$NHCH_3)B(pz)(C_6H_5)$ and $(C_6H_5)(pz)B(\mu\text{-}pz)_2B(pz)(C_6H_5)$.) Similarly, reaction of the borazine $[(CH_3)_2NBNCH_3]_3$ with a large excess of Hpz at room temperature gave $(CH_3)H_2N{\cdot}B(pz)_3$. This latter result shows that the terminal dimethylamino groups are readily displaced but the annular methylamine moiety of the original borazine is retained in the final product.

It is of interest to compare the ^1H NMR spectra of the two adducts $(CH_3)H_2N{\cdot}B(C_2H_5)(pz)_2$ and $(CH_3)H_2N{\cdot}B(pz)_3$. The former exhibited a signal for the N-bonded protons at 6.3 (2 H) ppm, whereas the latter exhibited two signals at 5.3 (1 H) and 7.55 (1 H) ppm, respectively. For the compound $(CH_3)_2HN{\cdot}B(pz)_3$, the (N)H signal was previously observed at 7.8 ppm and it was noted that in solution and at room temperature the (N)H is not localized and the N atoms of both the $(CH_3)_2N$ and the pz groups participate in the bonding; only at low temperatures the proton was found to be localized at the $(CH_3)N$ site.[6] Since at room temperature the CH_3 signal of $(CH_3)H_2N{\cdot}B(C_2H_5)(pz)_2$ is observed as a triplet, there is no doubt that the N-bonded H atoms with $\delta(^1H)$ 6.3 are located at the $N(CH_3)$ site. (Note that the (N)H signal of $(CH_3)H_2N{\cdot}B(CH_3)(pz)_2$ is also observed at 6.3 ppm.[9]) It is, therefore, reasonable to assume that for $(CH_3)H_2N{\cdot}B(pz)_3$ one (N)H is located at the $N(CH_3)$ site and gives rise to the signal at 6.3 ppm, whereas the other (N)H is fluxional and is evidenced at 7.5 ppm, migrating to 7.9 ppm at −39 °C. It is certainly surprising that the $B(pz)_3$ unit affects the (N)H protons of the coordinated CH_3NH_2 so differently as compared to the $B(pz)_2R$ ($R = CH_3$, C_2H_5) unit.

Finally, the reaction of $[(CH_3)_2NNH]_3B$ with excess of Hpz proceeded analogous to that of $[(CH_3)_2N]_3B$[6] to yield the complex $(CH_3)_2NNH_2{\cdot}B(pz)_3$. However, the latter is thermally much less stable than $(CH_3)_2HN{\cdot}B(pz)_3$ and it decomposed on attempts for purification. When heated to its melting point, it decomposed with the formation of what appeared to be (NMR and mass spectroscopic data) a mixture of $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ and $(pz)_2B(\mu\text{-}pz)[\mu\text{-}(CH_3)_2NNH]B(pz)_2$, which could not be separated.

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Resonance Raman Signatures of Oxomolybdenum Thiolate and Dithiolene Models of Molybdenum Proteins

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Resonance Raman (RR) data are reported for molybdenum compounds having ligands related to those which may be present at the active site of Mo redox enzymes: $Mo^{VI}O_2(dttd)$ (**1**) (dttd = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane), $Mo^{IV}(S_2C_2(CO_2Me)_2)_3^{2-}$ (**2**), and $Mo^{IV}O(S_2C_2(CO_2Me)_2)_2^{2-}$ (**3**). For **1** RR bands are observed at 922/865 and 375/356 cm^{-1} and are assigned to symmetric/asymmetric Mo═O and Mo—S(thiolate) stretchings, respectively. Excitation profiles (EP's) show the 922-cm^{-1} Mo═O band to reach maximum enhancement in resonance with a strong 410-nm electronic absorption of **1**, which is assigned to an O—Mo charge-transfer (CT) transition. In contrast, the 356-cm^{-1} Mo—S band EP has a dispersive shape with a maximum at 520 nm and a dip at 480 nm. This behavior is indicative of interference between scattering contributions from the strong 410-nm transition and a weaker transition at ~480 nm, attributed to thiolate–Mo CT. For **2**, the 647.1-nm-excited RR spectrum in resonance with a broad ~650-nm electronic absorption, shows a strong band at 365 cm^{-1} and a weaker one at 702 cm^{-1}, assigned to Mo—S and C—S stretching modes, respectively. Weak enhancement is also observed for bands at 1475, 1488, and 1525 cm^{-1}, one or more of which may arise from C═C stretching of the dithiolene ring. Replacement of a dithiolene ligand by an oxo ligand (giving **3**) produces marked RR changes. The Mo—S and C═C stretches, now at 393 and 1535 cm^{-1}, are seen with violet excitation, 406.7 nm, while yellow excitation (568.2 nm) reveals the Mo═O stretch, at 910 cm^{-1}, albeit weakly. The altered RR pattern implies a substantial electronic rearrangement, which is also reflected in the shifted ground-state vibrational frequencies.

