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RAMAN AND RESONANCE RAMAN SPECTRA OF SULFUR-BRIDGED BINUCLEAR MOLYBDENUM(V) COMPLEXES OF CYSTEINE-CONTAINING CHELATE ANIONS

Norikazu UEYAMA, Michio NAKATA, Takeo ARAKI, and Akira NAKAMURA*
Department of Polymer Science, Faculty of Science
Osaka University, Toyonaka, Osaka 560
Shinsuke YAMASHITA and Takuya YAMASHITA
Faculty of Pharmaceutical Sciences, Tokushima University,
Tokushima 770

μ-Disulfido-dioxodimolybdenum(V) complexes of $(Cys)^{2-}$, $(Cys\text{-}OMe)^{-}$, $(Ac\text{-}Cys)^{2-}$, $(Glutathione)^{2-}$ anions exhibit strong Raman bands at 930-950 cm^{-1} and 420 cm^{-1} assignable respectively to Mo=O and $Mo\text{-}S_{bridge}$ stretching vibrations. The resonance Raman spectra provide an excitation profile which is useful for assigning the broad electronic absorption due to the $Mo{<}^{S}_{S}{>}Mo$ moiety.

Molybdenum-sulfur bonding is an important feature of molybdenum enzymes in which molybdenum is bound to labile sulfide(S^{2-}) and/or cysteine thiolate[1)]. The investigation of the Mo active sites will be facilitated when the identification and information about the Mo-S linkages are obtainable by vibrational spectroscopy. The IR absorption due to the Mo-S vibration is too low in intensity to be applicable because of the covalency between two heavy atoms. By contrast, resonance Raman technique seems to be a powerful tool. In view of the importance of Mo complexes of cysteine-containing peptides as inorganic models of Mo enzymes, we have examined a variety of sulfur-bridged binuclear Mo(V) complexes by Raman and resonance Raman spectroscopy.

The Raman intensity enhancement at the resonance condition was found to be great enough to allow investigation of these complexes in dilute aqueous solutions and to detect Mo-S bonding in complexes such as Mo(V)/GSH (GSH=reduced glutathione), etc..

The Raman spectra(solid state) of complexes of type, $Na_2[Mo_2O_2S_2(Cys)_2]4H_2O$[2a)] (Fig.1), $Mo_2O_2S_2(Cys\text{-}OMe)_2$[2b)], $[Mo_2O_2S_2(Ac\text{-}Cys)_2][n\text{-}Bu_4N]_2$[2c)], and $Mo_2O_2S_2(GSH)_2$[2c)] exhibit strong bands at 930-950 cm^{-1} region and at 420 cm^{-1} region assignable respectively to $\nu_{Mo=O}$ and $Mo{<}^{S}_{S}{>}Mo$ vibrations (see Table I). The assignment of Mo=O stretching is corroborated by the IR spectra. However, the $Mo{<}^{S}_{S}{>}Mo$ vibration is not easily located in the low-frequency IR spectra of all of these sulfur-bridged Mo complexes. A medium-infrared band around 450-460 cm^{-1} has recently been tentatively assigned to the bridging Mo-S vibration[2a),3)].

Table I Raman bands of μ-oxo and μ-sulfido Mo(V) complexes in solid state (cm^{-1})

Complexes	$\nu_{Mo=O}$	$\mathrm{Mo}{<}^{S}_{S}{>}\mathrm{Mo}$	$\mathrm{Mo}{<}^{O}_{O}{>}\mathrm{Mo}$
$Na_2[Mo_2O_4(Cys)_2]5H_2O$	950(s)	-	738(w)
$Na_2[Mo_2O_2S_2(Cys)_2]4H_2O$	932(s)	417(vs)	-
$Mo_2O_2S_2(Cys\text{-}OMe)_2$	937(s)	424(vs)	-
$[Mo_2O_2S_2(Ac\text{-}Cys)_2][(n\text{-}Bu)_4N]_2$	955(s)	430(s)	-
$Na_2[Mo_2O_2S_2(GSH)_2]$	950(s)	420(s)	-

GSH: Reduced glutathione (γ-L-glutamyl-L-cysteinylglycine).

