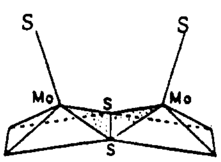
Table VIII. Comparison of the Metrical Details of Psuedooctahedral Mo_2S_4 Clusters (9)

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]



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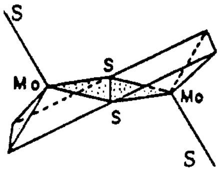

11

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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(27) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

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Preparation and Crystal Structure of Cyclic Dithiooxamides

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and GEORGE M. SHELDRICK

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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

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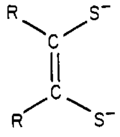
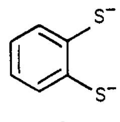
(**2**), are known.[1]



1



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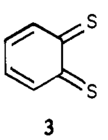

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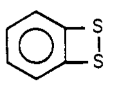
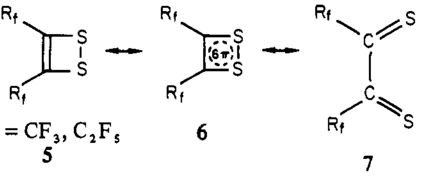


4

As far as we have been able to ascertain, there has been no report of a free ligand of the α-dithione type (**3**). Guha and Chakladar[2] reported the preparation of benzo-1,2-dithiete (**4**) by the oxidation of dithiocatechol with iodine in ethanol. Later work showed that the reaction product was a polymeric mixture and that the simplest substance isolated was the dimer.[3]

Krespan and collaborators[4] obtained bis(perfluoroalkyl)-1,2-dithietes (**5**) by the action of sulfur on the corresponding fluoroacetylenes. The high thermal stability of the dithiete **6** is explained by partial aromaticity as the ring system has 6 π electrons.



$R_f = CF_3, C_2F_5$

5 6 7

The formation of metal complexes from **5** probably takes place via the very reactive dithioketonic form **7**. Molecular orbital calculations suggest that the difference in stability between **6** and **7** is quite small.[5]

Attempts have also been made to trap reactive monomeric species by chemical reactions.[6] Although rubeanic acid and substituted dithiooxamides[7,8] have been known for some time, we were interested in α-dithiones containing a five- or six-membered ring. The 1,2-dithio analogue of squaric acid is known.[9]

Experimental Section

All reactions and separations were carried out with dry solvents and glass equipment. *N,N′*-Bis(trimethylsilyl)dithiooxamide was prepared according to the procedure reported in the literature.[8] ^{1}H NMR spectra were recorded with a Bruker 60-E (60-MHz) NMR spectrometer. Mass spectra were obtained with a Varian MAT CH5 70-eV mass spectrometer.

1,1-Dimethyl-2,5-bis(chlorodimethylsilyl)-1-sila-2,5-diazacyclopentane-3,4-dithione (8). To a stirred suspension of 3 g (25 mmol) of finely pulverized dithiooxamide in 100 mL of hexane and 15 mL (108 mmol) of triethylamine was added a solution of 13 mL (108 mmol) of dichlorodimethylsilane (in excess of stoichiometry) in 30 mL of hexane at room temperature. During the reaction triethylamine hydrochloride began to form slowly. The reaction mixture was stirred for about 48 h until no orange dithiooxamide could be detected. Evaporation of the solvent under vacuum afforded a light green powder, which was extracted with small amounts of methylene chloride. The combined extracts contained **8** and hydrochloride. A fractional crystallization of the eluate to separate hydrochloride gave 1 g (11%) of light olive green crystals, **8**: mp 150 °C (decomposition in a sealed tube); IR (Nujol) 1295, 1260, 1245, 1185, 1100, 965, 895, 865, 810 cm^{-1}; ^{1}H NMR (in CH_2Cl_2) 0.78 and 0.90 ppm (1:2); MS (150 °C) *m/e* 361, 359 (M*). Anal. Calcd for $C_8H_{18}Cl_2N_2S_2Si_3$: C, 26.58; H, 5.02; Cl, 19.61; S, 17.74. Found: C, 26.7; H, 5.1; Cl, 19.2; S, 18.1.

