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$Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$: A Novel Quadruply Bridged Binuclear Molybdenum Compound Containing a Disulfur Ligand

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Received February 12, 1982

One of the products from the reaction of $(NH_4)_2Mo_2O_7$ with benzoin and P_4S_{10} is shown to be the binuclear dithiolene complex $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ by single-crystal X-ray diffraction and chemical analysis. Green-black crystals of $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4 \cdot 1.5CH_2Cl_2$ crystallize in the triclinic space group $P\bar{1}$ with $a = 13.425$ (1) Å, $b = 14.067$ (2) Å, $c = 15.944$ (2) Å, $\alpha = 105.02$ (1)°, $\beta = 96.05$ (1)°, $\gamma = 91.41$ (1)°, and $Z = 2$. Each Mo atom is coordinated by seven S atoms in approximate monocapped-trigonal-prismatic geometry. The two Mo atoms are bridged by four S atoms of a shared square face of the trigonal prisms. Two of the bridging S atoms are supplied by a bridging disulfur (S_2) ligand, and two of the bridging S atoms are supplied by two bridging dithiolene ligands. The Mo···Mo distance is 2.778 (1) Å.

Introduction

The evidence that the molybdenum atoms of molybdoenzymes are ligated by one or more sulfur atoms has prompted general investigations of sulfur-rich molybdenum complexes in our laboratories.[2,3] In the course of these studies we decided to reinvestigate the sulfur-rich complexes containing molybdenum and dithiolene ligands.[4,5] Several formulations have been proposed for such complexes but none have been established by an X-ray structure determination. Herein we show that one of the products from the reaction of $(NH_4)_2Mo_2O_7$ with benzoin and P_4S_{10} is a binuclear disulfur (S_2) complex with the formula $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ (**1**), which has the molybdenum atoms bridged by four sulfur atoms. Several quadruply bridged binuclear molybdenum compounds are presently known,[6-10,26] but no previous example contains the $[Mo_2(S_2)(SR)_2]^{6+}$ cluster core of **1**. A preliminary report of portions of this work has appeared.[11]

Experimental Section

Synthesis of $Mo_2S_2[S_2C_2(C_6H_5)_2]_4 \cdot 1.5CH_2Cl_2$. A solution of ammonium paramolybdate tetrahydrate (2.3 g, 1.86 mmol) in degassed water (20 mL) was added to a dioxane solution (80 mL) of $[(C_6H_5)_2C_2S_2PS_2]_2$[25] (24.2 mmol) resulting from boiling benzoin (10 g) and P_4S_{10} (15 g) together for 2 h. The mixture was heated on a boiling water bath under argon for 1.5 h. After cooling, dichloromethane (35 mL) was added followed by ether (80 mL) to precipitate a black solid. Extraction with dichloromethane and addition of ether yielded green-black crystals of $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4 \cdot 1.5CH_2Cl_2$. Anal. Calcd: C, 51.05; H, 3.20; Cl, 7.86. Found: C, 50.59; H, 3.14; Cl, 7.43. IR (KBr): 498, 518 cm^{-1}. Visible spectrum (nm) in CH_2Cl_2: 750, 655, 533, 474; ratio $A_{553}/A_{474} = 1.4$.

Table I. Crystallographic Details for $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4 \cdot 1.5CH_2Cl_2$

