C_{11-16}$(av) | 1.380 (12) |
| $Mo_1$–$S_3$ | 2.530 (2) | C–$C_{31-35}$(av) | 1.391 (13) |
| $Mo_1$–$S_4$ | 2.489 (2) | $Mo_1$---$Mo_2$ | 3.073 (1) |
| $S_3$–$C_1$ | 1.701 (8) | $S_3$---$S_4$ | 2.812 (3) |
| $S_4$–$C_1$ | 1.683 (8) | $S_1$---$S_2$ | 3.120 (3) |
| Angles, deg | | | |
| $S_1$–$Mo_1$–$S_2$ | 84.27 (8) | $C_1$–$S_3$–$Mo_1$ | 88.81 (28) |
| $S_1$–$Mo_1$–$S_4$ | 131.72 (8) | $C_1$–$S_4$–$Mo_1$ | 90.60 (29) |
| $S_1$–$Mo_1$–$S_3$ | 87.52 (7) | $S_3$–$C_1$–$S_4$ | 112.38 (45) |
| $S_2$–$Mo_1$–$S_4$ | 86.90 (7) | $S_3$–$C_1$–$C_{11}$ | 124.14 (63) |
| $S_2$–$Mo_1$–$S_3$ | 137.36 (8) | $S_4$–$C_1$–$C_{11}$ | 123.43 (61) |
| $S_3$–$Mo_1$–$S_4$ | 68.13 (7) | $Mo_1$–$S_1$–$Mo_2$ | 82.84 (7) |

[a] Dihedral angle between planes $S_1$–$Mo_1$–$S_2$ and $S_1$–$Mo_2$–$S_2$ is 126.3°.

Both the monomeric and dimeric Mo(IV) complexes with $CpS_4$ ligation show sharp NMR spectra characteristic of diamagnetic complexes. This suggests a singlet ground state for the $d^2$ metal ions in each complex. The electrochemical behavior of these two complexes in $CH_3CN$ has been compared. While the monomeric derivative $C_5H_5Mo(S_2C(C_6H_5))(S_2C_6H_3(CH_3))$ undergoes two reversible reductions at −0.74 and −1.06 V vs. SCE,[8] the disulfido-bridged dimer shows no reduction activity at a Pt electrode. Each of the complexes undergoes a quasi-reversible oxidation near +0.7 V vs. SCE.[9] Several disulfido-bridged dimers of Mo(V) have been found to undergo one or two reversible reductions in nonaqueous solvents.[10-12] These have been associated with the formation

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[8] Cyclic voltammetry was carried out at a Pt electrode with 0.1 M $(n\text{-}C_4H_9)_4NBF_4$ in acetonitrile; scan rate = 0.10 V/s. For the reductions of $C_5H_5Mo(S_2CC_6H_5)(S_2C_6H_3CH_3)$, $\Delta E_p$ = 60 mV and $i_{pc}/i_{pa} \simeq 0.9$.

[9] For the oxidation of $C_5H_5Mo(S_2CC_6H_5)(S_2C_6H_3CH_3)$, the current intensity is approximately twice that of the reductions, suggesting a two-electron process; $\Delta E_p$ = 200 mV and $i_{pc}/i_{pa} \simeq 1$. For the oxidation of $[C_5H_5Mo(S)S_2CC_6H_5]_2$, $\Delta E_p$ = 130 mV.

[10] Bunzey, G.; Enemark, J. H.; Howie, J. K.; Sawyer, D. T. *J. Am. Chem. Soc.* **1977**, *99*, 4168.

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of Mo(V)–Mo(IV) and, in some cases, Mo(IV)–Mo(IV) dimers.

Table III. Positional Parameters for the Atoms of $[C_5H_5Mo(S)S_2CC_6H_5]_2$

| atom | *x* | *y* | *z* |
|---|---|---|---|
| $Mo_1$ | 0.72380 (4) | 0.176642 (28) | 0.15231 (11) |
| $Mo_2$ | 0.89779 (4) | 0.165390 (28) | 0.03685 (11) |
| $S_1$ | 0.84067 (13) | 0.14885 (9) | 0.3475 (3) |
| $S_2$ | 0.77906 (13) | 0.12522 (8) | −0.1143 (3) |
| $S_3$ | 0.73918 (14) | 0.27772 (9) | 0.3222 (3) |
| $S_4$ | 0.69502 (14) | 0.25853 (9) | −0.1019 (3) |
| $S_5$ | 0.93119 (14) | 0.26729 (9) | 0.1702 (3) |
| $S_6$ | 0.88309 (14) | 0.24147 (9) | −0.2468 (3) |
| $C_1$ | 0.7106 (5) | 0.3093 (3) | 0.0885 (13) |
| $C_2$ | 0.9099 (5) | 0.2943 (3) | −0.0711 (12) |
| $C_{11}$ | 0.7033 (5) | 0.3732 (3) | 0.0539 (12) |
| $C_{12}$ | 0.6949 (6) | 0.4118 (4) | 0.2197 (14) |
| $C_{13}$ | 0.6863 (6) | 0.4730 (4) | 0.1873 (16) |
| $C_{14}$ | 0.6877 (6) | 0.4941 (4) | −0.0108 (17) |
| $C_{15}$ | 0.6966 (6) | 0.4565 (4) | −0.1756 (14) |
| $C_{16}$ | 0.7037 (5) | 0.3960 (3) | −0.1392 (13) |
| $C_{21}$ | 0.9095 (5) | 0.3586 (3) | −0.1238 (13) |
| $C_{22}$ | 0.9187 (5) | 0.4004 (4) | 0.0343 (14) |
| $C_{23}$ | 0.9146 (7) | 0.4598 (4) | −0.0131 (17) |
| $C_{24}$ | 0.9015 (7) | 0.4783 (4) | −0.2224 (19) |
| $C_{25}$ | 0.8946 (7) | 0.4367 (4) | −0.3742 (16) |
| $C_{26}$ | 0.8974 (5) | 0.3771 (4) | −0.3263 (14) |
| $C_{31}$ | 0.5867 (6) | 0.1812 (4) | 0.1811 (18) |
| $C_{32}$ | 0.6020 (5) | 0.1336 (4) | 0.0552 (15) |
| $C_{33}$ | 0.6468 (6) | 0.0918 (4) | 0.1783 (16) |
| $C_{34}$ | 0.6604 (5) | 0.1128 (4) | 0.3782 (15) |
| $C_{35}$ | 0.6236 (7) | 0.1675 (5) | 0.3798 (17) |
| $C_{41}$ | 1.0320 (6) | 0.1572 (4) | −0.0015 (27) |
| $C_{42}$ | 0.9932 (10) | 0.1257 (8) | −0.1628 (18) |
| $C_{43}$ | 0.9562 (7) | 0.0773 (6) | −0.068 (3) |
| $C_{44}$ | 0.9753 (9) | 0.0839 (6) | 0.124 (3) |
| $C_{45}$ | 1.0192 (7) | 0.1301 (6) | 0.1732 (19) |

