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Circular Dichroism Spectra and Their Relation to Asymmetric Distortion of Some Dimeric Molybdenum(V) Complexes Containing Optically Active Amino Carboxylate

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Circular dichroism (CD) spectra of fifteen kinds of μ-X-μ-Y-bis(oxomolybdenum(V)) complexes, where X=Y=O, X=O and Y=S, and X=Y=S, containing optically active ligands such as (*S*)-cysteinate, its alkyl esters, (*R*)-penicillaminate (*R*-pen), (*S*)-histidinate, and (*R*)-propylenediaminetetraacetate, give two distinctive peaks with opposite signs at *ca.* 26000 and 33000 cm^{-1} in various media including KBr disks. Close examination of the known X-ray structural data of eight complexes indicated that the pseudo-octahedral coordination sphere of two molybdenum(V) ions are asymmetrically twisted around the Mo–Mo axis. The direction of such a twist for the complexes containing the ester ligands and *R*-pen, is opposite to that for the complexes with other ligands. The former and latter complexes give positive and negative, and negative and positive CD peaks at *ca.* 26000 and 33000 cm^{-1}, respectively. Thus the CD signs of the two peaks are related to the asymmetric distortion around the Mo–Mo axis.

Deviation of coordinated atoms from regular octahedron can cause a considerable effect on the circular dichroism(CD) spectra. Such an influence was demonstrated by the crystallographic data of some cobalt (III) complexes, *e.g.* tris(1,2-cyclopentanediamine)cobalt(III),[1] and also by theoretical considerations.[2,3] However, only a few examples are found,[1–4] which are limited to cobalt(III) complexes, and complexes of Schiff's bases with asymmetric diimine moiety.

Molybdenum(V) complexes give doubly bridged binuclear complexes with a μ-X-μ-Y-bis(oxomolybdenum (V)) core, $Mo_2O_2XY^{2+}$ (where X=Y=O, X=O and Y=S, and X=Y=S), and coordination number 5 or 6 depending on the ligands.[5] Their crystal structure exhibits considerable distortion from regular square pyramid or octahedron.[5–13] Such distortions can be asymmetrical when the ligand is optically active. The X-ray structure of $[Mo_2O_4(S\text{-cys})_2]^{2-}$,[8] $[Mo_2O_4(S\text{-hist})_2]$,[9] $[Mo_2O_4(S\text{-mecys})_2]$,[10] $[Mo_2O_2S_2(S\text{-cys})_2]^{2-}$,[11] $[Mo_2O_2S_2(S\text{-hist})_2]$[12], and $[Mo_2O_2S_2(S\text{-etcys})_2]$,[13] where *S*-cys^{2-}, *S*-hist^{-}, *S*-mecys^{-}, and *S*-etcys^{-} are (*S*)-cysteinate, (*S*)-histidinate, *O*-methyl- and *O*-ethyl-(*S*)-cysteinate, respectively, are schematically shown in Fig. 1a to 1c. They have chelate rings containing asymmetric carbon atoms at the basal edges. The complexes of *O*-alkyl-(*S*)-cysteinate give coordination number 5, whereas those of the others 6. We have examined carefully the crystallographic data of these complexes and found asymmetric distortions around the $Mo_2O_2XY^{2+}$ core.

We have also prepared three (*R*)-propylenediaminetetraacetate (*R*-pdta) complexes with di-μ-oxo,[14] μ-oxo-μ-thio, and di-μ-thio bridges and determined the X-ray structure (Fig. 1d).[15] These complexes have structurally different feature from the hitherto known carboxylate complexes, with asymmetric chelate ring bridging the molybdenum(V) ions across the two apical sites of the dimer. These *R*-pdta complexes also show considerable asymmetric distortions.

The CD and optical rotatory dispersion spectra (ORD) of molybdenum(V) complexes have been reported with only a limited variety of species[14,16–18] and their relation with the structure has not been discussed. We have measured CD spectra of various amino carboxylate and their ester complexes including those mentioned above in various media. We report here a remarkable correlation between the asymmetric distortion around the $Mo_2O_2XY^{2+}$ core and the CD pattern in the ultraviolet region. The CD studies also provide useful informations on the assignment of the electronic absorption bands of the doubly bridged molybdenum(V) complexes.

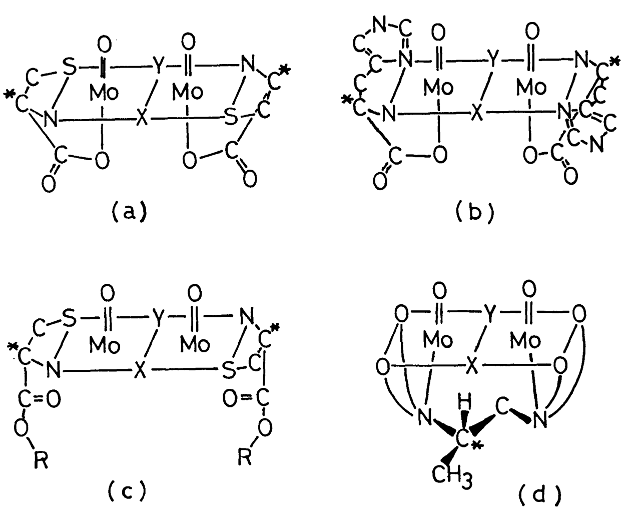


Fig. 1. Schematic drawings of the structure of $Mo_2O_2XY^{(2+)}$-type complexes (X=Y=O, X=O and Y=S, and X=Y=S). Asterisks indicate asymmetric carbons.
(a) $[Mo_2O_2XY(S\text{-cys})_2]^{2-}$, (b) $[Mo_2O_2XY(S\text{-hist})_2]$, (c) $[Mo_2O_2XY(S\text{-Rcys})_2]$ (R=CH_3 or C_2H_5), and (d) $[Mo_2O_2XY(R\text{-pdta})]^{2-}$.

Experimental

Preparation of the Complexes. The following seven complexes were prepared by the known methods; $Na_2[Mo_2O_4(S\text{-cys})_2]\cdot5H_2O$,[19] $[Mo_2O_4(S\text{-hist})_2]\cdot2H_2O$,[20] $[Mo_2O_4(S\text{-mecys})_2]$,[21] $[Mo_2O_4(S\text{-etcys})_2]$,[21] $Na_2[Mo_2O_4(R\text{-pdta})]\cdot3H_2O$,[14,22] $Na_2[Mo_2O_3S(S\text{-cys})_2]\cdot4H_2O$,[23] and $[Mo_2O_3S(S\text{-etcys})_2]$.[23]

The following three di-μ-thio-bis{oxomolybdenum(V)} complexes were prepared by modifying the methods in the literature.

*Sodium di-μ-thio-bis[{(*S*)-cysteinato}oxomolybdate(V)] Tetrahydrate,* $Na_2[Mo_2O_2S_2(S\text{-}cys)_2]\cdot 4H_2O$: A black solid was obtained by Mitchell's method,[19] which contained both soluble and insoluble components in *N,N*-dimethylformamide (DMF) (or dimethyl sulfoxide (DMSO)). The former seemed to be the expected complex. Insoluble component was not formed when the pH of the solution was adjusted carefully as follows. Hydrogen sulfide was slowly bubbled through 200 cm³ of the solution of $Na_2[Mo_2O_4(S\text{-cys})_2]\cdot 5H_2O$ (2 g; 3 mmol) in water for 1 h, the pH of the solution being kept at *ca.* 7 by the addition of aqueous NaOH solution. The resulting reddish brown solution was evaporated to 25 cm³ at 40 °C under a reduced pressure. Orange needles were collected after 3 days. Yield, 0.2 g. Found: C, 11.22; H, 2.71; N, 4.46%. Calcd for $C_6H_{18}N_2O_8S_4Na_2Mo_2$: C, 11.18; H, 2.82; N, 4.35%.

