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Synthesis and Molecular Structure of Molybdenum(V) Dimers with Mixed Oxo and Sulfido Terminal Ligands: Removal of Terminal Sulfide by Triphenylphosphine and Cyanide

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The complex $Mo_2OS(\mu\text{-}S_2)(S_2CNR_2)_2$ (R_2 = Me_2, Et_2, $n\text{-}Bu_2$, $(CH_2)_5$) was synthesized by the reaction of K_2MoS_4 and NaS_2CNR_2 in water in the presence of $Na_2S_2O_4$ and by the reaction of *cis*-$MoO_2(S_2CNR_2)_2$ or $Mo_2O_2(\mu\text{-}O)(S_2CNR_2)_4$ with hydrogen sulfide in chloroform. It could not be prepared by oxo–sulfido exchange with mixtures of $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ and $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ nor by the reaction of elemental sulfur with $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$. The structure of $Mo_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2$ was determined by X-ray crystallography. The compound crystallizes in space group $P2_1/a$ with a = 17.540 (3) Å, b = 6.859 (1) Å, c = 17.854 (2) Å, β = 104.67 (1)°, d_{obsd} = 1.916 (10) g cm^{-3}, d_{calcd} = 1.920 g cm^{-3}, and Z = 4. The stereochemistry of the dimer involves syn fusion of the basal edges of two tetragonal pyramids. The equatorial positions of each pyramid are occupied by the two bridging sulfido groups (S_b) and by two sulfur atoms from a S_2CNEt_2 ligand (S_l). The apical position of one pyramid is occupied by a terminal oxo group and that of the other pyramid by a terminal sulfido group. An approximate twofold disorder of the molecule in the crystal precludes accurate determination of the terminal Mo═O and Mo═S distances and obscures any differences between the two halves of the dimer. In view of the disorder, the least-squares refinement was terminated after convergence of the model with isotropic atoms with R_1 = 0.086 for the 1789 data with $F_o^2 \geq 3\sigma(F_o^2)$ and $2\theta \leq 40°$. The Mo···Mo distance is 2.826 (3) Å, the average Mo–S_b distance is 2.317 Å and the average Mo–S_l distance is 2.466 Å. The dihedral angle between the two $Mo(S_b)_2$ planes of the dimer is 149.4°. $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ reacted with triphenylphosphine or cyanide to give $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ and either triphenylphosphine sulfide or thiocyanate. This reaction with cyanide is reminiscent of the removal of sulfur from the molybdo enzymes xanthine oxidase and aldehyde oxidase. The possible interrelationships of these reactions is discussed and speculation concerning the function of the cyanide-labile sulfur atom in the enzymes is presented.

Introduction

The commonly held belief that molybdenum has a functional role at the substrate-binding sites of all the best-characterized molybdo enzymes[2,3] has led to considerable activity in the area of molybdenum coordination chemistry. Our studies[2,4–12] have concentrated on the higher oxidation states as being the most viable and, as part of that effort, we report the synthesis, characterization, and some chemistry of $Mo_2OS(\mu\text{-}S)_2(dtc)_2$ (dtc = S_2CNMe_2, S_2CNEt_2, $S_2CN(n\text{-}Bu)_2$, $S_2CN(CH_2)_5$). The determination of the structure of this complex with dtc = S_2CNEt_2 completes the series $Mo_2X_2(\mu\text{-}Y_2)(dtc)_2$ in which sulfido replaces oxo in the dinuclear core at both the terminal (X) and bridging (Y) positions. The structures of the compounds $Mo_2O_4(dtc)_2$ ($X_2 = Y_2 = O_2$),[13] $Mo_2O_2(\mu\text{-}O,S)(dtc)_2$ ($X_2 = O_2$, $Y_2 = \mu\text{-}O,S$),[14] $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ ($X_2 = O_2$, $Y_2 = S_2$),[15] and $Mo_2S_4(dtc)_2$ ($X_2 = Y_2 = S_2$)[16] have been reported previously as has a preliminary communication of our results.[17] Of particular interest is the possible relationship of some reactions of these mixed terminal oxo–sulfido compounds to the problem of the cyanide-labile sulfur atom[18–20] in xanthine oxidase and we report herein the first authenticated example of the replacement of a terminal sulfido ligand on molybdenum by oxo mediated by aqueous cyanide or triphenylphosphine.

Experimental Section

Materials and Physical Measurements. All reactions were carried out under an atmosphere of purified argon or nitrogen by using degassed analytical grade solvents. *cis*-Dioxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(VI),[21] μ-oxo-bis[oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(V)],[5] μ-disulfido-bis[oxo(*N*,*N*-diethyldithiocarbamato)molybdenum(V)],[12] μ-disulfido-bis[sulfido-(*N*,*N*-diethyldithiocarbamato)molybdenum(V)],[7] and potassium tetrathiomolybdate(VI)[22] were prepared by literature methods. Infrared spectra were recorded as KBr disks or Nujol mulls with a Beckman IR20A or a Perkin-Elmer 735 spectrophotometer, C, H, and N analyses were obtained with a Hewlett-Packard 185 CHN analyzer and S analyses were by Alfred Bernhardt, West Germany, mass spectra were obtained on a Hewlett-Packard 5930A spectrometer, and NMR spectra were obtained on a Varian A60 instrument.

Preparation of $Mo_2OS(\mu\text{-}S_2)(dtc)_2$. Two basic methods are available and typical procedures are described.