Table I. Atom Coordinates (× 10^4) and Temperature Factors (Å^2 × 10^3)

atom	*x*	*y*	*z*	U^a
S	0	20 (2)	1724 (1)	60 (1)
C(1)	0	1712 (6)	2141 (2)	38 (2)
N	0	3273 (5)	1905 (2)	35 (1)
Si(1)	0	3490 (2)	1082 (1)	42 (1)
C(2)	1512 (5)	2815 (7)	724 (2)	84 (2)
Cl(1)	0	6039 (2)	991 (1)	65 (1)
Si(2)	0	4816 (2)	2500	33 (1)
C(3)	1503 (5)	6014 (7)	2500	50 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Bond Lengths (Å) and Angles (Deg)

S-C(1)	1.637 (5)	C(1)-N	1.362 (6)
C(1)-C(1′)	1.535 (8)	N-Si(1)	1.770 (4)
N-Si(2)	1.784 (4)	Si(1)-C(2)	1.832 (5)
Si(1)-Cl(1)	2.075 (2)	Si(2)-C(3)	1.839 (5)
S-C(1)-N	125.2 (3)	S-C(1)-C(1′)	123.1 (2)
N-C(1)-C(1′)	111.7 (2)	C(1)-N-Si(1)	117.5 (3)
C(1)-N-Si(2)	112.8 (3)	Si(1)-N-Si(2)	129.8 (2)
N-Si(1)-C(2)	112.7 (2)	N-Si(1)-Cl(1)	101.1 (1)
C(2)-Si(1)-Cl(1)	105.0 (2)	C(2)-Si(1)-C(2′)	118.2 (3)
N-Si(2)-C(3)	111.7 (1)	N-Si(2)-N′	90.9 (3)
C(3)-Si(2)-C(3′)	116.3 (4)		

1,1-Dimethyl-2,5-bis(trimethylsilyl)-1-sila-2,5-diazacyclopentane-3,4-dithione (9). A stirred red solution of 3.66 g (13.9 mmol) and *N,N′*-bis(trimethylsilyl)dithiooxamide in 50 mL of hexane was cooled to −78 °C while the adduct began to crystallize. To this suspension was dropped 13.5 mL (28 mmol BuLi) of 20% BuLi/hexane solution over a period of 0.5 h. The reaction mixture began to turn light yellow with formation of the lithium salt of *N,N′*-bis(trimethylsilyl)dithiooxamide. The suspension was allowed to warm up to room temperature to complete the lithiation. The mixture was cooled again to −78 °C, and 2 mL (14 mmol) of dimethyldichlorosilane in 30 mL of hexane was slowly dropped onto the stirred suspension. While the mixture was warmed up slowly to room temperature, a reaction occurred with formation of the product and lithium chloride. **9** and lithium chloride were separated from the solution, washed several times with hexane, and then dried under vacuum. The product was eluted with methylene chloride and crystallized several times from small amounts of methylene chloride to provide 0.5 g (12%) of light olive green crystals, **9**: mp 220 °C dec; IR (Nujol) 1290, 1265, 1245, 1160, 1095, 950, 880, 850, 810 cm^1; ^{1}H NMR (in CH_2Cl_2) 0.46 and 0.61 ppm (3:1). Anal. Calcd for $C_{10}H_{24}N_2S_2Si_2$: C, 37.45; H, 7.54. Found: C, 36.4; H, 7.2.

Crystal Structure Determination. All crystallographic measurements were made at room temperature, with a Stoe-Siemens AED diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), from a crystal of approximate dimensions of 0.5 × 0.5 × 0.3 mm mounted in a Lindemann glass capillary. Unit cell dimensions, derived from 28 accurately centered reflections with $20 < 2\theta < 25°$, are $a = 10.390$ (3) Å, $b = 8.107$ (2) Å, $c = 21.387$ (4) Å, and $V = 1801.5$ Å^3. The space group is *Cmcm*, with $Z = 4$.

