concerted formation of the disulfide S–S bond without prior generation of high-energy mercaptide radicals.[20] The first-order decay of 1:1 Cu(tmpa)$^{2+}$–cysteine adducts therefore provides further confirmation that radical coupling is strongly hindered in this system. Even here, a bimolecular redox pathway is preferred when large excesses of cysteine are present. The mechanistic aspects of this and other copper(II) reductions by excess cysteine are still under investigation.[23,28]

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant D-735) is gratefully acknowledged. We thank Professor David McMillin for helpful criticisms of the manuscript.

Registry No. Cu(tmpa)$^{2+}$, 87207-95-2; cysteine, 52-90-4.

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Complexes Containing the $Mo_2O_5^{2+}$ Core: Preparation, Properties, and Crystal Structure of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$

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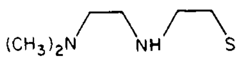
Mo(VI) complexes of the form $Mo_2O_5L_2$ have been prepared by reaction of $MoO_2(acac)_2$ with LH in methanol solution. The ligand L is a tridentate monoanion with one thiolate donor (L = $(CH_3)_2NCH_2CH_2NHCH_2CH_2S^-$, $(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S^-$, $(C_5H_4N)CH_2NHC_6H_4S^-$). ^{17}O NMR and IR spectra are consistent with a monooxo-bridged dinuclear structure, which is confirmed by X-ray crystallography in one case. Intensity data collected by using counter methods have led to the determination of the crystal and molecular structure of (μ-oxo)bis[dioxo(2,7-dimethyl-2,5-diazaoctane-7-thiolato)molybdenum(VI)], $Mo_2O_5(C_8H_{19}N_2S)_2$. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 11.711$ (2) Å, $b = 17.233$ (6) Å, $c = 24.778$ (7) Å, $V = 5000.8$ (22) Å^3, and $Z = 8$. Molybdenum centers are bridged by an oxo group, forming discrete dinuclear species in the unit cell. The molecule possesses a pseudo-twofold symmetry axis that passes through the bridging oxo group. The Mo–O$_b$–Mo angle is 143.8 (3)°; $(Mo-O_b)_{av} = 1.923$ (5) Å, and $(Mo{=}O)_{av} = 1.713$ (6) Å. The complex $Mo_2O_5(C_6H_{15}N_2S)_2$ reacts with C_6H_5SH and with $P(C_6H_5)_3$ to give the dinuclear Mo(V) complexes $Mo_2O_3(C_6H_{15}N_2S)_2(SC_6H_5)_2$ and $Mo_2O_4(C_6H_{15}N_2S)_2$, respectively.

Introduction

Oxo complexes of Mo(VI) have been under intense study[2-4] in part due to their potential relevance as model systems for Mo sites in enzymes. Ligands containing sulfur donors have been prominent in these studies as there is strong evidence that S is present in the enzymic Mo coordination sphere. Almost all of the attention with regard to ligands has focused on bidentate and tetradentate ligands,[5-13] which, respectively, form Mo(VI) complexes of the form MoO_2L_2 and MoO_2L containing the *cis*-MoO_2^{2+} core. In this paper we report complexes of some related tridentate ligands.

Tridentate ligands are of intrinsic interest because their complexes with the MoO_2^{2+} core should be of the form MoO_2L^+, leaving one open coordination site to potentially bind a substrate, a product, or an inhibitor.[14-16] Alternatively, the available site could be involved in bridging to a second molybdenum in a dinuclear complex. In this paper we report dinuclear Mo(VI) complexes of the tridentate ligands I–III and of a related potentially tetradentate ligand IV. These ligands each form dinuclear complexes of the form $Mo_2O_5L_2$ whose IR and NMR spectra are consistent with a bent Mo–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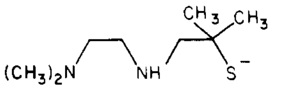
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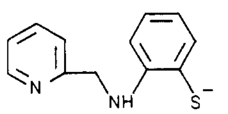
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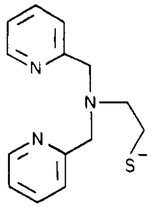
IV

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O–Mo bridge. This structure is confirmed for the case L = II by X-ray crystallography.

Experimental Section

Reagent grade solvents were used as received except for DMF, which was further purified by mixing with absolute ethanol, distilling at atmospheric pressure, and collecting the fraction boiling at 153 °C under argon. Thiol titrations using 0.5 N ethanolic I_2–KI (dead-stop end point) were adapted from the literature.[17]

$MoO_2(acac)_2$ was obtained from Climax Molybdenum Co. as a gift, which we gratefully acknowledge. Alternatively, $MoO_2(acac)_2$ was prepared by the method of Jones.[18] C, H, and N analyses were carried out by using a Perkin-Elmer 240 elemental analyzer equipped with a MC-341 microjector from Control Equipment Corp. Molecular weights were determined with use of a Hewlett-Packard Model HP302B vapor pressure osmometer. IR spectra were obtained from KBr pellets on a Beckman IR 20 spectrometer. Electronic spectra were measured in 1-cm path length quartz cells on a Cary 14 or Cary 118c spectrophotometer.

