Dioxomolybdenum(VI) Complexes Stabilized by Polydentate Ligands with NO_3, N_2O_2, and NS_2 Donor-Atom Sets

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Dioxomolybdenum(VI) complexes of the general formula $LMoO_2$ (L = $(OCH_2CH_2)_2N(CH_2CH_2OH)$ (**1**), $O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O$ (**2**), $HN(CH_2CH_2S)_2$ (**3**)) have been synthesized and characterized. The structures of all compounds have unambiguously been determined in solution with the use of NMR spectroscopy. Complexes **1** and **2** have a distorted octahedral coordination about Mo with *cis* oxo groups and two alkoxo oxygen atoms in the apical positions. The coordination sphere is completed by amino and alkoxo oxygen atoms in **1** and by two N atoms in **2**. Dissolution of **1** in H_2O promotes hydrolysis of the remaining hydroxy arm of the ligand to give the anionic species $H[MoO_2(OCH_2CH_2)_3N]$ in which all the alkoxo arms are equivalent. In **3**, the *cis*-MoO_2^{2+} core is coordinated in a distorted trigonal-bipyramidal arrangement by two sulfur atoms in axial positions, by a nitrogen atom, and by two *cis* oxygen atoms. As shown by a single-crystal X-ray diffraction analysis, **3** retains the trigonal-bipyramidal structure in the solid state: orthorhombic *Pnma*, a = 9.814(1) Å, b = 11.960(2) Å, c = 7.119(1) Å, $Z = 4$, $R = 0.031$. The reactions of **1–3** with some inorganic (PPh_3) and organic substrates (*p*-thiocresol, thioanisole, benzyl alcohol, benzaldehyde) have been investigated. Only complex **3** undergoes selective reduction of the metal center by triphenylphosphine and *p*-thiocresol converting to the dimer $Mo_2O_3[HN(CH_2CH_2S)_2]_2$. Our results confirm that a bulky ligand with sulfur donors is required to make $LMoO_2$ complexes capable of catalyzing oxygen-transfer reactions.

Introduction

Dioxomolybdenum(VI) complexes stabilized by polydentate ligands with mixed N,O,S-donor atom sets are of both practical and fundamental importance. Practical motivations arise from the fact that dioxo–Mo(VI) compounds are largely employed in oxidation reactions of inorganic and organic substrates.[1] From the fundamental perspectives, dioxo–Mo(VI) complexes with polydentate nitrogen, sulfur and oxygen ligands are considered valuable models for the active site of several Mo enzymes such as oxidases (xanthine oxidase, aldehyde oxidase) and reductases (nitrate reductase).[2]

In this paper we describe the synthesis, characterization, electrochemistry, and preliminary reactivity studies of some new MoO_2^{2+}-core complexes obtained by reaction of $MoO_2(acac)_2$ with the polydentate ligands $N(CH_2CH_2OH)_3$, $N(CH_2CH_2SH)_3$, $HN(CH_2CH_2SH)_2$, and $HO(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2OH$.

Of particular interest is the complex $MoO_2[HN(CH_2CH_2S)_2]$, which, despite the low steric hindrance of the thiolate ligand, exists as monomeric 14-electron species in the solid state, whereas analogous five-coordinate Mo systems are usually stabilized through either coordination of a solvent molecule or polymerization.

Experimental Section

Materials and Methods. Unless otherwise stated, all the manipulations were performed under a pure nitrogen atmosphere. $MoO_2(acac)_2$ and triethanolamine were purchased from Sigma-Aldrich; cysteamine was purchased from Fluka. Diethyl ether and CH_2Cl_2 were distilled from $LiAlH_4$ and P_2O_5, respectively. Tris(2-(*S*-isothioureido)ethyl)amine tetrahydrochloride, $N[CH_2CH_2SC(NH)NH_3]_3Cl_3 \cdot HCl$, and $HO(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2OH$ were prepared according to literature methods.[3,4] All the other chemicals were commercial products and were used as received without further purification. The solid compounds were collected on sintered-glass frits and washed with diethyl ether before being dried in a stream of nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer using samples mulled in Nujol between KBr plates.

Proton NMR spectra were recorded at 200.133 MHz on a Bruker ACP-200 spectrometer equipped with a variable-temperature control unit accurate to ± 0.1 °C. Chemical shifts are relative to tetramethylsilane as external reference. ^{31}P NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 121.42 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. ^{13}C NMR spectra were recorded on a Bruker ACP-200 spectrometer operating at 50.32 MHz. Chemical shifts were measured relative to the deuterated solvent resonance. ^{13}C-DEPT and 2D-HETCOR experiments were run on the Bruker ACP-200 spectrometer. Simulation of NMR spectra was achieved by using an updated version of the DAVINS program.[5] The initial choices of the shifts and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions better than 0.3 Hz.

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(1) (a) Garner, C. D.; Durant, R.; Mabbs, F. E. *Inorg. Chim. Acta* **1977**, *24*, L29. (b) Ueyama, N.; Yano, M.; Miyashita, H.; Nakamura, A.; Kamachi, M.; Nozakura, S. *J. Chem. Soc. Dalton Trans.* **1984**, 1447. (c) Ueyama, N.; Kamabuchi, K.; Nakamura, A. *J. Chem. Soc. Dalton Trans.* **1985**, 635. (d) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1977**, *16*, 3385. (e) Tanaka, K.; Honjo, M.; Tanaka, T. *Inorg. Chem.* **1985**, *24*, 2662. (f) Arzoumanian, H.; Corao, C.; Krentzien, H.; Lopez, R.; Teruel, H. *J. Chem. Soc., Chem Commun.* **1992**, 856. (g) Fusi, A.; Ugo, R.; Zanderighi, G. M. *J. Catalysis.* **1974**, *34*, 175. (h) Gullotti, M.; Pasini, A.; Zanderighi, G. M.; Ciani, G.; Sironi, A. *J. Chem. Soc. Dalton Trans.* **1981**, 902. (i) Coleman-Kammula, S.; Duim-Koolstra, E. T. *J. Organomet. Chem.* **1983**, *246*, 53. (l) Trifirò, F.; Forzatti, P.; Preite, S.; Pasquon, I. *J. Less-Commom Met.* **1974**, *36*, 319.

(2) (a) Newton, W. E. and Otsuka, S. eds. *Molybdenum Chemistry of Biological Significance*, Plenum, London, **1980**. (b) Coughlan, M. P. ed. *Molybdenum and Molybdenum-containing Enzymes*, Pergamon, New York, **1980**. (c) Hille, R.; Massey, V. in *Molybdenum Enzymes*, Spiro, T. G.; Ed., Wiley-Interscience, New-York, **1985**, p. 443. (d) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Ed.* **1985**, *62*, 943. (e) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235.

(3) Harley-Mason, J. *J. Chem. Soc.* **1947**, 320.

(4) Protiva, M.; Borovicka, M. *Chem. Listy* **1952**, *46*, 427.

(5) Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1980**, *37*, 395, 409.

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Conductivities were measured with a Model 990101 Orion conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M solutions at room temperature. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[6] When necessary, deaeration of solutions was performed by bubbling argon for 15 min. Unless otherwise stated, the potential values are relative to a saturated aqueous calomel electrode (SCE) and refer to controlled temperatures (see text). Under the present experimental conditions, the ferrocenium/ferrocene couple was located at + 0.38, + 0.40, and + 0.49 V in MeCN, DMSO, and DMF solutions, respectively. Gas chromatographic analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30-m (0.25-mm i.d., 0.25-μm FT) SPB-1 Supelco fused silica capillary column and coupled with a C-R6A Chromatopac operating in the corrected area method. UV/visible spectra were recorded on a Shimadzu UV-2100 spectrophotometer using quartz cells. Solutions were ca. 1×10^{-3} M in DMSO.