**Structural Study of $[C_5H_5Mo(S)S_2C(C_6H_5)]_2$.** The numbering scheme and a stereoview of the molecule are shown in Figures 1 and 2, respectively, and selected bond distances and angles and positional parameters are presented in Tables II and III, respectively. The idealized symmetry of the molecule is $C_{2v}$; no symmetry is imposed by the space group, but the bond distances and angles around the two molybdenum ions are very similar. The two dithiobenzoate ligands are aligned in a roughly parallel orientation with the average distance between phenyl rings equal to 3.70 Å. The bond distances and angles in these chelating dithio ligands are similar to those observed in other metal dithiobenzoate complexes.[13-15] In the previously characterized monomeric Mo(IV) complex, $Mo(S_2CC_6H_5)_4$, the S–Mo–S and S–$C_1$–S angles are slightly smaller (66.8 (1)° and 110.8°, respectively) and the Mo–S distances are longer than in the structure presented here.[15] These differences may be a result of the higher coordination number of the monomeric complex. Inspection of the data indicates that the two dithiobenzoate ligands in $[C_5H_5Mo(S)S_2CC_6H_5]_2$ are neither planar nor parallel. The planar phenyl ring numbered $C_{11}$–$C_{16}$ is twisted by 19.0° from the plane defined by $Mo_1$ and the $CS_2$ portion of the ligand. The plane of the second phenyl ring is rotated in the same direction from its $MoS_2C$ plane by 10.3°. A somewhat smaller ligand twist (6.6°) has been observed in the dithiobenzoate ligands of $Mo(S_2CC_6H_5)_4$.[15]

Several disulfido-bridged dimers of Mo(V) containing a $[Mo_2S_2Y_2]^{2+}$ unit (Y = O, NR, S) are known, and structural characterizations of both syn and anti isomers have been reported.[16,17] The nonplanar $Mo_2S_2$ ring of the Mo(IV) dimer reported here is structurally related to those of the syn Mo(V) dimers. Pertinent structural parameters of these complexes have been summarized previously;[16] they are presented again in Table IV with a recent addition.[17] While relatively little variation is observed in the tabulated structural parameters of the Mo(V) complexes, considerable differences are observed for some of these parameters in the Mo(IV) structure. For example, the $S_b$–Mo–$S_b$ angle and the $S_b$–$S_b$ distance in $[C_5H_5Mo(S)S_2CC_6H_5]_2$ are 84.34 (8)° and 3.120 (3) Å, respectively, considerably smaller than the average values in the Mo(V) dimers of 101° and 3.6 Å. These differences can be attributed to the larger coordination number of the Mo(IV) ions, each of which has a characteristic "piano-stool" geometry. For comparison, the OC–Mo–CO angles in monomeric complexes with related geometries, $C_5H_5Mo(CO)_3X$, are in the range of 75–78°.[18] Since the M–S distances in the $Mo_2S_2$ core of $[C_5H_5Mo(S)S_2CC_6H_5]_2$ do not vary significantly from those in the Mo(V) structures, the smaller $S_b$–Mo–$S_b$ angle results in an elongation of the core along the direction of the M–M axis. The Mo–Mo distance is increased to 3.07 Å, and the $Mo_1$–$S_b$–$Mo_2$ angle is 82.77 (7)° compared to average values of 2.82 Å and 76 (1)° in the Mo(V) systems.