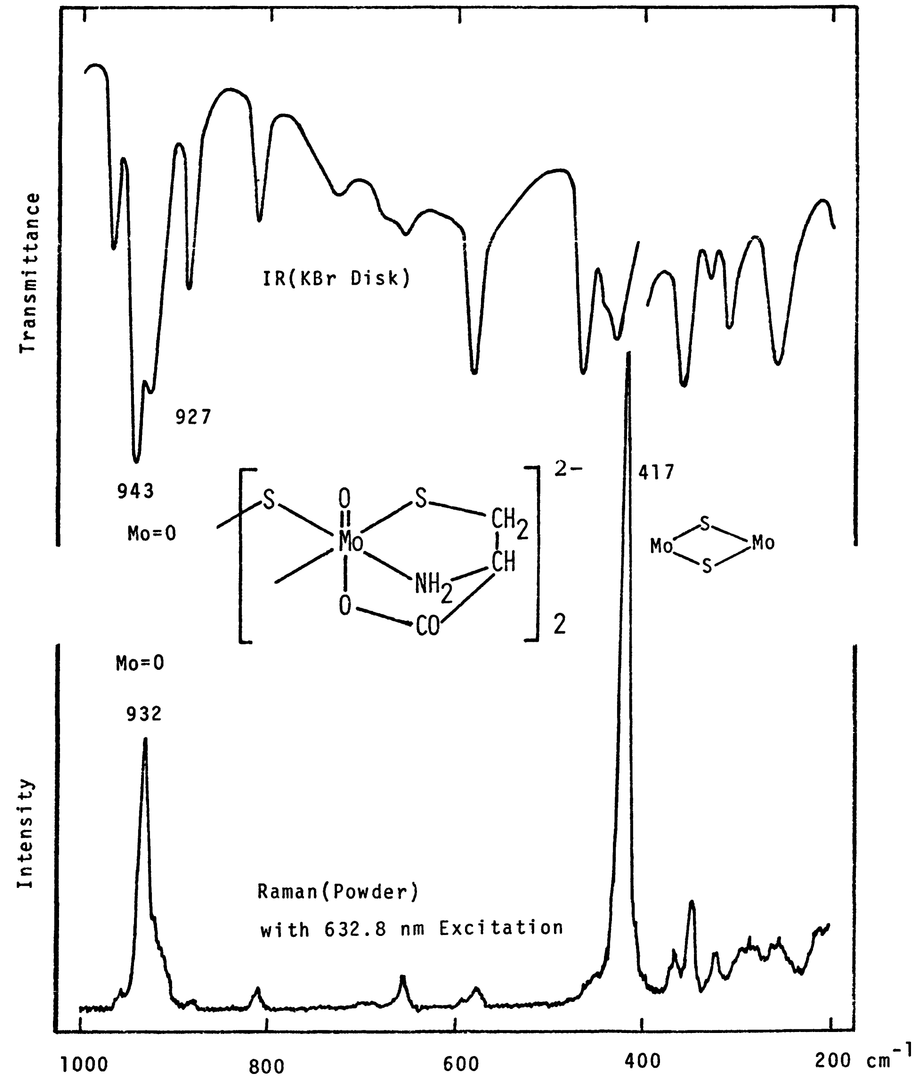

Fig.1 IR and Raman spectra of $Na_2[Mo_2O_2S_2(Cys)_2]4H_2O$ in solid state.

