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Structure of Tris[2-aminobenzenethiolato(2–)-*N*,*S*]molybdenum(VI), $Mo(NHC_6H_4S)_3$

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The crystal and molecular structure of tris[2-aminobenzenethiolato(2–)-*N*,*S*]molybdenum(VI), $Mo(NHC_6H_4S)_3$, has been determined from a single-crystal X-ray study. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell of dimensions $a = 10.644$ (1), $b = 11.459$ (2), $c = 15.113$ (2) Å. The observed and calculated densities are 1.66 (2) and 1.674 g cm^{-3}, respectively. Full-matrix least-squares refinement using 2084 unique reflections having $3.5° < 2\theta < 55°$ and $I > 3\sigma(I)$ converged at $R_1 = 0.027$ and $R_2 = 0.031$. Each molybdenum atom in the discrete monomers is in a distorted trigonal-prismatic coordination environment. The average Mo–S and Mo–N distances are 2.418 (6) and 1.997 (8) Å, respectively. The two triangular faces, formed by the three sulfur atoms and by the three nitrogen atoms, having the average S···S and N···N sides of 3.251 (30) and 2.793 (10) Å, respectively, are nearly parallel but are relatively twisted by the average angle of 12.3 (10)°. Distortion from a trigonal prism in this compound is slightly greater than that observed in $V(S_2C_2Ph_2)_3$. The molecule conforms to approximately C_3 point symmetry. Each 2-aminobenzenethiolate ligand is folded about its S···N vector. The protons of the NH groups are only 2.5 Å from the molybdenum atom and lie in the planes of the ligands.

Introduction

Molybdenum-containing enzymes are vitally important in nitrogen uptake, nitrogen metabolism, and several other biochemical reactions.[1] The coordination environment about the molybdenum atoms in such enzymes is still unknown because no molybdo enzyme has had its structure determined by X-ray crystallography. However, the molybdenum centers of the enzymes have been probed directly by electron paramagnetic resonance (EPR) spectroscopy[1] and very recently by X-ray absorption spectroscopy.[2] Comparison of the spectral data from enzymes with spectral data from coordination compounds suggests that sulfur atoms are coordinated to molybdenum in the enzymes.[1-3]

An important prerequisite for effective interpretation of the spectral results from enzymes is a series of compounds whose stoichiometry and stereochemistry have been definitively established by X-ray structure determination. One particularly interesting benchmark molecule is tris(2-aminobenzenethiolato)molybdenum(VI), $Mo(NHC_6H_4S)_3$, hereafter called $Mo(abt)_3$.[4] This compound contains only one kind of N atom and one kind of S atom. The X-ray absorption spectrum of $Mo(abt)_3$ has been obtained[5] and Mo–S and Mo–N distances have been deduced from the fine structure. In addition, reduction of $Mo(abt)_3$ by one electron yields $Mo(abt)_3^-$, a compound with a temperature-dependent EPR spectrum which exhibits hyperfine splitting from both ^{14}N and ^1H.[4] The structure of $Mo(abt)_3$ is of further interest because there are few structure determinations for tris-chelate MS_3N_3 complexes. Such compounds can adopt octahedral or trigonal-prismatic coordination geometries, and facial or meridional arrangements are possible for the ligands.

Experimental Section

Preparation of Crystals. All attempts to grow crystals of the title compound prepared according to previous methods[4] using usual diffusion techniques were unsuccessful because the compound decomposed in solutions in a few days,[4,6] even if carefully purified and degassed solvents were employed. Dark green crystals of $Mo(NHC_6H_4S)_3$ suitable for X-ray diffraction study were directly obtained from the following modification of the previous synthesis.[4]

To a solution of 2-aminobenzenethiol (0.31 g, 2.5 mmol) in benzene (15 mL), a filtered solution of dioxobis(acetylacetonato)molybdenum(VI)[7] (0.32 g, 1 mmol) in methanol (5 mL) was added dropwise. After the mixture was allowed to stand at room temperature for 6 h, the supernatant liquid was decanted. The remaining crystals were washed with a small amount of benzene and carbon tetrachloride and the liquid was decanted. These operations were repeated several times in order to remove microcrystals. Finally, the crystals were collected by filtration, washed with pentane, and dried in vacuo. The identity of the compound was confirmed by its IR spectrum.

Table I. Crystallographic Data at 24 °C[a]

formula	$C_{18}H_{15}N_3S_3Mo$
mol wt	465.47
space group	$P2_12_12_1$ (No. 19)
cell dimensions[b]	
a, Å	10.664 (1)
b, Å	11.459 (2)
c, Å	15.113 (2)
V, Å^3	1846.8 (4)
Z	4
d_{obsd},[c] g cm^{-3}	1.66 (2)
d_{calcd}, g cm^{-3}	1.674
crystal shape	rectangular parallelepiped
crystal dimensions, mm	0.10 × 0.12 × 0.29
radiation, Å	λ(Mo Kα) 0.710 73
monochromater	graphite crystal
supplied power	50 kV, 30 mA
data collection method	θ–2θ scan
scan speed, deg min^{-1}	variable (1.0–29.3 in the range $3.5° < 2\theta < 50°$; 0.7–29.3 in the range $50° < 2\theta < 55°$), determined as a function of peak intensity
scan range (2θ), deg	Mo Kα_1 – 0.8 to Mo Kα_2 + 0.8
ratio of total background time to peak scan time	0.5
std reflections	(200), (020), (002) after every 47 readings
std dev of standards	⩽2%
2θ limit, deg	3.5–55
no. of unique data	2496
no. of data used in the calculation	2084, $I > 3\sigma(I)$
absorption coeff (μ), cm^{-1}	10.30 (Mo Kα)
multiplier range of empirical absorption correction[d]	1.00–0.863

[a] The standard deviation of the least significant figure is given in the parentheses in this table and in following tables. [b] Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range from 15 to 25°. [c] Density was determined by the flotation method using a solution of carbon tetrachloride and bromoform. [d] Empirical absorption correction was applied using the program TAPER.[8]

Collection and Reduction of the X-ray Intensity Data. A well-formed crystal whose surface had been previously coated with epoxy glue[6] was mounted on a Syntex $P2_1$ autodiffractometer equipped with a scintillation counter and a graphite monochromator. The longest dimension of the crystal (*b* axis) was approximately parallel to the ϕ axis. The automatic centering, indexing, and least-squares routines[8,9] were carried out to obtain the cell dimensions which are given in Table I, together with other crystallographic data. A data set for the *hkl* octant was collected using conditions shown in Table I.