color	greenish black
habit	rectangular parallelepiped
dimens, mm	0.17 × 0.25 × 0.60
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	13.425 (1)
b, Å	14.067 (2)
c, Å	15.944 (2)
α, deg	105.02 (1)
β, deg	96.05 (1)
γ, deg	91.41 (1)
V, Å^3	2887.7 (6)
temp, °C	24.0
Z	2
mol wt	1352.9
ρ(obsd), g cm^{-3}	1.542 (6)[a]
ρ(calcd), g cm^{-3}	1.556
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator angle, deg	12.2[b]
takeoff angle, deg	6.0
reflctns measd	$+h, \pm k, \pm l$
2θ range, deg	4-50
scan technique	θ(crystal)-2θ(counter)
scan range, deg min^{-1}	2.00-29.30[c]
scan range, deg	$[2\theta(K\alpha_1) - 0.8]$-$[2\theta(K\alpha_2) + 0.8]$
bkgd measmt	at beginning and end of scan, each for half the total scan time
stds	3 every 97 reflctns[d]
no. of independent data collected	10 215
no. of data $\geq 3\sigma$	7518
no. of variables	276
final R	0.057[e]
final R_W	0.072[e]
abs coeff, cm^{-1}	9.49[f]
σ for reflctn of unit wt	2.76
overdetermination ratio	27.2

[a] Density was averaged over three trials by neutral bouyancy in aqueous zinc bromide. [b] Graphite-crystal monochromator. [c] Variable with more time spent on weaker reflections. [d] None of the standards showed any significant change in intensity during data collection. [e] For the 7518 data with $F_o^2 \geq 3\sigma(F_o^2)$. [f] An empirical absorption correction was performed (see text).

Synthesis of "$Mo_2S_2[S_2C_2(C_6H_5)_2]_2$". Ammonium paramolybdate (1.01 g, 0.88 mmol) in degassed water (20 mL) was heated at 100 °C for 1.5 h with a dioxane (118 mL) solution of $[(C_6H_5)_2C_2S_2PS_2]_2$ (12.5 mmol) under argon. The purple-black precipitate previously formulated[5] as $Mo_2S_4[S_2C_2(C_6H_5)_2]_2$ (0.95 g, 38% yield) (Anal. Calcd for $C_{28}H_{20}Mo_2S_8$: C, 41.8; H, 2.50. Found: C, 39.8; H, 2.22) was isolated by filtration and recrystallized from dichloromethane–

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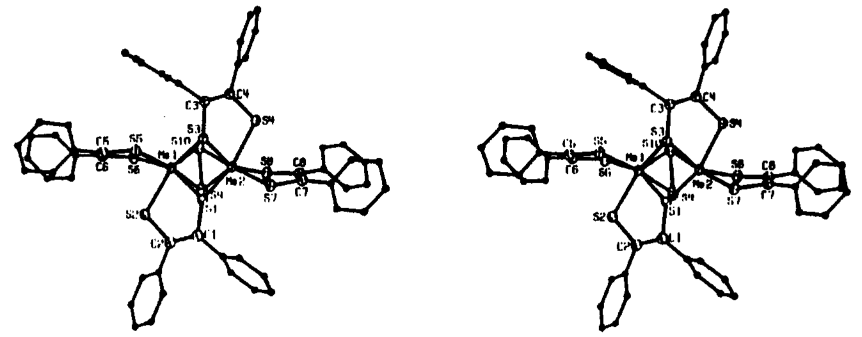

Figure 1. Stereoview of $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ parallel to the approximate C_2 axis of the molecule.

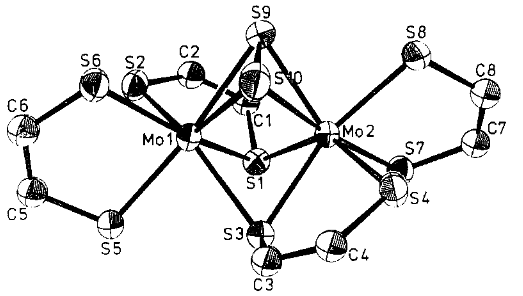

Figure 2. Perspective view of the coordination in $Mo_2(S_2)_2[S_2C_2(C_6H_5)_2]_4$. Phenyl groups have been omitted for clarity.

hexane (IR (KBr): 532 cm^{-1}). Dilution of the filtrate with degassed ethanol gave a green-black precipitate, which was isolated by filtration, washed with ethanol, and dried in vacuo. Visible and infrared spectra and chemical analysis showed this to be $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ (2.15 g, 58% yield).