(a) K_2MoS_4 (3.0 g, 9.92 mmol) and $NaS_2CNEt_2\cdot 2H_2O$ (3.22 g, 15.5 mmol) were dissolved in water (25 mL) and added with stirring to a solution of sodium dithionite (10.0 g, 57.4 mmol) in water (35 mL). After 1 h, the yellow precipitate (which formed immediately) was collected by filtration and washed with water (4 × 30 mL), ethanol (3 × 25 mL), and diethyl ether (3 × 25 mL). Dissolution in dichloromethane and aerobic chromatography on silica gel, using dichloromethane as eluant, gave a yellow solution which, on evaporation and diethyl ether addition, gave yellow-orange crystals of $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ (2.88 g, 96% yield). Anal. Calcd for $C_{10}H_{20}Mo_2N_2OS_7$: C, 20.0; H, 3.36; N, 4.66; S, 37.4. Found: C, 19.9; H, 3.55; N, 4.44; S, 37.1. The same product in similar yields was obtained on varying the molar ratio of $NaS_2CNEt_2\cdot 2H_2O$ to K_2MoS_4 from 1:1 to 4:1.

A similar reaction using $NaS_2CNMe_2\cdot 3H_2O$ (3.06 g, 15.5 mmol) gave $Mo_2OS(\mu\text{-}S_2)(S_2CNMe_2)_2$ (2.57 g, 95% yield), which was purified by Soxhlet extraction with boiling chloroform. Anal. Calcd for $C_6H_{12}Mo_2N_2OS_7$: C, 13.2; H, 2.22; N, 5.14; S, 41.2. Found: C, 13.5; H, 2.31; N, 4.88; S, 40.0.

(b) Hydrogen sulfide was bubbled through a solution of $Mo_2O_3(S_2CNEt_2)_4$ (1.0 g, 1.20 mmol) in chloroform (40 mL) for 30 min. The resultant mixture was stirred anaerobically for 18 h and reduced to half-volume. The yellow precipitate was then collected by filtration, washed with chloroform (1 × 25 mL) and hexane (4 × 20 mL), and dried in vacuo. The *product* may be crystallized directly (or after chromatography on silica gel with dichloromethane as eluant) from dichloromethane/ether to give orange crystals (0.45 g, 66% yield). Anal. Found: C, 19.9; H, 3.39; N, 4.58; S, 36.8.

Similarly, $Mo_2O_3(S_2CNMe_2)_4$ (1.0 g, 1.39 mmol) and hydrogen sulfide gave $Mo_2OS(\mu\text{-}S_2)(S_2CNMe_2)_2$ (0.65 g, 86% yield). Anal. Found: C, 13.3; H, 2.51; N, 5.20. Also, hydrogen sulfide and $Mo_2O_3(S_2CN(CH_2)_5)_4$ (1.0 g, 1.18 mmol) in chloroform (40 mL) gave yellow-orange $Mo_2OS(\mu\text{-}S_2)(S_2CN(CH_2)_5)_2$ (0.55 g, 74% yield). Anal. Calcd for $C_{12}H_{20}Mo_2N_2OS_7$: C, 23.1; H, 3.23; N, 4.48. Found: C, 23.3; H, 3.48; N, 4.51.

The same product in similar yield can be obtained when $MoO_2(dtc)_2$ replaces $Mo_2O_3(dtc)_4$. In this case, an initial change from yellow to purple indicates reduction to $Mo_2O_3(dtc)_4$. For example, $MoO_2[S_2CN(n\text{-}C_4H_9)_2]_2$ (0.10 g, 0.19 mmol) in chloroform (25 mL) with excess hydrogen sulfide was stirred for 18 h. Evaporation to 5 mL and addition of petroleum ether gave a yellow solid, which was

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chromatographed on silica gel with 1,2-dichloroethane as eluant to give $Mo_2OS(\mu\text{-}S_2)[S_2CN(n\text{-}C_4H_9)_2]_2$ (0.05 g, 75% yield). Anal. Calcd for $C_{18}H_{36}Mo_2N_2OS_7$: C, 30.3; H, 5.09; N, 3.93. Found: C, 30.4; H, 5.53; N, 4.11.

Attempted Reactions of $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ with Hydrogen Sulfide and Sodium *N,N*-Dialkyldithiocarbamate. (a) $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.5 g, 0.86 mmol) in chloroform (35 mL) was bubbled with hydrogen sulfide for 6 h. The light brown solid (0.4 g) which resulted was unchanged starting material (identified by analysis and infrared spectroscopy).

(b) $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.29 g, 0.5 mmol), sodium *N,N*-diethyldithiocarbamate trihydrate (0.23 g, 1.0 mmol) and sodium dithionite (0.17 g, 1.0 mmol) were boiled in degassed water for 1 h. The yellow solid was unchanged starting material (identified by analysis and infrared spectroscopy).

(c) Similar experiments with $Mo_2OS(\mu\text{-}S_2)(S_2CNMe_2)_2$ also produced no reaction.

Attempted Reaction of $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ and $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$. (a) These two compounds (~0.1 g, 0.16 mmol each) were stirred in dichloromethane solution for 60 h at 25 °C. The solvent was then removed to leave a mixture of unchanged starting materials (confirmed by its infrared spectrum). Extraction with dichloromethane (2 × 10 mL) left a residue of $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.05 g; identified by infrared spectroscopy), which on evaporation gave a mixture (0.13 g) of the starting materials enhanced with respect to $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$.

(b) No reaction occurred when a similar reaction mixture was boiled under reflux in 1,2-dichloroethane (30 mL) for 6 h with or without triphenylphosphine present.

Reactions of $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ with Triphenylphosphine. (a) A suspension of $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.20 g, 0.34 mmol) and triphenylphosphine (0.45 g, 1.71 mmol) was heated under reflux in chloroform (30 mL) for 19 h. The tan precipitate was washed with chloroform (2 × 10 mL), ethanol (4 × 25 mL), and diethyl ether (5 × 25 mL) and dried in vacuo. Chromatography on silica gel with dichloromethane as eluant gave lemon yellow $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.11 g, 57% yield). Anal. Calcd for $C_{19}H_{20}Mo_2N_2O_2S_6$: C, 20.6; H, 3.45; N, 4.79; S, 32.9. Found: C, 20.4; H, 3.33; N, 4.69; S, 33.7 (confirmed by infrared spectroscopy). Evaporation of the combined filtrate and washings to dryness gave a mixture of triphenylphosphine and triphenylphosphine sulfide (identified by its infrared spectrum). A similar experiment using equimolar amounts of triphenylphosphine and $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ required 48 h to go to completion but still gave $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ (67% yield; identified by infrared spectrum).