Synthesis of the Ligands. $N(CH_2CH_2SH)_3$. To a solution of tris(2-(*S*-isothioureido)ethyl)amine tetrahydrochloride $N[CH_2CH_2SC(NH)NH_3]_3Cl_3{\cdot}HCl$, (159.0 g, 0.34 mol) in water (200 mL) was added an aqueous solution of NaOH (54 g, 1.36 mol in 270 mL of H_2O). The resulting solution was heated at 80 °C using a thermostated bath under vigorous stirring. As soon as an oil formed (ca. 15 min), heating was stopped and the mixture was quickly cooled by means of an ice–salt bath. The organic phase containing $N(CH_2CH_2SH)_3$ was extracted with CH_2Cl_2 (3 × 200 mL) and dried over Na_2SO_4. The solvent was then removed under reduced pressure at 25 °C. The crude product was purified by bubbling HCl into its ethanol solution. Addition of diethyl ether gave the hydrochloride salt, which was recrystallized from methanol/diethyl ether. Anal. Calcd for $C_6H_{16}NClS_3$: H, 6.90; C, 30.82; N, 5.99; S 41.13. Found: H, 6.82; C, 30.76; N, 6.01; S 40.93. The free trithiol was obtained by dissolving the hydrochloride in 200 mL of $NaHCO_3$-saturated water solution. Extraction with CH_2Cl_2 (3 × 200 mL) and workup as described above gave 40 mL (72%, $d = 1.2$) of a colorless viscous product. Anal. Calcd for $C_6H_{15}NS_3$: H, 7.66; C, 36.51; N, 7.10; S, 48.73. Found: H, 7.56; C, 36.44; N, 7.02; S, 48.42. IR: 2560 (ν(S–H)) cm^{-1}. ^1H NMR (CD_3COCD_3, 294 K): AA'BB' spin system, δ(A) 2.84, δ(B) 2.76, $J(H_AH_{A'}) = -19.87$, $J(H_AH_B) = 7.07$, $J(H_{A'}H_B) = 6.34$, $J(H_{A'}H_{B'}) = -19.76$ Hz (data obtained by computer simulation); δ(S*H*) 2.14 (s, 3H, broad).

$HN(CH_2CH_2SH)_2$. Method A. Ethylene sulfide (19.6 mL, 0.33 mol) in benzene (50 mL) was added dropwise within 3 h to a stirred solution of cysteamine (23.15 g, 0.30 mol) in benzene (200 mL) at 80 °C. Heating was maintained for 24 h. The resulting solution, after cooling to room temperature, was washed with water (80 mL) and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the resulting crude product was purified by treatment with gaseous HCl in absolute ethanol to give the hydrochloride salt, which was precipitated with diethyl ether. The compound was recrystallized from absolute ethanol/diethyl ether. Anal. Calcd for $C_4H_{12}NClS_2$: H, 6.96; C, 27.66; N, 8.06; S, 36.91. Found: H, 7.01; C, 27.71; N, 8.04; S, 36.55. The free dithiol was obtained by dissolving the hydrochloride in 200 mL of $NaHCO_3$-saturated water solution, followed by extraction with CH_2Cl_2 (3 × 200 mL). The CH_2Cl_2 solution was dried over Na_2SO_4, and then the solvent was removed under reduced pressure to give the dithiol ligand in 80% yield as a colorless liquid.

Method B. The $HN(CH_2CH_2SH)_2$ ligand can be obtained by thermal decomposition of $N(CH_2CH_2SH)_3$ at 81–82 °C (1 mmHg) (80% yield). Anal. Calcd for $C_4H_{11}NS_2$: H, 8.08; C, 35.00; N, 10.20; S, 46.71. Found: H, 8.02; C, 34.92; N, 10.28; S, 46.54. IR: 3299 (ν(N–H)), 2547 (ν(S–H)) cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): AA'BB' spin system, δ(A) 2.84, δ(B) 2.68, $J(H_AH_{A'}) = -12.19$, $J(H_AH_B) = 5.90$, $J(H_{A'}H_B) = 6.74$, $J(H_{A'}H_{B'}) = -13.37$ Hz (data obtained by computer simulation); δ(S*H* + N*H*) 1.60 (s, 3H, broad).

Synthesis of the Complexes. $MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ (1). $MoO_2(acac)_2$ (2.45 g, 7.5 mmol) was dissolved in warm methanol (~60 °C) (25 mL). $N(CH_2CH_2OH)_3$ (1 mL, 7.5 mmol) in methanol (25 mL) was then added causing an immediate color change from yellow-orange to colorless. White crystals slowly separated in 87% yield. Anal. Calcd for $C_6H_{13}NMoO_5$: H, 4.76; C, 26.20; N, 5.09. Found: H, 4.71; C, 25.94; N, 5.06.

$MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (2). $MoO_2(acac)_2$ (1.96 g, 6.0 mmol) was dissolved in warm methanol (~60 °C)(25 mL). $HO(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2OH$ (0.98 mL, 6.0 mmol) in methanol (25 mL) was then added causing an immediate color change from yellow-orange to colorless. Slow diffusion of diethyl ether vapors into the resulting solution gave off-white crystals in 70% yield. Anal. Calcd for $C_8H_{18}N_2MoO_4$: H, 6.00; C, 31.80; N, 9.27. Found: H, 5.72; C, 31.89; N, 9.10.

$MoO_2[HN(CH_2CH_2S)_2]$ (3). $HN(CH_2CH_2SH)_2$ (0.25 mL, 2.0 mmol) in methanol (30 mL) was added dropwise to a solution of $MoO_2(acac)_2$ (0.65 g, 2.0 mmol) in warm methanol (~60 °C) (30 mL) causing an immediate color change from yellow-orange to yellow. After a small amount of brown powder was filtered-off, the resulting solution was cooled to room temperature. Yellow crystals slowly formed in 60% yield. A second crop of product was collected by adding diethyl ether (20 mL) to the mother liquor and cooling overnight at −20 °C. Anal. Calcd for $C_4H_9NS_2MoO_2$: H, 3.45; C, 18.26; N, 5.32; S, 24.36. Found: H, 3.37; C, 18.21; N, 5.35; S, 24.12.

Reaction of $N(CH_2CH_2SH)_3$ with $MoO_2(acac)_2$. To a solution of $MoO_2(acac)_2$ (0.65 g, 2.0 mmol) in warm DMF (15 mL), $N(CH_2CH_2SH)_3$ (340 μL, 2.0 mmol) in CH_3CN (25 mL) was slowly added. As a result, the color changed from yellow-orange to red-brown. Dark crystals rapidly formed in 42% yield. Anal. Calcd for $C_{12}H_{24}N_2S_6Mo_2O_3$: H, 3.85; C, 22.93; N, 4.46; S, 30.60. Found: H, 4.18; C, 23.58; N, 4.90; S, 31.12.

Reaction of $MoO_2[HN(CH_2CH_2S)_2]$ with PPh_3. A mixture of $MoO_2[HN(CH_2CH_2S)_2]$ (0.20 g, 0.75 mmol) and PPh_3 (0.20 g, 0.75 mmol) in DMF (5 mL) was heated at 80 °C for 2 h with stirring. The color of the solution quickly turned from yellow to dark red. After the solution cooled to room temperature, diethyl ether (20 mL) was added. Red-brown crystals of $Mo_2O_3[HN(CH_2CH_2S)_2]_2$ (4) formed in 87% yield. Anal. Calcd for $C_8H_{18}N_2S_4Mo_2O_3$: H, 3.55; C, 18.83; N, 5.49; S, 25.13. Found: H, 3.66; C, 19.04; N, 5.54; S, 25.23. The content of the mother liquor (1 mL) was analyzed by ^{31}P NMR spectroscopy after the ether was removed under reduced pressure and CD_3COCD_3 (0.5 mL) was added. PPh_3 and $OPPh_3$ were detected in a 1:1 ratio.