Crystal Structure Determination. A crystal of what proved to be $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4 \cdot 1.5CH_2Cl_2$ was mounted on a thin glass fiber attached to a goniometer head. The needle axis of the crystal (*a*) was nearly coincident with the ϕ axis of a Syntex P2$_1$ four-circle diffractometer. Peak widths at half-height of less than 0.25° for ω scans of several reflections indicated a satisfactory mosaic spread for the crystal. The reduced unit cell and details of data collection are given in Table I. Data were corrected for absorption by an empirical method;[12] the maximum correction was 1.24.

The structure was solved by direct methods, which revealed the coordinates of two molybdenum and ten sulfur atoms. All the remaining non-hydrogen atoms were located by subsequent structure factor calculations and difference electron density maps. Scattering factor tables for neutral non-hydrogen atoms[13] and spherically bonded hydrogen atoms[14a] were generated from the coefficients of analytical approximations. The effects of anomalous dispersion were included for Mo, S, and Cl,[14b] and these atoms were refined anisotropically. The carbon atoms were refined isotropically, and the phenyl groups were treated as rigid groups. Hydrogen atoms were included as fixed contributors in the final refinement. Additional details concerning computer programs and techniques of structure solution and refinement can be found in a previous publication.[15]

The final *R* factors are given in Table I for refinement of the data with $F_o^2 \geq 3\sigma(F_o^2)$. Refinement was based upon F_o with $\sum w(|F_o| - |F_c|)^2$ being minimized. The weights were taken as $w = 4F_o^2/\sigma^2(F_o^2)$, and a value of 0.04 was assigned to *p* in the expression for $\sigma(F^2)$.[16] The final positional and anisotropic thermal parameters for all the refined atoms are given in Table II. Parameters for the phenyl rings appear in Tables III and IV (Table IV appears in the supplementary material). A structure factor calculation for all 10 215 data gave $R = 0.080$ and $R_w = 0.075$. Tables of observed and calculated structure factors are also available as supplementary material. Selected interatomic distances and angles are collected in Tables V–VII (Table VII appears in the supplementary material).

Table II. Final Atomic Parameters for the Nongroup Atoms

atom	*x*	*y*	*z*
Mo(1)	0.74712 (4)	0.57177 (4)	0.77466 (3)
Mo(2)	0.72634 (4)	0.67720 (4)	0.94465 (3)
S(1)	0.83426 (12)	0.73236 (12)	0.84582 (10)
S(2)	0.73115 (13)	0.65229 (13)	0.65576 (10)
S(3)	0.86142 (11)	0.56743 (11)	0.90523 (10)
S(4)	0.73418 (13)	0.58626 (12)	1.05714 (10)
S(5)	0.88134 (12)	0.48552 (13)	0.71032 (10)
S(6)	0.65195 (12)	0.44831 (13)	0.66268 (11)
S(7)	0.81339 (12)	0.81518 (12)	1.04362 (11)
S(8)	0.59301 (12)	0.73811 (13)	1.02755 (11)
S(9)	0.59735 (13)	0.66399 (16)	0.82343 (11)
S(10)	0.61580 (14)	0.53404 (14)	0.85663 (11)
C(1)	0.7771 (5)	0.8164 (5)	0.7922 (4)
C(2)	0.7435 (5)	0.7796 (5)	0.7053 (4)
C(3)	0.8334 (4)	0.4603 (4)	0.9390 (4)
C(4)	0.7858 (4)	0.4736 (4)	1.0112 (4)
C(5)	0.8327 (5)	0.4181 (5)	0.6084 (4)
C(6)	0.7315 (5)	0.4020 (5)	0.5870 (4)
C(7)	0.7461 (5)	0.8476 (5)	1.1319 (4)
C(8)	0.6490 (5)	0.8106 (5)	1.1258 (4)
Cl(1)[a]	0.5554 (4)	1.0645 (5)	0.0762 (3)
Cl(2)[b]	0.8068 (5)	0.5746 (6)	0.2939 (4)
Cl(3)[b]	0.6273 (7)	0.6004 (6)	0.3658 (6)
C(9)[a]	0.5208 (20)	0.9620 (18)	0.0146 (18)
C(10-A)[b]	0.693 (5)	0.589 (4)	0.279 (4)
C(10-B)[b]	0.700 (3)	0.5217 (29)	0.3026 (24)

