that this contribution is geometry dependent and, in addition, may be important. Since the changes in J for the present compounds appear to be in the opposite direction of what would be expected upon consideration of the antiferromagnetic term only, it is possible that a description of the relative magnetic properties of Fe_2O_2 compounds requires an explicit consideration of both J_{AF} and J_F. Further work on additional members of this series of oxygen-bridged iron(III) compounds is in progress in order to elucidate this point.

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Registry No. $Fe_2L(OC_2H_5)_2Cl_2$, 91711-61-4; $Fe_2(acac)_4(OC_2H_5)_2$, 36107-36-5.

Supplementary Material Available: Listings of hydrogen atom coordinates, thermal parameters, and the observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

(38) Kahn, O.; Galy, J.; Journaux, Y.; Jaud, J.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165.

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Substituted Cysteamine Ligands and Their Complexes with Molybdenum(VI)

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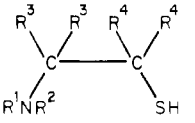
New bidentate cysteamine-based ligands containing CH_3-substituted carbon and nitrogen atoms have been synthesized. Together with known ligands the following complete set has now been prepared: $NH_2CH_2CH_2SH$, $CH_3NHCH_2CH_2SH$, $(CH_3)_2NCH_2CH_2SH$, $NH_2C(CH_3)_2CH_2SH$, $CH_3NHC(CH_3)_2CH_2SH$, $(CH_3)_2NC(CH_3)_2CH_2SH$, $NH_2CH_2C(CH_3)_2SH$, $CH_3NHCH_2C(CH_3)_2SH$, $(CH_3)_2NCH_2C(CH_3)_2SH$, $NH_2C(CH_3)_2C(CH_3)_2SH$, $CH_3NHC(CH_3)_2C(CH_3)_2SH$, and $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH$. Five of the ligands in this series are new, and their syntheses are reported in detail. Also $RNHCH_2C(CH_3)_2SH$ ligands with R = i-C_3H_7 and i-C_4H_9 are reported for the first time. These ligands, LH, were reacted in CH_3OH with $MoO_2(acac)_2$. In most cases the complex MoO_2L_2 resulted. However, in some cases this complex appears to be unstable. The syntheses and spectroscopic properties of the complexes are reported. The low values of ν(Mo–O) for some of the complexes are correlated either with H bonding or with the presence of a skew-trapezoidal-bipyramidal structure. Likewise electronic absorption spectra differ for complexes with octahedral as opposed to skew-trapezoidal-bipyramidal structures. For a given complex, ^{17}O and ^1H NMR spectroscopies are consistent with adoption in solution of the same octahedral or skew-trapezoidal-bipyramidal structure that is found in the solid state. Further, the skew-trapezoidal-bipyramidal complexes display temperature-dependent NMR spectra that are interpreted in terms of configurational averaging probably caused by Mo–N bond cleavage.

Introduction

Hexavalent molybdenum has been identified in several molybdoenzymes.[2-5] In sulfite oxidase,[6,7] xanthine oxidase,[8,9] and xanthine dehydrogenase,[10] structures containing oxo groups have been identified by EXAFS on the molybdenum absorption edge.[10] In addition to oxo, sulfur donors have been found[6-10] at distances commensurate with the presence of thiolate donors. Previous papers in this series[11-15] have reported Mo(VI) complexes of tri-[15] and tetradentate N,S donor ligands and have delineated attempts to structurally mimic the enzymic Mo site. Some of the complexes with tetradentate ligands show octahedrally based structures, with Mo–S and Mo–O distances quite similar to those found in sulfite oxidase.[11,13,14] However, in a preliminary paper[16] we reported that, with certain bidentate cysteamine-based ligands, unusual nonoctahedral complexes are obtained that have similar Mo–S and Mo–O distances. The accompanying paper[17] describes detailed structural studies of complexes in this class. This paper presents details of the preparation and spectroscopic characterization of a series of cysteamine-based ligands (I) and their Mo(VI) complexes.



I

Ligands based on cysteamine (I, $R^1 = R^2 = R^3 = R^4 = H$) have been well studied.[18,19] Kay and Mitchell[20] reported that

(1) (a) The Charles F. Kettering Research Laboratory. (b) Exxon Research and Engineering Co.
(2) Stiefel, E. I. In "Molybdenum and Molybdenum-Containing Enzymes"; Coughlan, M. P., Ed.; Pergamon Press: New York, 1980; p 41.
(3) Bray, R. C. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1980**, *51*, 107.
(4) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(5) Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59.
(6) Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1979**, *101*, 2772.
(7) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721.
(8) Tullius, T.; Kurtz, D. M., Jr.; Conradson, S. D.; Hodgson, K. O. *J. Am. Chem. Soc.* **1979**, *101*, 2776.
(9) Bordas, J.; Bray, R. C.; Garner, C. D.; Gutteridge, S.; Hasnain, S. S. *Biochem. J.* **1980**, *191*, 499.
(10) Cramer, S. P.; Hodgson, K. O.; Stiefel, E. I.; Newton, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 2748.
(11) Berg, J. M.; Hodgson, K. O.; Cramer, S. P.; Corbin, J. L.; Elsberry, A.; Pariyadath, N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 2774.
(12) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Pariyadath, P.; Heinecke, J.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York, 1980; p 279.
(13) Berg, J. M.; Hodgson, K. O.; Bruce, A. E.; Corbin, J. L.; Pariyadath, N.; Stiefel, E. I. *Inorg. Chim. Acta*, in press.
(14) Bruce, A.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Stiefel, E. I.; Spence, J. T.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917.
(15) Marabella, C. P.; Enemark, J. H.; Miller, K. F.; Bruce, A. E.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 3456.
(16) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.* **1980**, *102*, 3624.
(17) Berg, J. M.; Spira, D. M.; Hodgson, K. O.; Bruce, A. E.; Miller, K. F.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.*, following paper in this issue.
(18) Lindoy, L. F. *Chem. Soc. Rev.* **1975**, 421.

0020-1669/84/1323-3404$01.50/0

Table I. Color, Yield, and Analytical Data for MoO_2L_2 Complexes

L	color	yield, %	anal. calcd (found) % C	% H	% N
$H_2NCH_2CH_2S$[a]	golden yellow	76	17.15 (17.20)	4.32 (4.18)	10.00 (9.77)
$H_2NCH_2C(CH_3)_2S$	lemon yellow	82	28.58 (28.31)	5.95 (6.20)	8.34 (8.22)
$H_2NC(CH_3)_2CH_2S$	yellow	78	28.58 (28.42)	5.95 (5.94)	8.34 (8.11)
$H_2NC(CH_3)_2C(CH_3)_2S$	lemon yellow	82	36.73 (36.23)	7.19 (7.15)	7.14 (6.94)
$C_6H_5CH_2NHCH_2C(CH_3)_2S$	lemon yellow	85	51.18 (50.95)	6.20 (6.36)	5.43 (5.33)
$C_6H_5NHCH_2C(CH_3)_2S$	red-orange	70	44.25 (44.25)	5.16 (5.08)	3.44 (3.40)
$CH_3NHCH_2CH_2S$	orange-yellow	58	23.38 (22.90)	5.23 (5.23)	9.09 (8.91)
$CH_3NHCH_2C(CH_3)_2S$	yellow	56	32.96 (32.96)	7.69 (7.66)	6.64 (6.87)
$(CH_3)_2NCH_2C(CH_3)_2S$	yellow	61	36.73 (36.00)	7.14 (6.98)	7.14 (7.14)
$CH_3NHC(CH_3)_2C(CH_3)_2S$	yellow	81	39.99 (40.08)	7.67 (8.01)	6.66 (6.67)

[a] This complex was prepared previously from MoO_4^{2-} by Kay and Mitchell (1970).

cysteamine itself forms a Mo(VI) complex of the form $MoO_2(NH_2CH_2CH_2S)_2$, and similar complexes have been reported for the methyl and diethyl esters of cysteine. These complexes of N,S donor ligands also by EXAFS criteria bear distinct resemblance to the coordination sphere of Mo in sulfite oxidase.[9] In conjunction with our studies on tri- and tetradentate ligands we decided to look also at complexes of bidentate ligands for the sake of completeness as well as to provide simpler spectroscopic models for the complexes with multidentate ligands. As it developed, the chemistry of the cysteamine complexes proved to be not at all routine. We were led in stages to prepare a variety of substituted cysteamine ligands (some of which were never prepared before) and to investigate the spectroscopic and structural anomalies that were discovered during the course of the work.