Introduction

Molybdenum enzymes are distinguished by having extractable Mo-containing cofactors, which can reconstitute activity in Mo-deficient protein preparations.[1] The cofactors are of two kinds, the Fe–Mo cofactor of nitrogenase,[2,3] which contains Fe–Mo–S clusters, and the Mo–pterin cofactor of the Mo oxidase/reductase enzymes.[4-6] Although extractable, both cofactors are labile once extracted and have resisted definitive structural characterization, despite intense effort.

In the case of the Mo–pterin cofactor, for which model chemistry has been extensively investigated,[7] Rajagopalan[8,9] and coworkers have made the intriguing structural proposal shown in Figure 1, in which a *cis*-dioxo (or *cis*-oxo–sulfido) Mo(VI) unit (in the reduced Mo(IV)-containing form, an oxo or sulfido ligand is replaced by OH or SH$^-$) is bound via a dithiolene chelate to the pterin side-chain. The remaining Mo coordination sites presumably offer points of attachment for protein side-chain ligands, which are likely to be cysteine thiolate groups, as judged from EXAFS[10,11] and EPR[12] evidence, although nitrogen or oxygen ligands may sometimes be involved.[11] While based on compelling evidence from the chemical nature of cofactor degradation

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Table I. RR Frequencies and Assignments[a]

complex	ν_s(Mo—S)	ν_s(Mo═O)	ν_{as}(Mo═O)	ν(C═C)
$Mo^{IV}(mnt)^{2-}$ [b]	354			1497
$Mo^{IV}(S_2S_2C_2(CO_2Me)_2)_3^{2-}$ [c]	365			1525[e]
$Mo^{IV}O(S_2S_2C_2(CO_2Me)_2)_2^{2-}$ [c]	393	910		1535
$Mo^{VI}O_2(dttd)$ [c]	375[d]	922	890	
$Mo^{VI}O_2(L\text{-}cysOEt)_2$ [c]	380	921	890	

[a] $\nu_{s/as}$ = symmetric/asymmetric stretching. [b] Reference 14. [c] This work. [d] Asymmetric stretch at 355 cm^{-1}. [e] Other candidates at 1475 and 1488 cm^{-1}; see text.

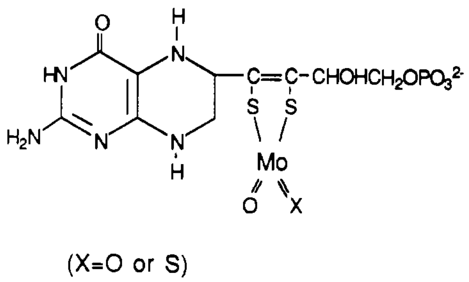

Figure 1. Structure proposed by Rajagopalan and co-workers[8,9] for the Mo-pterin cofactor.

products,[8,9] this structural proposal remains to be tested experimentally.

Resonance Raman (RR) spectroscopy might provide a useful test, because several bonding features of the proposed structure should have distinctive RR signatures. Thus Mo═O (and Mo═S), as well as Mo—S(thiolate or dithiolene), stretching modes are expected at characteristic frequencies and should be subject to RR enhancement via charge-transfer (CT) transitions.[13,14] The putative dithiolene C═C stretch should also be enhanced in resonance with electronic transitions of the Mo-dithiolene ring.[15] Pterin vibrations are also expected, but the pterin electronic transitions are in the ultraviolet region, while transitions associated with the dithiolene-MoO(S) unit might be expected in the visible region. The positions and strengths of these transitions are quite uncertain, however, since the absorption spectra of Mo proteins are generally dominated by other chromophoric cofactors: heme, flavin, and Fe-S clusters.[1] In a RR study of xanthine oxidase by Willis and Loehr[16] only Fe-S vibrational modes were detected. The Mo domain of sulfite oxidase, which can be separated from the cytochrome domain by tryptic cleavage, does show absorption bands at ~360 and ~480 nm, which might arise from CT transitions.[17] A preliminary RR spectrum[18] of this enzyme obtained with 514.5-nm excitation appears to show bands at 925 and 904 cm^{-1}, albeit on a strong fluorescence background, which have been attributed to a *cis*-$Mo^{VI}O_2$ unit.