The data were reduced to F_o^2 and $\sigma(F_o^2)$ by the procedures previously described.[10] Lorentz–polarization factors were calculated

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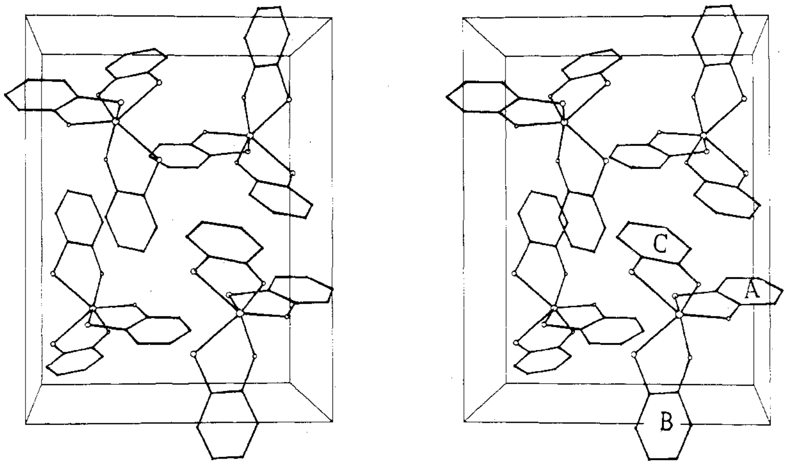

Figure 1. Stereoview of the molecular packing showing the contents of one unit cell. The positive direction of the *a* axis is perpendicular to the paper toward the reader. The positive direction of the *b* axis is horizontal to the right. Sulfur atoms have been arbitrarily assigned bigger thermal parameters than nitrogen atoms: A, C(1)–C(6); B, C(7)–C(12); C, C(13)–C(18).

on the assumption of 50% mosaicity and 50% perfection of the monochromator crystal. An absorption correction was applied[8] on the basis of absorption curves empirically obtained from θ–2θ scans, with ϕ varying from 0 to 360° at ca. 10° intervals, for 11 reflections at χ values of about 90° with 2θ in the range 7–52°. A slight increase in intensity was observed for all three standard reflections during the data collection. The increase was less than the estimated standard deviation of the mean intensity and therefore no correction for this increment was made.

Examination of the collected data set revealed the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$, consistent only with the acentric space group $P2_12_12_1$. In addition to the hkl data, a set of $\bar{h}\bar{k}\bar{l}$ reflections having $2\theta < 20°$ was collected and processed in the same manner as above, in order to assist in establishing the correct enantiomer. Equivalent reflections for the two forms were averaged after being individually corrected for absorption. The total number of the unique data obtained was 2496, of which 2084 reflections were considered significant using the criterion $I > 3\sigma(I)$. An estimate of the overall scale factor was obtained using Wilson's method and was subsequently refined.

Solution and Refinement of Structure. Neutral atomic scattering factors of Cromer and Waber[11a] were used for all atoms except hydrogen, for which the values of Stewart, Davidson, and Simpson[12] were taken. The values of real and imaginary components of anomalous dispersion corrections for the molybdenum and sulfur atoms were obtained from the tabulation of Cromer.[11b]

The structure was refined by full-matrix least-squares techniques,[13] minimizing the function $\sum w(|F_o| - |F_c|)^2$; the weights were assigned as $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$, where p, the factor to prevent overweighting of strong reflections, was set equal to 0.03.[14] The discrepancy indices, R_1 and R_2, are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The "goodness of fit" is defined by GOF $= [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where n is the number of reflections used in the refinement and m is the number of refined parameters.

The structure determination and preliminary least-squares refinement were based upon the 1643 significant reflections in the hkl octant within the 2θ range 4–50°. The structure was solved by the heavy-atom method, the position of the molybdenum atom being readily located from a three-dimensional Patterson map. One cycle of least-squares refinement of positional parameters for the molybdenum atom led to $R_1 = 0.354$ and $R_2 = 0.448$. A difference electron density map calculated from the molybdenum contributions revealed six possible positions for the three sulfur atoms, which were separable into two sets related to one another by a false center of symmetry at the molybdenum atom. One set of sulfur positions was arbitrarily chosen as a starting point for further refinements. The remaining 21 nonhydrogen atoms were located by successive refinements and difference electron density maps. Three cycles of isotropic refinement of all nonhydrogen atoms resulted in $R_1 = 0.048$ and $R_2 = 0.059$. Refining the molybdenum, sulfur, and nitrogen atoms anisotropically led to convergence in two cycles with $R_1 = 0.043$, $R_2 = 0.053$, and GOF = 1.934 ($m = 136$).

Since $P2_12_12_1$ is a noncentrosymmetric space group, there are two enantiomers possible. In order to determine the absolute configuration in the crystal selected for the present study, the anomalous dispersion terms for the molybdenum and sulfur atoms were introduced to the calculated structure factors. Two cycles of refinement using the data of the hkl octant and the $\bar{h}\bar{k}\bar{l}$ data which had been corrected for absorption converged to $R_1 = 0.042$, $R_2 = 0.051$, and GOF = 1.924 ($m = 136$). Changing the sign of the imaginary component of anomalous dispersion so as to generate the alternative enantiomer and refining the same parameters led to convergence in two cycles with $R_1 = 0.043$, $R_2 = 0.053$, and GOF = 1.978. A Hamilton's R factor test[11c,15] together with an analysis of the standard deviations of the parameters showed that the original model was preferred. This enantiomer was chosen for subsequent refinements.

