Circular dichroism spectrophotometric study of $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cysteinato})_2]^{2-}$ in aqueous micellar solutions

Yochi Sasaki* and **Moriya Miyashita**

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980 (Japan)

(Received September 24, 1990)

Abstract

$[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cys})_2]^{2-}$ (R-cys = (R)-cysteinate(2 −)) undergoes significant change in circular dichroism (CD) spectra on addition of cationic surfactants such as cetyltrimethylammonium bromide (CTAB), decyltrimethylammonium bromide (DTAB) and cetylpyridinium chloride (CPC). The CD dependence on [CTAB] occurs in two steps. At [CTAB] < cmc (critical micelle concentration), the change is interpreted by considering that R-cys partly liberates from $Mo_2(\mu\text{-}O)_2(O)_2^{(2+)}$. The change observed at [DTAB] > cmc is accounted for by the partial dissocation of a $-COO^-$ arm, while the complete liberation of the ligand is suppressed. The addition of a anionic surfactant and simple salts do not cause any change in the CD spectra. A similar CD change is observed for $[Mo_2(\mu\text{-}O)_2(O)_2(S\text{-pen})_2]^{2-}$ (S-pen = (S)-penicillaminate(2 −)), which is interpreted similarly. The sulfide bridged R-cys complexes, $[Mo_2(\mu\text{-}O)(\mu\text{-}S)(O)_2(R\text{-cys})_2]^{2-}$ and $[Mo_2(\mu\text{-}S)_2(O)_2(R\text{-cys})_2]^{2-}$, also undergo even more drastic CD changes on addition of CTAB. By contrast, $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-pdta})]^{2-}$ (R-pdta = (R)-1,2-propylenediaminetetraacetate(4 −)) which has a firmly coordinated hexadentate ligand does not show such CD changes on addition of CTAB.

Introduction

In their recent paper on the complexation of molybdenum(VI) by (R-cysteine [1], Gillard and coworkers discussed the solution behaviour of the molybdenum(V) dimer, $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cys})_2]^{2-}$ (R-cys = (R)-cysteinate dianion), on the basis of circular dichroism (CD) and ^1H and ^{13}C NMR spectra. The tridentate R-cys ligands as determined by X-ray structural analysis [2] partly dissociate via their carboxylate groups to become bidentate in aqueous solution [1]. We have measured the CD spectra of the complex in the presence of micelle forming cationic and anionic surfactants, and found remarkable and rather complicated changes in the spectra. These changes can be rationalized in terms of partial dissociation of the carboxylate group of R-cys [1]. Since understanding of the solution behaviour of the $Mo_2(\mu\text{-}O)_2(O)_2^{(2+)}$ complexes of R-cys and related ligands is important, we report our results in this area.

*Author to whom correspondence should be addressed at the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

Experimental

Materials

$Na_2[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cys})_2]\cdot 5H_2O$ [3], $Na_2[Mo_2(\mu\text{-}O)_2(O)_2(S\text{-pen})_2]\cdot 2H_2O$ (S-pen = (S)-penicillaminate(2 −)) [4], $Na_2[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-pdta})]\cdot 3H_2O$ (R-pdta = (R)-1,2-propylenediaminetetraacetate(4 −)), $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}S)(O)_2(R\text{-cys})_2]\cdot 4H_2O$ [5] and $Na_2[Mo_2(\mu\text{-}S)_2(O)_2(R\text{-cys})_2]\cdot 4H_2O$ [3, 4] were all prepared by literature procedures. All the surfactants, cetyltrimethylammonium bromide (CTAB, $(CH_3(CH_2)_{15}N(CH_3)_3Br)$, decyltrimethylammonium bromide (DTAB, $(CH_3(CH_2)_9N(CH_3)_3Br)$, cetylpyridinium chloride (CPC, $(CH_3(CH_2)_{15}C_5H_5NCl)$, and sodium dodecyl sulphonate (SDS, $(CH_3(CH_2)_{11}OSO_3Na)$ were used as received. Sodium perchlorate and other simple salts were also used as received.

Measurements

Electronic absorption spectra were measured with a Hitachi 323 Spectrophotometer. The CD spectra were obtained by the use of a JASCO J-40A automatic recording spectropolarimeter. Since the complexes were found to be less soluble

0020-1693/91/$3.50

in water in the presence of the surfactants, the concentrations employed were in the range (4–8) $\times 10^{-5}$M(1M = 1 mol dm^{-3}). The pH was not controlled, but was in the range 6.1–6.9. The measurements were carried out within 30 min of solution preparation, to avoid the effect of decomposition [1, 4]. ^{1}H and ^{13}C NMR measurements were not possible due to the low concentrations employed and the presence of surfactants.

