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Raman and Infrared Spectroscopic Studies of Dioxomolybdenum(VI) Complexes with Cysteamine Chelates

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A series of 13 dioxomolybdenum(VI) complexes with nitrogen and sulfur ligands was studied by Raman and infrared spectroscopy. The two structural classes identified previously, distorted octahedral and skew trapezoidal bipyramidal (STB), in general, could be distinguished by the position of the molybdenum–oxygen symmetric stretching vibration between 850 and 950 $\mathrm{cm^{-1}}$. Complexes having the distorted octahedral geometry with trans thiolate sulfur atoms exhibited $\nu_s(\mathrm{O{=}Mo{=}O})$ above 900 $\mathrm{cm^{-1}}$, whereas the skew-trapezoidal-bipyramidal complexes with cis thiolate sulfur atoms had values below 900 $\mathrm{cm^{-1}}$. The O=Mo=O vibrational frequencies are also sensitive to hydrogen bonding between the oxygens and amine hydrogens on the ligands. The compounds with known STB structure are sensitive to laser irradiation. They appear to revert to an octahedral structure upon laser irradiation of solution samples but are stable when measured as solids at ~90 K. Molybdenum–sulfur and molybdenum–nitrogen stretching vibrations have also been identified in the ranges 340–415 and 520–630 $\mathrm{cm^{-1}}$, respectively.

Introduction

Coordination compounds of molybdenum are of interest as models for molybdoenzymes that appear to contain sulfur, oxygen, and, possibly, nitrogen ligands bound to the molybdenum atom at the active center.[2] With the exception of nitrogenase, molybdoenzymes possess a common pterin-containing molybdenum cofactor with one or two terminal oxo ligands in the oxidized Mo(VI) state of the enzyme. However, EXAFS spectra of various molybdoenzymes, including xanthine oxidase and sulfite oxidase, show that the coordination environments around molybdenum have considerable variability.[3] As proteins influence the coordination geometry around an active-site metal ion, it is important to know how the properties of metal ion coordination compounds are affected by structural changes in the ligation sphere. We have, therefore, investigated the vibrational spectra (in solid and solution phases) of a number of dioxomolybdenum(VI) complexes with cysteamine-based chelates having nitrogen and sulfur ligands.

X-ray crystal structures have been reported for $\mathrm{MoO_2[CH_3NHCH_2C(CH_3)_2S]_2}$,[4,5] $\mathrm{MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2}$,[5] $\mathrm{MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2}$,[5] $\mathrm{MoO_2[tox]_2}$[6] (tox = thiooxine, the ligand derived from 8-mercaptoquinoline), $\mathrm{MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]}$,[7] $\mathrm{MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]}$,[8] $\mathrm{MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]}$,[9] and $\mathrm{Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2}$.[10] All but the first three are typical dioxomolybdenum(VI) complexes as shown in Figure 1: distorted octahedra with cis oxygen atoms, cis nitrogen atoms trans to the oxygen atoms, and trans thiolate sulfur atoms (or sulfur trans to bridging oxygen in the Mo(VI) dimer). The cis disposition of the two oxygen atoms enables maximum π-bonding to the molybdenum(VI) ion through orthogonal d orbitals. A trans arrangement of oxygen atoms would result in weakened Mo=O bonds necessitated by π-electron donation into the same d orbital of molybdenum. Structures with trans oxygen atoms in dioxomolybdenum(VI) complexes are unknown. The thiolates in simple complexes are found trans to each other due to a secondary electronic effect. The trans sulfur atoms, by not being coaxial with the strongly bound oxo groups, minimize competitions for molybdenum d levels. Fortunately, the trans arrangement is stable in the Mo(VI) complexes. A cis thiolate arrangement may undergo internal redox chemistry presumably owing to facile oxidation of the adjacent sulfur atoms.[3]

