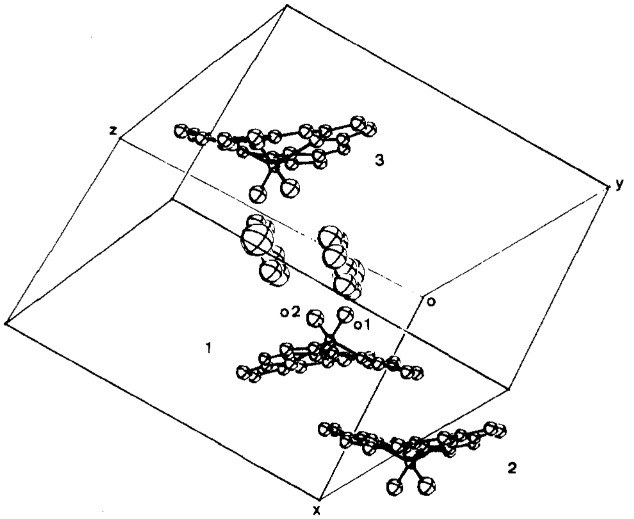

Figure 5. Packing of symmetry-related porphyrin cores in the unit cell.

atoms pointing toward each other and are separated by two symmetry-related toluene molecules of crystallization. Weak interactions occur between the methyl group of the toluene molecule and one of the oxygen atoms of the molybdenyl moiety, evidenced by the $O_2 \cdots C_{35}$ distance 3.61 (3) Å. Even shorter contacts are found between the oxygen atoms and the tolyl methyl groups of neighboring porphyrins: $O_1 \cdots C_{14}$ and $O_2 \cdots C_{21}$ respectively 3.23 (2) and 3.25 (2) Å, ensuring thus the crystal cohesion through weak hydrogen bonds.

The molecular structure of MoO$_2$(TTP) illustrates well the definite preference of complexes containing the d^0 MoO$_2^{2+}$ unit to adopt a cis geometry,[22] even at the expense of severe deformations of the porphyrin ligand. This is in agreement with the general tendency observed for strong σ- or π-bonding ligands to avoid sharing the same central-atom orbital.[23] The strained situation of the macrocycle is probably kept in solution. An approximate treatment[24] of the temperature-dependent ^{1}H NMR data[3c] gives an activation energy for the rotation of the tolyl groups $\Delta G_c^\ddagger = 13.8 \pm 1$ kcal mol^{-1} at the coalescence temperature $T_c = 290$ K. A low value of $\Delta G_c^\ddagger$ has been associated in several metalloporphyrins with a significant deviation from planarity of the macrocycle.[25]

The high reactivity of MoO$_2$(TTP), observed toward oxidation of phosphines,[26] may then be explained by the release of internal strain going from Mo^{VI}O$_2$(TTP) (Mo–Ct = 0.972 Å; Ct$\cdots$N = 1.967 Å) to Mo^{IV}O(TTP) (Mo–Ct = 0.639 Å; Ct$\cdots$N = 2.011 Å)[3c] during the oxygen atom transfer. Such an enhancement of the oxidizing properties, induced by internal steric-strain factors, may be relevant to the oxidation mechanisms of several metalloenzymes in which *cis*-dioxomolybdenum(VI) complexes are involved.[27] We are currently testing this hypothesis.

Acknowledgment. We thank Dr. I. Tkatchenko for helpful discussions. This work was supported by the Centre National de la Recherche Scientifique.

Registry No. MoO$_2$(TTP)·$^3/_2$C$_7$H$_8$, 73610-83-0.

Supplementary Material Available: A listing of the observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

---

(22) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 400.

(23) Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112.

(24) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

(25) Eaton, S. S.; Fishwild, D. M.; Eaton, G. R. *Inorg. Chem.* **1978**, *17*, 1542. Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 6594. Scheer, H.; Katz, J. J. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 398 and references therein.

