Preparation, Stereochemistry, and Kinetics of Isomerization and Racemization of Acetylacetonato Complexes of Chromium(III) Containing 2,2′-Bipyridine *N,N′*-Dioxide or Its 3,3′-Dimethyl Derivative

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New acetylacetonato (acac) chromium(III) complexes of the type, $[Cr(acac)_{3-n}L_n]^{n+}$ (n=1 and 2), where L denotes a seven-membered chelate ligand, 2,2′-bipyridine *N,N′*-dioxide (bpdo) or 3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide (*rac*- or *R*-mbdo), were prepared. Optically active $[Cr(acac)_2(R\text{-mbdo})]^+$ and $[Cr(acac)(R\text{-mbdo})_2]^{2+}$ yielded only one isomer and were assigned to $\Delta(\lambda)(lel)$ and $\Delta(\lambda\lambda)(lel_2)$, respectively, on the basis of the circular dichroism spectra and molecular models. The $[Cr(acac)(mbdo)_2]^{2+}$ complex prepared from *rac*-mbdo formed two racemates of diastereomers, $lel_2(\Delta(\lambda\lambda), \Lambda(\delta\delta))$ and $lel\cdot ob$ $(\Delta(\lambda\delta), \Lambda(\delta\lambda))$, whereas $[Cr(acac)_2(bpdo)]^+$ formed only $lel(\Delta(\lambda), \Lambda(\delta))$ isomer which was resolved by column chromatography. Both *rac*- and $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2\cdot H_2O$ resolved by a chemical method were found to crystallize in lel_2 isomer, but isomerize to the isomer in aqueous solution with the rate of 3.31×10^{-3} s^{-1} at 295.2 K, the rate constant for racemization ($\Delta \rightleftarrows \Lambda$) being 1.08×10^{-4} s^{-1} at 295.2 K. An intramolecular conformational inversion of the bpdo chelate ring for the isomerization and an intramolecular twist mechanism for the racemization were proposed.

In a metal complex, 2,2′-bipyridine *N,N′*-dioxide (bpdo) forms a skew seven-membered chelate ring of which conformation can exist in a pair of enantiomers, δ and λ (Fig. 1).[1] For a tris-bpdo complex, there are four possible racemic pairs of diastereomers (conformational isomers), $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$, $lel_2\cdot ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$, $lel\cdot ob_2(\Delta(\lambda\delta\delta), \Lambda(\delta\lambda\lambda))$, and $ob_3(\Delta(\delta\delta\delta), \Lambda(\lambda\lambda\lambda))$, and the diastereomerism is analogous to that in $[M(en)_3]^{n+}$ (en=ethlyenediamine).[2] However, it was found that tris-type chromium(III) complexes with bpdo[3] and its derivative, 3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide (mbdo)[4] give one and three diastereomers, respectively, and that $[Cr(bpdo)_3]^{3+}$ racemizes spontaneously in aqueous solution.[3] These results indicate that the bpdo chelate ring is flexible and changes its conformation ($\delta \leftrightarrows \lambda$) very easily. On the other hand, the mbdo chelate ring can not change its conformation because of the steric hindrance due to the methyl groups.[4]

This paper describes the preparation and stereochemistry of chromium(III) complexes of the type, $[Cr(acac)_{3-n}L_n]^{n+}$ (n=1, 2; L=bpdo, mbdo). Since the acac chelate ring is assumed to be planar, $[Cr(acac)_2L]^+$ and $[Cr(acac)L_2]^{2+}$ (L=bpdo or mbdo) have two $[lel(\Delta(\lambda), \Lambda(\delta))$ and $ob(\Delta(\delta), \Lambda(\lambda))]$ and three $[lel_2(\Delta(\lambda\lambda), \Lambda(\delta\delta))$, $lel\cdot ob(\Delta(\lambda\delta), \Lambda(\delta\lambda))$, and $ob_2(\Delta(\delta\delta), \Lambda(\lambda\lambda))]$ possible racemic pairs of diastereomers, respectively. In a preliminary paper, we have reported that the $[Cr(acac)(bpdo)_2]^{2+}$ complex isomerizes and racemizes spontaneously in aqueous solution at room temperature.[5] Kinetic studies for these reactions will be also described in detail in this paper.

Experimental

Since the new complexes are photosensitive causing hydrolysis, the following experiments were carried out in the dark.

Preparation and Resolution of $[Cr(acac)_2(bpdo)]^+$ and $[Cr(acac)_2(mbdo)]^+$. The complexes were prepared from $[Cr(acac)_3]$ and bpdo or mbdo according to a method similar to that for $[Cr(acac)_2(phen)]^+$ (phen=1,10-phenanthroline).[6] $[Cr(acac)_3]$ (4.0 g, 11.5 mmol) was added to 90% ethanol (400 cm^3) containing bpdo·H_2O[7] (2.4 g, 11.6 mmol) or racemic mbdo[4] (2.5 g, 11.6 mmol). The solution was adjusted to pH *ca.* 2 with hydrochloric acid and kept at 80 °C with stirring for 2d. The resulting solution was evaporated to a small volume under reduced pressure. The residue was diluted with water (500 cm^3) and the solution was applied on a column (ϕ3.0×50 cm) of SP-Sephadex C-25. The adsorbed species were eluted with a 0.8 mol/dm^3 NaCl solution to give three separate bands. The second green and the last green bands were found to contain bis-bpdo (or bis-mbdo) and tris-bpdo (or tris-mbdo) complexes, respectively. The first violet eluate was collected and mixed with $NaClO_4$ to give violet crystals, which were filtered, washed with a small amount of cold water, and recrystallized from warm water. Yield: bpdo-complex, 3.4g (54%); mbdo-complex, 1.6g (25%). Found for the bpdo complex: C, 44.67; H, 4.00; N, 5.26%. Calcd for $[Cr(acac)_2(bpdo)]ClO_4=C_{20}H_{22}N_2O_{10}ClCr$: C, 44.66; H, 4.12; N, 5.21%. Found for the mbdo complex: C, 46.69; H, 4.62; N, 4.94%. Calcd for $[Cr(acac)_2(mbdo)]ClO_4=C_{22}H_{26}N_2O_{10}ClCr$: C, 46.69; H, 4.63; N, 4.95%. Each of the bpdo and mbdo complexes gave only one racemic pair of diastereomers, no indication for the formation of the other isomer being detected on column chromatograms.

