Preparation and Properties of Tripodal and Linear Tetradentate N,S-Donor Ligands and their Complexes Containing the MoO_2^{2+} Core

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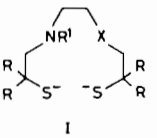
New linear and tripodal tetradentate ligands, LH_2, are reported and their syntheses are described. The new linear ligands L = $HSCH_2CH_2SCH_2CH_2NRCH_2CR_2SH$, R = H, CH_3) and the new tripodal ligands $N(CH_2CH_2SH)_2CH_2Z$, Z = CH_2NH_2, $CH_2N(CH_3)_2$, $CH_2N(C_2H_5)_2$, CH_2SCH_3 and CO_2^- were synthesized. The known linear ligands $HSCH_2CH_2NCH_3(CH_2)_nNCH_3CH_2CH_2SH$ (n = 2, 3) and $HSCR_2CH_2NHCH_2CH_2NHCH_2CR_2SH$ (R = H, CH_3) were also utilized. These ligands react with $MoO_2(acac)_2$ in CH_3OH to yield MoO_2L complexes in high yield. Infra-red and ^1H nmr spectra provide evidence to supplement X-ray crystallographic results reported elsewhere for selected numbers of the series. Octahedral structures with cis *MoO_2^{2+} groupings are assigned. Solution ^1H nmr studies are consistent with a* trans *placement of the two thiolate donors in agreement with the X-ray studies.*

Introduction

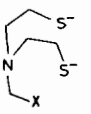
Multidentate ligands have played a key role in the development of modern coordination chemistry [2–5]. Recently, interest in multidentate ligands has been heightened by the realization that these ligands potentially provide to the metal a controlled coordination sphere which may mimic the function of the protein in metalloenzymes [6–8]. This paper presents some new N,S- and O-donor tetradentate ligands which may prove useful in tailoring or controlling metal coordination spheres. Complexes of these ligands with hexavalent MoO_2^{2+} cores are reported.

Coordination of molybdenum with S-donor ligands has been implicated at the active sites of molybdoenzymes [8–10]. In Mo-enzymes other than nitrogenase it is found that, in addition, oxo groups are bound directly to Mo [11–13]. In a number of cases the VI oxidation state has been identified in oxidized forms of the enzymes [9–14], leading us to investigate oxo molybdenum(VI) complexes with tetradentate ligands. These tetradentate ligands fall in two general categories, linear (**I**) and tripodal (**II**)



I

R = H, CH_3
R' = H, CH_3
X = NH, NCH_3, S



II

X = CH_2NH_2, $CH_2N(CH_3)_2$, $CH_2N(C_2H_5)_2$, SCH_3, COO^-

Of these ligands two of the linear variety were previously known [15, 16] and their Mo(VI) complexes have also been recently reported by Zubieta and coworkers [17, 18]. The remaining ligands were synthesized as part of this study.

The tripodal ligands are particularly significant. These ligands must, upon wrapping around a six-coordinate metal, leave two *cis* open sites in the metal coordination sphere. In hexacoordinate *cis*-MoO_2^{2+} complexes, the tripodal ligands are ideally suited to occupy the four remaining coordination sites. Moreover, if one of the oxo ligands is removed, the tripodal ligand (unlike the linear ligand) cannot rearrange to occupy the position *cis* to the remaining oxo. In a $4d_{z^2}$, Mo(IV) mono oxo complex the two 'd' electrons lie in a d_{xy} orbital where z is the oxo direction. By symmetry the two electrons are only available to a ligand or substrate that lies *cis* to the oxo. The tripodal ligand forces the remaining open site to be in the *cis*-position where the electron density is accessible.

This paper reports the synthesis of the ligands LH_2 and their Mo(VI) complexes, MoO_2L. Some of these results have been previously briefly communicated [19, 20]. Structural details of $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$ [21]. $MoO_2[(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2]$ [22] and

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$MoO_2[(SCH_2CH_2)_2NCH_2CH_2SCH_3]$ [22] are reported elsewhere. A structural study of $MoO_2(SCH_2CH_2SCH_2CH_2NHCH_2CH_2S)$ has been reported previously [18]. Independently, Zubieta *et al.* have also reported the synthesis [17] and structures [18] $MoO_2[SCH_2CH_2N(CH_3)(CH_2)_nN(CH_3)CH_2CH_2S]$, (n = 2, 3).

Experimental

Chemicals and Manipulations

Dioxomolybdenum(VI)bis(acetylacetonate), $MoO_2(acac)_2$, was prepared from ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and acetylacetone according to the procedure of Jones [23]. $H_2NCH_2CH_2SH\cdot HCl$ and $(CH_3)_2NCH_2CH_2SH\cdot HCl$ were purchased from Aldrich Chemical Co. and Parish Chemical Co., respectively. The latter was recrystallized twice from i-propanol/dioxane/$(C_2H_5)_2O$. $(C_4H_9)_4NPF_6$ was prepared from $(C_4H_9)_4NBr$ and KPF_6 according to the procedure of Sawyer and Roberts [24]. It was recrystallized from hot ethyl acetate/pentane. Acetonitrile was distilled from P_2O_5 and stored over molecular sieves. DMF was dried over molecular sieves, distilled under reduced pressure, and stored (−20 °C) over molecular sieves. N,N-dimethylethylenediamine, Adogen 464, bis(2-chloroethyl)amine hydrochloride and benzyl mercaptan were obtained from Aldrich Chem. Co. Other chemicals and solvents were reagent grade and used without further purification. H_2O labeled with ^{18}O (>90%) and ^{17}O(~40%) was obtained from Mound Laboratory. Manipulation of free thiols was done under argon. Thiol titrations were adapted from the literature [25] (0.05 *N* ethanolic I_2/KI, dead-stop endpoint).