Electrochemical measurements were carried out by using a PAR 173 potentiostat with a PAR 176 current voltage converter. An HP 3310B function generator was used for cyclic voltammograms, which were recorded on a MFE 815 X-Y recorder. A Pt-button electrode was used as the working electrode. Potentials are reported in V vs. a saturated calomel electrode. $[(C_4H_9)_4N]PF_6$ (0.1 M) was the supporting electrolyte, and samples were 1 mM in DMF. ^1H NMR spectra of ligands were obtained on a Varian Associates A-60 spectrometer; chemical shifts are in ppm downfield from tetramethylsilane, and coupling constants are reported in Hz. ^1H NMR spectra of complexes were obtained at 220 MHz at Indiana University. ^{17}O NMR spectra were obtained in CH_2Cl_2 solutions at Indiana University on a Varian Associates XL-100-15 FT spectrometer operating at 13.56 MHz. All resonances lie downfield from water and are assigned positive chemical shifts relative to external water. We are grateful to Prof. R. A. D. Wentworth and the NMR staff of Indiana University for their courtesy in allowing us to use the facility.

Synthesis of Ligands. *N*-(2-Pyridylmethyl)-2-mercaptoaniline (III) was prepared as described in the literature.[19] *N*,*N*-Dimethylethylenediamine, $(CH_3)_2NCH_2CH_2NH_2$, was obtained from Aldrich Chemical Co.

***N*-(2-Mercaptoethyl)-*N'*,*N'*-dimethylethylenediamine, $(CH_3)_2NCH_2CH_2NHCH_2CH_2SH$ (I).** The ligand was prepared along with $(HSCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$ from the reaction of $(CH_3)_2NCH_2CH_2NH_2$ and ethylene sulfide, CH_2SCH_2. A solution of $(CH_3)_2NCH_2CH_2NH_2$ (11.0 g, 0.125 mol) in 40 mL of dry toluene was mixed with a solution of ethylene sulfide[20] (15 g, 0.25 mol) in 50 mL of dry toluene at 40–50 °C and the resultant solution placed in a tube, which was sealed and immediately put in a 110 °C oven. (If the reaction was allowed to stand at room temperature, more polymer and less of the desired product resulted. If the reaction was never heated, more than 85% of the ethylene sulfide appeared as polymer. The desired reaction appears to be favored at higher temperatures.) After a 5-h reaction time, the solution was cooled and filtered to remove a small amount of poly(ethylene sulfide). The solvent was removed and the residual liquid fractionally distilled (Vigreux Column) under reduced pressure to give $(CH_3)_2NCH_2CH_2NHCH_2CH_2SH$, 4.8 g (26%), as a colorless liquid boiling at 40 °C (0.04 mm). Thiol titration gave 100% of the expected value. A ν(NH) band at 3300 and a ν(SH) band at ~2500 cm^{-1} are seen in the infrared spectrum. The NMR ($CDCl_3$) has a multiplet at 2.3–2.37 (CH_2), a singlet at 2.17 $[N(CH_3)_2]$, and a singlet at 1.63 (SH and NH). Treatment of the ligand with picric acid in CH_3OH gives the dipicrate derivative as yellow plates (mp 133–137 °C), 83.2% yield. Anal. Calcd for $C_{18}H_{22}N_8O_{14}S$: C, 35.65; H, 3.67; N, 18.48. Found: C, 35.37; H, 3.51; N, 18.29.

The tetradentate ligand $(HSCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$ was obtained in 45% yield (bp 102–4 °C (0.14 mmHg)) from this same reaction solution and will be fully described elsewhere.

***N*-(2-Mercapto-2-methylpropyl)-*N'*,*N'*-dimethylethylenediamine, $(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2SH$ (II).** A solution of 2,2-dimethylethylene sulfide[21] (105 mmol) in dry toluene (10 mL) was added over 3.5 h (argon atmosphere) to a refluxing solution of *N*,*N*-dimethylethylenediamine (105 mmol, in dry 40 mL of toluene). Reflux was continued for 15 h and the solvent removed from the cooled reaction solution. Vacuum distillation (Vigreux column) of the residue yielded the thiol as a colorless liquid (39.1%; bp 42–43 °C (0.04 mm)). Thiol titration showed 97% of the expected value.

NMR ($CDCl_3$) shows multiplets at ca. 2.75 and 2.42 $[(CH_2)_2]$, a singlet at 2.62 (CH_2), a singlet at 2.22 $[(CH_3)_2N]$, a singlet at 1.83 (SH and NH), and a singlet at 1.36 $[(CH_3)_2C]$.

***N*,*N*-Bis(2-pyridylmethyl)-2-mercaptoethylamine, $(C_5H_4NCH_2)_2NCH_2CH_2SH$ (IV).** Bis(2-pyridylmethyl)amine was prepared according to Romary et al.[22] except that benzene was used to separate the free base form of 2-(chloromethyl)pyridine. The pale yellow liquid amine product boiled at 126–130 °C (0.02 mm) (61.2%). This amine (50 mmol), ethylene sulfide (50 mmol), and toluene (50 mL) were heated (sealed tube) at 110 °C for 30 h. The reaction is slow, and the product cannot be distilled because of thermal lability (reverting to starting materials). "Purification" was effected by washing three times with water to remove ca. 10% unreacted amine (NMR), removing the solvent (vacuum), and finally pumping for 1 h (80 °C).