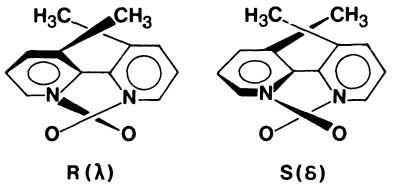

Fig. 1. A pair of enantiomers of mbdo.

The bpdo complex was resolved by DEAE-Sephadex A-25 column chromatography. The perchlorate of the complex (0.08g) was dissolved in water and the solution was applied on a column (ϕ3.8×140cm) of DEAE-Sephadex A-25 in the $[Sb_2(d\text{-tartrato})_2]^{2-}$ form.[8] The complex was eluted with

water, but only one band was observed on the column. However the front and rear fractions of the band showed positive and negative rotations at 546nm, respectively. Each of these fractions was collected separately and chromatographed repeatedly until no further increase in specific rotations at 546nm was observed. Each of the optically pure isomers was isolated as the perchlorate. The $(+)_{546}$- and $(-)_{546}$-isomers showed the following molar rotations in aqueous solutions: $[M]_{546}=+5750°$, $[M]_{546}=-5780°$. Found: C, 43.80; H, 3.94; N, 5.07%. Calcd for $(+)_{546}$-$[Cr(acac)_2(bpdo)]ClO_4\cdot 0.5H_2O=C_{20}H_{23}N_2O_{10.5}ClCr$: C, 43.93; H, 4.24; N, 5.12%.

The resolution of the mbdo complex was not achieved by the same chromatographic method. The optically pure mbdo complex was obtained from optically active mbdo[4] and $[Cr(acac)_3]$.

Preparation of $(+)_{546}$-$[Cr(acac)_2(R\text{-}mbdo)]^+$. The complex was obtained by the same method as that for the racemic complex using *R*-mbdo.[4] The perchlorate of the complex was obtained as violet crystals. Found: C, 46.62; H, 4.60; N, 4.75%. Calcd for $(+)_{546}$-$[Cr(acac)_2(R\text{-mbdo})]ClO_4=C_{22}H_{26}N_2O_{10}ClCr$: C, 46.69; H, 4.63; N, 4.95%.

Preparations of $[Cr(acac)(bpdo)_2]^{2+}$ *and* $[Cr(acac)(mbdo)_2]^{2+}$. The complexes were prepared by a method similar to that for the above bis-acac complexes using $[Cr(acac)_3]$ (4.0g, 11.5mmol) and bpdo·H_2O (4.8g, 23.3mmol) or racemic mbdo (5.2g, 24.0mmol). The complexes were obtained from the second green band on an SP-Sephadex column chromatograph (ϕ3.0×50cm, 0.8mol/dm^3 NaCl) and isolated as the perchlorate. Yield: bpdo-complex, 2.5g (29%); mbdo-complex, 2.8g (30%). Found for the bpdo complex: C, 40.51; H, 2.91; N, 7.24%. Calcd for $[Cr(acac)(bpdo)_2](ClO_4)_2\cdot H_2O=C_{25}H_{25}N_4O_{15}Cl_2Cr$: C, 40.33; H, 3.39; N, 7.53%. Found for the mbdo complex: C, 42.38; H, 4.35; N, 6.80%. Calcd for $[Cr(acac)(mbdo)_2](ClO_4)_2\cdot 2H_2O=C_{29}H_{35}N_4O_{16}Cl_2Cr$: C, 42.56; H, 4.31; N, 6.85%. For $[Cr(acac)(bpdo)_2]^{2+}$, attempts to separate possible diastereomers were all unsuccessful by column chromatography because of rapid isomerization of the complex (*vide post*). The $[Cr(acac)(mbdo)_2]^{2+}$ complex obtained from racemic mbdo was found to consist of two racemic pairs of diastereomers.[5]

Separation of Diastereomers of $[Cr(acac)(mbdo)_2]^{2+}$. The $[Cr(acac)(mbdo)_2]^{2+}$ complex (0.05g) was loaded on a column (ϕ2.2×130cm) of SP-Sephadex and eluted with a 0.1mol/dm^3 Na_2SO_4 solution. The column gave two bands, I and II in the order of elution. Each eluate was collected, diluted with water, and applied again on a small column (ϕ2.2×3cm) of SP-Sephadex. The adsorbed complex was eluted with a 1 mol/dm^3 NaCl solution. The eluate was collected and mixed with $NaClO_4$ to give crystals which were recrystallized from warm water. Found for isomer I: C, 42.53; H, 4.46; N, 6.77%. Calcd for $[Cr(acac)(mbdo)_2](ClO_4)_2\cdot 2H_2O=C_{29}H_{35}N_4O_{16}Cl_2Cr$: C, 42.56; H, 4.31; N, 6.85%. Found for isomer II: C, 43.50; H, 3.90; N, 6.77%. Calcd for $[Cr(acac)(mbdo)_2](ClO_4)_2\cdot H_2O=C_{29}H_{33}N_4O_{15}Cl_2Cr$: C, 43.51; H, 4.16; N, 7.00%. The formation ratio, I:II, was about 1:1.