*Di-μ-thio-bis[{(*S*)-histidinato}oxomolybdenum(V)] Dihydrate,* $[Mo_2O_2S_2(S\text{-}hist)_2]\cdot 2H_2O$: The procedure reported by Spivack and Dori,[24] which involves the passage of H_2S through the aqueous solution of $[Mo_2O_4(S\text{-hist})_2]$, gave a black material, from which the pure complex was not obtained. The pure complex was prepared as follows. Sodium molybdate (2.4 g; 10 mmol) and (*S*)-histidine (1.6 g; 10 mmol) were dissolved in 100 cm³ of water. Hydrogen sulfide was bubbled slowly through the solution for *ca.* 1 h, while 400 cm³ of water was added in small portions. The reddish brown solution was purged with nitrogen gas to remove excessive H_2S, and evaporated in a rotary evaporator until yellow solid deposited, which was washed with water until the washing became colorless. The yield of yellow powder was 0.45 g. Found: C, 22.46; H, 2.93; N, 13.05%. Calcd for $C_{12}H_{20}N_6O_6S_2Mo_2$: C, 22.79; H, 3.19; N, 13.29%.

*Di-μ-thio-bis[{O-methyl-(*S*)-cysteinato}oxomolybdenum(V)],* $[Mo_2O_2S_2(S\text{-}mecys)_2]$: This was prepared by one of the three methods given by Mitchell,[19] from sodium molybdate (1.2 g, 5 mmol), (*S*)-cysteine methyl ester hydrochloride (3.4 g; 20 mmol) and H_2S. The crude product (0.6 g) was dissolved in acetonitrile, a small amount of insoluble materials was removed, and the solution was kept in air for two days. The brown precipitate was filtered off. Addition of methanol or water to the filtrate gave orange crystals. Found: C, 17.13; H, 2.82; N, 4.97%. Calcd for $C_8H_{16}N_2O_6S_4Mo_2$: C, 17.27; H, 2.90; N, 5.04%.

Five new complexes were prepared by the following methods. The data of elemental analysis and important infrared absorption bands of the new complexes are summarized in Table 1. Each complex shows characteristic infrared bands for its skeletal structure, $Mo_2O_2XY^{2+}$.[23,25]

*Sodium di-μ-oxo-bis[{(*R*)-penicillaminato}oxomolybdate(V)] Dihydrate,* $Na_2[Mo_2O_4(R\text{-}pen)_2]\cdot 2H_2O$: The complex ion, $[Mo_2O_4(R\text{-pen})_2]^{2-}$, was described previously,[26] but the preparation method has not yet been reported. Molybdenum pentachloride (3.1 g; 11 mmol) was dissolved in 25 cm³ of 3 M (M=mol dm⁻³) HCl. (*R*)-Penicillamine (5 g; 33 mmol) in 20 cm³ of 3 M HCl was added to the solution. The pH was adjusted to 6—7 with 6 M NaOH, while the solution was cooled in an ice bath. Barium perchlorate (1.7 g; 5 mmol) in 20 cm³ of water was added to the solution to give orange precipitate of $Ba[Mo_2O_4(R\text{-pen})_2]\cdot 3H_2O$. This barium salt (2.6 g) and a cation exchange regin Dowex 50W-X8 (Na^+-form, 120 cm³) were stirred in 150 cm³ of water for *ca.* 5 h. The regin was filtered off, and the filtrate was treated with ethanol (50 cm³) to give orange precipitate (1.4 g). This was dissolved in a minimum amount of water and treated with acetonitrile to give first oily precipitate. The supernatant was removed by decantation and the oil was further treated with acetonitrile. Orange powder was collected and washed with acetonitrile and dried in air.

*μ-Oxo-μ-thio-bis[{(*S*)-histidinato}oxomolybdenum(V)] Trihydrate,* $[Mo_2O_3S(S\text{-}hist)_2]\cdot 3H_2O$: Hydrogen sulfide was bubbled slowly through the solution of molybdenum pentachloride (6.15 g; 23 mmol) in 100 cm³ of 3 M HCl for *ca.* 2 h. The solution was purged with nitrogen gas to remove excessive H_2S, and a small quantity of brown solid was filtered off. (*S*)-Histidine (1.7 g; 11 mmol) was added to the filtrate. The pH was adjusted to *ca.* 6 with 8 M NaOH solution. Greenish brown precipitate was filtered off, and the filtrate was kept in an ice bath to give yellow crystals. They were dissolved in 50 cm³ of 3 M HCl, and the pH was adjusted to *ca.* 6 with 8 M NaOH solution. The solution was filtered and kept in a refrigerator for 2 days to give yellow crystals.

*μ-Oxo-μ-thio-bis[{O-methyl-(*S*)-cysteinato}oxomolybdenum(V)],* $[Mo_2O_3S(S\text{-}mecys)_2]$: This was prepared by a similar method to that for the corresponding *S*-etcys complex.[23]

*Sodium μ-oxo-μ-{(*R*)-propylenediaminetetraacetato}-μ-thio-bis-{oxomolybdate(V)} Tetrahydrate,* $Na_2[Mo_2O_3S(R\text{-}pdta)]\cdot 4H_2O$: The procedure for the preparation of $[Mo_2O_3S(S\text{-hist})_2]\cdot 3H_2O$ was followed until the addition of ligand. A solution of (*R*)-propylenediaminetetraacetic acid monohydrate[27] (2.8 g; 9 mmol) in 25 cm³ of water was added to the molybdate solution, and the pH was adjusted to *ca.* 6 with 8 M NaOH solution. The solution was filtered to remove brown solid, and allowed to stand in a refrigerator for three days. A small quantity of black solid was removed, and the filtrate was evaporated to give first white solid, which was cooled in an ice-bath and filtered off, and then orange needles, which were recrystallized from water by adding ethanol.

Table 1. Elemental analysis and some infrared spectral data of the new compounds

Compound	Elemental analysis (%)			Infrared bands (cm⁻¹)[a]		
	C Found(Calcd)	H Found(Calcd)	N Found(Calcd)	(Mo=O$_t$)	(Mo–O$_b$)	(Mo–S$_b$)[b]
$Ba[Mo_2O_4(R\text{-pen})\cdot 3H_2O$	16.26 (16.19)	3.58 (3.26)	3.85 (3.78)			
$Na_2[Mo_2O_4(R\text{-pen})_2]\cdot 2H_2O$	11.53 (11.42)	3.35 (3.31)	4.64 (4.44)	939 s	735 m	
$[Mo_2O_3S(S\text{-hist})_2]\cdot 3H_2O$	22.68 (22.72)	3.39 (3.49)	13.49 (13.25)	946 s	733 m	467 m
$[Mo_2O_3S(S\text{-mecys})_2]$	17.56 (17.78)	2.91 (2.99)	5.31 (5.19)	939 s	738 m	450 w
$Na_2[Mo_2O_3S(R\text{-pdta})]\cdot 4H_2O$	19.17 (19.08)	3.44 (3.20)	3.96 (4.05)	940 s	740 m	460 m
$Na_2[Mo_2O_2S_2(R\text{-pdta})]\cdot 3H_2O$	18.65 (18.65)	2.93 (3.13)	3.96 (3.95)	941 s		480 s

a) Measured in KBr disks. b) Strongest band in the region 400—500 cm⁻¹, where several weak bands are also observed. The assignment should be tentative, according to the recent report on the resonance Raman spectra of some di-μ-thio complexes.[25]