In the Mo(V) dimers the terminal ligands bend back away from each other, and the dihedral angle between the $MoS_2$ planes of the core ranges from 147° to 161°. These geometric features have been attributed, in part, to the combination of effects produced by M–M bonding and ligand–ligand repulsions in the metal coordination spheres.[19,20] For example, in the dimers with terminal sulfido ligands, the distance between metal ions is less than the van der Waals contact distance

Table IV. Selected Structural Parameters of *syn*-$[LMo(\mu\text{-}S)Y]_2$ Complexes

| complex | Mo-Mo, Å | Mo-$Y_t$, Å | Mo-$S_b$, Å | Mo-L, Å | $S_b$-$S_b$, Å | Mo-$S_b$-Mo, deg | $S_b$-Mo-$S_b$, deg | dihedral angle, deg | ref |
|---|---|---|---|---|---|---|---|---|---|
| *syn*-$Mo_2S_4(S_2CN(C_4H_9)_2)_2$ | 2.801 (2) | 1.937 (6)[b] | 2.308 (4) | S 2.447 (6) | | 74.7 (1) | 101.8 (6) | 148 | 24 |
| *syn*-$Mo_2O_2S_2$(cysMe)$_2$[e] | 2.804 (4) | 1.71 (3)[a] | 2.30 (1) | S 2.38 (1)<br>N 2.24 (3) | 3.58 | 74.9 (4) | 101.8 (5) | 149 (1) | 25 |
| *syn*-$Na_2Mo_2S_2O_2$(cys)$_2$[f] | 2.82 (1) | 1.62 (3)[a] | 2.33 (1) | S 2.50 (1)<br>N 2.27 (3)<br>O 2.37 (3) | | 75 (1) | 103.0 (1) | 156.0 | 26 |
| *syn*-$Na_2Mo_2S_2O_2$(his)$_2$[g] | 2.82 (1) | 1.71 (2)[a] | 2.32 (2) | N 2.24 (2)<br>O 2.23 (2) | 3.64 (2) | 74.9 (5) | 103.8 (5) | 160.9 | 27 |
| *syn*-$Cs_2Mo_2S_2O_2$(EDTA) | 2.799 (1) | 1.683 (6)[a] | 2.294 (1) | O 2.111 (9)<br>N 2.448 (8)<br>O 2.37 (3) | | 75.2 (1) | 102.1 (1) | 152.3 | 28 |
| *syn*-$[(n\text{-}C_4H_9)_4N]_2$-$[Mo_2O_2S_2(i\text{-mnt})_2]$[c] | 2.821 (2) | 1.664 (7)[a] | 2.300 (1) | S 2.434 (3) | | 75.8 (1) | 101.6 (1) | 153.1 | 29 |
| *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ | 2.863 (2) | 2.100 (4)[b] | 2.320 (3) | S 2.406 (3) | 3.550 (4) | 76.22 (9) | 99.85 (10) | 146.9 (1) | 16 |
| *syn*-$(\eta^5\text{-}(CH_3)_5C_5)_2Mo_2S_2O_2$ | 2.808 (1) | 1.710 (5)[a] | 2.286 (2) | C 2.409 | | 75.8 | 101.5 | 152.0 | 17 |
| *syn*-$[C_5H_5Mo(S)S_2CC_6H_5]_2$ | 3.073 (1) | 2.505 (2)[d] | 2.324 (7) | C 2.313 (9) | 3.120 (3) | 82.77 (7) | 84.34 (8) | 126.3 | this work |

[a] Terminal oxo ligand. [b] Terminal sulfido ligand. [c] *i*-mnt is isomaleonitriledithiolate, $S_2C_2(CN)_2^{2-}$. [d] Average Mo–S distance of dithiobenzoate ligands. [e] CysMe, cysteine methyl ester. [f] Cys, cysteine. [g] his, histidine.

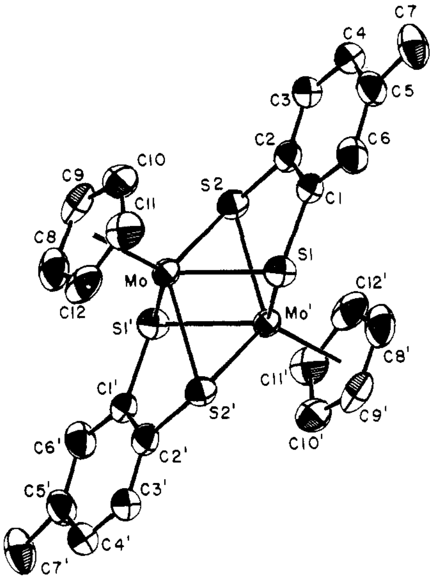

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Figure 3. Perspective drawing and numbering scheme for $[C_5H_5MoS_2C_6H_3(CH_3)]_2$. Thermal ellipsoids are drawn at the 50% probability level.

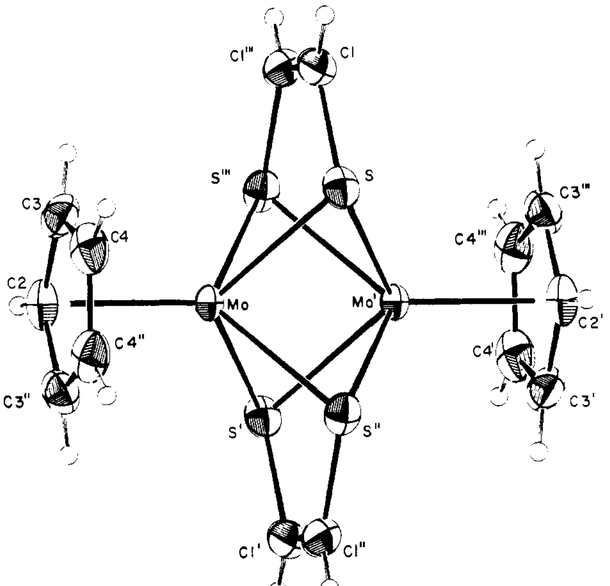

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Figure 4. Perspective drawing and numbering scheme for $[C_5H_5MoSC_2H_2S]_2$. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Table V. Atomic Positional Parameters