Preparation of $(-)_{589}$-$[Cr(acac)(R\text{-}mbdo)_2]^{2+}$. The complex was prepared by the same method as that for the racemic complex using *R*-mbdo and isolated as the perchlorate. Found: C, 43.48; H, 3.96; N, 6.81%. Calcd for $(-)_{589}$-$[Cr(acac)(R\text{-mbdo})_2](ClO_4)_2\cdot H_2O=C_{29}H_{33}N_4O_{15}Cl_2Cr$: C, 43.51; H, 4.16; N, 7.00%. The absorption spectrum of this complex coincides with that of isomer II. The complex corresponding to isomer I was not formed.

Resolution of $[Cr(acac)(bpdo)_2]^{2+}$. The resolution was achieved by use of the perchlorate of the complex and potassium $(+)_{589}$-tartratoantimonate(III). The resolving agent (0.9g, 1.3mmol) was added to a hot aqueous solution (70°C, 50 cm^3) of the complex (1g, 1.3mmol). The mixture was cooled in an ice bath with stirring to give white precipitate of $KClO_4$. The precipitate was filtered off and methanol (150 cm^3) was added to the filtrate. The resulting solution was cooled in a refrigerator to give green crystals, which were collected, washed with 80% methanol and then methanol, and air-dried. An aqueous solution of these crystals showed a negative rotation at 589nm but lost gradually the activity. Yield: 1.1g. Found: C, 33.63; H, 2.98; N, 4.58%. Calcd for $(-)_{589}$-$[Cr(acac)(bpdo)_2][Sb_2(d\text{-tartrato})_2]\cdot 6H_2O=C_{33}H_{39}N_4O_{24}CrSb_2$: C, 33.84; H, 3.36; N, 4.78%. The crystals were dissolved in a small amount of ice-cold water, and immediately $NaClO_4$ was added to the solution with stirring. Green crystals which resulted were collected, washed with ice-cold water and then ethanol, and air-dried. The complex showed a negative rotation at 589nm in aqueous solution but rapidly lost the activity. Found: C, 40.41; H, 2.94; N, 7.36%. Calcd for $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2\cdot H_2O=C_{25}H_{25}N_4O_{15}Cl_2Cr$: C, 40.33; H, 3.39; N, 7.53%.

Kinetic Runs. All kinetic experiments were carried out in the dark. Both racemic and $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2\cdot H_2O$ in aqueous solutions show a rapid absorption spectral change. The change of absorbance at 620nm was continuously recorded in the temperature range of 15.8—34.6°C on a Shimadzu MPS-50L spectrophotometer with a cell jacket to maintain the temperature constant within ±0.3°C. The pH and ionic strengths of the solutions were adjusted with an aqueous solution of NaCl-HCl. The complex concentrations were in the range of 1.8—2.8mmol/dm^3. The rate of change obeyed the first order kinetic law and the observed rate constant (k_{obsd}) is expressed as follows: $k_{obsd}=-\ln[(A_t-A_\infty)/(A_0-A_\infty)]/t$ where A's are absorbances at the time denoted by suffixes.

A decrease in optical activity at 589nm of $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2\cdot H_2O$ in aqueous solution was observed by similar procedures as described above using a Union PM-101 desital polarimeter. The temperature and the complex concentrations were in the range of 17.2—35.0°C and 1.4—2.5mmol/dm^3, respectively. The complex lost the optical activity in two steps with different rates, the first rapid and the subsequent slow steps (*vide post*).[5] In the latter step, the rate of decrease obeyed the first order kinetic law and the observed rate constant (k_{obsd}) is also expressed by the above equation where A's are degrees of optical rotation.

All kinetic data were treated by a least-squares method and all estimated errors are standard deviations.

Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Shimadzu MPS-50L spectrophotometer and a Jasco J-40 spectropolarimeter, respectively. Optical rotations were measured with a Union PM-101 desital polarimeter.

Results and Discussion

Preparation and Characterization of the Complexes. Four new complexes, $[Cr(acac)_{3-n}L_n]^{n+}$ (n=1 and 2; L= bpdo or mbdo) were prepared from $[Cr(acac)_3]$ and the dioxide ligand in 90% ethanol by a method similar to

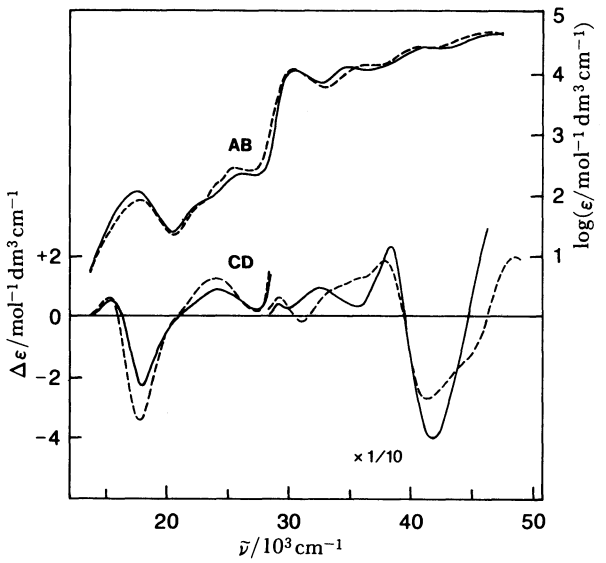

Fig. 2. Absorption (AB) and CD spectra of $(+)_{546}$-$[Cr(acac)_2(R\text{-mbdo})]^+$ (——) and $(+)_{546}$-$[Cr(acac)_2(bpdo)]^+$ (-----) in water.

that for $[Cr(acac)_2(phen)]^+$.[6] Each of the complexes was purified by SP-Sephadex column chromatography and isolated as the perchlorate. The complexes in aqueous solutions are stable in the dark, but undergo gradual hydrolysis in the light.