(26) Ledon, H.; Bonnet, M. *J. Mol. Catal.* **1980**, *7*, 309.

(27) Wentworth, R. A. D. *Coord. Chem. Rev.* **1976**, *18*, 1. Bizot Swedo, K.; Enemark, J. H. *J. Chem. Educ.* **1979**, *56*, 70. Tullius, T. D.; Kurtz, D. M., Jr.; Conradson, S. D.; Hodgson, K. O. *J. Am. Chem. Soc.* **1979**, *101*, 2776. Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *Ibid.* **1979**, *101*, 2772. Bowden, F. L. *Tech. Top. Bioinorg. Chem.* **1975**, 207. Raymond, K. N. *Adv. Chem. Ser.* **1977**, *No. 162*, Chapters 20–21.

Contribution from the Faculty of Chemistry, University of Bielefeld, D-4800 Bielefeld, West Germany,
and the Inorganic Chemistry Institute, University of Göttingen, D-3400 Göttingen, West Germany

Crystal and Molecular Structure of [N(CH$_3$)$_4$]$_2$[Mo$_2$O$_2$S$_2$(S$_2$)$_2$]: A Compound with Two S$_2^{2-}$ Ligands

WILLIAM CLEGG,[1a] NAGESWARAN MOHAN,[1b] ACHIM MÜLLER,*[1b] AXEL NEUMANN,[1a]
WALTER RITTNER,[1a] and GEORGE M. SHELDRICK*[1a]

Received July 23, 1979

The X-ray crystal and molecular structure of [N(CH$_3$)$_4$]$_2$[Mo$_2$O$_2$S$_2$(S$_2$)$_2$] has been determined by two independent data collection procedures (I, II). The compound crystallizes in the orthorhombic space group $Pca2_1$ with $Z = 4$. The unit cell dimensions are, for I, $a = 29.202$ (5) Å, $b = 6.546$ (1) Å, and $c = 10.875$ (2) Å and, for II, $a = 29.122$ (5) Å, $b = 6.529$ (1) Å, and $c = 10.884$ (2) Å. Full-matrix least-squares refinement resulted in a final R_1 index of 0.044 (I) or 0.069 (II) for 1774 (I) or 2728 (II) independent data. The structure contains discrete dimeric [Mo$_2$O$_2$S$_2$(S$_2$)$_2$]$^{2-}$ anions and [N(CH$_3$)$_4$]$^+$ cations. The two S$_2^{2-}$ ligands (S–S = 2.074–2.090 Å) are asymmetrically bonded to the central unit Mo$_2$O$_2$S$_2^{2+}$ (Mo–S 2.38 and 2.44 Å), the structure of which (*cis*-dioxo and nonplanar MoS$_2$Mo bridge) is nearly identical with that of other Mo$_2$O$_2$S$_2^{2+}$ compounds. The results indicate that the geometrical data derived from both measurements are internally consistent, although the temperature factors show significant differences.

Introduction

Not many coordination compounds with the disulfur moiety as ligand are known. But the S$_2^{2-}$ complex chemistry is interesting because there is no other simple ligand with such a large variety of modes of coordination.[2] The basic structural types are the side-on coordination (MS$_2$) and the bridging type (MS$_2$M). An interesting type of coordination occurs in [Mo$_4$(NO)$_4$S$_{13}$]$^{4-}$ where four S$_2^{2-}$ ligands are side-on and

---

(1) (a) University of Göttingen. (b) University of Bielefeld.

(2) A. Müller and W. Jägermann, *Inorg. Chem.*, **18**, 2631 (1979).