[a] These atoms are in the solvated dichloromethane molecule that is disordered about the center of symmetry. The space group imposes an occupancy factor of 0.5 on C(9). [b] These atoms are in the solvated dichloromethane molecule at the general position. C(10-B) is the alternate atom of C(10-A). Each atom was assigned an occupancy factor of 0.5.

Description of the Structure

A stereoview of one molecule of $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ (**1**) is shown in Figure 1, and a perspective view of the coordination environment appears in Figure 2. The approximate point group of **1** is C_2 although no symmetry is required by the space group. The two molybdenum atoms are bridged by four sulfur atoms. Two of the bridging sulfur atoms are supplied by the two bridging dithiolene ligands, and two of the bridging sulfur atoms are supplied by the bridging S_2 unit. Coordination about each molybdenum is completed by the two sulfur atoms from a chelating dithiolene and one sulfur atom from a bridging dithiolene ligand. Thus each molybdenum is coordinated by seven sulfur atoms. The approximate stereochemistry about each molybdenum atom is a monocapped trigonal prism. The two prisms share a rectangular face formed by the four bridging sulfur atoms. The Mo···Mo distance is 2.778 (1) Å.

The S(9)–S(10) distance of 2.044 (3) Å is similar to those found in other disulfur complexes.[17] The S(9)–S(10) vector is approximately perpendicular to the Mo–Mo vector (struc-

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Table III. Parameters for the Rigid Groups[a]

group	x_c	y_c	z_c	ϕ	θ	ρ
R1	0.7780 (3)	1.0159 (3)	0.89500 (25)	−1.735 (4)	−2.886 (4)	−0.626 (4)
R2	0.70882 (26)	0.89603 (25)	0.58208 (22)	2.104 (3)	2.783 (3)	2.363 (3)
R3	0.90494 (25)	0.28548 (24)	0.83032 (20)	1.9128 (29)	3.032 (3)	0.717 (3)
R4	0.77219 (26)	0.33615 (25)	1.11589 (21)	1.4708 (29)	−3.095 (3)	−0.644 (3)
R5	0.9721 (3)	0.33979 (28)	0.48611 (26)	0.557 (5)	2.521 (4)	1.994 (5)
R6	0.63884 (26)	0.28431 (26)	0.41966 (23)	0.605 (3)	3.125 (3)	1.024 (3)
R7	0.85704 (26)	0.97914 (26)	1.28449 (24)	2.910 (4)	−2.539 (3)	−1.136 (4)
R8	0.51548 (23)	0.85501 (24)	1.25958 (20)	−0.267 (3)	−2.9705 (28)	−0.901 (3)

[a] x_c, y_c, and z_c are the fractional coordinates of the center of the group. The angles ϕ, θ, and ρ (in radians) bring about alignment except for translation of an internal coordinate system within the group with a fixed external coordinate system.

Table V. Interatomic Distances (Å)

Mo(1)–Mo(2)	2.778 (1)	S(9)–S(10)	2.044 (3)
Mo(1)–S(1)	2.454 (2)	Mo(2)–S(3)	2.438 (2)
Mo(1)–S(2)	2.442 (2)	Mo(2)–S(4)	2.454 (2)
Mo(1)–S(3)	2.468 (2)	Mo(2)–S(1)	2.499 (2)
Mo(1)–S(5)	2.371 (2)	Mo(2)–S(7)	2.353 (2)
Mo(1)–S(6)	2.375 (2)	Mo(2)–S(8)	2.382 (2)
Mo(1)–S(9)	2.503 (2)	Mo(2)–S(10)	2.485 (2)
Mo(1)–S(10)	2.428 (2)	Mo(2)–S(9)	2.421 (2)
S(1)–S(3)	2.742 (2)	S(3)–S(10)	3.300 (2)
S(1)–S(9)	3.256 (3)		