One of the parameters that we varied was the degree of methyl substitution either on the carbon atoms of the cysteamine framework or on the nitrogen. Thus, dimethyl substitution on the sulfur-bearing carbon leads to a tertiary alkyl thiol and mono- or dimethyl substitution on N leads to a secondary or tertiary amine while dimethyl substitution on the N-bearing carbon leads to a primary amine without β-hydrogen atoms. These seemingly trivial substitutions lead to extreme differences in behavior. However, perusal of the literature reveals that these types of influences are not without precedent. For example, Wilkinson[21] stabilized transition-metal alkyl complexes by using ligands that lack β-elimination pathways. The absence of β-hydrogens is also a stabilizing feature of amino[22] and alkoxy[23] complexes. The situation for thiols is similar. Complexes of the tertiary alkyl thiols penicillamine or β,β-dimethylcysteamine compared, respectively, to those of cysteine or cysteamine are more stable toward redox decomposition in chemical[24,25] as well as in biological[26] systems. Our earlier work[27] on substituted cysteine complexes revealed the potentially enormous effects of methyl substitution on sulfur ligand framework. We investigated substituent effects on the activity of $Mo_2O_4(cys)_2^{2-}$ and its derivatives in molybdothiol catalyst systems.[28] β,β-Dimethyl substitution of cysteine led to total inactivation of the catalyst. β-Methyl substitution led stereospecifically to either retention of activity (for *threo*-β-methylcysteine) or loss of activity (for *erythro*-β-methylcysteine).[27]

In this paper we report MoO_2L_2 complexes of the substituted cysteamine ligands, I. The new and known ligands used in this study are listed in Table I. For some of the ligands, MoO_2^{2+} complexes stable at room temperature could not be prepared. In other cases, as determined by X-ray crystallography for $MoO_2[NH_2C(CH_3)_2CH_2S]_2$,[29] complexes of octahedral structure and normal spectroscopic behavior are found. In yet other cases, as determined crystallographically[16,17] for $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$, complexes of the unusual skew-trapezoidal-bipyramidal structure with short intramolecular S–S contacts are formed. Spectroscopic studies reported herein support the presence of these structures in solution as well as in the solid state. The variations in structure and spectra with ligand substituents have potential implications for multisulfur metal systems including certain enzymes.

Experimental Section

Reagents and Manipulations. Dioxobis(acetylacetonate)molybdenum(VI), $MoO_2(acac)_2$, was prepared from ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and acetylacetone according to the procedure of Jones.[30] $NH_2CH_2C(CH_3)_2SH\cdot HCl$ was prepared as in ref 31. $(CH_3)_2NCH_2CH_2SH\cdot HCl$ and $NH_2CH_2CH_2SH\cdot HCl$ were purchased from Aldrich Chemical Co. $(C_4H_9)_4NPF_6$ was prepared from $(C_4H_9)_4NBr$ and KPF_6 according to the procedure of Sawyer and Roberts[32] and was recrystallized from hot ethyl acetate/pentane. Acetonitrile was distilled from CaH_2 and stored over molecular sieves. Dichloroethane was distilled from P_2O_5 and stored over molecular

(19) Akbar Ali, M.; Livingstone, S. E. *Coord. Chem. Rev.* **1974**, *13*, 101.
(20) Kay, A.; Mitchell, P. C. H. *J. Chem. Soc.* **1970**, 2421.
(21) Wilkinson, G. *Science (Washington, D.C.)* **1974**, *185*, 109.
(22) Lane, B. C.; Lester, J. E.; Basolo, F. *J. Chem. Soc. D* **1971**, 1618.
(23) Krumpole, M.; Rocek, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.
(24) Rapp, H.; Seser, U. *Biochem. Biophys. Res. Commun.* **1976**, *72*, 223. Schugar, H. J.; Ou, C.; Thich, J. A.; Potenza, J. A.; LaLancette, R. A.; Furey, W., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 3048. Birker, P. J. M. W. L.; Freeman, H. C. *J. Am. Chem. Soc.* **1977**, *99*, 6890.
(25) Mastropaolo, D.; Thich, J. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1977**, *99*, 424. Brown, D. H.; McKinley, G. C.; Smith, W. E. *J. Chem. Soc., Dalton Trans.* **1978**, 199.
(26) Planas-Bohne, F. *Z. Naturforsch.* **1973**, *28*, 74.
(27) Corbin, J. L.; Pariyadath, N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1976**, *98*, 7862.
(28) Weathers, B. J.; Grate, J. H.; Strampach, N. A.; Schrauzer, G. H. *J. Am. Chem. Soc.* **1979**, *101*, 925.
(29) Berg, J. M.; Spira, D.; Wo, K.; McCord, B.; Lye, R.; Co, M. S.; Belmont, J.; Barnes, C.; Kosydar, K.; Raybuck, S.; Hodgson, K. O.; Bruce, A. E.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chim. Acta*, in press.
(30) Jones, M. M. *J. Am. Chem. Soc.* **1959**, *81*, 3180.
(31) Carroll, F. I.; White, J. D.; Wall, M. T. *J. Org. Chem.* **1963**, *28*, 1240.
(32) Sawyer, D. T.; Roberts, J. L., Jr. "Experimental Electrochemistry for Chemists"; Wiley Interscience: New York, 1974.

sieves. DMF was dried over molecular sieves, distilled under reduced pressure, and stored (−20 °C) over molecular sieves. Other chemicals and solvents were reagent grade and were used without further purification. Manipulation of free thiols was done under argon. Thiol titrations were adapted from the literature[33] (0.05 N ethanolic I_2/KI, dead-stop end point). Solvent removal was done below 45 °C on a rotary vacuum evaporator.

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 disks and/or Nujol mulls. 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 microejector from Control Equipment Corp. Reduction potentials were determined by cyclic voltammetry with a Princeton Applied Research Model 174 electrochemistry system equipped with a platinum-button vs. a saturated calomel 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/s. 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 (Hewlett-Packard VPO operation manual). Conductance measurements were made with a Radiometer conductivity meter and Radiometer CDC104 electrode. NMR spectra at 220 and 13.56 MHz for ^1H and ^{17}O, respectively, were run at Indiana University. ^{17}O spectra are reported as ppm downfield from 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 this facility. NMR spectra at 360 MHz were run at the Regional Biological NMR Center of Purdue University.

Preparation of Ligands. Ligands Made by Ag^+-Promoted Thiirane Ring Opening. Ag^+-promoted opening of thiiranes with primary amines proved useful in several of the syntheses. $CH_3NHCH_2C(CH_3)_2SH$ was prepared according to the reported procedure[47] of using Ag^+ to promote the reaction of 2,2-dimethylthiirane[35] and methylamine. Applying the same procedure with benzyl-, isopropyl-, or *tert*-butylamine resulted in the new ligands $R_1NHCH_2C(CH_3)_2SH$ (R_1 = $C_6H_5CH_2$, *i*-C_3H_7, *t*-C_4H_9), respectively. Additionally, the same method yielded $CH_3NHC(CH_3)_2C(CH_3)_2SH$ from reaction of 2,2,3,3-tetramethylthiirane[36] and methylamine. The amines were isolated as the hydrochloride salts and crystallized as described below. Thiol titration revealed 96–100% of the expected values. The only modifications in the literature procedure were the inclusion of 20–30% of a cosolvent (methanol or acetonitrile) and the stirring of the reaction mixtures overnight. The intermediate silver salts separated as solids, except in the benzylamine reaction. Here, the resulting yellow gum was triturated several times with water to obtain a solid product.

1-(Benzylamino)-2-methylpropane-2-thiol Hydrochloride, $C_6H_5CH_2NHCH_2C(CH_3)_2SH\cdot HCl$. The product was obtained in 56% yield from methanol/ether and melted with decomposition at 205–206 °C. NMR ($CDCl_3$) gave a multiplet at 7.3–7.8 (aromatic), a broad triplet at 4.35 with J = 5 Hz ($Ar-CH_2$), a multiplet at 2.9 (CH_2 + SH), and a singlet at 1.53 ppm [$(CH_3)_2$]. Anal. Calcd for $C_{11}H_{18}ClNS$: C, 57.00; H, 7.83; N, 6.04. Found: C, 57.25; H, 8.18; N, 6.04.

(Isopropylamino)-2-methylpropane-2-thiol Hydrochloride, $(CH_3)_2CHNHCH_2C(CH_3)_2SH\cdot HCl$. The product obtained in 74% yield from absolute ethanol/ether decomposed slowly above 130 °C. NMR ($CDCl_3$) gave a broad peak at 9.18 (NH_2^+), a multiplet at 3.67 (CH), a singlet at 3.45 (SH), a multiplet at 3.10 (CH_2), a singlet at 1.60 [$(CH_3)_2C$], and a doublet at 1.52 ppm, J = 7 Hz [$(CH_3)_2$]. Anal. Calcd for $C_7H_{18}ClNS$: C, 45.76; H, 9.87; N, 7.73. Found: C, 45.90; H, 10.29; N, 7.57.

1-(*tert*-Butylamino)-2-methylpropane-2-thiol, $(CH_3)_3CNHCH_2C(CH_3)_2SH\cdot HCl$. This product was obtained in 60% yield from absolute ethanol/ether and decomposes slowly above 145 °C. NMR ($CDCl_3$) showed a broad peak at 8.75 (NH_2^+), a multiplet at 3.12 (CH_2), and a multiplet at ca. 1.6 ppm (CH_3 + SH). Anal. Calcd for $C_8H_{20}ClNS$: C, 48.59; H, 10.19; N, 7.08. Found: C, 48.62; H, 10.33; N, 6.93.

3-(Methylamino)-2,3-dimethylbutane-2-thiol Hydrochloride, $CH_3NHC(CH_3)_2C(CH_3)_2SH\cdot HCl$. This compound was obtained in 68% yield from absolute ethanol/ether and melts with decomposition at 219–224 °C. NMR ($CDCl_3$) showed a broad peak at 8.92 (NH_2^+), a triplet at 2.78 with J = 5.5 Hz (CH_3N), a shoulder on the middle CH_3N peak at ca. 2.8 (SH), and singlets at 1.46 and 1.63 ppm [$(CH_3)_2CN$ and $(CH_3)_2CS$, assignment uncertain]. Anal. Calcd for $C_7H_{18}ClNS$: C, 45.76; H, 9.87; N, 7.62. Found: C, 45.93; H, 10.27; N, 7.40.