The residual red-brown oily product (93.4%) showed 96% of the expected thiol content (titration) and was sufficiently pure for use in the preparation of the Mo complex discussed below. The NMR spectrum ($CDCl_3$) shows a singlet at 2.98 (py–CH_2), a multiplet at ca. 1.9 $[(CH_2)_2]$, and a broad triplet at 0.78 (SH). The infrared spectrum shows ν(SH) at 2480 cm^{-1}.

Synthesis of Complexes. (μ-Oxo)bis[[*N*,*N*-dimethyl-*N'*-(2-mercaptoethyl)ethylenediamino]dioxomolybdenum(VI)], $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$. A solution of 2.8 g (15 mmol) of ligand in 15 mL of methanol was slowly added (over 20 min) to a filtered boiling solution of 4.5 g (13.8 mmol) of $MoO_2(acac)_2$ in 50 mL of methanol. The immediate color change of the solution to brown-yellow was followed by deposition of a bright yellow crystalline solid. This mixture was boiled for 30 min and filtered. The bright yellow crystalline compound was washed with methanol and ether and dried under vacuum (yield 84%). It is soluble in $C_2H_4Cl_2$, CH_2Cl_2, DMF, THF, and $CHCl_3$.

(μ-Oxo)bis[[*N*,*N*-dimethyl-*N'*-(2-methyl-2-mercaptopropyl)ethylenediamino]dioxomolybdenum(VI)], $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$. This compound was isolated as orange crystals in the above manner (yield 64%). It is in general more soluble than $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$.

(μ-Oxo)bis[[2-(2-picolyl)amino)benzenethiolato]dioxomolybdenum(VI)] Hydrate, $Mo_2O_5(SC_6H_4NHCH_2C_5H_4N)_2 \cdot H_2O$. A solution of 1.23 g (5.7 mmol) of ligand in 3 mL of methanol was slowly added (over 30 min) to a chilled, filtered solution of 1.99 g (6.1 mmol) of $MoO_2(acac)_2$ in 30 mL of methanol. A brown solid formed that was filtered, washed with methanol and ether, and dried in vacuo to obtain a light red powder (yield 73%). This compound is soluble in DMF and sparingly soluble in CH_2Cl_2 and $C_2H_4Cl_2$.

(μ-Oxo)bis[[2-(bis(2-picolyl)amino)ethanethiolato]dioxomolybdenum(VI)] Dihydrate, $Mo_2O_5[(C_5H_4NCH_2)_2NCH_2CH_2S]_2 \cdot 2H_2O$. A solution of 1.45 g (4.4 mmol) of $MoO_2(acac)_2$ in 200 mL of methanol was quickly added to a 50-mL solution of 1.15 g (4.4 mmol) of the ligand in methanol. The mixture was stirred for 2 min and filtered, and the clear orange-brown filtrate was collected (a brown solid was discarded). On cooling in the refrigerator overnight, this filtrate deposited golden yellow needles that were filtered, washed with methanol and ether, and dried under vacuum (yield 59%). This compound is insoluble in all solvents tested.

(μ-Oxo)bis[*N*,*N*-dimethyl-*N'*-(2-mercaptoethyl)ethylenediamino]bis(thiophenolato)dioxodimolybdenum(V), $Mo_2O_3(SC_6H_5)_2[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$. Excess thiophenol (14 mmol) was added to 30 mL of a CH_2Cl_2 solution of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ (1 mmol) to give a rapid color change from yellow to purple. After 2 h the solvent was removed by vacuum distillation, and 40 mL of degassed ether was added to give a brown precipitate and a purple solution. The purple solution was cooled to −10 °C for 4 days, and the well-formed purple crystals that deposited were recovered by filtration, washed with cold Et_2O, and dried under vacuum. The infrared spectrum of this complex displays absorbances

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Table I. Crystallographic Information for $Mo_2O_5(C_8H_{19}N_2S)_2$

mol formula	$Mo_2O_5(C_8H_{19}N_2S)_2$
fw	622.58
color	orange
radiation	Mo Kα
d_{calcd}, g/mL	1.65
d_{obsd}, g/mL	1.65
cryst size, mm	0.70 × 0.25 × 0.25
cell parameters	
a, Å	11.711 (2)[a]
b, Å	17.233 (6)
c, Å	24.778 (7)
V, $Å^3$	5000.8 (22)
Z, molecules/unit cell	8
space group	*Pbca* (No. 61[b])
data collcn mode	2θ-θ
2θ range of data, deg	4.0–50.0
scan rate (min, max), deg/min	4.0, 29.3
total bkgd/scan time	0.5
scan width	(Mo Kα_1 −0.8)–(Mo Kα_2 +1.0)
μ, cm^{-1}	11.74
abs cor	empirical
NO ($I > 3\sigma(I)$)/NV	2951/262
P	0.03
R_F	0.045
R_{wF}	0.058
GOF	2.16

[a] Numbers in parentheses here and elsewhere in the paper indicate the estimated standard deviation in the least significant digit. [b] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. I.

characteristic of the thiophenolate ligand and the $Mo_2O_3^{4+}$ structural unit [ν(Mo–O) at 930 cm^{-1}]. The complex is very soluble in CH_2Cl_2 and slightly soluble in ether.

