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Monomeric Molybdenum(V) Complexes. 1. Structure of Bis(2-aminobenzenethiolato)(diethyldithiocarbamato)molybdenum(V), $Mo(NHC_6H_4S)_2(S_2CN(C_2H_5)_2)$

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The crystal and molecular structure of bis(2-aminobenzenethiolato)(diethyldithiocarbamato)molybdenum(V), $Mo(NHC_6H_4S)_2(S_2CN(C_2H_5)_2)$, a compound with a rich EPR spectrum, has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions a = 17.246 (3) Å, b = 6.214 (1) Å, c = 19.284 (4) Å, and β = 93.384 (15)°. The observed and calculated densities are 1.576 (10) and 1.579 g cm^{-3}, respectively. Full-matrix, least-squares refinement using 2982 unique reflections having $3.5 \leq 2\theta \leq 50°$ and $I > 3\sigma(I)$ converged at $R_1 = 0.023$ and $R_2 = 0.029$. The compound exists as discrete monomers, and each molybdenum atom is six-coordinate. Chemically equivalent metal–ligand distances are nearly the same. The dithiocarbamate ligand has two identical Mo–S distances of 2.473 (1) Å. The 2-aminobenzenethiolate ligands have Mo–S distances of 2.376 (1) and 2.392 (1) Å and Mo–N distances of 2.001 (2) and 2.009 (2) Å. Chemically equivalent coordination angles differ significantly, producing an irregular coordination polyhedron which is approximately midway between a trigonal prism and an octahedron in which the two nitrogen atoms are trans to one another. The N–Mo–N angle is 157.5 (1)°. The protons of the NH groups were located directly by an electron density difference map, but their positions were not refined. The idealized intramolecular Mo···H distance is 2.5 Å.

Introduction

Molybdenum-containing enzymes are of current interest because of their vital importance in nitrogen uptake and nitrogen metabolism.[1] Initial genetic studies[2] suggested that all molybdoenzymes possess a common molybdenum cofactor. More recent results[3] indicate that nitrate reductase and xanthine oxidase share a common molybdenum cofactor which is different from the molybdenum cofactor in nitrogenase. However, the nature of the molybdenum centers in both these cofactors remains unknown.

The most general direct probe of molybdenum centers in enzymes to date has been the EPR spectra exhibited by several of the enzymes.[1] The molybdenum centers in xanthine oxidase have been extensively studied by EPR. During turnover the enzyme shows a distinctive EPR spectrum with a relatively high g value ($\langle g \rangle$ = 1.977) and a relatively small hyperfine splitting from ^{95,97}Mo ($\langle A \rangle$ = 34 G). EPR spectra with similar $\langle g \rangle$ and $\langle A \rangle$ values are observed[4] from the unstable solutions produced by the reaction of aqueous molybdate with thiols. These and other solution results have led to the hypothesis that xanthine oxidase contains mononuclear Mo(V) centers with each molybdenum atom ligated by one or more sulfur atoms. However, few discrete mononuclear Mo(V) complexes have been isolated because of the propensity of Mo(V) to form diamagnetic oxo-bridged dimers in the presence of water.[5,6] In fact, only one monomeric Mo(V) complex containing an Mo–S bond, namely, $MoOCl_3(SPPh_3)$, has previously had its stoichiometry and stereochemistry unequivocally established by x-ray crystallography.[7]

The general lack of definitive structural data for monomeric Mo(V) complexes has prompted us to undertake structural studies of a variety of monomeric Mo(V) complexes in order to provide a basis for correlating stoichiometry and stereochemistry with EPR spectra. Recently, Newton and Stiefel and their co-workers[8,9] have prepared several EPR-active monomeric Mo(V) complexes. Of particular interest is the title compound which has $\langle g \rangle$ = 1.990 and $\langle A \rangle$(^{95,97}Mo) = 38 G and which also shows well-resolved hyperfine splittings due to ^{14}N and ^{1}H in solution. The structure of this compound is described.

Experimental Section

Preparation of Crystal. The title compound was prepared by the reaction of μ-dioxo-bis[oxo(N,N-diethyldithiocarbamato)molybdenum(V)] with 2-aminobenzenethiol in dichloromethane as previously described.[9] Dark brown crystals, suitable for X-ray diffraction study, were obtained by a slow liquid diffusion of hexane into a saturated solution (10 mL) of the compound in dichloromethane containing a few drops of 2-aminobenzenethiol.[10] The identity of the compound was confirmed by its IR and EPR spectra.

Collection and Reduction of the X-ray Intensity Data. A well-formed crystal was mounted on a Syntex $P2_1$ autodiffractometer equipped with a scintillation counter and a graphite monochromator so that the longest dimension (b axis) was approximately parallel to the ϕ axis. The automatic centering, indexing, and least-squares routines[11] were used to obtain the cell dimensions which are given with other crystallographic data and data collection conditions in Table I.

The data were reduced to F_o^2 and $\sigma(F_o^2)$ by the following procedures. The integrated intensities were calculated with the formula $I = [C - (\mathrm{LB} + \mathrm{RB})/\mathrm{rt}]S$ where C is the peak count, LB the left-background count, RB the right-background count, rt the ratio of the total background time to the peak scan time, and S the scan rate. Their estimated standard deviations were assigned by the expression $\sigma(I) = [C + (\mathrm{LB} + \mathrm{RB})/(\mathrm{rt})^2]^{1/2}S$. In correcting for Lorentz and polarization effects the monochromator crystal was assumed to be 50% mosaic and 50% perfect. The Lorentz–polarization factor used was $LP(2\theta) = (P_m + P_p)/(2 \sin 2\theta)$ where $P_m = (1 + \cos^2 2\theta_m \cos^2 2\theta)/(1 + \cos^2 2\theta_m)$ and $P_p = (1 + |\cos 2\theta_m| \cos^2 2\theta)/(1 + |\cos 2\theta_m|)$; θ_m and θ represent the Bragg angles of the monochromator crystal ($2\theta_m$ = 12.2°) and the data crystal, respectively.[12] An empirical absorption correction was applied on the basis of ψ scans evaluated at 10° intervals from ψ = 0° to ψ = 350°, for 11 reflections with 2θ in the range 7–41°.