Results

$[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}cys)_2]^{2-}$

Careful experiments revealed that the CD strength at > 300 nm slightly decreased as the concentration of the complex was reduced as noted previously [1], and increased on addition of free (*R*)-cysteine. Thus at [complex] = 6.4×10^{-5} M, $\Delta\varepsilon$ was -10.6 M^{-1} cm^{-1} at 385 nm which increased in magnitude to -11.2 M^{-1} cm^{-1} on addition of the free ligand (8.8×10^{-4} M), a result consistent with a ligand dissociation equilibrium in aqueous solution.

The CD spectrum was practically the same in the absence and the presence of simple salts such as NaCl (9.5×10^{-2} M), $NaClO_4$ (9.5×10^{-2} M), NaBr (5.0×10^{-3}–9.5×10^{-2} M), $(C_2H_5)_4NBr$ (1.0×10^{-4}–6.4×10^{-3} M), $(C_2H_5)_4NCl$ (5.8×10^{-3} M) and $(C_2H_5)_4NClO_4$ (5.9×10^{-2} M). It did not change in the presence of an anionic surfactant SDS (8.0×10^{-3}–5.3×10^{-2} M). However, the CD spectrum was significantly affected by the cationic surfactant CTAB (Fig. 1), showing rather complicated dependence on [CTAB]. Dependence of the CD intensity on [CTAB] is shown in Fig. 2. Obviously there are two stages in the dependence. Since the critical micelle concentration (cmc) of CTAB is reported to be 9.2×10^{-4} M [6], the second stage appears to be related to the micelle formation. The effect at lower [CTAB] (<cmc) should arise from the interaction of the complex with the cetyltrimethylammonium ion. On addition of the free ligand (*R*)-cysteine (4.4×10^{-4} M), the CD spectra returned to the one without any added salt when the CTAB concentration was lower than cmc, but did not show any change when [CTAB] exceeded cmc. During these CD changes, the UV–Vis absorption spectra did not show significant change.

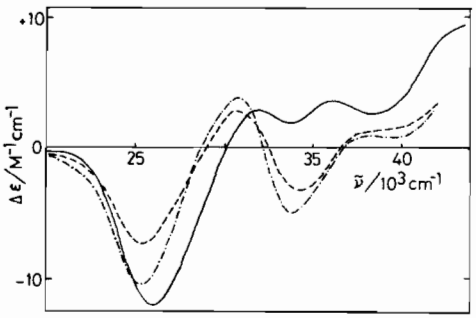


Fig. 1. Circular dichroism spectra of aqueous solution of $Na_2[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}cys)_2] \cdot 5H_2O$ at [CTAB) = 0 M (——), 1.6×10^{-4} M (– – – –), and 1.6×10^{-3} M (– · – · –).

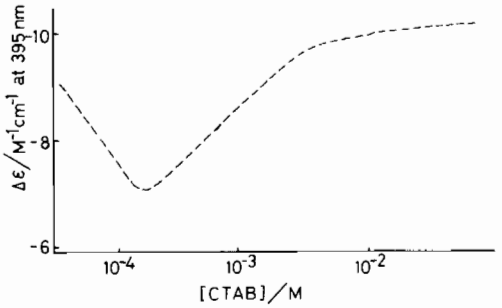


Fig. 2. The correlation of $\Delta\varepsilon$ at 395 nm of aqueous solutions of $Na_2[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}cys)_2] \cdot 5H_2O$ (6.4×10^{-5} M) with [CTAB].

Change in the CD spectrum was also observed in the presence of other cationic surfactants such as DTAB (1.8×10^{-4}–0.018 M) and CPC (0.071–0.126 M) at >cmc.