Bis(μ-oxo)bis[*N*,*N*-dimethyl-*N*-(2-mercaptoethyl)ethylenediamino]dioxodimolybenum(V), $Mo_2O_4[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$. Under argon a solution of 0.14 g of $P(C_6H_5)_3$ (0.53 mmol) in 5 mL of CH_2Cl_2 was added slowly to 0.29 g of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ (0.52 mmol) in 30 mL of CH_2Cl_2. The reaction mixture turned brown within 5 min. After being stirred at room temperature for 50 min, the reaction mixture was concentrated to about 30 mL and then cooled at −10 °C for several hours. The brown microcrystalline solid was filtered, washed with Et_2O until the wash was clear, and then dried in vacuo. More product was isolated from the filtrate by concentrating the solution. The total yield was 70%. Peaks at 950 and 940 and a shoulder at 925 cm^{-1} are assigned to the terminal MoO vibrations while a strong broad peak at 730 cm^{-1} is assigned to the Mo_2O_2 bridge. A white solid (tentatively identified by IR spectroscopy) as $(C_6H_5)_3PO$ was isolated from the Et_2O washes.

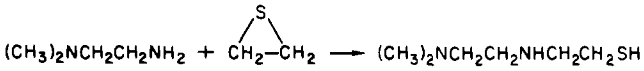
X-ray Data Collection. A crystal of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ was chosen from those isolated directly from the reaction mixture, mounted on a glass fiber, and placed on a Syntex $P2_1$ four-circle autodiffractometer. The unit cell was determined from the least-squares fit of 24 centered reflections, with 2θ values in the range 5.0–27.0°. ω scans indicated satisfactory mosaicity. Table I lists additional crystallographic information. During data collection, three standard reflections were monitored every 97 reflections and no significant loss of intensity was observed. A unique octant of data was collected, and Lorentz and polarization corrections were applied.[23] An empirical absorption correction was applied on the basis of 10 ψ scans with a 2θ range of 5–47°, each containing 36 points.[23,24]

Solution and Refinement of Structure. All computations were carried out on the CDC CYBER-175 computer at the University of Arizona with programs described previously.[24] The two crystallographically independent molybdenum atoms were located by standard Patterson methods. The remaining non-hydrogen atoms were located from successive structure factor calculations and difference electron density maps. All methylene hydrogen atoms were entered at idealized positions (C–H = 0.95 Å) as fixed contributors to the structure factor calculations. Hydrogen atom positions are listed in the supplementary data. Neutral-atom scattering factors[25] were applied to all non-hydrogen atoms, and the real and imaginary components of anomalous dispersion for the molybdenum and sulfur atoms were used in calculation of the structure factors. Hydrogen scattering factors used were those tabulated by Stewart et al.[26]

Residual (R) and weighted residual (R_w) indices were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ (where $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)]$ and $p = 0.03$), respectively. The goodness of fit parameter was determined by the equation $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of reflections with $F_o^2 > 3\sigma(F_o^2)$ and NV is the number of variables refined. A list of calculated and observed structure factors is included as supplementary material.

Results

Preparation of Ligands. Ligands were prepared by the reaction of the appropriate amine with ethylene sulfide or 2,2-dimethylethylene sulfide, e.g.



The tetradentate ligand $(CH_3)_2NCH_2CH_2N(CH_2CH_2SH)_2$ also is formed in this reaction, but when the isobutylene sulfide is used, only the corresponding tridentate ligand $(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2SH$ is isolated, apparently due to steric factors.

Preparation and Reactions of Complexes. The synthesis of the complexes is carried out according to

$$2MoO_2(acac)_2 + 2LH + H_2O \rightarrow Mo_2O_5L_2 + 4acacH$$

Although water was not explicitly added to the reaction mixture, no caution was exercised to exclude it from the CH_3OH solvent. This procedure gives good yields of products in a preparation that is presumed to be analogous to that of MoO_2L_2' and MoO_2L'' complexes where L′ and L″ are bi- and tetradentate ligands, respectively.[6-8] The colors and analyses of the complexes are shown in Table II. The analyses are consistent with the dinuclear formulation, and vapor pressure osmometry gives a molecular weight of 607 ± 8 for $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ where the calculated molecular weight is 622.

The reaction of $Mo_2O_5L_2$ (L = I) with reductants was pursued. With excess C_6H_5SH the purple reaction product is likely formed according to the reaction

$$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2 + 4C_6H_5SH \rightarrow 2H_2O + C_6H_5S\text{–}S\text{–}C_6H_5 + Mo_2O_3[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2(SC_6H_5)_2$$

The product is presumed to be the μ-oxo Mo(V) dimer. The solubility of this product in nonpolar solvents suggests a symmetrical structure and a *trans*-Mo_2O_3 bridge[3] may be present. The C_6H_5SH reactant formally removes one oxo from each Mo to convert the dinuclear oxo-bridged Mo(VI) complex to a dinuclear oxo-bridged Mo(V) complex.