$[C_5H_5MoS_2C_6H_3(CH_3)]_2$

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 0.06771 (6) | 0.0651 (1) | −0.04063 (5) |
| $S_1$ | 0.1103 (2) | −0.2588 (4) | 0.0462 (2) |
| $S_2$ | 0.0986 (2) | 0.1748 (4) | 0.1124 (1) |
| $C_1$ | 0.2200 (7) | −0.189 (2) | 0.1517 (6) |
| $C_2$ | 0.2147 (8) | 0.011 (2) | 0.1829 (6) |
| $C_3$ | 0.2943 (8) | 0.078 (2) | 0.2638 (6) |
| $C_4$ | 0.3827 (8) | −0.061 (2) | 0.3156 (6) |
| $C_5$ | 0.3880 (9) | −0.265 (2) | 0.2855 (6) |
| $C_6$ | 0.3069 (8) | −0.332 (2) | 0.2015 (6) |
| $C_{7a}$ | 0.480 (2) | −0.408 (3) | 0.348 (1) |
| $C_{7b}$ | 0.468 (2) | −0.007 (5) | 0.401 (2) |
| $C_8$ | 0.2518 (9) | 0.072 (2) | −0.0516 (7) |
| $C_9$ | 0.164 (1) | −0.002 (2) | −0.1332 (8) |
| $C_{10}$ | 0.0850 (9) | 0.160 (2) | −0.1709 (6) |
| $C_{11}$ | 0.1195 (10) | 0.337 (2) | −0.1155 (7) |
| $C_{12}$ | 0.222 (1) | 0.286 (2) | −0.0428 (7) |

$[C_5H_5MoSC_2H_2S]_2$

| atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| Mo | 0 | 0.08157 (1) | 0.06418 (2) |
| S | 0.14053 (5) | −0.06260 (4) | 0.11341 (4) |
| $C_1$ | 0.2918 (2) | −0.0271 (2) | 0.0498 (3) |
| $C_2$ | 0 | 0.2514 (2) | 0.0675 (3) |
| $C_3$ | 0.1093 (2) | 0.2199 (2) | 0.1339 (2) |
| $C_4$ | 0.0667 (3) | 0.1691 (2) | 0.2387 (2) |
| $HC_1$ | 0.355 (3) | −0.045 (2) | 0.096 (5) |
| $HC_2$ | 0 | 0.291 (3) | −0.009 (5) |
| $HC_3$ | 0.188 (4) | 0.216 (3) | 0.111 (6) |
| $HC_4$ | 0.117 (4) | 0.142 (3) | 0.291 (4) |

Table VI. Selected Bond Distances and Angles for 1,2-Arene- and 1,2-Alkenedithiolate-Bridged Dimers

| | | | |
|---|---|---|---|
| | $[C_5H_5MoS_2C_6H_3(CH_3)]_2$ | | |
| | Distances, Å | | |
| Mo–Mo′ | 2.580 (2) | $S_1$–$C_1$ | 1.788 (9) |
| Mo–$S_1$ | 2.449 (2) | $S_2$–$C_2$ | 1.784 (9) |
| Mo–$S_1'$ | 2.453 (2) | Mo–$C_{cp}$(av) | 2.299 (10) |
| Mo–$S_2$ | 2.454 (2) | C–$C_{aryl}$(av) | 1.398 (13) |
| Mo–$S_2'$ | 2.460 (2) | C–$C_{cp}$(av) | 1.414 (15) |
| $C_5$–$C_7$ | 1.509 (19) | $S_1$---$S_2'$ | 2.907 (3) |
| $S_1$---$S_2$ | 2.997 (3) | | |
| | Angles, deg | | |
| Mo–$S_1$–Mo′ | 63.51 (6) | $S_1$–$C_1$–$C_2$ | 117.4 (7) |
| Mo–$S_2$–Mo′ | 63.35 (6) | $S_2$–$C_2$–$C_1$ | 116.2 (7) |
| Mo–$S_1$–$C_1$ | 105.0 (3) | $S_1$–$C_1$–$C_6$ | 121.3 (8) |
| Mo′–$S_1$–$C_1$ | 103.9 (3) | $S_2$–$C_2$–$C_3$ | 122.3 (8) |
| Mo–$S_2$–$C_2$ | 105.5 (3) | C–C–$C_{aryl}$(av) | 120.0 (9) |
| Mo′–$S_2$–$C_2$ | 104.4 (3) | C–C–$C_{cp}$(av) | 108.0 (1) |
| $S_1$–Mo–$S_1'$ | 116.49 (6) | $S_1$–Mo–$S_2'$ | 72.73 (8) |
| $S_1$–Mo–$S_2$ | 75.25 (8) | $S_2$–Mo–$S_2'$ | 116.65 (6) |
| | $[C_5H_5MoSC_2H_2S]_2$ | | |
| | Distances, Å | | |
| Mo–Mo′ | 2.576 (1) | $C_1$–$C_1'''$ | 1.310 (6) |
| Mo–S | 2.463 (4) | C–$C_{cp}$(av) | 1.412 (4) |
| Mo–S′ | 2.458 (1) | | |
| Mo–$C_{cp}$(av) | 2.303 (2) | S---S‴ | 2.996 (1) |
| S–$C_1$ | 1.790 (3) | S---S″ | 2.934 (1) |
| | Angles, deg | | |
| S′–Mo–S″ | 73.29 (3) | Mo–S–$C_1$ | 103.70 (8) |
| S′–Mo–S | 116.87 (1) | Mo′–S–$C_1$ | 103.99 (9) |
| S′–Mo–S‴ | 74.99 (2) | S–$C_1$–$C_1'''$ | 118.09 (8) |
| S–Mo–S‴ | 73.11 (3) | C–C–$C_{cp}$(av) | 108.0 (2) |
| Mo–S′–Mo′ | 63.13 (1) | | |