1-(Dimethylamino)-2-(benzylthio)-2-methylpropane, $(CH_3)_2NCH_2C(CH_3)_2SCH_2C_6H_5$. The amine $NH_2CH_2C(CH_3)_2SCH_2C_6H_5$[31] was methylated (25 mmol) by using the $NaCNBH_3$/HCHO procedure of Borch and Hassid[37] as detailed for the preparation of $(CH_3)_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5$ (see below). After solvent removal, partitioning between ether and water, and washing (2 N NaOH, water), distillation gave the colorless product in 71.7% yield (83–84 °C (0.14 mm)). NMR ($CDCl_3$) showed a multiplet at 7.3 (aromatic), a singlet at 3.79 (SCH_2), a singlet at 2.42 (NCH_2), a singlet at 2.35 [$N(CH_3)_2$], and a singlet at 1.32 ppm [$C(CH_3)_2$].

Picrate Derivative. A 100-mg sample of the amine was added to 200 mg of picric acid in 2 mL of hot methanol. Chilling and scratching gave yellow needles (60 mg), which melted at 110.5–112 °C after two recrystallizations from methanol. Anal. Calcd for $C_{19}H_{24}N_4O_7S$: C, 50.43; H, 5.35; N, 12.38. Found: C, 50.52; H, 5.37; N, 12.20.

1-(Benzylthio)-2-amino-2-methylpropane, $NH_2C(CH_3)_2CH_2SCH_2C_6H_5$. A solution of 2,2-dimethylethyleneimine[38] (0.10 mol) in methanol (10 mL) was added over 20 min to a stirred solution of benzyl mercaptan (0.10 mol) in methanol (25 mL) at room temperature under an argon atmosphere. The reaction was somewhat exothermic. After the mixture was allowed to stand overnight, the solvent was removed and the residual oil distilled (Vigreux column) to give a small amount of $C_6H_5CH_2SH$ followed by 16 g (82%) of the colorless product, which boiled at 87–88 °C (0.04 mm). NMR ($CDCl_3$) gave a multiplet at 7.28 (aromatic), a singlet at 3.73 (benzyl CH_2), a singlet at 2.48 (CH_2), a singlet at 1.32 (NH_2), and a singlet at 1.12 ppm (CH_3).

Hydrochloride Salt. A 100-mg sample of the amine in 1 mL of absolute ethanol treated with HCl (0.06 mL) followed slowly by ether (6 mL) gave the hydrochloride as colorless crystals: 89 mg; mp 141–2 °C. Anal. Calcd for $C_{11}H_{18}ClNS$: C, 57.00; H, 7.83; N, 6.04. Found: C, 57.33; H, 8.05; N, 6.11.

2-Amino-2-methylpropanethiol Hydrochloride, $NH_2C(CH_3)_2CH_2SH\cdot HCl$. This known thiol[39] was prepared as the hydrochloride in 80% yield by Na/NH_3 cleavage of the previously unknown *S*-benzyl thioether, $NH_2C(CH_3)_2CH_2SCH_2C_6H_5$.

2-(Methylamino)ethanethiol, $CH_3NHCH_2CH_2SH$. This thiol was prepared by the reaction of anhydrous methylamine with thiirane (benzene solvent, 70 °C, sealed tube), rather than by the reported[34] method using H_2S and *N*-methylaziridine. The product (bp 65 °C (80 mm)) solidified on standing (lit. bp 134–6 °C, mp 48–54 °C) and exhibited the expected NMR spectrum and thiol content.

1-(Dimethylamino)-2-propane-2-thiol Hydrochloride, $(CH_3)_2NCH_2C(CH_3)_2SH\cdot HCl$. This thiol was prepared by Na/NH_3 cleavage of the above $(CH_3)_2NCH_2C(CH_3)_2SCH_2C_6H_5$. The product was isolated as the hydrochloride salt (91.6% yield), crystallizing from 2-propanol/ether. Calderbank and Ghosh[36b] reported obtaining the free-base form from 2,2-dimethylthiirane and dimethylamine (100 °C, sealed tube). We tried this reaction in toluene solvent (8 h, 110 °C), but only ca. 30% yield was obtained.

1-(Benzylthio)-2-(dimethylamino)-2-methylpropane, $(CH_3)_2NC(CH_3)_2CH_2SCH_2C_6H_5$. The amine $NH_2C(CH_3)_2CH_2SCH_2C_6H_5$ (25 mmol) was methylated by using the HCHO/$NaCNBH_3$ procedure as described below for $(CH_3)_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5$. After partitioning betwen 2 N NaOH and ether and washing (2 N NaOH, H_2O), removal of the ether and (simple) distillation gave the product in 78.8% yield as a colorless oil, bp 111–113 °C (0.1–0.08 mm). NMR ($CDCl_3$) gave a multiplet at 7.28 (aromatic) and singlets at 3.68 (benzyl CH_2), 2.52 (CH_2), 2.20 [$(CH_3)_2N$], and 1.04 ppm [$(CH_3)_2C$].

(33) Stone, K. G. "Determination of Organic Compounds"; McGraw-Hill: New York, 1956; pp 7–8, 190–192.
(34) Bergmann, E. P.; Kaluszyner, A. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 289.
(35) Snyder, H. R.; Stewart, J. M.; Ziegler, J. B. *J. Am. Chem. Soc.* **1947**, *69*, 2672.
(36) (a) Youtz, M. A.; Perkins, P. P. *J. Am. Chem. Soc.* **1929**, *51*, 3508. (b) Calderbank, A.; Ghosh, R. *J. Chem. Soc.* **1960**, 637.
(37) Borch, R. F.; Hassid, A. I. *J. Org. Chem.* **1972**, *37*, 1673.
(38) Cairns, T. L. *J. Am. Chem. Soc.* **1941**, *63*, 871.
(39) Handrick, G. R.; Atkinson, E. R.; Granchelli, F. E.; Bruni, R. J. *J. Med. Chem.* **1965**, *8*, 762.

Picrate Salt. Because the hydrochloride salt was not easily obtained in crystalline form, a picrate derivative was made for analysis. A mixture of picric acid (150 mg), the amine (0.11 mL), and methanol (3 mL) was warmed to effect solution. Chilling and scratching gave the crystalline picrate salt that was recrystallized (methanol) to give 69 mg of yellow prisms, mp 101–3 °C. Anal. Calcd for $C_{19}H_{24}N_4O_7S$: C, 50.43; H, 5.34; N, 12.38. Found: C, 50.49; H, 5.43; N, 12.32.

2-(Dimethylamino)-2-methylpropanethiol Hydrochloride, $(CH_3)_2NC(CH_3)_2CH_2SH\cdot HCl$. The *S*-benzyl compound $(CH_3)NC(CH_3)_2CH_2SCH_2C_6H_5$ (18.4 mmol) in ca. 100 mL of NH_3 was treated with Na. The solvent was blown off with argon and the residue partitioned between ether (25 mL) and 2 N HCl (30 mL). The aqueous phase was evaporated to dryness, treated with hot $CHCl_3$, and filtered to remove NaCl. The solution was evaporated and the residue recrystallized from absolute ethanol (10 mL) and ether (20 mL). As the salt appears to have a small temperature solubility coefficient, more ether (20 mL) was added after chilling (freezer). The crystalline product was filtered and washed with ether. Vacuum drying gave a hygroscopic product in 81.4% yield. Thiol titration showed >98% of the theoretical value. The melting point was indefinite, only slow decomposition above 150 °C (some softening) being observed.

NMR ($CDCl_3$) gave a broad peak at 12.5 (NH), a doublet at 3.05 with J = 8.8 Hz (CH_2), a doublet at 2.85 with J = 5 Hz [$(CH_3)_2N$], a triplet at 2.17 with J = 8.8 Hz (SH), and a singlet at 1.53 ppm [$(CH_3)_2C$]. Anal. Calcd for $C_6H_{16}ClNS$: 42.46; H, 9.50; N, 8.25. Found: C, 42.21; H, 9.80; N, 8.33.

1-(Benzylthio)-2-(methylamino)-2-methylpropane, $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5$. The intermediate methyleneimine derivative was formed by stirring $H_2NC(CH_3)_2CH_2SCH_2C_6H_5$ (46 mmol) and 37% aqueous formaldehyde (4.5 mL) in benzene (75 mL) at room temperature (1 h). The mixture was then refluxed for 12 h by using a Soxhlet extractor containing 3A molecular sieves to remove the water formed by the reaction. The resulting product, after solvent removal, was essentially pure (NMR) and could be distilled as a colorless liquid: bp 84–6 °C (0.04 mm); 85.1% yield.

