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Molybdenum Complexes of Aliphatic Thiols. The Structures of the Syn and Anti Isomers of the Di-μ-sulfido-bis(sulfido-1,2-dimercaptoethanatomolybdate(V)) Anion, $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$

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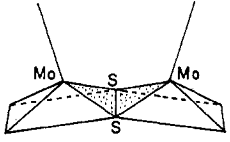
The structures of the tetraethylammonium salts of the syn and anti isomers of $[Mo_2S_4(dme)_2]^{2-}$ (where dme is the dianion of 1,2-dimercaptoethane) have been determined by x-ray crystallography. The syn isomer crystallizes in space group $P2_1/c$ with $a = 10.975$ (4) Å, $b = 19.158$ (6) Å, $c = 17.717$ (7) Å, $\beta = 115.95$ (3)°, and $Z = 4$. The calculated and observed densities are 1.537 and 1.528 (4) g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure using the 3258 data with $F_o^2 \geq 3\sigma(F_o^2)$ gave $R_1 = 0.061$ and $R_2 = 0.084$. The anti isomer crystallizes in space group $P2_1/n$ with $a = 10.234$ (2) Å, $b = 14.116$ (3) Å, $c = 11.347$ (3) Å, $\beta = 100.40$ (2)°, and $Z = 2$. The calculated and observed densities are 1.576 and 1.563 (4) g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure using the 1401 data with $F_o^2 \geq 3\sigma(F_o^2)$ gave $R_1 = 0.038$ and $R_2 = 0.049$. The inner coordination environments of the molybdenum atoms of the two isomeric binuclear anions are quite similar. Each molybdenum atom is ligated by five sulfur atoms in approximately tetragonal-pyramidal coordination geometry. The axial position of each pyramid is occupied by a terminal sulfido group (S_t); the equatorial positions are occupied by bridging sulfido groups (S_b) and the sulfur atoms from the dme ligands (S_l). The geometries of the four-membered Mo_2S_2 rings of the two isomers are different. The dihedral angle between the two MoS_2 planes of the syn isomer is 146.9 (3)° whereas the Mo_2S_2 ring of the anti isomer is required to be planar by the space group. The Mo···Mo distances in *syn*- and *anti*-$[Mo_2S_4(dme)_2]^{2-}$ are nearly identical, 2.863 (2) and 2.878 (2) Å, respectively. The average $Mo-S_b-Mo$ angles are 76.2 and 76.7°, respectively. The average S_b-Mo-S_b angle in the syn isomer is 99.9°, and the S_b-Mo-S_b angle in the anti isomer is 103.4°.

Introduction

Molybdenum is an essential element in nitrogenase and nitrate reductase, enzymes which catalyze the uptake of inorganic nitrogen by bacteria, plants, and fungi. Molybdenum is also present in enzymes involved in purine metabolism (xanthine oxidase) and sulfur metabolism (sulfite oxidase) in animals.[1] Recent genetic evidence suggests that all molybdenum-containing enzymes possess a common molybdenum cofactor.[2,3] The nature of the postulated molybdenum cofactor is still unknown, but both binuclear and mononuclear molybdenum centers must be considered as possibilities because many molybdo enzymes contain two molybdenum atoms per molecule.[1] Sulfur has been thought to be one of the atoms coordinated to the molybdenum atoms in xanthine oxidase since 1966 when it was shown[4] that thiols reduced molybdate to give EPR-active solutions whose spectral parameters resembled those of the enzyme.[5] Recent studies of the Mo(1s) extended x-ray absorption fine structure (EXAFS) of nitrogenase are also consistent with coordination of the molybdenum atoms by sulfur donor ligands.[6]

In order to be able to correlate the chemical reactivity and physical and spectroscopic properties of molybdenum complexes with their molecular structures we are investigating the stereochemistries of sulfur-rich molybdenum complexes. An especially interesting class of compounds are di-μ-sulfido-bridged binuclear Mo(V) complexes which undergo reversible oxidation–reduction reactions.[7,8] Each molybdenum atom in these stable binuclear species is also strongly bound to a terminal oxo or sulfido group, and two isomers are possible for complexes of the resulting $[Mo_2Y_2S_2]^{2+}$ core (where Y is O or S). Structure **1** arises from syn fusion of the basal edges of two tetragonal pyramids and has a bent Mo_2S_2 moiety with a dihedral angle between the two MoS_2 planes of ~150°. Structure **2** results from anti fusion of the basal edges of two tetragonal pyramids and has a planar Mo_2S_2 moiety.[9] Several compounds of structure **1** with Y = S or O are known,[10,11,13] and three cyclopentadienyl derivatives related to **2** have been reported.[14-16] However, there is no prior example of structures **1** and **2** both being observed with the same ligands. There is also no structurally characterized example of an $[Mo_2S_4]^{2+}$ complex for which the remaining donor atoms are exclusively sulfur atoms from aliphatic thiols. Herein we describe the structures of isomers **1** and **2** of the redox-active binuclear molybdenum(V) complexes with Y = S and having one 1,2-dimercaptoethanato ligand per molybdenum. A preliminary account of portions of this work has appeared.[17]



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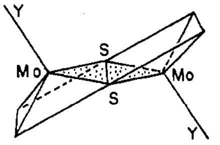

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Experimental Section

Suitable crystals of what proved to be the syn and anti isomers of tetraethylammonium di-μ-sulfido-bis(sulfido-1,2-dimercaptoethanatomolybdate(V)), $[(C_2H_5)_4N]_2[Mo_2S_4(S_2C_2H_4)_2]$ (hereafter abbreviated $[TEA]_2[Mo_2S_4(dme)_2]$) were prepared as previously described[17] by Dr. J. K. Howie and kindly provided by Professor D. T. Sawyer. The crystal data for both compounds are summarized in Table I. Data for both were collected on a Syntex $P2_1$ Fortran x-ray diffractometer equipped with an incident-beam monochromator containing a graphite crystal. Additional details concerning data collection and determination of the structures are given below.