Both $[Cr(acac)_2L]^+$ complexes of bpdo and racemic mbdo form only one racemic pair of diastereomers of two possible ones, *lel* and *ob*. No indication for the formation of the other isomer was found by column chromatography. The optical resolution of the bpdo complex was achieved by DEAE-Sephadex A-25 ($[Sb_2(d\text{-tartrato})_2]^{2-}$ form) column chromatography with water as an eluent, although repeated chromatography was necessary to obtain the optically pure isomers. On the other hand, the mbdo complex was hardly resolved by the same chromatographic method. Hence the optically pure mbdo complex was prepared from optically active *R*-mbdo.[4] The obtained *R*-mbdo complex gave also only one isomer and its absorption spectrum coincides with that of the racemate prepared from racemic mbdo. The active bpdo and mbdo complexes are optically stable in aqueous solution.

Figure 2 shows the absorption and CD spectra of $(+)_{546}$-$[Cr(acac)_2(R\text{-mbdo})]^+$ and $(+)_{546}$-$[Cr(acac)_2(bpdo)]^+$. The spectral data are given in Table 1. Both absorption spectra are nearly the same over the whole region. The bands at 17530cm^{-1} and 17670cm^{-1} for the mbdo and bpdo complexes, respectively, can be assigned to the first absorption band ($^4T_{2g}\leftarrow{}^4A_{2g}$). The band at *ca.* 26000cm^{-1} for each complex shows a clear shoulder on the low energy side and the band shape is similar to that of $[Cr(acac)_3]$, which was assigned to the $\pi^*\leftarrow\pi$ or $\pi^*\leftarrow n$ transition of acac$^-$.[9,10] The position of the second band ($^4T_{1g}\leftarrow{}^4A_{2g}$) is uncertain because of overlapping with this band. In the ultraviolet region, the complexes exhibit a strong band at 30300cm^{-1} which was also found in $[Cr(acac)_3]$ and assigned to involve both the $\pi^*\leftarrow\pi$ transition of acac$^-$ and the charge transfer (acac$^-$ to metal) transition.[9,10] In the higher energy region, the complexes show three strong bands characteristic of the chelated dioxide ligands.[3,4]

The CD spectra of the two $(+)_{546}$-isomers show a similar pattern over the whole region. This suggests that the isomers have the same absolute configuration including chirality of the skew dioxide chelate ring. The CD patterns in the region of the first absorption band are very similar to those of $(-)_{589}$-$[Cr(acac)_3]$,[11] $(-)_{546}$-$[Cr(acac)_2en]^+$,[10] and $(+)_{589}$-$[Cr(acac)_2tn]^+$ (tn= trimethylenediamine),[12] all of which were reported to have the *Δ* configuration. Thus both $(+)_{546}$-isomers of the dioxide complexes can be assigned to the *Δ* configuration. In the ultraviolet region, the isomers do not show clear exciton CD bands due to two acac$^-$ ligands in the region of 30000 to 35000cm^{-1}.[10-12]

As stated previously, *R*-mbdo forms a *λ* skew chelate ring in a complex.[4] Thus $(+)_{546}$-$[Cr(acac)_2(R\text{-mbdo})]^+$ can be assigned to the *Δ*(*λ*)(*lel*) isomer. The $(+)_{546}$-isomer of the bpdo complex which shows a CD spectrum very similar to that of the *R*-mbdo complex can be assigned to the same isomer. Thus both bpdo and *R*-mbdo complexes form only a *lel* isomer stereoselectively. The $[Cr(en)_2(bpdo)]^{3+}$[3] and $[Co(en)_2L]^{3+}$ complexes (L=2,2′-diaminobiphenyl[13,14] and its 6,6′-dimethyl derivative;[13] these ligands form a skew seven-membered chelate ring similar to the dioxide) give also only a *lel* isomer. On the other hand, bis(2,2′-bipyridine) and bis(1,10-phenanthroline) chromium(III) complexes containing bpdo or mbdo give only an *ob* isomer.[15] Examination with molecular models indicates that the difference in selectivity seems to come from steric conditions among the ligands.

Although $[Cr(acac)(rac\text{-mbdo})_2]^{2+}$ has three possible racemic pairs of diastereomers, lel_2, $lel\cdot ob$, and ob_2, the complex yielded two racemic pairs of diastereomers, isomer I and II. The formation ratio of the isomers, I:II was about 1: 1. On the other hand, the optically active $[Cr(acac)(R\text{-mbdo})_2]^{2+}$ complex prepared from *R*-mbdo gave only one isomer of two possible ones, *Δ*(*λλ*)(lel_2) and *Λ*(*λλ*)(ob_2), and its absorption spectrum coincides with that of isomer II. Since molecular models show that the ob_2 isomer has an extremely crowded structure, the *R*-mbdo complex can be assigned to the *Δ*(*λλ*)(lel_2) isomer. Therefore isomer I and II can be assigned to have the $lel\cdot ob$ and lel_2 structures, respectively. Attempts to resolve both isomers, I and II, were all unsuccessful. Isomer I and II are stable and the active *R*-mbdo complex is optically stable in aqueous solutions.