The structures of $\mathrm{MoO_2[CH_3NHCH_2C(CH_3)_2S]_2}$, $\mathrm{MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2}$, and $\mathrm{MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2}$ represent an unusual geometry for dioxomolybdenum(VI).[5] Described as a skew trapezoidal bipyramid (STB), this structure contains thiolate sulfur atoms in a cis configuration at an average S···S distance of 2.77 Å that suggests partial disulfide bond formation. At the same time, the O=Mo=O angle at 122° is larger than has ever been reported for dioxomolybdenum(VI). More typical values for this angle are ~109°.[3,6-10] The large O=Mo=O angle and somewhat longer Mo–O distance should result in a lowered frequency of vibration for $\nu(\mathrm{Mo({=}O)_2})$ for these three complexes with STB structure as compared to those of a normal octahedral complex. In a system of similar ligands ($\mathrm{MoO_2N_2{-}S_2}$), $\nu(\mathrm{Mo({=}O)_2})$ should vary inversely with the O=Mo=O angle. We report here Raman and infrared studies of molybdenum–oxygen stretching vibrations of these complexes, which generally serve to distinguish between STB and octahedral structures on the basis of their $\mathrm{Mo({=}O)_2}$ stretching frequencies. However, in a few cases, the $\mathrm{Mo({=}O)_2}$ frequencies are lower than expected for octahedral structures, and intramolecular hydrogen bonding is proposed to be responsible. In addition, we present evidence that the STB structures are unstable in solution upon laser irradiation and may preferentially convert to an octahedral geometry if that form is sterically possible.

Experimental Procedures

The synthesis of the complexes has been reported previously.[4,5,10-13] Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 621 grating infrared spectrometer. Raman data were collected on a Jarrell-Ash 25-300 spectrophotometer with modified grating and slit drives (RKB, Inc.) interfaced to a Computer Automation LSI-2 computer. This instrument has been described elsewhere.[14] Spectral data were recorded on solid samples cooled to ~90 K in a copper-rod cold finger immersed in liquid nitrogen, as described previously.[15] The scattered Stokes light was collected from the Dewar flask in a backscattering geometry. In general, the signal-to-noise ratio in Raman spectra was enhanced by repetitive scanning. NMR data were collected on samples at ambient

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Table I. Proposed Assignments for Selected Vibrational Frequencies (cm^{-1}) in Bidentate Ligand Complexes of Mo(VI)

complex		$Mo(=O)_2$ sym	$Mo(=O)_2$ asym	Mo—N sym	Mo—N asym	Mo—S sym	Mo—S asym
$MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$[a]	IR	882	856	600	555	378	350
	R	877	848	606		399	360
$MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$[a]	IR	878	847	624	557	408	388
	R	876		631	561	414	380
$MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$[a]	IR	893	855	606	562	373	357
	R	891	860	605	555	376	342
$MoO_2[NH_2CH_2CH_2S]_2$[b]	IR	888	850			387	351
	R	881	852				356
$MoO_2[tox]_2$[c]	IR	925	895	275		365	342
	R	916	891	276	251	366	342
$MoO_2[NH_2CH_2C(CH_3)_2S]_2$[b]	IR	907	872	590	539	404	363
	R	906	870	593		412	362
$MoO_2[C_6H_5CH_2NHCH_2C(CH_3)_2S]_2$[b]	IR	923	900	585	560	405	371
	R	924	903	597	566	414	368

[a] Complexes having the skew-trapezoidal-bipyramidal structure as determined from crystallography.[4,5] [b] Complexes assigned an octahedral structure (see text). [c] Complex having the octahedral structure as determined by crystallography.[5]

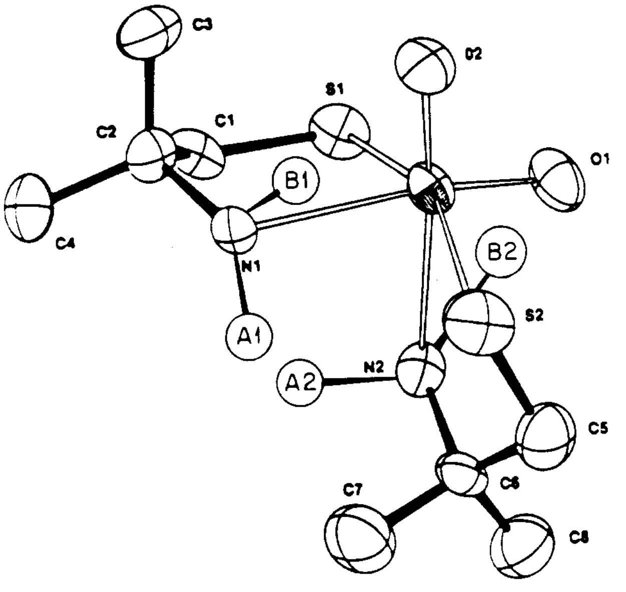

Figure 1. Generalized structural framework for octahedrally coordinated $Mo^{VI}O_2(N\text{-}S)_2$ complexes with substituted cysteamine ligands indicating the positions of the N-substituents A1, A2, B1, and B2 (adapted from ref 9).