Syn Isomer. Several crystals were rejected because preliminary ω scans showed them to be badly split. Eventually an acceptable crystal was found. The crystal was oriented with its long axis approximately parallel to the ϕ axis of the diffractometer. Unit cell parameters were determined by least-squares refinement of the setting angles of 20 reflections which had been automatically centered on the diffractometer. The ω-scan technique was chosen for data collection because of the mosaicity of the crystal (~0.5–0.7°). A variable-scan rate was selected after a rapid prescan of the reflection. Three standard reflections were checked after every 50 reflections. The stability of the standard reflections could not be analyzed in detail due to a disk failure that resulted in the loss of the standard-reflections data file. However, it is known that at no time during data collection did the intensity of any standard decrease by as much as 10%. Corrected intensities (I) and estimated standard deviations $\sigma(I)$ were calculated for each reflection with the program TAPER[18] using the formulas

$$I = [SC - \tau(B_1 + B_2)]SR$$

$$\sigma(I) = [SC + \tau^2(B_1 + B_2)^2]^{1/2}SR$$

where SC is the count during the scan, τ is the ratio of scan time to background time, B_1 and B_2 are the background counts on either side of the scan, and SR is the scan rate. The data were also corrected

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Table I. Crystal Data

	Syn isomer	Anti isomer
Habit	Rod	Rod
Dimensions	0.42 × 0.44 × 0.82 mm	0.08 × 0.05 × 0.33 mm
Space group	$P2_1/c$	$P2_1/n$
Cell parameters	$a = 10.975$ (4) Å $b = 19.158$ (7) Å $c = 17.717$ (7) Å $\beta = 115.95$ (3)°	$a = 10.234$ (2) Å $b = 14.116$ (3) Å $c = 11.347$ (3) Å $\beta = 100.40$ (2)°
Calcd density	1.527 g cm^{-3}	1.576 (2) g cm^{-3}
Obsd density	1.528 (4) g cm^{-3}	1.563 (4) g cm^{-3}
Z	4	2
λ	0.710 69(Mo K$\bar{\alpha}$) Å	0.710 69(Mo K$\bar{\alpha}$) Å
Scan technique	ω	θ–2θ
Scan width	1°	2.0°
Scan rate	2°/min for $I \leqslant 150$ counts/s to 29.3°/min for $I \geqslant$ 2500 counts/s	1.2°/min for $I \leqslant 150$ counts/s to 29.3°/min for $I \geqslant$ 13 000 counts/s
Background time:scan time	1:1	1:1
$2\theta_{max}$	50°	45°
No. of unique data	4701	2416
No. of data > 3σ	3258	1401
μ	12.39 cm^{-1}	12.66 cm^{-1}
Final R	0.061	0.038
Final R_w	0.084	0.049
σ for observn of unit wt	3.30	1.73

for Lorentz and polarization effects.[19] The polarization correction used was

$$P = (1 + \cos^2 2\theta_m \cos^2 2\theta_r)/(1 + \cos^2 2\theta_m)$$

where θ_m is the Bragg angle of the monochromator crystal (6.1°) and θ_r is the Bragg angle of the reflection. No correction was made for absorption. For this nearly cylindrical crystal the absorption coefficients will vary by about 10%. Examination of the data showed the systematic absences $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$, consistent with the space group $P2_1/c$ suggested by preliminary precession photographs (Mo Kα).

The positions of the two Mo atoms and the bridging S atoms were determined by direct methods. The remaining nonhydrogen atoms were located by subsequent structure factor calculations and difference electron density maps. Least-squares refinement of the structure was based upon F_o with $\sum w(|F_o| - |F_c|)^2$ being minimized. The weights were taken as $w = 4F_o/\sigma^2(F_o^2)$, and initially $\sigma(F_o^2)$ was based solely on counting statistics (vide supra). The atomic scattering factors for S, O, N, and C were from Ibers,[20] and those for Mo were from Cromer and Mann.[21] In the later cycles of refinement the effects of anomalous dispersion were included for Mo and S,[22] and these atoms were refined with anisotropic thermal parameters. All other atoms were refined isotropically. This model converged with $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.070$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.090$.

At this point the weighting scheme was modified to $\sigma(F_o^2) \geq 0.04F_o^2$ in order to prevent overweighting of low-angle intense reflections, and the idealized positions of the 24 hydrogen atoms on the methylene carbon atoms were determined (C–H = 0.95 Å[23]) and their calculated structure factors added as fixed contributions. Two additional cycles of least-squares refinement on this model with all atoms in the anion refined anisotropically gave $R_1 = 0.064$ and $R_2 = 0.090$ for the 3258 data with $F_o^2 \geq 3\sigma(F_o^2)$.

A difference electron density map revealed two peaks of relatively high electron density (1.2 e/Å^3) located near two of the methyl carbon atoms of one of the TEA cations. These peaks were assignable to conformational disorder of two ethyl groups of the TEA cation. Two cycles of full-matrix least-squares refinement of this disorder model with the total occupancy for the two positions of each disordered atom constrained to be 1.0 were well-behaved. Idealized positions for the 20 methylene hydrogen atoms not associated with the disordered methyl groups were redetermined and their calculated structure factors added as fixed contributions in the remaining refinements. Refinement of this model was terminated at $R_1 = 0.061$ and $R_2 = 0.084$ for the 3258 data with $F_o^2 \geq 3\sigma(F_o^2)$. In the final cycle R_2 decreased from 0.085 to 0.084. The shifts of the parameters of the molybdenum and sulfur atoms were all less than one estimated standard deviation and the maximum shift of a carbon atom parameter was 1.7σ. The largest peak in the final difference map contained 0.71 e/Å^3. A structure factor calculation using all 4701 data gave values of $R_1 = 0.084$ and $R_2 = 0.089$. Analysis of the weighting scheme showed somewhat larger values of $w|\Delta F|^2$ for the low-angle data. This may be due in part to the limitations of isotropic thermal parameters for describing the motion of the TEA cations and to ignoring the contributions of the methyl hydrogen atoms. Final atomic parameters and their estimated standard deviations are given in Table II, and a list of $10|F_o|$ and $10|F_c|$ is available.

