Preparation and Stereochemistry of Optical Isomers of the Tris-(3,3′-dimethyl-2,2′-bipyridyl *N,N′*-dioxide)chromium(III) Complex

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A new ligand, (*R*)- and (*S*)-3,3′-dimethyl-2,2′-bipyridyl *N,N′*-dioxide(mbdo) forms three diastereomers(I, II, and III) of $[Cr(mbdo)_3]^{3+}$ by the reaction with $[Cr(H_2O)_6]^{3+}$ in water. (I) was assigned to a pair of enantiomers, $\Delta(RRR)$ and $\Lambda(SSS)$, and (II) and (III) to either a diastereomeric pair of $\Delta(RRS)$ and $\Lambda(SSR)$ or $\Delta(SSR)$ and $\Lambda(RRS)$. While the racemic (I) was resolved by SP-Sephadex column chromatography, (II) and (III) isomerized in water to each other (II$\rightleftarrows$III) by exposure to ultraviolet light, were resolved by the reaction of $[Cr(H_2O)_4(R \text{ or } S)\text{-mbdo}]^{3+}$ with a stoichiometric amount of (*S* or *R*)-mbdo. The circular dichroism spectra of these optically active isomers were measured in aqueous solutions and compared with those of complexes of the $[CrO_6]$-type of known absolute configuration. The optically active free $(+)_{589}$- and $(-)_{589}$-mbdo were isolated by decomposing $\Lambda(SSS)$- and $\Delta(RRR)$-$[Cr(mbdo)_3]^{3+}$, respectively, with $edta^{4-}$. The active mbdo is optically stable even in boiling water.

2,2′-Bipyridyl *N,N′*-dioxide(bpdo) forms a skew seven-membered chelate ring upon coordination to a metal ion. Since the skew chelate ring is chiral (δ or λ), a tris-type complex of bpdo has four theoretically possible diastereomers, each of which has a pair of enantiomers (Δ and Λ).[1] By analogy with the stereoisomerism in $[Co(en)_3]^{3+}$(en=ethylenediamine),[2] these diastereomers can be designated as $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$, $lel_2ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$, $lelob_2$ $(\Delta(\lambda\delta\delta), \Lambda(\delta\lambda\lambda))$, and $ob_3(\Delta(\delta\delta\delta), \Lambda(\lambda\lambda\lambda))$. However, we have reported that $[Cr(bpdo)_3]^{3+}$ forms only one pair of enantiomers which racemize spontaneously in water at room temperature.[3] This indicates that the bpdo chelate ring is flexible, changing its conformation ($\delta\rightleftarrows\lambda$) very easily. If the rotation around the bond between the 2 and 2′ carbons of bpdo is prohibited by replacing the 3 and 3′ hydrogens with some bulky substituents, such a conformational change is forbidden and the complex ion is expected to exist in some optically stable isomers. This paper deals with the preparation and stereochemistry of the tris-chromium(III) complex with a new chelate ligand, (*R*)- and (*S*)-3,3′-dimethyl-2,2′-bipyridyl *N,N′*-dioxide(mbdo)(Fig. 1).

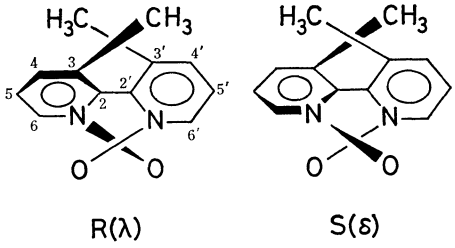

Fig. 1. A pair of enantiomers of mbdo.