Examination of the collected data set revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent with the space group $P2_1/c$. Of the 3664 unique data, 2982 reflections were considered significant using the criterion $I > 3\sigma(I)$ and were used in the subsequent solution and refinements of the structure.

Solution and Refinement of Structure. The major programs used in the course of the structure determination were as follows: MULTAN (locally modified, direct methods program, by G. Germain, P. Main, and M. M. Woolfson), Ibers' NUCLS (structure factor calculations and least-squares refinement, itself a modification of ORFLS, by W. R. Busing, K. O. Martin, and H. A. Levy), FORDAP (Fourier summation program, by A. Zalkin), ORFFE (locally modified, calculations of distances, angles, and least-squares planes with standard deviations, by Busing, Martin, and Levy), ORTEP (thermal ellipsoid plotting program, by C. K. Johnson). All calculations were performed on the CDC-6400 computer at the University of Arizona Computer Center.

Neutral atomic scattering factors of Cromer and Mann[13] were used for all atoms except hydrogen for which the values of Stewart, Davidson, and Simpson[14] were taken. The real and imaginary components of anomalous dispersion for the molybdenum and sulfur atoms were applied to the calculated structure factors using values of Cromer.[15]

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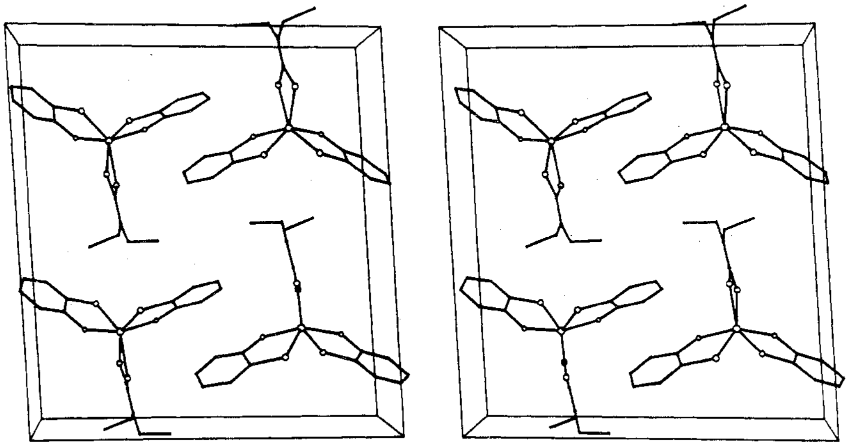

Figure 1. Stereoview of the molecular packing showing the contents of one unit cell. The positive direction of the *b* axis is into the page; the positive direction of the *a* axis is to the right.

Table I. Crystallographic Data at 25 °C[a]

Molecular formula	$C_{17}H_{20}N_3S_4Mo$
Mol wt	490.57
Space group	$P2_1/c$ (No. 14)
Cell dimensions[b]	
a, Å	17.246 (3)
b, Å	6.214 (1)
c, Å	19.284 (4)
β, deg	93.384 (15)
V, Å^3	2063.1 (6)
Z	4
d_{obsd}, g cm^{-3} [c]	1.576 (10)
d_{calcd}, g cm^{-3}	1.579
Crystal shape	Rod
Crystal dimensions, mm	0.23 × 0.17 × 0.34
Radiation, Å	λ(Mo Kα) 0.710 69
Monochromator	Graphite crystal
Supplied power	50 kV, 30 mA
Data collection method	θ–2θ scan
Scan speed, deg min^{-1}	Variable (2.0–29.3), determined as a function of peak intensity
Scan range (2θ), deg	Mo Kα_1 − 1.0 to Mo Kα_2 + 1.0
Ratio of total background time to peak scan time	0.5
Std reflections	(024), (204), (402) after every 97 readings
Std dev of standards	<2%
2θ limit, deg	3.5–50
No. of unique data	3664
No. of data used in the calculations	2982, $I > 3\sigma(I)$
Absorption coeff (μ), cm^{-1}	10.19 (Mo Kα)
Multiplier range of empirical absorption correction[d]	1.00–0.820

[a] The standard deviation of the least significant figure is given in parentheses in this table and in following tables. [b] Cell dimensions were obtained from a least-squares refinement of setting angles of 23 reflections in the 2θ range from 7 to 25°. [c] Density was determined by the flotation method using a solution of carbon tetrachloride and hexane. [d] Empirical absorption correction was applied using the program TAPER.

The structure was refined by full-matrix, least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$; the weights were taken 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.[16] The discrepancy indices, R_1 and R_2, are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. 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 variable parameters.

The positions of the molybdenum and sulfur atoms were obtained from an "*E* map" based on the solution with the highest combined form value (2.36) and the lowest residual index (42.7%) which was generated by the direct methods program MULTAN. One cycle of least-squares refinement of positional parameters for these atoms led to $R_1 = 0.433$ and $R_2 = 0.511$. The remaining 20 nonhydrogen atoms were located by successive least-squares refinements and difference electron-density maps. Two cycles of isotropic refinement resulted in $R_1 = 0.060$ and $R_2 = 0.079$. Refining the molybdenum, sulfur, and coordinated nitrogen atoms anisotropically reduced the discrepancy indices to $R_1 = 0.049$ and $R_2 = 0.067$. Anisotropic refinement of all nonhydrogen atoms converged with $R_1 = 0.039$, $R_2 = 0.060$, and GOF = 4.727 ($m = 226$). A difference electron-density map clearly revealed the positions of all 20 hydrogen atoms.