Anisotropic refinement of all nonhydrogen atoms gave $R_1 = 0.038$ and $R_2 = 0.046$. A difference electron density map calculated at this stage clearly revealed the positions of all 15 hydrogen atoms. These were then included as fixed contributors in idealized positions assuming trigonal geometry about the nitrogen and carbon atoms; C–H = 0.95 Å and N–H = 0.85 Å.[16] Each hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than the value for its bonded carbon or nitrogen atom. Two cycles of full-matrix least-squares refinement in which 226 parameters were allowed to vary led to final convergence with $R_1 = 0.027$, $R_2 = 0.031$, and GOF = 1.162; the overdetermination ratio (n/m) was 9.2. All parameter shifts during the final refinement were less than 0.05σ. The function $\sum w(|F_o| - |F_c|)^2$ was not significantly dependent either upon $(\sin\theta)/\lambda$ or upon $|F_o|$. The largest residual in the final difference electron density map was 0.58 e Å^{-3}, near the molybdenum atom. All other peaks were less than 0.5 e Å^{-3}. A structure factor calculation for all 2496 independent reflections yielded $R_1 = 0.039$ and $R_2 = 0.033$.

The final nonhydrogen atomic parameters with their standard deviations are given in Table II. Table III gives the root-mean-square amplitudes of vibration for the anisotropic atoms.[17] The fixed positional and thermal parameters for hydrogen atoms are listed in Table IV.[17] A listing of $10|F_o|$ and $10|F_c|$ values is also available.[17]

Description of Structure

Interatomic distances and angles with their estimated standard deviations are listed in Tables V and VI, respectively. The unit cell contains four monomeric $Mo(NHC_6H_4S)_3$ molecules as is shown in a stereoview of the crystal structure projected down the a axis (Figure 1). A stereoview of one molecule viewed down its approximate threefold (C_3) axis is shown in Figure 2, together with the labeling scheme.

The molybdenum atom is six-coordinate and bonded to the sulfur and nitrogen atoms from the three 2-aminobenzenethiolate ligands. The coordinated atoms are arranged about the molybdenum atom so as to roughly form a trigonal-prismatic polyhedron with the two triangular faces defined by the three sulfur atoms and by the three nitrogen atoms. This stereochemistry was suggested previously from solution

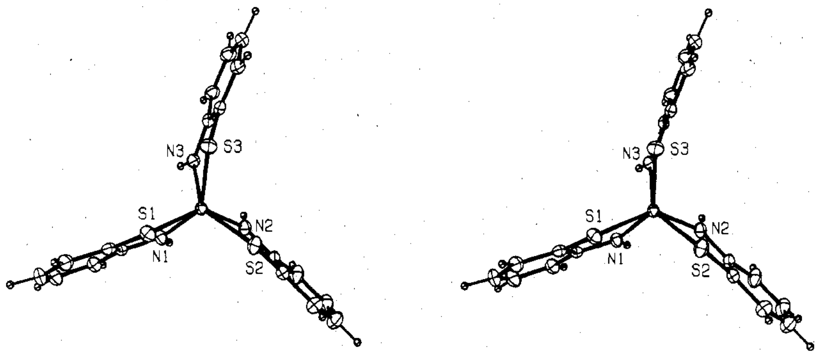

Figure 2. Stereoview of the Mo(abt)$_3$ molecule along the pseudo-C_3 axis. The hydrogen atoms have been assigned arbitrarily small thermal parameters for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

Table II. Final Atomic Coordinates and Anisotropic Thermal Parameters[a]

Atom[b]	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mo	.09530(4)	.20569(3)	.235942(27)	48.0(3)	37.56(25)	24.21(15)	-2.8(3)	2.70(21)	-.68(20)
S(1)	.31498(12)	.18887(12)	.20012(9)	52.9(11)	59.0(11)	40.7(6)	5.1(9)	.6(7)	-3.8(7)
S(2)	.13994(14)	.05228(12)	.34133(9)	84.5(14)	51.8(11)	37.3(7)	5.6(10)	6.6(8)	10.2(7)
S(3)	.07177(13)	.04919(11)	.12937(9)	72.1(14)	49.0(10)	34.7(6)	5.3(10)	-2.3(7)	-9.3(6)
N(1)	.1541(3)	.3704(3)	.24898(26)	51.(3)	45.4(29)	29.6(21)	-1.5(27)	7.4(27)	-4.3(20)
N(2)	-.0238(4)	.2411(4)	.33501(27)	50.(4)	53.(3)	33.0(19)	1.4(28)	5.5(23)	3.0(21)
N(3)	-.0366(4)	.2690(3)	.15624(25)	61.(4)	40.(3)	29.5(18)	-.5(28)	0.0(22)	1.0(19)
C(1)	.3531(5)	.3330(5)	.1892(3)	59.(4)	69.(4)	21.6(21)	-2.(4)	-6.8(26)	1.2(25)
C(2)	.4699(5)	.3741(6)	.1577(4)	56.(5)	109.(7)	35.4(27)	-2.(5)	3.(3)	-2.(4)
C(3)	.4949(6)	.4905(6)	.1587(4)	74.(6)	109.(7)	45.(3)	-44.(5)	6.(4)	10.(4)
C(4)	.4076(6)	.5705(5)	.1889(4)	94.(6)	78.(5)	50.(3)	-38.(6)	-7.(4)	4.(3)
C(5)	.2936(5)	.5348(5)	.2186(4)	82.(5)	66.(4)	38.(3)	-21.(4)	-1.(3)	0.(3)
C(6)	.2639(4)	.4147(4)	.21868(28)	54.(4)	56.(4)	19.4(23)	-11.(3)	-1.7(24)	-4.3(22)
C(7)	.0674(5)	.1069(4)	.4347(3)	69.(6)	57.(4)	30.1(23)	-19.(4)	-1.6(28)	1.7(25)
C(8)	.0794(6)	.0609(5)	.5204(4)	101.(7)	91.(6)	35.7(27)	-14.(6)	-8.(4)	12.(3)
C(9)	.0093(7)	.1055(8)	.5875(4)	159.(9)	110.(7)	28.5(28)	-44.(7)	1.(4)	5.(4)
C(10)	-.0742(7)	.1957(6)	.5726(4)	143.(8)	87.(6)	30.8(25)	-35.(7)	24.(4)	-17.(3)
C(11)	-.0879(6)	.2434(5)	.4918(4)	113.(7)	59.(4)	39.1(26)	-8.(5)	24.(4)	-5.1(26)
C(12)	-.0165(5)	.2007(5)	.4203(3)	70.(5)	57.(4)	26.3(20)	-18.(4)	4.9(25)	1.1(28)
C(13)	-.0749(5)	.0869(4)	.0887(3)	67.(5)	52.(4)	23.3(20)	-10.(4)	3.0(26)	7.3(22)
C(14)	-.1515(6)	.0126(5)	.0401(3)	95.(6)	66.(5)	27.4(24)	-16.(4)	2.(3)	-2.8(27)
C(15)	-.2634(5)	.0538(5)	.0056(4)	81.(6)	85.(5)	30.6(25)	-36.(5)	-2.(3)	2.(3)
C(16)	-.2984(5)	.1689(5)	.0186(4)	66.(5)	105.(6)	31.5(26)	-1.(5)	-6.1(29)	3.(3)
C(17)	-.2261(5)	.2427(5)	.0662(3)	65.(5)	75.(5)	29.7(24)	5.(4)	-3.2(29)	5.2(27)
C(18)	-.1141(4)	.2027(5)	.10417(29)	53.(4)	59.(4)	25.2(19)	-13.(4)	.5(23)	7.4(27)