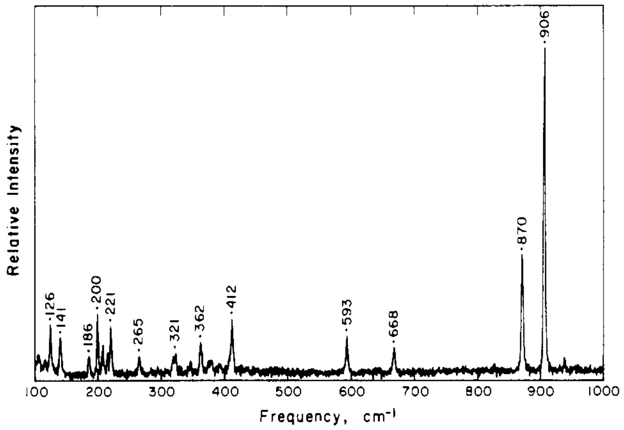

Figure 2. Raman spectrum of polycrystalline $MoO_2[NH_2CH_2C(CH_3)_2S]2$, representative of the relative signal intensities in the 100–1000-cm^{-1} region. Conditions: laser excitation 568.2 nm, ~30 mW at the sample Dewar; sample temperature ~90 K; bandpass 2.5 cm^{-1}; scan rate 2.5 cm^{-1} s^{-1}, 10 repetitive scans.

temperature with a JEOL FX90Q PFT-NMR spectrometer.

Raman studies of solutions of the Mo(VI) complexes were carried out at ambient temperature in three solvents (CH_2Cl_2, CH_3CN, and $(CH_3)_2SO$) over the range 800–1000 cm^{-1} to focus on the $Mo(=O)_2$ stretching frequencies. Because both CH_2Cl_2 and CH_3CN have a Raman band in this range, it was necessary to measure each complex in both solvents to observe all the Raman spectral features. However, Me_2SO was the only solvent used for $MoO_2[NH_2CH_2C(CH_3)_2S]_2$, $MoO_2[NH_2CH_2CH_2S]_2$, and $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$ because they are insoluble in CH_2Cl_2 and CH_3CN. Me_2SO has three Raman bands in this region at 899, 933, and 956 cm^{-1}. These three bands were deconvolved from $Mo(=O)_2$ bands through the use of a curve-fitting program that obtains a best fit to the observed spectrum by a trial and error procedure. Polarization data for selected $Mo(=O)_2$ frequencies were obtained by collecting Raman spectra back-to-back before and after rotation of the polarization of the incident radiation and passing the scattered light through a polarization scrambler.

Results and Discussion

Spectral Studies on Polycrystalline Complexes. The proposed assignments for the infrared and Raman frequencies of the $Mo(=O)_2$, Mo—N, and Mo—S stretching vibrations for the series of MoO_2^{2+} cysteamine complexes are listed in Table I. The $Mo(=O)_2$ stretching frequencies are generally intense and are in a region of the spectrum free from interferences by other modes (Figure 2). Isotopic studies of four compounds ($MoO_2[NH_2CH_2C(CH_3)_2S]_2$, $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$, and $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$) with ^{18}O enrichment have confirmed the assignments for the $Mo(=O)_2$ stretching vibrations.[16] Assignments for Mo–N and Mo–S frequencies are discussed later.

The values of the symmetric $Mo(=O)_2$ stretching frequency of these compounds vary from a low of 876 cm^{-1} to a high of 925 cm^{-1}. These values can be grouped into three approximate ranges: (1) a low range (876–891 cm^{-1}) that includes the three known STB structures of $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, and $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$; (2) a high range (916–925 cm^{-1}) that includes $MoO_2[C_6H_5CH_2NHCH_2C(CH_3)_2S]_2$ and $MoO_2[tox]_2$, the latter of which is known to possess an octahedral structure; (3) an intermediate value as represented by $MoO_2[NH_2CH_2C(CH_3)_2S]_2$ but having an unknown structure (Figure 2).