Anti Isomer. A dark red crystal measuring 0.083 × 0.050 × 0.330 mm was used for both space group determination and intensity data collection. Preliminary x-ray photographs using a precession camera and Mo Kα radiation (Zr filtered) showed systematic absences of $h0l$ for $h + l \neq 2n$ and $0k0$ for $k \neq 2n$, consistent with the monoclinic space group $P2_1/n$. This nonstandard setting of monoclinic space group $P2_1/c$ has equivalent positions $\pm(x, y, z)$; $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. Unit cell constants were determined by least-squares refinement of the setting angles of 25 reflections which were centered automatically on a Syntex $P2_1$ diffractometer. The experimental density (Table I) obtained by flotation in a mixture of CCl_4 and C_6H_5Br requires two formula units of $[TEA]_2[Mo_2S_4(dme)_2]$ per unit cell; hence each anion must lie on a center of symmetry.

Reflections were collected using the θ–2θ scan technique because ω scans on 12 of the centered reflections showed peak widths at half-height of less than 0.10°. The scan speed was variable and determined by the count rate of a rapid (29.3°/min) prescan of the reflection. The scan range was $2\theta_{MoK\alpha_1} - 1.0°$ to $2\theta_{MoK\alpha_2} + 1.0°$. Three standard reflections were checked after every 47 reflections. None of these check reflections had a standard deviation greater than 2.2% of its average intensity. Total exposure time for the crystal during data collection was 96 h, during which 3680 reflections with $2 < 2\theta < 45°$ were collected in two shells $3 \rightarrow 35°$ and $33 \rightarrow 45°$. The data from the two overlapping shells were merged to give 2416 independent reflections. Data were processed as described for the syn isomer (vide supra), and no correction was made for absorption.

The positions of the molybdenum and sulfur atoms of the anion were determined with some difficulty by direct methods. The preliminary procession photographs suggested that reflections with $h + k + l \neq 2n$ would be systematically weak. This body-centered intensity pattern was verified by the distribution of the normalized structure factors which showed $\langle E^2 \rangle << 1$ for reflections of odd parity. A satisfactory direct-methods solution was obtained after renormalizing the data so that $\langle E^2 \rangle = 1$ for each parity group. The solution had an approximately body-centered arrangement of the molybdenum atoms in the cell (vide infra).

The remaining nonhydrogen atoms were located by a series of structure factor calculations and difference electron density maps. Full-matrix least-squares refinement of the structure was carried out as described for the syn isomer. In the final cycles the atoms of the anion were refined anisotropically with anomalous dispersion effects included for Mo and S,[22] and the cation was refined isotropically. A difference electron density map computed with $R_1 = 0.046$ showed no peaks greater than 0.75 e/Å^3 and revealed several hydrogen atoms. Idealized coordinates were calculated for the 12 methylene hydrogen atoms, and they were included as fixed contributions to the structure. Refinement converged with $R_1 = 0.038$ and $R_2 = 0.049$ for the 1401 data with $F_o^2 \geq 3\sigma(F_o^2)$. In the final cycle of refinement all parameter shifts were less than one estimated standard deviation. A structure factor calculation using all 2197 data gave values of $R_1 = 0.074$ and $R_2 = 0.060$. No extinction correction was necessary. The final atomic parameters and their estimated standard deviations are given in Table III and a list of $10|F_o|$ and $10|F_c|$ is available as supplementary material.

Results

The determinations of the two crystal structures show unambiguously that both materials have the same chemical formula $[TEA]_2[Mo_2S_4(dme)_2]$ but syn (**1**) and anti (**2**) stereochemistries for the $[Mo_2S_4(dme)_2]^{2-}$ anion. Perspective views of the syn and anti isomers of the anion are shown in Figure 1. Selected distances are also included in the figure. Projected views of the syn and anti isomers and selected bond angles appear in Figure 2. Other distances and angles are given in Tables IV–VII. The idealized symmetry of the syn