Table 2. Torsion angles, θ_1, θ_2, θ_3, θ_4, and ξ,[a] and the chirality of the corresponding twist,[b] and the conformations of the gauche-like chelate rings of the ligands, for the $Mo_2O_2XY^{(2+)}$ type complexes

Complex	Torsion angles[c,d]					Chelate ring
	$\lvert\theta_1\rvert$	$\lvert\theta_2\rvert$	$\lvert\theta_3\rvert$	$\lvert\theta_4\rvert$	$\lvert\xi\rvert$	
$Na_2[Mo_2O_4(S\text{-cys})_2]\cdot 5H_2O$	4.0(8) Δ	1.5(7) Δ	1.7(7) Δ	11.7(5) Λ	0.1(4)* Δ	δ
$[Mo_2O_4(S\text{-etcys})_2]$	6.7(11) Λ	22.1(8) Λ	24.3(7) Λ		28.4(6) Λ	δ
$Na_2[Mo_2O_4(R\text{-pdta})]\cdot 3H_2O$	5.4(8) Δ	8.6(10) Δ	6.8(11) Δ	5.4(6) Δ	8.6(7) Δ	λ
$Na_2[Mo_2O_3S(R\text{-pdta})\cdot 4H_2O$	0.2(3)* Δ	10.0(3) Δ	11.6(4) Δ	9.1(2) Δ	11.5(2) Δ	λ
$Na_2[Mo_2O_2S_2(S\text{-cys})_2]\cdot 2H_2O$	4.7(14) Δ	1.4(11) Δ	0.6(11)* Δ	10.9(8) Λ	0.2(8)* Λ	δ
$[Mo_2O_2S_2(S\text{-mecys})_2]$	9.2(15) Λ	30.1(13) Λ	26.8(14) Λ		35.9(11) Λ	λ
$[Mo_2O_2S_2(S\text{-hist})_2]\cdot 1.5H_2O$	2.5(4) Δ	0.8(5) Δ	7.5(4) Δ	4.6(3) Λ	4.5(3) Δ	—
$Na_2[Mo_2O_2S_2(R\text{-pdta})]\cdot 4H_2O$	0.2(6)* Λ	9.3(6) Δ	9.2(7) Δ	10.8(4) Δ	10.4(5) Δ	λ

a) For the definition of θ_1, θ_2, θ_3, θ_4, and ξ, see Fig. 4a. b) See Fig. 4c. c) Estimated standard deviations in parentheses. d) Values with asterisks are too small to be valid for the discussion in the text.

Yield, 0.2 g.

Sodium μ-{(R)-Propylenediaminetetraacetato}-di-μ-thio-bis{oxomolybdate(V)} Trihydrate, $Na_2[Mo_2O_2S_2(\text{R-}pdta)]\cdot 3H_2O$: An aqueous solution (400 cm^3) of sodium molybdate (2.7 g; 10 mmol) and (*R*)-propylenediaminetetraacetic acid monohydrate[27] (1.6 g; 5 mmol) was treated with H_2S slowly until the color turned red, and then with nitrogen to remove excessive H_2S. The solution was evaporated under a reduced pressure to 50 cm^3 and kept in a refrigerator for a week to give orange crystals. Yield, 0.1 g.

The Aqua Complex Ions, $[Mo_2O_2XY(H_2O)_6]^{2+}$:[28] These ions were obtained in solution by dissolving the corresponding *S*-cys complexes in 2 M $HClO_4$. Complete disappearance of CD indicated complete loss of (*S*)-cysteinate ligand. The absorption spectra of the di-μ-oxo and di-μ-thio complexes were in reasonable agreement with those reported previously.[29,30] The spectrum of $[Mo_2O_3S(H_2O)_6]^{2+}$ is reported for the first time.

Measurements. All the measurements were carried out at room temperature. Electronic absorption and CD spectra of the complexes were measured in water, DMF and DMSO, whenever soluble, and also in KBr disks. The neutral complexes were insoluble in water. The spectra of *O*-alkyl-(*S*)-cysteinato complexes were measured in acetonitrile, too. The spectra in water were measured under nitrogen atmosphere; otherwise the spectra changed slowly.

The electronic absorption spectra were recorded on a Hitachi 323 Recording Spectrophotometer and a Hitachi 124 Spectrophotometer with a Hitachi Recorder QPD-34. The CD spectra were recorded on a JASCO J-40 Automatic Recording Spectropolarimeter, and a JASCO ORD-UV-5 Spectrophotometer with a CD attachment, for compounds either in solutions or in KBr disks. Nitrogen gas was passed through the cell compartment during the measurement in the KBr disk. The infrared absorption spectra were recorded on a JASCO IR-A1 and a JASCO IR-A2 Spectrophotometer in KBr disks. The PMR spectra were measured with a Varian T-60 Spectrometer in D_2O with sodium 3-(trimethylsilyl)propanesulfonate as an internal standard.

The torsion angles listed in Table 2 were calculated using the atomic coordinates given in the literature.[8,10–13,15] The details of positional parameters have not been found for $[Mo_2O_4(S\text{-hist})_2]$.[9]

Results and Discussion

In the following, the X-ray structures are closely examined, first. Then the nature of absorption bands and the corresponding CD bands are discussed. Finally, the correlation between the structure and the CD spectra is discussed.

Geometrical Isomerism of the Complexes. Several geometrical isomers are possible for the *S*-cys complex. We have fractionally crystallized the sodium salt of $[Mo_2O_4(S\text{-cys})_2]^{2-}$ from aqueous solution by adding ethanol slowly. Aqueous solutions of all the precipitates gave almost identical CD spectra. Thus either all the fractions contained the same geometrical isomer, or a rapid isomerization took place in aqueous solution to give an isomeric mixture with the same composition. The CD spectra of the crystalline complex in KBr disk and in aqueous solution show similar pattern (Fig. 2) in visible region to eliminate the latter possibility. The isomer illustrated in Fig. 1a should have been formed stereoselectively. All the other com-

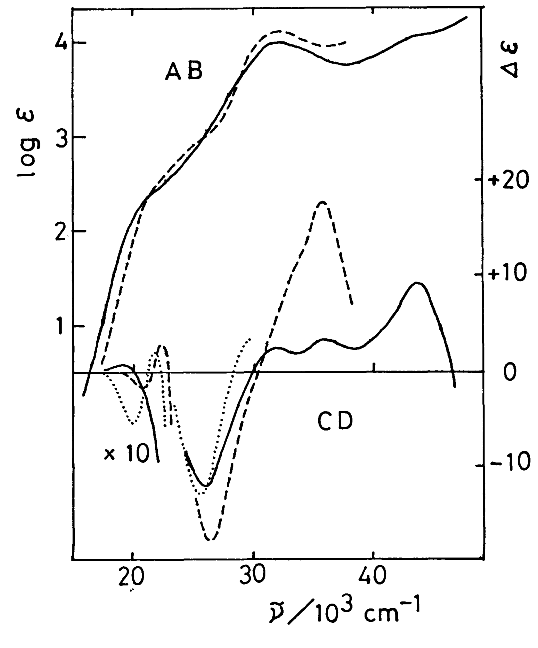


Fig. 2. Comparison in various media of absorption (AB) and CD spectra of $[Mo_2O_4(S\text{-cys})_2]^{2-}$; in water (——), in DMF (----), and in KBr disk (······).

plexes of *S*-cys, its alkyl esters, *S*-hist and *R*-pen are believed to give the geometrical isomers in Fig. 1 exclusively.