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(16) Partial ^{18}O enrichment (see ref 7, 8, 10, and 12) of these compounds leads to complicated patterns of isotopic shifts of the $Mo(=O)_2$ stretching modes in the Raman and infrared spectra of the polycrystalline samples. The origin of these up to seven peaks has been interpreted as a superposition of the coupled symmetric and asymmetric stretching vibrations involving single and/or double O atom substitutions at inequivalent sites (Willis, L. J.; Loehr, T. M. *Spectrochim. Acta*, in press). For example, the pair of lines at 906 and 870 cm^{-1} in $MoO_2[NH_2CH_2C(CH_3)_2S]_2$ (Figure 2) is replaced by peaks at 914, 902, 881, 870, 851, and 843 cm^{-1} (Raman) and corresponding features at 913, 900, 881, 867, 847, and 840 cm^{-1} (infrared) of the ^{18}O-enriched complex. The symmetric/asymmetric $Mo(=O)_2$ modes have been assigned at 914/881, [907]/843, 902/851, and 870/[836] cm^{-1} for the $^{16}O/^{16}O$, $^{16}O/^{18}O$, $^{18}O/^{16}O$, and $^{18}O/^{18}O$ species, respectively, having slightly different force constants for the two Mo=O bonds. Despite the apparent complexity of the isotopic splitting shifts, the data clearly support the assignment of these bands as Mo=O vibrations.

Table II. Proposed Assignments for Selected Vibrational Frequencies (cm^{-1}) in Tetradentate and Tridentate Ligand Complexes of Mo(VI)

		Mo(=O)$_2$		Mo—N		Mo—S		Mo-O-Mo	
complex		sym	asym	sym	asym	sym	asym	asym	sym
MoO$_2$[SC(CH$_3$)$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$C(CH$_3$)$_2$S]	IR	888	866	592		392	365		
	R	892	866	593		392	370		
MoO$_2$[SCH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$S]	IR	923	896	600	541	401	370		
	R	909	890	600	532	407	368		
MoO$_2$[(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_2$CH$_2$S)$_2$]	IR	923	896	548	526	412	362		
	R	919^a							
		916^a	894	545	526	415	366		
MoO$_2$[NH$_2$CH$_2$CH$_2$N(CH$_2$CH$_2$S)$_2$]	IR	913	881	532		410	365		
	R	909	884			407	370		
Mo$_2$O$_5$[(CH$_3$)$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$S]$_2$	IR	918	882	585	520	370		715	460
	R	914	884		521	378		706	462
Mo$_2$O$_5$[(CH$_3$)$_2$NCH$_2$CH$_2$NHCH$_2$C(CH$_3$)$_2$S]$_2$	IR	916	889	588	520	375		680	
	R	910	883			382			

^{a} Doublet.

The intermediate value of 906 cm^{-1} has been reported for a similar complex, MoO$_2$[NH$_2$C(CH$_3$)$_2$CH$_2$S]$_2$, which has identical values for the Mo(=O)$_2$ symmetric and antisymmetric stretching frequencies to the isomeric compound, MoO$_2$[NH$_2$CH$_2$C(CH$_3$)$_2$S]$_2$.[4] The structure of the former compound has recently been reported to have the octahedral structure with cis oxygen, trans sulfur, and cis nitrogen ligating atoms.[9] One can reasonably conclude from the vibrational frequencies that MoO$_2$[NH$_2$CH$_2$C(CH$_3$)$_2$S]$_2$ also has the distorted octahedral geometry and that the position of the methyl groups on the ethylene backbone does not create any steric hindrances that might alter the structure.

The unusual STB geometry of MoO$_2$[CH$_3$NHCH$_2$C(CH)$_3$S]$_2$ has been suggested to result from unfavorable steric or electronic interactions that would occur in a more normal octahedral complex with this ligand.[4] In the octahedral geometry, the methyl groups on the cis nitrogen atoms may interfere sterically with each other, preventing the formation of the octahedral complex. This hypothesis was examined by using Fisher–Hirschfelder–Taylor atom models.[17] The positions of the variable nitrogen substituents, A and B, are illustrated in Figure 1 by reference to the octahedral structure of MoO$_2$[NH$_2$C(CH$_3$)$_2$CH$_2$S]$_2$.[9] In the *N,N*-dimethyl complex, MoO$_2$[(CH$_3$)$_2$NCH$_2$C(CH$_3$)$_2$S]$_2$, the steric interference argument is very strong since the A1 and A2 positions must be filled with methyl groups making the octahedral geometry extremely unfavorable for this molecule; indeed, only the STB structure has been observed for this compound. In the mono-*N*-methyl complexes, the space-filling models indicate steric interference only in the A1–A2 arrangement of the four possible geometric configurations. However, three molecular isomers appear to be allowed for the octahedral geometry of the monomethyl-substituted amines: A1–B2, A2–B1, and B1–B2. Only the A1–A2 configuration is prohibited sterically. The ligand nitrogen itself does not favor any specific stereo configuration due to a low-energy barrier to inversion.[18] Since in the mono-*N*-methyl complexes, MoO$_2$[CH$_3$NHCH$_2$C(CH$_3$)$_2$S]$_2$ and MoO$_2$[CH$_3$NHC(CH$_3$)$_2$C(CH$_3$)$_2$S]$_2$, the STB structure predominates, some additional factor other than steric interference must be influencing the selection of structure.