Table II. Final Atomic Parameters for *syn*-$[TEA]_2[Mo_2S_4(dme)_2]$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
MO1	.91757(9)	.66242(4)	.17545(5)	110.9(15)	26.74(26)	49.1(4)	-.7(4)	37.7(6)	3.48(25)
MO2	1.20743(9)	.66290(4)	.24708(5)	105.4(15)	27.14(26)	47.2(4)	9.3(4)	41.2(6)	4.95(25)
S1	1.05805(28)	.74439(12)	.15718(16)	117.(4)	27.6(7)	56.8(12)	6.9(13)	46.1(17)	9.8(8)
S2	1.0687(3)	.61213(14)	.29996(17)	146.(4)	35.5(9)	56.6(13)	4.9(15)	52.1(19)	12.2(9)
S3	1.3706(3)	.64336(16)	.38997(17)	152.(5)	48.0(11)	48.8(13)	6.1(17)	33.0(19)	2.0(9)
S4	1.3520(3)	.76199(18)	.26410(23)	112.(5)	52.8(13)	96.3(21)	-16.3(18)	37.7(23)	17.7(13)
S5	.7715(3)	.76231(15)	.12613(20)	101.(4)	39.2(10)	78.3(17)	12.7(15)	32.5(20)	10.5(10)
S6	.7688(4)	.63817(22)	.23944(25)	152.(6)	69.4(15)	106.0(25)	12.6(22)	87.(3)	28.2(16)
S7	.8559(4)	.59122(17)	.07616(24)	251.(7)	40.1(11)	91.7(22)	-7.2(21)	68.(3)	-8.2(12)
S8	1.2473(3)	.58698(16)	.17418(18)	180.(5)	43.4(10)	58.7(14)	31.0(18)	56.0(21)	5.9(10)
C1	1.5113(15)	.6968(9)	.4024(11)	167.(25)	71.(7)	108.(11)	-19.(10)	-38.(13)	12.(7)
C2	1.5067(15)	.7399(12)	.3518(13)	99.(21)	135.(12)	163.(15)	-39.(13)	35.(14)	77.(12)
C3	.6223(15)	.7416(9)	.1431(13)	135.(25)	63.(7)	163.(15)	28.(10)	75.(14)	27.(8)
C4	.6116(15)	.6783(12)	.1670(13)	80.(21)	132.(12)	183.(16)	40.(13)	93.(15)	70.(12)
N1	-.3540(9)	.4657(4)	.3642(5)	6.08(19)					
C5	-.4329(13)	.4969(7)	.2783(8)	7.20(28)					
C6	-.4364(13)	.4129(6)	.3845(7)	6.52(26)					
C7	-.2301(13)	.4250(7)	.3666(7)	7.10(29)					
C8	-.3111(14)	.5228(7)	.4241(8)	7.6(3)					
C9	-.4995(15)	.4466(8)	.2064(9)	9.0(4)					
C10	-.5671(14)	.4408(7)	.3847(8)	7.5(3)					
C11(A)	-.1407(17)	.4619(8)	.3382(10)	7.7(5)					
C11(B)	-.076(7)	.403(4)	.469(5)	8.3(24)					
C12(A)	-.2249(20)	.5072(10)	.5077(12)	9.3(6)					
C12(B)	-.187(5)	.5815(24)	.4607(29)	5.7(14)					
N2	-.0828(10)	.3506(5)	.0933(6)	6.59(20)					
C13	-.0211(17)	.3620(9)	.1852(10)	10.3(4)					
C14	.0124(20)	.3525(9)	.0559(12)	11.7(5)					
C15	-.1511(17)	.2840(9)	.0777(10)	10.2(4)					
C16	-.1854(19)	.4078(9)	.0488(11)	11.4(5)					
C17	.0661(18)	.4301(10)	.2115(11)	11.3(5)					
C18	.1227(19)	.2888(10)	.0924(12)	12.3(5)					
C19	-.2387(15)	.2661(8)	-.0186(9)	8.9(4)					
C20	-.2984(17)	.4135(9)	.0839(10)	10.5(4)					

[a] All anisotropic temperature factors are × 10^4. A single temperature factor entry indicates that the atom was refined isotropically. Temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviation of the least significant digit is given in parentheses. C11 and C12 are the disordered carbon atoms of two of the ethyl groups of a TEA cation. The occupancies of these positions are C11(A) = 0.77 (4) and C12(A) = 0.78 (2).

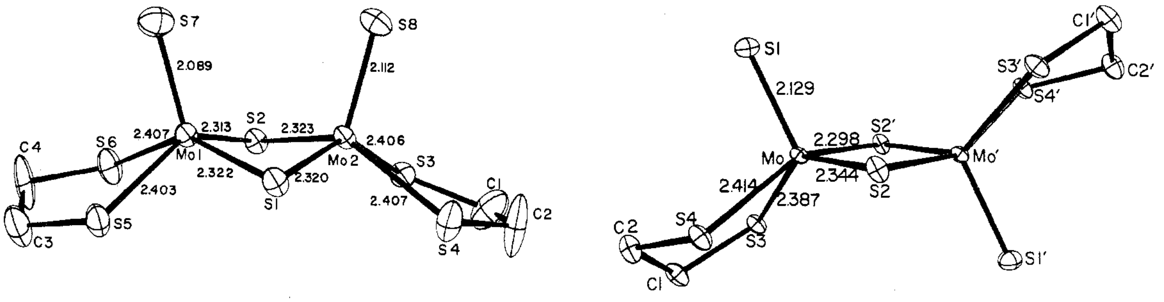


Figure 1. Perspective view of the syn (left) and anti (right) isomers of the $[Mo_2S_4(dme)_2]^{2-}$ anion showing the numbering schemes and some selected bond lengths. For the anti isomer the primed atoms are related to the unprimed atoms by a center of symmetry. Ellipsoids enclose 50% of the probability distribution.

and anti isomers are C_{2v} and C_{2h}, respectively (exclusive of the methylene groups of the dme ligands). No symmetry is imposed on the syn isomer; the anti isomer is required to have $\bar{1}$ symmetry by the space group.

The inner coordination environments of the molybdenum atoms of the two isomeric anions are quite similar (Table VIII). Each molybdenum atom is ligated by five sulfur atoms in approximately tetragonal-pyramidal (TP) coordination geometry. The axial position of each TP is occupied by a terminal sulfido group (S_t); the equatorial positions are occupied by bridging sulfido groups (S_b) and the sulfur atoms from the dme ligands (S_l).