The diamine part of the three *R*-pdta complexes is known to form a distorted λ gauche structure with the methyl group at equatorial direction.[15] The gauche structure of $[\mathrm{Mo_2O_4(pdta)}]^{2-}$ was claimed to be fixed at 0—90 °C by the measurements of ^{1}H[31] and ^{13}C NMR spectra[32] in aqueous solution. Molecular model studies also indicated that the inversion of the gauche structure is difficult owing to the steric hindrance of methyl group with the oxide bridges.[31,32] We thus believe that the diamine part of all the three *R*-pdta complexes is fixed in aqueous solutions as found by X-ray crystallography.[15]

Two geometrical isomers are possible for $[\mathrm{Mo_2O_3S}(R\text{-pdta})]^{2-}$ due to relative positions of the bridging oxo and sulfido ligands. The proton NMR spectrum of the complex in $\mathrm{D_2O}$ gave only one methyl signal (doublet), indicating only one isomer in the solution. Fractional crystallization failed to give any evidence for the existence of two isomers. The structure of stereoselectively formed isomer determined by X-ray diffraction method,[15] is shown in Fig. 1d.

Close Examination of the X-Ray Structures. Asymmetry caused by the arrangement of coordinated atoms around the $\mathrm{Mo_2O_2XY^{2+}}$ core is considered first. A view of $[\mathrm{Mo_2O_4}(R\text{-pdta})]^{2-}$ along the Mo–Mo axis (Fig. 3a, the axis perpendicular to the paper plane) clearly shows that the pseudo-octahedron of the molybdenum ion over the paper plane is rotated clockwise around the Mo–Mo axis from that underneath the paper plane. The extent of such a rotation may be expressed by the four torsion angles, θ_1, θ_2, θ_3, and θ_4, defined by the four pairs of metal ligand bonds, Mo–$\mathrm{O_t}$, Mo–$\mathrm{O_c}$, Mo–$\mathrm{O_c}'$, and Mo–N, respectively (Fig. 4a). The direction of rotation of each pair can be represented by the sign (P and M, suggested by IUPAC,[33] Fig. 4c) of the torsion angles.

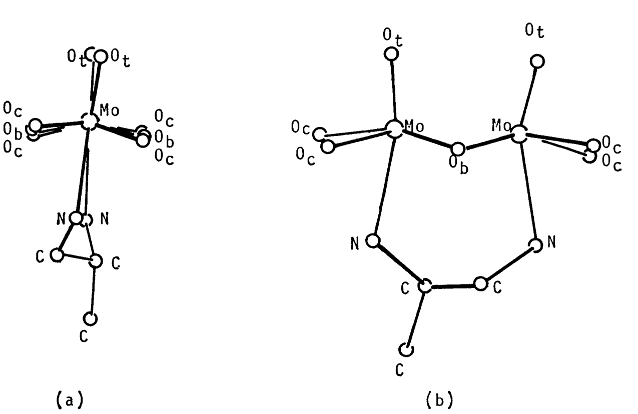


Fig. 3. (a) The projection from the Mo-Mo axis for $[\mathrm{Mo_2O_4}(R\text{-pdta})]^{2-}$, and (b) the projection from the axis connecting two oxide bridges for the same ion. Acetate arms are omitted for clarity. ($\mathrm{O_t}$=terminal oxide oxygen, $\mathrm{O_b}$=bridging oxide oxygen, $\mathrm{O_c}$=ligand carboxylate oxygen).

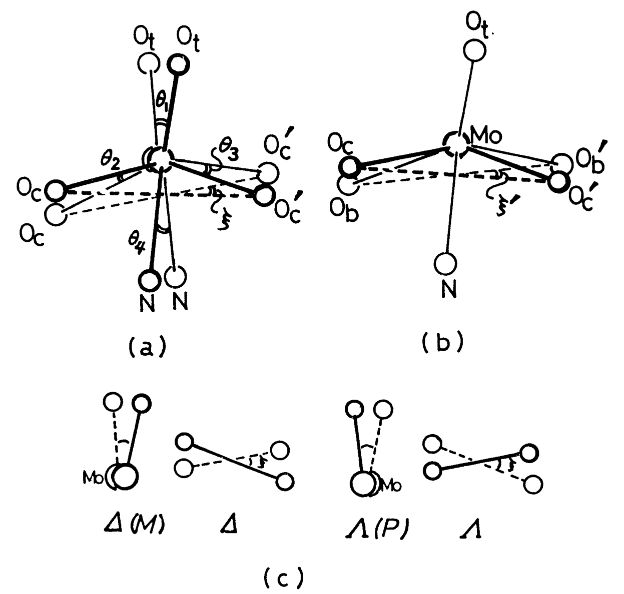
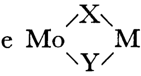


Fig. 4. (a) (b) The definition of torsion angles for $[\mathrm{Mo_2O_4}(R\text{-pdta})]^{2-}$. ($\mathrm{O_t}$, $\mathrm{O_b}$, and $\mathrm{O_c}$ ($\mathrm{O_c}'$), see legend of Fig. 3). (c) The definition of chirality used in this paper.

Figure 3b shows the view of the same complex along the axis connecting two bridging oxygens. The coordinated four carboxylate oxygens show alternating deviations from the mean plane of these four oxygen atoms. Such a distortion can be understood as a distortion of two basal edges, connecting two carboxylate oxygens, $\mathrm{O_c}$ and $\mathrm{O_c}'$, on a given molybdenum ion, and represented by the angle, ξ (Fig. 4a). These two basal edges give a skew arrangement, and the chirality of such a distortion can be expressed by the symbol, Δ or Λ.[34] The direction of the distortion of each Mo–ligand bond pair (Mo–$\mathrm{O_t}$, Mo–$\mathrm{O_c}$, Mo–$\mathrm{O_c}'$, and Mo–N) can be also expressed by use of Δ or Λ (Fig. 4c). Since the present asymmetry deals with 'conformation' of the two octahedrons of molybdenum(V) ions, δ and λ might be prefered to Δ and Λ. However, δ and λ are used for the conformation of ligand itself. Thus, the symbols, Δ and Λ, are tentatively used hereafter in this paper rather than P and M, since the latters are not always related to asymmetry. Table 2 lists the values of $|\theta_1|$, $|\theta_2|$, $|\theta_3|$, $|\theta_4|$, and $|\xi|$, and the 'chirality of the twist' for various doubly-bridged molybdenum(V) complexes containing optically active ligands. The angle ξ is closely related to θ_2 and θ_3, and is used hereafter as representing these angles.

The chirality of the twist of two Mo–$\mathrm{O_t}$ bonds (θ_1), and of the two basal edges (ξ), are the same for a given complex, except for $[\mathrm{Mo_2O_2S_2}(S\text{-cys})_2]^{2-}$ and $[\mathrm{Mo_2O_2S_2}(R\text{-pdta})]^{2-}$ whose ξ and θ_1, respectively, are negligibly small. It should be noted that the chirality of these twists of the bidentate *S*-cys ester complexes are different from those of the terdentate *S*-cys and *S*-hist complexes, despite of the same absolute configuration of these ligands themselves. The values of $|\xi|$ vary depending on the complex, and those for the *S*-cys ester complexes are considerably big as compared with those of the others. Variation in $|\theta_1|$ values is smaller. The chirality of the twist of two apical bonds (trans to terminal oxo bonds) is Δ for the *R*-pdta complexes, and Λ for the *S*-cys and *S*-hist complexes, despite that the chirality of the twist of Mo–O_t bonds is Δ for all these complexes.

The asymmetries around each metal ion of the dimer are complicated by the highly distorted structure from the regular octahedron. The asymmetry of the basal plane involving two basal atoms and two bridging ligands may be most important, since the bond trans to Mo–O_t is longer than the others or fails to exist. Such asymmetry may be defined by the angle, ξ', in Fig. 4b. Under the definition the asymmetry around each metal ion of the dimer is considered similarly as that around the dimeric core defined by ξ. The five membered chelate rings at the basal edge form gauche like structure, whose absolute conformations are given in Table 2. The diamine part of *R*-pdta bridging the two apical sites of the $Mo_2O_2XY^{2+}$ core also form gauche like structure, whose absolute conformation is also given in Table 2.