Other complexes

$[Mo_2(\mu\text{-}O)_2(O)_2(S\text{-pen})_2]^{2-}$ showed CD spectral changes in the presence of CTAB ([CTAB] > cmc) (the CD spectrum is enantiometic to that of the *R*-cys complex due to different absolute configuration of the ligand). On the other hand, $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-pdta})]^{2-}$ showed no CD spectral change on addition of CTAB. The changes in the CD spectra of $[Mo_2(\mu\text{-}O)(\mu\text{-}S)(O)_2(R\text{-cys})_2]^{2-}$ and $[Mo_2(\mu\text{-}S)_2(O)_2(R\text{-cys})_2]^{2-}$ were also studied briefly in the presence of CTAB at >cmc (Figs. 3 and 4). The changes

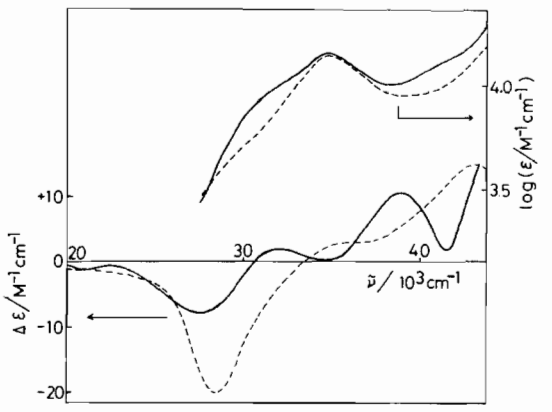


Fig. 3. Electronic absorption and circular dichroism spectra of aqueous solutions of $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}S)(O)_2(R\text{-}cys)_2] \cdot 4H_2O$ at [CTAB] = 0 M (——) and 4.7×10^{-3} M (– – – –).

TABLE 1. The CD spectral data (peak in 10^{-3} cm^{-1} and $\Delta\varepsilon$ in M^{-1} cm^{-1}) for some Mo(V) dimer complexes in the presence of cationic surfactants

Complex Surfactant (conc.)	$\Delta\varepsilon$ (M^{-1} cm^{-1})
$[Mo_2O_4(R\text{-cys})_2]^{2-}$	
None	26.1 (−10.6), 31.7 (+3.0), 36.0 (+3.5)
(*R*-cys(8.8×10^{-4} M))	26.1 (−12.0)
CTAB (1.6×10^{-4} M)	25.8 (−7.0), 31.7 (+3.0)
CTAB (1.6×10^{-3} M)	25.3 (−10.4), 30.5 (+3.8), 33.9 (−5.0)
DTAB (0.126 M)	25.3 (−10.0), 30.8 (+3.5), 33.9 (−2.5)
CPC (1.8×10^{-2} M)	25.1 (−12.2), 30.3 (+5.0), 34.2 (−8.0)
$[Mo_2O_4(S\text{-pen})_2]^{2-}$	
None	26.6 (+10.4), 31.9 (−4.2), 35.8 (−3.2)
CTAB (1.6×10^{-3} M)	25.4 (+10.4), 30.5 (−4.6), 33.8 (+1.6)
$[Mo_2O_4(R\text{-pdta})]^{2-}$	
None, CTAB (0.009 M)	26.0 (−5.5), 33.3 (+5.1), 37.1 (−1.6), 40.6 (+3.9)
$[Mo_2O_3S(R\text{-cys})_2]^{2-}$	
None	27.7 (−8.0), 31.7 (+2.2), 39.0 (+10.3)
CTAB (4.7×10^{-3} M)	28.6 (−20.2), 35.3 (+2.8), 43.3 (+14.9)
$[Mo_2O_2S_2(R\text{-cys})_2]^{2-}$	
None	25.0 (+4.0), 27.8 (−7.9) 31.5 (+15.7), 37.8 (−16.8)
CTAB (2.6×10^{-3} M)	24.5 (+1.0), 27.9 (−16.8), 33.1 (+15.0), 37.7 (−16.1)

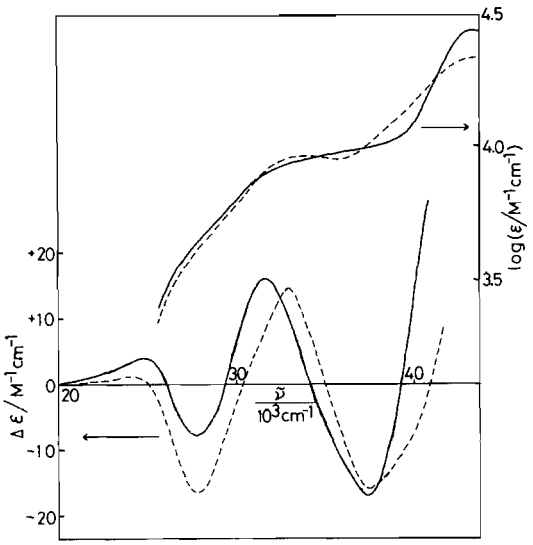


Fig. 4. Electronic absorption and circular dichroism spectra of aqueous solutions of $Na_2[Mo_2(\mu\text{-}S)_2(O)_2(R\text{-cys})_2] \cdot 4H_2O$ at [CTAB] = 0 M (——) and 2.6×10^{-3} M (– – – –).

are even more significant than those of the di(μ-oxo) complex, $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cys})_2]^{2-}$. In these two μ-S complexes, changes in the visible absorption spectra also occur (Figs. 3 and 4).