The two crystallographically independent TP fragments of the syn isomer are nearly identical. The range of the four

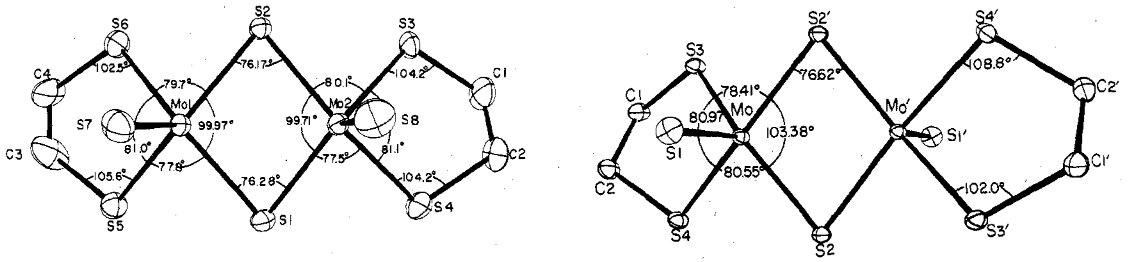


Figure 2. Projected views of the syn (left) and anti (right) isomers of the $[Mo_2S_4(dme)_2]^{2-}$ anion showing selected bond angles. Ellipsoids enclose 50% of the probability distribution.

Table III. Final Atomic Parameters for *anti*-$[TEA]_2[Mo_2S_4(dme)_2]$

	x	y	z	β_{11} [a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.57925(7)	0.99669(6)	0.11841(6)	6.31(8)	2.55(4)	4.34(6)	-0.54(7)	1.68(5)	-0.30(5)
S1	0.7297(3)	0.8905(2)	0.1444(2)	10.06(3)	3.99(2)	9.62(3)	0.09(2)	2.00(3)	-0.27(2)
S2	0.3790(2)	0.9231(2)	0.0518(2)	8.19(3)	4.00(1)	5.12(2)	-2.18(2)	1.93(2)	-0.14(1)
S3	0.6603(2)	1.1454(2)	0.2052(2)	10.13(3)	3.43(1)	6.06(2)	-1.75(2)	2.92(2)	-0.93(1)
S4	0.4963(2)	0.9895(2)	0.0159(3)	10.59(3)	4.53(1)	5.04(2)	-1.81(2)	3.03(2)	-0.39(2)
C1	0.6399(10)	1.1498(8)	0.3562(9)	12.87(14)	5.67(7)	6.67(9)	-2.96(8)	3.28(10)	-2.1(6)
C2	0.6247(10)	1.0538(8)	0.4065(9)	14.05(20)	5.66(7)	5.30(9)	-2.11(8)	1.54(9)	-0.30(7)
N	0.0953(7)	1.1444(5)	0.2414(6)	1.98(15)					
C3	0.1512(10)	1.1531(7)	0.3723(9)	4.23(22)					
C4	0.2083(10)	1.1447(7)	0.1723(9)	4.17(22)					
C5	0.0162(10)	1.0528(8)	0.2145(9)	4.24(22)					
C6	-0.0014(9)	1.2275(7)	0.2076(9)	3.83(21)					
C7	0.0520(12)	1.1461(9)	0.4576(11)	6.10(29)					
C8	0.2849(11)	1.2387(8)	0.1762(10)	5.18(28)					
C9	0.0932(11)	0.9622(9)	0.2552(10)	5.70(28)					
C10	-0.0575(11)	1.2353(8)	0.0717(10)	5.37(27)					

[a] All anisotropic atomic temperature factors $\times 10^3$. A single temperature factor entry indicates the atom was refined isotropically.

Table IV. Interatomic Distances (Å) for the *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ Anion

Mo1-Mo2	2.863 (2)	S3-C1	1.78 (2)
Mo1-S1	2.322 (3)	S4-C2	1.78 (2)
Mo1-S2	2.313 (3)	S5-C3	1.83 (2)
Mo2-S1	2.320 (3)	S6-C4	1.81 (2)
Mo2-S2	2.323 (3)	C1-C2	1.21 (2) (1.51)[a]
Mo1-S7	2.089 (4)	C3-C4	1.31 (2) (1.54)[a]
Mo2-S8	2.112 (3)	S1-S2	3.550 (4)
Mo1-S5	2.403 (3)		
Mo1-S6	2.407 (3)		
Mo2-S3	2.406 (3)		
Mo2-S4	2.407 (3)		

[a] Interatomic distance averaged over the thermal motion, with the atoms assumed to move independently.

Table V. Bond Angles (deg) for the *syn*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ Anion

Mo1-S1-Mo2	76.17 (8)	S3-C1-C2	123 (1)
Mo1-S2-Mo2	76.28 (9)	S4-C2-C1	122 (1)
S1-Mo1-S2	99.97 (10)	S5-C3-C4	118 (1)
S1-Mo2-S2	99.72 (10)	S6-C4-C3	116 (1)
S3-Mo2-S4	81.1 (1)	S1-Mo1-S5	77.8 (1)
S5-Mo1-S6	81.0 (1)	S2-Mo1-S6	79.7 (1)
Mo2-S3-C1	104.2 (6)	S1-Mo2-S4	77.5 (1)
Mo2-S4-C2	104.2 (6)	S2-Mo2-S3	80.1 (1)
Mo1-S5-C3	105.6 (5)	Mo2-Mo1-S7	105.3 (1)
Mo1-S6-C4	102.5 (6)	Mo1-Mo2-S8	102.4 (1)

Dihedral Angle between Planes S2-Mo1-S1 and S1-Mo2-S2: 146.9 (1)

Table VI. Interatomic Distances (Å) for the *anti*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ Anion

Mo-Mo'	2.878 (2)	S3-C1	1.805 (10)
Mo-S1	2.129 (3)	S4-C2	1.828 (10)
Mo-S2	2.298 (2)	C1-C2	1.490 (14)
Mo-S2'	2.344 (2)	S2-S2'	3.658 (4)
Mo-S3	2.387 (2)		
Mo-S4	2.414 (2)		

Table VII. Bond Angles (deg) for the *anti*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ Anion

S2-Mo-S2'	103.38 (7)	S3-C1-C2	112.3 (7)
S3-Mo-S4	80.97 (9)	S4-C2-C1	108.7 (7)
Mo-S2-Mo'	76.62 (7)	S2-Mo-S4	80.55 (8)
Mo-S3-C1	108.8 (3)	S2'-Mo-S3	78.41 (8)
Mo-S4-C2	102.0 (3)	Mo-Mo'-S1	115.04 (9)

independent Mo–S_b distances is 0.009 Å, and the range of Mo–S_t distances is 0.005 Å. The S_b and S_t atoms of each TP fragment are nearly coplanar (Table IX), and in both TP fragments the Mo atom is 0.72 Å out of the basal plane toward the S_t ligand.

