

Figure 2. Plot of $\log k_{\text{OH}}$ against the $\text{p}K_{\text{a}}$ of the leaving oxime for the alkaline hydrolysis of acetyl esters of various oximes measured at 25 °C. The $\text{p}K_{\text{a}}$ values are taken from the literature.⁵ The data presented are the rates for $\text{Zn}^{2+}\cdot\mathbf{1}(\text{O})$ and the acetyl esters of benzaldoxime³ (■), 2-, 3-, or 4-pyridinecarboxaldoxime³ (▲), and 3- or 4-(hydroxyimino)methyl-*N*-methylpyridinium internal salt⁶ (●). The linear line has a slope (β_{LG}) of -0.65 .

$K \ll 1/[\text{Zn}^{2+}]$, and the linearity seen in Figure 1 indicates $K \ll 5 \text{ M}^{-1}$. The small formation constant for $\text{Zn}^{2+}\cdot\mathbf{1}$ can be ascribed to the low electron density on the nitrogens of $\mathbf{1}$. The $\text{p}K_{\text{a}}$ value for the pyridyl nitrogen of $\mathbf{1}$ was 2.29 ± 0.04 as measured by spectral titration (not shown).

Mechanisms compatible with the observed rate data and the complex formation are indicated in 4-6. The only catalytic role of zinc ion proposed in 4 is to increase the leaving ability of the oxime ion ($\text{p}K_{\text{a}}$ of the oxime is lowered from 10.04 to 6.52 upon complexation with zinc ion⁴). For the mechanism of 4, k' of eq 2 represents the attack of the hydroxide ion on the complex ($k_{\text{OH}}[\text{OH}^-]$), and the corresponding pseudo-first-order rate constant under the condition of $K \ll 1/[\text{Zn}^{2+}]$ is

$$k_0 = k_{\text{OH}}K[\text{Zn}^{2+}][\text{OH}^-] \quad (4)$$

Comparison of eq 4 with eq 1 discloses $k_{\text{OH}} \gg 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ as $K \ll 5 \text{ M}^{-1}$. The plot of $\log k_{\text{OH}}$ against $\text{p}K_{\text{a}}$ of the leaving oxime for the alkaline hydrolysis of various oxime esters is illustrated in Figure 2. The data point for $\text{Zn}^{2+}\cdot\mathbf{1}$ represents the lowest limit estimated above. The large deviation seen with the data point for $\text{Zn}^{2+}\cdot\mathbf{1}$ indicates that other catalytic factors in addition to simple decrease in the basicity of the leaving group is needed to explain the high reactivity of $\text{Zn}^{2+}\cdot\mathbf{1}$.

The most probable mechanism is, therefore, that of 5 or 6. In these mechanisms, polarization of the carbonyl group by the zinc ion and the nucleophilic attack by the neighboring zinc-bound hydroxide ion are also proposed. These two factors have been proposed in several other instances,⁷ although differentiation between them has not been successful.

In summary, the zinc ion catalyzed hydrolysis of $\mathbf{1}$ involves two cooperative catalytic factors: increased leaving ability of the oxime and enhanced nucleophilic attack of the hydroxide ion at the carbonyl carbon.

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Contribution from the Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan, and Faculty of Pharmaceutical Science, Tokushima University, Tokushima 770, Japan

Raman and Resonance Raman Spectra of Oxomolybdenum(VI) and -(V) Complexes of Cysteine and Related Thiolate Ligands¹

Norikazu Ueyama,² Michio Nakata,^{2a} Takeo Araki,^{2a} Akira Nakamura,^{*2a} Shinsuke Yamashita,^{2b} and Takuya Yamashita^{2b}

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Active sites of molybdoenzymes were recently investigated by X-ray absorption edges and EXAFS to reveal the nature of coordinating atoms around the molybdenum.³ The oxidases, e.g., xanthine oxidase, were found to involve $\text{Mo}=\text{O}$ and Mo -thiolate bonds. The coexistence of the hard (oxo) and soft (thiolate) ligands on the same molybdenum(VI) ion has been considered responsible for their high catalytic activity in O atom transfer oxidations and dehydrogenations. Stiefel et al. actively synthesized structural models of such enzymes.⁴ By contrast, the active site of nitrogenase has no $\text{Mo}=\text{O}$ moiety and consists of MoFe -mixed sulfur cluster where bridging inorganic sulfides (sulfido ligand) play an important role.⁵

We have prepared a series of oxomolybdenum complexes of cysteine-containing oligopeptides and here the $\text{Mo}=\text{O}$, $\text{Mo}-\text{S}-\text{Mo}$, and $\text{Mo}-\text{S}-\text{CH}_2$ bondings were investigated by Raman and resonance Raman spectra. These techniques have a distinct advantage over the infrared spectra in that information about vicinity of heavy-metal and sulfur atoms can be obtained. The resonance Raman spectra can detect presence of metal-metal or metal-sulfur bonds even in dilute aqueous solutions.