0020-1669/80/1319-2066$01.00/0

Table I. Crystal Data and Structure Determination

	I		II
formula		$[N(CH_3)_4]_2[Mo_2O_2S_2(S_2)_2]$	
mol wt		564.6	
cryst system		orthorhombic	
a, Å	29.202 (5)		29.122 (5)
b, Å	6.546 (1)		6.529 (1)
c, Å	10.875 (2)		10.884 (2)
temp of measmt		20 °C	
U, Å^3	2079		2069
d_{calcd}, g cm^{-3}	1.83		1.81
d_{measd}, g cm^{-3}			1.86
Z		4	
space group		$Pca2_1$	
radiation		Mo Kα graphite monochromator	
λ, Å		0.710 69	
diffractometer	Syntex $P2_1$ (four-circle)		Stoe STADI-2 (Weissenberg geometry)
cryst dimens, mm	ca. 0.6 × 0.1 × 0.1		0.27 × 0.73 × 0.56 and 0.27 × 0.52 × 0.58
scan mode	$\theta-2\theta$		ω
$2\theta_{max}$, deg	48		70
abs cor	none		Gaussian integration, $\mu = 17.3$ cm^{-1}
no. of unique obsd reflctns	1474		2728
criterion for observn	$I > 1.96(I)$		based on prescan; all measd reflctns had $I > 3\sigma(I)$
discrepancy among equiv reflctns	ca. 5%		ca. 7%
computer program	Syntex XTL		Syntex SHELXTL
weighting scheme for refinement		$1/\sigma^2(F_o)$	
quantity minimized[a]		$\Sigma w\Delta^2$	
final R_1[b,d]	0.044		0.069
final R_2[c,d]	0.053		0.093
largest shift/esd in final cycle	0.5		0.02

[a] $\Delta = |F_o| - |F_c|$. [b] $R_1 = \Sigma|\Delta|/\Sigma|F_o|$. [c] $R_2 = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. [d] Unobserved reflections not included.

end-on bonded to different metal atoms.[3] A bridging S_2^{2-} group external and roughly perpendicular to a metal–metal bond is of importance for the stabilization of metal–metal bonds as for example in $[Mo_2(S_2)_6]^{2-}$ (the first complex containing only S_2^{2-} ligands)[4] and $[Mo_3S(S_2)_6]^{2-}$ (the first isolated discrete transition-metal sulfur cluster).[5,6] As the type of metal–ligand interaction is not well-known for S_2^{2-} complexes, it seems to be important to characterize more complexes from the structural point of view. In this paper we report the crystal and molecular structure of the compound $[(CH_3)_4N]_2[Mo_2O_2S_2(S_2)_2]$, the complex anion of which was obtained by a novel intramolecular redox reaction from $MoO_2S_2^{2-}$.[7]

Experimental Section

$[(CH_3)_4N]_2[Mo_2O_2S_2(S_2)_2]$ was obtained by the method described in ref 7.

Data Collection. The red crystals were rectangular parallelepipeds. Preliminary investigation by oscillation and Weissenberg photography gave initial cell parameters. Systematic absences ($0kl$ for l odd; $h0l$ for h odd) indicated space group $Pca2_1$ (No. 29) or $Pcam$ (alternative orientation of $Pbcm$, No. 57). The former was confirmed by successful structure solution and refinement. The density was measured by flotation in iodomethane–dichloromethane.

The two independent data collection procedures and sets of crystal data are given in Table I. For I, cell parameters were obtained from angle measurements of 15 reflections with $45 < 2\theta < 28°$, and intensity data were collected from a single-crystal setting. For II, intensities were measured from two crystals, mounted about b and c, respectively, and final cell parameters were calculated from the ω angles of the 269 $h0l$ and 230 $hk0$ reflections. Only reflections registering more than a preset intensity on a 1-s prescan at the calculated peak center were measured. The two sets of data (layers $h0l$ to $h,13,l$ and $hk0$ to $hk2$) were merged after absorption corrections had been applied. All the experimental details are summarized in Table I.

Structure Solution and Refinement. In both cases, the structure was solved by Patterson and Fourier methods and refined by least-squares techniques with all nonhydrogen atoms anisotropic. Atomic scattering factors, including corrections for anomalous scattering, were taken from ref 8. Hydrogen atoms were not located.