The geometry of the TP fragments of the anti isomer is less regular than those of the syn isomer. In the anti isomer the two independent Mo–S_b and Mo–S_t distances differ by 0.046 and 0.027 Å, respectively, and the four equatorial sulfur atoms show substantial deviations from planarity (Table VIII). The Mo atom is 0.66 Å above the basal plane of the TP.

The four-membered Mo_2S_2 rings of the two isomers have different geometries. In *syn*-$[Mo_2S_4(dme)_2]^{2-}$ the dihedral angle between the two MoS_2 planes of the Mo_2S_2 ring is 146.9 (3)°. The Mo_2S_2 ring of *anti*-$[Mo_2S_4(dme)_2]^{2-}$ is required to be planar by the space group. Since the Mo–S_b distances for the two isomers are nearly identical, the Mo···Mo and/or the S_b···S_b distances must differ. Table VII shows that the S_b···S_b distance of the syn isomer is 0.108 Å longer than that of the

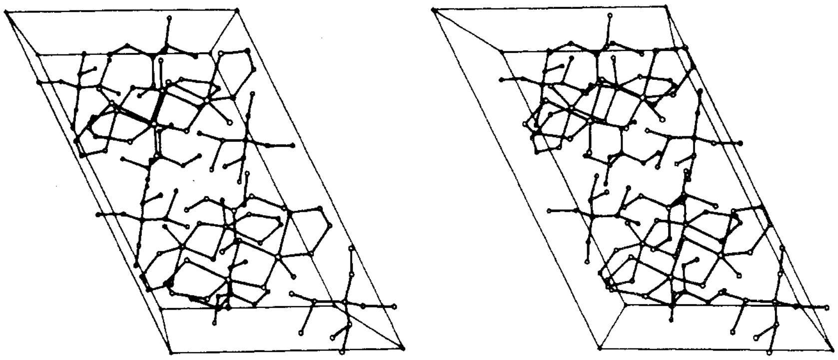


Figure 3. Packing diagram for *syn*-$[TEA]_2[Mo_2S_4(dme)_2]$ viewed along the *b* axis. Both conformations of the disordered TEA cation are shown.

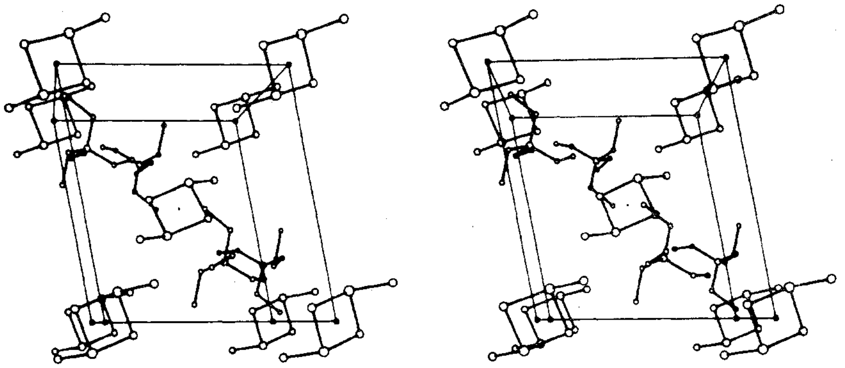


Figure 4. Packing diagram for *anti*-$[TEA]_2[Mo_2S_4(dme)_2]$ viewed along the *b* axis. For clarity only the Mo_2S_4 cores of the anions are shown.

Table VIII. Equations for Least-Squares Planes in the *syn*- and *anti*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ Anions[d]

Atom	Dist, Å	Atom	Dist, Å
Syn Isomer			
Plane 1: $0.4768x - 0.6779y - 0.5596z + 6.0851 = 0$[a]			
S1	0.0188	S4	−0.0213
S2	−0.0183	Mo2	0.72
S3	0.0208		
Plane 2: $0.0936x - 0.6620y - 0.7437z + 10.3393 = 0$[b]			
S1	0.0604	S6	0.0672
S2	−0.0589	Mo1	0.72
S5	−0.0686		
Anti Isomer			
Plane: $-0.7167x + 0.6862y - 0.1243z - 6.0744 = 0$[c]			
S2	0.089	S4	−0.066
S2′	−0.205	Mo	0.66
S3	0.181		

[a] Rms deviation of the fitted atoms from the plane is 0.02 Å.
[b] Rms deviation of the fitted atoms from the plane is 0.06 Å.
[c] Rms deviation of the fitted atoms from the plane is 0.15 Å.
[d] Equations fit to sulfur atom coordinates only.