Reaction of $MoO_2[HN(CH_2CH_2S)_2]$ with p-$CH_3C_6H_4SH$. To a solution of $MoO_2[HN(CH_2CH_2S)_2]$ (0.20 g, 0.75 mmol) in DMF (5 mL) at room temperature was added p-$CH_3C_6H_4SH$ (0.18 g, 1.50 mmol) with stirring. The yellow solution immediately turned brown. GC analysis showed the mixture to contain p-$CH_3C_6H_4S$-SC_6H_4-p-CH_3 and p-$CH_3C_6H_4SH$ in a 1:1 ratio. On addition of diethyl ether (20 mL) red-brown crystals of 4 were obtained.

X-ray Data Collection and Processing. Crystal and intesity data for $MoO_2[HN(CH_2CH_2S)_2]$ (3) are reported in Table 1. X-ray measurements were performed on a Enraf-Nonius CAD4 diffractometer. The cell constants and orientation matrix were determined by least-squares refinement of the setting angles for 25 reflections. The intensities of three standard reflections were measured every 120 min of X-ray exposure (Mo Kα). No decay was observed. The data were corrected for Lorentz and polarization effects. An empirical correction for the absorption effect was made by using the program DIFABS.[7]

Solution and Refinement of the Structure. All the calculations were carried out on a Digital DEC 5000/200 computer by using the SHELX76[8] and ORTEP[9] programs. Atomic scattering factors for non-hydrogen atoms were taken from ref 10 and for hydrogen atoms from ref 11.

Table 1. Crystal Data for $MoO_2[HN(CH_2CH_2S)_2]$ (3)

formula	$C_4H_9NMoO_2S_2$
M_r	263.19
space group	*Pnma*
a (Å)	9.814(1)
b (Å)	11.960(2)
c (Å)	7.119(1)
V (Å^3)	835.6(2)
Z	4
D_{calc} (g cm^3)	2.09
μ(Mo Kα) (cm^{-1})	19.57
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)
R	0.031
R_w	0.031

(6) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P. *Organometallics* **1991**, *10*, 636.

(7) Walker, N.; Stuart, D. *Acta Cryst.* **1983**, *A39*, 158.

(8) Sheldrick, G. M., SHELX76, *System of Computing Programs*, University of Cambridge, Cambridge, England, **1976**.

(9) Johnson, C. K., ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (U.S.) **1976**.

(10) *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, **1974**, Vol. 4, 99.

Table 2. Atomic Parameters and U Values (Å^2) for the Structure of $MoO_2[HN(CH_2CH_2S)_2]$ (3)[a]

atom	x	y	z	U or U_{eq}
Mo	1191(1)	2500	1291(1)	25(1)[b]
S	657(1)	658(1)	2233(2)	35(1)[b]
O1	-41(5)	2500	-382(6)	46(2)[b]
O2	2753(4)	2500	304(6)	44(2)[b]
C1	1756(5)	466(3)	4245(6)	37(2)[b]
C2	1616(5)	1487(3)	5503(6)	37(2)[b]
N	1932(5)	2500	4405(6)	26(2)[b]

[a] Thermal parameters multiplied by 1000, and coordinates, by 10000. [b] U_{eq} defined as one-third of the trace of the orthogonalized thermal tensor.

Anomalous dispersion terms, both real and imaginary, were included for non-hydrogen atoms.[12] The function $\Sigma w(F_o - F_c)^2$ was minimized during the least-squares refinements, the weight w being defined as $1/\sigma^2(F_o)$. The structure was solved by the heavy-atom method. Full-matrix least-squares refinements were carried out by assigning anisotropic thermal parameters to molybdenum, nitrogen, sulfur, and oxygen atoms. Hydrogen atoms were detected from ΔF maps and successfully refined. The refinement converged to $R = 0.031$ and $R_w = 0.031$ factors. The ΔF final maps appeared essentially featureless. Final positional parameters of non-hydrogen atoms of **3** are reported in Table 2.

Results and Discussion

Synthesis of the Ligands. The syntheses of the thiol ligands $N(CH_2CH_2SH)_3$ and $HN(CH_2CH_2SH)_2$ have been improved on their previously reported procedures.[3] In particular, heating was carefully controlled during the synthesis of $N(CH_2CH_2SH)_3$, while the purification of the latter compound was achieved through the isolation of the hydrochloride. A rigorous control of the temperature prevents the decomposition of the ligand to the corresponding dithiol *via* elimination of ethylene sulfide. Indeed, the loss of ethylene sulfide from high-boiling mercaptans is a well-documented reaction.[13] As a matter of fact, the ligand $HN(CH_2CH_2SH)_2$ is almost quantitatively obtained by distillation of the trithiol. In a previous paper, the formation of some dithiol in the synthesis of the trithiol was erroneously attributed to the presence of some diethanolamine impurities in the starting triethanolamine.[3] Alternatively, the ligand $HN(CH_2CH_2SH)_2$ can be prepared by reaction of cysteamine with ethylene sulfide.

Synthesis of the Complexes. Dioxomolybdenum complexes of the formula MoO_2L [L = $(CH_2CH_2O)_2N(CH_2CH_2OH)$ (**1**), $O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O$ (**2**), $HN(CH_2CH_2S)_2$ (**3**)] have been prepared by the known ligand-exchange reaction 1 using $MoO_2(acac)_2$ as starting reagent.

$$MoO_2(acac)_2 + LH_2 \xrightarrow{MeOH} MoO_2L + 2acacH \quad (1)$$

According to the stoichiometry of reaction 1, treatment of $MoO_2(acac)_2$ with $N(CH_2CH_2OH)_3$ causes the deprotonation of only two OH groups.

Extreme care is necessary for handling $N(CH_2CH_2SH)_3$ and $HN(CH_2CH_2SH)_2$ due to their ability to act as either reductants or ligands. Indeed, in the synthesis of $MoO_2[HN(CH_2CH_2S)_2]$ (**3**), thiol oxidation may compete with the substitution of the acac ligand. As a result, small amounts of $Mo_2O_3[HN(CH_2CH_2S)_2]_2$ (**4**) may form during the reaction. This behavior has already been observed for $HSCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2SH$[14,15] and $(HSCH_2CH_2)_2NCH_2CH_2SCH_3$.[15] In order to minimize this side reaction, it is convenient to use a deficiency of the thiol as well as warm solutions of polar solvents.

The reaction of $MoO_2(acac)_2$ with $N(CH_2CH_2SH)_3$ in warm DMF gives extremely air-sensitive dichroic microcrystals. The composition and the structure of this compound could not be determined due to both fast decomposition in solution and the extensive broadening of the ^1H NMR resonances (most likely caused by unknown paramagnetic impurities). The IR data (strong band at 780 cm^{-1}) indicate the presence of an $O{=}Mo^V{-}O{-}Mo^V{=}O$ moiety,[16] which suggests that two thiols arms of the ligand have displaced acac (see reaction 1), while the third thiol arm has acted as a reductant.