Examination of individual values of $|F_o|$ and $|F_c|$ showed that several low-angle intense reflections had $|F_o| \ll |F_c|$. A correction for secondary extinction was therefore included in the refinement in the form[12,17] $F_c = zF_o$, where $z = \{c\beta(2\theta)I + [1 + (c\beta(2\theta)I)^2]^{1/2}\}^{1/2}$, $\beta(2\theta) = (1 + \cos^2 2\theta_m)(1 + \cos^2 2\theta_m \cos^4 2\theta)/(1 + \cos^2 2\theta_m \cos^2 2\theta)^2$, and $\sum w(|F_o| - |F_c|/z)^2$ is minimized. Three additional cycles of full-matrix refinement gave $R_1 = 0.038$, $R_2 = 0.052$, GOF = 4.11 ($m = 227$), and a secondary extinction coefficient of $c = 2.55\ (9) \times 10^{-6}$ mm^{-1} e^{-2}. Despite the inclusion of an extinction parameter three of the strongest reflections, (002), (110), and (200), still had $|F_o| \ll |F_c|$. Reexamination of the crystal at low X-ray power showed that the reflections in question were seriously affected by coincidence loss. Therefore, all reflections in the range $3.5 < 2\theta < 16°$ were re-collected at reduced X-ray power (40 kV, 10 mA). These data were processed as previously described and used to apply a linear correction for coincidence losses of the strong reflections. The estimated losses at full power (50 kV, 30 mA) for the (002), (110), and (200) reflections were 30, 19, and 27%, respectively.

Refinement was continued using the coincidence-corrected data. Hydrogen atoms were included as fixed contributors in idealized positions (C–H = 0.95 Å, N–H = 0.85 Å)[18] assuming trigonal geometry about the nitrogen atoms and the phenyl carbon atoms and tetrahedral geometry about the methyl and methylene carbon atoms. Each hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than the atom to which it was attached. In the final cycle of full-matrix least-squares refinement 227 parameters were varied, and all parameter shifts were less than 0.05σ. Final discrepancy indices were $R_1 = 0.023$, $R_2 = 0.029$, and GOF = 1.249. The overdetermination ratio (n/m) was 13.1. The final value of the refined extinction coefficient was $5.7\ (9) \times 10^{-7}$ mm^{-1} e^{-2}. An analysis of $\sum w(|F_o| - |F_c|)^2$ showed no appreciable dependence either upon $(\sin \theta)/\lambda$ or upon $|F_o|$. The final difference electron-density map revealed no peaks greater than 0.46 e Å^{-3}. A structure factor calculation using all 3664 independent reflections yielded $R_1 = 0.035$ and $R_2 = 0.031$.

A listing of $10|F_o|$ and $10|F_c|$ values is available as supplementary material. The final nonhydrogen atomic parameters with their standard deviations are given in Table II, while the fixed positional and thermal parameters for hydrogen atoms are listed in Table III. Interatomic distances and angles are given in Tables IV and V.

Description of Structure

A stereoview of the crystal structure projected down the *b* axis is shown in Figure 1. The unit cell contains four discrete molecules of $Mo(NHC_6H_4S)_2(S_2CN(C_2H_5)_2)$, which are packed so that the S(1)–S(2) vector is approximately parallel to the shortest axis (*b*). A stereoview of one molecule, showing

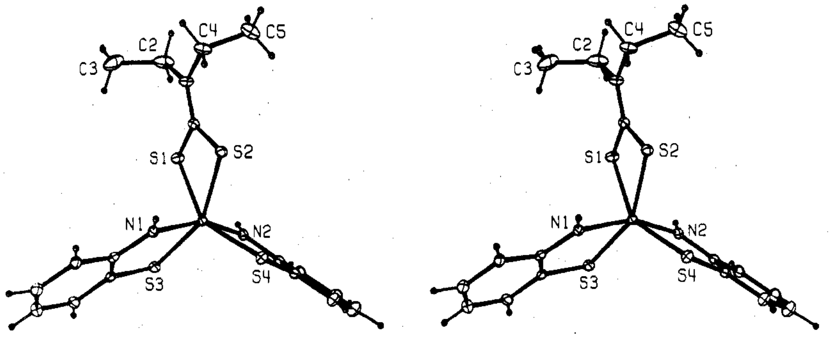

Figure 2. Stereoview of the Mo(abt)$_2$(dedtc) molecule. The hydrogen atoms have been assigned arbitrarily small thermal parameters for clarity. Thermal ellipsoids are drawn to enclose 15% of the probability distribution.