In contrast, reaction with $P(C_6H_5)_3$ according to

$$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2 + P(C_6H_5)_3 \rightarrow OP(C_6H_5)_3 + Mo_2O_4[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$$

leads to the presumed bis(μ-oxo) Mo(V) dimer. In these reactions, C_6H_5SH and $P(C_6H_5)_3$ yield different Mo(V) dinuclear products upon reaction with the $Mo_2O_5^{2+}$ core. Reduction with thiophenol provides the necessary anionic ligand needed to achieve a neutral complex containing the $Mo_2O_3^{4+}$ core. Addition of thiophenol to the $Mo_2O_4L_2$ complex leads to a purple solution indicative of the presence of the $Mo_2O_3^{4+}$ core. The reactions observed here contrast with those of $MoO_2(dtc)_2$ where either C_6H_5SH or $P(C_6H_5)_3$ gives the

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Table II. Color and Analytical Data of Dinuclear Complexes

complex	color	anal.	% C	% H	% N
$Mo_2O_5[(C_5H_4NCH_2)_2NCH_2CH_2S]_2 \cdot H_2O$	golden yellow	calcd	40.79	4.40	10.19
		found	40.93	3.96	10.16
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$	bright yellow	calcd	25.45	5.00	9.89
		found	24.98	5.34	9.88
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$	orange	calcd	30.87	6.15	9.00
		found	30.63	5.95	9.01
$Mo_2O_5(C_5H_4NCH_2NHC_6H_4S)_2 \cdot 2H_2O$	light red	calcd	40.01	3.36	7.78
		found	39.96	3.16	7.81
$Mo_2O_3[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2(C_6H_5S)_2$	purple	calcd	38.30	5.36	7.44
		found	38.45	5.42	6.87
$Mo_2O_4[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$	brown	calcd	26.19	5.49	10.12
		found	26.45	5.35	9.56

Table III. Infrared Data for Dinuclear Complexes

complex	$\nu(Mo-O_t)$, cm^{-1}	$\nu(Mo_2O)$, cm^{-1}
$Mo_2O_5[(C_5H_4NCH_2)_2NCH_2CH_2S]_2 \cdot H_2O$	920, 910, 890	720
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$	911, 870	707
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$	900, 860	665
$Mo_2O_5(C_5H_4NCH_2NHC_6H_4S)_2 \cdot 2H_2O$	918, 894	770
$Mo_2O_4[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$	950, 940, 925	730
$Mo_2O_3[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$-$(SC_6H_5)_2$	930	

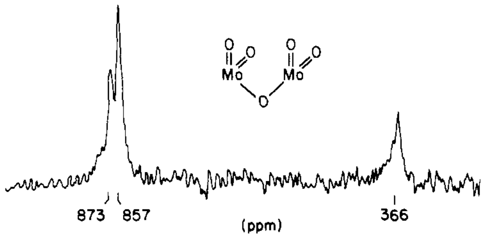

Figure 1. ^{17}O NMR spectrum of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$.

Table IV. Electronic Absorptions of $Mo_2O_5L_2$ Complexes[a]

complex	λ, nm	$\bar{\nu}$, cm^{-1}	ε, L mol^{-1} cm^{-1}
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$	420	23 800	2 660
	350	28 600	12 100
	274	36 500	11 300
	229	43 700	15 300
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$	418	23 900	2 650
	350	28 600	10 700
	281	35 600	10 200
	228	43 900	14 600

[a] CH_2Cl_2 solutions.

monooxo-bridged $Mo_2O_3(dtc)_4$ complex.[18]

Electrochemically, $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ and $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ each display an irreversible reduction wave at ~−1.0 V.

Spectroscopic Properties. Complexes containing the $Mo_2O_5^{2+}$ core display characteristic IR and NMR absorptions that are useful in identifying the presence of that core. Infrared spectral absorptions in the Mo–O stretching region are listed in Table III. The strong infrared band between 650 and 770 cm^{-1} is assigned to the asymmetric Mo–O–Mo stretch in agreement with previous studies.[3] The assignment has been confirmed for $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ by ^{18}O labeling, which shifts the bridging band from 707 to 670 cm^{-1}. ^{18}O labeling is accomplished by exchange of the complex in $C_2H_4Cl_2$ with a small amount of $H_2{}^{18}O$. In addition to the bridging vibrations, the two terminal oxo groups on each Mo give rise to a doublet centered around 900 cm^{-1} with a splitting of about 30–40 cm^{-1} characteristic of the symmetric and asymmetric stretches of the *cis*-dioxo grouping.

^{17}O NMR has been utilized to glean structural and bonding information from oxomolybdenum complexes.[27-30] The spectrum of ^{17}O-labeled $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ in a saturated CH_2Cl_2 solution is shown in Figure 1. The obvious assignment attributes the 873 and 857 ppm peaks to the terminal $Mo-O_t$ linkages while the single lower intensity peak at 366 ppm downfield from H_2O is assigned to the single bridging oxygen ligand. The ^{17}O NMR spectrum of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ does not show as much resolution of the $Mo-O_t$ resonances; however, separate signals are resolvable at 868, 856, and 367 ppm. The exchange of $H_2{}^{17}O$ into $Mo_2O_5L_2$ complexes proceeds rapidly in CH_3CN, with no preferential incorporation into terminal or bridging sites.