Characterization of Molybdenum Complexes. All the alkoxo complexes are air-stable in both the solid state and solution. In contrast, $MoO_2[HN(CH_2CH_2S)_2]$ (**3**), though slow, decomposes in solutions exposed to air. $MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (**2**) is soluble in common organic solvents with the exception of alcohols, while $MoO_2[HN(CH_2CH_2S)_2]$ is soluble only in DMF, DMSO, and, to a lesser extent, $CHCl_3$ and CH_3CN. $MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ (**1**) is soluble only in DMSO, water, and hot DMF. All the complexes are nonelectrolytes in solution with the exception of $MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ in water solution where the compound behaves as a 1:1 electrolyte (Λ_M = 352 Ω^{-1} cm^2 mol^{-1}).

The dimeric complex **4** is only sparingly soluble in DMSO where it behaves as a nonelectrolyte.

Infrared and UV/Visible Spectra. Selected infrared and UV/visible spectral data for **1**–**3** are reported in Tables 3 and 4, respectively.

The IR and UV spectral data are unexceptional and in good correlation with those reported for several *cis*-$Mo^{VI}O_2L$ species.[14,17-21]

In particular, the UV bands in the range from 270 to 470 nm are attributed to ligand → Mo(VI) charge transfers.[22] The IR absorptions at ~920 and 890 cm^{-1} are attributed to ν(Mo=O) symmetric and asymmetric vibrations of C_{2v} *cis*-MoO_2^{2+} groups, respectively.[14,17,20]

The IR spectrum of **4** (Table 3) displays a strong broad band at 942 cm^{-1} and a medium-intensity band at 778 cm^{-1}, which are readily assigned to ν(Mo=O) and ν(Mo–O–Mo) vibrations, respectively.[14,16,23]

Structure of 3. An X-ray analysis has been carried out on $MoO_2[HN(CH_2CH_2S)_2]$ (**3**). The structure consists of independent mononuclear molecules. An ORTEP view is reported in Figure 1, while selected bond distances and angles are reported in Table 5. The coordination geometry around the metal center approximates a distorted trigonal bipyramid in which the S atoms occupy the axial positions and the O1, O2, and N atoms lie in the equatorial plane. The crystallographic imposed σ plane contains the Mo, O1, O2 core as well as the N and H5 atoms. Under this symmetry, only one of the two SCH_2CH_2N arms is symmetry independent. The MoO_2 framework adopts a *cis* arrangement with the Mo–O distances essentially equivalent [1.697(4) and 1.687(4) Å] and an O1–Mo–O2 angle of

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(12) *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, **1974**, Vol. 4, 149.
(13) Snyder, H. R.; Stewart, J. H.; Ziegler, J. B. *J. Am. Chem. Soc* **1947**, *69*, 2672.
(14) Pickett, C.; Kumar, S.; Vella, P. A.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 908.
(15) Corbin, J. L.; Miller, K. F.; Pariyadath, N.; Wherland, S.; Bruce, A. E.; Stiefel, E. I. *Inorg. Chim. Acta* **1984**, *90*, 41.
(16) Newton, W. D.; Corbin, J. L.; Bravard, D. C.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* **1974**, *13*, 1100.
(17) Willis, L. J.; Loehr, T. M.; Miller, K. F.; Bruce, A. E.; Stiefel, E. I. *Inorg. Chem.* **1986**, *25*, 4289.
(18) Subramanian, P.; Spence, J. T.; Ortega, R.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 2564.
(19) Hinshaw, C. J.; Peng, G.; Singh, R.; Spence, J. T.; Enemark, J. H.; Bruck, M.; Kristofzski, J.; Merbs, S. L.; Ortega, R. B.; Wexler, P. A. *Inorg. Chem.* **1989**, *28*, 4483.
(20) Stiefel, E. I. *Progr. Inorg. Chem.* **1977**, *22*, 1.
(21) (a) Stiefel, E. I. in *Comprehensive Coordination Chemistry*, Wilkinson, G.; Gillard, R. D.; McCleverty, J. A.; Eds., Pergamon Press, Oxford, **1987**, Vol. 3, p. 1375. (b) Garner, C. D.; Bristow, S. in *Molybdenum Enzymes*, Spiro, T. G.; Ed., Wiley-Interscience, New-York, **1985**, p. 343.
(22) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917.
(23) Kamenar, B.; Korpar-Colig, B.; Cindric, M.; Penavic, M.; Strukan, N. *J. Chem. Soc. Dalton Trans.* **1992**, 2093.

Table 3. Selected IR Spectral Data for Molybdenum Complexes[a]

complex	ν(Mo=O)	ν(Mo–O–Mo)	others
$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ (1)	930 (s), 904 (s)		2900 (s), ν(O–H)[b]
$MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (2)	914 (s), 878 (s)		
$MoO_2[HN(CH_2CH_2S)_2]$ (3)	930 (s), 885 (s)		3173 (m), ν(N–H)
$Mo_2O_3[HN(CH_2CH_2S)_2]_2$ (4)	942 (s, br)	778 (m)	3173 (m), ν(N–H)

[a] Nujol mulls, cm^{-1}. [b] Very broad.

Table 4. UV/Visible Spectral Data for Molybdenum Complexes[a]

complex	λ_{max} (nm) (ϵ_M (cm^{-1} mol^{-1} L))
$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ (1)	274 (6770)
$MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (2)	272 (6500)
$MoO_2[HN(CH_2CH_2S)_2]$ (3)	271 (9180), 414 (sh, broad), 479 (sh)
$Mo_2O_3[HN(CH_2CH_2S)_2]_2$ (4)	262 (4110), 303 (sh), 468 (1780)

[a] DMSO solutions at 21 °C in the range 190–900 nm.

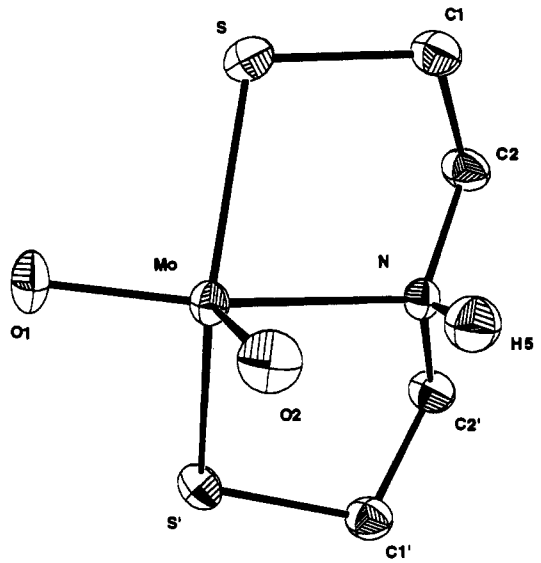

Figure 1. Ortep drawing of the complex $MoO_2[HN(CH_2CH_2S)_2]$ (3).

Table 5. Selected Bond Distances (Å) and Angles (deg) for $MoO_2[HN(CH_2CH_2S)_2]$ (3)

Mo–O1	1.697(4)	Mo–S	2.361(1)
Mo–O2	1.687(4)	Mo–N	2.333(4)
O1–Mo–O2	110.8(2)	S–Mo–O2	108.6(1)
S–Mo–N	78.4(1)	S–Mo–S'	137.8(1)
N–Mo–O1	152.7(2)	O2–Mo–N–S	72.2(1)
N–Mo–O2	96.5(2)	S–Mo–N–C2	–6.2(3)
S–Mo–O1	92.4(1)		

110.8(2)°. The N–Mo–O angles are substantially different [152.7(2) and 96.5(2)° for O1 and O2, respectively]. This feature and the value of the O2–Mo–N–S torsion angle of 72.2(1)° represent the major deviations from the idealized trigonal-bipyramidal geometry and indicate that the molecule approaches a "butterfly-like" geometry in which the two SCH_2CH_2N arms are bent toward each other and toward the O2 atom.