There is no significant asymmetric spiral arrangement of more than two chelate rings in a given complex. No appreciable asymmetric distortion is seen within the  $\mathrm{Mo}\overset{X}{\underset{Y}{\diamond}}\mathrm{Mo}$ core for all the complexes.

Medium Effects on the CD Spectra. The data of absorption and CD spectra of the di-μ-oxo complexes in various media are summarized in Table 3. The CD spectra in the region $<30000\ \mathrm{cm}^{-1}$ for all the complexes are characterized by the strong peaks at *ca.* $26000\ \mathrm{cm}^{-1}$. The CD pattern of a given complex in this region is very similar to one another regardless of the medium, although the peak in KBr disk shifts always to slightly lower wave number (Fig. 2). Such a similarity suggests that the basic skeletal structure of the complexes in crystals should be retained in the solutions; *i.e.* isomerization and ligand dissociation are not feasible upon dissolution, and the extent of donor atom distortion does not seem to change significantly. Similar conclusion was derived also for the μ-oxo-μ-thio and di-μ-thio complexes.

The CD spectrum of $[Mo_2O_4(S\text{-cys})_2]^{2-}$ in DMSO changed considerably as its concentration changed in less than 0.001 M solution. However, addition of free (*S*)-cysteine to the solution restored a pattern similar to that in solutions of higher complex concentration and that in DMF. Reversible ligand dissociation must take place in dilute DMSO solutions. A similar trend was observed also for $[Mo_2O_3S(S\text{-cys})_2]^{2-}$ in DMSO, but not for the other complexes in any of the solvents examined.

The CD spectrum of $[Mo_2O_4(S\text{-cys})_2]^{2-}$ in water is different from that in DMF in the region $>30000\ \mathrm{cm}^{-1}$ (Fig. 2). Also the CD spectrum of $[Mo_2O_4(R\text{-pen})_2]^{2-}$ in water in the same region is significantly different from those in DMF and DMSO, the spectra in the latter two solvents being very similar to each other. Such a difference seems to be due to the difference in strength in the CD band at *ca.* $36000\ \mathrm{cm}^{-1}$, the CD strength in DMF being *ca.* 5 times bigger than that in water. The origin of such a solvent effect is not certain. However, it is unlikely that the difference indicates the significant change in skeletal structure of the complex, since no significant change in the CD band in $26000\ \mathrm{cm}^{-1}$ region, which is sensitive to the skeletal structure (*vide infra*), is observed. The CD spectra of two other *S*-cys complexes, $[Mo_2O_3S(S\text{-cys})_2]^{2-}$ and $[Mo_2O_2S_2(S\text{-cys})_2]^{2-}$, have similar patterns in water to those in the organic solvents. No significant change in CD spectra was observed for the *R*-pdta complexes in aqueous media and in DMF and DMSO.

The CD patterns of $[Mo_2O_4(S\text{-cys})_2]^{2-}$ and $[Mo_2O_4(R\text{-pen})_2]^{2-}$ are almost completely enantiomeric in a given solvent, suggesting that the replacement of two hydrogens with methyl groups at the adjacent carbon to -S^- does not give significant influence on the CD spectrum.

The *S*-cys ester complexes have vacant apical sites (trans to terminal oxo), which might interact with solvent molecules. However, the solvent effects on the CD spectra of $[Mo_2O_4(S\text{-Rcys})_2]$ ($R=CH_3$, C_2H_5) is very small. No significant change was observed even in pyridine which has a strong donor ability. Probably the oxygen atoms of the ester ligands situate near the apical positions as in crystals,[10,13] to prevent the interaction of the solvent molecules.

The Nature of the Absorption Bands of the Di-μ-oxo Complexes. The $Mo_2O_4^{2+}$ complexes give different spectral patterns from those of the monomeric and single-bridged μ-oxo dimeric molybdenum(V) complexes.[5] The $Mo_2O_4^{2+}$ dimers are diamagnetic, indicating the interaction of the d-orbitals of the two metal ions.[5] The absorption spectrum of $[Mo_2O_4(R\text{-pdta})]^{2-}$ has two bands at 25800 and $33600\ \mathrm{cm}^{-1}$, and a shoulder at *ca.* $20800\ \mathrm{cm}^{-1}$ in water. Similar absorption patterns are observed for the complexes with the same core, $[Mo_2O_4(H_2O)_6]^{2+}$ (see Fig. 9),[29] $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$,[35] $[Mo_2O_4(\mathrm{edta})]^{2-}$,[36] and $[Mo_2O_4(\mathrm{hedta})(H_2O)]^{-}$,[37] where edta^{4-} and hedta^{3-} stand for ethylenediaminetetraacetate ion and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetate ion, respectively.

All the other complexes in this study also have absorption peaks at *ca.* $33000\ \mathrm{cm}^{-1}$, but none in lower wave number region. However, they give CD bands in the region $<30000\ \mathrm{cm}^{-1}$, suggesting the presence of electronic transitions of corresponding energies. The electronic transition energies of all the complexes can be estimated from either the absorption or the CD peaks, and are summarized in Table 3. Four common transitions are observed in the region from 12000 to $40000\ \mathrm{cm}^{-1}$. The energies of these bands change only slightly from one complex to another. It is concluded that these transitions are mainly due to the $Mo_2O_4^{2+}$ core and to a much less extent to the variety of other ligands. Brown *et al.* calculated the electronic transition energies of $[Mo_2O_4(S\text{-cys})_2]^{2-}$ by the SCF-MO method and gave five transition energies, 13250, 20320, 27390, 30870, and $35700\ \mathrm{cm}^{-1}$.[17] These transitions were claimed to involve the orbitals mainly located on the two molybdenum atoms, and hence common to other $Mo_2O_4^{2+}$ complexes.[17] The absorption and CD peaks at *ca.* $13250\ \mathrm{cm}^{-1}$ should be very weak, if existed, since our results failed to indicate the transition at this wave number in <0.1 M aqueous solutions. The four transitions with the higher wave number

Table 3. The absorption (AB) and CD spectral data for of the di-μ-oxo-bis{oxomolybdenum(V)} complexes (Wave number/10^3 cm^{-1}; absorption intensity ($\log \varepsilon$) and CD strength ($\Delta\varepsilon$) in parenthesis).[a,b]