The statistical weighting scheme gave an even analysis of variance.[9] No significant peaks were found in a final difference synthesis. There is no evidence for significant extinction effects.

Observed and calculated structure factors are tabulated as supplementary material. Positional and thermal parameters are given in Table II and bond lengths and angles in Table III. The structure determination II was actually carried out with the a and c axes interchanged for computing convenience. Results have been transformed to the standard setting in Tables I and II, but in the structure factor tables the experimental orientation has been retained (i.e., h and l are interchanged).

Because the space group is noncentrosymmetric, the question of absolute polarities of the crystals must be considered, as must the relative polarities of the two crystals used in the determination II. To investigate this, we have made further refinements: (i) refinement with the data unchanged and all atomic coordinates inverted; (ii) refinement based on the data from one crystal of II alone; (iii) as ii but with atomic coordinates inverted. The residuals from i were virtually identical (i.e., within 0.0001) with those of the original refinement, and there were no significant shifts in any of the refined parameters. The refinements ii and iii also produced results which were insignificantly different from one another. It is thus clear that the polarities of the individual crystals are irrelevant to this structure determination. This is not surprising, in view of the fact that the largest imaginary term in the atomic scattering factors for Mo Kα radiation

---

(3) A. Müller, W. Eltzner, and N. Mohan, *Angew. Chem., Int. Ed. Engl.*, **18**, 168 (1979).

(4) A. Müller, W.-O. Note, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **17**, 279 (1978).

(5) A. Müller, R. G. Bhattacharyya, and B. Pfefferkorn, *Chem. Ber.*, **112**, 778 (1979).

(6) A. Müller, S. Sarkar, R. G. Bhattacharyya, S. Pohl, and M. Dartmann, *Angew. Chem., Int. Ed. Engl.* **17**, 535 (1978).

(7) W. Rittner, A. Müller, A. Neumann, W. Bäther, and R. C. Sharma, *Angew. Chem., Int. Ed. Engl.*, **18**, 530 (1979).

(8) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 99; D. T. Cromer and J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, p 149.

(9) W. C. Hamilton, ref 7, p 293.