When one considers importance of the sulfur coordination at the molybdenum enzyme active sites, a correct assignment of $\text{Mo}=\text{O}$, $\text{Mo}-\text{S}-\text{Mo}$, or $\text{Mo}-\text{S}-\text{CH}_2$ vibrations in some relevant model complexes will contribute to further investigation and understanding of the enzymes.

Experimental Section

The dioxobis(acetylacetonato)molybdenum(VI) was purchased from Nakarai Chemical Co. The dioxomolybdenum(VI) complexes of cysteine methyl ester and cysteine ethyl ester were prepared by the method reported by Kay and Mitchell.⁶ Dioxobis(benzyl cysteinato-*S*)molybdenum(VI), $\text{MoO}_2(\text{cysOBzl})_2$, was synthesized by the following method. L-Cysteine benzyl ester hydrochloride (0.36 g) which was prepared by the procedure of Erlanger et al.⁷ was dissolved in 1 mL of water. The solution was added to 1-mL aqueous solution of Na_2MoO_4 (0.21 g). A yellow precipitate was collected, washed with water, and dried over P_2O_5 under reduced pressure. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2\text{Mo}$: C, 43.80; H, 4.41; N, 5.11. Found: C, 43.2; H, 4.39; N, 5.01. Dioxobis(isopropyl cysteinato-*S*)molybdenum(VI), $\text{MoO}_2(\text{cysO-}i\text{-Pr})_2$, was synthesized by the same method mentioned above for the $\text{MoO}_2(\text{cysOBzl})_2$. Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2\text{Mo}$: C, 31.86; H, 5.35; N, 6.19. Found: C, 31.56; H, 5.35; N, 6.40. The dioxomolybdenum(VI) complexes of dimethyldithiocarbamate ($\text{S}_2\text{CNMe}_2^-$) and diethyldithiocarbamate ($\text{S}_2\text{CNEt}_2^-$) ligands were

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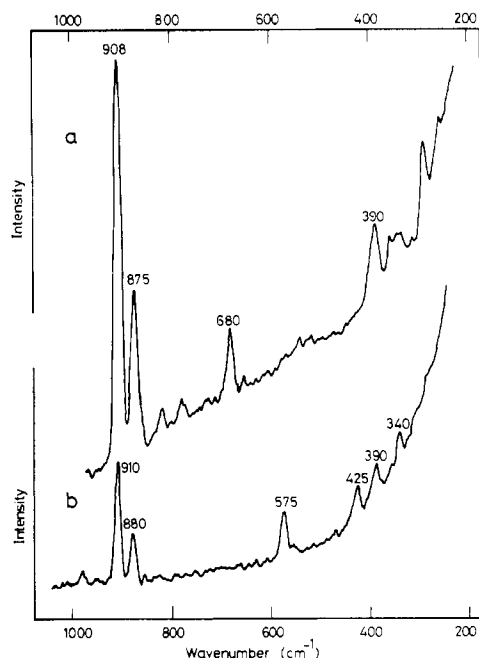


Figure 1. Raman spectra of (a) $\text{MoO}_2(\text{cysOEt})_2$ and (b) $\text{MoO}_2(\text{S}_2\text{CNET}_2)_2$ in the solid state (6328-Å excitation, 10 mW, 32 scans).

prepared by the methods reported in the literature.⁸

Sodium di- μ -oxo-bis[oxo(cysteinato)molybdate(V)] pentahydrate, $\text{Na}_2\text{Mo}_2\text{O}_7(\mu\text{-O})_2(\text{cys})_2 \cdot 5\text{H}_2\text{O}$, was prepared by the dithionite reduction procedure of Kay and Mitchell.⁶ Sodium di- μ -sulfido-bis[oxo(cysteinato)molybdate(V)] tetrahydrate, $\text{Na}_2\text{Mo}_2\text{O}_7(\mu\text{-S})_2(\text{cys})_2 \cdot 4\text{H}_2\text{O}$, was prepared by the procedure reported by Schultz et al.⁹ Sodium di- μ -oxo-bis[oxo(L-histidinato)molybdate(V)] was prepared by the method of Melby.¹⁰