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	.750327(12)	.77274(4)	.260670(11)	17.55(9)	141.4(7)	14.52(7)	-1.33(18)	1.70(5)	4.52(16)
S(1)	.73678(5)	.94504(11)	.37489(4)	40.3(3)	138.4(18)	18.32(21)	4.6(6)	5.41(20)	2.3(5)
S(2)	.76057(4)	.49438(11)	.35240(4)	28.27(26)	144.2(18)	17.28(20)	10.5(5)	2.33(17)	5.2(5)
S(3)	.68860(4)	1.06602(11)	.19895(4)	23.85(26)	150.1(18)	20.09(21)	-7.2(5)	.24(18)	10.3(5)
S(4)	.81932(4)	.53009(12)	.19168(4)	25.49(26)	185.0(20)	20.23(21)	-3.5(6)	4.71(18)	-6.0(5)
N(1)	.64544(12)	.6499(3)	.23430(11)	22.1(8)	139.(6)	19.1(7)	-6.9(18)	2.5(6)	12.1(16)
N(2)	.84867(12)	.9388(4)	.24897(12)	21.2(8)	182.(6)	18.1(7)	-3.7(19)	-.7(6)	-4.8(17)
N(3)	.72895(16)	.6543(4)	.47657(12)	45.9(12)	173.(7)	12.9(7)	-7.7(23)	.7(7)	1.5(17)
C(1)	.74100(15)	.6915(4)	.41098(14)	24.1(10)	152.(7)	16.6(8)	-6.7(22)	-.8(7)	2.9(19)
C(2)	.7110(3)	.8298(6)	.52448(17)	103.(3)	188.(10)	16.6(10)	-7.(4)	6.2(13)	-10.7(25)
C(3)	.6271(4)	.8840(7)	.52341(24)	115.(4)	357.(15)	41.7(17)	66.(6)	45.1(20)	8.(4)
C(4)	.73681(22)	.4378(5)	.50647(15)	58.0(17)	184.(9)	16.4(9)	-14.(3)	-1.1(9)	10.6(22)
C(5)	.81812(28)	.3968(7)	.53521(21)	74.4(23)	323.(13)	33.1(13)	6.(5)	-14.6(14)	26.(3)
C(6)	.59684(15)	.9614(4)	.17792(13)	19.9(9)	173.(7)	15.2(7)	4.3(21)	3.2(6)	-.7(19)
C(7)	.53833(17)	1.0740(5)	.14067(16)	30.0(11)	207.(8)	22.1(9)	16.8(26)	.1(8)	11.3(22)
C(8)	.46666(18)	.9783(6)	.12653(18)	24.0(12)	346.(12)	28.9(11)	19.(3)	-3.4(9)	6.5(29)
C(9)	.45319(17)	.7705(6)	.14933(17)	19.9(10)	343.(11)	26.6(10)	-9.7(29)	-.3(8)	-8.7(28)
C(10)	.51083(16)	.6553(5)	.18482(15)	22.7(10)	220.(8)	21.8(9)	-10.6(24)	3.7(7)	-6.1(22)
C(11)	.58386(14)	.7494(4)	.19903(13)	20.5(9)	172.(7)	13.5(7)	3.1(22)	3.2(6)	-3.3(19)
C(12)	.90033(16)	.6831(5)	.17480(15)	20.9(10)	236.(9)	18.4(8)	3.8(24)	2.3(7)	11.3(22)
C(13)	.95816(19)	.6144(6)	.13225(17)	31.7(13)	348.(12)	27.0(10)	8.(3)	10.9(9)	-3.0(29)
C(14)	1.01961(22)	.7494(8)	.12085(22)	32.9(14)	528.(18)	38.4(14)	7.(4)	19.0(11)	11.(4)
C(15)	1.02374(20)	.9524(7)	.15011(21)	25.7(13)	470.(15)	37.7(14)	-26.(4)	7.7(10)	27.(4)
C(16)	.96775(17)	1.0239(5)	.19186(17)	21.9(10)	298.(10)	28.6(10)	-25.9(28)	-1.8(8)	14.1(27)
C(17)	.90541(15)	.8874(5)	.20534(14)	18.3(9)	226.(8)	17.5(8)	-7.3(23)	-2.3(7)	12.3(21)

[a] x, y and z are in fractional monoclinic coordinates. Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] The ring carbon atoms are numbered so that C(6) and C(12) are attached to S(3) and S(4), respectively, and C(11) and C(17) are attached to N(1) and N(2), respectively.

Table III. Parameters for Fixed Hydrogen Atoms[a]

Atom[b]	x	y	z	B, Å^2
H(N1)	0.6379	0.517	0.2466	3.0
H(N2)	0.8557	1.054	0.2741	3.0
H(C2)-1	0.7291	0.792	0.5711	6.0
H(C2)-2	0.7400	0.957	0.5125	6.0
H(C3)-1	0.6160	0.986	0.5584	7.5
H(C3)-2	0.6094	0.945	0.4790	7.5
H(C3)-3	0.5958	0.758	0.5301	7.5
H(C4)-1	0.7007	0.419	0.5424	5.0
H(C4)-2	0.7233	0.331	0.4711	5.0
H(C5)-1	0.8547	0.407	0.5007	7.0
H(C5)-2	0.8320	0.502	0.5710	7.0
H(C5)-3	0.8216	0.257	0.5561	7.0
H(C7)	0.5483	1.218	0.1247	4.1
H(C8)	0.4254	1.058	0.1009	4.9
H(C9)	0.4033	0.705	0.1393	4.6
H(C10)	0.5008	0.510	0.2006	3.8
H(C13)	0.9537	0.475	0.1096	5.0
H(C14)	1.0602	0.696	0.0932	6.1
H(C15)	1.0659	1.048	0.1393	5.9
H(C16)	0.9710	1.168	0.2126	4.7

[a] See Solution and Refinement of Structure in text. [b] Symbols in parentheses refer to atoms to which the hydrogen atoms are bonded.