The Mo–ligand bond distances and angles in **3** are in the range normally observed for several complexes containing the MoO_2^{2+} core.[21a,24] It is worth noticing that **3** represents the second example of a monomeric five-coordinate dioxo Mo(VI) complex. The first complex of this class, $MoO_2[C_5H_3N\text{-}2,6\text{-}(CH_2CPh_2S)]$, has recently been described by Berg and Holm and contains an NS_2 donor atom set.[22] This coordination number is very uncommon for both alkoxo and thiolato $Mo^{VI}O_2$ complexes with tridentate ligands since six-coordinate species are generally formed by either coordination of a solvent molecule[18,22,24-28] or polymerization through unsymmetrical Mo=O···Mo bridges with the next neighbors.[24,29,30]

The value of the O1–Mo–O2 angle [110.8(2)°] in **3** is very similar to that [110.5(3)°] found in Berg and Holm's complex which adopts a distorted TBP geometry with the sulfur atoms in the axial position.[22,31] In contrast, the O1–Mo–N and O2–Mo–N angles are significantly different. This indicates that our complex is more distorted toward a square-pyramidal geometry (with the O2 atom in axial position and the sulfur atoms in *trans* to each other) than Berg and Holm's one.

As discussed below, all the spectroscopic data show that **3** does not change structure on going from the solid state to solution.

Magnetic Resonance Spectra. ^1H NMR and ^{13}C NMR data for all complexes are reported in Tables 6 and 7, respectively; the labeling scheme used is shown in Figure 2. Unambiguous assignment of the ^1H NMR resonances was made on the basis of computer fittings of the experimental data. This procedure was necessary in view of the complexity of the proton NMR spectra due to the presence of several different types of CH_2 groups in the complexes. All the assignments were confirmed by ^{13}C–^1H 2D-HETCOR and homonuclear decoupling experiments.

$MoO_2[HN(CH_2CH_2S)_2]$ (3). The NMR data of $MoO_2[HN(CH_2CH_2S)_2]$ are fully consistent with the solid-state structure. In particular, the ^{13}C NMR spectrum (DMSO-d_6, 294 K) displays single sets of resonances for the $HNCH_2$ (β) and CH_2S (α) carbon atoms, respectively, which is consistent with the magnetic equivalence of the two SCH_2CH_2N arms. The proton resonances (DMSO-d_6, 294 K) have successfully been computed using an ABCDM spin system where M stands for the amino proton N*H* and ABCD are the four methylenic protons of each arm. The hydrogen atoms of each CH_2 group are chemically inequivalent as imposed by the crystallographic symmetry. All the proton resonances are shifted downfield as compared to those of the free thiol.

$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ (1). In the ^{13}C NMR spectrum (DMSO-d_6, 294 K) of **1** the CH_2O (α) and NCH_2 (β) carbon nuclei display a single set of resonances, indicating the chemical equivalence of the two coordinated arms also in this complex. In this case, however, two other peaks appear with chemical shifts only slightly downfield compared to those of the free ligand and in a 1:2 intensity ratio with the resonances of C_α and C_β. These resonances are assigned to the carbons of the CH_2CH_2OH arm ($C_{f\alpha}$ and $C_{f\beta}$). The ^{13}C NMR spectrum nicely correlates with the ^1H NMR spectrum (DMSO-d_6, 294 K). In fact, two distinct spin systems are observed: the first (ABCD pattern) is attributed to the methylenic protons of the two chemically equivalent arms coordinated to Mo (these exhibit large downfield shifts compared to the signals of the free ligand); the second (A_2M_2X pattern) is attributed to the third arm ($C_{f\alpha}H_A$

(24) Bhattacharjee, S.; Bhattacharyya, R. *J. Chem. Soc. Dalton Trans.* **1993**, 1151.
(25) Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 660.
(26) Boyd, I. W.; Spence, J. T. *Inorg. Chem.* **1982**, *21*, 1602.
(27) Berg, J. M.; Holm, R. M. *Inorg. Chem.* **1983**, *22*, 1768.
(28) Craig, J. A.; Harlan, E. W.; Snyder, B. S.; Whitener, M. A.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 2082.
(29) Wilson, A. J.; Penfold, B. R.; Wilkins, C. J. *Acta Cryst.* **1983**, *C39*, 329.
(30) Topich, J.; Lyon, J. T. *Polyhedron* **1984**, *3*, 55.
(31) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 3035.

Table 6. ^{1}H NMR Spectral Data for Molybdenum Complexes[a]

complex	chem shifts (ppm) and coupling consts J (Hz)	pattern
$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$[b] (1)	8.07 (O*H*)	A
	3.86 ($C_{f\alpha}H_A$), 3.14 ($C_{f\beta}H_M$), $J(H_AH_M)$ = 5.43	A_2M_2
	4.75 ($C_\alpha H_A$), 4.60 ($C_\alpha H_B$), 3.68 ($C_\beta H_C$), 3.30 ($C_\beta H_D$), $J(H_AH_B)$ = 10.77, $J(H_AH_C)$ = 8.49, $J(H_AH_D)$ = 5.65, $J(H_BH_C)$ = 7.41, $J(H_BH_D)$ = 3.65, $J(H_CH_D)$ = 12.21	ABCD
$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$[c] (1)	7.68 (O*H*), 3.62 ($C_{f\alpha}H_A$), 2.97 ($C_{f\beta}H_M$), J (OHH_A) = 3.40, J(OHH_M) = 0.00, $J(H_AH_M)$ = 5.48	A_2M_2X
	4.62 ($C_\alpha H_A$), 4.48 ($C_\alpha H_B$), 3.50 ($C_\beta H_C$), 3.17 ($C_\beta H_D$), $J(H_AH_B)$ = 10.75, $J(H_AH_C)$ = 8.50, $J(H_AH_D)$ = 5.65, $J(H_BH_C)$ = 7.41, $J(H_BH_D)$ = 3.61, $J(H_CH_D)$ = 12.23	ABCD
$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$[d] (1)	3.95 ($C_\alpha H_A$), 3.48 ($C_\beta H_M$), $J(H_AH_M)$ = 5.23	A_2M_2
$MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$[e] (2)	2.91 (s, 6H, CH_3)	A
	4.57 ($C_\alpha H_A$), 4.51 ($C_\alpha H_B$), 3.44 ($C_\beta H_C$), 2.81 ($C_\beta H_D$), $J(H_AH_B)$ = 11.10, $J(H_AH_C)$ = 7.12, $J(H_AH_D)$ = 5.27, $J(H_BH_C)$ = 7.25, $J(H_BH_D)$ = 5.51, $J(H_CH_D)$ = 12.19	ABCD
	2.83 ($C_\gamma H_A$), 2.76 ($C_\gamma H_B$), $J(H_AH_{A'})$ = 2.59, $J(H_AH_B)$ = 11.76, $J(H_AH_{B'})$ = 2.03, $J(H_BH_{B'})$ = 1.72	AA'BB'
$MoO_2[HN(CH_2CH_2S)_2]$[c] (3)	3.70 ($C_\beta H_A$), 3.45 ($C_\alpha H_B$), 3.29 ($C_\alpha H_C$), 2.85 ($C_\beta H_D$), 6.51 (NH_E), $J(H_AH_B)$ = 2.04, $J(H_AH_C)$ = 4.32, $J(H_AH_D)$ = 11.13, $J(H_AH_E)$ = 3.84, $J(H_BH_C)$ = 12.54, $J(H_BH_D)$ = −3.89, $J(H_BH_E)$ = 0.73, $J(H_CH_D)$ = −12.84, $J(H_CH_E)$ = −0.1, $J(H_DH_E)$ = 10.77	ABCDE

[a] Data for second-order patterns were measured by computer simulations. [b] In DMF-d_7, 294 K. [c] In DMSO-d_6, 294 K. [d] In D_2O, 294 K. [e] In $CDCl_3$, 294 K.