The Raman and the resonance Raman spectra were recorded by using a Jasco R-800 spectrometer in conjunction with Spectra-Physics Model 164 Ar^+ laser and Kimmon Electric Co. Model KLG-103 laser with photon-counting systems. The resonance Raman spectra in solution were taken in a liquid cell. The enhancements of all resonance Raman vibrations were normalized to the 1630- cm^{-1} vibration of water or the 1000- cm^{-1} vibration of urea.

Results and Discussion

Dioxomolybdenum(VI) Complexes. The Raman spectra of $\text{MoO}_2(\text{cysOEt})_2$, shown in Figure 1, exhibit two intense peaks at 908 and 875 cm^{-1} , which are also observable in the corresponding IR spectra. These are therefore assigned to $\text{Mo}=\text{O}$ stretching in mutually cis (C_{2v}) geometry. Dioxomolybdenum(VI) complexes have a pronounced tendency to adopt *cis*-dioxo orientation. For example, the Raman spectra of typical dioxomolybdenum(VI) complexes, e.g., $[\text{MoO}_2\text{S}_2]^{2-}$ ¹¹ and $[\text{MoO}_2\text{F}_4]^{2-}$,¹² have also been reported to exhibit two intense peaks assigned for $\text{Mo}=\text{O}$ stretching. The Raman frequencies (Table I) for $\text{MoO}_2(\text{cys-OR})_2$, (R = CH_3 , C_2H_5 , isopropyl, benzyl) reflect the electronic property of the auxiliary ligands. Thus, the thiolato or sulfido (S^{2-}) ligand lowers the frequency in comparison with more electronegative ligands such as F^- or O^{2-} .

The band observed at 680 cm^{-1} for $\text{MoO}_2(\text{cysOMe})_2$ is assigned to C-S stretching vibration of the *cys* ligand, and the Raman spectrum of $\text{Hg}(\text{cysOMe})_2$ ¹³ has a peak at 680 cm^{-1} . On the lower frequency side for $\text{MoO}_2(\text{cysOR})_2$, a medium-intensity band appears at 385–390 cm^{-1} which is tentatively

Table I. Selected Vibrational Frequencies (cm^{-1}) for Dioxobis(alkyl L-cysteinato-S)molybdenum(VI) Complexes, Dioxobis(dialkyldithiocarbamato)molybdenum(VI) Complexes, and Dioxobis(acetylacetonato)molybdenum(VI) Complexes^a

complexes	$\nu_s(\text{MoO})$	$\nu_a(\text{MoO})$	$\nu(\text{SC})$	$\nu(\text{MoS})$
$\text{MoO}_2(\text{cysOMe})_2$	906 s	875 m	694 w	385 m
$\text{MoO}_2(\text{cysOEt})_2$	908 s	875 m	680 w	390 m
$\text{MoO}_2(\text{cysO-}i\text{-Pr})_2$	905 s	875 m	685 m	395 w
$\text{MoO}_2(\text{cysOBzl})_2$	902 s	874 m	680 m	387 w
$\text{MoO}_2(\text{S}_2\text{CNMe}_2)_2$	923 s	885 m	578 m	390 m
$\text{MoO}_2(\text{S}_2\text{CNET}_2)_2$	910 s	880 m	575 m	390 m
$\text{MoO}_2(\text{acac})_2$	925 s	898 m		

^a Abbreviations: ν_s , symmetric stretching; ν_a , asymmetric stretching; s, strong; m, medium; w, weak.

assigned to the Mo-S stretching. Davis¹³ also reported that the $\nu(\text{Hg-S})$ of $\text{Hg}(\text{cysOMe})_2(\text{HCl}) \cdot \text{H}_2\text{O}$ was found at 310 cm^{-1} . Thus, the assignment of the $\nu(\text{Mo-S})$ at 385–390 cm^{-1} may be reasonable for the Mo-S bond, when the mass effect of the metal was considered.