Experimental

Preparation of Ligand. 3,3′-Dimethyl-2,2′-bipyridyl *N,N′*-dioxide(mbdo) was prepared from 3,3′-dimethyl-2,2′-bipyridyl[4] according to a method similar to that for 2,2′-bipyridyl *N,N′*-dioxide(bpdo).[5] An acetic acid solution(75 cm³) of 3,3′-dimethyl-2,2′-bipyridyl(18 g, 0.1 mol) was mixed with 30% aqueous hydrogen peroxide(60 cm³). The solution was refluxed for 4 h, then mixed with another 50 cm³ of 30% aqueous hydrogen peroxide and refluxed for 3 h. The resulting pale yellow solution was evaporated under reduced pressure to give an oily residue. A small amount of ethanol was added to the residue and the mixture was evaporated. This procedure was repeated several times to remove water contained in the product. White precipitate was obtained upon addition of a small amount of acetone and then ether to the oily residue. The precipitate was filtered, washed with acetone and then ethanol, and air-dried. Recrystallization from a small amount of hot ethanol gave white cubic crystals. Yield: 12.3 g (60%), mp 212—214 °C (sublimation); IR(KBr disk) 1255 and 1242(ν_{N-O}) and 802 cm^{-1}(δ_{N-O}); ^{1}H-NMR(D_2O) δ=2.17 ppm(s, CH_3). The mbdo ligand exists in a pair of enantiomers. The optically active ligand was obtained by decomposing an optically active $[Cr(mbdo)_3]^{3+}$ complex (*vide post*).

Preparation of $[Cr(mbdo)_3]^{3+}$. A 10^{-2} mol/dm³ hydrochloric acid solution (40 cm³) containing $Cr(NO_3)_3 \cdot 9H_2O$ (1.2 g, 3 mmol) and racemic mbdo(2.4 g, 11 mmol) was heated at 80 °C for 5 h. After cooling, sodium perchlorate (2 g, 16 mmol) was added to the solution to give green precipitate, which was filtered, washed with water and then ethanol, and recrystallized from warm water. Yield: 1.1 g (73%). This complex perchlorate consists of three pairs of diastereomers of $[Cr(mbdo)_3]^{3+}$.

Separation of Optical Isomers of $[Cr(mbdo)_3]^{3+}$. The $[Cr(mbdo)_3]^{3+}$ complex obtained above was dissolved in water, and the solution was poured on a column(ϕ2.7×130 cm) of SP-Sephadex C-25 resin in the Na^+ form. By eluting the adsorbed band with a 0.2 mol/dm³ sodium $(+)_{589}$-tartratoantimonate(III) solution, the column gave three separate bands, Ia,Ib, and Ic in the order of elution (Fig. 2a). All the fractions of Ia and of Ib gave positive and negative, respectively, rotations at sodium D line, the CD patterns of Ia and Ib fractions being enantiomeric to each other. Thus, the Ia and Ib bands were assigned to a pair of enantiomers (diastereomer I(Ia, Ib)). The fractions of Ic band were collected and rechromatographed. The adsorbed complex on an SP-Sephadex column(ϕ2.7×130 cm) was eluted with a 0.15 mol/dm³ Na_2SO_4 solution. Two separate bands (II and III) were obtained (Fig. 2b). The diastereomers in these bands isomerize to each other on exposure to light (II$\rightleftarrows$III), so that the chromatography should be carried out in the dark. The isomers Ia and Ib in solution are stable in the light. The diastereomers II and III were found to be partially resolved by column chromatography. The fractions of Ia, Ib, II, and III bands were collected separately, diluted several times with water, and poured on small columns of SP-Sephadex resin. The adsorbed isomers were eluted with a 2 mol/dm³ NaCl solution, and the eluates

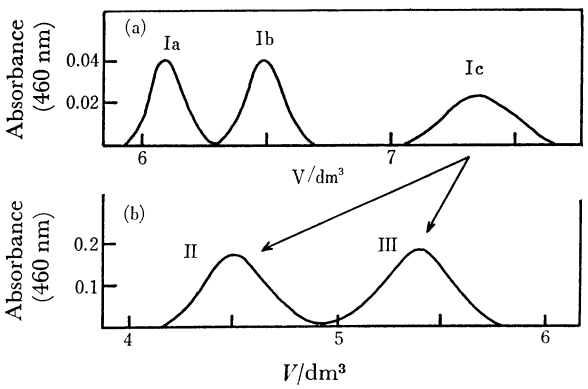

Fig. 2. (a) Elution curve of $[Cr(mbdo)_3]^{3+}$. Eluent: 0.2 mol/dm³ sodium $(+)_{589}$-tartratoantimonate(III). (b) Elution curve of Ic. Eluent: 0.15 mol/dm³ sodium sulfate.

were mixed with $NaClO_4$ to give green crystals, which were filtered, washed with a small amount of cold water, and air-dried. The formation ratio, I(Ia+Ib):II:III was 4 : 1 : 1.