This imine, $CH_2{=}NC(CH_3)_2CH_2SCH_2C_6H_5$ (39 mmol), in benzene (20 mL) was reduced by *slow* addition (1.5–2 h) to a refluxing solution of lithium aluminum hydride (2.8 g) in dry THF (125 mL). If the addition was too rapid (e.g., 20 min), the product contained some unreacted imine. After it was refluxed for 12 h, the mixture was hydrolyzed by addition of sodium potassium tartrate (50 mL of saturated solution). Benzene (100 mL) was added and the organic phase washed twice with water. After solvent removal, distillation (Vigreux column) gave the desired amine (56%) as a colorless liquid (bp 91–3 °C (0.17 mm). NMR ($CDCl_3$) gave a multiplet of 7.3 (aromatic), singlets at 3.71 (benzyl CH_2), 2.53 (CH_2), 2.2 (N-CH_3), 1.36 (broad, NH), and 1.05 ppm [$C(CH_3)_2$].

Hydrochloride Salt. A 100-mg sample of the amine in 1 mL of absolute ethanol was treated with concentrated HCl (0.06 mL) and then ether (5 mL). After chilling, the solid product was filtered and washed with ether; mp 116–18 °C. Anal. Calcd for $C_{12}H_{20}ClNS$: C, 58.63; H, 8.20; N, 5.70. Found: C, 58.89; H, 8.43; N, 5.62.

2-(Methylamino)-2-methylpropanethiol Hydrochloride, $CH_3NHC(CH_3)_2CH_2SH\cdot HCl$. The *S*-benzyl compound, $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5$ (21 mmol), was dissolved in 10 mL of ether, and the cleavage was carried out exactly as for the dimethylamino analogue (above). The crude hydrochloride salt was recrystallized (freezer) from ethanol (10 mL), dioxane (20 mL), and ether (10 mL) to give 71.4% (mp 124–5 °C) after washing with dioxane/ether. NMR ($CDCl_3$) gave a broad peak at 9.4 ($-NH_2^+$), a doublet at 4.63 with J = 9 Hz (CH_2), a triplet at 4.33 with J = 6 Hz ($-NCH_3^+$), a triplet at 2.0 with J = 9 Hz (SH), and a singlet at 1.48 ppm [$(CH_3)_2$].

2-(Benzylthio)-3-amino-2,3-dimethylbutane, $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5$. 2,2,3,3-Tetramethylethyleneimine was prepared essentially by the method given by Closs and Brois.[40] During the reduction step, after the reaction temperature began to fall, external heat was applied to maintain 55 °C for 1 h. The crude product from the final (cyclization) step was used after removal of the ether, no further purification being done. The yield was estimated by titration of an aliquot with HCl (phenol red).

Crude 2,2,3,3-tetramethylethyleneimine (81 mmol), methanol (25 mL), and benzyl mercaptan (12 mL) were heated for 24 h in a sealed tube. The reaction mixture was filtered and partitioned between H_2O (150 mL) and ether (50 mL). The ether layer was extracted with 1 N HCl (70 and 30 mL), the combined HCl extracts were washed with ether and made basic with NaOH, and the free amine was extracted into ether. Removal of the solvent gave the product as a pale yellow oil that crystallized (yield 74%). Although the product distilled (bp ca. 115 °C (0.2 mm)), it was sufficiently pure for the subsequent preparations without distillation. NMR ($CDCl_3$) shows a multiplet at 7.36 (aromatic), a singlet 5.57 (SCH_2), a peak at 1.55 [$SC(CH_3)_2$ + NH_2], and a singlet at 1.37 ppm [$NC(CH_3)_2$]. Assignment of the two *gem*-dimethyl groups is based on the assumption that $NC(CH_3)_2$ would exhibit a greater downfield shift on formation of the HCl salt.

The hydrochloride salt $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5\cdot HCl$ was prepared and recrystallized from 2-propanol/ether (mp 149–59 °C). Anal. Calcd for $C_{13}H_{22}NSCl$: C, 60.09; H, 8.54; N, 5.39. Found: C, 59.94; H, 8.81; N, 5.49.

2-(Benzylthio)-3-(dimethylamino)-2,3-dimethylbutane Hydrochloride, $(CH_3)_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5\cdot HCl$. The general procedure of Borch and Hassid[37] was followed. $NaCNBH_3$ (23.9 mmol) was added in one portion to a well-stirred mixture of the amine $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5$ (15 mmol), 36% aqueous formaldehyde (6 mL, 72 mmol), and acetonitrile (45 mL). After 15 min, the pH was adjusted to 7 with concentrated CH_3COOH and maintained there for 1.5 h. The solvent was removed and the residue shaken with 2 N NaOH (50 mL) and ether (50 mL). The aqueous phase was extracted with more ether (2 × 25 mL), and the combined organic phases were washed with 0.5 N NaOH. The amine was then extracted into 1 N HCl (3 × 30 mL), the aqueous solution evaporated, and the residue dried to give 3.61 g (83.7%) of the crude hydrochloride. The compound, although pure by NMR standards, always analyzed ca. 1% low in carbon, and this was not improved by recrystallization (benzene/hexane); mp 132–3 °C, softening at ca. 127 °C. It was, however, used effectively for preparation of the thiol. NMR ($CDCl_3$) gave a very broad peak at 10.55 (NH^+), a multiplet at 7.28 (aromatic), a singlet at 3.87 (SCH_2), a doublet at 3.0 with J = 5 Hz [$N(CH_3)_2^+$], and singlets at 1.58 and 1.62 ppm [$NC(CH_3)_2$ and $SC(CH_3)_2$, assignment uncertain].

Attempted Methylation Using HCHO/HCO_2H. A solution of $H_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5$ (13.1 mmol), 37% aqueous HCHO (2.6 mL), and 90% formic acid (10 mL) was refluxed for 11 h and cooled, concentrated HCl (1 mL) added, and the solution evaporated to dryness. The residue was recrystallized from 1-propanol (6 mL) by adding ether (15 mL) to give an off-white solid: 82.5%, mp ca. 220 °C dec. I_2 titration showed no thiol. The product is evidently 3,4,4,5,5-pentamethyl-1,3-thiazolidine hydrochloride, consistent with the NMR, titration, and analysis. Anal. Calcd for $C_8H_{12}ClNS$: C, 49.09; H, 9.27; N, 7.16. Found: C, 48.85; H, 9.24; N, 7.06. The identical product could be obtained by treating $CH_3NHC(CH_3)_2C(CH_3)_2SH\cdot HCl$ in the same manner.

3-Amino-2,3-dimethylbutane-2-thiol Hydrochloride, $NH_2C(CH_3)_2C(CH_3)_2SH\cdot HCl$. The *S*-benzyl compound $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5$ (13.4 mmol) was cleaved with Na in liquid NH_3 (100 mL). The crude HCl salt was recrystallized from $CHCl_3$ (15 mL, hot filtration) and hexane (10 mL) added to give the thiol hydrochloride as colorless prisms in 78.6% yield (mp indefinite, slow decomposition above 150 °C). Thiol titration gave 99.5% of the expected value. The compound is slightly hygroscopic. NMR ($CDCl_3$) showed a broad singlet at 8.5 (NH_3^+), a broad singlet at 2.29 (SH), and a broad singlet at 1.57 ppm (CH_3). Anal. Calcd for $C_6H_{16}ClNS$: C, 42.46; H, 9.50; N, 8.25. Found: C, 42.48; H, 9.97; N, 8.13.

3-(Dimethylamino)-2,3-dimethylbutane-2-thiol Hydrochloride, $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH\cdot HCl$. The *S*-benzyl compound $(CH_3)_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5$ (11.0 mmol) was cleaved with Na in liquid NH_3 (100 mL) in the usual manner. The crude HCl salt was taken up in hot $CHCl_3$/absolute ethanol (50 and 20 mL) and filtered to remove NaCl, and the solvent was removed. The product was recrystallized from $CHCl_3$ (15 mL, hot filtration) and ether (20 mL, added last) to give 76.9% of the thiol hydrochloride as a white solid (mp 147–49 °C dec). Thiol titration showed 98.8% of the expected value. NMR ($CDCl_3$) gave a very broad peak at 10.5 (NH^+), a broad singlet at 3.35 (SH), singlets at 1.58 and 1.67 [$(CH_3)_2C$], and a doublet at 3.02 ppm with J = 5 Hz [$(CH_3)_2N^+$]. The NMR of the free base gave a singlet at 2.42 [$(CH_3)_2N$], a broad singlet at 2.13 (SH), a singlet at 1.34 [$SC(CH_3)_2$], and a singlet at 1.2 ppm [$NC(CH_3)_2$]. Anal. Calcd for $C_8H_{20}ClNS$: C, 48.58; H, 10.19; N,

(40) Closs, G. L.; Brois, S. J. *J. Am. Chem. Soc.* **1960**, *82*, 6068.

7.12. Found: C, 48.23; H, 10.56; N, 7.22.

Preparation of Complexes. The MoO_2L_2 complexes were prepared by the following general procedure. Slight variations for several of the complexes are indicated. Table I lists the complexes, their yields, colors, and analytical data.