Table VI. Selected Interatomic Angles (Deg) for Atoms in the Coordination Polyhedron

S(2)–Mo(1)–S(1)	78.71 (6)	S(4)–Mo(2)–S(3)	77.71 (5)
S(5)–Mo(1)–S(6)	81.29 (6)	S(7)–Mo(2)–S(8)	81.41 (6)
S(1)–Mo(1)–S(3)	67.73 (5)	S(1)–Mo(2)–S(3)	67.48 (5)
S(9)–Mo(1)–S(10)	48.95 (7)	S(9)–Mo(2)–S(10)	49.23 (7)
Mo(1)–S(1)–Mo(2)	68.24 (5)	Mo(1)–S(3)–Mo(2)	69.00 (4)
Mo(1)–S(9)–Mo(2)	68.68 (5)	Mo(1)–S(10)–Mo(2)	68.86 (5)

ture type III[17]), but the Mo–S distances are not equivalent. For example, Mo(1)–S(9) = 2.503 (2) Å, whereas Mo(1)–S(10) = 2.428 (2) Å. Similar differences are found for the Mo(2)–S(10) and Mo(2)–S(9) distances (Table V). Asymmetric bonding of S_2^{2-} ligands with a similar range of Mo–S distances also occurs in $Mo_2(S_2)_6^{2-}$ [8] and seems to be a general feature of type III $M_2(S_2)$ structures.[17] The Mo–S distances in $Mo(S_2)Cl_3$ are 2.40–2.46 Å.[7]

The Mo–S distances involving the dithiolene ligands are 2.353–2.499 Å. The shortest Mo–S distances occur for dithiolene ligands chelated to a single molybdenum atom (average 2.370 (12) Å). The Mo–S distances for the dithiolene ligands that are involved in bridging the molybdenum atoms range from 2.438 to 2.499 Å. Another feature of interest is the distance between the bridging S atoms of two different dithiolene ligands (S(1)–S(3) = 2.742 (2) Å). This distance is substantially longer than an S–S single-bond distance (~2.05 Å) but substantially shorter than the estimated sum of van der Waals radii for nonbonded S atoms (3.70 Å).[18] Similar short S···S interactions are known for a number of other sulfur-containing compounds.[19] All other S···S distances in **1** are ≥3.05 Å.

Discussion

As in other facets of molybdenum–sulfur chemistry it seems likely that a variety of sulfur-rich dithiolene complexes can be obtained from the reactions of simple molybdenum compounds with benzoin and P_4S_{10}, depending upon the exact reaction conditions and the procedures for isolation and purification of the compounds. The infrared spectra show that at least two different complexes can be prepared, sensitive to apparently minor changes in experimental conditions. The major product of our synthesis (**1**) was produced by a procedure similar to that of McCleverty and co-workers[5] but has a different chemical composition than the material isolated by them. Analytical data and visible spectra indicate that **1** is identical with the compound of the same formula prepared by Schrauzer and co-workers[4] from an alternative reaction involving $MoCl_5$, benzoin, and P_4S_{10}, but the bis(μ-sulfido) structure proposed by them is shown to be incorrect by our crystal structure determination. It is ironic that **1** has the structural feature of four bridging S atoms proposed by McCleverty and co-workers[5] and the chemical formula, $Mo_2S_2[S_2C_2(C_6H_5)_2]_4$, of the compound obtained by Schrauzer and co-workers.[4]