Preparation of $Cr(mbdo)Cl_3 \cdot 5H_2O$. A 10^{-2} mol/dm³ hydrochloric acid solution(50 cm³) containing $Cr(NO_3)_3 \cdot 9H_2O$(0.8 g, 2.0 mmol) and racemic mbdo(0.5 g, 2.3 mmol) was heated at 70 °C for 3 h. After cooling, the resulting solution was poured on a column (ϕ 2.5×80 cm) of SP-Sephadex C-25 resin. The adsorbed product was eluted with a 0.5 mol/dm³ NaCl solution to give three separate bands. The last blue-green band was a mixture of the mono-mbdo complex and $[Cr(H_2O)_6]^{3+}$, which were separated by similar SP-Sephadex column chromatography using a 0.2 mol/dm³ Na_2SO_4 solution as an eluent. The green fraction of the mono-mbdo complex was again poured on a small column(ϕ 2.7×5 cm) of SP-Sephadex after dilution with water. The column was washed well with 10^{-2} mol/dm³ hydrochloric acid in order to replace Na^+ ions on the resin with H^+, and the adsorbed complex was eluted with 3 mol/dm³ hydrochloric acid. The eluate was evaporated to dryness in a vacuum desiccator over P_2O_5 and NaOH to give violet crystals. They were washed with ethanol and air-dried. Yield: 60%. This complex has the composition of $Cr(mbdo)Cl_3 \cdot 5H_2O$, and turns from violet to green in water, indicating that some chloride ions coordinate to the chromium(III) ion in the solid state. On heating an aqueous solution of the complex at 60 °C for a few hours, the absorption spectrum coincides with that of the green fraction ($(Cr(H_2O)_4(mbdo)]^{3+}$) separated by chromatography.

Resolution of mbdo. Optically active mbdo was obtained from the $(+)_{589}$-Ia or $(-)_{589}$-Ib isomer. To an aqueous solution (20 cm³) of the Ia or Ib isomer(50 mg, 0.05 mmol) was added $Na_2H_2edta \cdot 2H_2O$ (100 mg, 0.27 mmol) and the solution was heated at 70 °C for 10 h. During the course of heating, the color of the solution gradually turned from green to red violet. The resulting solution was diluted with 500 cm³ of water, adjusted to pH 9—10 with NaOH. The solution was passed through first a column of Dowex 1X8 anion exchange resin in the Cl^- form (ϕ 2.7×20 cm) to remove $[Cr(OH)(edta)]^{2-}$ produced and other anions, and then through a column of Dowex 50W cation exchange resin in the H^+ form (ϕ 2.7×10 cm) to remove cations such as Na^+ and the unreacted mbdo-chromium(III) complex. The solution was then evaporated to dryness under reduced pressure to give optically active mbdo. The $(+)_{589}$-Ia isomer gave $(+)_{589}$-mbdo ($[\alpha]_{589}^{23} = +10.6°$). The active mbdo is optically stable in solution.

Preparation of Optically Active $[Cr(H_2O)_4((+)_{589}$- *or* $(-)_{589}$-*mbdo)]^{3+}$. This complex was prepared from $[Cr(H_2O)_6]^{3+}$ and optically active mbdo by the method described for the racemic $[Cr(H_2O)_4(mbdo)]^{3+}$ complex. Its isolation was not achieved because of the small amount obtained. The quantitative circular dichroism(CD) spectrum of this complex was determined with the aid of the ε values of the racemate.