The changes in the CD spectra are summarized in Table 1.

Discussion

Gillard and coworkers [1] convincingly demonstrated by ^{1}H NMR spectra that $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-cys})_2]^{2-}$ ([complex] = 0.2 M) partially dissociates its $-COO^-$ group (*c.* 75% of the ligand is in the dissociated form, while no free ligand is observed). Although the concentration of the solution used for the NMR measurements was significantly higher than that for the CD measurements, we expect a similar $-COO^-$ dissociation at the lower complex concentration although to a different degree since the $-COO^-$ dissociation processes occur intramolecularly or with proton assistance.

The dissociation equilibrium becomes important at lower complex concentrations. Shifting to the complex formation at higher complex concentration makes the dissociation negligible at the concentration of the NMR measurements.

The present observations on the *R*-cys complex can be accounted for by Scheme 1*.

$[Mo_2O_4(R\text{-cys-}N,S,COO)_2]^{2-}$ (**1**)

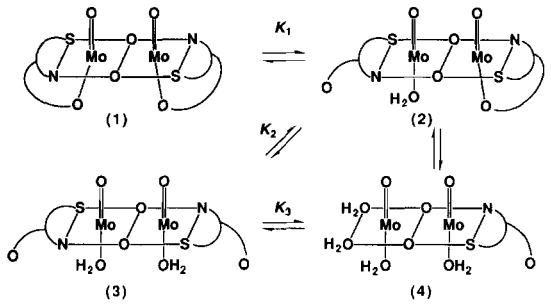
$\overset{K_1}{\rightleftharpoons}$ $[Mo_2O_4(R\text{-cys-}N,S)(R\text{-cys-}N,S,COO)]^{2-}$ (**2**)

$\overset{K_2}{\rightleftharpoons}$ $[Mo_2O_4(R\text{-cys-}N,S)_2]^{2-}$ (**3**)

$\overset{K_3}{\rightleftharpoons}$ $[Mo_2O_4(R\text{-cys-}N,S)]$(**4**) + $R\text{-cys}^{2-}$

Here, *R*-cys-*N,S,COO* and *R*-cys-*N,S* represent the tridentate ligand with coordinated $-NH_2$, S^-, and $-COO^-$ (as found by the crystal structure

*The dissociation of both the ligands is unlikely because the aqua complex of $Mo_2(\mu\text{-}O)_2(O)_2^{(2+)}$ is known to cause precipitation at the pH studied (pH, *c.* 6) [7].



Scheme 1

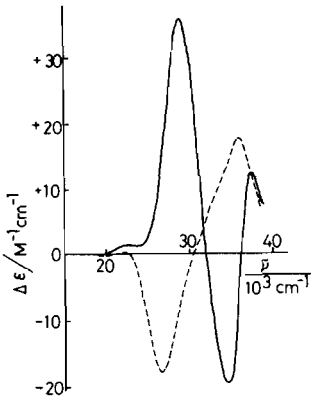


Fig 5 Circular dichroism spectra of $Na_2[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}cys)_2]\ 5H_2O$ in DMF (- - - -) and $Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}etcys)_2$ in DMF (——) [4]

determination [2]) and bidentate with uncoordinated $-COO^-$, respectively Under the micelle forming condition, equilibria K_1 and K_2 shift to the right Complete liberation of the ligand (K_3) is unlikely, since the addition of the free ligand did not cause any change in the CD spectrum In the region [CATB] < cmc, however, one of the *R*-cys ligands dissociates from $Mo_2(\mu\text{-}O)_2(O)_2$*, since the addition of the free ligand gives the original CD spectrum

The dinegative *R*-cys complex would be incorporated into the positively charged micelle of CTAB, DTAB and CPC In the cationic micelles, the more polar structure with free $-COO^-$ groups would be more stable from the electrostatic point of view, so that the species **2** and **3** would be favored over **1** The presence of CTAB at <cmc facilitates the complete dissociation of *R*-cys from $Mo_2(\mu\text{-}O)_2O_2^{(2+)}$, which is more difficult to explain It has been suggested that the complete dissociation as well as partial $-COO^-$ dissociation occurs to a higher extent at lower pH [1] The pH of the solution ($[Mo_2] = 7\,5 \times 10^{-5}$ M) changed only slightly on addition of CTAB (6 6 at [CTAB] = 0 M and 6 1 at $1\,0 \times 10^{-2}$ M), and the pH alone cannot be responsible for the observed ligand dissociation It is possible that the hydrophobicity of cetyltrimethylammonium ions may play a role