Complex	Medium[c]	AB or CD	Band classification				
			I	II	III	IV	V
$[\mathrm{Mo_2O_4}(S\text{-cys})_2]^{2-}$	water	AB	21.0 s (2.31);		32.3 (4.03);		43.7 (4.05)
		CD	19.2 (+0.07);	26.1 (−12.2);	31.7 (+2.6);	36.0 (+3.1);	43.8 (+9.30)
	DMF	AB	21.0 s (2.25);	25.4 s (2.92);	32.0 (4.10);		— — — —
		CD	20.8 (−0.19); 22.6 (+0.3)	26.4 (−18.0);		36.0 (+17.9);	— — — —
	KBr	CD	20.0 (−) ; 21.8 (+)	25.5 (−)	— — — —	— — — —	— — — —
$[\mathrm{Mo_2O_4}(R\text{-pen})_2]^{2-}$	water	AB	21.0 s (2.25);		32.2 (4.09);		44.4 (4.09)
		CD	18.6 (−0.07);	26.6 (+11.4);	31.9 (−4.4) ;	35.8 (−4.9);	43.6 (−11.7)
	DMF	AB			31.7 (4.06);		— — — —
	(DMSO)	CD	20.5 (+0.15); 22.4 (−0.29)	26.8 (+14.4);	30.0 s (−9.0) ;	36.0 (−22.0);	— — — —
$[\mathrm{Mo_2O_4}(S\text{-hist})_2]$	DMSO	AB	21.1 s (1.87);	26.1 s (2.52);	33.0 (3.79);		— — — —
		CD	20.4 (+0.14);	26.9 (−3.0) ;	33.6 (+3.9);	38.0 (+7.3);	— — — —
	KBr	CD	20 (+) ;	26.7 (−)	— — — —	— — — —	— — — —
$[\mathrm{Mo_2O_4}(S\text{-mecys})_2]$	AN	AB			34.0 s (3.95);	36.0 s (3.97);	45.5 (4.21)
		CD	22.3 (+0.85);	28.9 (+29.0);	34.4 (−22.0);	37.3 (+11.1);	40.5 (−4.20) 43.8 (+8.0) 46.9 (−9.2)
	DMF	AB	21.6 s (2.75);	29.2 s (3.48);	34.5 (3.94);		— — — —
		CD	22.4 (+1.42);	29.0 (+35.8);	34.0 (−22.0);	37.4 (+14.8);	— — — —
	KBr	CD	22.0 s (+) ;	27.5 (+) ;	32.6 (−) ;	— — — —	— — — —
$[\mathrm{Mo_2O_4}(S\text{-etcys})_2]$	AN	AB		29.0 s (3.29);	34.2 s (3.95);	36.2 s (3.95);	45.0 s (4.20)
		CD	22.2 (+1.03);	28.8 (+30.5);	34.4 (−21.5);	37.4 (+10.2);	40.4 (−4.6) 44.0 (+10.0) 46.7 (−6.5)
	DMF	AB	22.1 s (2.18);	28.7 s (3.48);	34.4 (3.98);		— — — —
		CD	22.4 (+1.45);	29.0 (+36.2);	34.3 (−19.8);	37.6 (+12.5);	— — — —
	KBr	CD	22.5 s (+) ;	27.9 (+) ;	33.3 (−) ;	— — — —	— — — —
$[\mathrm{Mo_2O_4}(R\text{-pdta})]^{2-}$	water	AB	20.8 s (2.00);	25.8 (2.60);	33.6 (4.00);		
		CD	20.8 s (−0.48);	26.0 (−5.5) ;	33.3 (+5.1) ;	37.1 (−1.6) ;	40.6 (+3.85) 45.2 (−5.10)
	DMF	AB		25.6 (2.60);	33.0 (3.99);		— — — —
		CD	20.6 (−0.38);	25.6 (−6.4) ;	32.8 (+5.7) ;		— — — —
	KBr	CD	19.8 (−) ;	25.2 (−) ;	31.8 (+) ;	35.9 (−) ;	— — — —

a) s indicates "shoulder". b) Dashed lines indicate the region where data cannot be obtained due to solvent absorption. c) DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, AN = acetonitrile, KBr = KBr disk.

must correspond to our four common transitions. These are denoted hereafter as band I, II, III, and IV from the low wave number (Table 3).

The band II of the two complexes containing the esters of *S*-cys are somewhat different from those of the other complexes: *i.e.* the position of the band is at a large wave number by nearly 3000 cm^{-1}, and the absorption strength is almost ten times of those of the other complexes. Such differences may be accounted for by the greater distortion of the *S*-cys ester complexes and the absence of apically ligating atoms. The nature of the band is not very different from those of the other complexes.[17]

Characteristics of the CD Spectra of the Di-μ-oxo Complexes. The CD data of the six $Mo_2O_4^{2+}$ complexes are listed in Table 3. The CD spectra in the band I region are weak in intensity and sensitive to the medium. There seems to be more than two components of electronic transitions, as judged from the CD spectra.

The CD sign of band II at *ca.* 26000 cm^{-1} are positive for $[Mo_2O_4(S\text{-mecys})_2]$, $[Mo_2O_4(S\text{-etcys})_2]$, and $[Mo_2O_4(R\text{-pen})_2]^{2-}$, and negative for the others. The CD pattern of this band is least affected by the medium. The $\Delta\varepsilon/\varepsilon$ value of this band is the biggest among those of the four transitions; *i.e.* the values are larger than those of the other bands by five to ten times except for the *S*-cys ester complexes. Therefore the band II should be the most important in considering the optical activity of the complexes. The CD signs at band III are always opposite to those at band II. Hence, the asymmetric source for these two transitions can be common.

No absorption peak is observed at band IV region, but one CD band is always observed. The CD sign of the band IV does not related to those of band II and III. In higher wave number region than 40000 cm^{-1}, a few absorption and CD peaks are observed, but the CD patterns are complicated. No further discussion is made in this study.

Relation between the CD Sign and the Structure of Di-μ-oxo Complexes. Comparison of the CD data in Table 3 with the structural data in Table 2 of three $Mo_2O_4^{2+}$ complexes, leads to the following findings.

The CD signs of the band II and III are related to the chirality of the twist of two Mo–O$_t$ bonds (angle θ_1) and of the twist of the two basal edges (angle ξ). The negative and positive CD peaks at the band II and III regions, respectively, for the *S*-cys and *R*-pdta complexes reflect the Δ chirality of these twists, while the reverse CD signs for the *S*-etcys complex are related to the Λ chirality. It should be noted that the relationship is found for the three complexes which have different ligand environments. Such a relationship for the important band II transition suggests that the distortion around the Mo–Mo axis difined by the torsion angles, θ_1, θ_2, θ_3, and ξ, must be the most important asymmetric source of $Mo_2O_4^{2+}$ complexes.

The CD sign at band IV seems to be related to the absolute configuration of the ligand itself; *i.e.* positive CD peaks for the *S*-cys, *S*-hist, *S*-mecys, and *S*-etcys complexes, and negative CD peaks for the *R*-pdta and *R*-pen complexes. The CD sign at band IV seems to be also related to the conformation of the five membered chelate ring; *i.e.* positive and negative CD peaks corresponding to δ and λ conformations (Table 2), respectively. However, these relations concerning the band IV should be taken as tentative, since the location of relevant asymmetric centers in the molecules are different between the *R*-pdta complex and the others.

The twist of the two bonds trans to Mo–O$_t$ (apical bond) would not be important in determining the CD patterns. These bonds are considerably longer, if existed, than the other bonds and would not give significant influence on the electronic transitions of the $Mo_2O_4^{2+}$ moiety. The asymmetry around each metal ion of the dimer represented by the torsion angle ξ', is parallel to the distortion of the dimer represented by ξ, and thus can also explain the CD signs of band II and III. However, such an explanation is less attractive since the nature of the absorption bands are now assigned to involve the transitions within the dimeric core rather than those within the orbitals of one metal ion.

Absorption and CD Spectra of the μ-Oxo-μ-thio and the Di-μ-thio Complexes. The absorption and CD spectra of $Mo_2O_4^{2+}$, $Mo_2O_3S^{2+}$, and $Mo_2O_2S_2^{2+}$ complexes containing *S*-cys, *S*-mecys, *S*-hist, and *R*-pdta are compared with one another in Figs. 5—8. Absorption spectra of $[Mo_2O_2XY(H_2O)_6]^{2+}$ are shown in Fig. 9. The numerical data of the μ-oxo-μ-thio and di-μ-thio complexes are summarized in Table 4 and 5, respectively.