Preparation of Optical Isomers of $[Cr((+)_{589}$-*mbdo*$)_2((-)_{589}$-*mbdo*$)]^{3+}$. To an aqueous solution of $[Cr(H_2O)_4((-)_{589}$--mbdo$)]^{3+}$ was added twice the equivalent amount of $(+)_{589}$-mbdo. The solution was heated at 50 °C for 7 h and poured on an SP-Sephadex column (ϕ 2.0×50 cm). The adsorbed product was eluted with a 0.5 mol/dm³ NaCl solution in order to separate the tris-complex from the starting material. The fractions of the second band were collected and rechromatographed. By elution with a 0.2 mol/dm³ Na_2SO_4 solution, two bands(IIa and IIIa) were obtained, corresponding to enantiomers of diastereomers II and III, respectively, described for the racemic complex. Both isomers show positive rotation at 589 nm and epimerize to each other in the light (IIa$\rightleftarrows$IIIa) as observed for the racemic II and III. Diastereomer I was not formed, indicating that no disproportionation took place.

Analytical data of all the new compounds are given in Table 1.

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40 spectropolarimeter, respectively. Optical rotations were determined with a JASCO DIP-40 digital polarimeter.

Results and Discussion

A new ligand mbdo can exist in a pair of enantiomers, since free rotation around the common axis connecting the two rings is prohibited by the presence of the methyl and NO groups. The ligand molecule has no functional group to form diastereomers with resolving agents, but the optical resolution was achieved by forming optically active $[Cr(mbdo)_3]^{3+}$, the ligands

Table 1. Analytical data

	C/%		H/%		N/%	
	Found	Calcd	Found	Calcd	Found	Calcd
mbdo[a]	66.64	66.64	5.26	5.60	12.84	12.95
Ia: $[Cr(mbdo)_3](ClO_4)_3 \cdot 5H_2O$	39.67	39.69	4.06	4.27	7.72	7.72
II: $[Cr(mbdo)_3](ClO_4)_3 \cdot 2H_2O$	41.68	41.77	3.99	3.90	8.26	8.16
III: $[Cr(mbdo)_3](ClO_4)_3 \cdot 3H_2O$	40.85	41.05	3.92	4.03	7.90	7.98
$CrCl_3(mbdo) \cdot 5H_2O$	30.83	31.01	4.41	4.78	6.05	6.03

a) mbdo = $C_{12}H_{12}N_2O_2$.

in which have the same chirality (*vide infra*). The resolved mbdo is optically stable even in boiling water. The enantiomers are denoted by *R* and *S*,[6] as shown in Fig. 1. The *R*-(or *S*-) ligand forms a λ(or δ) skew chelate ring stereoselectively upon coordination. In this paper, the chilarity of the ligand is represented by the symbols δ and λ.

The $[Cr(mbdo)_3]^{3+}$ complex has eight theoretically possible optical isomers; $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$, $lel_2ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$, $lelob_2(\Delta(\lambda\delta\delta), \Lambda(\delta\lambda\lambda))$, and ob_3 $(\Delta(\delta\delta\delta), \Lambda(\lambda\lambda\lambda))$. In the *lel* structure, the line joining the two nitrogen atoms of the mbdo ligand is nearly parallel to the C_3 axis of the complex ion, while in the *ob* structure, it is extremely oblique to the same axis so that the line and the axis are almost perpendicular to each other.