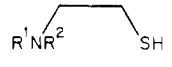
A solution of 2 mmol of ligand dissolved in 2 mL of CH_3OH was added dropwise at room temperature to a filtered, stirred solution of 1 mmol of $MoO_2(acac)_2$ in 6 mL of CH_3OH. If the ligand was in the form of the hydrochloride, 2 mmol of $(C_2H_5)_3N$ was also added. Most complexes are insoluble in CH_3OH, and a yellow precipitate formed immediately. The reaction mixtures were cooled to 0 °C for $^1/_2$ h to complete the precipitation. Complexes containing the ligands $CH_3NHCH_2C(CH_3)_2S^-$, $CH_3NHC(CH_3)_2C(CH_3)_2S^-$, and $(CH_3)_2NCH_2C(CH_3)_2S^-$ are slightly soluble in CH_3OH. In these cases the total volume of CH_3OH was decreased from 8 to 5 mL, and the reaction mixtures were cooled overnight at 0 °C to complete the precipitation. In all cases the product was isolated by filtration, washed with CH_3OH and $(C_2H_5)_2O$, and dried under vacuum. The complex of the $CH_3NHCH_2CH_2S^-$ ligand was prepared in cold (0 °C) methanol and was isolated from a deep red-orange solution. In all other cases the products were isolated from yellow solutions. $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ solutions in CH_3OH slowly deposit a white salt formulated as $[(CH_3)_2NHCH_2C(CH_3)_2SSC(CH_3)_2CH_2NH(CH_3)_2]_2Mo_8O_{26}$. Anal. Calcd for $C_{24}H_{60}N_2S_2Mo_8O_{26}$: C, 16.19; H, 3.52; N, 3.14. Found: C, 16.60; H, 3.53; N, 3.26.

The preparation of MoO_2L_2 complexes was also attempted with the following ligands: $(CH_3)_2NCH_2CH_2SH\cdot HCl$, $(CH_3)_2NC(CH_3)_2CH_2SH\cdot HCl$, $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH\cdot HCl$, $CH_3NHC(CH_3)_2CH_2SH\cdot HCl$, *i*-$C_3H_7NHCH_2C(CH_3)_2SH\cdot HCl$, and *t*-$C_4H_9NHCH_2C(CH_3)_2SH\cdot HCl$. When the above preparative reaction was used, the initial bright-yellow solution turned deep red within 1–10 min. The only product that could be isolated by solvent evaporation or by addition of a countersolvent, e.g., $(C_2H_5)_2O$ or $CHCl_3$, was a dull yellow insoluble and presumably polymeric solid. When the reactions were carried out at −75 °C under Ar, the initial yellow color of the reaction mixture was stabilized and a yellow solid precipitated. However, attempts to isolate the yellow solid while keeping the reaction vessels cold were unsuccessful. With a slight rise in temperature, the solid dissolved and the solutions began to turn orange-red.

Results

Ligand Syntheses. The framework of cysteamine $S–C_S–C_N–N$ is present in all of the ligands used in this study. The subscripts S and N are used to designate the skeleton carbons bonded to sulfur and nitrogen, respectively. [This avoids the inconsistency associated with the fact that a so-called "tertiary" thiol is connected to a carbon with three carbon groups on it (a tertiary carbon) whereas a tertiary amine has the amine nitrogen itself connected to three carbon atoms.] We use the designation tertiary to refer to an atom that is threefold carbon bound. The ligands differ in the degree of methyl substitution in the framework. Each framework carbon atom is either CH_2 or $C(CH_3)_2$. There are four possible combinations: (1) both primary; (2) C_S primary, C_N tertiary; (3) C_N primary, C_S tertiary; (4) both tertiary. For each of these combinations the amino group can be tertiary $[RN(CH_3)_2]$, secondary $[RHN(CH_3)]$, or primary $[RNH_2]$. Of these 12 possibilities, seven were known and we report here the syntheses of the remaining five ligands plus three additional new ligands containing substituents other than CH_3 on N.

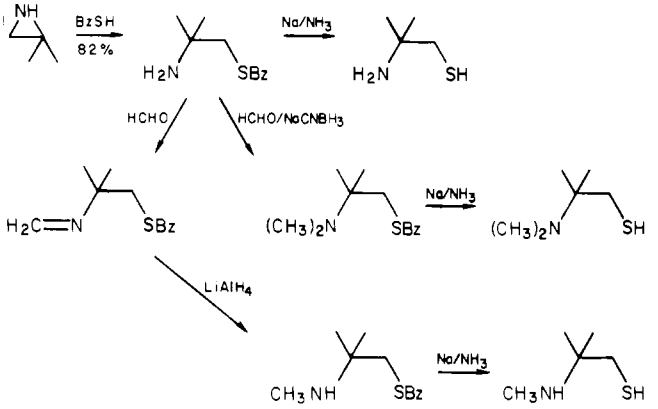
Case 1: C_N and C_S Both Primary. In this case

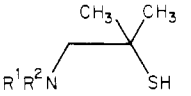


the ligands had all been synthesized previously, and the cases where $R^1 = R^2 = H$ or CH_3 are commercially available.

Case 2: C_N Primary, C_S Tertiary. Ligands of this type were also all known compounds. The method of Wall et al.[41] was used to prepare the *S*-benzyl derivative $NH_2CH_2C(CH_3)_2S$-$CH_2C_6H_5$. This intermediate was N,N-dimethylated to give the unreported 1-(dimethylamino)-2-(benzylthio)-2-methylpropane, which was debenzylated with Na/NH_3 to give $NH_2CH_2C(CH_3)_2SH$.

Scheme I

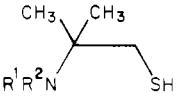




$R^1 = R^2 = H$
$R^1 = H$, $R^2 = CH_3$
$R^1 = R^2 = CH_3$

In addition to the complex with $R^1 = H$, $R^2 = CH_3$, we also synthesized some analogues in which the single *N*-methyl group was replaced by phenyl, benzyl, isopropyl, and *tert*-butyl. While the *N*-phenyl compound had been reported by us earlier,[42] the remaining compounds are new. These were conveniently synthesized in the same manner as $CH_3NHCH_2C(CH_3)_2SH$, i.e., the silver ion catalyzed addition of the appropriate primary amine to 2,2-dimethylthiirane.

Case 3: C_N Tertiary, C_S Primary. The only reported member of this series is the primary amine R^1, $R^2 = H$, $NH_2C(CH_3)_2CH_2SH$.[39]

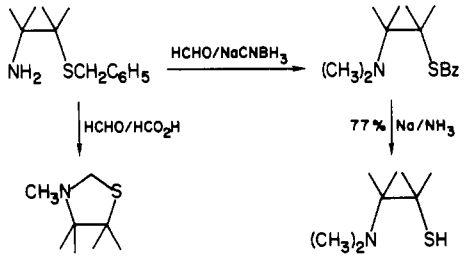


We prepared this and other members of this series by a scheme utilizing a common intermediate $[NH_2C(CH_3)_2CH_2SCH_2C_6H_5]$ prepared by addition of benzyl mercaptan to 2,2-dimethylaziridine. By analogy with the ring opening with thiophenol[43] or H_2S[44] the thiol adds to the least substituted carbon atom, giving the desired isomer (Scheme I). Monomethylation was possible because the Schiff base formed by reacting $H_2NC(CH_3)CH_2SCH_2C_6H_5$ with formaldehyde was particularly stable due to the presence of a tertiary carbon next to nitrogen.[45] This Schiff base could be isolated and reduced to the methyl amine, which upon debenzylation yields $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5$. The *N,N*-dimethyl ligand was obtained from $NH_2C(CH_3)_2CH_2SCH_2C_6H_5$ by using the mild methylation procedure of Borch and Hassid[37] followed by debenzylation.

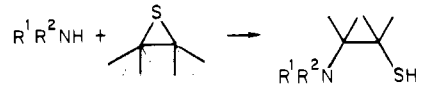
Case 4: C_N and C_S Tertiary. In the series with completely methylated backbones, none of the compounds were known. Based on the work of Snyder et al.,[35] the most direct approach

(41) Carroll, F. I.; White, J. D.; Wall, M. T. *J. Org. Chem.* **1963**, *28*, 1240.
(42) Corbin, J. L.; Work, D. E. *J. Org. Chem.* **1976**, *41*, 489.
(43) Meguerian, G.; Clapp, L. B. *J. Am. Chem. Soc.* **1951**, *73*, 2121.
(44) Larice, J. R.; Roggero, J.; Metzger, J. *Bull. Soc. Chim. Fr.* **1967**, 3637.
(45) Hurwitz, M. D. U.S. Patent 2 582 128, 1952; *Chem. Abstr.* **1952**, *46*, 8146*f*.

Scheme II

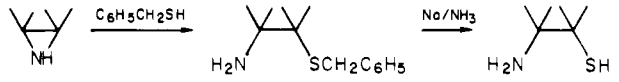


appeared to be addition of the amines (R^1R^2NH) to the thiirane according to



A trial reaction of CH_3NH_2 with the thiirane yielded virtually no thiol (20 h, 80 °C, benzene), possibly for steric reasons. Published rate data[46] showed that tetramethylthiirane was indeed much less reactive than lesser substituted thiiranes, thus ruling out this simple synthetic approach. However, the addition of primary amines to thiiranes has been shown to be catalyzed by silver ion,[47] and this reaction at least allowed us to obtain $CH_3NHC(CH_3)_2C(CH_3)_2SH$ in good yield from tetramethylthiirane and CH_3NH_2.