Proton NMR spectra of the $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ and $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ complexes were obtained at 220 MHz in $CDCl_3$. The $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ complex displays a pair of sharp signals at 1.53 and 1.58 ppm for the $C(CH_3)_2$ group and a pair of broad signals ($\nu_{1/2}$ = 15 Hz at 220 MHz) at 2.5 and 2.9 ppm for the $N(CH_3)_2$ group. The inequivalence of these geminal methyl groups is consistent with the persistence of the solid-state structure in solution. The $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$ complex also displays a pair of sharp signals at 2.43 and 2.88 ppm ($\nu_{1/2}$ = 5 Hz at 220 MHz) for the $N(CH_3)_2$ group. The ^1H NMR results indicate the structural similarity of these complexes in solution and the probable similarity of solid-state and solution structures.

The electronic spectra of two $Mo_2O_5L_2$ complexes are given in Table IV. The spectra resemble those of other complexes containing the MoO_2^{2+} core, and, although the general assignment of the transitions to S → Mo and O → Mo charge transfer is likely, detailed assignments have not been attempted.

Discussion of Structure

Final positional parameters for $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ are shown in Table V. Anisotropic thermal parameters are included in the supplementary data. The structure and labeling scheme of the molecule are presented in Figure 2. Each molybdenum atom is six-coordinate with approximately octahedral geometry. Discrete dinuclear species are formed through bridging oxo groups between crystallographically independent molybdenum atoms.

The terminal and bridging oxo groups adopt *fac* stereochemistry. The three remaining *fac* positions are occupied by

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Table V. Final Atomic Coordinates

atom	*x*	*y*	*z*
Mo1	−0.03233 (6)	0.18042 (4)	0.113331 (26)
Mo2	0.25125 (7)	0.09537 (4)	0.130959 (24)
S1	−0.17585 (19)	0.26780 (14)	0.14882 (10)
S2	0.45158 (19)	0.09832 (14)	0.10771 (9)
OB	0.0910 (4)	0.10639 (27)	0.11713 (20)
O11	−0.1276 (5)	0.1396 (4)	0.06908 (24)
O12	0.0443 (5)	0.2506 (3)	0.08020 (22)
O21	0.2603 (4)	0.1707 (3)	0.17592 (20)
O22	0.2646 (5)	0.0126 (3)	0.16841 (23)
N12	0.0344 (6)	0.2163 (4)	0.19746 (25)
N11	−0.1087 (7)	0.0825 (4)	0.17922 (29)
N22	0.2579 (6)	0.1678 (4)	0.04998 (25)
N21	0.2275 (7)	0.0002 (5)	0.05477 (29)
C11	−0.2304 (8)	0.0923 (6)	0.1940 (5)
C12	−0.0897 (10)	0.0015 (5)	0.1570 (4)
C13	−0.0364 (9)	0.0928 (6)	0.2275 (4)
C14	−0.0208 (8)	0.1732 (5)	0.2422 (3)
C15	0.0250 (8)	0.3027 (5)	0.2026 (4)
C16	−0.0898 (8)	0.3381 (5)	0.1892 (4)
C17	−0.1659 (9)	0.3618 (6)	0.2393 (4)
C18	−0.0720 (11)	0.4111 (6)	0.1541 (5)
C21	0.1115 (9)	−0.0352 (6)	0.0554 (4)
C22	0.3103 (11)	−0.0678 (7)	0.0623 (6)
C23	0.2496 (11)	0.0414 (8)	0.0060 (4)
C24	0.2083 (11)	0.1178 (7)	0.0050 (4)
C25	0.3720 (9)	0.1960 (7)	0.0321 (5)
C26	0.4659 (8)	0.1952 (6)	0.0767 (4)
C27	0.4637 (12)	0.2590 (5)	0.1185 (5)
C28	0.5819 (9)	0.1991 (7)	0.0477 (4)

Table VI. Selected Interatomic Distance (Å) for $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$

atoms	dist	atoms	dist
Mo1-O11	1.715 (6)	Mo2-O21	1.714 (5)
Mo1-O12	1.715 (6)	Mo2-O22	1.709 (6)
Mo1-OB	1.929 (5)	Mo2-OB	1.917 (5)
Mo1-N11	2.513 (7)	Mo2-N21	2.516 (7)
Mo1-N12	2.310 (6)	Mo2-N22	2.364 (6)
Mo1-S1	2.422 (3)	Mo2-S2	2.416 (3)

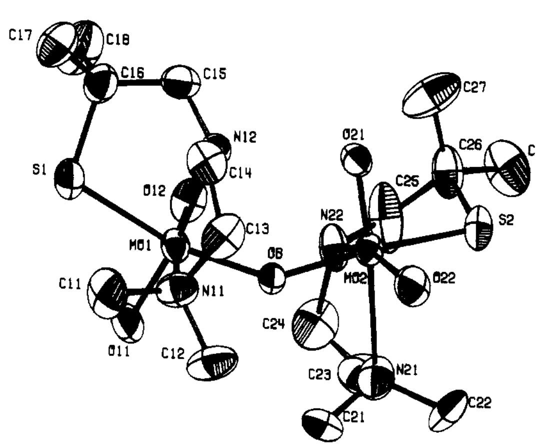

Figure 2. Perspective view and labeling scheme for $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$; hydrogen atoms omitted for clarity.