[a] Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})]$.

[b] The ring carbon atoms are numbered so that C(1), C(7) and C(13) are attached to S(1), S(2) and S(3), respectively and C(6), C(12) and C(18) are attached to N(1), N(2) and N(3), respectively.

Table V. Interatomic Distances (Å) in Mo(NHC$_6$H$_4$S)$_3$

Mo-S(1)	2.412 (1)	C(4)-C(5)	1.359 (8)
Mo-S(2)	2.419 (1)	C(5)-C(6)	1.412 (7)
Mo-S(3)	2.424 (1)	C(6)-C(1)	1.407 (7)
Mo-N(1)	1.998 (4)	C(7)-C(8)	1.404 (7)
Mo-N(2)	2.005 (4)	C(8)-C(9)	1.359 (9)
Mo-N(3)	1.989 (4)	C(9)-C(10)	1.383 (9)
S(1)-C(1)	1.709 (6)	C(10)-C(11)	1.346 (8)
S(2)-C(7)	1.728 (5)	C(11)-C(12)	1.410 (7)
S(3)-C(13)	1.735 (5)	C(12)-C(7)	1.415 (7)
N(1)-C(6)	1.356 (6)	C(13)-C(14)	1.390 (7)
N(2)-C(12)	1.371 (6)	C(14)-C(15)	1.385 (8)
N(3)-C(18)	1.370 (6)	C(15)-C(16)	1.385 (8)
C(1)-C(2)	1.415 (7)	C(16)-C(17)	1.352 (8)
C(2)-C(3)	1.360 (9)	C(17)-C(18)	1.402 (7)
C(3)-C(4)	1.383 (9)	C(18)-C(13)	1.411 (7)
S(1)-N(1)	2.796 (4)	N(3)-N(1)	2.729 (6)
S(2)-N(2)	2.781 (4)	S(1)-N(2)	4.191 (4)
S(3)-N(3)	2.801 (4)	S(2)-N(3)	4.188 (4)
S(1)-S(2)	3.239 (2)	S(3)-N(1)	4.193 (4)
S(2)-S(3)	3.285 (2)	S(1)-N(3)	3.917 (4)
S(3)-S(1)	3.230 (2)	S(2)-N(1)	3.906 (4)
N(1)-N(2)	2.736 (5)	S(3)-N(2)	3.941 (4)
N(2)-N(3)	2.724 (6)		

studies.[4] The mean Mo–S and Mo–N distances are 2.418 (6) and 1.997 (8) Å, respectively. The average values for the S–Mo–S and N–Mo–N angles are 84.5 (8) and 86.2 (2)°.

The S_3N_3 polyhedron is somewhat distorted from the idealized trigonal-prismatic geometry as can be seen clearly in Figure 2. One kind of distortion arises from the different dimensions of the triangular faces. The triangle defined by the sulfur atoms has the average S···S distance of 3.251 (30) Å, while the smaller triangle of the nitrogen atoms has the mean N···N side of 2.730 (6) Å. Thus, the polyhedron is severely tapered. Tapered trigonal-prismatic structures have been reported before.[18,19]

The two triangular faces are almost parallel to one another, the dihedral angle between them being only 0.5°. The molybdenum atom lies close to the pseudo-C_3 axis and is 1.525 (1) and 1.227 (2) Å from the triangular planes of sulfur atoms and nitrogen atoms, respectively. The two triangles, however, are rotated about the pseudo-C_3 axis with respect to one another (vide infra).

One descriptor of distortion in tris-chelate complexes is the chelate projection (twist) angle. Figure 3 shows a projection