(b) A similar experiment with $Mo_2OS(\mu\text{-}S_2)(S_2CNMe_2)_2$ (0.20 g, 0.35 mmol) and triphenylphosphine (0.4 g, 1.77 mmol) in boiling chloroform (35 mL) for 21 h produced $Mo_2O_2(\mu\text{-}S_2)(S_2CNMe_2)_2$ (0.15 g, 77% yield), which was washed with chloroform and hexane and dried in vacuo. Anal. Calcd for $C_6H_{12}Mo_2N_2O_2S_6$: C, 13.6; H, 2.29; N, 5.30. Found: C, 14.2; H, 2.21; N, 4.87. The combined filtrate and washings were evaporated to dryness and taken up in a minimum of carbon tetrachloride, and hexane was added. The white crystals of triphenylphosphine sulfide (0.05 g; identified by its infrared spectrum) were filtered off, and on evaporation of the filtrate, triphenylphosphine (0.31 g; identified by its infrared spectrum) crystallized.

Reactions of $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ with Triphenylphosphine. A mixture of $Mo_2S_2(\mu\text{-}S_2)[S_2CN(n\text{-}Bu)_2]_2$ (0.19 g, 0.25 mmol) and triphenylphosphine (0.33 g, 1.27 mmol) was heated under reflux in chloroform (35 mL) for 18 h. After evaporation, the dark brown precipitate was washed with diethyl ether (3 × 25 mL) and dried in vacuo. Its infrared spectrum contained bands due to the dithiocarbamate ligands but none assignable to terminal or bridging molybdenum–oxygen or molybdenum–sulfur vibrations. A similar experiment with $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ gave a similar result.

Attempted Reaction of Sulfur with $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$. $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.20 g, 0.34 mmol) and elemental sulfur (0.05 g, 1.56 mg atom) were heated under reflux in chloroform (40 mL) for 5 h. The brown precipitate was collected by filtration, washed with chloroform (2 × 15 mL) when it lightened to yellow, and dried in vacuo. Infrared spectroscopy and elemental analysis indicated it to be unreacted starting material.

Reaction of $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ with Cyanide. $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.22 g, 0.35 mmol), potassium cyanide (0.023 g, 0.35 mmol), and tetraethylammonium bromide (0.074 g, 0.35 mmol) were heated under reflux for 60 h in a mixture of chloroform (30 mL), ethanol (10 mL), and water (5 mL). The solvents were removed by evaporation and the residue was washed with water (5 × 10 mL), ethanol (2 × 15 mL), and diethyl ether (2 × 15 mL). The yellow residue of $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ (0.14 g, 71% yield) was dried in vacuo. Anal. Found: C, 20.9; H, 3.47; N, 4.59 (confirmed by infrared spectrum). The combined washings were evaporated to dryness and taken up in 1 M hydrochloric acid (5 mL). To 2 drops of this solution were added 2 drops of 1% aqueous ferric chloride solution to give a blood red coloration (soluble in diethyl ether), which confirms the presence of thiocyanate. A similar reaction in which the potassium cyanide is omitted allows the starting material to be recovered unchanged. A reaction in which the tetraethylammonium bromide and the additional water are omitted does produce $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ but the yield is lower and the reaction time is increased.

Table I. Atomic Parameters for $Mo_2OS_3(S_2CN(C_2H_5)_2)_2$ [a]

atom	x	y	z	B, Å^2
Mo(1)	0.60729 (12)	0.7447 (3)	0.30885 (11)	1.99 (5)
Mo(2)	0.67086 (12)	0.8542 (3)	0.18455 (12)	2.07 (5)
S(1)[b]	0.4921 (5)	0.7189 (13)	0.2637 (5)	5.99 (19)
S(2)	0.6754 (4)	0.5493 (10)	0.2420 (4)	2.54 (14)
S(3)	0.6441 (4)	1.0532 (9)	0.2798 (4)	2.00 (13)
S(4)	0.6418 (4)	0.4848 (11)	0.4082 (4)	2.83 (15)
S(5)	0.6289 (4)	0.8908 (10)	0.4387 (4)	2.52 (14)
S(6)	0.7819 (4)	0.7227 (11)	0.1392 (4)	3.38 (16)
S(7)	0.7604 (4)	1.1217 (10)	0.1728 (4)	2.40 (14)
O[b]	0.5882 (10)	0.8668 (25)	0.0990 (10)	1.8 (4)
N(1)	0.6507 (12)	0.621 (3)	0.5516 (11)	2.5 (4)
N(2)	0.8702 (12)	1.008 (3)	0.0997 (11)	2.6 (4)
C(1)	0.6407 (13)	0.660 (4)	0.4756 (13)	1.8 (5)
C(2)	0.6588 (16)	0.414 (4)	0.5827 (16)	3.4 (6)
C(3)	0.5777 (20)	0.322 (5)	0.5667 (19)	5.1 (8)
C(4)	0.6579 (17)	0.776 (4)	0.6125 (16)	3.3 (6)
C(5)	0.5833 (20)	0.795 (5)	0.6399 (19)	5.2 (8)
C(6)	0.8117 (14)	0.959 (4)	0.1314 (14)	2.3 (5)
C(7)	0.9191 (17)	0.854 (4)	0.0713 (17)	3.8 (6)
C(8)	0.8900 (23)	0.829 (6)	−0.0112 (23)	6.9 (10)
C(9)	0.8909 (16)	1.221 (4)	0.0921 (16)	3.6 (6)
C(10)	0.9624 (19)	1.273 (5)	0.1528 (18)	4.9 (7)

[a] x, y, and z are in fractional monoclinic coordinates. The standard deviation of the least significant figure is given in parentheses. [b] Disordered atoms (see Experimental Section).