The MoO$_2$[C$_6$H$_5$CH$_2$NHCH$_2$C(CH$_3$)$_2$S]$_2$ complex differs from MoO$_2$[CH$_3$NHCH$_2$C(CH$_3$)$_2$S]$_2$ by the addition of a phenyl ring to each of the *N*-methyl groups. These benzyl groups should create even greater steric interferences than the *N*-methyl groups. If steric considerations were dominant, an STB geometry might have been expected together with a symmetric Mo(=O)$_2$ stretching frequency within the low range. However, MoO$_2$[C$_6$H$_5$CH$_2$NHCH$_2$C(CH$_3$)$_2$S]$_2$ exhibits a frequency at 924 cm^{-1} at the top of the high range that is indicative of an octahedral geometry and a configuration that should have the benzyl groups in the A1–B2, A2–B1, or B1–B2 positions. In view of the similarity of the C$_6$H$_5$CH$_2$NHCH$_2$C(CH$_3$)$_2$S$^-$ and CH$_3$NHCH$_2$C(CH$_3$)$_2$S$^-$ ligands, it is surprising that their complexes do not have similar structures. The formation of the STB geometry is disfavored by the addition of the phenyl substituents. The reason for this difference could lie in the hydrogen-bonding pattern found in the STB complexes,[4,5] which may be precluded by the presence of benzyl groups.

The symmetric Mo(=O)$_2$ stretching frequency for MoO$_2$[NH$_2$CH$_2$CH$_2$S]$_2$ is observed in the low range at 881 cm^{-1}. Since complexes of known STB geometry exhibit frequencies in the low range, assignment of an STB structure to this complex might appear reasonable. However, with the absence of methyl groups on the nitrogen and the ethylene backbone of the ligand, there are no steric interferences that can prevent the formation of either structure. The STB geometry is presently known only when the amine ligand has one or two methyl groups attached to it, a condition that is not present in the NH$_2$CH$_2$CH$_2$S$^-$ ligand. For an octahedral structure, the low symmetric Mo(=O)$_2$ stretching frequency that is observed is explainable by intramolecular hydrogen bonding. The two amine hydrogens would occupy both the A and B positions, and the latter would be ideally situated to hydrogen bond to the nearby oxygen atoms. Such interactions would tend to reduce electron density between the oxygen ligands and Mo(VI), leading to a lowering of the vibrational frequency. For example, large falls in ν(C=O), ν(P=O), and the frequencies of other acceptors due to hydrogen-bonding interactions are well-known.[19] In the respiratory protein, oxyhemerythrin, hydrogen bonding between the hydroperoxide ligand and the oxo bridge of the Fe–O–Fe cluster has been suggested to be responsible for the large drop in ν_s(Fe–O–Fe) relative to that of other methemerythrin adducts.[20] Such significant lowering in frequencies is probably not observed for MoO$_2$[NH$_2$C(CH$_3$)$_2$CH$_2$S]$_2$ and MoO$_2$[NH$_2$CH$_2$C(CH$_3$)$_2$S]$_2$ because the methyl groups on the ethylene backbone may create enough steric interference to inhibit rearrangement of the ligand that would be necessitated in the hydrogen-bonded forms; however, it may be the reason why these two complexes exhibit an intermediate value for ν_s(Mo(=O)$_2$). In the case of MoO$_2$[C$_6$H$_5$CH$_2$NHCH$_2$C(CH$_3$)$_2$S]$_2$, at least one of the amine hydrogens must occupy an A site to prevent the steric interaction of both benzyl groups in A sites, and hence, the lowering of the frequency is not observed. Although the crystal structure of MoO$_2$[NH$_2$CH$_2$CH$_2$S]$_2$ is not known at present, solution studies of this complex (see below) indicate that the octahedral geometry very likely predominates in the solid state.

The complexes listed in Table II consist of Mo(VI) monomers with tetradentate ligands and Mo(VI) dimers with tridentate ligands and a bridging oxygen ligand. With the exception of

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(17) The FHT atom model for the metal ion has a strict octahedral geometry and was, therefore, unsuitable for observing the ligand-enforced distortions upon coordination. Instead, a piece of modeling clay of the same size was substituted. Its flexibility allowed attachment of the ligands at angles other than the strict 90° required by the rigid model and gave a better indication of the likely bonding conditions in the complex.