In this situation it would be helpful to know the RR enhancement patterns of model compounds in order to anticipate the optimum excitation wavelengths for protein studies. Unfortunately no close replica of the structure shown in Figure 1 has yet been prepared, but compounds are available that exemplify some of the bonding features separately. In this study we report RR characteristics for three of these compounds: $MoO_2(dttd)$[19] (**1**) (dttd = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane), in which a *cis*-$Mo^{VI}O_2$ is bound to a chelate having two thiolate and two thioether ligands, $Mo(S_2C_2(CO_2Me)_2)_3^{2-}$ [20] (**2**), a tris(dithiolene)molybdenum(IV) complex, and $MoO(S_2C_2(CO_2Me)_2)_2^{2-}$ [21] (**3**), a $Mo^{IV}O$ complex with two dithiolene ligands. The expected vibrational modes are seen for these compounds, and interesting variations in enhancement patterns are encountered.

Experimental Section

$MoO_2(dttd)$ (**1**) was synthesized according to Kaul et al.,[19] except that the CH_2Cl_2 extract of the solid formed from Mo and dttd was oxidized with *tert*-butyl hydroperoxide (3.0 M in 2,2,4-trimethylpentane (Aldrich), diluted 25× in CH_2Cl_2) for 5 min; the solvent was removed with a rotary evaporator, and the sample was redissolved in CH_2Cl_2. The purity of the dttd was checked by NMR spectroscopy, and that of the final product by electrochemistry.[19] The triethylammonium (TEA^+) salts of $Mo(S_2C_2(CO_2Me)_2)_3^{2-}$ (**2**) and $MoO(S_2C_2(CO_2Me)_2)_2^{2-}$ (**3**) were prepared by the methods of Coucouvanis and co-workers.[20,21] $MoO_2(L\text{-}cysOEt)_2$ was prepared by established procedures.[22,23] Electronic absorption spectra were recorded in CH_2Cl_2 with a HP 8451A diode array spectrophotometer.

Raman spectra were obtained with Kr^+ or Ar^+ CW laser excitation in backscattering geometry using spinning solution or solid sample holders. The spectra were collected with a Spex 1401 double monochromator equipped with a cooled RCA 31034 photomultiplier and photon-counting electronics (Ortec 9325), under computer control. They were analyzed with the aid of Spectra-Calc software.

Results

$Mo^{VI}O_2$(dttd). A structural diagram of $MoO_2(dttd)$ (**1**)[19] is shown in Figure 2, along with RR spectra of a CH_2Cl_2 solution excited at 406.7 and 520.8 nm. At these wavelengths selective enhancement is observed for bands associated with Mo═O (922 cm^{-1}) and Mo—S(thiolate) (375 cm^{-1}) stretching, respectively. These are the symmetric stretches, for which maximal enhancement is expected. Weaker bands are seen, at 890 and 350 cm^{-1}, which are assignable to the respective asymmetric stretches. The frequencies are in the range reported by Willis et al.[24] for a series of $Mo^{VI}O_2$ cysteamine complexes. As shown in Table I, we find essentially the same frequencies for the RR bands of $MoO_2(L\text{-}cysOEt)$ (L-cysOEt = L-cysteine *O*-ethyl ester), whose methyl analogue has Mo═O and Mo—S(thiolate) bond distances (1.714 and 2.414 Å)[25] that are the same as those of **1**.[18] (Raman frequencies reported by Ueyama et al.[14] for solid $MoO_2(L\text{-}cysOEt)_2$ differ by 5-15 cm^{-1}, probably due to solid-state effects.[24]) The Mo—S stretches are attributable to the thiolate groups of **1**. The thioether ligands should give rise to additional Mo—S stretches, but these are expected at lower frequencies, since the thioether bonds are longer than the thiolate bonds, 2.68 vs 2.40 Å.[19] Application of Badger's rule[26] to the Mo—S bonds suggest that the Mo—S(thioether) frequencies should be ~30% lower than the Mo—S(thiolate) frequencies, and therefore should fall at ~250 cm^{-1}. This region is obscured by a solvent peak in our spectra. A weak unassigned mode is observed at 390 cm^{-1} with 406.7-nm excitation; it may arise from a ligand deformation.