Table VI. Interatomic Angles (deg) in $Mo(NHC_6H_4S)_3$

S(1)-Mo-N(1)	78.06 (11)	C(3)-C(4)-C(5)	120.8 (5)
S(2)-Mo-N(2)	77.28 (12)	C(4)-C(5)-C(6)	119.6 (6)
S(3)-Mo-N(3)	78.13 (12)	C(5)-C(6)-C(1)	119.8 (5)
S(1)-Mo-S(2)	84.18 (5)	N(1)-C(6)-C(1)	116.2 (4)
S(2)-Mo-S(3)	85.43 (5)	N(1)-C(6)-C(5)	124.0 (5)
S(3)-Mo-S(1)	83.82 (5)	S(2)-C(7)-C(8)	125.2 (5)
N(1)-Mo-N(2)	86.22 (16)	S(2)-C(7)-C(12)	115.6 (4)
N(2)-Mo-N(3)	86.01 (15)	C(12)-C(7)-C(8)	119.0 (5)
N(3)-Mo-N(1)	86.38 (16)	C(7)-C(8)-C(9)	119.8 (6)
S(1)-Mo-N(2)	143.03 (12)	C(8)-C(9)-C(10)	120.9 (6)
S(2)-Mo-N(3)	143.40 (12)	C(9)-C(10)-C(11)	121.4 (6)
S(3)-Mo-N(1)	142.83 (12)	C(10)-C(11)-C(12)	119.7 (6)
S(1)-Mo-N(3)	125.46 (12)	C(11)-C(12)-C(7)	119.1 (5)
S(2)-Mo-N(1)	124.03 (12)	N(2)-C(12)-C(7)	115.9 (4)
S(3)-Mo-N(2)	125.48 (12)	N(2)-C(12)-C(11)	125.0 (5)
Mo-S(1)-C(1)	100.09 (19)	S(3)-C(13)-C(14)	124.4 (4)
Mo-S(2)-C(7)	100.74 (18)	S(3)-C(13)-C(18)	116.3 (4)
Mo-S(3)-C(13)	98.31 (17)	C(18)-C(13)-C(14)	119.3 (5)
Mo-N(1)-C(6)	126.2 (3)	C(13)-C(14)-C(15)	119.7 (5)
Mo-N(2)-C(12)	126.7 (3)	C(14)-C(15)-C(16)	120.3 (5)
Mo-N(3)-C(18)	124.9 (3)	C(15)-C(16)-C(17)	121.2 (5)
S(1)-C(1)-C(2)	124.3 (4)	C(16)-C(17)-C(18)	119.9 (5)
S(1)-C(1)-C(6)	116.9 (4)	C(17)-C(18)-C(13)	119.5 (5)
C(6)-C(1)-C(2)	118.7 (5)	N(3)-C(18)-C(13)	116.0 (4)
C(1)-C(2)-C(3)	119.7 (6)	N(3)-C(18)-C(17)	124.5 (5)
C(2)-C(3)-C(4)	121.4 (5)		
S(2)-S(1)-S(3)	61.04 (4)	N(2)-N(1)-N(3)	59.80 (14)
S(3)-S(2)-S(1)	59.35 (4)	N(3)-N(2)-N(1)	59.98 (15)
S(1)-S(3)-S(2)	59.61 (4)	N(1)-N(3)-N(2)	60.21 (15)

Table VII. Dihedral Angles (deg)

plane 1	plane 2	angle
S(1), S(2), S(3)	N(1), N(2), N(3)	0.5
Mo, S(1), N(1)	Mo, S(2), N(2)	117.5
Mo, S(2), N(2)	Mo, S(3), N(3)	118.8
Mo, S(3), N(3)	Mo, S(1), N(1)	118.4
Mo, S(1), N(1)	ligand skelton A[a]	11.8
Mo, S(2), N(2)	ligand skelton B	14.7
Mo, S(3), N(3)	ligand skelton C	21.5
ligand skelton A[a]	ligand skelton B	114.6
ligand skelton B	ligand skelton C	112.4
ligand skelton C	ligand skelton A	127.9

[a] Ligand skelton A: S(1), C(1), C(2), C(3), C(4), C(5), C(6), N(1); ligand skelton B: S(2), C(7), C(8), C(9), C(10), C(11), C(12), N(2); ligand skelton C: S(3), C(13), C(14), C(15), C(16), C(17), C(18), N(3).

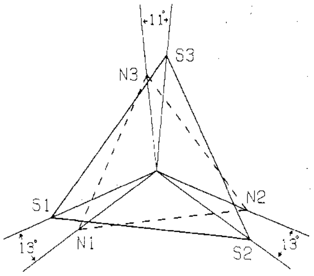

Figure 3. Projection of the coordination polyhedron onto the mean plane defined by the triangular faces S(1), S(2), S(3) and N(1), N(2), N(3). The mean plane and the chelate projection (twist) angles are defined in ref 10. The average chelate projection angle is 12.3 (10)°.

along the approximate C_3 axis normal to the mean plane defined by the above pair of triangular faces and gives the individual chelate projection angles (ϕ's).[10] These angles should be 0° for the trigonal-prismatic limit and 60° for the octahedral limit. The individual values observed here are $\phi(S(1),Mo,N(1)) = 12.8°$, $\phi(S(2),Mo,N(2)) = 13.0°$, and $\phi(S(3),Mo,N(3)) = 11.1°$. Although these distortions from the idealized tapered trigonal prism are fairly large, it is nevertheless clear that the compound is closer to trigonal-prismatic geometry than to octahedral geometry.

The expected coordination geometry of tris-chelate compounds can be calculated by minimizing the total repulsion energy of the donor atoms, taking into account the constraints of the chelate bite.[20,21] The average chelate bite angle in $Mo(abt)_3$ is 77.8 (5)°, and the calculated chelate projection angle is 45°, considerably greater than the observed angles. For comparison, in octahedral *fac*-tris(4,6-dimethylpyrimidine-2-thiolato)cobalt(III)[22] the chelate bite angle is 72°, and the observed mean chelate projection angle is 45°.

Another useful measure of the distortion is the dihedral angle, ρ, between the mean plane defined above and the coordination plane formed by the metal atom and the two donor atoms in the chelate.[10] The angles $\rho(S(1),Mo,N(1)) = 82.0°$, $\rho(S(2),Mo,N(2)) = 81.8°$, and $\rho(S(3),Mo,N(3)) = 83.1°$ are close to the ideal value of 90° in trigonal-prismatic geometry. In an octahedron these angles are 54.7°. Other angular descriptors of the coordination polyhedron, such as the dihedral angles between the coordination planes given in Table VII and the pseudotrans and pseudocis S–Mo–N angles shown in Table VI, also emphasize that $Mo(abt)_3$ belongs to the group of compounds with approximate trigonal-prismatic coordination geometry. The trigonal distortion is somewhat larger than that in $V(S_2C_2Ph_2)_3$.[23]

The approximate point symmetry of the S_3N_3 coordination polyhedron is C_3. The ligand skeletons of the three chelate rings span the S···N edges of the trigonal prism. Each abt ligand is folded in the same direction about its S···N vector so that the gross symmetry of the entire molecule remains nearly C_3. However, close examination of the dihedral angles between the mean planes of the ligand atoms and their respective coordination planes reveals that there are significant variations among the three chelate rings (Table VII).

Inspection of the packing diagram and the intra- and intermolecular contacts suggest that the variation in dihedral angles results from the intermolecular repulsions between phenyl rings in the solid state. Figures 1 and 4 show that the molecules pack with the phenyl rings of ligands A and C aligned approximately perpendicular to the *c* axis. The plane of ring B is nearly parallel to this axis. Two kinds of inter-ring contacts occur. The major contact involves rings A and C.