between sulfurs, and the terminal sulfido ligands are bent back to give a $S_t$–$S_t$ distance of 3.8–3.9 Å. In the molybdenum(IV) dimer presented here, it appears that the longer M–M and M–$S_{dithiobenzoate}$ distances help to decrease the potential for contact repulsions between sulfur atoms in the coordination spheres. As a result, the structure has a smaller dihedral angle as well as a more acute angle between bridging and apical sulfurs. Other electronic effects may also be contributing to the structural differences observed for this disulfido-bridged dimer.

**Synthesis and Characterization of Dimercaptotoluene Complexes.** The reaction of bis(cyclopentadienyltricarbonylmolybdenum) with 3,4-dimercaptotoluene in refluxing methylcyclohexane yields as the major product a dimer containing the anion of dimercaptotoluene as well as carbonyl ligands.

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(13) Bonamico, M.; Dessy, G. *Chem. Commun.* **1968**, 483.

(14) Coucouvanis, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1968**, *90*, 3281; **1969**, *91*, 307.

(15) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. *J. Chem. Soc., Dalton Trans.* **1975**, 2079.

(16) Bunzey, G.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 682.

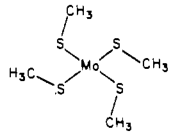
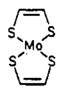
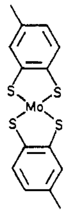
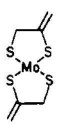
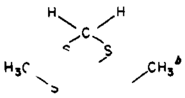
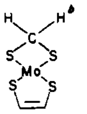
(17) Dahl, L. F., private communication.

(18) (a) Churchill, M. R.; Fennessey, J. R. *Inorg. Chem.* **1967**, *6*, 1213. (b) *Ibid.* **1968**, *7*, 953. (c) Dahl, L. F.; de Gil, E. R. *J. Am. Chem. Soc.* **1969**, *91*, 3751.

(19) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 52.

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

Table VII. Selected Structural Data for the $Mo_2S_4$ Cores of Neutral and Cationic Dimers of Formula $[C_5H_5Mo(SR)_2]_2$

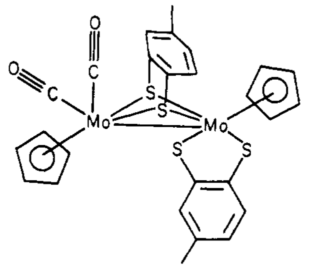
| core of $[CpMo(SR)_2]_2$[a] | M-M, Å | M-S (av), Å | M-S-M, deg | S---S$_{intra}$ | S---S$_{inter}$ | ref |
|---|---|---|---|---|---|---|
|  1 | 2.603 (2) | 2.46 (1) | 64.0 (2) | | 2.96 (1) | 30 |
|  2 | 2.576 (1) | 2.460 (1) | 63.13 (1) | 2.996 (1) | 2.934 (1) | this work |
|  3 | 2.580 (1) | 2.454 (2) | 63.51 (6) | 2.997 (3) | 2.907 (3) | this work |
|  4 | 2.592 (1) | 2.435 (2) | 64.28 (4) | 2.969 (2) | 2.860 (2) | 31 |
|  5 | 2.596 (1) | 2.450 (1) | 64.00 (4) | 2.673 (2), 2.823 (2) | 3.119 (2) | 22 |
|  6 | 2.601 (1) | 2.460 (1) | 63.90 (4) | 2.866[c] | 3.035[c] | 22 |

[a] A view down the metal-metal vector is shown; Cp ligands have been omitted. [b] Structure contains $CH_3C_5H_4$ ligands. [c] Structure is disordered; average values are given.

Table VIII. Crystal Data

| | | | |
|---|---|---|---|
| formula | $C_{24}H_{20}Mo_2S_6$ | $C_{24}H_{22}Mo_2S_4$ | $C_{14}H_{14}Mo_2S_4$ |
| $M_r$ | 694.704 | 630.58 | 502.403 |
| space group | $P2_1/n$ | $P2_1/c$ | $Cmca$ |
| $a$, Å | 16.708 (4) | 12.065 (2) | 10.440 (1) |
| $b$, Å | 22.510 (4) | 6.403 (2) | 13.199 (2) |
| $c$, Å | 6.465 (1) | 16.134 (3) | 11.015 (2) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 94.88 (1) | 111.53 (1) | 90 |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 2422.4 (8) | 1159.5 (5) | 1517.8 (4) |
| $d_c$, g cm$^{-3}$ | 1.90 | 1.81 | 2.20 |
| $d_o$, g cm$^{-3}$ | 1.88 | 1.80 | 2.18 |
| $Z$ | 4 | 2 | 4 |
| $F$(000) | 1376 | 628.0 | 984 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 15.22 | 14.13 | 21.3 |