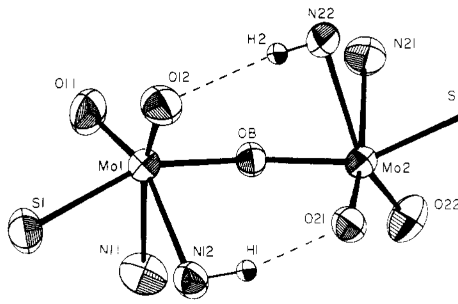

Figure 3. View of the coordination sphere of $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$ along the pseudo-twofold axis showing the intramolecular hydrogen-bonding interactions.

Table VII. Selected Interatomic Angles (deg) for $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$

atoms	angle	atoms	angle
O11-Mo1-O12	108.9 (3)	O21-Mo2-O22	105.9 (3)
O11-Mo1-OB	104.3 (3)	O22-Mo2-OB	105.6 (3)
O11-Mo1-N12	155.0 (3)	O22-Mo2-N22	154.0 (3)
O11-Mo1-S1	92.1 (2)	O22-Mo2-S2	93.4 (2)
O11-Mo1-N11	84.7 (3)	O22-Mo2-N21	82.7 (3)
O12-Mo1-OB	95.6 (3)	O21-Mo2-OB	95.9 (2)
O12-Mo1-N12	93.8 (3)	O21-Mo2-N22	98.6 (3)
O12-Mo1-S1	95.6 (2)	O21-Mo2-S2	94.5 (2)
O12-Mo1-N11	166.1 (3)	O21-Mo2-N21	171.2 (3)
OB-Mo1-N12	83.1 (2)	OB-Mo2-N22	80.1 (2)
OB-Mo1-S1	155.9 (2)	OB-Mo2-S2	154.9 (2)
OB-Mo1-N11	77.9 (2)	OB-Mo2-N21	79.8 (2)
N12-Mo1-S1	75.0 (2)	N22-Mo2-S2	75.8 (2)
N12-Mo1-N11	73.4 (2)	N22-Mo2-N21	73.2 (3)
S1-Mo1-N11	86.3 (2)	S2-Mo2-N21	86.7 (2)

coordination of the N,N,S ligand. The sulfur atoms (S1, S2) are trans to the bridging oxygen atom (OB). Although no symmetry is imposed upon the molecule, there is a pseudo-twofold axis that passes through the bridging oxygen and is perpendicular to the Mo–Mo vector (Figure 3). The list of chemically equivalent bond distances and angles (Tables VI and VII) illustrates the approximate twofold symmetry of the molecule. Distances and angles within the ligand framework are unexceptional and are included in the supplementary material.

Oxo-bridged dinuclear Mo(VI) complexes are known both in compounds in which there are additional bridging ligands (such as in Mo_2O_5(9,10-phenanthrenesemiquinone)[31] and in compounds where only a single oxo bridge connects the two Mo atoms.[32–37] In this latter class the Mo–O–Mo angle ranges from strictly 180° in $Mo_2O_5(C_2O_4)_2(H_2O)_2{}^{2-}$[32] to 136° in $Mo_2O_3(O_2)_4(H_2O)_2{}^{2-}$[36] with intermediate values for $Mo_2O_5(dmf)_4Cl_2$ (171°),[38] $Mo_2O_5(phen)_2(NCS)_2$ (162.7°),[35] and $Mo_2O_3(CH_3CH(O)CH(O)CH_3)_2(CH_3CH(O)CH(OH)CH_3)_2$ (162°).[33] The Mo–O–Mo linkage in $Mo_2O_5(Hnta)_2{}^{2-}$ also appears to be close to linear.[33] The present structure has an Mo1–OB–Mo2 angle of 143.8°.

The bridging Mo–OB distances at 1.92–1.93 Å are comparable to but slightly longer than the distances found in other complexes containing the $Mo_2O_5{}^{2+}$ core shown in Table VIII. This is likely due to the presence of sulfur in the position trans to the bridging oxo. As a strong σ- and π-donor, sulfur competes with the bridging O atom for the Mo 4d and 5p orbitals and hence causes the Mo–OB bond to be somewhat weaker and longer. This implies the presence of more electron density on the bridging O atom, which in turn is consistent with the bent structure around OB.

The terminal Mo–O distance of ~1.71 Å is close to distances found in other $Mo_2O_5{}^{2+}$ complexes and in mononuclear complexes containing the $MoO_2{}^{2+}$ core structure. The O_t–Mo–O_t angles of 105.9 and 108.9° are also typical of those

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Table VIII. Comparison of Distances and Angles in $Mo_2O_5^{2+}$ Complexes

	Mo–O_b–Mo, deg	Mo–O_b, Å	Mo–O_t, Å	ref
$Mo_2O_5(C_2O_4)_2(H_2O)_2$	180	1.876	1.68, 1.70	32
$Mo_2O_5(dmf)_4Cl_2$	171	1.90	1.68	38
$Mo_2O_5(phen)_2(NCS)_2$	162.7	1.865, 1.885	1.685, 1.688, 1.691, 1.694	35
$Mo_2O_5(Hnta)_2$	180	1.88	1.68, 1.71	34
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$	143.8	1.929, 1.917	1.715, 1.715, 1.714, 1.709	this work

found in $Mo_2O_5^{2+}$ and MoO_2^{2+} complexes. The deviation from the octahedral angle of 90° is attributable to the repulsion between the tightly bound O_t atoms.