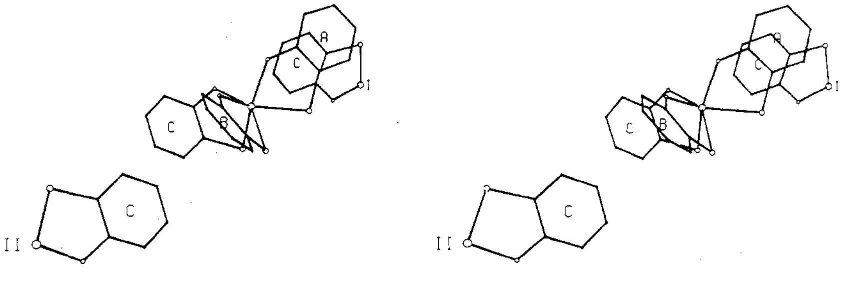

Figure 4. Stereoview of the molecular packing showing the selected intermolecular contacts. The positive direction of the *c* axis is perpendicular to the paper toward the reader. The positive direction of the *a* axis is horizontal to the right. Sulfur atoms have been arbitrarily assigned bigger thermal parameters than nitrogen atoms: A, C(1)–C(6); B, C(7)–C(12); C, C(13)–C(18). I: $0.5 + x, 0.5 - y, -z$. II: $-0.5 - x, -y, 0.5 + z$.

Table VIII. Selected Intermolecular Contacts (Å)

atoms	symmetry operation[a] on the second atom	distance
C(1) - - - C(15)	I	3.449 (7)
C(1) - - - C(16)	I	3.532 (7)
C(2) - - - C(14)	I	3.507 (8)
C(2) - - - C(15)	I	3.600 (8)
C(3) - - - C(14)	I	3.387 (8)
C(3) - - - C(15)	I	3.744 (8)
C(4) - - - C(14)	I	3.645 (8)
C(4) - - - C(15)	I	3.741 (8)
C(5) - - - C(15)	I	3.590 (8)
C(6) - - - C(15)	I	3.422 (7)
C(8) - - - C(15)	II	3.624 (9)
C(9) - - - C(15)	II	3.427 (10)
C(10) - - - C(15)	II	3.493 (9)
C(11) - - - C(15)	II	3.763 (8)

[a] I: $0.5 + x, 0.5 - y, -z$. II: $-0.5 - x, -y, 0.5 + z$.

Ring A of one molecule lies over the ring C of an adjacent molecule. These two rings are nearly parallel to one another (dihedral angle ~16°). The nonbonded contacts among the atoms in the two rings (Table VIII) are shorter than the van der Waals distance (3.70 Å).[24] The stereochemistry of the intermolecular contacts between A and C (Figure 4) favors an increase in the dihedral angle between C and the Mo, S(3), N(3) plane and a decrease in the dihedral angle between A and the Mo, S(1), N(1) plane. A second inter-ring contact involves C(15) of ring C with ring B of an adjacent molecule. This can be described as an edge-to-face contact, and the dihedral angle between the rings is ~46°. The stereochemistry of this contact would tend to slightly decrease the dihedral angle between C and the Mo, S(3), N(3) plane and increase the dihedral angle between B and the Mo, S(2), N(2) plane. The intermolecular contacts between ring A and the edge of ring B in a neighboring molecule are comparable to van der Waals distances (the shortest C···H contact is ~2.96 Å). The qualitative features of the inter-ring contacts are consistent with the observed pattern (Table VII) of dihedral angles between the planes of the ligand skeletons and their respective coordination planes, i.e., C > B > A. Packing forces are also probably responsible for the slight deviation of the S_3N_3 coordination polyhedron from exact C_3 point symmetry.

Discussion

To our knowledge, tris(2-aminobenzenethiolato)molybdenum(VI), $Mo(abt)_3$, is the first compound with a trigonal-prismatic structure containing both coordinated sulfur and nitrogen atoms to be definitively characterized by X-ray crystallography, although other tris-chelate compounds with the S_3N_3 framework have been assigned trigonal-prismatic geometry from spectroscopic data.[4,25] The structure of the molybdenum(V) compound containing the 2-aminobenzenethiolate ligands, $Mo(abt)_2(dedtc)$ where dedtc denotes the diethyldithiocarbamate anion, has been recently determined.[10] In contrast to the present structure, its geometry is midway between a trigonal prism and an octahedron with two nitrogen atoms trans to one another. It is interesting, however, that $Mo(abt)_2(dedtc)$ has one abt ligand close to the trigonal-prismatic limit and the other abt ligand close to the octahedral limit. Some pertinent average distances and angles for both compounds and the related trigonal-prismatic compound, $Mo(S_2C_6H_4)_3$,[26] are summarized in Table IX.

The average Mo–N distance of 1.997 (8) Å in $Mo(abt)_3$ is almost identical with that of 2.005 (6) Å found in $Mo(abt)_2(dedtc)$[10] where considerable multiple character of the Mo–N bond has been suggested. The Mo–N distances for coordinated amines are usually 0.2 Å longer than those observed for these abt complexes.[27,28] Shorter Mo–N distances of 1.80 and 1.62 Å have been found in the $MoNN(CH_3)_2$ and MoN groupings, respectively.[29]

The average Mo–S distance of 2.418 (6) Å is longer than the 2.367 (6) Å in $Mo(S_2C_6H_4)_3$[26] and the 2.374 (8) and 2.357 (4) Å for maleonitriledithiolate ligands (mnt) in $Mo(mnt)_3^{2-}$ and $Mo(mnt)_2(dedtc)^-$.[30] The Mo–S distances of coordinated dithiocarbamate ligands are ~2.47 Å,[27] and the Mo–S distance is 2.460 (1) Å in $MoOCl_3(SPPh_3)$.[31] Average Mo–S distances similar to those in $Mo(abt)_3$ have recently been observed for coordinated aliphatic thiols in the syn and anti binuclear Mo(V) isomers (2.405 (2) and 2.401 (19) Å)[32] and for coordinated mercaptoquinolinate ligands in $MoO_2(tox)_2$ (2.411 (1) Å).[33] The mean Mo–S distance of 2.384 (11) Å