X-ray Analysis. Orange crystals suitable for X-ray diffraction were obtained by slow liquid diffusion of pentane into a saturated dichloromethane solution of the compound prepared by the action of hydrogen sulfide on *cis*-$MoO_2(S_2CNEt_2)_2$ followed by chromatography on silica gel. Cell dimensions and diffraction data were obtained on a Syntex $P2_1$ autodiffractometer using graphite monochromated Mo K$\bar{\alpha}$ radiation at 24 °C.[23,24] Crystal data: $C_{10}H_{20}N_2OS_7Mo_2$; mol wt 600.6; monoclinic; $a = 17.540$ (3), $b = 6.859$ (1), $c = 17.854$ (2) Å; $\beta = 104.67$ (1)°; $d_{\text{obsd}} = 1.916$ (10), $d_{\text{calcd}} = 1.920$ g cm^{-3}; $Z = 4$; space group $P2_1/a$. The data were processed in a manner described previously.[24] The positions of the Mo atoms and most of the S atoms were located by direct methods.[24,25] Subsequent least-squares refinements and difference electron density maps revealed the positions of the remaining nonhydrogen atoms. The magnitude of the electron density at the two terminal positions suggested partial disorder of the terminal O and terminal S atoms. Isotropic refinement of an ordered model having a terminal oxo group and a terminal sulfido group, using 1789 independent reflections with $I \geq 3\sigma(I)$ and $2\theta \leq 40°$, resulted in $R_1 = 0.086$ and $R_2 = 0.119$.[26] The temperature factors for the terminal O and S atoms in this model were 1.8 and 6.0 Å^2, respectively, and the Mo–S$_t$ and Mo–O$_t$ distances were chemically unreasonable (vide infra), confirming the partial disorder of the terminal atoms. Refinement of a disordered model in which the Mo–O$_t$ and Mo–S$_t$ distances were constrained to 1.68 and 2.00 Å, respectively, gave occupancies which suggested a 75:25 disorder of the terminal atoms. Since the partial overlap of the terminal O and S atoms precluded a meaningful determination of the Mo–S$_t$ and Mo–O$_t$ distances, refinement was stopped at the isotropic model, which established the stoichiometry and stereochemistry of the compound.

The atomic parameters with their standard deviations are listed in Table I. Selected interatomic distances and angles are given in Table II, and a listing of $10|F_o|$ and $10|F_c|$ values is also available.[27]

Table II. Selected Interatomic Distances (Å) and Angles (deg)

Mo(1)–Mo(2)	2.826 (3)	Mo(2)–S(6)	2.461 (9)
Mo(1)–S(2)	2.317 (8)	Mo(2)–S(7)	2.459 (7)
Mo(1)–S(3)	2.309 (8)	C(1)–S(4)	1.706 (25)
Mo(2)–S(2)	2.322 (7)	C(1)–S(5)	1.705 (25)
Mo(2)–S(3)	2.320 (8)	C(6)–S(6)	1.718 (26)
Mo(1)–S(4)	2.479 (7)	C(6)–S(7)	1.715 (27)
Mo(1)–S(5)	2.466 (7)		
S(2)–Mo(1)–S(3)	101.8 (3)	S(2)–Mo(2)–S(3)	101.3 (3)
Mo(1)–S(2)–Mo(2)	75.1 (3)	Mo(1)–S(3)–Mo(2)	75.2 (3)
S(4)–Mo(1)–S(5)	70.6 (3)	S(6)–Mo(2)–S(7)	70.7 (4)
S(2)–Mo(1)–S(4)	83.6 (3)	S(2)–Mo(2)–S(6)	82.8 (3)
S(3)–Mo(1)–S(5)	81.6 (3)	S(3)–Mo(2)–S(7)	82.9 (3)
S(2)–Mo(1)–S(5)	138.0 (4)	S(2)–Mo(2)–S(7)	139.4 (4)
S(3)–Mo(1)–S(4)	142.0 (4)	S(3)–Mo(2)–S(6)	141.3 (4)
Mo(1)–S(4)–C(1)	87.3 (10)	Mo(2)–S(6)–C(6)	87.9 (11)
Mo(1)–S(5)–C(1)	87.7 (10)	Mo(2)–S(7)–C(6)	88.1 (10)
S(2)–Mo(1)–S(1)[a]	110.1 (4)	S(2)–Mo(2)–O[a]	110.1 (7)
S(3)–Mo(1)–S(1)[a]	107.7 (4)	S(3)–Mo(2)–O[a]	108.7 (7)
S(4)–Mo(1)–S(1)[a]	105.4 (4)	S(6)–Mo(2)–O[a]	105.6 (7)
S(5)–Mo(1)–S(1)[a]	108.4 (4)	S(7)–Mo(2)–O[a]	106.4 (7)

[a] Angle contains disordered atoms.

Results

Preparations and Reactions. The reaction of potassium tetrathiomolybdate(VI) with 1, 2, or 4 mol of sodium *N*,*N*-dialkyldithiocarbamate in the presence of sodium dithionite in water at 25 °C produces a molybdenum(V) dimer containing a di-μ-sulfido bridge and mixed oxo and sulfido terminal ligands, $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ (eq 1). The same compound is precipitated when hydrogen sulfide is passed through a chloroform solution at 25 °C of either *cis*-dioxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(VI) or μ-oxo-bis[oxobis(*N*,*N*-dialkyldithiocarbamato)]molybdenum(V) (eq 2).

$$2MoS_4^{2-} + 2dtc^- + S_2O_4^{2-} \xrightarrow{H_2O} Mo_2OS(\mu\text{-}S_2)(dtc)_2 \quad (1)$$

$$Mo_2O_2(\mu\text{-}O)(dtc)_4 \xrightarrow{H_2S} Mo_2OS(\mu\text{-}S_2)(dtc)_2 \quad (2)$$

These complexes are inert to further reaction with hydrogen sulfide and excess dithiocarbamate ligand and could not be prepared by a ligand exchange reaction as appropriate mixtures of the $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ and $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ are recovered unchanged from boiling 1,2-dichloroethane after 6 h.