Unfortunately, isolation of the Mo(VI) complex of the acetyl cysteinato anion or benzyl cysteinato-S anion presumably involving SO- or NO-chelation has been unsuccessful. The Raman spectrum of $\text{MoO}_2(\text{acac})_2$ containing OO-chelation was taken in solid state. The typical bands are listed in Table I.

The medium-intense band at 460 cm^{-1} assignable to $\nu(\text{Mo-O})$ was observed.

The Raman spectra of closely related $\text{MoO}_2(\text{S}_2\text{CNR})_2$ (R = Me, Et (Figure 1)) also revealed two intense bands at the $\text{Mo}=\text{O}$ stretching region. The frequencies for the methyl derivative are definitely higher than those of the ethyl derivative (Table I). The double bonding at the $\text{Mo}=\text{O}$ moiety is sensitive to the electronic effect of the alkyl group on the N atom of the dithiocarbamato ligand. There are medium-intensity bands at 578 and 575 cm^{-1} assignable to the C-S stretching.

Three bands at 425, 390, and 340 cm^{-1} are tentatively assigned to $\delta(\text{NCC})$, $\nu(\text{Mo-S})$, and $\delta(\text{SCS}) + \nu(\text{Mo-S})$, respectively, on the basis of the detailed IR and resonance Raman spectroscopic studies on $\text{Ni}(\text{S}_2\text{CNET}_2)_2$, $\text{Pt}(\text{S}_2\text{CNET}_2)_2$, and $\text{Cu}(\text{S}_2\text{CNET}_2)_2$.¹⁴ Such complexes were reported to provide the bands of $\nu(\text{Ni-S})$ and $\nu(\text{Cu-S})$ at 363 and 367 cm^{-1} , respectively. In comparison with the sensitivity of the $\text{Mo}=\text{O}$ stretching frequency, these lower frequency bands are not affected by the electronic effect of the alkyl group.

Binuclear Oxomolybdenum(V) Complexes. The Raman spectrum of a typical binuclear oxomolybdenum complex of cysteinato(2-) is shown in Figure 2a. A single band of the $\text{Mo}=\text{O}$ stretching appears at 950 cm^{-1} in accord with the previous IR data.⁶ A weak band faintly observed at 738 cm^{-1} due to the Mo_2O_2 ring vibration was observed, but this assignment is ambiguous because many bands between 700 and 800 cm^{-1} were observed. The band also appears in the IR spectrum in medium intensity. This IR band has been reported by Kay and Mitchell⁶ (735 cm^{-1}) and by Melby¹⁰ (730 cm^{-1}). The theoretical interpretation of vibrations for the di- μ -oxo molybdenum ring system reported by Wing¹⁵ has indicated that a Raman band should be observed at 700–750 cm^{-1} . The Raman line at 667 cm^{-1} seems due to C-S stretching which is also observed at 660 cm^{-1} for $\text{Mo}_2\text{O}_7(\mu\text{-S})_2(\text{cys})_2^{2-}$. At least one of two clear medium bands at 390 and 313 cm^{-1} , always observed with repeated measurements, may be ascribed to Mo-S stretching. Figure 2b shows the spectrum of Mo_2O_7

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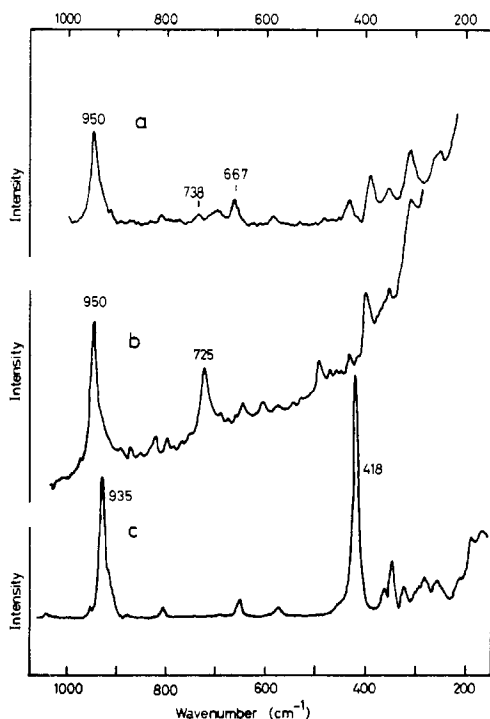


Figure 2. Raman spectra of (a) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-O})_2(\text{cys})_2]\cdot 5\text{H}_2\text{O}$, (b) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-O})_2(\text{his})_2]$, and (c) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{cys})_2]\cdot 4\text{H}_2\text{O}$ in the solid state (6328-Å excitation, 10 mW, 32 scans).