Table IX. Comparison of the *syn*- and *anti*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ Anions[a]

Atoms	Syn	Anti
Average Interatomic Distances, Å		
Mo-Mo	2.863 (2)	2.878 (2)
Mo-S_b	2.320 (5)	2.321 (33)
Mo-S_t	2.101 (16)	2.129 (3)
Mo-S_l	2.406 (2)	2.401 (19)
C_l-S_l	1.80 (2)	1.817 (16)
S_b-S_b	3.550 (4)	3.658 (4)
Mo displacement	0.72	0.66
C_l-C_l	1.26 (7) 1.52[b]	1.490 (14) 1.56[b]
Average Bond Angles, Deg		
Mo-S_b-Mo	76.23 (7)	76.62 (7)
S_b-Mo-S_b	99.85 (8)	103.38 (7)
S_l-Mo-S_l	81.1 (1)	80.97 (9)
Mo-S_l-C_l	104.1 (13)	105.4 (48)
Dihedral angle	146.9 (3)	180
Mo-Mo-S_t	109.1 (1)	115.04 (9)

[a] For multiple measurements, the number given in parentheses is the estimated standard deviation of the mean $\sigma = [\Sigma_i(x_i - \bar{x})^2 / n(n-1)]^{1/2}$, where x_i is an individual observation, $\bar{x}$ is the unbiased estimate of the mean, and n is the number of observations.
[b] Interatomic distances averaged over thermal motion with the atoms assumed to move independently.

anti isomer, whereas the Mo⋯Mo distances differ by only 0.015 Å. Expressed in terms of bond angles, the Mo–S_b–Mo angles for the syn and anti isomers are essentially the same (76.2 and 76.6°, respectively), but the S_b–Mo–S_b angles differ by 3.6° (35σ).

The geometry of the dme ligand is very similar in the two isomers. The apparent C–C distances in the syn isomer of 1.21 (2) and 1.31 (2) Å are unrealistically short for carbon–carbon single bonds. However, Figure 1 shows that the C atoms have large thermal displacements normal to the ring. Correction for thermal motion assuming independent motion[24] of the atoms leads to C–C distances of 1.51 and 1.54 Å. The maximum root-mean-square amplitudes of vibration for the C atoms of the dme ligands of the anti isomer are only half as large as for the syn isomer and the uncorrected C–C bond length is 1.49 Å. Correction assuming independent thermal motion lengthens the bond to 1.56 Å.

The packing diagrams for the two structures are shown in Figures 3 and 4. The anions of the anti isomer (Figure 4) are packed in an approximately body-centered arrangement as suggested by the intensity distribution. The efficient packing of the cations and the anions in the anti isomer makes its density 3% higher than that of the syn isomer. The higher density of the anti isomer probably accounts in part for its better behaved dme rings. The lower density of the crystals of the syn isomer is also manifested in the disorder of one of the TEA cations (Figure 3).

The ordered cation in the syn structure has approximately D_{2d} symmetry. The other cation in the syn structure and the cation of the anti structure show no apparent symmetry in the crystal. The distances and angles in the cations are included as supplementary information.

Discussion

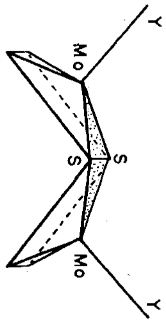
The two forms of the $[Mo_2S_4(dme)_2]^{2-}$ anion described here are the first documented examples of syn–anti isomerism in binuclear Mo(V) complexes. There is only one other report of a binuclear Mo(V) complex in which each molybdenum atom is ligated exclusively by sulfur atoms,[25] although several di-μ-sulfido-bridged dimers containing the $[Mo_2Y_2S_2]^{2+}$ core are known. Important distances and angles for such compounds are tabulated in Table X.

One point of interest from Table X is the variation of Mo–S_t distances, which range from 1.937 (6) to 2.141 Å. It is unclear whether this variation is a property of Mo–S_t distances or is perhaps due to other factors. For example, recent work in our laboratory[26] has shown that partial occupancy of terminal sulfido sites by terminal oxo ligands can lead to apparent Mo–S_t distances as short as 1.82 Å. It would seen prudent to forego making conclusions concerning Mo–S_t distances until additional structure determinations become available.

As has been emphasized previously,[27] di-μ-sulfido-bridged binuclear Mo(V) complexes have essentially invariant Mo–S_b distances; the unweighted average of the entries in Table X is 2.32 (2) Å. The Mo···Mo distances show somewhat wider variation, ranging from 2.79 (1) to 2.920 (1) Å with an unweighted average of 2.84 (4) Å. The average S_b···S_b distance is 3.62 (5) Å. The Mo–S_b–Mo angles are remarkably constant [average 76 (1)°], as has been noted elsewhere.[16] A direct Mo–Mo bond has previously been postulated to explain the short intermetallic distances and the diamagnetism of binuclear di-μ-sulfido-bridged complexes of Mo(V). However, the similarity of the Mo–S_b–Mo angles in the syn and anti isomers is equally compatible with a model involving strong antiferromagnetic coupling through the bridging sulfido ligands. At present there are neither suitable experimental data nor appropriate theoretical calculations to evaluate these two descriptions. The S_b–Mo–S_b angles show no obvious correlation with syn and anti geometry. The largest and smallest S_b–Mo–S_b angles in Table X occur in syn compounds: 103.8 (5)° in *syn*-$[Mo_2S_2O_2(histidine)_2]^{2-}$; 99.85 (10)° in *syn*-$[Mo_2S_4(dme)_2]^{2-}$.

The relative stabilities of the syn and anti isomers remain unknown. Previously it was suggested[10] that steric factors may play a role in selection of one isomer over the other in some cases. The low yields of syn and anti isomers of the $[Mo_2S_4(dme)_2]^{2-}$ anion have precluded appropriate dynamic studies of their possible interconversion. Cyclic voltammograms of the two isomers are similar with both showing reversible one-electron reductions.[17] The small amounts of available material and the very negative reduction potentials have prevented isolation of the reduced species.