The reported CD spectrum of $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}cys)_2]^{2-}$ in pure water [4] should represent the initial two equilibrium states involving **1**, **2** and **3**** It should be noted that the CD spectra of $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}cys)_2]^{2-}$ show significant solvent dependence [4] The spectrum in DMF (Fig 5) relates essentially to species **1**, because $-COO^-$ dissociation is less favoured in this less polar solvent It is known that (*R*)-cysteinate ethyl ester (*R*-etcys) coordinates to $Mo_2(\mu\text{-}O)_2(O)_2$ as a bidentate ligand via its $-NH_2$ and $-S^-$ groups as determined crystallographically for $[Mo_2(\mu\text{-}O)_2(O)_2(R\text{-}etcys)_2]$ [8] This complex shows a nearly enantiomeric CD pattern with an appreciable blue shift (Fig 2) when compared with that of the *R*-cys complex in DMF This effect is due to the inversed absolute configuration of the asymmetric distortion around the Mo–Mo axis [4, 9] On dissociation of $-COO^-$, we would expect **2** and **3** to adopt a structure similar to that of the *R*-etcys complex (namely the inversion of the asymmetric distortion around the Mo–Mo axis takes place from Δ in **1** to Λ in **3**) Thus, **3** would show a similar CD spectral pattern to the *R*-etcys complex The structure of **2** would be somewhere between **1** and **3** The CD spectrum of **2** is difficult to estimate, but may be intermediate between those of **1** and **3** The CD spectra of the *R*-cys complex in water is intermediate between those in DMF and of the *R*-etcys complex On addition of CTAB, the spectrum appears to shift to the direction of that of the *R*-etcys complex These considerations are consistent with the suggested shift in the equilibria

The behaviour of $[Mo_2(\mu\text{-}O)_2(O)_2(S\text{-pen})_2]^{2-}$ is similarly understood, since the ligand possesses a very similar structure to *R*-cys The pdta ligand is firmly coordinated to $Mo_2(\mu\text{-}O)_2(O)_2^{2-}$ [9] and is not expected to show such flexible behaviour and thus no effect by the CTAB micelle is observed The changes in CD spectra of the two *R*-cys complexes with μ-S on addition of CTAB are large The CD spectra of these complexes are more complicated [4] and discussions similar to those given for the di(μ-oxo) complexes are not feasible However, the spectral change should be related to the similar structural change as discussed above The phenomena seem to be characteristic for the complexes with the *R*-cys ligand

The contribution of species **4 is excluded, since the addition of the ligand does not affect the CD spectrum

which has a highly stressed conformation when it acts as a terdentate

Acknowledgements

The authors are grateful to Professor Kazuo Saito, International Christian University, Tokyo, for valuable discussions Helpful comments from Professors R W Hay (The University of St Andrews) and Tasuku Ito (Tohoku University) are also acknowledged This work was supported by a Grant-in-Aid for Scientific Research (No 02245106) on Priority Area of 'Molecular Approaches to Non-equilibrium Processes in Solutions' from the Ministry of Education, Science, and Culture, Japan

References

1 A M V S V Cavaleiro, J D Pedrosa de Jesus, V M S Gil, R D Gillard and P A Williams, *Inorg Chim Acta, 172* (1990) 25
2 J R Knox and C K Prout, *Acta Crystallogr , Sect B, 25* (1969) 1857
3 A Kay and P C H Mitchell, *J Chem Soc A*, (1970) 2421
4 K Z Suzuki, Y Sasaki, S Ooi and K Satio, *Bull Chem Soc Jpn , 53* (1980) 1288
5 V R Ott, D S Swieter and F A Schultz, *Inorg Chem , 16* (1977) 2538
6 J H Fendler and E J Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1970, Ch 2
7 R Iwata, A Nagasawa and Y Sasaki, *Nippon Kagaku Kaishi (Tokyo)*, (1988) 604
8 M G B Drew and A Kay, *J Chem Soc A*, (1971) 1851
9 A Kojima, S Ooi, Y Sasaki, K Z Suzuki, K Saito and H Kuroya, *Bull Chem Soc Jpn , 54* (1981) 2457