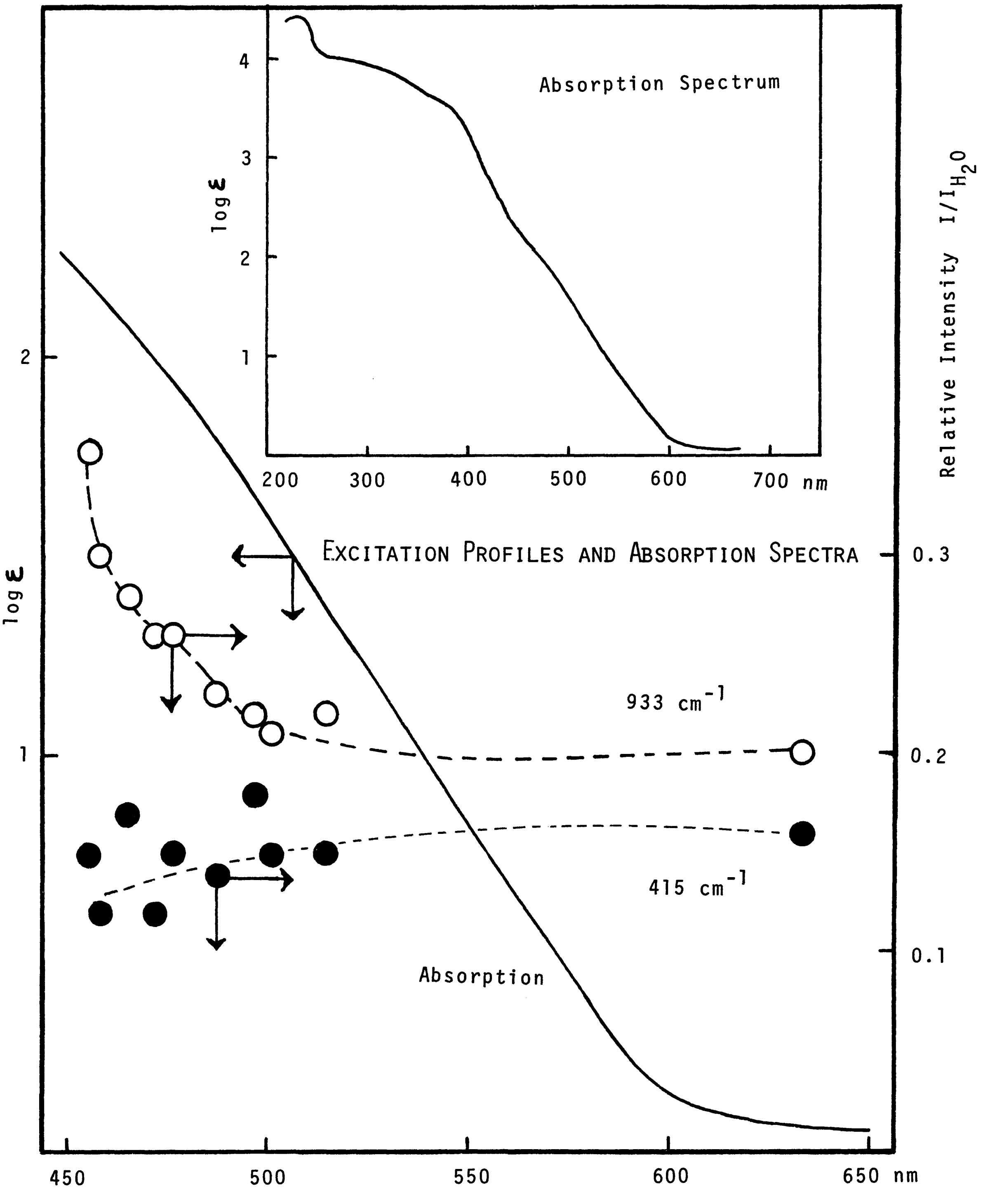

Fig.2 Excitation profiles and absorption spectra of $Na_2[Mo_2O_2S_2(Cys)_2]4H_2O$ in aqueous solution; concentration for Raman measurement: 3.6 x 10^{-3}M; experimental points; (o) 933, (●) 415 cm^{-1}, respectively. The ratios of I/I_{H_2O} were measured relative to the band of water at 1635 cm^{-1}.

Depolarization experiment showed that these Raman bands are due to totally symmetric vibrations. The intensity of these two bands are enhanced even at the ordinary solid state condition of the measurement. Variation of the exciting wavelength allows the excitation profiles shown in Figure 2. The profile for the 415 cm^{-1} band indicates that the electronic absorption attributable to the $\mathrm{Mo}{<}^{\mathrm{S}}_{\mathrm{S}}{>}\mathrm{Mo}$ system is very broad and weak extending from 400 to 600 nm. The excitation profile for the $\nu_{Mo=O}$ vibration at 933 cm^{-1} shows an intensity increase at lower excitation wavelengths. The electronic bands mainly concerned with the Mo=O system is therefore at $\sim$ 400 nm region.

The previous IR assignment[4] of 738 cm^{-1} band of $Na_2[Mo_2O_4(Cys)_2]5H_2O$[2d] to one of the $\mathrm{Mo}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Mo}$ vibrations is confirmed by the resonance Raman intensity variation at the 775 cm^{-1} peak utilizing excitations tuned at various wavelengths. The oxo-bridged Mo(V) complexes, $Na_2[Mo_2O_4(Cys)_2]5H_2O$, for example, lack strong Raman bands at 420 cm^{-1} region but have bands at 950 cm^{-1} assignable to $\nu_{Mo=O}$.

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