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Table III. Comparison of Solid-State and Solution Raman Frequencies (cm^{-1}) for Bidentate Ligand Complexes of Mo(VI)

		soln		
complex	solid	CH_2Cl_2	CH_3CN	Me_2SO
$MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$	877 (sym)	928		
	848 (asym)		893	
$MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$	876 (sym)	926		
			895	
$MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$	891 (sym)	899[a]		
	860 (asym)			
$MoO_2[NH_2CH_2CH_2S]_2$	881 (sym)			912 p
	852 (asym)			885 dp
				853 p
$MoO_2[tox]_2$	916 (sym)	931		
	891 (asym)		898	
$MoO_2[NH_2CH_2C(CH_3)_2S]_2$	906 (sym)			912
	870 (asym)			882
$MoO_2[C_6H_5CH_2NHCH_2C(CH_3)_2S]_2$	924 (sym)	931		
	903 (asym)		895	

[a] Upon successive scans, the intensity of the 899-cm^{-1} peak decreases and no new peaks appear; $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ appears to decompose in solution; see text.

Table IV. Comparison of Solid-State and Solution Raman Frequencies (cm^{-1}) for Tetradentate and Tridentate Ligand Complexes of Mo(VI)

		soln		
complex	solid	CH_2Cl_2	CH_3CN	Me_2SO
$MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$	892 (sym)			915
	866 (asym)			888
$MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]$	909 (sym)	925 p		
	890 (asym)		900	
$MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$	919,[a] 916[a] (sym)	928 p		
	894 (asym)	898 dp[b]	900	
$MoO_2[NH_2CH_2CH_2N(CH_2CH_2S)_2]$	909 (sym)			
	884 (asym)		927	
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$	914 (sym)	919		
	884 (asym)	888	888	
$Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2C(CH_3)_2S]_2$	910 (sym)	920		
	883 (asym)	886	886	

[a] Doublet. [b] Precise quantitation of depolarization is difficult because of an underlying, weakly polarized solvent band.

$MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$, all of these complexes exhibit the symmetric $Mo(=O)_2$ stretching vibration above 900 cm^{-1}, indicating that the structures are octahedral with trans thiolate ligands. This conclusion is borne out by the X-ray crystal structure determinations of $MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]$[8] and $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$.[7] The structure of $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$ has also been determined to be the octahedral geometry,[9] yet the major bands in the region of the $Mo{=}(O)_2$ stretching frequencies appear at 892 and 866 cm^{-1} as the symmetric and antisymmetric vibrations, respectively. These lowered values might also be explained through intramolecular hydrogen bonding. Although they are not pictured in the ORTEP drawing of $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$, the positions of the two amine hydrogens can easily be envisioned on the approximately sp^3-hybridzed nitrogen atoms. These amine hydrogens appear to be in good proximity to each of the oxygens to allow intramolecular hydrogen bonding. Such a structural arrangement is also supported by space-filling models. Although both $MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]$ and $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$ have nearly the same O=Mo=O angle (~110°), their Mo=O bond lengths are significantly different. In the latter, which has the necessary amine hydrogens for hydrogen bonding, they average 1.712 Å vs. 1.688 Å for the former complex having the *N*-methyl substituents. This >0.02-Å difference is consistent with our proposal of intramolecular hydrogen bonding leading to lowered $Mo(=O)_2$ frequencies of vibration.

Solution Raman Studies. All of the octahedral complexes exhibit solution Raman frequencies that are some 5–15 cm^{-1} *higher* than the corresponding values in the solid state (Tables III and IV). These increases can be attributed to a relaxation of solid-state effects in which coupling of vibrational modes between molecules in a unit cell results in a lower force constant.[16] The frequency increases are not attributable simply to the change in sample temperature (~90 K for the solids and room temperature for the solutions); in a series of Raman spectra obtained between 100 and 298 K in the 800–900-cm^{-1} region for $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, the $Mo(=O)_2$ vibration at 878 cm^{-1} and a ligand mode at 866 cm^{-1} exhibited identical frequencies and peak shapes at all temperatures. The occurrence of $\nu_s(O{=}Mo{=}O)$ at 919–931 cm^{-1} (values at or above the high range observed in the solids) indicates that these complexes retain an octahedral coordination geometry in solution.