Table 7. ^{13}C NMR Spectral Data for Molybdenum Complexes

complex	chem shifts (ppm)
$MoO_2[(OCH_2CH_2)_2$-$N(CH_2CH_2OH)]$[a] (1)	76.95 (C_α), 63.89 (C_β), 61.39 ($C_{f\alpha}$), 60.18 ($C_{f\beta}$)
$MoO_2[O(CH_2)_2NMe$-$(CH_2)_2NMe(CH_2)_2O]$[b] (2)	73.57 (C_α), 64.18 (C_β), 58.82 (C_γ), 51.95 (CH_3)
$MoO_2[HN(CH_2CH_2S)_2]$[a] (3)	60.97 (C_α), 38.11 (C_β)

[a] In DMSO-d_6, 294 K. [b] In $CDCl_3$, 294 K.

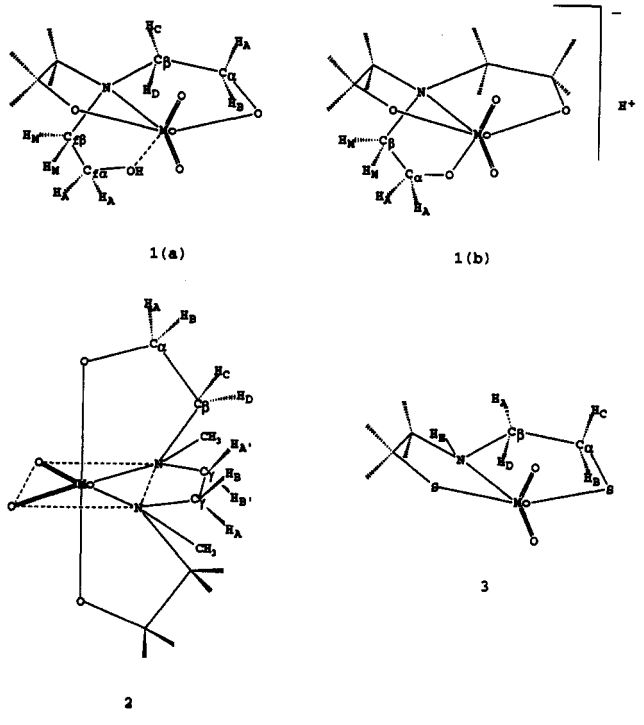

Figure 2. Sketches of complexes **1–3** with the labeling scheme adopted for the NMR assignments [**1(a)**, DMSO-d_6 or DMF-d_7 solutions; **1(b)**, D_2O solution].

and $C_{f\beta}H_M$ in Figure 2). The label × represents the hydrogen of the O*H* group, which originates as a triplet at 7.68 ppm. This pattern shows the structural nonrigidity of the hydroxy arm. On the other hand, the downfield shifts of 3.37 ppm for the O*H* hydrogen, and of ca. 0.2 ppm for the $C_{f\alpha}H_A$ and $C_{f\beta}H_M$ hydrogens, respectively, compared to the corresponding resonances of the free ligand, indicate that this arm is weakly bound to the metal center. A similar ^{1}H NMR spectrum is displayed in DMF-d_7, the only difference being that the O*H* hydrogen appears as a broad singlet. In contrast, only an A_2B_2 spin system is shown in D_2O solution (294 K), indicating that all the arms are equivalent, while no O*H* resonance is observed. This behavior is consistent with a fast proton exchange on the NMR time scale between the solvent and the intact OH group of the ligand, which, ultimately, results in a rapid interconversion of all the arms. The structure of **1** has been a matter of debate in the past years. On the basis of IR measurements, Voronkov and Lapsyn[32] formulated **1** as the neutral species $MoO(OH)(OCH_2CH_2)_3N$ containing the Mo–OH group. More recently, Atovmyan and Krasochka[33] proposed the anionic formulation $H[MoO_2(OCH_2CH_2)_3N]$ on the basis of an X-ray analysis, attributing the existence of two different Mo–O(alkyl) lengths to nonbonding repulsion interactions. Our spectroscopic and conductivity data are therefore consistent with the anionic formulation in water solution. However, in aprotic solvents such as DMF or DMSO, our data are consistent with the neutral structure $MoO_2[(CH_2CH_2O)_2N(CH_2CH_2OH)]$ where the *cis*-MoO_2 group, two alkoxo arms of the ligand (magnetically equivalent due to the presence of a symmetry plane containing the *cis*-MoO_2N moiety) and a weakly interacting amino–alcohol arm give rise to an approximate octahedral coordination around the metal center.

$MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (2). A DEPT-^{13}C spectrum ($CDCl_3$, 294 K) of **2** shows four resonances for the four different types of carbons, namely C_α, C_β, C_γ, and CH_3. Thus, the two alkoxo arms as well as the two carbon atoms C_γ of the bridging arm are magnetically equivalent. This assignment was confirmed by a computer simulation of the ^{1}H NMR spectrum ($CDCl_3$, 294 K) which was successfully interpreted as containing two identical ABCD spin systems, originated by the $NC_\beta H_2C_\alpha H_2O$ protons, and an AA'BB' spin system due to the hydrogen atoms of the $NC_\gamma H_2C_\gamma H_2N$ bridge. The ^{1}H NMR spectrum is complicated by superimposition of the two spin systems in the high-field region. The experimental and computed ^{1}H NMR spectra of **2** are reported in Figure 3. On the basis of ^{13}C and ^{1}H NMR data, **2** is assigned an octahedral geometry with a local C_2 symmetry about Mo where the 2-fold rotation axis lies in the MoO_2N_2 plane and bisects the O=Mo=O angle. Under this symmetry, each of the $C_\gamma H_2$ protons are evidently inequivalent.

In conclusion, irrespective of the ligand, complexes **1–3** contain

(32) Voronkov, M. G.; Lapsyn, A. F. *Khim. Geterotsikl. Soedinenii* **1967**, 561.
(33) Atovmyan, L. O.; Krasochka, O. N. *Chem. Commun.* **1970**, 1670.

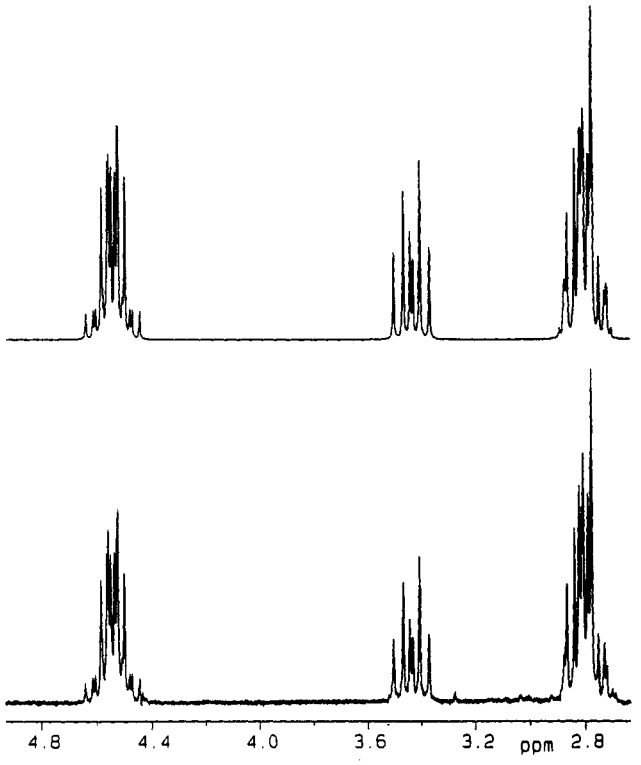

Figure 3. Experimental (lower) and simulated (upper) ^1H NMR spectra of $MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (**2**) ($CDCl_3$, 294 K). The resonances of the methyl groups were digitally removed for simplicity.