The lone terminal sulfido group could be removed either by tertiary phosphine in boiling chloroform (eq 3) or by cyanide in a boiling chloroform–ethanol–water mixture (eq 4). In contrast, $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ decomposes to unidentifiable products under similar conditions. As these phosphine and cyanide reactions are reminiscent of sulfur atom transfers,[28] an attempt was made to prepare $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ by boiling $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ with an excess of sulfur in chloroform, but this was unsuccessful.

$$Mo_2OS(\mu\text{-}S_2)(dtc)_2 \xrightarrow{PPh_3} Mo_2O_2(\mu\text{-}S_2)(dtc)_2 + S{=}PPh_3 \quad (3)$$

$$Mo_2OS(\mu\text{-}S_2)(dtc)_2 \xrightarrow{CN^-} Mo_2O_2(\mu\text{-}S_2)(dtc)_2 + SCN^- \quad (4)$$

Infrared Spectra. All four complexes of the type $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ (dtc = S_2CNMe_2, S_2CNEt_2, $S_2CN(n\text{-}Bu)_2$, $S_2CN(CH_5)_5$) have bands at ~960 and ~545 cm^{-1}, assigned to the terminal molybdenum–oxygen and –sulfur stretching vibrations,[5,12,29] and at ~470 and ~340 cm^{-1} due to the di-μ-sulfido bridge.[12] Selected infrared data for these and related compounds are listed in Table III. These data show that an equimolar mixture of $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ and $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ can easily be distinguished from $Mo_2OS(\mu\text{-}S_2)(dtc)_2$, particularly in the regions of ~470 cm^{-1}, i.e., the highest energy bridge vibration, and ~965 cm^{-1}, the terminal molybdenum–oxygen stretching vibrations.

Table III. Selected Infrared Spectral Data[a]

compound	$\nu(Mo{=}O)$	$\nu(Mo{=}S)$	$\nu(MoS_2Mo)$
$Mo_2O_2(\mu\text{-}S_2)(dtc)_2$[b]	967 vs, 952 m		477 m, . . ., 340 m
$Mo_2S_2(\mu\text{-}S_2)(dtc)_2$		548 s, 538 sh	. . ., 463, 334 m
1:1 mixture[c]	967 s, 952 m	548 m, 538 sh	476 m, 464 m, 336 m
$Mo_2OS(\mu\text{-}S_2)(dtc)_2$	962 s, 956 sh	544 s	471 m, 337 m

[a] KBr disks. Key: vs = very strong, s = strong, m = medium, sh = shoulder. [b] dtc = *N*,*N*-diethyldithiocarbamate, other ligands gave very similar values. [c] 1:1 mixture of $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ and $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ after dissolution in dichloromethane and evaporation to dryness.

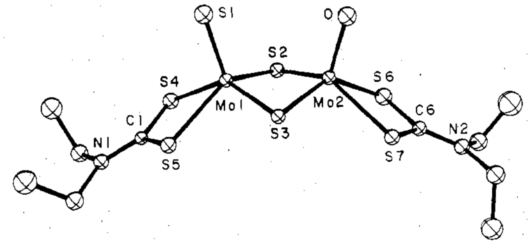


Figure 1. Perspective view of $Mo_2OS(\mu\text{-}S)_2(S_2CN(C_2H_5)_2)_2$. The disordered terminal atoms have been assigned arbitrary thermal parameters for clarity. The respective distances and angles in the coordination sphere are listed in Table II. The dihedral angle between planes S(2)–Mo(1)–S(3) and S(2)–Mo(2)–S(3) is 149.4°.

NMR Spectra. A comparison of saturated solutions in pyridine-d_5 of $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$, $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$, and $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ (dtc = S_2CNEt_2), together with the product from reaction (both total and partial) of the last compound with triphenylphosphine, indicated a small shift of the methyl resonances of the dithiocarbamate ethyl group to lower field when the terminal oxo groups are replaced by sulfido. A similar trend is observed as bridging oxo ligands are replaced sequentially by sulfido groups.[30] The chemical shifts (downfield from Me_4Si) of these methyl proton triplets are 67 Hz for $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$, 71 Hz for $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$, and a doublet of triplets at 67 and 69 Hz for $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$. An equimolar mixture of $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ and $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$, when extracted with pyridine, gave a spectrum consisting mainly of that for $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$ which is consistent with the higher solubility of this compound in organic solvents.

Mass Spectrum. No mass peaks above the parent molecular ion $[Mo_2OS_3(S_2CNEt_2)_2]^+$, *m*/*e* 592–608, are observed in the spectrum of $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$, but a fragment of mass (parent − 16), consistent with the ion $[Mo_2S_3(S_2CNEt_2)_2]^+$, is observed.

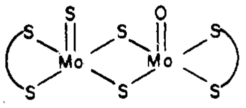
Structure of the Compound. A perspective view of the molecule is shown in Figure 1. The X-ray structural determination together with other physical measurements establishes the stoichiometry to be $Mo_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2$. The geometry about each of the molybdenum atoms in this binuclear molecule is best described as a distorted square pyramid. Two bridging sulfur atoms (S_b) and two sulfur atoms (S_l) from the dithiocarbamate ligands form a basal plane of each square pyramid. However, atoms in the axial positions are different, one axial site being occupied by a sulfur atom and the other by an oxygen atom. The general features are similar to those found in related compounds having $[Mo_2O_2(\mu\text{-}O)_2]^{2+}$, $[Mo_2O_2(\mu\text{-}OS)]^{2+}$, $[Mo_2O_2(\mu\text{-}S_2)]^{2+}$, and $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ groups.[3,14-16,31,32] The molecule adopts the syn conformation[32] and each molybdenum atom is displaced 0.7 Å from the basal plane toward the axial atom. The