For the STB complexes $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ and $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, however, shifts in $\nu_s(O{=}Mo{=}O)$ of ~50 cm^{-1} from values in the low range into the high range suggest structural rearrangements to some other geometry in solution, possibly octahedral. However, Corbin et al.[11] have reported NMR studies indicating that these complexes retain the STB structure in solution. The possibility must be considered that these compounds are unstable in solution owing to thermal and/or photochemical decomposition in the laser beam used for the Raman excitation. Thus, we noted that the $\nu_s(Mo(=O)_2)$ band for $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (891 cm^{-1} in the solid) shifts upward in frequency to 899 cm^{-1} during the first scan of the CH_2Cl_2 solution sample (Table III). However, in successive scans, the 899-cm^{-1} peak decreases and finally disappears. No new peaks are observed in the $Mo(=O)_2$ stretching region. Since the octahedral structure is sterically forbidden owing to the dimethyl substituents, the loss of the vibrational spectrum indicates decomposition. The NMR spectra of Corbin et al.[11] showed that this complex also retains its STB structure in solution. We believe that the STB structure is unstable in solution owing to decomposition during the Raman experiment. This proposal was tested by recording the NMR spectrum of a solution sample of $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ before and after laser irradiation and finding that it was significantly different. After exposure to

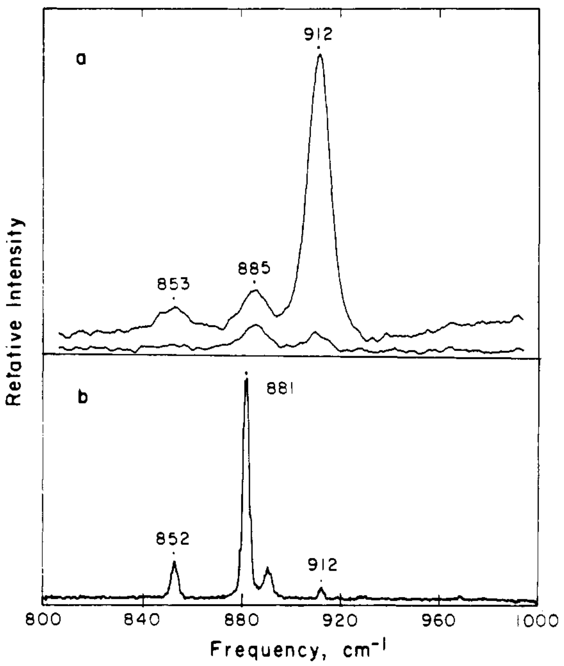

Figure 3. Raman spectra of solution and solid samples of $MoO_2[NH_2CH_2CH_2S]_2$ in the $Mo(=O)_2$ stretching region: (a) difference spectrum of solute in Me_2SO after subtraction of solvent spectrum (647.1-nm excitation, 90 mW, bandpass 5 cm^{-1}, scan rate 1.0 cm^{-1} s^{-1}, 6 scans; upper spectrum, perpendicular polarization; lower spectrum, parallel polarization); (b) polycrystalline solid, spectrum obtained at 90 K (conditions as in Figure 2).

the laser, the NMR spectrum showed a larger number of peaks and the major peaks due to the two types of methyl groups in the ligand exhibited significantly lower intensities. These NMR data confirm that decomposition of the complex had occurred.[21]

The solution Raman spectrum for $MoO_2[NH_2CH_2CH_2S]_2$ shows three peaks at 912 p, 885 dp, and 853 p cm^{-1} which are very similar in frequency to three peaks at 912, 881, and 852 cm^{-1} in the spectrum of the solid (Figure 3). The difference between these two sets of data lies in the relative intensities of these three peaks. In the solution spectrum, the 912-cm^{-1} peak is much more intense than the 885-cm^{-1} peak; yet in the solid-state spectrum, the strongest peak is at 881 cm^{-1} and the band at 912 cm^{-1} is weak (~90 K) or completely absent (at room temperature). The 31-cm^{-1} upward shift in frequency is significantly lower than the ~50-cm^{-1} shifts exhibited by the STB complexes, $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ and $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, yet considerably higher than the typical 5–15-cm^{-1} shifts experienced by the octahedral complexes on going from the solid to the solution phases. The one member of known octahedral geometry, $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$, whose low $Mo(=O)_2$ frequency at 892 cm^{-1} in the solid state is attributed to intramolecular hydrogen bonding, also exhibits an intermediate upshift (23 cm^{-1}) for this frequency in Me_2SO solution. Intramolecular hydrogen bonding in both of these compounds ($MoO_2[NH_2CH_2CH_2S]_2$ and $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$) could be disrupted by the aprotic polar solvent, Me_2SO, permitting the oxygen atoms to regain electron density, thus allowing stronger bonds to Mo and the subsequent increase in frequency.