The empirical formula $C_5H_5Mo(CO)S_2C_6H_3(CH_3)$ has been established by elemental analyses, and the dimeric nature has been confirmed by mass spectral data. In the NMR spectrum two singlets are attributed to the cyclopentadienyl ligands, and two carbonyl stretches are observed in the infrared spectrum (Table I). The data indicate either that the complex is of low symmetry with inequivalent ligand environments or that two isomers, each with symmetrically equivalent cyclopentadienyl ligands, are present in solution. It has been proposed that the related nitrosyl complex $[CpMo(NO)S_2C_6H_3(CH_3)]_2$ exists as a mixture of isomers.[21] However, we believe that the carbonyl analogue is a species of low symmetry on the basis of spectral data that suggest a structure with two different metal environments such as that shown below (I). The chemical shifts of the two cyclopentadienyl resonances at 5.50 and 4.66 ppm are comparable to those observed for two monomeric derivatives with coordination spheres similar to the ones proposed for I. The Cp resonance of $CpMo(CO)_2S_2CC_6H_5$ occurs at 5.50 ppm and that of $CpMo(S_2CC_6H_5)(S_2C_6H_3CH_3)$ at 4.90 ppm. In addition, the relative intensities and frequencies of the infrared carbonyl stretches are similar for the dimer and the dicarbonyl monomeric complex (Table I).



I

Attempts to thermally substitute the carbonyl ligands in the dimer with other $\pi$ acceptors, such as isonitriles, were unsuccessful. Upon irradiation with ultraviolet light, the above purple complex loses carbon monoxide to form the green dimer

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(21) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 3308.

Table IX. Crystallographic Data: Experimental Conditions and Solution and Refinement Details

| | $C_{24}H_{20}Mo_2S_6$ | $C_{24}H_{22}Mo_2S_4$ | $C_{14}H_{14}Mo_2S_4$ |
|---|---|---|---|
| cryst size, mm | 0.45 × 0.34 × 0.02 | 0.4 × 0.4 × 0.6 | 0.48 × 0.85 × 0.64 |
| cell parameter, refinement, no. of reflcns | 25 | 10 | 25 |
| $2\theta$ limits, deg | $3.0 < 2\theta < 45.0$ | $2.0 < 2\theta < 50.0$ | $3.0 < 2\theta < 70.0$ |
| scan speed, deg min$^{-1}$ | 2.0–24.0 | 4.0–24.0 | 2.0–24.0 |
| scan range, deg | 0.8 below $K\alpha_1$ to 0.8 above $K\alpha_2$ | 1.2 below $K\alpha_1$ to 1.4 above $K\alpha_2$ | 1.0 below $K\alpha_1$ to 1.0 above $K\alpha_2$ |
| no. of data points | | | |
| measd | 3862 | 2155 | 1763 |
| obsd ($F_o^2 < 3.0\sigma(F_o^2)$) | 2240 | 1519 | 1476 |
| absorption correction | yes | none | none |
| max, min, transmission coeff | 0.970, 0.561 | | |
| phase determination | direct methods, MULTAN 78 | Patterson methods | direct methods, MULTAN 78 |
| least-squares refinement | full matrix | full matrix | full matrix |
| hydrogen contribution | fixed idealized isotropic | not included | isotropic refined |
| weighting scheme | | based on counting statistics | |
| final residuals | | | |
| $R$ | 0.036 | 0.053 | 0.027 |
| $R_w$ | 0.044 | 0.065 | 0.035 |
| no. of variables | 289 | 145 | 64 |
| ratio of observations to parameters | 8 | 10 | 23 |
| esd of an observation of unit weight | 1.217 | 1.87 | 1.131 |

$[C_5H_5MoS_2C_6H_3(CH_3)]_2$. A single cyclopentadienyl resonance is observed in the NMR spectrum of this complex, and its visible spectrum is simlar to those observed for dimers with bridging alkenedithiolate ligands.[2]

**Crystallographic Characterizations of 1,2-Arenedithiolate- and 1,2-Alkenedithiolate-Bridged Dimers.** X-ray diffraction studies of the bis(mercaptotoluene) derivative have been completed. The compound is isostructural with previously characterized Mo(III) dimers and is most closely related in structure to the bis(ethenedithiolate) complex $[C_5H_5MoSC_2H_2S]_2$.[2] The structural characterizations of both complexes are presented here. Perspective drawings of the two molecules shown in Figures 3 and 4 illustrate the basic similarities of the dimers, both of which have the two dithiolate ligands situated in a plane perpendicular to the metal–metal vector. Positional parameters and bond distances and angles for the two complexes are listed in Tables V and VI, respectively. $[C_5H_5MoSC_2H_2S]_2$ is located in the unit cell about a position of $2/m$ symmetry with the midpoint between the molybdenum atoms situated at the center of inversion at (000). This is consistent with the density that indicated one-fourth of a molecule per asymmetric unit or four molecules per unit cell. $[C_5H_5MoS_2C_6H_3(CH_3)]_2$ crystallizes in the centrosymmetric space group $P2_1/c$ with a symmetry of $C_{2h}$.

It is instructive to compare these two structures with those of other neutral cyclopentadienylmolybdenum(III) dimers with bridging thiolate ligands. Selected data for a series of these isostructural complexes are summarized in Table VII. Many of the structural parameters are comparable for the entire series of compounds. For example, the Mo–S bond distances are generally in the range of 2.45–2.46 Å, and the M–S–Mo′ angles are 63–64°.