Table IX. Summary of Average Distances (Å) and Angles (deg)[a] in $Mo(NHC_6H_4S)_3$ and Related Compounds

	$Mo(NHC_6H_4S)_3$[b]	$Mo(NHC_6H_4S)_2(S_2CN(C_2H_5)_2)$[c]	$Mo(S_2C_6H_4)_3$[d]
		Distances	
Mo–S	2.418 (6)	2.384 (11) [2.392 (1), 2.376 (1)][e]	2.367 (6)
Mo–N	1.997 (8)	2.005 (6) [2.001 (2), 2.009 (2)]	
S–C(1)	1.724 (13)	1.736 (1) [1.736 (3), 1.736 (3)]	1.727 (6)
N–C(6)	1.366 (8)	1.370 (6) [1.374 (3), 1.366 (4)]	
C(1)–C(2)	1.403 (12)	1.394 (2) [1.392 (4), 1.395 (4)]	1.399 (11)
C(2)–C(3)	1.368 (15)	1.382 (3) [1.384 (4), 1.379 (5)]	1.359 (12)
C(3)–C(4)	1.384 (1)	1.385 (4) [1.388 (4), 1.382 (6)]	1.404 (12)
C(4)–C(5)	1.352 (7)	1.371 (5) [1.375 (4), 1.367 (5)]	=(C2)–C(3)[f]
C(5)–C(6)	1.408 (5)	1.403 (3) [1.401 (4), 1.406 (4)]	=(C1)–C(2)
C(6)–C(1)	1.411 (4)	1.401 (1) [1.401 (4), 1.401 (4)]	1.412 (6)
chelate bite	2.793 (10)	2.795 (12) [2.787 (2), 2.804 (2)]	3.110 (8)
side(S–S)	3.251 (30)	*g*	3.091 (15)
side(N–N)	2.730 (6)	*g*	
		Angles	
Mo–S–C(1)	99.7 (12)	101.4 (5) [101.8 (1), 101.1 (1)]	106.2 (23)
Mo–N–C(6)	126.0 (10)	127.0 (13) [127.9 (2), 126.1 (2)]	
S–C(1)–C(6)	116.3 (6)	116.5 (3) [116.3 (2), 116.7 (2)]	119.4 (4)
N–C(6)–C(1)	116.0 (2)	116.0 (3) [115.8 (2), 116.2 (2)]	
bite	77.8 (5)	78.6 (6) [78.2 (1), 79.0 (1)]	82.1 (4)

[a] In this table and the text, the estimated standard deviation (esd) for a mean value ($\overline{x}$) is given in parentheses and is obtained from the expression $\sigma = [\Sigma(x_i - \overline{x})^2/(N-1)]^{1/2}$, where $\overline{x}$ is the mean of N measurements and x_i is the ith such measurement. [b] This work. [c] Reference 10. [d] Reference 26. [e] Left-side values in square brackets are obtained for the $NHC_6H_4S^{2-}$ ligand closer to the octahedral conformation and right-side values for the ligand closer to the trigonal-prismatic geometry. Values in parentheses refer to esd's on individual parameters. [f] The molecule has mirror symmetry; space group *Pnam*. [g] The molecule has an irregular coordination polyhedron with the two nitrogen atoms trans to one another.

for the coordinated abt ligands in Mo(abt)$_2$(dedtc)[10] deviates slightly, but significantly, from that found here. The relatively short Mo–S distances indicate a significant charge delocalization over both ligand and metal.

The Mo–S and Mo–N distances in Mo(abt)$_3$ have recently been independently determined from analysis of the fine structure of the Mo 1s X-ray absorption spectrum.[5] The distances obtained from the EXAFS experiment (Mo–N = 1.996 Å and Mo–S = 2.419 Å) are in good agreement with those from the present single-crystal X-ray structure determination.

Chemically equivalent distances and angles of the abt ligands are nearly the same and are not significantly different from those found in Mo(abt)$_2$(dedtc).[10] The mean S–C distance of 1.724 (13) Å is comparable to that of 1.727 (6) Å in Mo(S$_2$C$_6$H$_4$)$_3$[26] and slightly shorter than the average S–C distance of 1.742 (6) Å in MoO$_2$(tox)$_2$.[33] The average N–C bond length of 1.366 (8) Å is very similar to the longer of two kinds of N–C distances in coordinated hydroxyquinolinate and mercaptoquinolinate ligands.[28,33,34] The short S–C and N–C distances indicate considerable double-bond character for these bonds. The average S–C and N–C distances in Mo(abt)$_2$(dedtc) are 1.736 (1) and 1.370 (6) Å.[10] The average C–C bond distance is 1.388 (24) Å, close to that of benzene and its derivatives,[35] although the individual C–C distances vary widely in the phenyl ring. Similar variations are observed for Mo(abt)$_2$(dedtc),[10] Mo(S$_2$C$_6$H$_4$)$_3$,[26] and related compounds.[36–38]

An interesting feature of the structure is the folding of the ligand planes along the S···N vectors. Similar deviations from planarity have been observed for trigonal-prismatic tris(dithiolate) compounds.[26,36–40] A recent structural study has shown that octahedral tris(catecholate) compounds also have a slight bending of the ligand system due to packing forces.[41] As mentioned previously, the irregular magnitude of the bendings in Mo(abt)$_3$ is probably due to packing effects. From the intermolecular contacts, however, it seems unlikely that packing forces alone are responsible for the observed bending of the ligand systems. In this regard, the structure of Mo(abt)$_2$(dedtc) is of particular interest.[10] Nonplanar geometry has been found for the abt ligand which is closer to a trigonal prism whereas a planar conformation occurs for the abt ligand which is closer to an octahedron. Ligand folding may be an inherent feature of trigonal-prismatic compounds of highly delocalized chelating ligands. The protons of the NH groups in Mo(abt)$_3$ lie in the planes of the abt ligands as was observed previously for the abt ligands of Mo(abt)$_2$(dedtc).[10]