Intensities were collected for 1721 reflections with $7 < 2\theta < 50°$, in the θ/ω scan mode, by means of a profile-fitting procedure.[10] After equivalents were merged ($R_M = \{\sum[n\sum w(F - \bar{F})^2]/\sum[(n-1)\cdot(\sum wF^2)]\}^{1/2} = 0.033$, $R_S = \sum\sigma(F)/\sum F = 0.037$, where *n* is the number of equivalents averaged), there remained 863 unique reflections, of which 706 with $F > 3\sigma(F)$ were used for all calculations.[11]

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(1) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303.

(2) Guha, P. C.; Chakladar, M. N. *Q. J. Indian. Chem. Soc.* **1925**, *2*, 318.

(3) Field, L.; Stephens, W. D.; Lippert, E. L. *J. Org. Chem.* **1961**, *26*, 4782.

(4) Krespan, C. G.; McKusick, B. C.; Cairns, T. L. *J. Am. Chem. Soc.* **1960**, *82*, 1515. Krespan, C. G. *Ibid.* **1961**, *83*, 3434. Hencher, J. L.; Shen, Q.; Tuck, D. G. *Ibid.* **1976**, *98*, 899.

(5) Schrauzer, G. N. *Transition Met. Chem. (N.Y.)* **1968**, *4*, 299.

(6) Kusters, W.; de Mayo, P. *J. Am. Chem. Soc.* **1974**, *96*, 3502. Jacobsen, N.; de Mayo, P.; Weedon, A. C. *Nouv. J. Chim.* **1978**, *2*, 331. Fanghänel, E.; Ebisch, R.; Adler, B. *Z. Chem.* **1973**, *13*, 431.

(7) Wheatly, P. J. *J. Chem. Soc.* **1965**, 396.

(8) Rinne, D.; Thewalt, U. *Z. Anorg. Allg. Chem.* **1978**, *443*, 185.

(9) Seitz, G.; Morck, H.; Mann, K.; Schmiedel, R. *Chemiker-Ztg.* **1974**, *98*, 459.

(10) Clegg, W. *Acta Crystallogr., Sect. A* **1981**, *A37*, 22.

(11) Programs used in this study were written by G. M. Sheldrick (SHELXTL system) and W. Clegg (diffractometer control program).

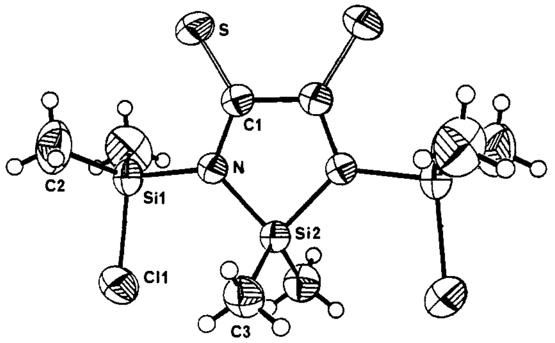


Figure 1. The molecule of **8**, with 50% probability ellipsoids for the anisotropic atoms.

No corrections were applied for absorption (μ = 0.76 mm^{-1}).

The structure was solved by multisolution tangent refinement and refined to a minimum value of $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F_o) + 0.0004|F_o|^2$). Scattering factors were taken from ref 12. The methyl groups were refined with *restraints* to hold all C–H distances equal and all H···(C)···H distances equal. A common isotropic temperature factor was employed for the hydrogen atoms, with anisotropic thermal parameters for all other atoms. The final R ($=\sum|\Delta|/\sum|F_o|$) was 0.0527 and the final R_w ($=\sum w^{1/2}|\Delta|/\sum w^{1/2}|F_o|$) was 0.0498. The rms deviation of a reflection on an absolute scale of F_o ($=(\sum w\Delta^2/\sum w)^{1/2}$) was 1.68 electrons and showed no systematic trends as a function of indices, sin θ, or $|F_o|$.