Table II. Atomic Coordinates ($\times 10^4$)[a,b] and Anisotropic Thermal Parameters (Å^2, $\times 10^3$)[a-c]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	1456 (1)	587 (2)	0[d]	37 (1)	34 (1)	27 (1)	−5 (1)	1 (1)	3 (1)
	1456 (1)	580 (2)	0[d]	26 (1)	26 (1)	26 (1)	−4 (1)	1 (1)	5 (1)
Mo(2)	1542 (1)	2256 (2)	2385 (2)	32 (1)	31 (1)	27 (1)	−1 (1)	−2 (1)	0 (1)
	1543 (2)	2255 (2)	2385 (2)	22 (1)	23 (1)	24 (1)	−2 (1)	−1 (1)	0 (1)
S(1)	1441 (1)	4015 (5)	542 (4)	48 (2)	30 (2)	34 (2)	4 (2)	3 (2)	−1 (2)
	1440 (1)	4020 (5)	537 (4)	43 (2)	26 (1)	28 (2)	2 (1)	1 (2)	−4 (1)
S(2)	1290 (2)	−992 (6)	1865 (4)	69 (3)	23 (2)	37 (2)	3 (2)	−2 (2)	0 (2)
	1288 (1)	−976 (5)	1877 (4)	51 (2)	15 (1)	36 (2)	3 (1)	−2 (2)	−1 (1)
S(3)	1016 (2)	1269 (8)	−1843 (4)	72 (3)	62 (3)	39 (3)	−3 (3)	−13 (2)	8 (3)
	1012 (2)	1277 (8)	−1840 (5)	61 (3)	54 (2)	35 (2)	−5 (2)	−13 (2)	8 (2)
S(4)	873 (2)	−1440 (8)	−929 (5)	93 (4)	63 (3)	54 (3)	0 (3)	−27 (3)	−31 (3)
	869 (2)	−1449 (8)	−923 (6)	85 (4)	60 (3)	51 (3)	−1 (3)	−26 (3)	−27 (3)
S(5)	1165 (2)	4938 (7)	3481 (4)	59 (3)	40 (2)	39 (2)	−5 (2)	6 (2)	6 (2)
	1160 (2)	4920 (6)	3483 (4)	49 (2)	31 (2)	35 (2)	−4 (2)	5 (2)	8 (2)
S(6)	1125 (2)	2078 (7)	4327 (4)	70 (3)	54 (3)	39 (2)	9 (2)	15 (2)	5 (3)
	1129 (2)	2063 (7)	4312 (4)	69 (3)	44 (2)	31 (2)	8 (2)	16 (2)	1 (2)
O(1)	1981 (4)	−185 (18)	−395 (9)	62 (7)	87 (8)	36 (7)	−18 (7)	6 (6)	17 (7)
	1988 (4)	−186 (21)	−405 (12)	36 (5)	79 (8)	46 (7)	−4 (8)	10 (6)	8 (6)
O(2)	2105 (3)	2208 (15)	2713 (10)	34 (5)	53 (7)	55 (8)	−4 (6)	−9 (5)	9 (5)
	2114 (4)	2223 (17)	2707 (12)	34 (5)	51 (6)	46 (8)	−14 (6)	−2 (5)	2 (5)
N(1)	2884 (4)	6506 (23)	1406 (12)	28 (7)	58 (8)	40 (8)	−8 (8)	−6 (6)	−3 (7)
	2873 (4)	6494 (18)	1428 (13)	22 (5)	36 (6)	36 (7)	−4 (6)	−10 (5)	2 (5)
C(1)	2498 (6)	7310 (24)	2169 (13)	56 (9)	80 (11)	21 (10)	−22 (9)	8 (8)	2 (11)
	2496 (6)	7377 (25)	2192 (16)	39 (7)	70 (9)	32 (9)	−1 (8)	23 (7)	19 (9)
C(2)	2679 (6)	5166 (30)	419 (15)	83 (14)	95 (14)	47 (11)	−45 (11)	6 (10)	−37 (13)
	2674 (6)	5219 (35)	404 (18)	60 (11)	106 (15)	32 (8)	−26 (12)	9 (8)	−44 (11)
C(3)	3191 (6)	5239 (32)	2132 (18)	72 (14)	110 (17)	71 (14)	19 (13)	−19 (12)	61 (13)
	3192 (8)	5343 (46)	2202 (33)	57 (12)	143 (22)	111 (24)	51 (22)	−36 (16)	32 (14)
C(4)	3129 (7)	8247 (25)	804 (19)	90 (15)	43 (11)	95 (17)	−13 (12)	49 (13)	−42 (11)
	3135 (10)	8265 (28)	829 (29)	137 (22)	39 (9)	99 (21)	−10 (12)	51 (19)	−51 (12)
N(2)	5110 (4)	3257 (20)	5948 (10)	56 (9)	64 (9)	16 (7)	8 (8)	−4 (6)	−6 (8)
	5116 (4)	3178 (19)	5944 (13)	28 (6)	48 (7)	34 (7)	15 (6)	−8 (6)	3 (5)
C(5)	4823 (6)	2101 (27)	6888 (18)	46 (11)	73 (14)	90 (15)	25 (12)	0 (10)	4 (10)
	4816 (6)	2026 (33)	6878 (28)	39 (9)	88 (14)	109 (20)	31 (16)	29 (12)	−32 (10)
C(6)	4821 (7)	4467 (35)	5139 (20)	102 (16)	133 (20)	70 (15)	72 (16)	−7 (14)	16 (16)
	4809 (9)	4483 (47)	5112 (30)	111 (20)	133 (23)	82 (20)	39 (20)	−58 (19)	−7 (19)
C(7)	5464 (7)	4591 (37)	6486 (20)	109 (18)	142 (23)	81 (17)	7 (17)	−30 (14)	−89 (17)
	5450 (10)	4585 (46)	6583 (26)	114 (20)	149 (25)	70 (17)	60 (19)	−42 (16)	−82 (19)
C(8)	5408 (9)	1723 (34)	5412 (26)	158 (23)	84 (17)	179 (28)	28 (19)	129 (22)	38 (17)
	5389 (13)	1474 (38)	5316 (44)	196 (29)	69 (15)	235 (41)	31 (24)	172 (30)	40 (18)