$(\mu\text{-O})_2(\text{his})_2$ in solid state. A strong band assignable to $\nu(\text{Mo-O}_b)$ was observed at 725 cm^{-1} . Melby¹⁰ reported that the IR bands for $\nu(\text{Mo-O}_b)$ were observed at 750 and 475 cm^{-1} .

The doubly sulfur-bridged di- μ -sulfido oxomolybdenum complex also exhibits strong Raman lines at 935 cm^{-1} ($\nu(\text{Mo=O})$) and at 418 cm^{-1} . The latter intense peak always appears in the Raman spectra of various doubly sulfur-bridged binuclear molybdenum complexes examined by us and may be utilized for diagnostic purpose. The depolarization experiment in aqueous solution indicated that the 935 - and 418-cm^{-1} bands are due to symmetric vibrations as expected. In the IR spectra, the identification of the sulfur bridge has been ambiguous although there is a tentative assignment of the IR band at 466 cm^{-1} to this group.⁹

In view of the importance of $\mu\text{-oxo}$ and $\mu\text{-sulfido}$ coordination at the active sites of molybdenum enzymes, we have examined the resonance Raman spectra in dilute aqueous solutions ($9 \times 10^{-4}\text{ M}$). Figure 3a shows a resonance Raman spectrum of $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-O})_2(\text{cys})_2]$ in aqueous solution. The relative intensity of the 775-cm^{-1} band of the di- $\mu\text{-oxo}$ complex was remarkably enhanced (ca. 3-fold relative to other bands). For the di- $\mu\text{-sulfido}$ complex, the intensity enhancement is quite different and the 935-cm^{-1} ($\nu(\text{Mo=O})$) and the 417-cm^{-1} ($\nu(\text{Mo-S}_b)$) bands are both greatly enhanced in intensity.

The excitation profiles are shown in Figure 4. The 775-cm^{-1} band is intensified by irradiation at shorter wavelengths. This result indicated that the electronic bands associated with the 775-cm^{-1} vibration $\nu(\text{Mo-O}_b)$ exist at wavelengths shorter than 470 nm .

The MO calculation of Brown et al.¹⁶ on the di- $\mu\text{-oxo}$ and di- $\mu\text{-sulfido}$ molybdenum(V) complexes have indicated that an electronic absorption at 313 nm of the di- $\mu\text{-oxo}$ complex is due to a transition from the filled Mo-Mo bonding orbital to a vacant Mo-Mo antibonding orbital. The observed reso-

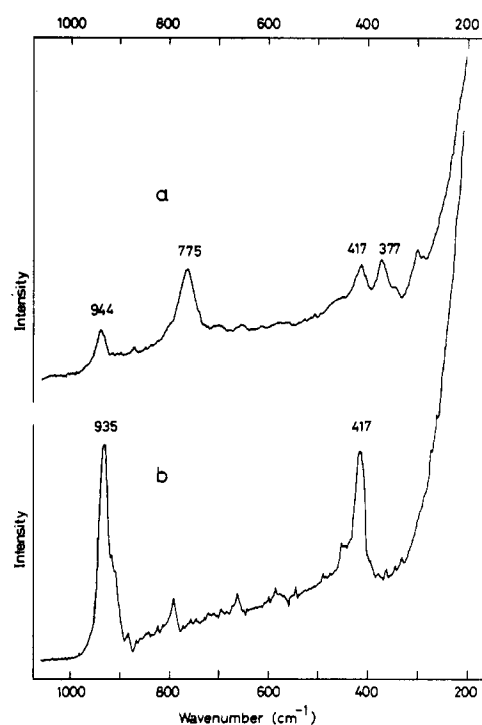


Figure 3. Resonance Raman spectra of (a) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-O})_2(\text{cys})_2]$ and (b) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{cys})_2]$ in aqueous solutions (concentration, 2 mg/mL , 4545-Å excitation, 90 mW , 8 scans).