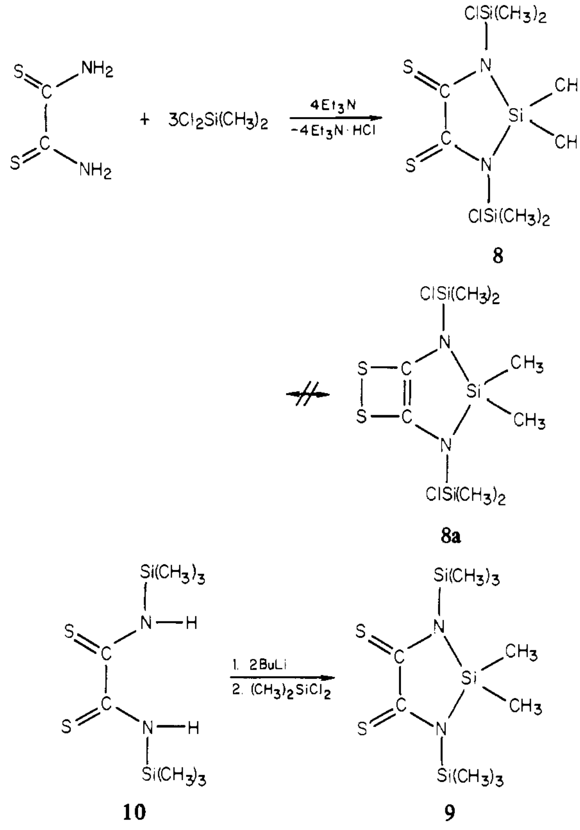
Observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom parameters are available as supplementary material. Atomic coordinates are reported in Table I and bond lengths and angles in Table II.

Results and Discussion

The molecule possesses crystallographic *mm* symmetry, with all atoms except four carbons and twelve hydrogens lying on special positions in the mirror planes. The five-membered ring and the sulfur and silicon substituents are thus exactly coplanar. The $-SiMe_2Cl$ groups are staggered with respect to the C–S bonds and dimethylsilyl units. The C–C bond length of 1.538 (8) Å is the same as that found[8] in *trans-N,N'*-bis(trimethylsilyl)dithiooxamide (**10**); however, the C–S bond is significantly shorter in **8** (1.637 (5) Å) than in **10** (1.659 (4) Å). This is consistent with a π interaction between N and the additional Si atom (Si(2)) in **8**, reducing the π character in the N–C bond and thereby increasing it in the C–S bond.

1,1-Dimethyl-2,5-bis(chlorodimethylsilyl)-1-sila-2,5-diazacyclopentane-3,4-dithione (**8**) and 1,1-dimethyl-2,5-bis(trimethylsilyl)-1-sila-2,5-diazacyclopentane-3,4-dithione (**9**) appear to be the first compounds isolated that possess a five-membered ring containing a dithiooxamide group. Silicon was used for the ring formation because it is known that, e.g., $(H_3Si)_3N$ has a planar structure and reduced basicity vs. that of tertiary amines, which may be explained by assumption of multiple bonding between the nitrogen and the silicon atoms. This leads to a reduction of electron density at the sulfur atoms in compounds **8** and **9** so that they can be arranged in cis positions. On the basis of an X-ray analysis it was shown that rubeanic acid in the solid state has a cis–trans configuration.

Scheme I



The syntheses of **8** and **9** were performed according to the reaction sequence shown in Scheme I. **8** was prepared in hexane in 11% yield. Compounds **8** and **9** are surprisingly thermally stable but very sensitive to moisture and can be handled only under dry nitrogen. They are soluble in methylene chloride and THF without obvious decomposition. A temperature-dependent ^{1}H NMR investigation did not show equilibrium between the α-dithione **8** and dithiete form **8a**. Mass spectral studies by field ionization confirmed the monomeric structure of **8**, and the molecular ion was observed at *m/e* 361 and 359 in agreement with two chlorine atoms in the molecule. The chelating properties of **8** and **9** are under investigation.

Acknowledgment. We are grateful to Dr. E. Hädicke, BASF Ludwigshafen, for the use of his Data General Eclipse computer and to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial assistance.

Registry No. 8, 82665-15-4; **9**, 82665-16-5; **10**, 58065-72-8; ethanedithioamide, 79-40-3; dichlorodimethylsilane, 75-78-5.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(12) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 99. Cromer, D. T.; Ibers, J. A. *Ibid.*, p 149.