Figure 3 shows the absorption spectra of the two isomers of $[Cr(acac)(rac\text{-mbdo})_2]^{2+}$ and the CD spectrum of $(-)_{589}$-$[Cr(acac)(R\text{-mbdo})_2]^{2+}$. The spectral data are given in Table 1. The absorption spectra of the two isomers fairly differ from each other in the visible region, while those in the ultraviolet region are similar. The absorption bands at 17390cm^{-1} with a shoulder

TABLE 1. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption	CD
	$\tilde{\nu}/10^3\,cm^{-1}$ (log ε)	$\tilde{\nu}/10^3\,cm^{-1}$ ($\Delta\varepsilon$)
$(+)_{546}$-[Cr(acac)$_2$(*R*-mbdo)]$^+$	17.53(2.03)	15.50(+0.52)
	23.0 (1.9)sh	17.86(−2.30)
	25.6 (2.3)sh	24.57(+0.87)
	26.18(2.33)	28.99(+4.37)
	30.33(4.03)	32.47(+9.98)
	34.54(4.08)	38.46(+23.7)
	40.90(4.39)	42.02(−39.9)
	46.0 (4.6)sh	
$(+)_{546}$-[Cr(acac)$_2$(bpdo)]$^+$	17.67(1.91)	15.24(+0.59)
	23.0 (1.9)sh	17.78(−3.43)
	25.38(2.43)	23.92(+1.27)
	29.8 (4.0)sh	29.24(+6.09)
	30.30(4.03)	31.06(−1.96)
	37.0 (4.1)sh	35.3 (+12)sh
	40.73(4.40)	37.88(+18.5)
	45.87(4.60)	41.32(−26.9)
		44.0 (−16)sh
		48.31(+20.0)
lel·ob-[Cr(acac)(*R*-mbdo)(*S*-mbdo)]$^{2+}$	16.5 (1.7)sh	
	17.39(1.71)	
	22.8 (1.8)sh	
	24.3 (2.0)sh	
	25.25(2.05)	
	29.5 (3.6)sh	
	30.03(3.63)	
	30.40(3.63)	
	34.60(4.24)	
	40.82(4.53)	
	45.5 (4.7)sh	
$(-)_{589}$-*lel*$_2$-[Cr(acac)(*R*-mbdo)$_2$]$^{2+}$	16.18(1.87)	15.85(+2.08)
	17.0 (1.8)sh	18.25(−0.35)
	22.42(1.91)	21.69(+0.67)
	25.8 (2.0)sh	28.25(−0.35)
	29.9 (3.6)sh	30.40(+6.05)
	30.40(3.65)	34.72(−20.3)
	30.77(3.65)	39.22(−33.6)
	34.72(4.19)	41.5 (−15)sh
	40.82(4.55)	47.06(+88.8)
	45.45(4.74)	
$(-)_{589}$-[Cr(acac)(bpdo)$_2$]$^{2+}$ [a]	16.34(1.82)	16.75(+2.25) [b]
	17.24(1.81)	17.92(+2.43)
	22.73(1.91)	23.15(−0.41)
	24.0 (2.0)sh	29.5 (−5.5)sh
	25.32(2.07)	30.77(−8.34)
	30.40(3.71)	37.0 (−26)sh
	35.84(4.24)	38.76(−35.7)
	40.65(4.58)	42.74(+58.0)
	45.87(4.75)	

a) These data correspond to the spectra of an equilibrium mixture of *lel*$_2$ and *lel·ob* isomers (see text).
b) The $\Delta\varepsilon$ values were extrapolated to time zero. sh: Shoulder.

(16500cm^{-1}) and at 16180cm^{-1} with a shoulder (17000 cm^{-1}) for isomer I and II, respectively, can be assigned to the first absorption band ($^4T_{2g}\leftarrow{}^4A_{2g}$). The band of isomer II (*lel*$_2$) is more intense than that of isomer I (*lel·ob*). The *lel*$_3$ isomer of [Cr(mbdo)$_3$]$^{3+}$ also shows the most intense and the narrowest first absorption band among those of the three isomers, *lel*$_3$, *lel*$_2$·*ob*, and *lel·ob*$_2$.[4]

Figure 4 compares the absorption and CD spectra of a series of [Cr(acac)$_{3-n}$(*R*-mbdo)$_n$]$^{n+}$ (n=0—3). The first absorption band shifts to lower wavenumbers by replacing acac with mbdo. The intensities of bands in the region from 23000 to 50000 cm^{-1} are related to the number of dioxide and acac ligands. The CD spectra in the region of the first absorption band show a gradual change with an increasing number of n in [Cr(acac)$_{3-n}$(*R*-mbdo)$_n$]$^{n+}$, indicating the same absolute configuration. The $(-)_{589}$-[Cr(acac)$_3$][11] and [Cr(*R*-mbdo)$_3$][3+4] complexes have been assigned to the Δ and $\Delta(\lambda\lambda\lambda)$(*lel*$_3$) configurations, respectively. Thus our preceding assignments of $\Delta(\lambda)$(*lel*) and $\Delta(\lambda\lambda)$(*lel*$_2$), respectively, for [Cr(acac)$_2$(*R*-mbdo)]$^+$ and [Cr(acac)(*R*-

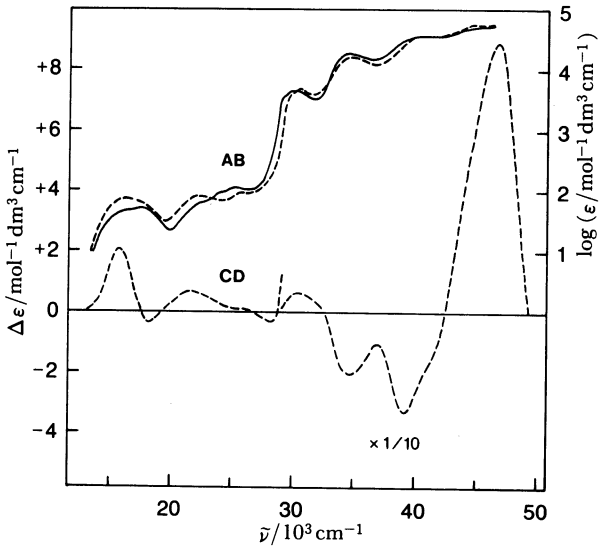

Fig. 3. Absorption (AB) spectrum of $[Cr(acac)(R\text{-mbdo})(S\text{-mbdo})]^{2+}$ (isomer I) (——), and absorption and CD spectra of $(-)_{589}$-$[Cr(acac)_2(R\text{-mbdo})_2]^{2+}$ (isomer II) (-----) in water.