The intensities of the 922-cm^{-1} Mo═O and 375 cm^{-1} Mo—S bands were measured relative to a solvent band at several

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Table II. Estimated RR Peak Height Intensities Expressed in Units of Cross Section (Millibarns per Steradian per Molecule) at the Indicated Excitation Wavelength, λ_0 (nm)

complex	σ(Mo—S);[c] λ_0	σ(μo=O);[d] λ_0	σ(C=C); λ_0
$Mo^{IV}(S_2S_2C_2(CO_2Me)_2)_3^{2-}$[a]	0.13 (±25%); 647.1		0.03 (±25%); 647.1
$Mo^{IV}O(S_2S_2C_2(CO_2Me)_2)^{2-}$[a]	0.03 (±6%); 406.7	0.01 (±19%); 568.2	0.07 (±25%); 406.7
$Mo^{VI}O_2$(dttd)[b]	58 (±20%); 520.8	103 (±4%); 413.1	

[a] Measured against the TEA$^+$ ion band at 449 cm^{-1} (solid sample), which was in turn referenced against the CH_2Cl_2 band at 284 cm^{-1} in a 1.2 M solution of TEA$^+$Cl$^-$ in CH_2Cl_2. The CH_2Cl_2 band was in turn referenced against the benzene 998-cm^{-1} band in a mixture of the two solvents. The benzene cross sections are given in ef 35. [b] Measured against the CH_2Cl_2 (solvent) band at 284 cm^{-1}. [c] Mo—S symmetric stretch for **1**; MoS_6 or MoS_4 breathing modes for **2** and **3**. [d] MoO_2 symmetric stretch for **1**. [e] Uncertainty estimated from the peak height measurement confidence level.

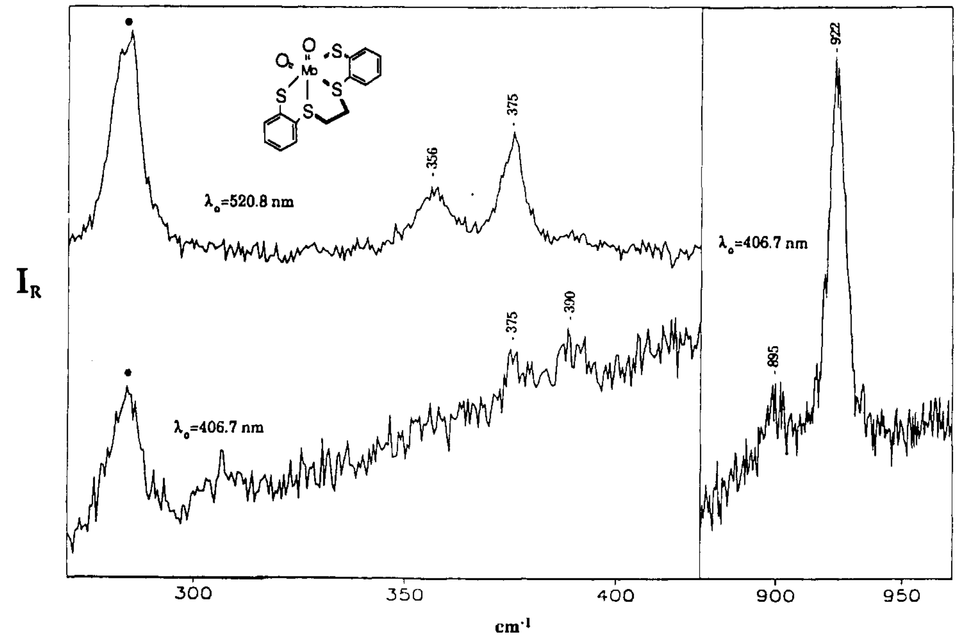

Figure 2. RR spectra of MoO_2(dttd) in CH_2Cl_2 (3 mM) with excitation at 406.7- and 520.8-nm excitation, showing selective enhancement of Mo=O and Mo—S stretching bands. (Bands with asterisks are from the solvent.) Conditions: 100-mW laser power, 3-cm^{-1} slit width, 2-s dwell time/0.5-cm^{-1} step.