Early molecular orbital descriptions of trigonal-prismatic complexes[42] pointed out that two kinds of ligand π interactions can contribute significantly to the stabilization of trigonal-prismatic geometry: (1) the interaction between the d_{z^2} orbital of the metal and the ligand π_h orbitals (the lone pair of the coordinated atoms in the ligand plane); (2) the interaction of d_{xy}, $d_{x^2-y^2}$ with the delocalized π_v orbitals which are perpendicular to the ligand plane. A series of structural studies of tris(benzenedithiolate) complexes[26,36–38] has emphasized the importance of interaction (2) in stabilizing trigonal-prismatic geometry. A recent paper by Hoffmann and co-workers[43] also points out that interaction (2) can be an important stabilizing factor in trigonal-prismatic complexes. Their results further emphasize that trigonal-prismatic geometry enables all five d orbitals to participate in σ bonding and is most likely to occur in formally d^0–d^2 complexes with d orbitals of low energy. The structure of Mo(abt)$_3$ is consistent with interaction (2) being an important factor in the stabilization of trigonal-prismatic geometry. Clearly interaction (1), metal d_{z^2} with ligand π_h, cannot be very important in Mo(abt)$_3$ because the π_h orbitals of the nitrogen atoms are involved in bonding to the hydrogen atoms which lie in the planes of the ligands.[4]

In solution Mo(abt)$_3$ can be readily reduced to Mo(abt)$_3^-$. The solution EPR spectra of Mo(abt)$_3^-$ and the related compound Mo(abt)$_2$(dedtc) have been extensively studied.[4,44–46] Both compounds show hyperfine splittings due to the ^{1}H and ^{14}N nuclei of the coordinated amido groups. The solution spectrum of the monoanion is resolved at low temperature with isotropic splittings of $A(^1\text{H}) = 6.4$ and $A(^{14}\text{N}) = 2.1$ G.[4,44] The EPR spectrum of Mo(abt)$_2$(dedtc) is clearly resolved at room temperature with $A(^1\text{H}) = 7.4$ and $A(^{14}\text{N}) = 2.4$ G.[44] The short Mo–N distances in these compounds which result in intramolecular Mo···H distances of ~2.5 Å undoubtedly are an important factor in the relatively large ^{1}H hyperfine splittings. The possible implications of the ^{1}H splittings for molybdo enzymes have been discussed previously.[4,10,44]

The low-temperature EPR spectrum of Mo(abt)$_3^-$ shows that all three ligands are equivalent on the EPR time scale. This strongly suggests that the stereochemistry of the monoanion is similar to that in Figure 2. However, the trigonal distortion of Mo(abt)$_3^-$, which is formally a Mo(V) complex, could differ significantly from Mo(abt)$_3$, which is formally a Mo(VI) complex. Attempts to obtain crystalline derivatives of the Mo(abt)$_3^-$ anion suitable for X-ray structure determination have thus far been unsuccessful.

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Supplementary Material Available: Table III, the root-mean-square amplitudes of vibration, Table IV, the fixed positional and thermal parameters for hydrogen atoms, and a listing of the observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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K. O. Martin, and H. A. Levy), ORFFE (locally modified, calculations of distances, angles, and least-squares planes with standard deviations by Busing, Martin, and Levy), and ORTEP (thermal ellipsoid drawing program, by C. K. Johnson).
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Synthesis, Structure, and Properties of Asymmetric Benzoyldiazenido and Thiobenzoyldiazenido Complexes of Molybdenum

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The synthesis of the compounds of general formula $[Mo_2O(S_2CNR)_2(YC_6H_4CXN_2)_2]\cdot Sol$, X = S and O, Y = H and Cl, and Sol = CH_2Cl_2 and $CHCl_3$, is reported. The compounds were characterized by elemental analyses and infrared, electronic, and ^1H NMR spectroscopy. The ^1H NMR spectra exhibited a number of alkyl resonances, suggesting that the dithiocarbamate ligands are nonequivalent. The molecular structures of the compounds $[Mo_2O(S_2CNEt_2)_2(C_6H_5CON_2)_2]\cdot CH_2Cl_2$ and $[Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2]\cdot CHCl_3$ were revealed in single-crystal X-ray diffraction studies. The structures are analogous and shown to be asymmetric dinuclear complexes with bridging benzoyldiazendio or thiobenzoyldiazenido ligands. The nonplanar Mo_2N_2 rhombus is common to both structures and exhibits a nearly identical geometry in the two derivatives. The geometries about the square-pyramidal Mo2 sites are also constant. The Mo1 sites are approximately trigonal prismatic, the coordination polyhedra constrained by the geometric requirements of sulfur vs. oxygen coordination. Voltammetric studies of the dimers indicate a reversible one-electron reduction, followed by an irreversible cathodic process at more negative potentials. The redox behavior of the dimers is discussed and contrasted with that of the symmetrical dimers $Mo_2O_3(S_2CX)_4$, X = $-NR_2$, $-OR$, and $-SR$.

Introduction

The coordination chemistry of molybdenum in its higher oxidation states (IV to VI) has received a great deal of attention, particularly because of the possible relationship of these species to the redox-active molybdoenzymes[2,57] and the general interest in polynuclear metal compounds.[3,59] In particular, the iron–molybdenum protein component of nitrogenase from *Azotobacter vinelandii*,[4] *Clostridium pasteurianum*,[5] and *Klebsiella pneumoniae*[6] and xanthine oxidase[7] all contain two molybdenum atoms per mole of enzyme. The proposal has been made that the two molybdenum atoms are at the active site and function in a concerted fashion during catalysis.[8] Although a number of oxidation states have been postulated for the molybdenum atoms in the native proteins,[7b] there is no direct evidence for the oxidation state in the nitrogenase systems.

The importance of molybdenum in these redox-active proteins and the speculation that dimeric species involving sulfur coordination may be relevant to the active-site geometry[2,7b] have prompted a number of studies on the chemical,[8-10] electrochemical,[11] and structural aspects[12-23] of dimeric molybdenum complexes with sulfur-containing ligands.

The structural chemistry of dimeric molybdenum complexes in the higher oxidation states is dominated by oxo- or sulfido-bridged groupings (**1a**–**2e**). A number of complexes with the μ-oxo geometry **1a**[14] or **1b**[12,13,15,24] have been structurally

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