[a] Estimated standard deviations in the last place of figures are given in parentheses. [b] For each atom, the first row of figures is for I and the second for II. [c] The anisotropic temperature factor takes the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$. [d] Fixed to define the origin.

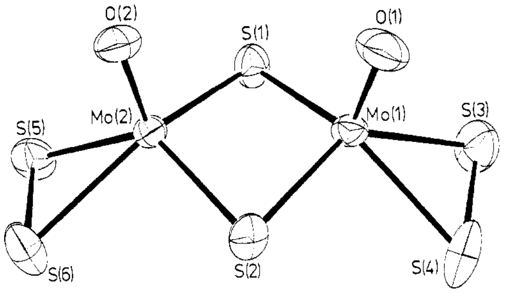

Figure 1. Structure of the $[Mo_2O_2S_2(S_2)_2]^{2-}$ anion, with thermal motion depicted as 50% probability ellipsoids.

is $\Delta f'' = 0.688$ for Mo atoms, and $\sum \Delta f''$ for all the heavy atoms (Mo and S) in one unit cell is only 8.48, compared with $F(000)$ of 1128 electrons.

Results and Discussion

The structure contains discrete dimeric $[Mo_2O_2S_2(S_2)_2]^{2-}$ anions and $[N(CH_3)_4]^+$ cations. The structure of the $[Mo_2O_2S_2(S_2)_2]^{2-}$ anion is shown in Figure 1 by using the thermal parameters of II, which are represented as 50% probability ellipsoids.[10]

The two sets of refined coordinates are not significantly different. Figure 2 shows a half-normal probability plot for

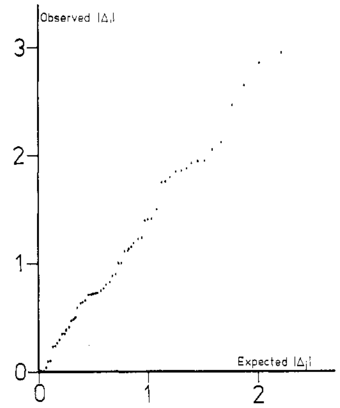

Figure 2. Half-normal probability plot for the two sets of refined coordinates. Slope = 1.39.

these parameters. The gradient of 1.39 indicates a systematic underestimation of the standard deviations in one or both of the structure determinations.[9,11]

Thermal parameters, on the other hand, are considerably less comparable. In particular, the U_{11} values of the heavier atoms are markedly higher for I than for II. This can be traced to the elongation of the crystal along the a axis for I, which

---

(10) C. K. Johnson, "ORTEP", Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(11) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157 (1971).