A different approach was needed for the syntheses of $NH_2C(CH_3)_2C(CH_3)_2SH$ and $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH$. Fortunately, the opening of the aziridine ring with thiol is apparently much easier than opening the thiirane ring with amine.[48] Adding benzyl mercaptan to 2,2,3,3-tetramethylaziridine yielded the thioether, which in turn was debenzylated to give $NH_2C(CH_3)_2C(CH_3)_2SH$.



Methylation of $H_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5$ by the $HCHO/NaCNBH_3$ procedure[37] produced the *N,N*-dimethyl *S*-benzyl compound, which in turn yielded $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH$ upon debenzylation. Methylation by the Clarke–Eschweiler procedure,[50] surprisingly, gave only the thiazolidine (Scheme II). This presumably arises from cleavage of the *S*-benzyl group and reaction of the resulting aminethiol with formaldehyde.

Synthesis of Complexes. The reaction of most of the substituted cysteamine ligands with $MoO_2(acac)_2$ proceeds smoothly by substitution, giving MoO_2L_2 complexes in pure form and good yield (eq 1).

$$MoO_2(acac)_2 + 2LH \xrightarrow{CH_3OH} MoO_2L_2 + 2acacH \quad (1)$$

The formulation of the products as mononuclear Mo(VI) dioxo complexes containing two bidentate ligands in the coordination sphere is consistent with the reaction conditions, elemental analyses, spectroscopic data, molecular weight determinations, and, in four cases, X-ray structural analyses.[16,17,29]

For some of the S,N bidentate ligands, MoO_2L_2 complexes do not form according to eq 1. In these cases addition of the ligand to $MoO_2(acac)_2$ gives a yellow solution that quickly changes to a deep red. It would appear that the ligand coordinates to the MoO_2^{2+} unit to give an unstable product. At low temperature under Ar the initial yellow product appears to be stabilized, although attempts at isolation have been unsuccessful. The ligands for which no complexes could be isolated are $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH$, $(CH_3)_2NC(CH_3)_2CH_2SH$, $(CH_3)_2NCH_2CH_2SH$, $CH_3NHC(CH_3)_2CH_2SH$, and $R_1NHCH_2C(CH_3)_2SH$ (R_1 = *i*-C_3H_7, *t*-C_4H_9). These ligands have a substituted amino group as their common feature.

Table II. Reduction of MoO_2L_2 Complexes Measured by Cyclic Voltammetry[a]

L	E_{red},[b] V
$(CH_3)_2NHCH_2C(CH_3)_2S$	−0.893, −1.296
$C_6H_5CH_2NHCH_2C(CH_3)_2S$	−1.414
$CH_3NHCH_2CH_2S$	−1.426
$CH_3NHCH_2C(CH_3)_2S$	−1.452
$H_2NCH_2CH_2S$	−1.458
$CH_3NHC(CH_3)_2C(CH_3)_2S$	−1.478
$H_2NCH_2C(CH_3)_2S$	−1.150
$H_2NC(CH_3)_2CH_2S$	−1.561
$H_2NC(CH_3)_2C(CH_3)_2S$	−1.598

[a] Pt button electrode vs. SCE; 1 mM solutions in DMF with 0.1 M $(C_4H_9)_4NPF_6$; scan rate 0.5 V/s; range +0.5 to −2.0 V. [b] Peak potential of irreversible reduction arranged according to decreasing potential.

The complexes containing ligands with the lowest degree of alkyl substitution are the least soluble in chlorinated hydrocarbons. Methyl substitution on the carbon adjacent to the nitrogen increases the solubility of the complexes. Substitution on the nitrogen and on one or both of the carbons increases the solubility still further. Ranking the MoO_2L_2 complexes according to increasing solubility in CH_2Cl_2 gives $NH_2CH_2CH_2S^- < CH_3NHCH_2CH_2S^- < NH_2CH_2C(CH_3)_2S^- < NH_2C(CH_3)_2C(CH_3)_2S^- < NH_2C(CH_3)_2C(CH_3)_2S^- < C_6H_5CH_2NHCH_2C(CH_3)_2S^- < (CH_3)_2NCH_2C(CH_3)_2S^- < CH_3NHC(CH_3)_2C(CH_3)_2S^-$.

All of the complexes are nonelectrolytes in CH_3CN, and most of the complexes decompose slowly (over several days) in solutions exposed to air to give white solids. The decomposition of $MoO_2[(CH_3)_2NH_2CH_2C(CH_3)_2S]_2$ is most rapid and is accompanied by an increase in conductivity. Here, a white crystalline solid was isolated from the decomposition and is identified by its analysis and infrared spectrum as an isopolymolybdate salt of the disulfide diammonium salt of the ligand, $[(CH_3)_2NHCH_2C(CH_3)_2SSC(CH_3)_2CH_2NH(CH_3)_2]_2[Mo_8O_{26}]$.

The molecular weights of $MoO_2[C_6H_5CH_2NHCH_2C(CH_3)_2S]_2$, $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ were determined in dichloroethane by vapor pressure osmometry (calcd): 505 (517), 348 (364), 390 (421), 433 (393). The results are within 3–10% of the molecular weights calculated for monomeric Mo dioxo complexes. The other complexes were not soluble enough in solvents suitable for vapor pressure osmometry.

All complexes display irreversible cyclic voltammetry at potentials listed in Table II. All complexes except $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ undergo one irreversible reduction in the range −1.4 to −1.6 V. $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ is most easily reduced (i.e., its reduction potential is the least negative) and undergoes two irreversible reductions at ~−0.9 and −1.3 V. Coulometric or chemical reductions, although not exhaustively pursued, appeared to yield dinuclear Mo complexes containing $Mo_2O_4^{2+}$ cores.

The infrared spectra of the MoO_2L_2 complexes provide qualitative evidence for the coordination of the thiolate and amine groups of the ligand to the Mo. The S–H absorption at ~2500 cm^{-1} in the free ligand is absent in the spectra of the complexes. For primary and secondary amines the N–H absorption shifts from ~3400 to ~3200 cm^{-1} upon coordination of the nitrogen to Mo. Infrared spectra show no ab-

(46) Oddon, A.; Wylde, J. *Bull. Soc. Chim. Fr.* **1967**, 1603.
(47) Luhowy, R.; Meneghini, F. *J. Org. Chem.* **1973**, *38*, 2405.
(48) Hahn, C. S. *Taehan Hwahakhoe Chi* **1963**, *7*, 230.

Table III. Electronic and Infrared Absorptions of MoO_2L_2 Complexes

L	electronic spectra[a] λ, cm^{-1}	λ, nm (ε, M^{-1} cm^{-1})	IR[b] λ, cm^{-1}
$H_2NCH_2CH_2S$	28 250	354 (4000)	891
	36 760 sh	272 (4200)	866
	40 650 sh	246 (4400)	
	43 480 sh	230 (5100)	
$H_2NCH_2C(CH_3)_2S$	28 170	355 (5600)	907
	38 460 br	260 (7200)	872
	43 860 sh	228 (8000)	
$H_2NC(CH_3)_2CH_2S$	28 900	346 (5090)	907
	37 740	265 (5800)	882
	43 480 sh	230 (5860)	
$H_2NC(CH_3)_2C(CH_3)_2S$	28 570	350 (7000)	906
	38 020	263 (8800)	872
$C_6H_5CH_2NHCH_2C(CH_3)_2S$	28 570	350 (2980)	925
	37 040	270 (4700)	900
	37 880	264 (4900)	
$CH_3NHCH_2CH_2S$	28 170	355 (4400)	902
	35 970 sh	278 (4500)	873
	39 370 sh	254 (5800)	
	43 860 sh	228 (7550)	
$CH_3NHCH_2C(CH_3)_2S$	28 250	354 (2600)	882
	38 170 sh	262 (3700)	856
$(CH_3)_2NCH_2C(CH_3)_2S$	30 580 br	327 (2800)	893
	35 970 sh	278 (3200)	879
$CH_3NHC(CH_3)_2C(CH_3)_2S$	29 410 sh	340 (3980)	878
	30 300	330 (4430)	847
	37 040 sh	270 (4340)	

[a] In CH_3CN. [b] As KBr pellets. [c] Measured anaerobically to prevent decomposition of the solution.

sorption between 1600 and 1500 cm^{-1} due to residual acac ligand in the complexes.

The MoO_2L_2 complexes show two strong absorptions (of unequal intensity) in the 950–850-cm^{-1} region (Table III) that are characteristic of the MoO_2^{2+} stretching frequencies. Large variation (~50 cm^{-1}) in the positions of these absorptions is observed in this series of complexes. Except for $MoO_2(NH_2CH_2CH_2S)_2$, those complexes having absorptions occurring at the lowest energy are known to have skew-trapezoidal-bipyramid (STB) structures. The difference in energy between the two ν(Mo–O) absorptions ranges from 25 to 35 cm^{-1} for all complexes except $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ where the difference is only 14 cm^{-1}.

In addition to their lower energy, the ν(Mo–O) infrared absorptions for the STB complexes display band envelopes that differ significantly from those of the normal octahedral complexes. The symmetric (higher energy) stretch is relatively less intense in the STB complexes. Insofar as the STB complexes can be viewed as more closely derived from a trans octahedral dioxo complex,[16,17] this intensity difference is explainable. In the trans octahedral dioxo complex, only the asymmetric stretch will be infrared active and only a single peak should be observed. The decrease in the intensity of the symmetric stretch is consistent with the opening of the O–Mo–O angle. An opposite effect is expected in the Raman spectra, and indeed such an effect is clearly seen.[49]

For all complexes, except $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ and $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, the lowest energy electronic absorption occurs near 350 nm (28 570 cm^{-1}) and tails into the visible region. The lowest energy absorptions for $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ and $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ occur at approximately 330 nm (30 000 cm^{-1}).