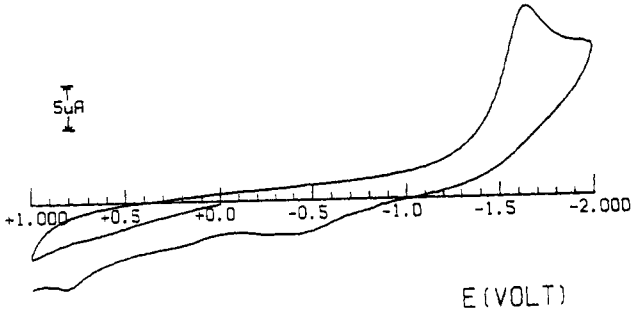

Figure 4. Cyclic voltammetric responses recorded at a platinum electrode on a deaerated DMSO solution containing **1** (1.6×10^{-3} M) and $(NBu_4)ClO_4$ (0.2 M). Scan rate = 0.2 V s^{-1}. T = 294 K.

a pair of NCH_2CH_2X (X = S, O) symmetry-related arms in which the hydrogens of each CH_2 group are inequivalent. An ABCD pattern is therefore observed for these rigid CH_2CH_2 arms in the ^1H NMR spectra. Interestingly, according to the spectral data (Table 6) and heteronuclear ^{13}C–^1H 2D experiments, the A and B hydrogens are those bonded to the C_α atom in **1** and **2** and to the C_β and C_α atoms in **3**. All these hydrogen nuclei show a downfield shift of ca. 0.5 ± 1 ppm as compared to the corresponding resonances of the free ligands in the same solvent.

Electrochemical Studies. The electrochemical behavior of **1–3** has been investigated in view of the ease of dioxomolybdenum(VI) complexes to accede to the Mo(V), Mo(IV), and Mo(III) oxidation states through either one-electron or multielectron steps. This redox aptitude is relevant to some electron-transfer properties of molybdoenzymes.[22,24,34]

Figure 4 shows the cyclic voltammetric response exhibited by **1** in dimethyl sulfoxide solution. The reduction process at E_p = −1.65 V does not exhibit any directly associated response in the reverse scan even at a scan rate of 20 V s^{-1}. This indicates that very fast chemical complications are coupled to the Mo(VI)/Mo(V) step, as confirmed also by controlled potential coulometry at E_W = −1.7 V.

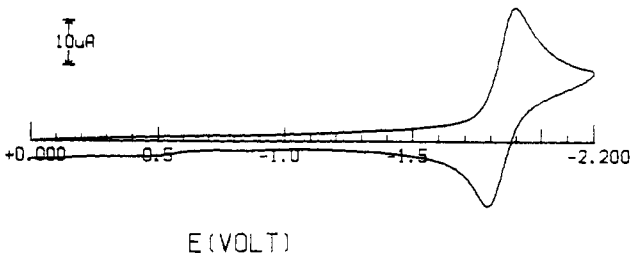

Figure 5. Cyclic voltammetric responses recorded at a platinum electrode on a deaerated DMSO solution containing **2** (1.2×10^{-3} M) and $(NBu_4)ClO_4$ (0.2 M). Scan rate = 0.5 V s^{-1}. T = 294 K.

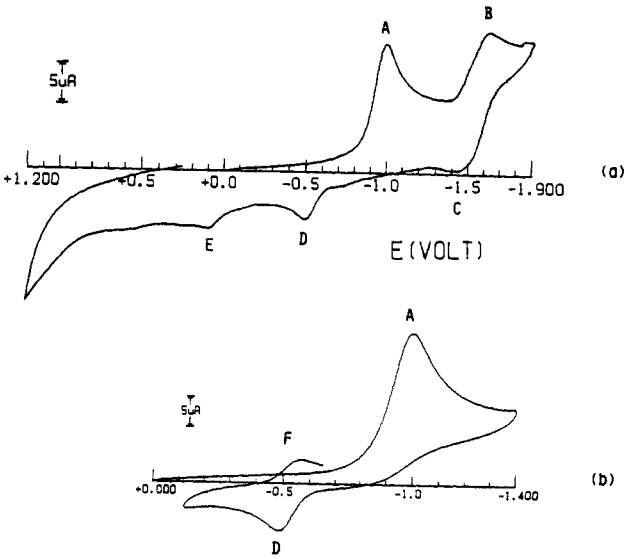

Figure 6. Cyclic voltammetric responses recorded at a platinum electrode on a deaerated DMSO solution containing **3** (1.8×10^{-3} M) and $(NBu_4)ClO_4$ (0.2 M). T = 294 K. Scan rates: (a) 0.2 V s^{-1}; (b) 0.5 V s^{-1}.

As shown in Figure 5, also complex **2** displays a single reduction process, which likely involves a one-electron step. Actually, 1.3 electrons/molecule were consumed in the course of the exhaustive electrolysis (E_W = −1.95 V) likely because of a partial contribution of the neighboring solvent discharge. In spite of the apparent chemical reversibility, the i_{pa}/i_{pc} ratio is significantly lower than 1 at lower scan rates (i.e., 0.60, 0.75, and 0.85 at 0.05, 0.1, and 0.2 V s^{-1}, respectively). This evidence once again denunciates the occurrence of chemical complications following the primary electron transfer MoO_2^{2+}/MoO_2^{+}. A rough evaluation[35] of the lifetime of the monoanion $[2]^-$ leads to a value of $t_{1/2} \sim 6$ s.

Finally, Figure 6 shows that **3** possesses a richer redox propensity. In fact, this complex undergoes a first reduction step at peak A, which consumes one electron/molecule in controlled-potential coulometry (E_W = −1.1 V). This reduction peak does not display a directly associated reoxidation response in the reverse scan even at 20 V s^{-1}, except for the peak-system D/F. This system is clearly attributable to the redox processes of an unidentified Mo(V) species arising from significant rearrangement of the unstable MoO_2^{+} species $[3]^-$. Such a species in turn undergoes a further one-electron reduction at peak B, which exhibits some features of chemical reversibility.

Table 8 summarises the electrode potentials of the redox changes described above.

(34) (a) Isbell, A. F., Jr.; Sawyer, D. T. *Inorg. Chem.* **1971**, *10*, 2449. (b) Bristow, S.; Garner, C. D.; Pickett, C. J. *J. Chem. Soc. Dalton Trans.* **1984**, 1617. (c) Dowerah, D.; Spence, J. T.; Singh, R.; Wedd, A. G.; Wilson, G. L.; Farchione, F.; Enemark, J. H.; Kristofzki, J.; Bruck, M. *J. Am. Chem. Soc.* **1987**, *109*, 5655.

(35) Brown, E. R.; Sandifer, J. R. in *Physical Methods of Chemistry. Electrochemical Methods*, Rossiter, B. W. and Hamilton, J. F. Eds., Vol. 2, Wiley, New York, **1986**, Chapt. 4.

Table 8. Electrode Potentials (V *vs* SCE) for the Redox Changes Exhibited by the Molybdenum Complexes 1–3

complex	$E°'$(Mo(VI)/Mo(V))	$E°'$(Mo(V)/Mo(IV))	solvent
$MoO_2[(OCH_2CH_2)_2N(CH_2CH_2OH)]$ (1)	−1.64[a]		DMSO
$MoO_2[O(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2O]$ (2)	−1.89[b]		DMF
	−1.84[b]		DMSO
	−1.93[b]		MeCN
$MoO_2[HN(CH_2CH_2S)_2]$ (3)	−0.98[a]	−1.05[b]	DMSO
	−1.02[a]	*c*	MeCN

[a] Fully irreversible. [b] Complicated by relatively slow reactions. [c] Ill-defined processes.