Table IV. Interatomic Distances (Å)

Mo-S(1)	2.473 (1)	C(2)-C(3)	1.485 (7)
Mo-S(2)	2.473 (1)	C(4)-C(5)	1.499 (5)
Mo-S(3)	2.392 (1)	C(6)-C(7)	1.392 (4)
Mo-S(4)	2.376 (1)	C(7)-C(8)	1.384 (4)
Mo-N(1)	2.001 (2)	C(8)-C(9)	1.388 (4)
Mo-N(2)	2.009 (2)	C(9)-C(10)	1.375 (4)
S(1)-C(1)	1.722 (3)	C(10)-C(11)	1.401 (4)
S(2)-C(1)	1.713 (3)	C(11)-C(6)	1.401 (4)
S(3)-C(6)	1.736 (3)	C(12)-C(13)	1.395 (4)
S(4)-C(12)	1.736 (3)	C(13)-C(14)	1.379 (5)
N(1)-C(11)	1.374 (3)	C(14)-C(15)	1.382 (6)
N(2)-C(17)	1.366 (4)	C(15)-C(16)	1.367 (5)
C(1)-N(3)	1.314 (3)	C(16)-C(17)	1.406 (4)
N(3)-C(2)	1.474 (4)	C(17)-C(12)	1.401 (4)
N(3)-C(4)	1.467 (4)		
S(1)-S(2)	2.867 (1)	S(4)-N(1)	3.242 (2)
S(3)-N(1)	2.787 (2)	S(1)-N(1)	3.563 (2)
S(4)-N(2)	2.804 (2)	S(1)-S(4)	4.664 (1)
S(1)-S(3)	3.526 (1)	S(2)-N(2)	3.778 (2)
S(1)-N(2)	3.190 (2)	S(2)-S(3)	4.742 (1)
S(3)-N(2)	2.977 (2)	S(3)-S(4)	4.029 (1)
S(2)-S(4)	3.325 (1)	N(1)-N(2)	3.933 (3)
S(2)-N(1)	3.087 (2)		

the labeling scheme, appears in Figure 2.

The molybdenum atom is six-coordinate and bonded to four sulfur atoms and two nitrogen atoms. The chemically equivalent Mo-S distances are similar (Table IV). However, the two Mo-S distances from the diethyldithiocarbamate (dedtc) ligands of 2.473 (1) Å are substantially longer than the two Mo-S distances of 2.392 (1) and 2.376 (1) Å from the 2-aminobenzenethiolate (abt) ligands. The Mo-N distances of 2.001 (2) and 2.009 (2) Å are not significantly different from one another.

Table V. Interatomic Angles (deg)

S(1)-Mo-S(2)	70.86 (3)	C(2)-N(3)-C(1)	121.6 (2)
S(3)-Mo-N(1)	78.18 (6)	C(4)-N(3)-C(1)	121.6 (2)
S(4)-Mo-N(2)	79.00 (7)	C(2)-N(3)-C(4)	116.8 (2)
S(1)-Mo-S(3)	92.90 (3)	C(3)-C(2)-N(3)	113.5 (4)
S(2)-Mo-S(4)	86.54 (3)	C(5)-C(4)-N(3)	111.3 (3)
S(1)-Mo-S(4)	148.25 (3)	S(3)-C(6)-C(7)	123.7 (2)
S(2)-Mo-S(3)	154.12 (3)	S(3)-C(6)-C(11)	116.3 (2)
S(1)-Mo-N(1)	105.08 (7)	C(11)-C(6)-C(7)	119.9 (3)
S(2)-Mo-N(2)	114.48 (7)	C(6)-C(7)-C(8)	119.8 (3)
S(1)-Mo-N(2)	90.13 (7)	C(7)-C(8)-C(9)	120.1 (3)
S(2)-Mo-N(1)	86.57 (6)	C(8)-C(9)-C(10)	120.8 (3)
S(3)-Mo-S(4)	115.32 (3)	C(9)-C(10)-C(11)	119.7 (3)
S(3)-Mo-N(2)	84.64 (7)	C(10)-C(11)-C(6)	119.5 (3)
S(4)-Mo-N(1)	95.20 (7)	N(1)-C(11)-C(6)	115.8 (2)
N(1)-Mo-N(2)	157.47 (9)	N(1)-C(11)-C(10)	124.6 (3)
Mo-S(1)-C(1)	87.69 (9)	S(4)-C(12)-C(13)	123.6 (3)
Mo-S(2)-C(1)	87.88 (9)	S(4)-C(12)-C(17)	116.7 (2)
Mo-S(3)-C(6)	101.76 (9)	C(17)-C(12)-C(13)	119.7 (3)
Mo-S(4)-C(12)	101.10 (10)	C(12)-C(13)-C(14)	119.4 (3)
Mo-N(1)-C(11)	127.93 (17)	C(13)-C(14)-C(15)	120.8 (3)
Mo-N(2)-C(17)	126.12 (19)	C(14)-C(15)-C(16)	121.0 (3)
S(1)-C(1)-S(2)	113.14 (15)	C(15)-C(16)-C(17)	119.2 (3)
S(1)-C(1)-N(3)	123.0 (2)	C(16)-C(17)-C(12)	119.9 (3)
S(2)-C(1)-N(3)	123.9 (2)	N(2)-C(17)-C(12)	116.2 (2)
		N(2)-C(17)-C(16)	123.8 (3)
S(3)-S(1)-N(2)	52.33 (4)	S(4)-S(2)-N(1)	60.62 (4)
S(1)-S(3)-N(2)	58.01 (5)	S(2)-S(4)-N(1)	56.06 (4)
S(1)-N(2)-S(3)	69.66 (5)	S(2)-N(1)-S(4)	63.32 (5)

The coordination angles about the molybdenum atom vary widely (Table V) and show that the complex has no symmetry in the solid state. Differences between chemically related interchelate coordination angles show variations ranging from 3.6° between the S(1)–Mo–N(2) and S(2)–Mo–N(1) angles to as large as 10.6° between the S(3)–Mo–N(2) and S(4)–Mo–N(1) angles. These differences are 51 and 151σ, respectively.

The irregular coordination polyhedron about the molybdenum atom is approximately midway between a trigonal prism and an octahedron with the two nitrogen atoms trans to one another (N–Mo–N = 157.47 (9)°). The plane containing the atoms S(1), S(3), and N(2) is nearly parallel to the plane containing S(2), S(4), and N(1) (dihedral angle = 3.5°). A view along the "pseudotrigonal" axis normal to the mean plane defined by this pair of triangles is shown in Figure 3. Also shown in this projection of this tris chelate complex are chelate projection (twist) angles.[19] These angles should be 0° for a trigonal prism and 60° for an octahedron. The differing projection angles of 16 and 34° for the two abt ligands further emphasize the absence of symmetry in the molecule in the solid state.