Physical Measurements

Melting points were taken on a hot stage microscope and are corrected. Infrared spectra were recorded with a Beckman IR 20A spectrometer. Solid state spectra were obtained from KBr discs and also from nujol mulls in some cases. Solution spectra were obtained in CH_3CN. Ultraviolet–visible spectra were recorded with a Cary 118 spectrophotometer using 1 cm quartz cells. Elemental analyses were carried out (at CFKRL) on a PE 240 elemental analyzer equipped with an MC 240 microjector from Control Equipment Corporation. Reduction potentials *vs.* a saturated calomel electrode were determined by cyclic voltammetry with a Princeton Applied Research Model 174 Electrochemistry System equipped with a platinum button electrode. The electrolyte solution, 0.1 *M* $(C_4H_9)_4NPF_6$ in DMF, was degassed with Ar. Sample concentration was 10^{-3} *M* and scan rates varied from 50 to 500 mV/sec. Molecular weights were determined in $C_2H_4Cl_2$ with a Hewlett-Packard 302B Vapor Pressure Osmometer at 37 °C calibrated with benzil. Data were analyzed by a least squares statistical method (H–P VPO operation manual). Conductance measurements were made with a Radiometer conductivity Meter and a Radiometer CDC104 electrode. ^1H NMR spectra of the ligands and some complexes were measured at 60 MHz on a Varian A60 Spectrometer. Chemical shifts are given in ppm downfield from internal tetramethylsilane and coupling constants are in Hz. ^1H nmr at 220 MHz were obtained at Indiana University, ^{17}O NMR Spectra were obtained in CH_2Cl_2 solutions also 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.

Ligand Preparations

N,N′-bis(2-mercaptoethyl)ethylenediamine [26], N,N′-bis(2-mercapto-2-methylpropyl)ethylenediamine [27], N,N′-bis(2-mercaptoethyl)-N,N′-dimethyl-ethylenediamine [15, 26], and N,N′-(2-mercaptoethyl)-N,N′-dimethylpropylenediamine [16] were prepared according to the literature. The last named ligand was further purified by vacuum distillation (b.p. 122–125 °C/0.05 mm).

N,N-bis(2-Mercaptoethyl)-N′,N′-diethylethylenediamine, $(HSCH_2CH_2)_2NCH_2CH_2N(C_2H_5)_2$

A solution of N,N-diethylethylenediamine (14.5 g, 0.125 mol, Eastman Chem.) in 40 ml of dry toluene was mixed with a solution of ethylene sulfide [28] (15 g, 0.25 mol) in 50 ml of dry toluene and allowed to stand 6–8 hr (sealed tube, argon flushed). The reaction mixture was then heated (110 °C oven) for 15 hr, cooled, and filtered to remove a small amount of polyethylene sulfide. The solvent was removed and the residual liquid fractionally distilled (Vigreux column) under reduced pressure to give N,N-bis(2mercaptoethyl)-N′,N′-diethylethylenediamine, 15.2 g (51%) as a colorless liquid boiling at 120 °C/0.12 mm. Thiol titration showed >92% of the expected value. NMR($CDCl_3$) showed a multiplet at 2.6 [$(CH_2)_2$ + CH_2(ethyl)], a singlet at 1.87 (SH) and a triplet with J = 7 at 1.02 [CH_3(ethyl)]. The dipicrate derivative separated from methanol as yellow needles (m.p. 151–52 °C, dec.) in 71% yield. *Anal.* Calcd. for $C_{22}H_{30}N_8O_{14}S_2$: C, 38.03; H, 4.35; N, 16.13. Found: C, 38.20; H, 4.37; N, 16.16.

The tridentate ligand $HSCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$ [29] was also recovered from this reaction in 22% yield as a colorless liquid boiling at 60 °C/0.12 mm. NMR($CDCl_3$) showed a multiplet at 2.7 [$(CH_2)_2$ + CH_2(ethyl)], a singlet at 1.67 (NH + SH) and a triplet at 1.02 with J = 7 [CH_3(ethyl)]. The

dipicrate derivative was obtained (methanol) as an oil (69.4%) which solidified on standing (m.p. 110–111 °C). *Anal.* Calcd. for $C_{20}H_{26}N_8O_{14}S$: C, 37.86; H, 4.13; N, 17.66; Found: C, 38.21; H, 4.19; N, 17.44.

N,N-bis-(2-Mercaptoethyl)-N',N'-dimethylethylenediamine, $(HSCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$

The reaction was carried out in the same manner (same scale) as used for the diethyl compound, except that the solutions of the reagents were mixed warm (40–50 °C) and immediately put in the 110 °C oven. If the reaction was allowed to stand at room temperature, more polymer and less product resulted. If the reaction was never heated, more than 85% of the ethylene sulfide appeared as polymer. Thus the desired reaction appeared to be favored by higher temperature. A reaction time of 5 hr was sufficient. Work up as above and distillation gave, N,N-bis(2-mercaptoethyl)-N',N'-dimethylethylenediamine, 11.8 g (45.4%) as a colorless liquid boiling at 102–4 °C/0.14 mm. Thiol titration showed >94% of the expected value. IR showed no ν(N–H) band and ν(S–H) as a broad band at 2520 cm^{-1}. NMR ($CDCl_3$) showed a multiplet at 2.4–2.8 [$(CH_2)_2$], a singlet at 2.23 [$(CH_3)_2N$] and a singlet at 1.90 (SH). A dipicrate derivative was obtained 79% yield (methanol). The yellow solid melted at 151.5–153.5°. *Anal.* Calcd. for $C_{20}H_{26}N_8O_{14}S_2$: C, 36.04; H, 3.93; N, 16.81. Found: C, 36.20; H, 3.86; N, 16.82.

N,N-bis(2-mercaptoethyl)2-methylthioethylamine $(HSCH_2CH_2)_2NCH_2CH_2SCH_3$

The reaction was run in the same manner as above but on one-half scale. A reaction time of 30 hr (110 °C) was used. The starting 2-methylthioethylamine was prepared by the addition of methyl mercaptan to ethyleneimine (76%, b.p. 48–50 °C/27 mm). Work up as before and distillation gave N,N-bis-(2-mercaptoethyl)2-methylthioethylamine, 7.1 g (61.3%) as a colorless liquid boiling at 114–116 °C/0.03 mm. Thiol titration showed 94% of the expected value. NMR ($CDCl_3$) showed a multiplet at 2.5–2.9 [$(CH_2)_2$], a singlet at 2.12 (CH_3-S), and a singlet at 1.04 (S-H). A picrate derivative was obtained from methanol in 88% yield. It separated as an oil which solidified on cooling (m.p. 95–100 °C). *Anal.* Calcd. for $C_{13}H_{20}N_4O_7S_3$: C, 35.44; H, 4.58; N, 12.72. Found: C, 35.32; H, 4.47; N, 12.73.