A perusal of the redox chemistry of known six-coordinate Mo(VI) complexes does not allow one to rationalize the redox propensity in terms of the different donor atom sets around the MoO_2^{2+} unit. In particular, as regards the first Mo(VI)/Mo(V) or Mo(VI)/Mo(IV) step, one may find (i) The $MoO_2[O_4]$ assembly exhibits either reversible[34a,36a,b] or irreversible[36c] electron transfers. The same result is observed for the $MoO_2[S_4]$ (reversible, ref 37a; irreversible, ref 37b-d), $MoO_2[N_2S_2]$ (reversible, refs 14, 34c, 38a, 39a; irreversible, refs 18, 38a, 39b-e), and $MoO_2[N_2SO]$ sets.[18,39c] (ii) The $MoO_2[N_2O_2]$,[18,34b,38] $MoO_2[S_2O_2]$,[37d,40] and $MoO_2[N_3S]$[41] systems undergo an irreversible reduction. (iii) The $MoO_2[N_3Br]$ system undergoes a reversible reduction.[42] A minor uncertainty apparently holds for the formally five-coordinate Mo(VI). In fact, (i) the $MoO_2[NSO]$[14,24,43] complexes as well as the $MoO_2[NO_2]$[22,44] ones are always irreversibly reduced, and (ii) the $MoO_2[NS_2]$ system is reversibly reduced.[22] It is therefore evident that subtle stereochemical features govern the redox aptitude of dioxomolybdenum(VI) complexes.

Reactivity. The potential of **1–3** to act as oxidants toward triphenylphosphine and some substrates of biological interest (*p*-thiocresol, thioanisole, benzyl alcohol, benzaldehyde) has been investigated in either DMF or DMSO solutions.

Irrespective of the solvent, complex **3** reacts only with triphenylphosphine and *p*-thiocresol. Analysis of the reaction products shows the reactions to have the following stoichiometries:

$$2MoO_2[HN(CH_2CH_2S)_2] + PPh_3 \rightarrow OPPh_3 + Mo_2O_3[HN(CH_2CH_2S)_2]_2 \quad (2)$$

$$2MoO_2[HN(CH_2CH_2S)_2] + 2CH_3C_6H_4SH \rightarrow CH_3C_6H_4S\text{–}SC_6H_4CH_3 + Mo_2O_3[HN(CH_2CH_2S)_2]_2 + H_2O \quad (3)$$

The reaction with *p*-thiocresol is immediate at room temperature, whereas PPh_3 is oxidized to $OPPh_3$ only at temperatures higher than 60 °C (at 80 °C the reaction is complete in ca. 2 h). In the course of both reactions the starting Mo(VI) complex is transformed into the dimeric Mo(V) complex $Mo_2O_3[HN(CH_2CH_2S)_2]_2$ (**4**).

Dimerization of the molybdenum precursor commonly occurs in similar oxidation reactions, particularly when the complex carries a nonbulky ligand.[1a,14,45,46] In contrast, stable monomeric $Mo^{IV}O^{2+}$ complexes are generally obtained with sterically hindered ligands. In this case, the reactions of the Mo(VI) precursors are stoichiometric in DMF solutions and generally catalytic in DMSO due to oxygen abstraction from the solvent, which thus regenerates the starting dioxomolybdenum(VI) species.[22,47-51]

Complexes **1** and **2** do not react with any of the substrates under investigation even at 100 °C. This finding suggests that the oxo-transfer ability of dioxomolybdenum(VI) complexes depends on the donor-atom set, in particular, the presence of at least one sulfur donor atom seems to be of mandatory importance.[22,24,41]

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Supplementary Material Available: Table S1 provides hydrogen atom locations for **3**, and Table S2 lists a complete set of crystallographic data for **3** (2 pages). Ordering information is given on any current masthead page.

(36) (a) Charney, L. M.; Schultz, F. A. *Inorg. Chem.* **1980**, *19*, 1527. (b) Charney, L. M.; Finklea, H. O.; Schultz, F. A. *Inorg. Chem.* **1982**, *21*, 549. (c) Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 1322.
(37) (a) Kaul, B. B.; Enemark, J. H.; Merbs, S. L.; Spence, J. T. *J. Am. Chem. Soc.* **1985**, *107*, 2885. (b) De Hayes, L. J.; Faulkner, H. C.; Doub, W. H., Jr.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 2110. (c) Chaudhury, M. *J. Chem. Soc. Dalton Trans.* **1984**, 115. (d) Ueyama, N.; Yoshinaga, N.; Nakamura, A. *J. Chem. Soc. Dalton Trans.* **1990**, 387.
(38) (a) Taylor, R. D.; Street, J. P.; Minelli, M.; Spence, J. T. *Inorg. Chem.* **1978**, *17*, 3207. (b) Rajan, O. A.; Spence, J. T.; Leman, C.; Minelli, M.; Sato, M.; Enemark, J. H.; Kroneck, P. M. H.; Sulger, K. *Inorg. Chem.* **1983**, *22*, 3065. (c) Mohanty, R. N.; Chakravorty, V.; Dash, K. C. *Polyhedron* **1991**, *10*, 33.
(39) (a) Spence, J. T.; Minelli, M.; Kroneck, P. *J. Am. Chem. Soc.* **1980**, *102*, 4538. (b) Purohit, S.; Koley, A. P.; Prasad, L. S.; Manoharan, P. T.; Ghosh, S. *Inorg. Chem.* **1989**, *28*, 3735. (c) Purohit, S.; Koley, A. P.; Ghosh, S. *Polyhedron* **1990**, *9*, 881. (d) Corbin, J. L.; Miller, K. F.; Pariyadath, N.; Heinecke, J.; Bruce, A. E.; Wherland, S.; Stiefel, E. I. *Inorg. Chem.* **1984**, *23*, 3404. (e) Küsthardt, U.; Albach, R. W.; Kiprof, P. *Inorg. Chem.* **1993**, *32*, 1838.
(40) (a) Cliff, C. A.; Fallon, G. D.; Gatehouse, B. M.; Murray, K. S.; Newman, P. J. *Inorg. Chem.* **1980**, *19*, 773. (b) Llopis, E.; Doménech, A.; Ramirez, J. A.; Cervilla, A.; Palanca, P.; Picher, T., Sanz, V. *Inorg. Chim. Acta.* **1991**, *189*, 29.
(41) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 3044.
(42) Backes-Dahman, G.; Herrmann, W.; Wieghardt, K.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 485.
(43) (a) Bhattacharjee, S.; Bhattacharyya, R. *J. Chem. Soc. Dalton Trans.* **1992**, 1357. (b) Bustos, C.; Burckhardt, O.; Schrebler, R.; Carrillo, D.; Arif, A. M.; Cowley, A. H.; Nunn, C. M. *Inorg. Chem.* **1990**, *29*, 3996.
(44) Topich, J. *Inorg. Chem.* **1981**, *20*, 3704.
(45) Speier, G. *Inorg. Chim. Acta* **1979**, *32*, 139.
(46) Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057.
(47) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925.
(48) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401; and reference therein.
(49) Xiao, Z.; Young, C. G.; Enemark, J. H.; Wedd, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 9194.
(50) Schultz, B. E.; Holm, R. H. *Inorg. Chem.* **1993**, *32*, 4244.
(51) Schultz, B. E.; Gheller, S. F.; Muetterties, M. C.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 2714.