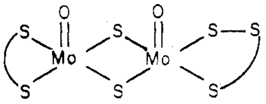
Mo···Mo distance of 2.826 (3) Å and the average Mo–S_b distance of 2.317 Å are in the range observed for other compounds with Mo_2S_2 bridges,[31,32] as are the average angles Mo–S_b–Mo (75.2°) and S_b–Mo–S_b (101.6°). The average Mo–S_l distance (2.466 Å) is comparable to those found in other Mo(V) compounds with dithiocarbamate ligands.[31]

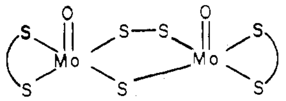
The Mo–S_t and Mo–O_t distances cannot be accurately determined for this structure because the disorder of the molecules in the crystal results in partial "overlap" of the terminal O and terminal S positions which precludes a meaningful least-squares refinement of their coordinates. The "apparent" Mo–S_t and Mo–O_t distances from the present refinement are 1.98 (1) and 1.82 (2) Å, respectively. Compared to other well-defined structures,[16,31,32] this Mo–S_t distance is ~0.1 Å too short and this Mo–O_t distance is ~0.1 Å too long. The approximate twofold disorder also rules out detailed comparisons between other parameters of the $MoOS_4^{2+}$ and MoS_5^{2+} fragments.

Discussion

The product from the anaerobic reactions of hydrogen sulfide with either the *cis*-dioxomolybdenum(VI) or the μ-oxo-bis[oxomolybdenum(V)] core ligated with dithiocarbamates was found to be identical with that obtained from aqueous, anaerobic mixtures of tetrathiomolybdate(VI), sodium dithiocarbamate, and sodium dithionite on the basis of elemental analysis and IR and NMR spectroscopy. Microanalysis indicated seven sulfur atoms (four from two dithiocarbamate ligands) per dinuclear molybdenum unit and infrared spectroscopy showed the presence of a di-μ-sulfido bridge. The seventh sulfur atom could then be either a terminal ligand (I) or a persulfide (II or III).


I


II

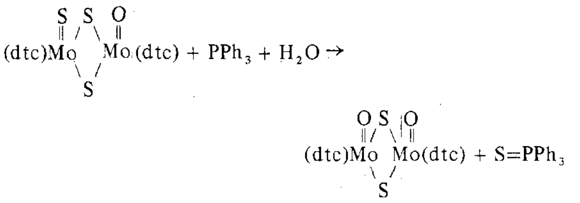

III

The mass spectrum showed a peak consistent with the parent ion of I, but loss of an oxygen atom from II or III would yield the same ion. Moreover, reactions in mass spectrometer probes are known to occur and can lead to unexpected products.[33] The additional complication of an equimolar mixture of $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ and $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ was eliminated by (i) resolving mixtures by extraction with dichloromethane, (ii) proton NMR spectrometry in pyridine solution, and (iii) infrared spectroscopy (see Table III). However, a definitive choice between I, II, and III could still not be made using these data. In the infrared region, for example, both the sulfur–sulfur[28,34,35] and the molybdenum–sulfur[7,12] stretching vibrations are expected at ~500 cm^{-1} while the Mo=O stretch[29] absorbing at ~960 cm^{-1} in our reaction product has a lower frequency, poorly resolved shoulder reminiscent of the $[Mo_2O_2X_2]^{2+}$ (X = O, S) core,[29] i.e., supportive of II or III. Reaction with triphenylphosphine to abstract sulfur and produce $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ also appeared to support II, although its slowness relative to other persulfides[28,36] and the lack of readdition of sulfur to this product[28] was disturbing. In addition, electrochemical results[12] were more compatible with I, being intermediate between those for $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ and $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ (dtc = S_2CNEt_2). It became apparent that an X-ray structural determination was the only solution.

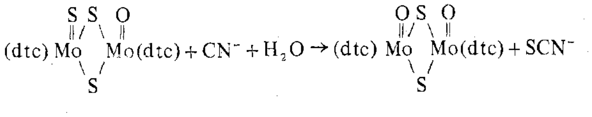
The preliminary crystallographic data strongly suggested that the correct structure was I because the measured density (1.916 g cm^{-3}) was much closer to the calculated density for I (1.92 g cm^{-3}) than for II or III (1.97 g cm^{-3}). Structure I was confirmed by the complete X-ray structure determination. The structure is shown in Figure 1 and distances and angles appear in Table II. Unfortunately, disorder prevents extensive refinement of the structure, but the overall stereochemistry is unambiguously determined as I. Once the molecular weight and stereochemistry have been established, it became obvious that the two ν(Mo=O) bands in the infrared spectrum could arise from two different lattice sites occupied by the oxo groups in the disordered structure. In all other known cases,[37,38] the $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ compounds form disordered crystals, thereby obscuring any structural differences between the two different molybdenum centers of the molecule. In view of the unusual reactivity of this species and its possible implication (vide infra), it is very unfortunate that well-ordered crystals of I are not available.

Others have produced similar compounds by the hydrogen sulfide route and both formulations, I[35,39] and II,[40] have been suggested. This preparative method, however, can give mixtures of not easily separable products,[35,39] particularly when performed aerobically,[35] which can result in misinterpretation of experimental data (compare, e.g., the data in ref 12 with that in ref 39a). This problem can be overcome by using the tetrathiomolybdate(VI) route, whereby good yields of a single product are obtained. A product similar to I (rather than $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$) was probably obtained previously[41] with $MoO_2[S_2CN(n\text{-}Bu)_2]_2$ and hydrogen sulfide. Our work[5,12,29] shows that the single infrared band at 967 cm^{-1} assigned in that work[41] to ν(C—S) of the dithiocarbamate is certainly ν(Mo=O) while the band assigned to ν(Mo=O) is an internal ligand vibration. Another product, which was formulated as the mixed terminal molybdenum(V) compound,[42] $Mo_2OS(\mu\text{-}O_2)(dtc)_2$, is certainly $Mo_2O_2(\mu\text{-}OS)(dtc)_2$, with bridging rather than terminal sulfide. Those authors were misled by the molybdenum–oxygen bridge vibration[29] at 520 cm^{-1} which they assigned as ν(Mo=S). Our attempts to prepare I by ligand exchange with 1:1 mixtures of $Mo_2O_2(\mu\text{-}S_2)(dtc)_2$ and $Mo_2S_2(\mu\text{-}S_2)(dtc)_2$ in boiling 1,2-dichloroethane were unsuccessful. Our work again emphasizes the critical importance of X-ray structure determination for establishing the stoichiometry as well as the stereochemistry of coordination compounds.