General Features: The most characteristic feature of the absorption spectra is the remarkable increase in absorption intensity with increase in the number of bridging sulfide in the band II region (*ca.* 26000 cm^{-1}) except for the *S*-mecys complexes. The change in

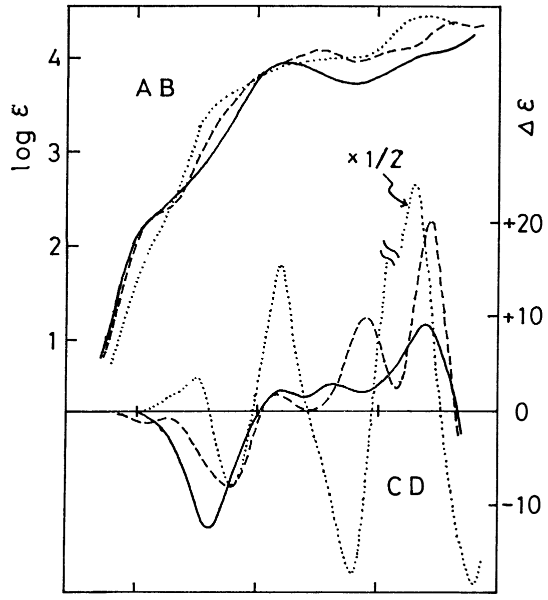


Fig. 5. Absorption (AB) and CD spectra of $[Mo_2O_2XY(S\text{-cys})_2]^{2-}$ in water; X=Y=O (——), X=O and Y=S (----), and X=Y=S (······).

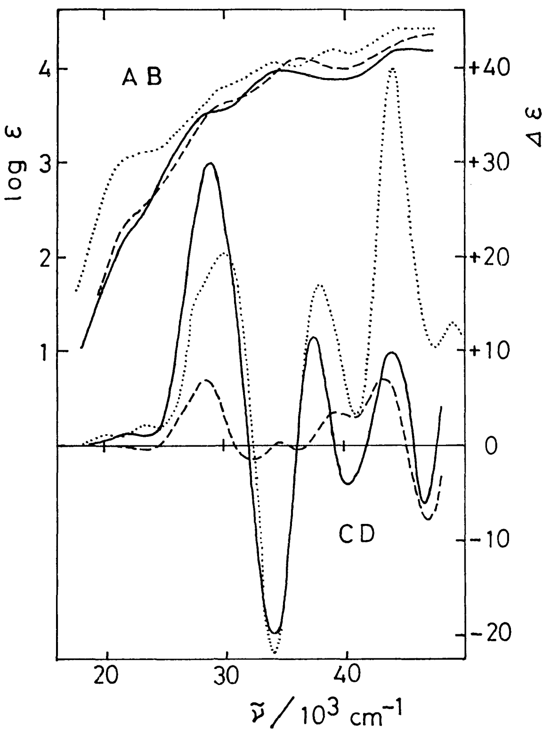


Fig. 6. Absorption (AB) and CD spectra of $[Mo_2O_2XY(S\text{-mecys})_2]$ in acetonitrile; X=Y=O (——), X=O and Y=S (----), and X=Y=S (······).

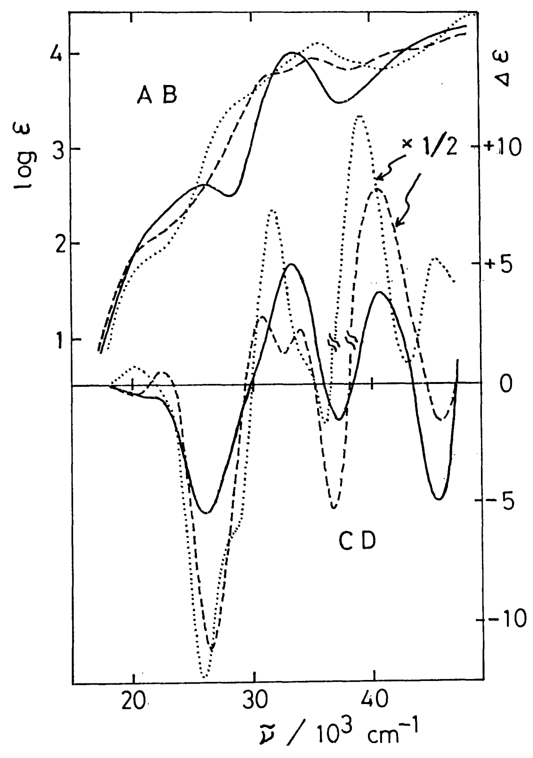


Fig. 8. Absorption (AB) and CD spectra of $[Mo_2O_2XY(R\text{-pdta})]^{2-}$ in water; X=Y=O (——), X=O and Y=S (----) and, X=Y=S (······).

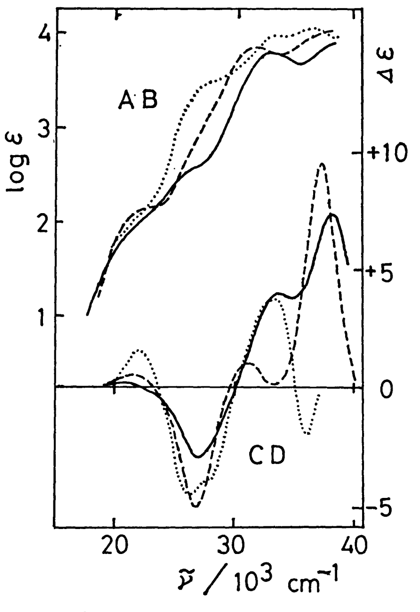


Fig. 7. Absorption (AB) and CD spectra of $[Mo_2O_2XY(S\text{-hist})_2]$ in DMSO; X=Y=O (——), X=O and Y=S (----), and X=Y=S (······).

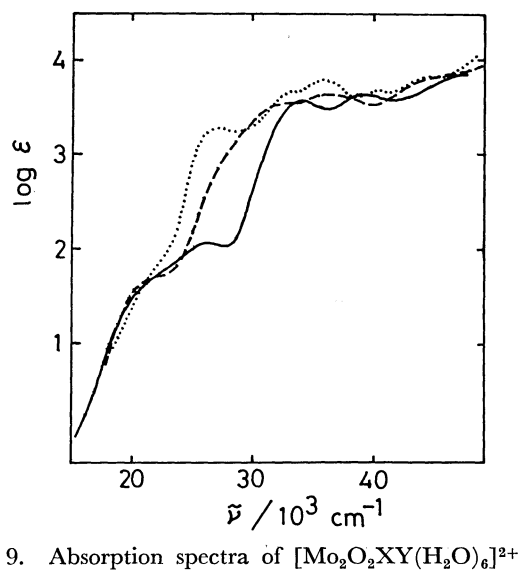


Fig. 9. Absorption spectra of $[Mo_2O_2XY(H_2O)_6]^{2+}$ in 2 M aqueous perchloric acid solution; X=Y=O (——), X=O and Y=S (----), and X=Y=S (······).

CD spectra with change in the bridging group is rather modest in the band II and III region (25000—35000 cm^{-1}). The general pattern for the di-μ-oxo complexes (two distinctive CD bands with opposite signs) is also appreciated for the μ-oxo-μ-thio and di-μ-thio complexes. Such facts suggest that the nature of CD sensitive transitions at the band II and III region is common to all the complexes, regardless of the bridging groups. The difference in absorption spectra at the band II region is interpreted by the appearance of a strong new band which is less sensitive to CD, in the μ-thio complexes.

The following interpretations for the increase in absorption intensity at band II region, are not feasible, since the corresponding CD change is not accompanied; *i.e.* a) the intensity of 'band II' itself increased, and b) the 'band III' shifted its position to the band II region as the number of sulfide bridge increased.