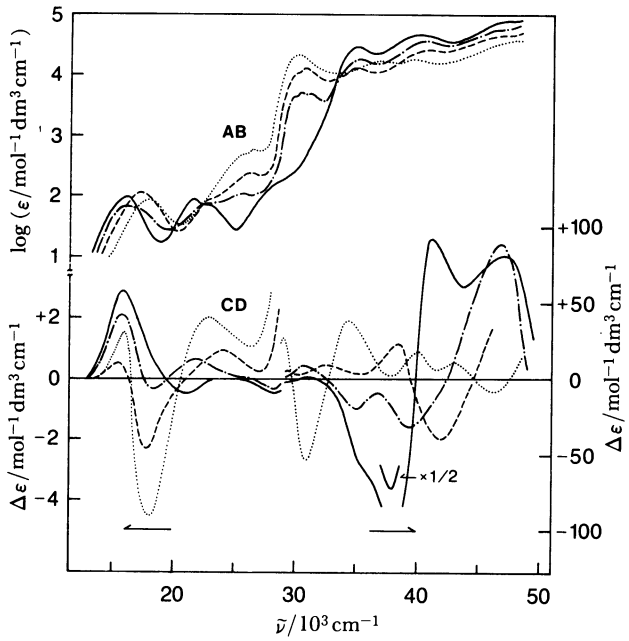

Fig. 4. Absorption (AB) and CD spectra of a series of Δ-$[Cr(acac)_{3-n}(R\text{-}mbdo)_n]^{n+}$ complexes in water; $(-)_{589}$-$[Cr(R\text{-mbdo})_3]^{3+}$ (——), $(-)_{589}$-$[Cr(acac)(R\text{-mbdo})_2]^{2+}$ (-·-·-), $(+)_{546}$-$[Cr(acac)_2(R\text{-mbdo})]^{+}$ (-----), and $(-)_{589}$-$[Cr(acac)_3]$ in ethanol (·····).[11]

mbdo)$_2]^{2+}$ are consistent with these CD spectra. The CD strength of the negative component in $[Cr(acac)_3]$ is gradually reduced by replacing acac with *R*-mbdo, $[Cr(R\text{-mbdo})_3]^{3+}$ showing only positive CD band. A similar CD change occurring with replacement of a seven-membered chelate ligand is observed in CD spectra of a series of $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ ($x+y+z=3$), where tmd denotes tetramethylenediamine which forms a seven-membered chelate ring upon coordination.[16]

The $[Cr(acac)(bpdo)_2]^{2+}$ complex has three possible racemic pairs of diastereomers as well as the corresponding *rac*-mbdo complex. However, attempts to separate such isomers were all unsuccessful by column chromatography because of rapid isomerization of the complex (*vide post*).[5] The optically active complex which was obtained by the chemical method with $K_2[Sb_2(d\text{-tartrato})_2]$ loses gradually its activity in aqueous solution at room temperature.

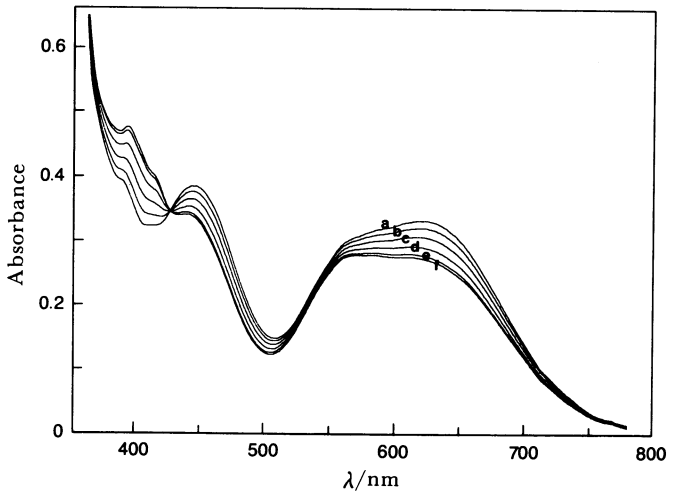

Fig. 5. Absorption spectral change of $[Cr(acac)(bpdo)_2]$-$(ClO_4)_2\cdot H_2O$ in water (pH 7) at 18.0 °C. Reaction time (min): a, 1; b, 3; c, 6; d, 12; e, 24; f, ∞.

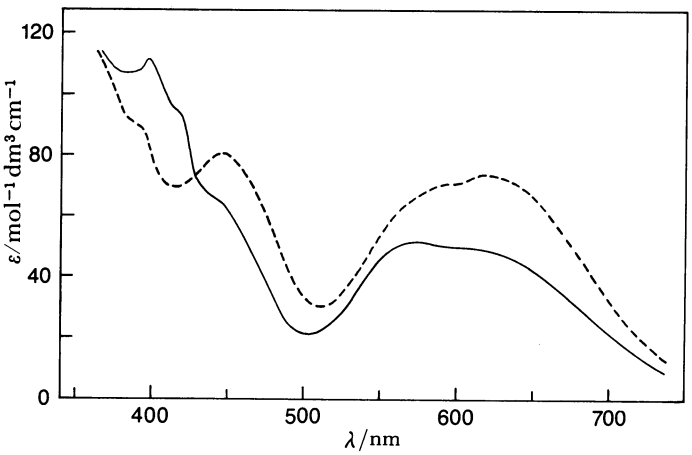

Fig. 6. Absorption spectra of two diastereomers of $[Cr(acac)(rac\text{-mbdo})_2]^{2+}$ in the visible region in water; isomer I(*lel·ob*) (——) and isomer II(lel_2) (-----).