N-(2-mercaptoethyl)-2-methylthioethylamine, 1 g (12%) was also obtained from the reaction as a colorless liquid boiling at 68 °C/0.04 mm. Thiol titration showed 96.9% of the expected value. NMR ($CDCl_3$) showed an A_2B_2 pattern at 2.75 [$(CH_2)_2$], a singlet at 2.12 (SCH_3) and a singlet at 1.69 (S-H + N-H). A picrate derivative did not separate from methanol. A crystalline disulfide dihydroiodide derivative was formed from the thiol titration in ethanol (m.p. 210.5–212 °C). *Anal.* Calcd. for $C_{10}H_{26}I_2N_2S_4$: C, 21.58; H, 4.71; N, 5.03. Found: C, 21.45; H, 4.87; N, 4.97.

If a 1:1 ratio of amine and ethylene sulfide was used in the reaction, the tridentate ligand was obtained in 48% yield and the tetradentate ligand in only 15% yield.

Bis(2-benzylthioethyl)amine, $(C_6H_5CH_2SCH_2CH_2)_2NH$

This compound was the first intermediate required in the preparation of $(HSCH_2CH_2)_2NCH_2CH_2NH_2$ and $(HSCH_2CH_2)_2NCH_2COOH$.

A solution of sodium ethoxide (from 32.3 g of Na and 460 ml abs. ethanol) was dropped into a stirred ice-cold solution of bis(2-chloroethyl)amine hydrochloride (0.465 mol) and benzyl mercaptan (0.94 mol) in 460 ml abs. ethanol. The solution was slowly heated to reflux, then stirred and refluxed for 2.5 hr. After chilling, NaCl was filtered off and washed with ethanol. The solvent was evaporated, and the residual oil taken up in benzene (250 ml) and washed with two 50-ml portions of water. Purification was effected via the hydrochloride salt. Benzene was removed, the crude product was dissolved in abs. ethanol (400 ml), and conc. HCl (42 ml) added. After addition of ether (800 ml) and chilling to –20 °C the crystalline (flat needles) salt was filtered, washed (6:1 ethanol–ether, then ether), and vacuum dried (66.9% yield, m.p. 127–127.5 °C). *Anal.* Calcd. for $C_{18}H_{23}ClNS_2$: C, 61.25; H, 6.57; N, 3.97. Found: C, 61.00; H, 6.68; N, 3.86.

To obtain the free base the hydrochloride salt (0.1 mol) was stirred with 200 ml of benzene and 55 ml of 2 *N* NaOH until no solid remained. Removal of the solvent from the organic phase gave the free ligand as an essentially colorless oil. During the course of this work, an independent synthesis of this compound appeared, using a different method [30].

N,N'-bis(2-Benzylthioethyl)-2-aminoacetonitrile·hydrochloride, $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CN\cdot HCl$

This molecule is a precursor to the ligands $(HSCH_2CH_2)_2NCH_2COOH$ and $(HSCH_2CH_2)_2NCH_2CH_2NH_2$. Aqueous HCHO (50 mmol, 4.2 ml) was dropped into a rapidly stirred mixture of $NaHSO_3$ (50 mmol) and DMF (15 ml). Stirring was continued while the mixture was heated (50 °C) for 30 min. After 30 additional min at room temperature, the amine $(C_6H_5CH_2SCH_2CH_2)_2NH$ (free base form, 40 mmol) was added along with 5 ml DMF followed by aqueous KCN (54 mmol in 6 ml of water). Efficient stirring was continued for 10 hr while heating (oil bath) at 50– 55 °C. The crude product was separated by addition of ether (3 × 60 ml), stirring, and decanting the upper phase. The

hydrochloride salt was obtained by passing HCl gas into this ether solution. After chilling, filtering and washing (ether) the yield was 89% of crystalline product, m.p. 116–118 °C (rapid heating). The compound was essentially analytically pure at this stage but could be recrystallized from chloroform–ether. *Anal.* Calcd. for $C_{20}H_{25}ClN_2S_2$: C, 61.12; H, 6.41; N, 7.13. Found: C, 61.06; H, 6.69; N, 7.06.

NMR ($CDCl_3$ + few drops CF_3CO_2H) displays a singlet at 7.32 (aromatic H), a singlet at 4.20 (CH_2-CN), a singlet at 3.77 (benzyl-CH_2) and multiplet at 1.99 [$(CH_2)_2$].

N,N'-bis(2-Benzylthioethyl)ethylenediamine, $(C_6H_5CH_2SCH_2CH_2)NCH_2CH_2NH_2$

The nitrile hydrochloride $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CN{\cdot}HCl$ (50.9 mmol) was first converted to the free base by stirring with 200 ml $CHCl_3$ and 60 ml of 1 *N* NaOH. The organic layer was separated, the solvent removed, and the oily base dissolved in dry ether (100 ml). This solution was added (30 min) to a stirred suspension of $LiAlH_4$ (0.10 mol) in dry ether (100 ml), refluxed for 2.5 h, and hydrolyzed by the careful addition of saturated aqueous sodium potassium tartrate (100 ml). The ether layer was washed with water, (2 × 50 ml) dried (K_2CO_3), and the solvent removed to yield the crude amine as a colorless oil. Purification was effected *via* the dipicrate salt. (A crystalline hydrochloride could not be obtained). The crude amine in ethanol (100 ml) was added to a boiling solution of picric acid (109 mmols) in ethanol (250 ml), the crystalline picrate filtered after chilling (freezer), washed (ethanol), and vacuum dried (yield, 86.5%, m.p. 160–61 °C). An analytical sample was recrystallized from ethanol. *Anal.*: Calcd. for $C_{32}H_{34}N_8O_{14}S_2$: C, 46.94; H, 4.19; N, 13.68. Found: C, 46.79; H, 4.04; N, 13.73.

The dipicrate was converted to the free amine by stirring with benzene (500 ml) and 0.2 *N* NaOH (750 ml). The organic layer was further washed with NaOH (2 × 100 ml), water (100 ml), and dried over K_2CO_3. Removal of the solvent yielded the amine as a pale amber oil.

NMR ($CDCl_3$) displayed a singlet at 7.32 (aromatic-H), a singlet at 3.72 (benzyl-CH_2) a multiplet at 2.53 [$(CH_2)_2$] and a broad singlet at 1.37 (N-H).