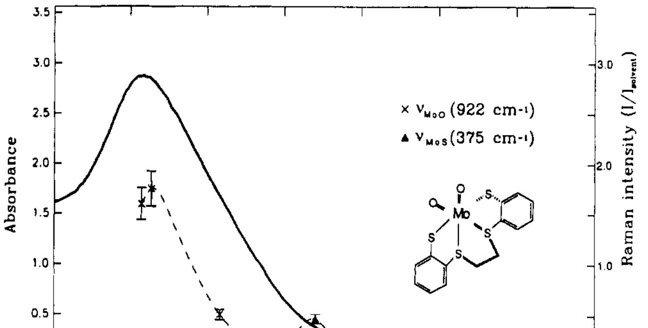

Figure 3. Absorption spectra of MoO_2(dttd) (0.1 mM in CH_2Cl_2) and excitation profiles of the 922-cm^{-1} Mo=O and 375-cm^{-1} Mo—S stretching RR bands. RR intensities were ratioed to the 284-cm^{-1} CH_2Cl_2 band in 3 mM solution.

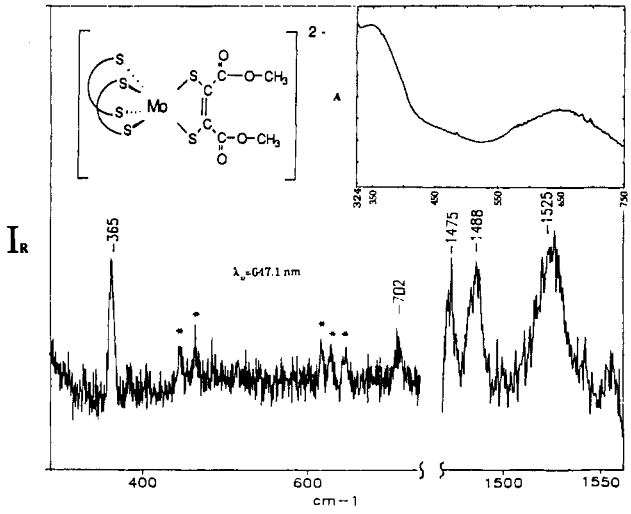

Figure 4. Absorption spectrum in CH_2Cl_2 solution (0.1 mM) (inset) and 647.1-nm-excited RR spectrum of solid $(TEA)_2[Mo(S_2C_2(CO_2Me)_2)_3]$. Asterisks mark TEA$^+$ (tetraethylammonium) bands, and conditions are as in Figure 2.

wavelengths. They are plotted as Raman excitation profiles (EP's) in Figure 3 and compared with the absorption spectrum. Clearly the Mo=O profile tracks the 410-nm absorption band, which is therefore assigned to an O—Mo charge-transfer (CT) transition. The Mo—S EP of **1** does not show a 410-nm peak but instead gives a maximum (weaker than the Mo=O EP maximum) at ~520 nm. The absorption spectrum shows no feature at this wavelength, but the 410-nm band is skewed to the red, and its shape suggests the presence of a weaker band at ~480 nm. We assign a S—Mo CT transition near this wavelength. The red shift of the Mo—S EP maximum (520 nm) as well as the dip at the resonant wavelength (480 nm) can be explained by destructive interference[27] between scattering contributions from the local weak Mo—S CT state and stronger higher lying excited states. This behavior is well precedented in other systems.[28] The Mo=O and M—S (bridging) EP's reported by Ueyama et al.[14] for the binuclear complex $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]$ are quite consistent with