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

	I	II
	Bond Lengths	
Mo(1)···Mo(2)	2.825 (2)	2.829 (2)
Mo(1)–S(1)	2.320 (4)	2.321 (4)
Mo(2)–S(1)	2.330 (4)	2.338 (4)
Mo(1)–S(2)	2.327 (4)	2.333 (4)
Mo(2)–S(2)	2.320 (4)	2.304 (4)
Mo(1)–S(3)	2.422 (5)	2.426 (5)
Mo(1)–S(4)	2.382 (6)	2.384 (6)
Mo(2)–S(5)	2.392 (5)	2.388 (4)
Mo(2)–S(6)	2.441 (5)	2.423 (5)
S(3)–S(4)	2.075 (7)	2.083 (8)
S(5)–S(6)	2.090 (6)	2.074 (6)
Mo(1)–O(1)	1.670 (11)	1.688 (11)
Mo(2)–O(2)	1.680 (9)	1.698 (11)
N(1)–C(1)	1.494 (20)	1.492 (22)
N(1)–C(2)	1.510 (22)	1.507 (24)
N(1)–C(3)	1.455 (23)	1.465 (32)
N(1)–C(4)	1.498 (22)	1.533 (26)
N(2)–C(5)	1.523 (22)	1.537 (28)
N(2)–C(6)	1.455 (24)	1.532 (33)
N(2)–C(7)	1.474 (26)	1.508 (31)
N(2)–C(8)	1.451 (27)	1.528 (37)
	Bond Angles	
S(1)–Mo(1)–S(2)	101.8 (2)	101.3 (2)
S(1)–Mo(1)–S(3)	91.3 (2)	90.9 (2)
S(1)–Mo(1)–S(4)	129.2 (2)	129.0 (2)
S(1)–Mo(1)–O(1)	112.0 (4)	111.8 (5)
S(2)–Mo(1)–S(3)	133.8 (2)	133.9 (2)
S(2)–Mo(1)–S(4)	88.5 (2)	88.7 (2)
S(2)–Mo(1)–O(1)	106.3 (4)	107.0 (5)
S(3)–Mo(1)–S(4)	51.2 (2)	51.3 (2)
S(3)–Mo(1)–O(1)	109.3 (4)	109.2 (5)
S(4)–Mo(1)–O(1)	112.2 (4)	112.6 (5)
S(1)–Mo(2)–S(2)	101.7 (2)	101.7 (2)
S(1)–Mo(2)–S(5)	90.4 (2)	90.6 (2)
S(1)–Mo(2)–S(6)	134.8 (2)	134.9 (2)
S(1)–Mo(2)–O(2)	108.4 (4)	108.0 (4)
S(2)–Mo(2)–S(5)	130.4 (2)	129.5 (2)
S(2)–Mo(2)–S(6)	90.5 (2)	90.0 (2)
S(2)–Mo(2)–O(2)	110.2 (4)	110.8 (4)
S(5)–Mo(2)–S(6)	51.2 (2)	51.1 (2)
S(5)–Mo(2)–O(2)	111.0 (4)	111.3 (4)
S(6)–Mo(2)–O(2)	107.7 (4)	108.0 (5)
Mo(1)–S(1)–Mo(2)	74.8 (1)	74.8 (1)
Mo(1)–S(2)–Mo(2)	74.9 (1)	75.2 (1)
Mo(1)–S(3)–S(4)	63.5 (2)	63.3 (2)
Mo(1)–S(4)–S(3)	65.4 (2)	65.4 (2)
Mo(2)–S(5)–S(6)	65.6 (2)	65.3 (2)
Mo(2)–S(6)–S(5)	63.2 (2)	63.6 (2)
C(1)–N(1)–C(2)	107.5 (12)	110.1 (12)
C(1)–N(1)–C(3)	111.3 (13)	110.2 (17)
C(1)–N(1)–C(4)	109.6 (12)	108.2 (13)
C(2)–N(1)–C(3)	107.4 (13)	112.8 (17)
C(2)–N(1)–C(4)	108.7 (13)	107.1 (16)
C(3)–N(1)–C(4)	112.1 (13)	108.2 (16)
C(5)–N(2)–C(6)	110.9 (13)	109.3 (15)
C(5)–N(2)–C(7)	114.5 (14)	111.0 (17)
C(5)–N(2)–C(8)	104.8 (14)	103.6 (18)
C(6)–N(2)–C(7)	109.0 (14)	108.1 (18)
C(6)–N(2)–C(8)	118.8 (15)	116.4 (22)
C(7)–N(2)–C(8)	98.6 (15)	108.3 (19)

produces a systematic absorption error. Anisotropic thermal parameters are known to be very sensitive to systematic errors and, indeed, act as a convenient "sink" for them when corrections either are not made or are inadequate. It is noteworthy, and encouraging, that the coordinates, which are usually of greater interest, are not noticeably affected.