N,N'-bis(2-Mercaptoethyl)ethylenediamine, $(HSCH_2CH_2)_2NCH_2CH_2NH_2$

The amine $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CH_2NH_2$ (8.58 mmol) in ether (10 ml) was added to 100 ml of liquid NH_3. With stirring Na was added until a permanent blue color was obtained. The NH_3 solvent was swept away with argon, and the residue partitioned between ether (70 ml) and 1 *N* HCl (70 ml). The aqueous phase was evaporated to dryness leaving the dihydrochloride salt of the product which was extracted into boiling absolute ethanol:2-propanol (2:1, 100 ml) and filtered hot to remove salt. $CHCl_3$ (50 ml) was added and, after chilling, filtration and washing with 2-propanol the product was obtained as colorless plates (57%, m.p. 113–115 °C). Titration showed 95% of the expected thiol. *Anal.*: Calcd. for $C_6H_{18}Cl_2N_2S_2$: C, 28.46; H, 7.16; N, 11.06. Found: 28.34; H, 7.33; N, 10.86.

N,N'-bis(2-Benzylthioethyl)-2-aminoacetic acid, $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CO_2H$

The nitrile hydrochloride $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CN{\cdot}HCl$ (15 mmol) in abs. ethanol (100 ml) was stirred and saturated with HCl gas (40 °C). The solution was further stirred and warmed (oil bath, 40 °C) for 18–20 hr, and the solvent removed. The residue was taken up in $CHCl_3$, washed with water, 5% $NaHCO_3$ (2 × 30 ml), and again water. Evaporation of the organic phase left the ester $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CO_2C_2H_5$ as a pale yellow oil. It was not further characterized (except for NMR). NMR ($CDCl_3$) showed a singlet at 7.31 (Ar-H); a quartet at 4.15 (ester CH_2), a singlet at 3.71 (benzyl CH_2), a singlet at 3.32 (CH_2CO_2) and a triplet at 2.91 (ester CH_3).

Hydrolysis was accomplished by refluxing with 1 *N* NaOH (40 ml), ethanol (20 ml), and Adogen 464 (150 mg) as the phase transfer catalyst, for 1½ hr. (Hydrolysis was very slow otherwise, apparently due to insolubility of the ester.) A single phase resulted. Water (30 ml) was added and the mixture was extracted with benzene (25 ml). The benzene was extracted with 20% ethanol–water (3 × 20 ml) and the combined aqueous phase was adjusted to pH 3.5 with conc. HCl. The product acid precipitated in 85.3% yield and was washed with water. It could be recrystallized from 2:1 methanol–water (m.p. 113.5–114 °C). *Anal.*: Calcd. for $C_{20}H_{25}NO_2S_2$: C, 63.96; H, 6.71; N, 3.73. Found: C, 64.01; H, 6.89; N, 3.86. NMR in 2:1, $CDCl_3$:CF_3COOH showed a singlet at 7.38 (aromatic-H) and a complex multiplet for the methylene protons.

N,N-bis(2-Mercaptoethyl)2-aminoacetic acid, $(HSCH_2CH_2)_2NCH_2COOH$

The acid $(C_6H_5CH_2SCH_2CH_2)_2CH_2COOH$, (5.34 mmol) was cleaved in the same manner as the amine $(C_6H_5CH_2SCH_2CH_2)_2NCH_2CH_2NH_2$ using 100 ml of NH_3 and 10 ml of ether. The aqueous acidic phase was evaporated to give a gum plus salt. The gum was extracted into abs. ethanol, and the solvent removed. Attempted crystallization of the residual gum from ethanol–ether was not successful. The gum was dissolved in water (5 ml) and the pH adjusted to *ca.* 4 with NaOH. This solution of the product was deemed sufficiently pure to be used for preparation of the Mo(VI) complex (*vide infra*).

TABLE I. Analytical Data for MoO_2L Complexes.

Complex	Color	Yield		C	H	N
L = $SCH_2CH_2NHCH_2CH_2NHCH_2CH_2S$	yellow	93%	c	23.54	4.57	9.15
			f	23.92	4.98	9.01
L = $SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S$	orange	83%	c	28.74	5.43	8.38
			f	28.83	5.39	8.40
L = $SCH_2CH_2N(CH_3)CH_2CH_2CH_2N(CH_3)CH_2CH_2S$	orange	66%	c	31.03	5.79	8.04
			f	30.24	6.04	7.88
L = $SC(CH_3)_2CH_2NCH_2CH_2NCH_2C(CH_3)_2S$	yellow	81%	c	33.15	6.12	7.73
			f	32.85	6.26	7.79
L = $SCH_2CH_2NHCH_2CH_2SCH_2CH_2S$	orange-brown	93%	c	22.30	4.02	4.33
			f	22.40	4.14	4.22
L = $SCH_2CH_2N(CH_3)CH_2CH_2SCH_2CH_2S$	orange	86%	c	24.93	4.45	4.15
			f	25.05	4.55	4.05
L = $(SCH_2CH_2)_2NCH_2CH_2NH_2$	orange	85%	c	23.53	4.61	9.15
			f	23.36	4.90	8.62
L = $(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$	orange	77%	c	28.74	5.43	8.38
			f	28.48	5.47	8.43
L = $(SCH_2CH_2)_2NCH_2CH_2N(C_2H_5)_2$	orange	65%	c	33.15	6.12	7.73
			f	32.79	6.17	7.81
L = $(SCH_2CH_2)_2NCH_2CH_2SCH_3$	orange	88%	c	24.92	4.48	4.15
			f	25.38	4.52	4.18
L = $[(SCH_2CH_2)_2NCH_2COO^-][(C_6H_5)_4As^+$ salt]	orange		c	51.21	4.30	2.00
			f	51.62	4.20	1.99

S-(2-Mercaptoethyl)-2-aminoethanethiol, $NH_2CH_2CH_2SCH_2CH_2SH$

A solution of ethyleneimine (0.22 mol) in 50 ml of methanol was added over 1 hr (20–30 °C) to a stirred solution of 1,2-ethanedithiol (0.505 mol) in methanol (50 ml). After stirring overnight, the solvent was removed and the residue fractionally distilled (Vigreux column). After the excess dithiol was collected, the product boiling at 64 °C/0.05 mm (21.14 g, 70.3%) was collected as a colorless oil which solidified on standing (m.p. 36–41 °C). NMR ($CDCl_3$) displayed an A_2B_2 pattern at 2.70 [$S(CH_2)_2N$], a singlet at 2.68 [$S(CH_2)_2S$] and a singlet at 1.49 (NH + SH).