Finally, we wish to point out that careful inspection of exact molecular models suggests that there may be a second conformation (3) available to the syn isomer.[28] Conformation 3



3

has a dihedral angle between MoS_2 planes of approximately

Table X. Relevant Structural Parameters of Disulfido-Bridged Molybdenum Complexes

Complex	Mo–Mo, Å	Mo–Y_t, Å	Mo–S_b, Å	Mo–L,[e] Å	S_b–S_b, Å	Mo–S_b–Mo, deg	S_b–Mo–S_b, deg	Mo–Mo–O_t, deg	Dihedral angle, deg	Mo displacement, Å	Ref
anti-$(\eta^5\text{-}C_5H_5)_2Mo_2S_2O_2$	2.894 (5)	1.679 (6)[a]	2.317 (3)	C 2.41	3.616 (9)	77.3 (1)	102.7 (1)	112.4 (1)	180		14
anti-$(\eta^5\text{-}C_5H_5)_2Mo_2S_2(NC(CH_3)_3)_2$	2.920 (1)	1.733 (4)[b]	2.342 (1)	C 2.383	3.661 (2)	77.1 (1)	102.9 (1)	109.3 (1)[b]	180		16
anti-$(\eta^5\text{-}C_5H_5)_2Mo_2S_4$		2.141[c]							180		15
syn-$Mo_2S_4(S_2CN(C_4H_9)_2)_2$	2.801 (2)	1.937 (6)[c]	2.308 (4)	S 2.447 (6)		74.7 (1)	101.8 (6)	104.3 (2)[c]	148	0.72	25
syn-$Mo_2O_2S_2$(cysteine methyl ester)$_2$	2.804 (4)	1.71 (3)[a]	2.30 (1)	S 2.38 (1) N 2.24 (3)	3.58	74.9 (4)	101.8 (5)	105 (1)	149 (1)	0.38	32
syn-$Na_2Mo_2S_2O_2$(cysteine)$_2$	2.82 (1)	1.62 (3)[a]	2.33 (1)	S 2.50 (1) N 2.27 (3) O* 2.37 (3)		75 (1)	103.0 (1)	100 (1)	156.0	0.42	33
syn-$Na_2Mo_2S_2O_2$(histidine)$_2$	2.82 (1)	1.71 (2)[a]	2.32 (2)	N 2.24 (2) O* 2.23 (2)	3.64 (2)	74.9 (5)	103.8 (5)	105 (1)	160.9		34
syn-$Cs_2Mo_2S_2O_2$(EDTA)	2.799 (1)	1.683 (6)[a]	2.294 (1)	O 2.111 (9) N* 2.448 (8) O* 2.37 (3)		75.2 (1)	102.1 (1)	100.5	152.3	0.37	35
syn-$[(n\text{-}C_4H_9)_4N]_2$-$[Mo_2O_2S_2(i\text{-mnt})_2]$[d]	2.821 (2)	1.664 (7)[a]	2.300 (1)	S 2.434 (3)		75.8 (1)	101.6 (1)	108.4 (2)	153.1	0.72	10
syn-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$	2.863 (2)	2.100 (4)[c]	2.320 (3)	S 2.406 (3)	3.550 (4)	76.22 (9)	99.85 (10)	103.8 (1)[c]	146.9 (1)	0.72	This work
anti-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$	2.878 (2)	2.129 (3)[c]	2.321 (2)	S 2.400 (2)	3.658 (4)	76.62 (7)	103.38 (7)	115.04 (9)[c]	180	0.66	This work

[a] Terminal oxo ligand. [b] Terminal imido group. [c] Terminal sulfido ligand. [d] *i*-mnt is isomaleonitriledithiolate, $S_2C_2(CN)_2^{2-}$. [e] Asterisk denotes atom trans to Y in six-coordinate complexes.

210° (measured from the side of the anion with the terminal sulfido ligands). All other distances and angles of **3** are identical with those of the syn conformer whose structure has been described above. No example of conformer **3** has yet been reported for binuclear Mo(V) complexes in which the Mo atoms are five-coordinate. For six-coordinate binuclear Mo centers conformer **3** becomes two distorted octahedra sharing a face. Three structures of such triply bridged binuclear Mo(V) complexes have been described.[29-31] The largest dihedral angle in such complexes is 196°.[29]

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Registry No. *syn*-$[TEA]_2[Mo_2S_4(dme)_2]$, 65137-01-1; *anti*-$[TEA]_2[Mo_2S_4(dme)_2]$, 65045-66-1.

Supplementary Material Available: Tables of distances and angles in the TEA cations and structure factor tables (24 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tris[tetra-μ-formato-diaquodichromium(II)] Decahydrate: A Case of an Unusually Good False Minimum in a Structure Solution

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The title compound, $[Cr_2(O_2CH)_4(H_2O)_2]_3 \cdot 10H_2O$, crystallizes from a dilute aqueous solution of chromium(II) formate in the tetragonal space group $I4_1/acd$. The unit cell has the dimensions $a = 17.929$ (3) Å, $c = 25.198$ (3) Å, $V = 8100$ (4) Å^3, $d_x = 1.87$ g/cm^3, and $Z = 8$ for the formula given. The 48 chromium atoms in the unit cell are all present in $Cr_2(O_2CH)_4(H_2O)_2$ units and these are of two crystallographically independent types having Cr–Cr distances of 2.373 (2) and 2.360 (2) Å, while the respective Cr–O$_{ax}$ distances are 2.268 (4) and 2.210 (6) Å. The structure initially refined to a false minimum ($R_1 = 0.0551$, $R_2 = 0.0805$), but this was recognized because of unreasonable values of some internuclear distances. A structure with reasonable values of these bond lengths and significantly lower residuals ($R_1 = 0.0505$, $R_2 = 0.0684$) was found to be stable under refinement and is reported in detail.

Introduction

Among the carboxylato complexes of both chromium(II) and copper(II), of the general formula $M(O_2CR)_2(L)_x$, the hydrated formato complexes $M(O_2CH)_2(H_2O)_x$ are remarkable for the range of values x may assume.[1,2] Both color and magnetic properties vary with x. At least four distinct hydrates have been reported for chromium(II) formate[1] and two for copper(II) formate,[2] in addition to the anhydrous metal

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