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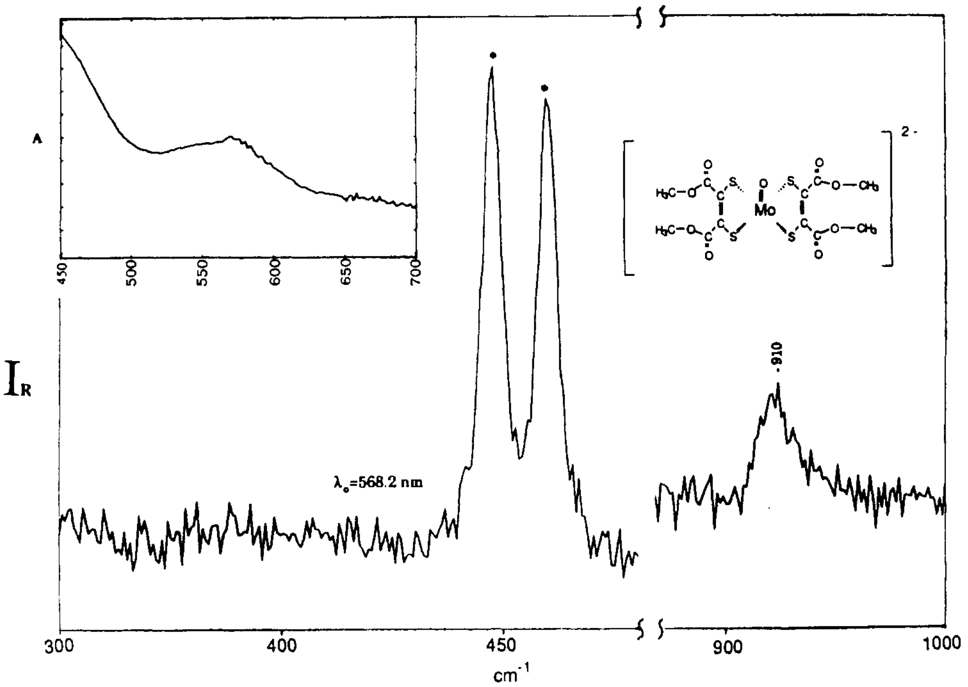

Figure 5. Absorption spectrum in CH_2Cl_2 solution (0.4 mM) (inset) and 568.2-nm-excited RR spectrum of solid $(TEA)_2[MoO(S_2C_2(CO_2Me)_2)_2]$ showing weak enhancement only of the 910-cm^{-1} Mo═O stretching mode. Asterisks mark TEA peaks, and conditions are as in Figure 2.

the behavior shown in Figure 3, but the critical wavelengths where the extrema occur are missing from their plots.

When absolute intensities are determined by comparing the solvent band with benzene, whose Raman cross section is known, the enhancement factors for Mo═O and Mo—S stretching are found to be modest. Expressed in cross section units, millibarns per steradian per molecule (Table II), the Mo═O and Mo—S RR intensities are 103 and 58 when measured at their EP maxima. For comparison, the RR intensities for the strong bands of tryptophan are in the 1400–2000 range in resonance with the allowed 220-nm π–π^* transition of the indole ring.

$Mo(S_2C_2(CO_2Me)_2)_3^{2-}$. A structural diagram of $Mo(S_2C_2(CO_2Me)_2)_3^{2-}$ (**2**) is shown in Figure 4, along with the absorption spectrum (in CH_2Cl_2) and the 647.1-nm-excited RR spectrum of the tetraethylammonium (TEA^+) salt. The absorption and RR spectra are similar to those of the analogous tris(dithiolene) complex $Mo(mnt)_3^{2-}$ (mnt = 1,2-dicyanoethylenedithiolato), for which Clark and Turtle[15] report enhancement of the MoS_6 breathing mode, at 354 cm^{-1}, with red excitation. The dominant RR band in Figure 4, at 365 cm^{-1}, is likewise assigned to this mode. Its 11-cm^{-1} upshift in **2** is surprising, since the Mo—S bonds are 0.02 Å longer in **2** than in $Mo(mnt)_3^{2-}$ (2.39[19] vs 2.37 Å[29]). The geometries of the two complexes differ, however. **2** is a trigonal prism,[20] while in $Mo(mnt)_3^{2-}$ the S_3 triangles are twisted halfway to an octahedral configuration.[29] The principal effect of this twist is to increase the S--S separation within each dithiolene ring, from 3.09[19] to 3.14 Å[29] (the interligand S--S distances are nearly the same, 3.18–3.20 Å). The S--S nonbonded force constants should consequently be larger for **2**, leading to an increase in the MoS_6 breathing frequency. This effect evidently overrides the expected decrease in the Mo—S stretching force constant.