N,S-bis(2-Mercaptoethyl)-2-aminoethanethiol, $HSCH_2CH_2NHCH_2CH_2SCH_2CH_2SH$

A solution of $HSCH_2CH_2SCH_2CH_2NH_2$ (50.2 mmol) and ethylene sulfide (50.5 mmol) in dry toluene (40 ml) was heated in a sealed tube (argon) for 20 hr at 110–115 °C. Removal of the solvent and vacuum fractional distillation (Vigreux column) gave 5.4 g (54.6%) of product boiling at 142–4 °C/0.02 mm. Thiol titration showed more than 93% of the expected value.

NMR($CDCl_3$) displayed a multiplet at 2.5–3 [$(CH_2)_2$] and a singlet 1.6 (NH + SH).

S-2-(2-Mercaptoethyl)-N-methyl-2-aminoethanethiol, $CH_3NHCH_2CH_2SCH_2CH_2SH$

N-(2-methylaminoethyl)sulfuric acid [31] (0.10 mol), ethanedithiol (0.10 mol), 25 ml H_2O, and 20 ml of 10 *N* NaOH were stirred at room temperature (2 hr) under argon, then refluxed for 5 hr. The upper oily layer was separated and fractionated under vacuum (Vigreux) to give the desired thiol in 18% yield (b.p. 64–5 °C/0.03 mm). Titration showed 98.6% of the expected thiol content. NMR ($CDCl_3$) displayed a multiplet at 2.77 [$(CH_2)_2$], a singlet at 2.46 (CH_3N) and NMR ($CDCl_3$) a singlet at 1.58 (NH + SH).

A higher boiling fraction (114–17 °C/0.03 mm), apparently (by NMR) S,S'-bis(2-methylaminoethyl)-ethanedithiol, $CH_3NHCH_2CH_2SCH_2CH_2SCH_2CH_2NHCH_3$, was obtained in 18.2% yield.

N,S-bis(2-Mercaptoethyl)-N-methyl-2-aminoethanethiol, $HSCH_2CH_2N(CH_3)CH_2CH_2SCH_2CH_2SH$

The above *N*-methylamine $CH_3NHCH_2CH_2SCH_2CH_2SH$ (17.2 mmol) was mercaptoethylated in a manner identical to that used for the N–H analog. Simple distillation of the product gave an 88% yield of the desired thiol (b.p. 110–30 °C/0.2–0.25 mm) as a colorless liquid. Thiol titration gave >99% of the expected value. NMR ($CDCl_3$) gave a multiplet at 2.6–2.8 [$(CH_2)_2$], a singlet at 2.27 (NCH_3) and a broad singlet at 1.77 (SH).

Preparation of Complexes

All complexes were prepared by essentially the same method. The preparation of one complex is given in detail.

[N,N'-bis(2-methyl-2-thiolatopropyl)ethylenediamine]dioxomolybdenum(VI), $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$

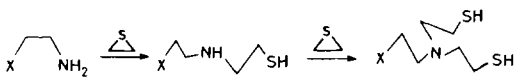
A solution of 2.63 g (11.2 mmol) of ligand in 25 ml of CH_3OH was added slowly to a filtered solution of 3.63 g (11.1 mmol) of $MoO_2(acac)_2$ in 75 ml of warm (~60 °C) CH_3OH. The color changed to brown-yellow and a bright yellow crystalline solid was deposited. The methanol was boiled for 30 minutes, allowed to cool to room temperature and filtered. The crystalline product was washed with methanol and dried with diethylether.

The complex $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SCH_3]$ was prepared at 0 °C in methanol due to its relative sensitivity toward reduction to $Mo_2O_3[(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2]$. Table I presents the analytical data, colors and yields for the complexes.

Results and Discussion

Synthesis of Ligands

Where applicable, direct mercaptoethylation of the appropriate amine with ethylene sulfide was found to be an extremely useful reaction. The tripodal tetradentate ligands resulted directly from this simple approach. Substantial amounts of the intermediate tridentate ligands were also formed, even though a 2:1 ratio of ethylene sulfide to amine was used:

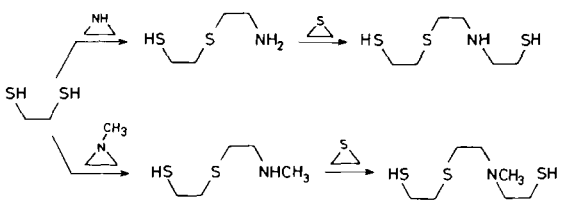


X = $N(CH_3)_2$, N , SCH_3

The tridentate ligands were also characterized and are discussed elsewhere [29]. Temperature control was found to be critical for X = $CH_2N(CH_3)_2$ as polyethylene sulfide was formed as the major product if care was not taken.

Attempted extension of this procedure to the tertiary thiol (by use of 2,2-dimethylethylene sulfide with N,N-dimethyl-ethylenediamine) resulted only in the tridentate ligand $(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2SH$ [29]. There was no evidence of the corresponding tripodal tetradentate being formed, possibly because of steric hindrance.

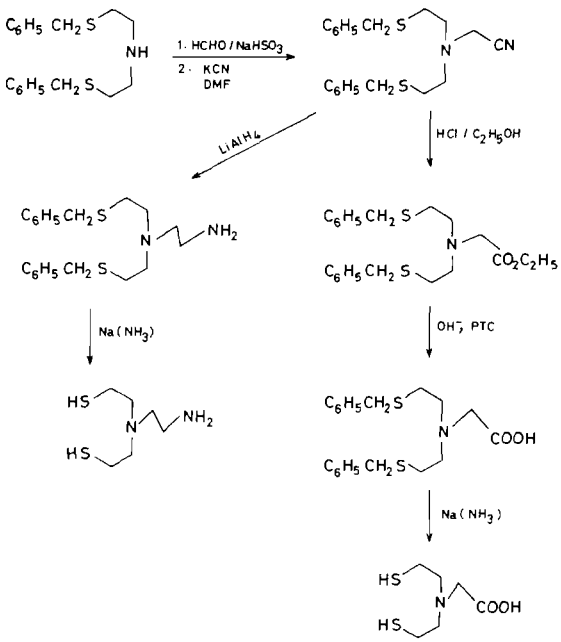
Linear tetradentate ligands could also be prepared by the mercaptoethylation reaction. The tridentate precursors were formed by the reaction of 1,2-ethanedithiol with ethyleneimine or N-methyl-ethyleneimine



(generated *in situ*) and then reacted with ethylene sulfide.