However, some structural trends are observed as the nature of the thiolate ligands is varied. In particular, a comparison of the structures with two alkenedithiolate ligands, **2**, **3**, and **4**, with that of the monothiolate-bridged derivative, **1**, shows that the intraligand S–S distances are longer and the interligand distances shorter in the dithiolate derivatives. These distortions can be attributed to the angles required at the $sp^2$-hybridized carbons in the hydrocarbon linkages of the ligands. Since the metal–sulfur distances do not change very much in **1**, **2**, or **3**, the sulfur atom distortions result in a corresponding change in M–M distances. As the span of the dithiolate ligand is increased, the M–S–M angles are compressed slightly and the M–M distance is decreased from 2.60 Å in **1** to 2.58 Å in **2** and **3**. Complex **4** involves relatively short M–S distances compared to the other dimers. These short bonds contribute to the short interligand distances between sulfur atoms in this dimer. The most striking structural features in the complexes with a methanedithiolate ligand, **5** and **6**, are the extremely short intraligand S–S distances. These structures have been discussed in more detail elsewhere.[22]

## Experimental Section

**Reagents.** Reagent grade bis(cyclopentadienyltricarbonylmolybdenum) was purchased from Strem Chemicals. Technical grade (98%) 3,4-dimercaptotoluene was purchased from Aldrich and used without further purification. (Perthiobenzoato)zinc(II), $Zn(S_3C_7H_5)_2$, was prepared by the method reported previously.[5] Most solvents were reagent grade and used without further purification. Chloroform was passed through an alumina column just prior to use, and acetonitrile used in cyclic voltammetric experiments was distilled from $CaH_2$ and $P_2O_5$. Electrometric grade tetra-*n*-butylammonium tetrafluoroborate was purchased from Southwestern Analytical Chemicals Inc. and dried under vacuum before use. Reagent grade alumina (pH 6–8) from Baker was used for all column chromatography.

**Physical Measurements.** Proton NMR were recorded at 90 MHz on a Varian EM-390 spectrometer. Reported chemical shifts are referenced to tetramethylsilane. Infrared spectra of Nujol mulls or of $CCl_4$ solutions were measured on a Perkin-Elmer 337 spectrophotometer. Mass spectra were recorded on a Varian MAT-CH5 spectrometer and reported as $m/e$'s based on $^{96}Mo$. A Cary 219 spectrophotometer was used to obtain visible spectra. Cyclic voltammetry was carried out by using a conventional three-electrode cell supplied by Princeton Applied Research and a PAR 174A polarographic analyzer. A platinum wire was used as the working electrode. Elemental analyses were provided by Spang Laboratory.

**X-ray Crystallography.** Data for the structures (Table VIII) were collected at 25 °C on a Syntex $P\bar{1}$ autodiffractometer using Mo $K_\alpha$ radiation monochromatized by a graphite crystal. The procedures, which were similar for all three structures, are summarized in Table IX. The cell parameters were refined by least-squares fit of the parameters as noted in the table. The measured data were corrected for Lorentz and polarization effects.[23] Data were corrected for absorption as noted in Table IX. Salient features of the solution and refinement of the structures are also given in the table.

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(22) McKenna, M.; Miller, D. J.; Wright, L. L.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(23) The data reduction routine was written in this laboratory. All other programs used in the solution and refinement of these structures are contained or based on Dr. J. A. Ibers' Northwestern University Crystallographic Computing Package and Dr. P. Main's MULTAN78 package. The scattering factors used were for neutral atoms as given in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

**Syntheses. $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$.** $[C_5H_5Mo(CO)_3]_2$ (2.3 g, 4.7 mmol) and 3,4-dimercaptotoluene (1.5 g, 9.6 mmol) were refluxed in 50 mL of methylcyclohexane under nitrogen for 18 h to form a dark purple solution. The solvent was removed by rotoevaporation, and the resulting solid was chromatographed without protection from air on a 2.5 × 25 cm column. Elution with benzene gave first a minor green fraction ($[C_5H_5MoS_2C_6H_3(CH_3)]_2$) and then the purple product. The solvent was removed and the sample was dried in vacuo for 12 h; yield 2.7 g, 84%. Anal. Calcd for $C_{26}H_{22}O_2S_4Mo_2$: C, 45.58; H, 3.23; S, 18.68. Found: C, 45.54, H, 3.43; S, 18.62. Yield of $[C_5H_5MoS_2C_6H_3(CH_3)]_2$: 0.3 g, 10%.

**$[C_5H_5MoS_2C_6H_3(CH_3)]_2$.** $[C_5H_5Mo(CO)S_2C_6H_3CH_3]_2$ (0.69 g, 1.0 mmol) was photolyzed with a Hanovia 450-W Hg arc lamp in a quartz submersible well in 350 mL of toluene for 3.5 h. The resulting green solution was rotoevaporated to dryness, and the solid was washed with acetone to remove any remaining starting complex; yield 0.47 g, 74%. Anal. Calcd for $C_{24}H_{22}S_4Mo_2$: C, 45.71; H, 3.52; S, 20.33. Found: C, 45.85; H, 3.58; S, 20.35.