The reaction of I, $Mo_2OS(\mu\text{-}S_2)(dtc)_2$ (dtc = S_2CNMe_2, S_2CNEt_2), with triphenylphosphine as described by eq 3 is apparently unique to this mixed terminal oxo–sulfido ligand species. The observation that this is not a simple sulfur atom abstraction (cf. ref 28) and that yields up to 75% are obtained indicates that oxo groups are supplied externally, probably by minute amounts of water in the solvent chloroform. Thus, the reaction is probably better represented by reaction 5.


$$(dtc)\overset{S}{\overset{\|}{Mo}}(\mu\text{-}S)_2\overset{O}{\overset{\|}{Mo}}(dtc) + PPh_3 + H_2O \rightarrow (dtc)\overset{O}{\overset{\|}{Mo}}(\mu\text{-}S)_2\overset{O}{\overset{\|}{Mo}}(dtc) + S{=}PPh_3 \quad (5)$$

Similarly, the rather slow reaction with cyanide may be represented by reaction 6. We have been unable to resubstitute the terminal oxygen by sulfur by using hydrogen sulfide or elemental sulfur on the di-μ-sulfido dimers.[7,12]


$$(dtc)\overset{S}{\overset{\|}{Mo}}(\mu\text{-}S)_2\overset{O}{\overset{\|}{Mo}}(dtc) + CN^- + H_2O \rightarrow (dtc)\overset{O}{\overset{\|}{Mo}}(\mu\text{-}S)_2\overset{O}{\overset{\|}{Mo}}(dtc) + SCN^- \quad (6)$$

Biochemical Implications

These reactions may be relevant to the inactivation of the molybdo enzymes, xanthine oxidase and aldehyde oxidase, by cyanide treatment.[18] Although the inactivation is known to remove a sulfur atom as thiocyanate, the nature of this cyanide-labile sulfur atom and the mechanism of its removal are still unclear. The cyanide-labile sulfur atom has been postulated to be: (a) part of a persulfide group[18] (but as such species should give hydrogen sulfide on acidification, which is not observed in xanthine oxidase, this suggestion is questionable), (b) a cysteinyl sulfur ligated to molybdenum[43] (but cleavage of a C–S band with cyanide appears very unlikely), and (c) a ligand (initially unspecified in nature[19,20] but more recently formulated as a terminal sulfide[44]) of molybdenum, which is replaced by oxygen during inactivation. The substitution of sulfur by oxygen is in line with the changes in the *g* value and $a(^1H)$ of the EPR signal observed for cyanide-treated, inactivated xanthine oxidase as compared with the normal signal.[20] Our observation that terminal sulfide ligands on molybdenum can be substituted by oxo on treatment with aqueous cyanide solutions is the first well-characterized example of this reaction. It adds considerable support to postulate (c) and strongly suggests that the sulfur atom in question in these enzymes is a terminal sulfido ligand on molybdenum. The possibility of terminal sulfido groups on these enzymes has been mentioned before[3,45] and the removal of sulfide from molybdenum complexes by cyanide in aqueous solution has also been inferred.[46] Bray and his co-workers suggest that reaction 7 operates in xanthine oxidase in exact

$$\text{(Enz)Mo}{=}\text{S} + \text{CN}^- + \text{H}_2\text{O} \rightarrow \text{(Enz)Mo}{=}\text{O} + \text{SCN}^- + 2\text{H}^+ + 2\text{e}^- \quad (7)$$

analogy with reaction 6 we believe to operate in our synthetic system. Bray's work[44] should be consulted for details as to how this change in ligands fits other observations for these two forms of xanthine oxidase. The possibility that the terminal sulfur (or oxygen) atom is the location of the exchangeable, EPR-coupled proton in the active (or cyanide-inactivated) enzyme formed by transfer of the aldehydic proton (or the proton from the 8-carbon atom of xanthine) to the enzyme contrasts with the suggestion that this site might be an ever-present ligated nitrogen (or possibly oxygen) on molybdenum.[8] This point is still controversial.

A further complication has recently arisen in that analysis of the X-ray absorption fine structure (EXAFS) of the molybdenum component of both xanthine oxidase[47] and sulfite oxidase[48] has indicated preliminarily the presence of ca. two oxo groups at ~1.7 Å from molybdenum and two to three thiolate-type sulfur donors in the oxidized (Mo(VI)) state of both enzymes. No peak was assigned as corresponding to a molybdenum–terminal sulfide distance. The absence of such a peak in the EXAFS spectrum of sulfite oxidase may not be too surprising as sulfur-assisted C–H bond cleavage, the suggested[44] function for the cyanide-labile sulfur atom, is obviously not required for the oxidation of sulfite to sulfate. Its absence in the xanthine oxidase sample used for EXAFS analysis does, however, raise questions. The presence of substantial amounts of desulfo xanthine oxidase[19,20] in this sample might explain this inconsistency but the activity of the sample appears to rule out this suggestion. Further refinement of these theories and results and correlation of the EXAFS data with the enzymic and synthetic chemical reactivity data will no doubt be forthcoming from the continued efforts in all these areas.