Of the four possible diastereomers, three (I, II, and III) were obtained by the reaction of $[Cr(H_2O)_6]^{3+}$ with racemic mbdo. No indication was found for the presence of more than three diastereomers by column chromatography. The isomers show absorption spectra differing from each other in the region of the first absorption band (Fig. 3). Diastereomer I is completely resolved into enantiomers Ia and Ib by SP-Sephadex column chromatography. The enantiomers are optically stable in solution. On the other hand, diastereomers II and III isomerize to each other in solution by exposure to ultraviolet light. Since the chirality of the ligand is retained in the complexes and no disproportionation takes place, the isomerization between II and III can be attributed to inversion in the arrangement of ligands around the metal ion ($\Delta \rightleftarrows \Lambda$, epimerization). Such epimerization will arise in the following two systems; (1) $lel_3 \rightleftarrows ob_3[\Delta(\lambda\lambda\lambda)(\text{or } \Lambda(\delta\delta\delta)) \rightleftarrows \Lambda(\lambda\lambda\lambda)(\text{or } \Delta(\delta\delta\delta))]$ and (2) $lel_2ob \rightleftarrows lelob_2$ $[\Delta(\lambda\lambda\delta)(\text{or } \Lambda(\delta\delta\lambda)) \rightleftarrows \Lambda(\lambda\lambda\delta)(\text{or } \Delta(\delta\delta\lambda))]$. Reaction (1) does not seem to take place, since molecular models show that the ob_3 isomer forms an extremely crowded structure, while reaction (2) appears to arise without difficulty from the studies of molecular models. Thus, diastereomer I which is stable in solution can be assigned to the lel_3 isomer, and diastereomers II and III to two isomers of the lel_2ob and $lelob_2$. The assignments are supported by the following experimental results. Diastereomer I assigned to the least crowded lel_3 structure is obtained in the largest amount (*vide ante*). The reaction of $[Cr(H_2O)_6]^{3+}$ with optically active mbdo obtained from the Ia (or Ib) enantiomer gives only the Ia (or Ib) enantiomer. Thus, the ligand recovered from Ia (or Ib) is proved to be optically pure, and diastereomer I should be the lel_3 isomer. On the other hand, the tris-complex prepared from $[Cr(H_2O)_4((-)_{589}\text{-mbdo})]^{3+}$ and $(+)_{589}$-mbdo consists of two optically active IIa and IIIa isomers, no diastereomer I being formed (see Experimental). Isomers IIa and IIIa thus formed should be enantiomers of diastereomers II and III, respectively, corresponding to either group of $\Delta(\delta\lambda\lambda)$ and $\Lambda(\delta\lambda\lambda)$ or $\Delta(\delta\delta\lambda)$ and $\Lambda(\delta\delta\lambda)$. The isomers isomerize (epimerize) to each other in solution by exposure to ultraviolet light, distributing in almost equal amounts at equilibrium. Thus, the equilibration study gives no information on the assignment of the structures of diastereomers II and III. In the column chromatography, diastereomer I(lel_3) eluates most quickly. If the elution order of the diastereomers is proportional to the number of the *lel* ligand, diastereomers II and III are assigned to the lel_2ob and $lelob_2$ isomers, respectively.

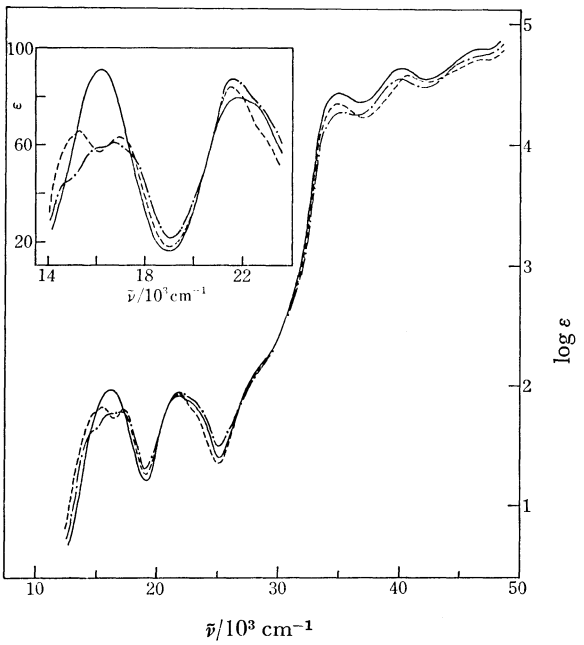

Fig. 3. Absorption spectra of three diastereomers of $[Cr(mbdo)_3]^{3+}$, Ia(——), II(----), and III(—·—).

Figure 3 shows the absorption spectra of diastereomers Ia, II, and III. Their spectral patterns in the region of the first absorption band differ remarkably, while those in the other region are similar to each other. The first absorption band of Ia is sharp and symmetrical, but those of II and III split into three components. All the diastereomers belong to the $[CrO_6]$-type in which the ligating oxygen atoms are the same kind. However, the actual symmetry of the lel_3 isomer will be D_3, and those of both lel_2ob and $lelob_2$ isomers will lower to C_2. In the fields of D_3 and C_2 symmetries, the first absorption band ($^4T_{2g}$) will split into two ($^4A_1$, ^4E) and three (2^4A, ^4B) components, respectively. Although diastereomer Ia shows no splitting in the first absorption band, the fact that diastereomers II and III exhibit the presence of three components in these bands supports the previous assignment for structures of these diastereomers. The absorption spectrum of diastereomer Ia is very similar to that of $[Cr(bpdo)_3]^{3+}$ over the whole region.[3] This indicates that the latter complex in which the ligands can easily change the conformation exists in the lel_3 form in solution. The spectral data are given in Table 2.