A different synthetic approach was needed for the tripodal tetradentate ligands where one of the pendent arms contains a COOH or NH_2 group. We devised Scheme I below which utilized a common intermediate.

Scheme I



The carboxylate-containing tripod was a gum which was characterized as the tetraphenylarsonium salt of its Mo(VI) complex (*vide infra*). All ligands gave satisfactory analyses and their nmr spectra are consistent with their respective formulations.

Synthesis and Properties of Complexes

The MoO_2L complexes were generally prepared by the reaction of $MoO_2(acac)_2$ with one equivalent of ligand in warm (~60 °C) methanol solution.

$$MoO_2(acac)_2 + LH_2 \longrightarrow MoO_2L + 2acacH$$

When the complex of the $-SCH_3$ tripod ligand was prepared from a warm solution, the product contained a small amount of a red-brown impurity which was tentatively identified as $Mo_2O_3[(CH_3SCH_2CH_2)N(CH_2CH_2S)_2]_2$ by electronic and infrared spectra. The electronic spectrum showed an absorption at 470 nm while the infrared showed weak bands at ~940 and 770 cm^{-1} due, respectively, to the terminal and bridging Mo–O stretches of the $Mo_2O_3^{4+}$ core. Reduction of $MoO_2[CH_3SCH_2CH_2N(CH_2CH_2S)_2]$ with $P(C_6H_5)_3$ [32] gave a complex presumed to be the Mo(V) complex $Mo_2O_3[CH_3$-

TABLE II. Infrared Spectra MoO_2L Complexes.[a]

Complex	IR	
	ν_a	ν_s
L = $SCH_2CH_2(CH_3)NCH_2CH_2CH_2N(CH_3)CH_2CH_2S$	932, 897	
L = $(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$	921, 893	
L = $(SCH_2CH_2)_2NCH_2CH_2SCH_3$	921, 891	
L = $SCH_2CH_2(CH_3)NCH_2CH_2SCH_2CH_2S$	917, 887	
L = $SCH_2CH_2NHCH_2CH_2SCH_2CH_2S$	916, 878, 870	
L = $SCH_2CH_2(CH_3)NCH_2CH_2N(CH_3)CH_2CH_2S$	913, 886	
L = $(SCH_2CH_2)_2NCH_2CH_2NH_2$	911, 888	
L = $[(SCH_2CH_2)_2NCH_2COO^-]$ $[(C_6H_5)_4As^+$ salt]	910, 885	
L = $SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S$	893, 870	
L = $SCH_2CH_2NHCH_2CH_2NHCH_2CH_2S$	892, 855	

[a]Arranged according to decreasing energy of the symmetric absorption.

$SCH_2CH_2N(CH_2CH_2S)_2]$ which displayed IR and electronic absorptions identical to those of the contaminant. Preparation of the Mo(VI) complex at 0 °C led to the isolation of pure MoO_2^{2+} complex. Other preparative reactions proceeded in good yield without complication. Analytical data are shown in Table I.

Solvents which proved useful for these complexes include CH_2Cl_2, $C_2H_4Cl_2$, CH_3CN, DMF and DMSO. In general complexes with methyl substituted nitrogen atoms are more soluble than the corresponding complexes which contain NH groups. The molecular weight of $MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)$-$CH_2CH_2S]$ was determined by vapor pressure osmometry in $C_2H_2Cl_2$ as 331 (calc. 334) confirming the mononuclear formulation for this complex. There is no reason to doubt the mononuclear nature of any of the complexes reported here.

Table II displays the infrared absorptions in the ν(Mo–O) region. Each of the complexed display intense absorptions in the 850–930 cm^{-1} region of the infrared spectrum. The two band pattern with a separation of ~30 cm^{-1} is assigned to the symmetric (a_1) and antisymmetric (b_1) stretching modes of a C_{2v} *cis*-MoO_2^{2+} group [9]. Isotopic labelling studies and Raman spectra (taken in collaboration with L. Willis and T. Loehr) are consistent with this assignment. For $MoO_2[(SCH_2CH_2)_2N(CH_2CH_2N(CH_3)_2]$, isotopic labelling with ^{18}O was accomplished by carrying out the preparation in the presence of a few drops of H_2O [18]. In the resultant complex, bands at 912 and 859 are assigned to the ^{16}O, ^{18}O substituted complex whereas bands at 874 and 851 cm^{-1} are assigned to the ^{18}O, ^{18}O substituted complex. The shifts are as expected for the mass difference between ^{16}O and ^{18}O. The lowest values for ν(Mo–O) are found in $MoO_2(SCH_2CH_2NHCH_2CH_2NHCH_2CH_2S)$ and may be due to intermolecular H bonding in the solid state.

The electronic spectral maxima are listed in Table III. The complexes with linear tetradentate ligands all

TABLE III. Electronic Absorptions of MoO_2L Complexes in CH_3CN.