There are no detectable absorptions in the visible or near-infrared regions of the spectrum. Although most of the complexes have absorptions in approximately the same position,

(49) Loehr, T.; Willis, L., personal communication.
(50) Moore, M. L. *Org. React. (N.Y.)* **1949**, *5*, 307.

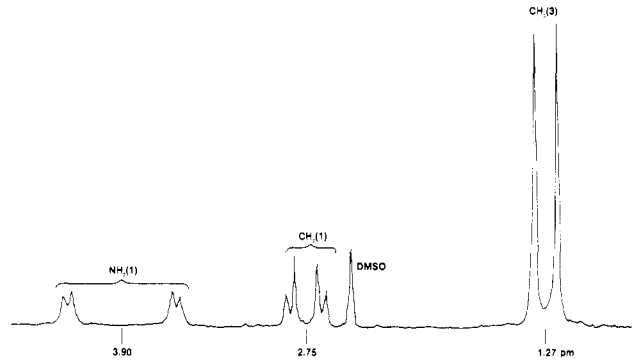
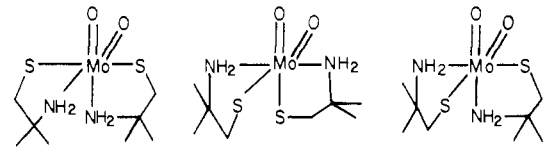


Figure 1. 220-MHz ^1H NMR spectrum of $MoO_2[NH_2C(CH_3)_2CH_2S]_2$ in Me_2SO-d_6.

the molar absorptivities of the skew-trapezoidal-bipyramidal complexes appear smaller by a factor of ~2.

NMR and Dynamical Considerations. The background provided by the structural work allows us to look at 220-MHz ^1H and ^{17}O NMR data for complexes in this class. The spectra can be used both for structural and dynamical evaluation of the complexes.

The spectrum of $MoO_2[NH_2C(CH_3)_2CH_2S]_2$ shown in Figure 1 establishes the equivalence of the two bidentate ligands. The NMR spectrum of the free ligand, $NH_2C(CH_3)_2CH_2SH$, contains three singlets of relative intensity 6:2:3, which are attributed respectively to the two equivalent methyl groups, to the methylene group, and to a common resonance for the two amino and one sulfhydryl proton. Coordination to molybdenum eliminates the SH signal and removes the equivalence of the methyl groups, the two methylene protons, and the two amino protons, respectively. As displayed in Figure 1 the spectrum in Me_2SO-d_6 shows two methyl resonances centered at 1.27 ppm and separated by 32 Hz. The inequivalence of the two methylene protons and of the two amino protons give rise to AB patterns centered at 2.74 ppm (J_{AB} = 12 Hz) and 3.89 ppm (J_{AB} = 11 Hz), respectively. A structural isomer of type **1** or **2** will account for the observed



1 2 3

spectrum. However, isomer **3** in the absence of exchange would be expected to yield a spectrum containing four distinct methyl resonances and a pair of AB patterns for each methylene and amino group. Structure **1** is the structure determined by X-ray diffraction in the solid state,[29] and the NMR indicates its probable presence in solution as well.

In contrast to $MoO_2[NH_2C(CH_3)_2CH_2S]_2$, other MoO_2L_2 complexes display spectra where equivalent methyl substituents and equivalent methylene protons are observed at room temperature (17 °C) and, in some cases, this equivalence is maintained at low temperatures. The spectrum of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ in $CDCl_3$ in Figure 2 consists of a singlet at 1.48 ppm, a broad peak at 2.94 ppm, a doublet at 3.03 ppm, and a very broad singlet at 3.62 ppm. Consistent with the integration, these peaks are assigned to the two methyl groups on the carbon adjacent to sulfur, the methylene group, the amine methyl group, and the amine proton, respectively. The addition of D_2O results in the collapse of the doublet at 3.03 ppm to a singlet and the disappearance of the peak at 3.62 ppm, which is the behavior anticipated upon exchanging the amine proton for a deuteron.

The crystal structure of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ shows that the methyl groups of the tertiary carbon adjacent

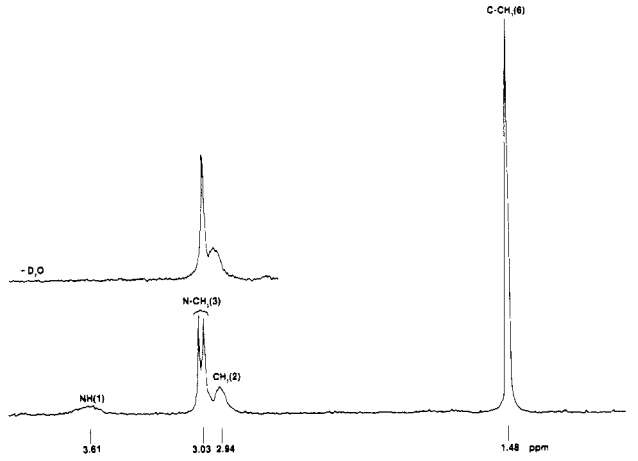


Figure 2. 220-MHz ^1H NMR spectrum of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ in $CDCl_3$.

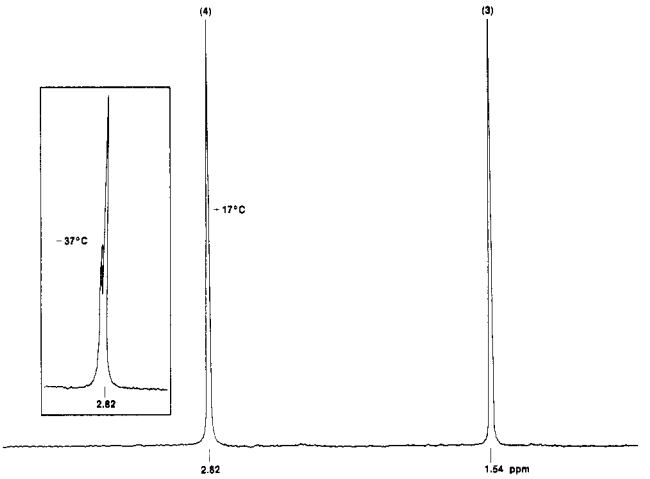


Figure 3. 220-MHz ^1H NMR spectrum of $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ in $CDCl_3$.

to sulfur as well as the two methylene protons are inequivalent in the solid state. However, the spectrum of this complex in solution reveals that the solid-state inequivalence of the two methyl groups and the two methylene protons have each been removed. In addition, any complexity that results from diastereoisomerism of the MoO_2L_2 complex, due to chiral centers associated with the nitrogen and molybdenum atoms, was not observed. Consequently, a molecular rearrangement process must exist to average the environments of both the methyl groups and the methylene protons.

The ^1H NMR spectrum of the skew-trapezoidal-bipyramidal complex $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ shown in Figure 3 is deceptively simple. At room temperature the spectrum displays only two sharp peaks. Lowering the temperature reveals the source of the deception. There is accidental isochronicity of the peaks due to the CH_2 and $N(CH_3)_2$ protons, which is removed due to a differing temperature dependence in the shifts of the two chemically different sets of protons. The low-temperature spectrum, while still very simple, is in agreement with the X-ray crystallographic structure of the solid. Specifically, the skew-trapezoidal-bipyramidal structure of $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]$ has C_2 symmetry, and ring inversions of relatively small amplitude would produce an average C_{2v} symmetry that would make all $N(CH_3)_2$, all CH_2, and all $C(CH_3)_2$ protons equivalent. The ^{17}O NMR spectrum of $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ consists of a single sharp peak consistent with this argument.

It was, however, somewhat puzzling to look at the ^1H and ^{17}O NMR of the STB complex $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, which are significantly more complex. At room

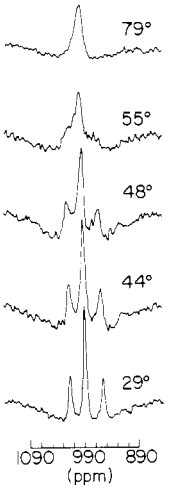


Figure 4. Variable-temperature ^{17}O NMR spectrum of $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$ in 1,2-dichloroethane.

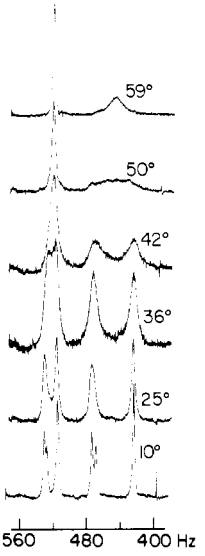


Figure 5. Variable-temperature 360-MHz ^1H NMR spectrum of $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$ in $CDCl_3$ showing only the carbon-bound (C_S and C_N) methyl protons.

temperature the ^{17}O NMR spectrum (Figure 4) consists of *three* peaks in approximate 1:2:1 intensity ratio. The ^1H NMR is extremely complex in the CH_3 region (Figure 5) containing at least six signals due to the CH_3 protons at room temperature. These multiple signals must be due to chemical shift inequivalence since spin–spin coupling is small between the $(CH_3)_2$ groups on tertiary carbons. Temperature dependence of the ^{17}O and ^1H NMR spectra shown in Figures 4 and 5, respectively, reveal that the complexity disappears (or lessens) at high temperature.