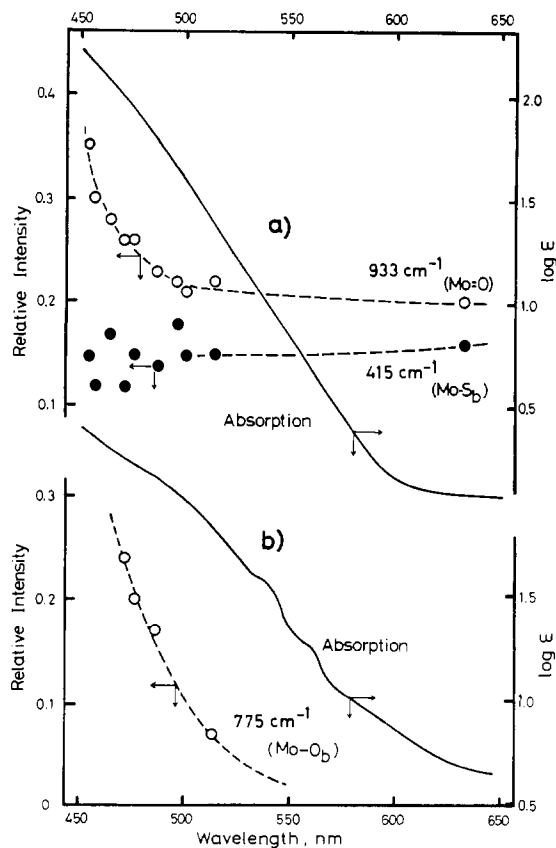


Figure 4. Excitation profiles and absorption spectra of (a) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-O})_2(\text{cys})_2]$ and (b) $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{cys})_2]$ in aqueous solutions. Relative intensity refers to the enhancement normalized to the water band at 1635 cm^{-1} .

nance Raman spectra (Figures 3a and 4a) thus support their conclusion although Raman studies by excitation at the shorter wavelengths remain to be done. In the resonance Raman

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spectra of the di- μ -sulfido complexes (see Figure 3b), the excitation profile of the 935-cm⁻¹ band indicates that the electronic absorption involving the Mo=O bonding is at wavelengths shorter than 470 nm. By contrast, the profile for the 417-cm⁻¹ band (Figure 4a) exhibits no clear maximum in the range studied. The electronic absorption in this range has no maximum but only weak tailing. The scattered intensity data around 500 nm may indicate presence of a vibrational fine structure. Clearly further detailed study is needed to clarify these points.

The MO calculation of Brown et al.¹⁷ on the di- μ -sulfido complex indicated extensive mixing of the individual ligand atomic orbitals at the lowest vacant MO which is responsible for the absorption occurring at the visible region. The CD spectra of various oligopeptide complexes involving di- μ -sulfido bridges always show extrema in the 400-450-nm range.¹⁸ Contribution of chirality at the cysteine residue to the electronic absorption is apparent.

Two strong Raman lines were observed for the di- μ -sulfido molybdenum(V) complex of glutathione (GSH), [Mo₂O₂S₂(γ -Glu-cys-Gly)₂]²⁻,¹⁹ at 950 and 425 cm⁻¹. A weak peak at 295 cm⁻¹ and the 425-cm⁻¹ peak were intensified by irradiation at 457.9 nm. The former peak may be due to the Mo-S_b or Mo-SC stretching. An indication of incorporation of di- μ -sulfido-bis(oxomolybdenum) ion into cys-containing proteins such as papain (M_r 23 400)²⁰ is readily obtainable by the Raman spectrum. Thus, our preliminary results show weak peaks at 930 and 420 cm⁻¹ for this macromolecular Mo(V) complex.

The observation of a highly enhanced Raman line assigned to the di- μ -sulfido bridge helps to detect or identify its presence in metalloenzymes or metalloproteins. The frequency dependence could also give clues to the coordination environment at the metal and strengths of the participating bonds.

Registry No. MoO₂(cysOMe)₂, 29683-37-2; MoO₂(cysOEt)₂, 22775-78-6; MoO₂(cysO*i*-Pr)₂, 76832-60-5; MoO₂(cysOBzl)₂, 76832-61-6; MoO₂(S₂CNMe₂)₂, 39248-36-7; MoO₂(S₂CNMe₂)₂, 18078-69-8; MoO₂(acac)₂, 21884-95-7; Na₂[Mo₂O₂(μ -O)₂(cys)₂], 23331-32-0; Na₂[Mo₂O₂(μ -S)₂(cys)₂], 29683-41-8; Mo₂O₂(μ -O)₂(his)₂, 26658-23-1; Na₂MoO₄, 7631-95-0.