**$C_5H_5Mo(CO)_2S_2CC_6H_5$ and $[C_5H_5Mo(S)S_2CC_6H_5]_2$.** $[C_5H_5Mo(CO)_3]_2$ (1.0 g, 2.0 mmol) and $Zn(S_3CC_6H_5)_2$ (0.87 g, 2.0 mmol) were refluxed under nitrogen in 50 mL of benzene for 20 h. The purple solution was filtered in air; the resulting brown precipitate was washed with $CH_2Cl_2$ until washings were colorless and then discarded. The filtrate was evaporated to dryness. Addition of 75 mL of diethyl ether dissolved the red purple complex $C_5H_5Mo(CO)_2S_2CC_6H_5$. The ether solution was filtered and evaporated; the monomeric product was further purified by column chromatography eluting with 10:1 hexanes/$CH_2Cl_2$; yield 0.74 g, 49%. Anal. Calcd for $C_{14}H_{10}O_2S_2Mo$: C, 45.40; H, 2.72; S 17.32. Found: C, 45.54; H, 2.82; S, 17.17. The black ether-insoluble product was recrystallized from $CH_2Cl_2$ and found to be $[C_5H_5Mo(S)S_2CC_6H_5]_2$; yield 0.34 g, 24%. Anal. Calcd. for $C_{24}H_{20}S_6Mo_2$: C, 41.62; H, 2.91; S, 27.77. Found: C, 41.44; H, 2.98; S, 27.60.

**Photolytic Reaction of $C_5H_5Mo(CO)_2S_2CC_6H_5$ with Sulfur.** The monomeric complex (0.71 g, 1.9 mmol) and sulfur (0.36 g, 1.4 mmol) were photolyzed under nitrogen in the apparatus described above in 350 mL of toluene for 2 h. $[C_5H_5Mo(S)S_2CC_6H_5]_2$ was isolated by using the procedure described above; yield 0.28 g, 43%. No reaction was observed when toluene solutions of the monomeric complex were refluxed under nitrogen with excess sulfur for 48 h.

**$C_5H_5Mo(S_2CC_6H_5)(S_2C_6H_3(CH_3))$.** $C_5H_5Mo(CO)_2S_2CC_6H_5$ (0.51 g, 1.4 mmol) and 3,4-dimercaptotoluene (0.11 g, 0.70 mmol) were photolyzed under nitrogen in the apparatus described above in 400 mL of toluene for 3 h. The solvent was removed by rotoevaporation, and the residue was chromatographed with a 4:1 toluene/hexanes solution to give the red product; yield 0.11 g, 35%. Anal. Calcd. for $C_{19}H_{16}S_4Mo$: C, 48.72; H, 3.42; S, 27.35. Found: C, 48.88; H, 3.56; S, 27.26.

**Attempted Reactions of $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$ with an Isocyanide.** The molybdenum complex (0.10 g, 0.14 mmol) and excess *n*-butyl isocyanide (0.4 mmol) were refluxed in $CHCl_3$ for 6 days. The starting complex was recovered and identified by IR and NMR spectra.

**Acknowledgment.** Support for this work from the donors of the Petroleum Research Fund, administered by the American Chemical Society, from the National Science Foundation, and, in part, from the Department of Energy, Office of Basic Energy Sciences, and the University of Colorado Computing Center is gratefully acknowledged.

**Registry No.** I, 86885-25-8; II, 86885-24-7; III, 86885-22-5; IV, 86885-23-6; V, 86885-26-9; $C_5H_5Mo(S_2CC_6H_5)[S_2C_6H_3(CH_3)]$, 86900-63-2.

**Supplementary Material Available:** Complete listings of bond lengths and angles, tables of thermal parameters, and tables of observed and calculated structure amplitudes (96 pages). Ordering information is given on any current masthead page.

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# Crystal Structure and Low-Temperature Crystal Spectra of Dicesium *trans*-Dichlorotetraaquotitanium(III) Chloride

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*Received January 26, 1983*

$Cs_2TiCl_5{\cdot}4H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.565$ (1) Å, $b = 9.3077$ (8) Å, $c = 9.2813$ (8) Å, $\beta = 116.44$ (1)°, and $Z = 2$. The structure was refined by full-matrix least squares to $R = 0.048$ for 1205 reflections having $I > 3\sigma(I)$ and $2\theta < 50°$. The crystals contain *trans*-$[TiCl_2(H_2O)_4]^+$ ions that lie on crystallographic centers of symmetry. The Ti–Cl, Ti–O(1), and Ti–O(2) distances are 2.400 (2), 2.033 (5), and 2.046 (6) Å, respectively. The $Cs^+$ ions are coordinated to eight chloride ligands at the corners of a distorted square antiprism; the average Cs–Cl distance is 3.62 (1) Å. The optical spectra that originate from the $^2E_g$ ($D_{4h}$) ground state are vibronic in nature; the $\sigma$ spectrum is much weaker than the $\pi$. The tetragonally split $^2E_g$ ($O_h$) yields excited states at 14 970 ($^2A_{1g}$) and 19 220 ($^2B_{1g}$) cm$^{-1}$. The upper band has a shoulder 2640 cm$^{-1}$ above the peak; this is due to coupling of a water vibration with the ligand field transition.

## Introduction

Many halo–aquo complexes of the first-row transition metals contain the *trans*-dihalotetraaquometal chromophore.[2] Recently we reported the structure and spectra of $Cs_2CrCl_5{\cdot}4H_2O$[2] and $Cs_3VCl_6{\cdot}4H_2O$,[3] both of which contain this chromophore. Here we extend the study to be titanium(III) analogue, $Cs_2TiCl_5{\cdot}4H_2O$. This compound forms large crystals

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