The coalescence patterns reveal that there is averaging of all three ^{17}O resonances into one and of all CH_3 proton resonances into two signals. This behavior we believe is explicable in terms of isomeric forms of the STB structure as shown schematically in Figure 6. In the $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ complex, the single ^{17}O resonance and the single $N(CH_3)_2$ resonances are seen to be due to the chemical equivalence of the protons involved (Figure 6a). However, in the $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$ complex there are two possible isomers of the STB structures (Figure 6b). These are syn and anti with respect to the NCH_3 (or NH) groups. The syn isomer should have inequivalent ^{17}O resonances whereas the oxygens are equivalent in the anti form. If the syn and anti forms are present in roughly equal amounts, then the observed three-peak 1:2:1 pattern would be expected in

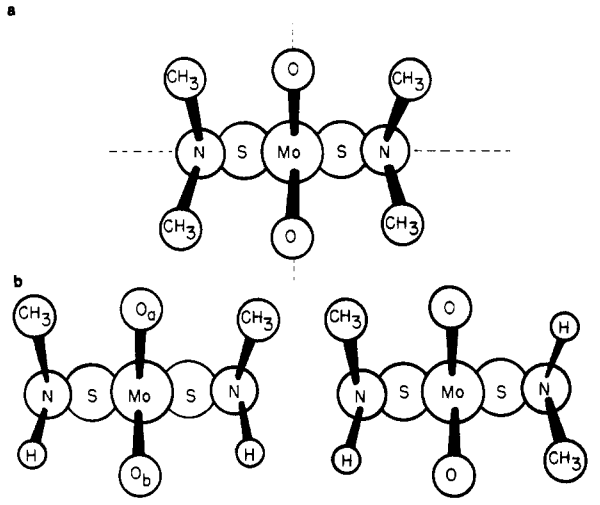


Figure 6. Schematic representation of skew-trapezoidal-bipyramidal structures: (a) $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$; (b) $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$.

the ^{17}O NMR spectrum. Upon heating, the observed coalescence (Figure 4) is attributed to averaging the environments in the two STB structure (possibly by N–Mo bond-breakage inversion about N followed by Mo–N bond re-formation). The same explanation holds for the CH_3 resonances. Thus, there are four types of carbon-bound CH_3 groups in each of the two structures, leading to a maximum of eight resonances. The same averaging process between the two STB structures would leave only two types of CH_3 groups, i.e., those on C_N and those on C_S. Clearly, the static and dynamic NMR data are both consistent with the STB structure. The NMR data show that the STB structure is likely present in solution as well as in the solid state.

Acknowledgment. We are grateful to the National Science Foundation for support of this work through Grants CHE 77-07026 and 79-26021.

Registry No. $C_6H_5CH_2NHCH_2C(CH_3)_2SH\cdot HCl$, 82626-95-7; $(CH_3)_2CHNCH_2C(CH_3)_2SH\cdot HCl$, 91229-26-4; $(CH_3)_3CNHCH_2C(CH_3)_2SH\cdot HCl$, 91229-27-5; $CH_3NHC(CH_3)_2C(CH_3)_2SH\cdot HCl$, 91229-28-6; $(CH_3)_2NCH_2C(CH_3)_2SCH_2C_6H_5$, 91229-29-7; $NH_2CH_2C(CH_3)_2SCH_2C_6H_5$, 59681-09-3; $(CH_3)_2NCH_2C(CH_3)_2SCH_2C_6H_5$ picrate, 91229-30-0; $NH_2C(CH_3)_2CH_2SCH_2C_6H_5$, 91237-78-4; $NH_2C(CH_3)_2CH_2SCH_2C_6H_5\cdot HCl$, 91237-79-5; $NH_2C(CH_3)_2CH_2SH\cdot HCl$, 4146-00-3; $CH_3NHCH_2CH_2SH$, 10061-40-2; $(CH_3)_2NCH_2C(CH_3)_2SH\cdot HCl$, 91229-31-1; $(CH_3)_2NC(CH_3)_2CH_2SCH_2C_6H_5$, 91229-32-2; $(CH_3)_2NC(CH_3)_2CH_2SCH_2C_6H_5$ picrate, 91229-33-3; $(CH_3)_2NC(CH_3)_2CH_2SH\cdot HCl$, 91229-34-4; $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5$, 91229-35-5; $CH_2{=}NC(CH_3)_2CH_2SC_6H_5$, 91229-36-6; $CH_3NHC(CH_3)_2CH_2SCH_2C_6H_5\cdot HCl$, 91229-37-7; $CH_3NHC(CH_3)_2CH_2SH\cdot HCl$, 91229-38-8; $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5$, 91229-39-9; $NH_2C(CH_3)_2C(CH_3)_2SCH_2C_6H_5\cdot HCl$, 91229-41-3; $(CH_3)_2NC(CH_3)_2C(CH_3)_2SCH_2C_6H_5\cdot HCl$, 91229-42-4; $NH_2C(CH_3)_2C(CH_3)_2SH\cdot HCl$, 79797-08-3; $(CH_3)_2NC(CH_3)_2C(CH_3)_2SH\cdot HCl$, 91229-44-6; $MoO_2(H_2NCH_2S)_2$, 29836-54-2; $MoO_2(H_2NCH_2C(CH_3)_2S)_2$, 76757-49-8; $MoO_2(H_2NC(CH_3)_2CH_2S)_2$, 91279-42-4; $MoO_2(H_2NC(CH_3)_2C(CH_3)_2S)_2$, 79799-79-4; $MoO_2(C_6H_5CH_2NHC(CH_3)_2S)_2$, 91229-45-7; $MoO_2(C_6H_5NHCH_2C(CH_3)_2S)_2$, 91229-46-8; $MoO_2(CH_3NHCH_2CH_2S)_2$, 91229-47-9; $MoO_2(CH_3NHCH_2C(CH_3)_2S)_2$, 74005-67-7; $MoO_2((CH_3)_2NCH_2C(CH_3)_2S)_2$, 74005-68-8; $MoO_2(CH_3NHC(CH_3)_2C(CH_3)_2S)_2$, 76772-96-8; $MoO_2(acac)_2$, 17524-05-9; 2,2-dimethylthiirane, 3772-13-2; benzylamine, 100-46-9; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9; 2,2,3,3-tetrramethylthiirane, 17066-32-9; methylamine, 74-89-5; 2,2-dimethylethylene imine, 2658-24-4; benzyl mercaptan, 100-53-8; thiirane, 420-12-2; tetramethylethylene imine, 5910-14-5; 3,4,4,5,5-pentamethyl-1,3-thiazolidine, 91229-43-5.

Contribution from the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387, Department of Chemistry, Stanford University, Stanford, California 94305, and Exxon Research and Engineering Company, Corporate Research-Science Laboratory, Annandale, New Jersey 08801

Six-Coordinate Dioxomolybdenum(VI) Complexes Containing a Nonoctahedral Structure with a Short Sulfur–Sulfur Contact

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The structures of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ (**1**), $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]$ (**2**), and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (**3**) have been determined by using X-ray diffraction intensity data collected by counter techniques. **1** crystallizes in space group $P2_1/c$ with $a = 10.688$ (3) Å, $b = 11.923$ (2) Å, $c = 14.032$ (3) Å, $\beta = 106.65$ (2)°, and $Z = 4$. **2** crystallizes in space group $P2_1/c$ with $a = 10.771$ Å, $b = 11.281$ (4) Å, $c = 16.021$ (3) Å, $\beta = 90.43$ (2)°, and $Z = 4$. **3** crystallizes in space group $Fdd2$ with $a = 18.441$ (b) Å, $b = 22.998$ (6)Å, $c = 8.006$ (1) Å, and $Z = 8$. The six-coordinate structures are remarkably similar with an unusual nonoctahedral geometry described as a skew trapezoidal bipyramid. An approximate N_2S_2 plane contains the Mo atom with equivalent oxygen atoms above and below the plane. Average distances in the first coordination sphere are Mo–O = 1.72, Mo–N = 2.30, and Mo–S = 2.42 Å. An additional unusual feature of the structures is the short S–S contact of 2.73–2.82 Å with an S–Mo–S angle of 68.8–71.0°. This is attributed to partial disulfide bond formation. The *N*-methyl substitution on the cysteamine ligand would cause severe steric hindrance were an octahedral structure adopted. The resultant skew-trapezoidal structure minimizes the steric repulsion without causing any electronically unfavorable interactions.

The coordination chemistry of hexavalent molybdenum is dominated by complexes of coordination number 6.[2,3] Of these, there are large numbers of both mononuclear and homo- and heteropolynuclear oxomolybdates and a few dinuclear complexes. Virtually all of the mononuclear complexes contain a dioxomolybdenum group and, almost without exception, possess octahedral (or distorted octahedral) coordination wherein the two oxo ligands occupy cis positions in the Mo coordination sphere.[2-4] This paper presents three complexes

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(2) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(3) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.

0020-1669/84/1323-3412$01.50/0