The chemical literature[22] on six-coordinate complexes is replete with other angular descriptors of distortion in addition to the projection angles described above. The dihedral angle ρ is defined as the angle between the mean plane of Figure 3 and the chelate planes defined by the molybdenum atom and two donor atoms. In the trigonal-prismatic limit $\rho = 90°$, and in the octahedral limit $\rho = 54.7°$. The angles found here are ρ(S(1),Mo,S(2)) = 66.8°, ρ(N(1),Mo,S(3)) = 67.8°, and ρ(N(2),Mo,S(4)) = 80.2°. Another indicator of angular distortions is the angle between chelate planes. Thse angles should be 120° in a trigonal prism and 90° in an octahedron. Table VI shows the interchelate angles range from 104.9 to 114.8°. Muetterties and Guggenberger[23] have used δ, the angle between adjacent faces of a coordination polyhedron, to describe its shape. For a trigonal prism the δ's at the b_1 and b_2 edges are 0 and 120°, respectively, whereas in an octahedron $\delta = 70.5°$. The δ angles for the molecule appear in Table VI.

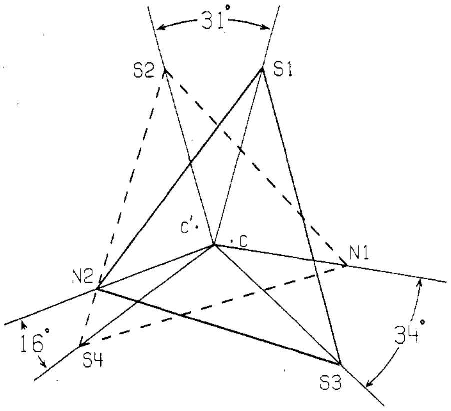

Figure 3. Projection of the coordination polyhedron onto the mean plane defined by the triangular faces S(1), S(3), N(2) and S(2), S(4), N(1). The centroids of these faces are C and C′, respectively. The mean plane and the chelate projection (twist) angles are defined in ref 19.

Table VI. Dihedral Angles

Atoms in plane 1	Atoms in plane 2	Angle, deg
S(1), S(3), N(2)	S(2), S(4), N(1)	3.5
Mo, S(1), S(2)	Mo, S(3), N(1)	104.9
Mo, S(1), S(2)	Mo, S(4), N(2)	112.3
Mo, S(3), N(1)	Mo, S(4), N(2)	114.8
Mo, S(1), S(2)	S(1), S(2), C(1), N(3), C(2), C(4)	7.5
Mo, S(3), N(1)	S(3), N(1), C(6), C(7), C(8), C(9), C(10), C(11)	1.6
Mo, S(4), N(2)	S(4), N(2), C(12), C(13), C(14), C(15), C(16), C(17)	6.8
S(1), S(2), C(1), N(3), C(2), C(4)	S(3), N(1), C(6), C(7), C(8), C(9), C(10), C(11)	96.6
S(1), S(2), C(1), N(3), C(2), C(4)	S(4), N(2), C(12), C(13), C(14), C(15), C(16), C(17)	125.5
S(3), N(1), C(6), C(7), C(8), C(9), C(10), C(11)	S(4), N(2), C(12), C(13), C(14), C(15), C(16), C(17)	111.8
S(1), S(2), N(1)	S(3), N(1), S(1)	37.6
S(1), S(2), N(2)	S(4), N(2), S(2)	27.3 $\}$ δ's at b_1[a]
S(3), S(4), N(1)	S(3), S(4), N(2)	49.4
S(3), N(1), S(1)	S(3), N(1), S(4)	91.1
S(4), N(2), S(2)	S(4), N(2), S(3)	90.9 $\}$ δ's at b_2
S(1), S(2), N(1)	S(1), S(2), N(2)	104.3

[a] δ's are defined in ref 23. The remaining δ's are 66.6, 71.1, 72.8, 76.5, 80.3, and 91.5°.

All of the angular descriptors of the coordination polyhedron of the molecule show that it has very irregular coordination geometry and that the two abt ligands are not equivalent in the solid state. The nonbonded intramolecular contacts shown in Table IV also emphasize the irregular coordination polyhedron and the inequivalence of the two abt ligands, e.g., S(1)···S(3) = 3.53 and S(2)···S(4) = 3.33 Å.

The structure can be best summarized as having the dedtc ligand and one abt ligand more closely related to octahedral geometry and the other abt ligand more closely related to a trigonal prism. A similar chelate ligand stereochemistry has been found in the tris(dithiolate) complexes $V(S_2C_2(CN)_2)_3^{2-}$,[24] $Mo(S_2C_2(CN)_2)_3^{2-}$,[22] $W(S_2C_2(CN)_2)_3^{2-}$,[22] and $Zr(S_2C_6H_4)_3^{2-}$.[25] A coordination polyhedron in which two chelate ligands are closer to the trigonal-primatic limit and one ligand is closer to the octahedral limit has been found for $Ta(S_2C_6H_4)_3^{-}$.[26]

Dihedral angles between the mean planes of the chelate skeletons and their respective coordination planes are given in Table VI. It is interesting to note that the Mo, S(3), N(1) plane has an angle of 1.6° with the mean plane of its chelate skeleton, whereas the angle between the Mo, S(4), N(2) plane and its mean chelate skeletal plane is 6.8°. The latter abt ligand is also the one which is closer to the trigonal-prismatic limit. Similar deviations from planarity have been observed in chelate systems of trigonal prismatic tris(dithiolate) compounds.[27-30]

Intermolecular contacts involving hydrogen atoms are comparable to van der Waals contacts. The shortest non-hydrogen intermolecular contact is 3.496 (1) Å and involves an S(1) atom of one molecule and the S(2) atom of an adjacent molecule at x, $1 + y$, z.