Figure 4 shows the CD spectra of $(+)_{589}$-$[Cr((+)_{589}\text{-mbdo})_3]^{3+}$ (Ia), $(+)_{589}$-$[Cr((+)_{589}\text{-mbdo})_2((-)_{589}\text{-mbdo})]^{3+}$(IIa), and $(+)_{589}$-$[Cr((+)_{589}\text{-mbdo})_2((-)_{589}\text{-mbdo})]^{3+}$(IIIa). The Ia isomer gives strong CD in the regions of the first and the ligand absorption bands. On the other hand, isomers IIa and IIIa show very similar spectra to each other over the whole

Table 2. Absorption and CD spectral data

	Absorption $\tilde{\nu}/10^3\ cm^{-1}$ (log ε)	CD $\tilde{\nu}/10^3\ cm^{-1}$ ($\Delta\varepsilon$)
$(+)_{589}$-mbdo	38.61 (4.32)	32.47 (+0.19)
	45.87 (4.57)	36.36 (−2.05)
		38.61 (+5.26)
		42.8 (−0.4)sh
		45.05 (−1.40)
		46.73 (+1.80)
Ia	16.23 (1.96)	16.00 (−2.86)
	21.81 (1.90)	21.21 (+0.46)
	22.5 (1.9)sh	28.65 (+0.45)
	35.09 (4.42)	31.30 (−0.61)
	39.92 (4.46)	36.0 (+63)sh
	46.08 (4.79)	38.10 (+142)
		41.15 (−93.9)
		46.95 (−79.9)
IIa	14.9 (1.8)sh	14.71 (−1.26)
	15.27 (1.82)	15.20 (−1.17)
	16.98 (1.80)	17.24 (+1.21)
	21.51 (1.93)	21.05 (−0.40)
	22.9 (1.8)sh	28.49 (+0.08)
	35.09 (4.33)	34.90 (+13.2)
	40.40 (4.59)	38.54 (+24.4)
	46.30 (4.72)	41.49 (−8.55)
		46.08 (−20.7)
IIIa	14.8 (1.6)sh	14.58 (−0.57)
	15.97 (1.76)	15.22 (−0.63)
	16.92 (1.78)	17.36 (+0.71)
	21.69 (1.94)	21.19 (−0.30)
	23.2 (1.8)sh	28.41 (+0.06)
	35.21 (4.28)	35.46 (+9.47)
	40.00 (4.55)	38.46 (+16.3)
	46.3 (4.8)sh	42.02 (−8.20)
		46.51 (−12.6)
IV	16.89 (1.36)	15.77 (−0.14)
	23.64 (1.55)	16.95 (+0.08)
	34.48 (3.90)	21.23 (−0.01)
	41.49 (4.19)	23.36 (+0.02)
	45.87 (4.38)	27.50 (+0.01)
		34.13 (−0.81)
		38.50 (−9.73)
		41.93 (+11.5)
		46.73 (−12.6)

Ia: $(+)_{589}$-$[Cr((+)_{589}$-mbdo$)_3]^{3+}$
IIa: $(+)_{589}$-$[Cr((+)_{589}$-mbdo$)_2((-)_{589}$-mbdo$)]^{3+}$
IIIa: $(+)_{589}$-$[Cr((+)_{589}$-mbdo$)_2((-)_{589}$-mbdo$)]^{3+}$
IV: $[Cr(H_2O)_4((+)_{589}$-mbdo$]^{3+}$
sh: shoulder.