Both racemic and $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2$-$H_2O$ in aqueous solution show a rapid absorption spectral change with an isosbestic point at 427 nm as Fig. 5 shows. The complexes are not hydrolyzed during the change of spectra, since any hydrolyzed product was not detected in the resulting solutions by column chromatography. The species corresponding to absorption spectra a and f in Fig. 5 can be assigned by comparing these spectra with those of the isomers of $[Cr(acac)(rac\text{-mbdo})_2]^{2+}$ in Fig. 6. Spectrum a quite resembles that of the lel_2 isomer of the mbdo complex, and spectrum f seems to be an intermediate one between

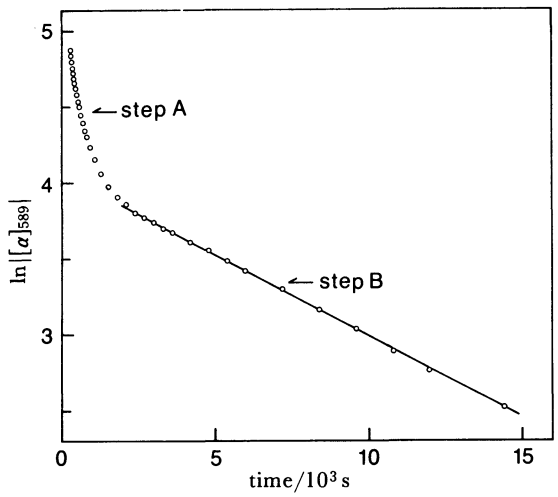

Fig. 7. Decrease in optical rotation of $(-)_{589}$-[Cr(acac)(bpdo)$_2$](ClO$_4$)$_2$·H$_2$O with time in water (pH 7) at 22.0°C.

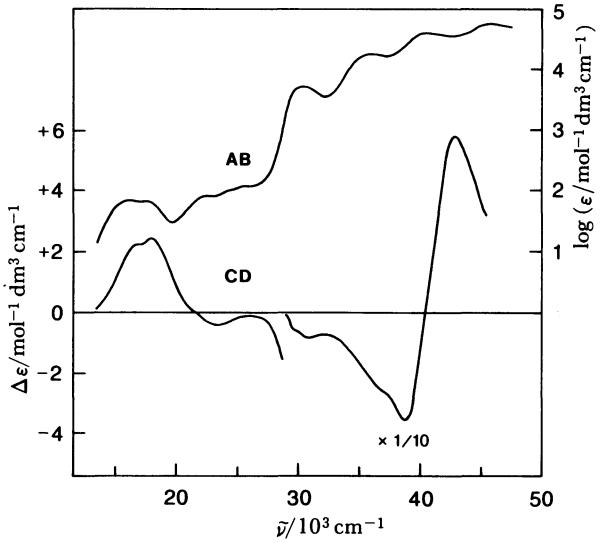

Fig. 8. Absorption (AB) and CD spectra of $(-)_{589}$-[Cr(acac)(bpdo)$_2$]$^{2+}$ in water. These were recorded after an equilibrium of *lel*$_2$ ⇌ *lel·ob* had been reached, and the CD spectrum was corrected for racemization (see text).

those of the two isomers (*lel*$_2$ and *lel·ob*). Thus the spectral change should be caused by isomerization of the complex, *lel*$_2$ ⇌ *lel·ob*. The bpdo chelate ring was shown to be flexible and change its conformation, $\delta \rightleftharpoons \lambda$, very easily.[2,3] Molecular models indicate that the *lel*$_2$ isomer seems to isomerize easily to the *lel·ob* one and *vice versa*, but the *ob*$_2$ isomer will be never formed because of its crowded structure.

As shown in Fig. 7, an aqueous solution of $(-)_{589}$-[Cr(acac)(bpdo)$_2$](ClO$_4$)$_2$·H$_2$O loses the optical activity in two steps with different rates, the first rapid (step A) and the subsequent slow (step B) steps.[5] In step A, the decrease in optical activity accompanies the absorption spectral change, while no spectral change is observed in step B. These results suggest that step A involves the isomerization reaction between the diastereomers, *lel*$_2$ ⇌ *lel·ob*, and step B the racemization reaction between the enantiomers, $\Delta \rightleftharpoons \Lambda$, of the complex.

Figure 8 shows the absorption spectrum of $(-)_{589}$-[Cr(acac)(bpdo)$_2$]$^{2+}$ in aqueous solution at 31°C at 20min after dissolution, when no more change in the absorption spectrum was observed. After the equilibrium was reached, the CD spectrum changed with time by step B (the racemization, $\Delta \rightleftharpoons \Lambda$), thus it was extrapolated to time zero by using the k_{obsd}(racemization) value (*vide post*). The corrected CD spectrum is also shown in Fig. 8. The spectral data are given in Table 1. The absorption spectrum in the ultraviolet region is also an intermediate one between those of the *lel*$_2$ and *lel·ob* isomers of [Cr(acac)(mbdo)$_2$]$^{2+}$. The first absorption band gives two components at 16340 and 17240 cm^{-1}. Corresponding to these components, the complex shows two positive CD bands and can be assigned to the Δ configuration. Thus it is concluded that $(-)_{589}$-[Cr(acac)(bpdo)$_2$](ClO$_4$)$_2$·H$_2$O crystallizes in the $\Delta(\lambda\lambda)$-(*lel*$_2$) structure and isomerizes in aqueous solution to the $\Delta(\lambda\delta)$(*lel·ob*) structure in step A.