MoO_2L Complex	λ		ϵ
	nm	cm^{-1}	
L = $SCH_2CH_2NHCH_2CH_2NHCH_2CH_2S$	390	25,640	sh
	356	28,100	4400
	281	35,600	4600
	245	40,800	6900
L = $SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S$	368	27,200	5130
	290	34,500	5130
	253	39.500	7180
	228	43,860	sh

(continued overleaf)

TABLE III. *(continued)*

MoO_2L Complex	λ		ϵ
	nm	cm^{-1}	
L = $SCH_2CH_2N(CH_3)CH_2CH_2CH_2N(CH_3)CH_2CH_2S$	368	27,200	4490
	270	37,000	sh 4620
	237	42,200	6620
L = $SC(CH_3)_2CH_2NCH_2CH_2NCH_2C(CH_3)_2S$	367	27,250	5710
	280	35,700	sh 4230
	250	40,000	sh 5750
L = $SCH_2CH_2NHCH_2CH_2SCH_2CH_2$	395	25,300	sh
	365	24,700	4900
	315	31,750	sh
	293	34,100	sh 3700
	249	40,200	sh
	234	43,700	8300
L = $SCH_2CH_2(CH_3)NCH_2CH_2SCH_2CH_2S$	360	27,800	4920
	320	31,250	sh 3750
	291	34,400	sh 4000
	252	39,700	sh
	235	42,550	10,200
L = $(SCH_2CH_2)_2NCH_2CH_2NH_2$	379	26,400	broad 3340
	315	31,750	sh
	286	35,000	5540
	233	42,900	9540
L = $(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$	391	25,600	broad 2930
	325	30,800	sh
	287	34,800	4430
	236	42,400	9530
L = $(SCH_2CH_2)_2NCH_2CH_2SCH_3$	366	27,300	sh
	350	28,600	sh
	326	30,600	sh
	286	35,000	sh
	248	40,300	sh

have λ_{max} at ~360 nm (range 356 to 368 nm) with extinction coefficients ~5000 (range 4400 to 5700.) The spectra of the tripodal ligand complexes show a broad absorption at ~380 (range 371 to 387 nm). The spectra are in most cases slightly solvent dependent. For example in $MoO_2(SCH_2CH_2N(CH_3)CH_2CH_2SCH_2CH_2S)$ the three bands at 360, 320 and 291 in CH_3CN shift to 371, 324 and 296 nm, respectively, in DMF. In one case, $MoO_2[CH_3SCH_2CH_2N(CH_2CH_2S)_2]$ a more dramatic effect is seen on changing from CH_3CN to CH_2Cl_2. The spectrum in CH_2Cl_2 appears simpler with a band at 375 and shoulder at 313 nm. The $-SCH_3$ arm of the tripod may be very weakly bound (Mo–S is ~2.8 Å [19, 22]) and in CH_3CN we may be observing a complex in which a CH_3CN ligand has replaced the thioether in the Mo coordination sphere.

Electrochemical data is shown in Table IV. All of the MoO_2L complexes with the exception of $MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]$, display irreversible behavior under the conditions employed. We confirm the finding of Zubieta and coworkers [17] that $MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]$ has a quasi-reversible wave (Δ = 69 mV) at −1.22 V. This is approximately in the middle of the range of reduction potentials for the MoO_2L complexes studied. $MoO_2[(SCH_2CH_2)_2NCH_2CH_2SCH_3)]$ has the highest reduction potential (least negative) and $[(C_6H_5)_4As]$ $MoO_2[(SCH_2CH_2)_2NCH_2COO^-]$ has the lowest reduction potential. The reason for the reversibility of the wave in the one exceptional case was not understood by Zubieta *et al.* [17] and unfortunately, we have no insight to add in this regard.

TABLE IV. Reduction Potentials of MoO_2L Complexes Measured by Cyclic Voltammetry.[a]

Complex	E_p
$MoO_2(SCH_2CH_2)_2NCH_2CH_2SCH_3$	−0.959[c]
$MoO_2SCH_2CH_2(CH_3)NCH_2CH_2SCH_2CH_2S$	−1.173[c]
$MoO_2(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2$	−1.202[c]
$MoO_2SCH_2CH_2NHCH_2CH_2SCH_2CH_2S$	−1.215[c]
$MoO_2SCH_2CH_2(CH_3)NCH_2CH_2N(CH_3)CH_2CH_2S$	−1.257, −1.188[d]
$MoO_2(SCH_2CH_2)_2NCH_2CH_2NH_2$	−1.292[c]
$MoO_2SCH_2CH_2NHCH_2CH_2NHCH_2CH_2S$	−1.351[c]
$MoO_2SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S$	−1.416[c]
$MoO_2[(SCH_2CH_2)_2NCH_2COO^-][(C_6H_5)_4As^+$ salt]	−1.505[c]
$MoO_2[SCH_2CH_2(CH_3)NCH_2CH_2CH_2N(CH_3)CH_2CH_2S]$	−1.667[c]

[a]Pt button *vs.* S.C.E., 1 m*M* solutions in DMF with 0.1 *M* $[(C_4H_9)_4N][PF_6]$; scan rate 0.5 V/sec, range (+0.5)–(−2.0) V. [b]Peak potential of reduction arranged according to decreasing potential. [c]Irreversible. [d]Quasi-reversible, 69 mV peak separation.

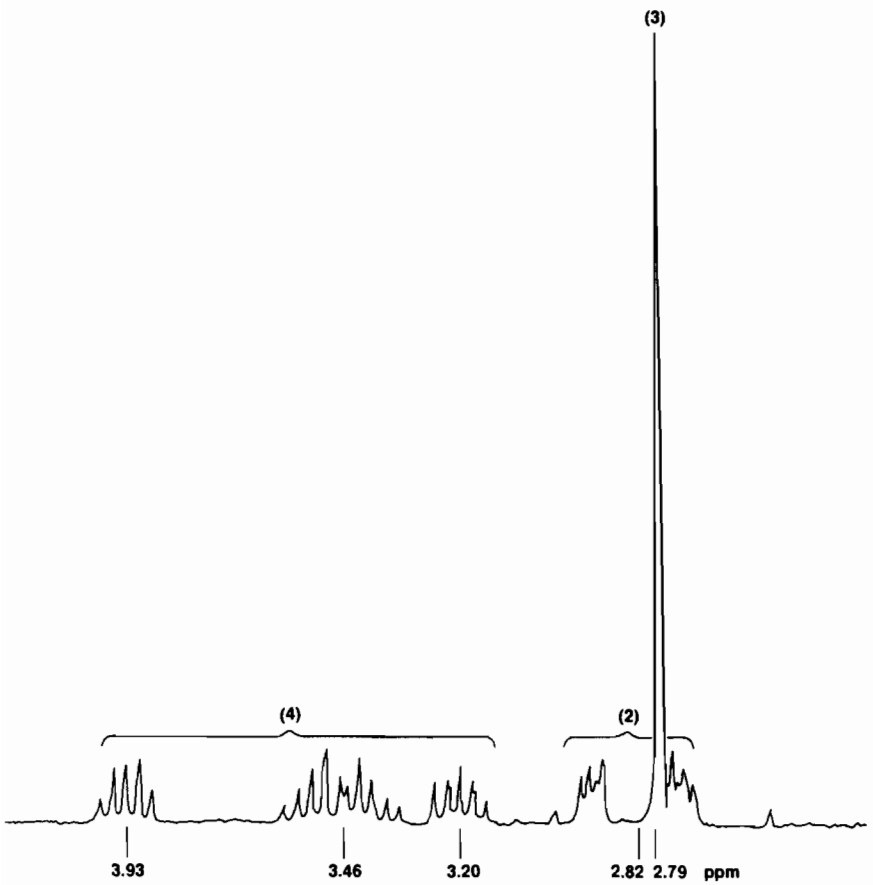


Fig. 1. 220 MHz ^1H nmr of $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$.