region, although the strength of the former is somewhat larger. Both isomers consist of the same ligands, two $(+)_{589}$-mbdo and one $(-)_{589}$-mbdo. However, these isomers are antipodal to each other in the arrangement of the ligands around the metal ion. If one is Δ-configuration, the other is Λ-configuration. The similarity in the CD spectra suggests that the circular dichroism in these isomers is mainly caused by the contribution due to the vicinal effect of the chiral mbdo ligand (δ,λ) rather than to the configurational

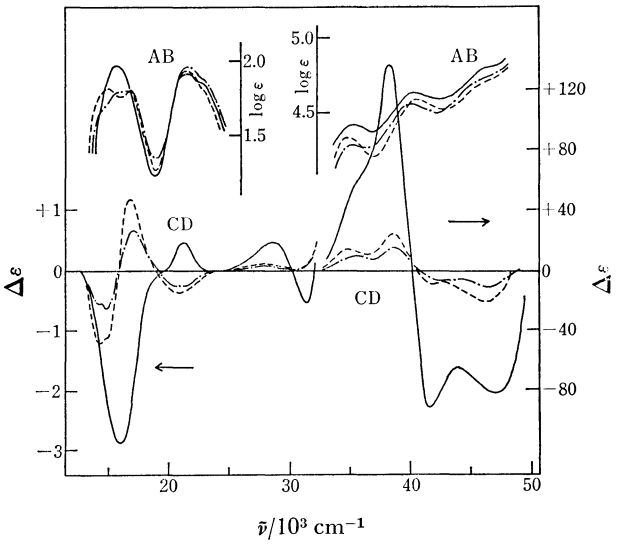

Fig. 4. Absorption(AB) and CD spectra of $(+)_{589}$-$[Cr((+)_{589}$-mbdo$)_3]^{3+}$ (Ia)(——), $(+)_{589}$-$[Cr((+)_{589}$-mbdo$)_2((-)_{589}$-mbdo$]^{3+}$ (IIa)(----), and $(+)_{589}$-$[Cr((+)_{589}$-mbdo$)_2((-)_{589}$-mbdo$)]^{3+}$ (IIIa)(—·—).

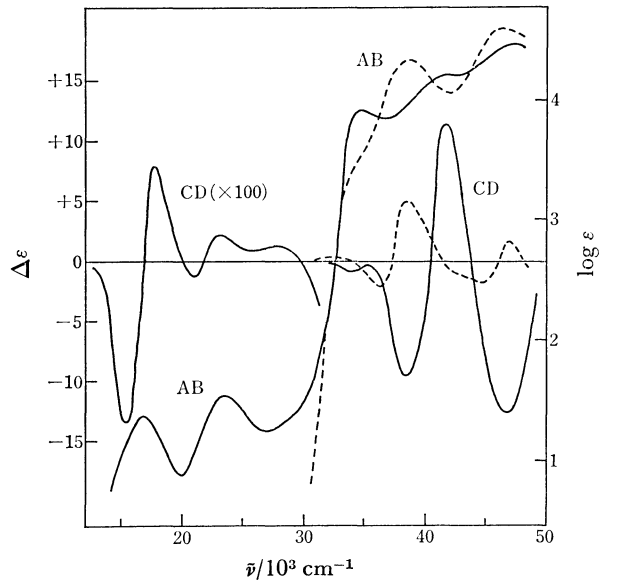

Fig. 5. Absorption(AB) and CD spectra of $[Cr(H_2O)_4$-$((+)_{589}$-mbdo$)]^{3+}$(——) and $(+)_{589}$-mbdo(----).

effect (Δ, Λ). Since these isomers contain two $(+)_{589}$-mbdo and one $(-)_{589}$-mbdo, the vicinal effect would come from one $(+)_{589}$-mbdo, if such effects of chiral ligands function additively. The $[Cr(H_2O)_4((+)_{589}$-mbdo$)]^{3+}$ complex of the $[CrO_6]$-type is a good example for knowing the vicinal effect of $(+)_{589}$-mbdo. However, as Fig. 5 shows, the CD spectrum of this complex is similar in pattern but much weaker in intensity than that of isomers IIa and IIIa, in the region of the first absorption band. In the ultraviolet region, its spectrum differs remarkably from that of the isomers. This indicates that the configurational and vicinal effects do not contribute additively to the CD spectra of these complexes. The additivity rule has been reported to hold for a number of five-membered chelate complexes.[7] The chiral conformation of the mbdo chelate ring does not cause inversion.