Several binuclear molybdenum compounds that are quadruply bridged by four sulfur atoms are now known.[6-10,26] However, compound **1** is the first example with both a bridging disulfur ligand and bridging SR groups. Compound **1** can be formally described as two Mo(V) ions bridged by an S_2^{2-} ligand and two SR^- groups. Other structures involve four different levels of oxidation of the Mo_2S_4 bridging system: $[Mo_2(S_2)_6]^{2-}$ (**2**)[8] and $Mo(S_2)Cl_3$ (**3**)[7] formally contain two Mo(V) ions bridged by two S_2^{2-} ligands; $(\eta\text{-}CH_3C_5H_4)_2Mo_2S_2(SCH_3)_2$ (**4**)[26] formally contains two Mo(IV) ions bridged by two SR^- groups and two S^{2-} ligands; $[(\eta\text{-}C_5H_5)_2Mo_2(SCH_3)_4]^+$ (**5**)[6] and $[(\eta\text{-}C_5H_5)_2Mo_2(SC_3H_6S)_2]^+$ (**6**)[10] formally contain one Mo(III), one Mo(IV), and four SR^- groups; $(\eta\text{-}C_5H_5)_2Mo_2(SCH_3)_4$ (**7**)[6] and $[(\eta\text{-}CH_3C_6H_5)_2(SCH_3)_4]^{2+}$ (**8**)[9] formally contain two Mo(III) ions and four SR^- groups.

Compounds **1**–**8** all contain the pseudooctahedral Mo_2S_4 cluster[20] with the Mo atoms at opposite vertices (**9**). Vari-

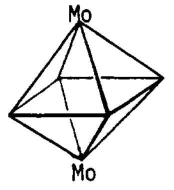

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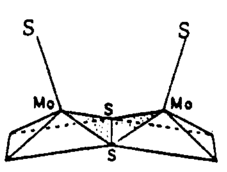
Table VIII. Comparison of the Metrical Details of Psuedooctahedral Mo_2S_4 Clusters (9)

compd	formula	cluster	Mo···Mo, Å	Mo-SR, Å	Mo-(S_2), Å	no. of S-S bonds[a]	other S···S, Å	ref
2	$[Mo_2(S_2)_6]^{2-}$	$[Mo_2(S_2)_2]^{6+}$	2.827 (2)		2.38-2.45	2	3.401-3.453	8
3	$Mo(S_2)Cl_3$	$[Mo_2(S_2)_2]^{6+}$	2.833 (2)		2.40-2.46	2	3.384	7
1	$Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$	$[Mo_2(S_2)(SR)_2]^{6+}$	2.778 (1)	2.44-2.50	2.42-2.50	1	2.742 (2), 3.28	this work
4	$(\eta\text{-}CH_3C_5H_4)_2Mo_2S_2(SCH_3)_2$	$[Mo_2S_2(SR)_2]^{2+}$	2.582 (1)	2.48	*b*	0	2.758 (3), 3.014 (3)	26
5	$[(\eta\text{-}C_5H_5)_2Mo_2(SCH_3)_4]^+$	$[Mo_2(SR)_4]^{3+}$	2.617 (4)	2.44		0	2.90	6
6	$[(\eta\text{-}C_5H_5)_2Mo_2(SC_3H_6S)_2]^+$	$[Mo_2(SR)_4]^{3+}$	2.599 (1)	2.417-2.427		0	2.838 (3), 2.939 (3)	10
7	$(\eta\text{-}C_5H_5)_2Mo_2(SCH_3)_4$	$[Mo_2(SR)_4]^{2+}$	2.603 (2)	2.46		0	2.96	6
8	$[(\eta\text{-}CH_3C_6H_5)_2Mo_2(SCH_3)_4]^{2+}$	$[Mo_2(SR)_4]^{2+}$	2.614 (1)	2.451-2.462		0	*c*	9

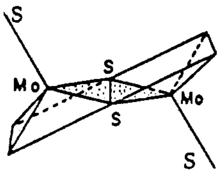
[a] S-S distances of 1.9-2.1 Å. [b] The bridging Mo-S distances are 2.352 (2) Å. [c] From the published Mo-S and Mo-Mo distances it can be calculated that S···S ⩽ 2.95 Å.