Other Vibrational Assignments. Values assigned to ν(Mo–S) in Tables I and II are based upon literature values that have been reported in the range 350–400 cm^{-1}.[22] The use of a general valence force field (GVFF) normal-coordinate analysis program on complexes $MoO_2[tox]_2$ and $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, for which X-ray crystal structures are known, confirms these approximate assignments. Within the 350–400-cm^{-1} range, more than two bands appear in the Raman spectra of most of these complexes and, therefore, the assignments must be considered tentative.

Values assigned to ν(Mo–N) in the literature are rare, but reported values are as high as 600 cm^{-1} owing to multiple Mo–N bonding.[23] Other complexes exhibit ν(Mo–N) at 553 and 528 cm^{-1}.[23] On the basis of these few reported values, ν(Mo–N) for amine nitrogens can be expected over a wide range of frequencies from about 500 to 650 cm^{-1}. This region in all of the Raman and infrared spectra of the complexes reported here is relatively void of peaks. Therefore, those peaks observed in this region were assigned to ν(Mo–N).

The one exception to this general assignment is $MoO_2[tox]_2$ whose values for ν(Mo–N) are listed at 276 and 251 cm^{-1}. The ligand contains nitrogen as part of a heterocyclic molecule that constrains the nitrogen from a pure Mo–N stretching vibration. The effect is to impart a larger mass to the nitrogen ligand, which reduces the frequency of vibration. This effect has been observed previously.[24,25] The value at 276 cm^{-1} has been assigned previously to ν(Mo–N) on the basis of molybdenum isotopic shifts,[26] but the peak at 251 cm^{-1} is a new assignment and is based upon normal-coordinate analysis.

Conclusions

In dioxomolybdenum(VI) complexes with nitrogen and thiolate sulfur ligands, the frequency of the symmetric O=Mo=O vibration can be used as an indicator of probable structural type. Values above about 900 cm^{-1} reflect a distorted octahedral structure wherein the thiolate sulfurs coordinate trans to one another and the nitrogens coordinate cis to each other and trans to the two cis oxygens. Values below 900 cm^{-1} may represent a skew-trapezoidal-bipyramid structure as for the complex $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$ or an octahedral structure with significant intramolecular hydrogen bonding between the amine hydrogen atoms and the oxygen ligands to molybdenum, as suggested for the complex $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$. Although it was anticipated that information on the structure of the molybdenum cofactor of xanthine oxidase could be obtained by resonance Raman spectroscopy, studies to date have not revealed any resonance-enhanced modes due to the molybdenum center.[27] Nevertheless, infrared and Raman analyses could yield useful information when the molybdenum cofactor from molybdoenzymes such as xanthine oxidase and sulfite oxidase can be isolated in sufficient quantity and purity for spectroscopic analyses.

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Registry No. $MoO_2[CH_3NHCH_2C(CH_3)_2S]_2$, 74005-67-7; $MoO_2[CH_3NHC(CH_3)_2C(CH_3)_2S]_2$, 76772-96-8; $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$, 74005-68-8; $MoO_2[NH_2CH_2CH_2S]_2$, 29836-54-2; $MoO_2[tox]_2$, 69779-05-1; $MoO_2[NH_2CH_2C(CH_3)_2S]_2$, 76757-49-8; $MoO_2[C_6H_5CH_2NHCH_2C(CH_3)_2S]_2$, 91229-45-7; $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$, 67598-35-0; $MoO_2[SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S]$, 80287-02-1; $MoO_2[(CH_3)_2NCH_2CH_2N(CH_2CH_2S)_2]$, 70612-67-8; $MoO_2[NH_2CH_2CH_2N(CH_2CH_2S)_2]$, 93774-14-2; $Mo_2O_5[(CH_3)_2NCH_2CH_2NHCH_2CH_2S]_2$, 87145-26-4; $Mo_2O_5[(CH_3)_2NHCH_2CH_2NHCH_2C(CH_3)_2S]_2$, 87145-27-5; Mo, 7439-98-7.

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(21) Additional evidence for the sensitivity of the STB compounds to laser intensity came from the solid samples, several of which revealed scorching where the laser light was focused unless the power was reduced and the temperature of the sample was lowered to liquid-nitrogen temperatures.

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