Discussion

To our knowledge $Mo(abt)_2(dedtc)$ is the first *monomeric* Mo(V) complex containing both coordinated sulfur and nitrogen atoms to be definitively characterized by X-ray crystallography. Moreover, there appears to be only one other structural report of a monomeric Mo(V) complex containing an Mo–S bond, a preliminary communication of the structure of the triphenylphosphine sulfide complex $MoOCl_3(SPPh_3)$.[7] The $Mo(S_2CNEt_2)_4^+$ cation has been extensively studied and probably has the same eight-coordinate structure as the related tungsten complex.[31] Several structures of binuclear Mo(V) compounds containing Mo–S bonds have been determined in recent years.[6,32]

In $Mo(abt)_2(dedtc)$ the Mo–S distance of the coordinated dedtc ligand (2.473 Å) is similar to those found in binuclear Mo(V) complexes.[6] The average Mo–S distance of the abt ligands (2.384 Å) is similar to the average Mo–S distance of 2.374 Å in $Mo(S_2C_2(CN)_2)_3^{2-}$[22] and 2.367 Å in $Mo(S_2C_6H_4)_3$[27] and only slightly shorter than the Mo–S distances of 2.401 and 2.406 Å recently observed for coordinated aliphatic thiols.[32] The Mo–S distance in $MoOCl_3(SPPh_3)$ is 2.460 (1) Å.[7]

The average Mo–N distance (2.005 Å) is more than 0.2 Å shorter than Mo–N distances commonly observed for four-coordinate nitrogen atoms[6] and is also substantially shorter than the 2.205 Å observed for the Mo–N distance of the trigonal nitrogen atom of coordinated quinolinate ion.[33] An Mo–N distance of 1.80 Å has been observed for the $Mo–NN(CH_3)_2$ grouping.[34] The short Mo–N distance for the coordinated abt ligand suggests that the Mo–N bond has considerable multiple character.

The two abt ligands of the molecule are nearly identical. The maximum difference between chemically equivalent pairs of distances in the two rings is 0.008 Å (2.5σ). The mean S–C distance (1.736 Å) and the mean C–NH distance (1.370 Å) are both consistent with a delocalized electronic structure for the chelate ring. Similar S–C (1.724 Å) and C–NH (1.366 Å) distances have subsequently been observed for $Mo(abt)_3$, which adopts a distorted trigonal-prismatic structure.[40] There appear to be no other reports of structures of metal complexes of the abt ligand.

It was emphasized above that the solid-state geometry of $Mo(abt)_2(dedtc)$ is irregular and that the two abt ligands are not equivalent. The inequivalence could be a consequence of the formally d^1 electron configuration of the Mo(V) center or could be due to packing forces in the solid.

The solution EPR spectra of $Mo(abt)_2(dedtc)$ have been extensively studied[9] and show that in solution the two abt ligands are equivalent on the EPR time scale. This could be due to a rapid averaging of irregular conformers or to the existence of a symmetric complex in solution in the absence of the packing forces of the solid. The temperature dependence exhibited by the EPR spectrum of $Mo(abt)_2(dedtc)$ and by other presumed monomeric Mo(V) complexes[35] suggests that equilibria among irregular conformers may be an important process in monomeric Mo(V) complexes. Intramolecular rearrangements of six-coordinate complexes are extensively reviewed elsewhere.[36] Here it is sufficient to emphasize that such rearrangements will convert the two NH groups from pseudotrans to pseudocis geometry. A particularly interesting feature of the reported EPR spectrum of $Mo(abt)_2(dedtc)$ is the hyperfine splitting of 7.4 G from the proton on the coordinated amido group.[9] The short Mo–N distance (vide supra) which results in an intramolecular Mo···H distance of only 2.5 Å is undoubtedly an important factor in ^1H hyperfine splitting of this magnitude being observed in this compound.

Single-crystal X-ray structure determinations of monomeric Mo(V) complexes open up the possibility of single-crystal EPR experiments in a diamagnetic host lattice to establish the orientations of the **g** and **A** tensors of the molybdenum atom relative to its coordination environment. Such knowledge of the anisotropies of pertinent complexes should be a useful aid for interpreting the anisotropies of the EPR signals from molybdoenzymes. Figure 1 shows that $Mo(abt)_2(dedtc)$ crystallizes so that all four molecules in the unit cell have their pseudotrigonal axis nearly parallel to the crystallographic b axis. Thus, the structure is crystallographically well suited to a single-crystal EPR study. However, the presence of 18 protons in each molecule in addition to the NH protons may lead to broadening of the signals which would obscure the anisotropic information.[37]

Finally, it is pertinent to comment on the possible relationship of the structure of $Mo(abt)_2(dedtc)$ to the molybdenum centers in enzymes, particularly xanthine oxidase. It has been previously emphasized that $Mo(abt)_2(dedtc)$ is not a direct model of the molybdenum environment in xanthine oxidase.[9] However, the properties of the molecule do provide definitive evidence that monomeric complexes with sulfur atoms coordinated to Mo(V) can approximate the isotropic g and A values of the enzyme.[4] This structure and the EPR spectroscopy[9] also support the hypothesis[38,39] that the ^1H hyperfine splitting observed in xanthine oxidase during turnover arises from protons on a ligand donor atom. It should also be noted that $Mo(abt)_2(dedtc)$ contains no terminal oxo group but is in fact preferentially formed from an oxo complex.[8,9] A terminal oxo group is usually assumed to be present in xanthine oxidase and to be responsible for the strong anisotropy of the EPR signal from the enzyme.[1] The nearly isotropic EPR signals of $Mo(abt)_2(dedtc)$[37] and $Mo(S_2CNEt_2)_4^+$[31] are consistent with this assumption. However, further attempts to ascribe the EPR spectrum of xanthine oxidase to a specific monomeric Mo(V) center must await the determination of the structures of additional monomeric Mo(V) complexes and the elucidation of the anisotropies of their EPR spectra.