ations in the structural details of the Mo_2S_4 clusters of **1-8** are given in Table VIII. The formal addition of a pair of electrons to cluster **2** to produce cluster **1** results in rupture of one of the S-S bonds of **2** and a shortening of the Mo···Mo distance by 0.049 Å (25σ). Compounds **4-8** have shorter Mo···Mo distances and no S-S bonds. The formal reduction of the $[Mo_2(S_2)_2]^{6+}$ clusters of **2** and **3** to the $[Mo_2(SR)_4]^{2+}$ clusters of **7** and **8** requires the addition of eight electrons to cluster unit **9**. This implies the existence of a series of compounds containing Mo_2S_4 clusters that encompass at least *nine different oxidation levels*. The stability of particular clusters should be capable of modulation by the nature of the R groups attached to the bridging S atoms and by the nature and number of the ancillary ligands attached to the Mo atoms.

In an examination of the data of Table VIII it should also be borne in mind that a number of compounds containing the $Mo_2S_4^{2+}$ core are known. To date all known structures exhibit geometry **10** or **11**.[3,27] There are as yet no examples of an $Mo_2S_4^{2+}$ complex with structure **9**. This stereochemistry has been proposed for the red isomer of $(\eta\text{-}C_5H_5)_2Mo_2S_4$,[21] but molecular orbital calculations on the compound suggest that structure **11** is more stable.[22]



10



11

The structure of $Mo_2S_4[S_2C_2(C_6H_5)_2]_2$ orginally prepared by McCleverty and co-workers remains unknown. There are no examples of compounds with $[Mo_2S_4]^{4+}$ units in Table VIII. The IR band at 532 cm^{-1} suggests the presence of a disulfur ligand.[17] The S-S stretching vibration of **1** occurs at 518 cm^{-1}.

Conclusion

The structure of **1** further underscores the complexities of the chemistry of molybdenum-sulfur compounds and the diverse structures that can occur. Binuclear molybdenum-sulfur compounds which are singly,[23] doubly, triply, and quadruply bridged are known.[24] The pathways for interconversion of these various species and their relationships to monomeric molybdenum complexes in various oxidation states should continue to be a fruitful area of study. Knowledge of the relationships between the various dimers and monomers may also provide important insight for understanding molybdenum desulfurization catalysts and the behavior of molybdenum centers in molybdoenzymes.

Acknowledgment. We thank the National Institutes of Environmental Health Sciences (Grant No. ES 00966) for support and the University of Arizona Computer Center for a generous allocation of computer time.

Registry No. **1**·1.5CH_2Cl_2, 82639-20-1; $[(C_6H_5)_2C_2S_2PS_2]_2$, 82639-19-8; ammonium paramolybdate, 12027-67-7.

Supplementary Material Available: Listings of observed and calculated structure factors, final thermal parameters, derived group parameters (Table IV), and bond angles in ligands (Table VII) (34 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Cyclic Dithiooxamides

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Received April 7, 1982

The first cyclic five-membered dithiooxamides **8** and **9** were synthesized by different routes, starting from dithiooxamide and chloromethylsilanes. **8** and **9** are obtained in small yield and are very sensitive to moisture. Crystals of **8** are orthorhombic, *Cmcm*, with $a = 10.390$ (3) Å, $b = 8.107$ (2) Å, $c = 21.387$ (4) Å, and $Z = 4$ based $C_8H_{18}Cl_2N_2S_2Si_3$. The molecule possesses crystallographic *mm* symmetry, with all atoms except those of the methyl groups coplanar.

Over the past two decades there has been a considerable increase in the study of the chemistry of transition-metal complexes containing 1,2-dithiolates as ligands. Two main types of 1,2-dithiolates, the ethane (**1**) and benzene derivatives

0020-1669/82/1321-3798$01.25/0