Aside from bands due to the TEA^+ counterions (marked with asterisks), the RR spectrum of **2** also contains weakly enhanced bands at 702, 1475, 1488, and 1525 cm^{-1}. The 702-cm^{-1} band is assigned to a stretching mode of the dithiolene C—S bonds. It is ~20 cm^{-1} higher than bands assigned by Ueyama et al.[14] to C—S stretching in $Mo^{VI}O_2$ complexes of several cysteine esters, consistent with the more delocalized bonding in the dithiolene ring. The frequency is too low to be the MoS_6 breathing mode overtone ($2 \times 365 = 730$ cm^{-1}), anharmonicity being negligible for dithiolene M—S stretching overtones.[15]

The trio of bands near 1500 cm^{-1} are in the dithiolene C═C stretching region.[15,30] It is possible that all three are C═C stretches, since there are three dithiolene rings in the complex. In D_{3h} (trigonal prismatic) symmetry these stretches transform as A_1' and E'; the 1475/1488 cm^{-1} doublet could be the E' mode, split by solid-state effects, while the 1525-cm^{-1} band could be the A' mode. This assignment implies significant electronic coupling to explain the 50-cm^{-1} spread in frequency, since they are separated by several bonds and kinematic coupling is negligible. Electronic coupling is not seen in the centrosymmetric bis(dithiolene) complex $Ni(nmt)_2^{2-}$, whose Raman[32] and IR[30] C═C modes (A_{1g} and B_{2u}) are at almost the same frequency, 1480–1485 cm^{-1}. Mo(IV), however, has empty d_π orbitals, which can provide a pathway for electronic coupling, whereas the d_π orbitals are filled on (low-spin) Ni(II).

Clark and Turtle[15] report a single C═C stretching RR band for $Mo(mnt)_3^{2-}$, at 1497 cm^{-1}, and it is enhanced in resonance with the next higher absorption band, at 500 nm, not with red excitation. Evidently the character of the excited states is altered somewhat between **2** and $Mo(mnt)_2^{2-}$, due to the different ligand orbital energies and their altered overlaps with the Mo orbitals in the twisted geometry of $Mo(mnt)_2^{2-}$.

The absolute RR intensities are low (Table II), only ca. 0.1 and 0.03 for Mo—S and C═C stretchings, respectively, measured at 647.1 nm, the only wavelength at which the RR bands were detected. The red absorption band of the complex (Figure 4) is very broad, and it is possible that resonance enhancement is diminished by interferences among the multiple expected Mo–dithiolene electronic transitions.[31]

$Mo^{IV}O(S_2C_2(CO_2Me)_2)_2^{2-}$. Replacement of one dithiolene ligand in **2** with an oxo ligand, to give $MoO(S_2C_2(CO_2Me)_2)_2^{2-}$ (**3**), produces marked spectral alterations. As shown in Figure 5, the 650-nm absorption band of **2** is missing and is replaced by a very broad band at ca 580 nm. Excitation within this band (568.2 nm, Figure 5) does not produce RR enhancement of a Mo—S stretch, as observed for **2**, but the Mo═O stretch is observed, albeit weakly (see the stronger Raman signal for the unenhanced TEA^+ bands) at 910 cm^{-1}. On the other hand, excitation at 406.7 nm, at the edge of the strong near-UV ab-

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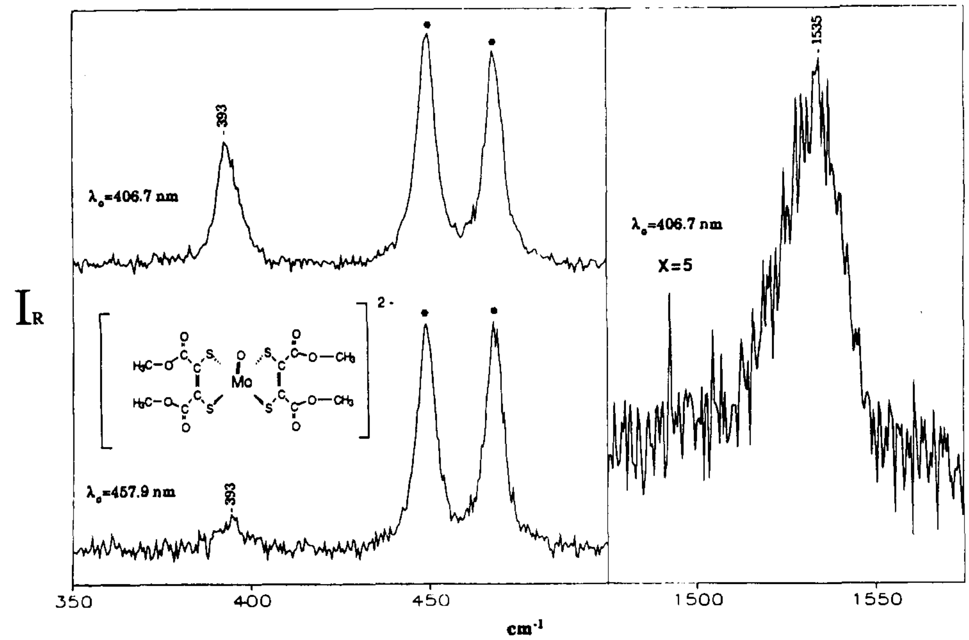