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Registry No. $Mo_2OS(\mu\text{-}S_2)(S_2CNEt_2)_2$, 69779-01-7; $Mo_2OS(\mu\text{-}S_2)(S_2CNMe_2)_2$, 69796-02-7; $Mo_2OS(\mu\text{-}S_2)(S_2CN(CH_2)_5)_2$, 69706-32-7; $Mo_2OS(\mu\text{-}S_2)[S_2CN(n\text{-}C_4H_9)_2]_2$, 69779-87-9; $Mo_2O_2(\mu\text{-}S_2)(S_2CNEt_2)_2$, 69779-02-8; $Mo_2S_2(\mu\text{-}S_2)(S_2CNEt_2)_2$, 67814-43-1; $Mo_2S_2(\mu\text{-}S_2)[S_2CN(n\text{-}Bu)_2]_2$, 69779-03-9; $Mo_2O_2(\mu\text{-}S_2)(S_2CNMe_2)_2$, 69706-33-8; $Mo_2O_3(S_2CNEt_2)_4$, 20023-86-3; $Mo_2O_3(S_2CNMe_2)_4$, 20023-85-2; $Mo_2O_3(S_2CN(CH_2)_5)_4$, 20023-87-4; $MoO_2[S_2CN(n\text{-}C_4H_9)_2]_2$, 18078-71-2; K_2MoS_4, 13718-35-9.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(26) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
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Monomeric Molybdenum(V) Complexes. 2. Comparison of the Structures of *cis*-Oxochlorobis(8-mercaptoquinolinato)molybdenum(V) and *cis*-Dioxobis(8-mercaptoquinolinato)molybdenum(VI)

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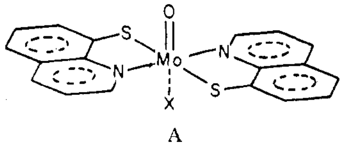
The crystal and molecular structures of $MoOCl(tox)_2$ (**1**) and $MoO_2(tox)_2$ (**2**), where tox is the anion of 8-mercaptoquinoline, have been determined by X-ray crystallography. Crystal data for **1**: monoclinic; space group $P2_1/c$; $a = 15.144$ (2), $b = 8.498$ (2), $c = 13.840$ (3) Å; $\beta = 100.436$ (15)°; $Z = 4$; $d_{obsd} = 1.765$ (10), $d_{calcd} = 1.774$ g cm^{-3}. Crystal data for **2**: orthorhombic; space group $Pbca$; $a = 9.038$ (3), $b = 14.825$ (4), $c = 25.210$ (7) Å; $Z = 8$; $d_{obsd} = 1.758$ (10), $d_{calcd} = 1.763$ g cm^{-3}. Full-matrix least-squares refinement of **1** by use of 1592 independent reflections with $3.5° < 2\theta \leq 45°$ and $I \geq 3\sigma(I)$ gave final discrepancy indices $R_1 = 0.040$ and $R_2 = 0.043$. Refinement of **2** based on the 1398 unique data having $3.5° < 2\theta \leq 50°$ and $I \geq 3\sigma(I)$ converged at $R_1 = 0.047$ and $R_2 = 0.046$. Compounds **1** and **2** have similar geometries. Both are monomeric with distorted octahedral geometry around each molybdenum atom. The MoO_2^{2+} grouping in **2** has the expected cis configuration with an O–Mo–O angle of 106.3 (3)°. The $MoOCl^{2+}$ unit of **1** also has a cis configuration, contrary to earlier proposals, with a Cl–Mo–O angle of 103.0 (2)°. In **1** Mo–Cl = 2.342 (2) Å and Mo–O = 1.716 (4) Å. The average Mo–O distance in **2** is 1.703 (12) Å. The Mo–N bonds trans to the oxo groups (2.408 (6) Å in **1** and 2.374 (9) and 2.382 (9) Å in **2**) are ~0.2 Å longer than the Mo–N bond of **1** which is trans to the chlorine atom (2.210 (6) Å). The mean Mo–S distances are 2.409 (7) Å for **1** and 2.411 (1) Å for **2**, respectively. The 8-mercaptoquinolinate ligands are folded along their S···N vectors in both compounds.

Introduction

The molybdenum centers of a number of molybdenum-containing enzymes have been probed by EPR spectroscopy.[1–4] In particular, xanthine oxidase has been extensively studied.[1] During turnover, this 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). The interpretation of such EPR spectra in terms of a specific molybdenum coordination environment in the enzyme has been hampered by a lack of definitive data from simple discrete mononuclear molybdenum complexes. Early solution EPR studies of molybdenum(V) in the presence of thiol ligands[5] led to the general assumption that sulfur ligation is important in the enzymes. However, few discrete mononuclear molybdenum(V) complexes of sulfur-containing ligands have been isolated and structurally characterized so that the stoichiometry and stereochemistry of the complex could be related to the observed spectrum.[6–8]

One of the most promising mimics of the EPR spectrum of xanthine oxidase is the species which is extracted into organic solvents when 8-mercaptoquinolinate (tox) reacts with molybdenum(V) in aqueous acid.[9] The EPR parameters of this compound are similar to those observed for xanthine oxidase under certain conditions,[1] and structure A with X, a unidentate monoanion, trans to an oxo ligand has been proposed for this complex. Recently $MoOCl(tox)_2$ (**1**) has been prepared in pure form and the kinetics of its oxidation by nitrate have been investigated.[10] Herein we show that the stereochemistry of $MoOCl(tox)_2$ is not A but that the Cl ligand is cis to the oxo group. The structure of the closely related molybdenum(VI) complex, $MoO_2(tox)_2$ (**2**), is also described. Compounds **1** and **2** are the first pair of monomeric molybdenum(V) and molybdenum(VI) compounds having common chelate ligands to be structurally characterized. The stereochemistries of such redox-related pairs are of fundamental interest for evaluating the consequences of electron transfer in molybdo enzymes.



A

Experimental Section

Preparation of Crystals. All preparative manipulations were carried out in a dry nitrogen atmosphere. Solvents were dried and degassed by standard procedures. 8,8′-Diquinolyl disulfide was prepared as previously described.[11]

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