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Registry No. $Mo(NH_6H_4S)_2(S_2CN(C_2H_5)_2)$, 66322-07-4.

Supplementary Material Available: Listings of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(19) In the present work, the chelate projection angles, $\phi_{ii'}$, are defined as the angles between the projections of the metal–ligand vectors, M–L_i and M–$L_{i'}$, onto the mean plane of the two triangular faces: face 1 (L_1, L_2, L_3) and face 2 ($L_{1'}$, $L_{2'}$, $L_{3'}$), where L_i and $L_{i'}$ ($i = 1, 2, 3$) represent the donor atoms in the same chelate. The mean plane is formed by the three points whose coordinates are expressed in the general formula, $U_{ii'} = (d_{i'}(1)U_i + d_i(2)U_{i'})/(d_i(2) + d_{i'}(1))$ ($U = X, Y, Z$), where $d_i(2)$ and $d_{i'}(1)$ represent the distances of L_i from face 2 and $L_{i'}$ from face 1, respectively. Several other definitions of the chelate projection angle are summarized in ref 20 and 21. However, those definitions are not useful if the vector defined by the centroids of face 1 and face 2, C and C′, is far from normal to the faces. Typical examples of this condition are (1) the present compound, where face 1 and face 2 are approximately parallel but slipped relative to each other, and (2) $Ta(S_2C_6H_4)_3^-$ anion, where the two faces deviate from being parallel. The method which Dymock and Palenik[20] recommend for computing the individual chelate projection angles defines the dihedral angles between the planes formed by L_i, C, and C′ and by $L_{i'}$, C, and C′. This method results in ϕ_{S1S6} of 28°, ϕ_{S2S3} of 30°, and ϕ_{S4S5} of 43° for $Ta(S_2C_6H_4)_3^-$ and ϕ_{S1S2} of 21°, ϕ_{N1S3} of 35°, and ϕ_{N2S4} of 26° for the present compound. These values differ from those calculated according to our definition ($\phi_{S1S6} = 52°$, $\phi_{S2S3} = 18°$, and $\phi_{S4S5} = 19°$ for $Ta(S_2C_6H_4)_3^-$; see text and Figure 3 for the present compound).

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Crystal and Molecular Structure of Tris(*p*-fluorophenyl isocyanide)bis(trimethyl phosphite)cobalt(I) Tetrafluoroborate, $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$

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The structure of $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$ has been determined using three-dimensional X-ray diffractometer data collected at −40 °C. The pale yellow crystals are orthorhombic, space group *Pnna*, with $a = 17.168$ (2) Å, $b = 17.034$ (3) Å, $c = 12.051$ (2) Å, $Z = 4$, density (X-ray, −40 °C) = 1.427 g cm^{-3}, and density (measured, 21 °C) = 1.422 g cm^{-3}. The structure was refined by full-matrix least squares using 1372 reflections with $I \geq 2\sigma(I)$ to a final weighted R of 0.088. The coordination around the Co(I) is very nearly trigonal bipyramidal with the complex lying on a twofold crystallographic axis and the phosphite ligands occupying the axial positions. The axial Co–P bond distance is 2.137 (3) Å; the two independent Co–C bond distances are 1.83 (2) and 1.85 (1) Å. The P–Co–P bond angles are 90.3 (1), 90.3 (4), and 89.4 (4)°; the two independent equatorial angles are 115.7 (5) and 122.2 (4)°.

Introduction

Distortions of bond distances and angles from idealized trigonal-bipyramidal geometry have been observed in pentakis(aromatic isocyanide)cobalt(I) compounds including $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$,[1] $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$,[2] $[Co(CNC_6H_5)_5]ClO_4$,[3,4] and $[Co\{CNC_6H_2(CH_3)_3\text{-}2,4,6\}_5]ClO_4$.[5] Recently, trialkyl phosphites have been shown to readily replace aromatic isocyanide ligands in $[Co(CNR)_5]ClO_4$ and $[Co(CNR)_5]BF_4$ to yield $[Co(CNR)_3\{P(OR')_3\}_2]ClO_4$ and $Co(CNR)_3\{P(OR')_3\}_2]BF_4$.[6] On the basis of infrared and ^{59}Co NQR data, Becker[6] predicted these compounds to have strict D_{3h} symmetry in solution but to have distorted trigonal-bipyramidal geometry in the solid state. To learn more about the geometries of these complexes and the extent of distortion, if any, the X-ray structural determination of tris(*p*-fluorophenyl isocyanide)bis(trimethyl phosphite)cobalt(I) tetrafluoroborate, $[Co(CNC_6H_4F\text{-}p)_3\{P(OCH_3)_3\}_2]BF_4$, was undertaken. Also of interest was the linearity of the Co—C≡N and −C≡N—C bonds, found to be bent in the pentakis(phenyl isocyanide) compounds. Additionally, it was hoped that this investigation of the structure at −40 °C would yield improved bond distances and angles for the trimethyl phosphite ligand, which in previous structures was found to have very large thermal motions.

Experimental Section

Collection and Reduction of Data. The compound $[Co(CNC_6H_4F)_3\{P(OCH_3)_3\}_2]BF_4$ was prepared by Dr. C. A. L. Becker in a procedure described elsewhere.[6,7] Crystals were obtained by slow

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