However, the chelate ring is large and would be flexible in a certain range. The most stable conformation of the ring may differ more or less from each other in each complex to minimize steric interactions among ligands. The different conformations would bring about different vicinal effects in CD spectra. The reason why the additive rule fails in the mbdo complexes can be attributed to such flexible conformation of the chelate ring. The free $(+)_{589}$-mbdo ligand which should be in a different conformation from those in the complexes exhibits a quite different CD spectrum in the ultraviolet region from that of the complexes. The absolute configurations of isomers IIa and IIIa can not be assigned from the CD spectra.

Isomer Ia, $(+)_{589}$-$[Cr((+)_{589}\text{-mbdo})_3]^{3+}$ shows a strong negative CD band in the region of the first absorption band. The $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ isomer which gives a similar CD pattern in this region was assigned to the *Λ*-configuration[3] from comparison of the CD patterns of a series of complexes, $[Cr(bpdo)_n(en)_{3-n}]^{3+}$. Figure 6 shows a comparison of the CD spectrum of Ia isomer with that of *Λ*-$[Cr(ox)_3]^{3-}$ (ox= oxalate ion)[8,9] and *Λ*-$[Cr(mal)_3]^{3-}$ (mal=malonate ion).[8,9] The spectral changes for these five-, six-, and seven-membered chelate complexes, are similar to those observed for a series of complexes, $[Co(NH_2(CH_2)_nNH_2)_3]^{3+}$ (n=2, 3, and 4).[10] In the ultraviolet region, the Ia (or Ib) isomer exhibits a characteristic CD pattern with strong intensity; a positive (or negative) and a negative (or positive) CD band from the smaller wavenumber side. The other complexes of mbdo show no such strong CD in this region. The CD bands in this region may be assigned to the $\pi \rightarrow \pi^*$ transitions of the ligand. Since the Ia isomer consists of ligands with the same chirality, $(+)_{589}$-mbdo, such strong CD might be caused by the exciton interaction among the ligands as observed for $[M(phen)_3]^{n+}$ (phen=1,10-phenanthroline).[11] Although the exciton CD for the system consisting of ligands with a twist conformation is unknown, the CD pattern of the Ia isomer resembles that of *Λ*-$[Cr(phen)_3]^{3+}$,[11,12] and the isomer can be assigned to the *Λ*-configuration. The assignment agrees with that based on the CD sign in the region of the first absorption band. If the isomer has the *Λ*-configuration, the $(+)_{589}$-mbdo ligand should be in the *δ*-skew conformation to form the lel_3 structure. Hence the $(+)_{589}$-mbdo can be assigned to the *S*-configuration.

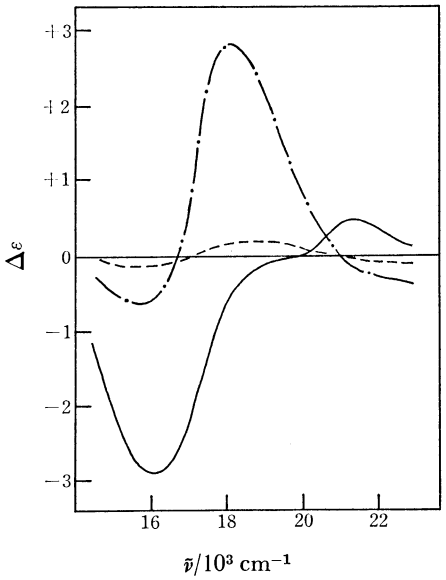

Fig. 6. CD spectra of $[CrO_6]$ complexes in the region of the first absorption band, $(+)_{589}$-$[Cr((+)_{589}\text{-mbdo})_3]^{3+}$ (Ia)(——), *Λ*-$[Cr(mal)_3]^{3-}$ (----), and *Λ*-$[Cr(ox)_3]^{3-}$ (—·—).

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