TABLE 4. THE NUMERICAL DATA OF ABSORPTION (AB) AND CD SPECTRA OF THE μ-OXO-μ-THIO-BIS{OXOMOLYBDENUM(V)} COMPLEXES[a)]

Complex (solvent)	AB $\lambda/10^3$ cm^{-1} (log ε)	CD[b)] $\lambda/10^3$ cm^{-1} ($\Delta\varepsilon$)	
$[Mo_2O_3S(S\text{-cys})_2]^{2-}$	21.5 s (2.35)	21.0 (−1.10)	
(water)	30.5 s (3.92)	27.7 (−8.00)*	
	35.0 (4.12)	31.7 (+2.19)*	
	41.0 s (4.10)	39.0 (+10.3)	
	46.3 (4.40)	44.3 (+20.1)	
$[Mo_2O_3S(S\text{-hist})_2]$	22.4 s (2.13)	21.7 (+0.18)	31.6 (+2.6)*
(DMF)	31.4 (3.85)	26.9 (−3.8)*	
$[Mo_2O_3S(S\text{-mecys})_2]$	23.0 s (2.50)	23.5 (−0.41)	36.2 (−0.3)
(acetonitrile)	30.0 s (3.63)	28.6 (+6.9)*	39.4 (+3.4)
	36.4 (4.10)	32.2 (−1.5)	43.3 (+7.0)
		34.8 (+0.2)	46.8 (−7.9)
$[Mo_2O_3S(S\text{-etcys})_2]$	23.4 s (2.63)	23.4 (−0.42)	36.2 (−0.2)
(acetonitrile)	29.4 s (3.55)	28.6 (+6.7)*	39.4 (+3.4)
	36.2 (4.09)	32.0 (−1.9)	43.5 (+6.7)
	47.2 (4.34)	34.7 (+0.4)	47.0 (−7.7)
$[Mo_2O_3S(R\text{-pdta})]^{2-}$	21.6 s (2.05)	20.1 (−0.45)	34.0 (+2.2)
(water)	32.0 s (3.77)	22.5 (+0.51)	36.5 (−5.4)
	35.3 (3.93)	26.1 (−11.1)*	40.7(+16.4)
	43.2 s (4.00)	30.8 (+2.8)*	45.5 (−3.5)

a) Data in only one solvent are given. Those in other solvents show similar values. b) Asterisk indicates the band which is assigned to have common nature to band II or III of the corresponding di-μ-oxo complex.

TABLE 5. THE NUMERICAL DATA OF ABSORPTION (AB) AND CD SPECTRA OF THE DI-μ-THIO-BIS{OXOMOLYBDENUM(V)} COMPLEXES[a)]

Complex (solvent)	AB $\lambda/10^3$ cm^{-1} (log ε)	CD[b)] $\lambda/10^3$ cm^{-1} ($\Delta\varepsilon$)	
$[Mo_2O_2S_2(S\text{-cys})_2]^{2-}$	21.0 s (2.00)	19.3 (−0.04)	42.9 (+48.2)
(water)	26.3 s (3.53)	25.0 (+3.95)	47.6 (−36.9)
	32.0 s (3.96)	27.8 (−7.88)*	
	35.8 (4.25)	31.5 (+15.7)*	
	43.7 (4.47)	37.8 (−16.8)	
$[Mo_2O_2S_2(S\text{-hist})_2]$	22.2 s (2.13)	22.1 (+1.49)	36.0 (−2.02)
(DMSO)	27.4 s (3.40)	26.3 (−4.63)	
	33.6 (3.97)	28.2 s (−3.75)*	
	36.2 (4.03)	33.3 (+3.66)*	
$[Mo_2O_2S_2(S\text{-mecys})_2]$	22.9 s (3.11)	17.0 (−0.05)	34.2 (−22.1)*
(acetonitrile)	30.5 s (3.84)	20.2 (+1.08)	38.0 (+17.0)
	34.3 (4.09)	23.6 (+2.18)	44.0 (+40.0)
	39.1 (4.20)	28.2 s (+17.2)*	49.1 (+13.2)
	45.1 s (4.44)	30.1 (+20.4)	
$[Mo_2O_2S_2(R\text{-pdta})]^{2-}$	21.0 s (1.82)	20.2 (+0.78)	36.0 (−1.8)
(water)	28.6 s (3.62)	25.6 (−12.3)*	39.1 (+22.5)
	35.8 (4.08)	28.0 s (−6.4)	45.2 (+10.5)
	38.8 s (3.88)	31.7 (+7.4)*	
	48.4 (4.37)	34.4 s (+0.85)	

a) Data in only one solvent are given. Those in other solvents show similar values. b) Asterisk indicates the band which is assigned to have common nature to band II or III of the corresponding di-μ-oxo complex.

The absorption and CD spectra in the other regions (band I, IV, and V regions) do not show any systematic trend, the number and the energies of absorption or CD bands depending on the bridging structure and the ligand. The *S*-mecys complex gives only slight increase in absorption intensity with increase in the number of bridging sulfide in the band II region. However, the absorption intensity of the di-μ-thio *S*-mecys complex in the band I region is more than five times bigger than those of di-μ-oxo and μ-oxo-μ-thio *S*-mecys complexes.

Ott *et al.* claimed on the basis of absorption spectra that the absorption bands I—IV shift to higher wave number with increase in the number of sulfide bridge. However, the CD spectra do not conform with such a trend.

Band II Region: The CD bands for all the di-μ-thio complexes split into two components. They have opposite signs for the *S*-cys complex, and the same sign for the other complexes. The splitting is accounted for by the appearance of a new band. A comparison of the absorption spectra with the CD spectra suggests that the CD component corresponding to the new band is the higher and lower wave number component for the *S*-cys and *S*-hist complexes, and for the *S*-mecys and *R*-pdta complexes, respectively. It is seen that the 'band II' not only remains at almost the same position as that for the di-μ-oxo complexes, but also keeps its sign unchanged, regardless of the change in bridging ligand. The new band has much smaller $\Delta\varepsilon/\varepsilon$ than the 'band II' does.

Band III Region: The CD peaks of μ-oxo-μ-thio and di-μ-thio complexes have same sign as those of the di-μ-oxo complexes, except for [Mo_2O_3S(*S*-etcys)$_2$] and [Mo_2O_3S(*S*-mecys)$_2$] which have no strong CD band in this region. Asymmetric distortion related to the CD strength at this region would be small for the μ-oxo-μ-thio *S*-cys ester complexes.

Relation between the CD Sign and the Structure of the μ-Thio Complexes. The CD bands with common nature to those of the di-μ-oxo complexes in band II and III region, are indicated with asterisks in Table 4 and 5. The same relation to that found for the di-μ-oxo complexes is also found for the μ-thio complexes. The negative and positive CD peaks for the 'band II' and 'band III', respectively, reflect the Δ chirality of the twist of two Mo–O_t bonds and of two basal edges, and the reverse CD patterns are related to Λ chirality of these twists. The relation is thus established for all the complexes regardless of the bridging structure, di-μ-oxo, μ-oxo-μ-thio and di-μ-thio.

Table 2 shows that $|\xi|$ values are much bigger than the $|\theta_1|$ values for most of the complexes. However, the ξ values for the di-μ-oxo and di-μ-thio cys complexes are nearly zero, and thus the twist of the two Mo–O_t bonds must be important in determining CD sign. On the other hand, the θ_1 values of μ-oxo-μ-thio and di-μ-thio complexes of *R*-pdta are practically zero. The donor atom distortion of the basal plane should be important for them. Intensity of the CD peaks of these complexes are not very different. These facts tell that neither the twist of Mo–O_t bonds nor the tetrahedral distortion of the basal plane alone can be the controlling factor of the CD sign at band II and III region. The CD sign must reflect the overall asymmetry caused by the twist of the two molybdenum coordination spheres around the Mo–Mo axis.

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