There is a significant difference in the cell parameters for I and II, though this is not reflected in the derived results (bond lengths and angles), because the contribution to their esd's from the least-squares inverse matrix is greater. Although this could indicate that the esd's of the cell parameters are grossly underestimated, an alternative explanation is that the crystals were obtained from different preparations and there may be some variation of unit cell dimensions: the difference in *a* and *b* is some 0.26% and in *c* 0.08%.

The two sets of bond lengths and angles are also not significantly different, especially in view of the gradient of the half-normal probability plot for the coordinates.

The structure (*cis*-dioxo group and nonplanar MoS_2Mo bridge) of the central unit $Mo_2O_2S_2^{2+}$ is very similar to that in corresponding complexes containing ligands like histidine, cysteine, edta, or dtc (average $Mo–O_t$ bond distance 1.68 ± 0.01 Å; $Mo–S_b = 2.30 \pm 0.03$ Å; $Mo–Mo = 2.82 \pm 0.03$ Å; $MoS_2–MoS_2$ dihedral angle 150–160°).[12] But it is worth mentioning that the derivative with cyclopentadienyl ligands is centrosymmetric with a planar Mo_2S_2 unit and trans oxo as well as trans cyclopentadienyl groups.[13] It should be noted that the $Mo_2O_2S_2^{2+}$ group has a high formation tendency[14,15] and that it is formed during a novel dimerization redox process from $MoO_2S_2^{2-}$ in aqueous solution, too.[7]

The Mo–S bond distance variation in $MoO_2S_2^{2+}$ complexes with sulfur-containing ligands is highly dependent on the position of the sulfur donor atoms with respect to the terminal oxygen atom.[12] In the case of the $[Mo_2O_2S_2(S_2)_2]^{2-}$ complex, the Mo–S distances are rather short resulting in rather long S–S bond distances of the S_2^{2-} ligands (2.074–2.090 Å). (The S–S bond lengths in most S_2^{2-} complexes vary between 2.00 and 2.05 Å.[2]) The two S_2^{2-} ligands are asymmetrically bonded as in $[Mo_2^{V}(S_2)_6]^{2-}$[4] but have shorter Mo–S and longer S–S bond distances than the terminal ligands in the above-mentioned compound[4] in which the electron population of the π_v^* level[2] of the S_2^{2-} ligand is smaller.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung (NRW) for financial support and Dr. E. Hädicke (BASF) for computing facilities.

Registry No. $[N(CH_3)_4]_2[Mo_2O_2S_2(S_2)_2]$, 73557-92-3.

Supplementary Material Available: Listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

---

(12) B. Spivack, A. P. Ganghan, and Z. Dori, *J. Am. Chem. Soc.*, **93**, 5266 (1971); D. H. Brown and J. A. D. Jeffreys, *J. Chem. Soc., Dalton Trans.*, 732 (1973); B. Spivack and Z. Dori, "Proceedings of the First International Conference on Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Climax Molybdenum Co., 1973, p 131; A. Müller, N. Mohan, and R. C. Sharma, to be submitted for publication.

(13) D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3721 (1967).

(14) B. Spivack and Z. Dori *J. Chem. Soc., Chem. Commun.*, 909 (1973).

(15) A. Müller, R. G. Bhattacharyya, N. Mohan, and B. Pfefferkorn, *Z. Anorg. Allg. Chem.*, **454**, 118 (1979).