Figure 6. 406.7- and 457.9-nm-excited RR spectra of solid (TEA)$_2$[MoO(S$_2$C$_2$(CO$_2$Me)$_2$)$_2$] showing enhancement of Mo—S (393 cm^{-1}) and C═C (1535 cm^{-1}; scale factor expanded ×5) stretching modes with violet excitation. Asterisks mark TEA modes, and conditions are as in Figure 2.

sorption, does reveal a prominent 393-cm^{-1} band, assignable to Mo—S stretching (Figure 6). Its intensity decreases markedly when the excitation is shifted to 457.9 nm. With 406.7-nm excitation, a band was also detected at 1535 cm^{-1} (Figure 6), which is assigned to C═C stretching. Detailed excitation profiles could not be obtained due to limitations of spectral quality, but the resonance enhancement pattern shows the excited states to be qualitatively different for **3** than for **2**.

The Mo═O frequency, 910 cm^{-1}, is very low compared to other Mo^{IV}O complexes.[33] For example, it is at 1008 cm^{-1} in the isoelectronic complex MoOCl$_4{}^{2-}$.[34] The ~100-cm^{-1} difference is a reflection of the greater π-donating ability of two dithiolene ligands relative to four chlorides. The dithiolenes compete with the oxo ligand for the Mo d$_\pi$ acceptor orbitals, thereby lowering the Mo═O bond strength. Mo—S bonds are 0.01 Å shorter (2.38 Å[21b]) in **3** than in **2**. This small difference, which may result from the decreased steric crowding in the 5-coordinate **3**, indicates that an oxo group and a dithiolene ligand are comparable in their donor strengths. The higher Mo—S stretching frequency in **3** than in **2**, 393 vs 365 cm^{-1}, is attributable partly to the 0.01-Å bond shortening and partly to altered kinematics; the Mo atom moves somewhat during the MoS$_4$ breathing mode of **3**, which has a domed structure[21b] and an asymmetric mass distribution, but not during the MoS$_6$ breathing mode of **2**.

Again, the absolute RR intensities are very low (Table II), values of 0.03 and 0.07 being estimated for Mo—S and C═C stretching at 406.7 nm, similar to the values for **3** measured at 647.1 nm, and 0.01 for Mo═O stretching at 568.2 nm. Interferences from multiple-electronic transition, contributing to the very broad visible absorption (Figure 5), may limit the enhancements.

Discussion

What implications do these results have for RR characterization of the Mo–pterin cofactor? Clearly, the identification of a C═C stretching band would provide key evidence in favor of the proposed dithiolene link[8,9] between the pterin and the molybdenum. Our measurements suggest that enhancement factors for this and other dithiolene modes are likely to be low and that relatively high protein concentrations will be needed for their detection. Nevertheless, it may be possible to detect them by using long-wavelength laser excitation, since only the dithiolene electronic transitions are expected to produce detectable enhancement in the red region.

Mo—S stretching vibrations are expected in the 350–400-cm^{-1} region for the Mo–dithiolene bonds, and also for Mo–thiolate bonds from protein cysteine ligands. It may be possible to distinguish them via their enhancement patterns: the Mo–dithiolene stretches should be enhanced in resonance with long-wavelength dithiolene transitions, while Mo–thiolate stretches should be more strongly enhanced in resonance with thiolate–Mo charge-transfer transitions. These are expected at shorter wavelengths, although the influence of the dithiolene ligand on the charge-transfer energies (via its tuning of the d-orbital energies) is unknown. Also, for this reason the optimum wavelength for enhancing the Mo═O stretches is difficult to anticipate, although it is clearly in the violet region if the thiolate/thioether, complex (**1**), is a guide. The RR spectra of **2** indicate that dithiolene transitions can also enhance Mo═O stretching, albeit weakly.

The Mo═O frequencies should be in the 900–1000-cm^{-1} range, although the spectrum of **2** shows that dithiolene coordination has the effect of depressing the frequency toward the lower end of the range, at least for Mo(IV). The Mo^{VI}═O stretches of oxidized cofactor may be similarly downshifted.

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