The arrangement of atoms in the coordination sphere of each Mo atom is consistent with previous results in oxomolybdenum chemistry. The geometry of terminal and bridging oxo groups at the three *fac* positions leaves them approximately mutually perpendicular allowing each a maximal share of the Mo 4d and 5p orbitals.[3] Viewed in terms of the *cis*-MoO_2^{2+} core on each Mo, the next strongest donors are the bridging O atom ligand and the thiolate S atom. These occupy positions cis to the Mo–O_t linkages and hence trans to each other. The remaining coordination positions are occupied by the N atom donors of the ligands trans to oxo. The two Mo–N distances in each Mo sphere are quite different, with the dimethyl-substituted N terminus of the ligand displaying at 2.51 Å a substantially longer bond than the central N atom of the ligand. In work on bidentate and tetradentate N,S-donor complexes with the MoO_2^{2+} core, severe repulsions of $N(CH_3)_2$ groups were found to have a pronounced effect on the structure and/or bond lengths.[5-7] In the present case we attribute the greater length of the Mo1–N11 and Mo2–N21 bonds to repulsion between the $N(CH_3)_2$ methyl groups and the respective sulfur atom and/or the O12 and O22 atoms, respectively.

The synthesis of the $Mo_2O_5L_2$ complexes in the present study and their apparent persistence in polar solvents contrast with results reported by Topich[15] and by Rajan and Chakravorty,[14,16] who also studied Mo(VI) complexes of tridentate ligands. These authors observe mononuclear $MoO_2L(D)$, complexes where L is a tridentate dianionic Schiff's base ligand and D is a molecule of solvent (although no crystallographic information is available). The dianionic Schiff base ligands can neutralize the charge on the MoO_2^{2+} core and hence favor mononuclear complexes. The monoanionic tridentate ligands used in the present study are insufficient to neutralize the charge on the MoO_2^{2+} core. Hence, an additional oxide ion is probably scavenged from trace water to act as a bridge between the two Mo atoms and neutralize the excess charge on both Mo atoms.

An additional structural feature possibly favoring the stability of the $Mo_2O_5L_2$ complexes of the present study is the weak intramolecular hydrogen bonds between the central NH group coordinated to one molybdenum atom and the terminal oxo group on the other molybdenum atom (Figure 3). Such bonds are indicated by short nonbonded contacts N12···O21 = 2.81 Å and N22···O12 = 2.98 Å. Attempts to locate the hydrogen atoms on N12 and N22 in the final difference electron density map were unsuccessful. Calculation of idealized coordinates for these hydrogen atoms gave N–H···O bond angles of 148 and 165°. Weak bridging by hydrogen bonds would also favor the relatively small Mo1–OB–Mo2 angle of 143.8° (Table VIII). The proposed hydrogen-bonding interaction does *not* result in two kinds of Mo–O_t distances (Table VI). Similar NH···O hydrogen bonds, albeit intermolecular, are seen in the structures of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ and $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$.[6]

The structural findings in these $Mo_2O_5L_2$ complexes may have implications for the chemistry of molybdoenzymes. Certain dioxomolybdenum(VI) complexes of thiolate ligands have been shown to substantially reproduce the EXAFS spectra of the oxidized form of sulfite oxidase.[5] The most recent proposal[39] for the structure of the molybdenum center of the oxidized form of sulfite oxidase is a mononuclear unit containing $MoO_2(SR)_2$. Explicit EXAFS features assignable to a dinuclear molybdenum center are not observed for the enzyme. However, the ability of the EXAFS[40] technique to detect atoms falls off rapidly with increasing distance, and atoms that are only weakly coupled to the absorber (or not coupled at all) are seldom detected. The $Mo_2O_5L_2$ structure described here has a Mo···Mo distance of 3.66 Å, and the Mo atoms are not held rigidly with respect to each other. Similar Mo···Mo separations might not be detected in the EXAFS analysis of the enzyme. Therefore, although their presence remains unlikely, oxo-bridged dinuclear molybdenum centers of the type reported here cannot by EXAFS criteria alone be eliminated from consideration as structural models for the molybdenum centers of sulfite oxidase and other Mo enzymes.

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Registry No. I, 87145-32-2; II, 87145-33-3; IV, 87145-34-4; $Mo_2O_5[(C_5H_4NCH_2)_2NCH_2CH_2S]_2$, 87145-29-7; $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$, 87145-26-4; $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$, 87145-27-5; $Mo_2O_5(C_5H_4NCH_2NHC_6H_4S)_2$, 87145-28-6; $Mo_2O_4[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$, 87145-31-1; $Mo_2O_3(SC_6H_5)_2[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$, 87145-30-0; $MoO_2(acac)_2$, 17524-05-9; $(HSCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$, 70662-55-4; $(CH_3)_2NCH_2CH_2NH_2$, 108-00-9; CH_2SCH_2, 420-12-2; 2,2-dimethylethylene sulfide, 3772-13-2; bis(2-pyridylmethyl)amine, 1539-42-0.

Supplementary Material Available: Listings of hydrogen atom positions, observed and calculated structure factor amplitudes, anisotropic thermal parameters, and bond distances and angles in the ligand skeleton (16 pages). Ordering information is given on any current masthead page.

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