Kinetics of Isomerization and Racemization of [Cr(acac)(bpdo)$_2$]$^{2+}$. The kinetic experiments were carried out in the dark so as to avoid photoinduced reactions.

The rate of the isomerization of [Cr(acac)(bpdo)$_2$]$^{2+}$, *lel*$_2$ ⇌ *lel·ob*, was followed by monitoring the absorption spectral change at 620nm with time (in step A) in aqueous solution under the conditions described in Experimental part. The rate of spectral change obeyed the first order kinetic law for at least four half-lives and the rate constant (k_{obsd}) was obtained from the slope of $\log(A_t - A_\infty)$ *vs.* time where A's are absorbances at 620nm. The rate for the $(-)_{589}$-isomer agreed with that for the racemate within the experimental error. The values of k_{obsd} are given in Table 2. Arrhenius treatment of $\log(k_{obsd})$ *vs.* T^{-1} yielded an activation energy of (77.3±1.2) kJ mol^{-1}) and Eyring treatment of $\log(k_{obsd}/T)$ *vs.* T^{-1} gave an activation enthalpy of (74.9±1.1) kJ mol^{-1} and an activation entropy of (−38.5±3.7) JK^{-1}mol^{-1}. The rate was independent of concentrations of H$^+$ and the free ligands. Hence it is suggested that the isomerization proceeds by an intramolecular mechanism. The small negative activation entropy value seems to reflect such a mechanism. This is consistent with the preceding conclusion that the isomeri-

Table 2. Rate constants for the isomerization of [Cr(acac)(bpdo)$_2$](ClO$_4$)$_2$·H$_2$O in aqueous solutions (I=0.1[a])

t/°C	k_{obsd}×10^3/s^{-1}	t/°C	k_{obsd}×10^3/s^{-1}
15.8	1.69±0.01[b]	22.0[f]	3.30±0.03
18.0[c]	2.14±0.02	22.1[c]	3.31±0.02
22.0	3.31±0.02	27.4[c]	5.64±0.07
22.0[d]	3.31±0.02	34.6	12.2±0.2
22.0[e]	3.30±0.03		

a) Ionic strength adjusted with NaCl. b) Errors are standard deviations estimated by least squares. c) For $(-)_{589}$-isomer. d) In 0.1 mol/dm^3 HCl. e) In 0.05 mol/dm^3 bpdo. f) In 0.02 mol/dm^3 Hacac.

TABLE 3. RATE CONSTANTS FOR THE RACEMIZATION OF $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ IN AQUEOUS SOLUTIONS (I=0.1[a])

t/°C	$k_{obsd} \times 10^4$/s^{-1}	t/°C	$k_{obsd} \times 10^4$/s^{-1}
17.2	0.621±0.006[b]	28.4[d]	2.22±0.01
22.0	1.08±0.01	28.4[e]	2.21±0.02
25.0	1.51±0.02	30.0	2.64±0.02
28.1[c]	2.20±0.02	35.0	4.76±0.03
28.2	2.20±0.01		

a) Ionic strength adjusted with NaCl. b) Errors are standard deviations estimated by least squares. c) In 0.1 mol/dm^3 HCl. d) In 0.05 mol/dm^3 bpdo. e) In 0.02 mol/dm^3 Hacac.

zation occurs by the conformational inversion ($\lambda \rightleftharpoons \delta$) of the bpdo chelate ring in the $\Delta(\lambda\lambda)(lel_2)$ isomer to afford the $\Delta(\lambda\delta)(lel \cdot ob)$ isomer. The difference in free energy between the lel_2 and $lel \cdot ob$ isomers of the complex is small in aqueous solution because of the almost equal formation ratio between the two isomers of $[Cr(acac)(rac\text{-}mbdo)_2]^{2+}$.

For $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ in aqueous solution, the rate of decrease in optical activity was followed under the conditions described in experimental part. As Fig. 7 shows, the rate in step B obeyed the first order kinetic law for at least three half-lives and the rate constant (k_{obsd}) was obtained from the slope of $\log|\alpha_t|$ *vs.* time where α is degrees of optical rotation at 589 nm. The values of k_{obsd} are given in Table 3. The estimated values of activation energy, enthalpy, and entropy are (84.8±1.2) kJ mol^{-1}, (82.4±1.2) kJ mol^{-1}, and (−41.7±3.9) J K^{-1} mol^{-1}, respectively. The rate was independent of concentrations of H^+ and the free ligands. Thus the racemization ($\Delta \rightleftharpoons \Lambda$) will also proceed by an intramolecular mechanism. In a previous paper,[3] the rate of racemization of $[Cr(bpdo)_3]^{3+}$ in aqueous solution was found to be 1.40×10^{-4} s^{-1} at 26.9 °C with an activation energy and entropy of 81.3 kJ mol^{-1} and −49 J K^{-1} mol^{-1}, respectively, and the racemization was suggested to proceed *via* an intramolecular twist mechanism from a comparison of these kinetic parameters with those of other complexes such as $[Cr(phen)_3]^{3+}$,[17] for which the same mechanism was proposed. The rate constant and the activation parameters of $[Cr(acac)(bpdo)_2]^{2+}$ are very similar to those of $[Cr(bpdo)_3]^{3+}$, and the racemization will also proceed *via* a twist mechanism. The small negative activation entropy value seems to be consistent with such an intramolecular twist mechanism.

Tables 2 and 3 show that the rate of racemization ($\Delta \rightleftharpoons \Lambda$) is 30 times slower than that of the isomerization ($\delta \rightleftharpoons \lambda$); the complex in aqueous solution isomerizes from the lel_2 isomer to the $lel \cdot ob$ one prior to the racemization. Several different twist mechanisms have been proposed for the intramolecular racemization of a tris(chelate)-type complex.[18] However, it is difficult to determine which mechanism is the most probable for the racemization of the present complex.

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