Five of the complexes discussed here have been subjected to full X-ray crystallographic determinations [18–22]. The two tripodal complexes and the three linear complexes have been shown to have six-coordinate near octahedral structures with *cis*-MoO_2^{2+} grouping. The thiolate donors occupy the sites which are *cis* to both oxo groups and are displayed *trans* to each other. Evidence from proton nmr is consistent with the adoption of the same structure in solution.

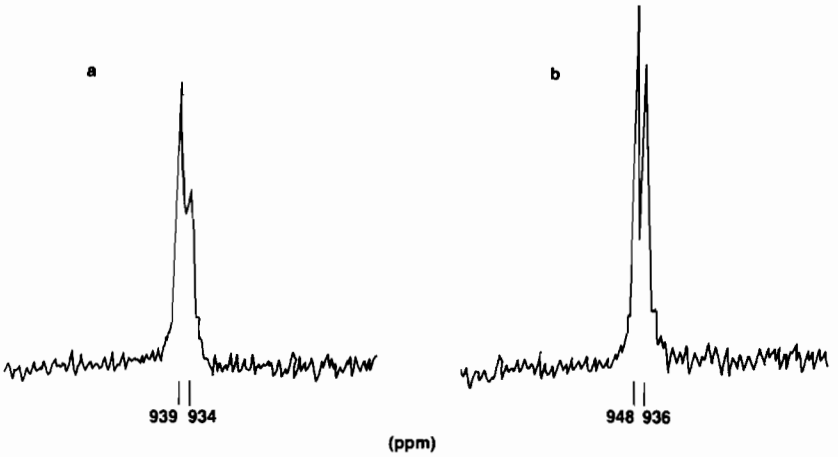


Fig. 2. ^{17}O nmr spectra of MoO_2L complexes.

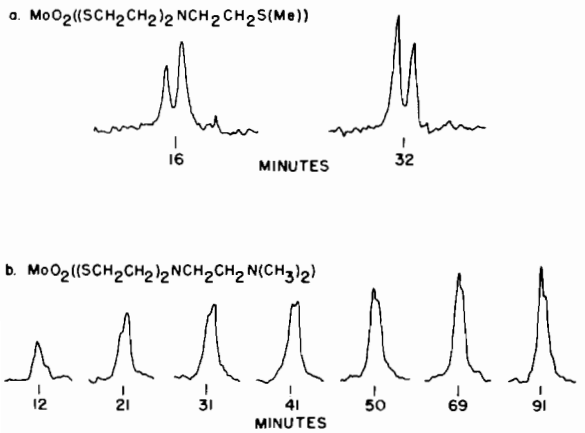


Fig. 3. Time dependence of the appearance of the ^{17}O nmr spectra of MoO_2L_2 complexes.

NMR Studies

Both proton and ^{17}O nmr spectra have been obtained for most of the complexes. The proton nmr spectra as might be expected are quite complex due to the presence of several different kinds of CH_2 groups in each of the complexes. As an example the nmr spectrum of $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$ is displayed in Fig. 1. It is clear that, even though this complex is expected on the average to have a mirror plane the spectrum is still quite detailed. However, the observation of a single peak at 1.79 ppm assignable to the N-CH_3 protons suggests that in solution in a time averaged sense the complex has Cs symmetry. The remaining complexity arises from the presence of four distinct types of CH_2 groups which are adjacent to S, tripod N (two different types) and $N(CH_3)_2$ respectively. Further, in each CH_2 in the thiolate arms of the ligand, ring flipping does not average the CH_2 protons. Therefore a complex ABCD pattern might be expected for the $(CH_2)_2$ grouping of the thiolate arms while a simpler A_2B_2 pattern might be expected for the $N(CH_3)_2$ arm of the tripod. We have not attempted detailed assignment of the spectrum which, nonetheless, is consistent with the presence of a solution structure similar to that found in the solid state.

^{17}O NMR spectroscopy has given valuable information on oxo molybdenum compounds [33, 34]. Complexes labeled with ^{17}O could be readily obtained by adding a few drops of labeled H_2O^{17} during the preparation. ^{17}O nmr spectra for two of the tripodal-ligand complexes are displayed in Fig. 2. The tripodal ligands have inequivalent oxygen atoms and indeed each displays a doublet in the terminal oxo region. As shown in Fig. 3, if H_2O^{17} is added to the solution of natural abundance $MoO_2[(SCH_2CH_2)_2NCH_2CH_2N(CH_3)_2]$ in CH_3CN the low field ^{17}O signal appears earlier than the high field signal indicating a differential rate of exchange of the two oxygen atoms. In the absence of further information a specific assignment of the peaks cannot be made. However, we may speculate that the oxygen *trans* to the more closely bound tripodal nitrogen would exchange more rapidly than the oxygen *trans* to the more weakly bound $N(CH_3)_2$ group. This would be consistent with the general finding [33, 34] that more tightly bound oxygen atoms give signals at lower field.

Conclusions

New tetradentate ligands LH_2 have been reported as have their MoO_2^{2+} complexes. The ligand preparations and the ligands themselves should serve others interested in the design and synthesis of polydentate ligands. The MoO_2L complexes whose X-ray structures are discussed elsewhere have solution behavior consistent with relative rigidity on the nmr time scale. ^{17}O NMR spectra show that oxo ligands display a range of chemical shifts and ex-

change rates which may be useful in the characterization of new oxo molybdenum complexes, molybdoenzymes and their cofactors.

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