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(19) The [Mo₂O₂(μ -S)₂(GSH)₂]²⁻ ion was synthesized by the addition of glutathione to a solution of [Mo₂O₂(μ -S)₂]²⁺ at pH 7. Isolation of the complex as a sodium salt was carried out by the addition of methanol to the aqueous solution.

(20) Papain and the [Mo₂O₂(μ -S)₂]²⁺ ion were mixed in water at pH 6.5. The metal complex was purified by dialysis. The binding site of the [Mo₂O₂(μ -S)₂]²⁺ ion should be located in a pocket having one each of thiolato and imidazole ligands (Ueyama, N.; Nakamura, A., unpublished results). Formation of this complex was also supported by the CD spectrum in water.

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Matrix Isolation Investigation of the Methylfluorosilicate Anions

Bruce S. Ault* and Uly Tandoc

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The Lewis acid or acceptor properties of inorganic fluorides such as BF₃, SiF₄, and PF₅ are well-known, including thorough ion cyclotron resonance and mass spectral studies of the fluoride affinities of these species.¹⁻³ The product anions such

as SiF₅⁻, have also been well characterized in condensed-phase studies.⁴ More recently, attention has been directed toward the effects of alkyl substitution on the Lewis acid; studies have shown that the fluoride affinity drops off dramatically as the number of methyl groups increases for the fluoromethylsilanes.¹ Only one of the possible product anions, (CH₃)₃SiF₄⁻, has been observed in solution,^{5,6} and characterized by ¹H and ¹⁹F NMR. The SiF₅⁻ anion has also been characterized in argon matrices after formation through the salt/molecule technique, in which CsF is reacted with SiF₄ to form the Cs⁺SiF₅⁻ ion pair.⁷ Since the fluoride ion is known to catalyze a number of organosilicon reactions^{8,9} and gas-phase studies indicate at least some stability for alkylfluorosilicate anions,¹⁻² a similar study was conducted to attempt to isolate and characterize these anions in inert-gas matrices.

Experimental Section

All of the experiments conducted in this study were performed on a conventional matrix isolation apparatus which has been described previously.¹⁰ CsF (Alfa) and CsCl (Fisher) were the salts employed in this study, and both were vaporized from a stainless-steel Knudsen cell at roughly 500 °C. (CH₃)₃SiF₃, (CH₃)₂SiF₂, and (CH₃)₃SiF were purchased from PCR, Inc., and used after purification through a freeze-thaw cycle under vacuum. Argon was used as the matrix gas in all experiments and was used without further purification. Matrix samples were deposited for 20-24 h before final scans; both survey and high resolution scans were recorded on a Beckman IR-12 infrared spectrophotometer.

Results

Before salt/molecule reactions were undertaken with the fluoromethylsilanes, blank experiments were conducted at representative dilutions with each of the silane compounds; the recorded spectra agreed well with literature spectra.^{11,12} When CsF was vaporized and codeposited with a sample of Ar/(CH₃)₃SiF₃ = 1000, four new bands were observed in the spectrum, which could not be attributed to parent species, at 742, 825, 837, and 862 cm⁻¹. When the concentration was increased to 400/1, the same set of bands appeared, with increased intensity, and a weaker band was observed near 450 cm⁻¹. These experiments were repeated several times, using different CsF levels, and the five bands appeared consistently and maintained a constant relative intensity.

CsF was codeposited with samples of Ar/(CH₃)₂SiF₂ in several experiments, with concentrations ranging from 1000/1 to 250/1. A number of medium-to-weak bands were detected in each experiment, reproducibly at 674, 695, and 868 cm⁻¹, along with bands which appeared as shoulders on parent bands at 787 and 834 cm⁻¹. The spectra of the reaction products of CsF with (CH₃)₃SiF₃ and (CH₃)₂SiF₂ are shown in the traces of Figure 1. CsF was also codeposited with samples of Ar/(CH₃)₃SiF in several experiments, and in each case, weak bands were detected at 749 (sh), 986, and 1248 cm⁻¹. Even in the most concentrated experiments, M/R = 200, these bands had at most an optical density of 0.05.

For a test of the effect of chlorine atom substitution, CsCl was codeposited with a sample of Ar/(CH₃)₃SiF₃ = 400, and no bands were detected in the spectrum which could be attributed to a reaction product. Likewise, when CsF was reacted with a sample of Ar/(CH₃)₃SiCl₃ = 400 in one experi-

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