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Isomerization and Racemization of the Tris(4,4′-dimethyl-2,2′-bipyridine *N,N′*-dioxide)chromium(III) Complex

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A new chromium(III) complex, $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ (4,4′-Me_2bpdo=4,4′-dimethyl-2,2′-bipyridine *N,N′*-dioxide) was prepared and resolved into a pair of enantiomers by an SP-Sephadex column chromatographic method using an achiral eluting agent Na_2SO_4. Both perchlorate and nitrate of the complex were found to crystallize in the $lel_2 \cdot ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$ form. Upon dissolution in water, the complexes isomerized to the $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$ form with a rapid change in absorption spectra, and then racemized ($\Delta \rightleftarrows \Lambda$) slowly. The rate constants at 35.0 °C were $4.39 \times 10^{-3}\,s^{-1}$ for the isomerization and $3.46 \times 10^{-5}\,s^{-1}$ for the racemization. These inversion reactions including conformational change ($\delta \rightleftarrows \lambda$) and configurational change ($\Delta \rightleftarrows \Lambda$) are supposed to proceed by intramolecular mechanisms. The rates of isomerization and racemizatioin of the 4,4′-Me_2bpdo complex are ca. two and ten times slower than those of $[Cr(bpdo)_3]^{3+}$ (bpdo=2,2′-bipyridine *N,N′*-dioxide), respectively.

The skew seven-membered chelate ring of 2,2′-bipyridine *N,N′*-dioxide (bpdo) in metal complexes has been confirmed by X-ray analyses of $[La(bpdo)_4](ClO_4)_3$[1] and $[UO_2(NO_3)_2(bpdo)]$.[2] The skew conformation of bpdo can exist in a pair of enantiomers, δ and λ as shown in Fig. 1. Hence a tris(bpdo) complex has four possible racemic pairs of diastereomers, $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$, $lel_2 \cdot ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$, $lel \cdot ob_2(\Delta(\lambda\delta\delta), \Lambda(\delta\lambda\lambda))$, and $ob_3(\Delta(\delta\delta\delta), \Lambda(\lambda\lambda\lambda))$. Bertini et al.[3] reported that the dominant isomers of $[M(bpdo)_3](PF_6)_2$ ($M=Co^{2+},Ni^{2+}$) in acetonitrile will be either the lel_3 or ob_3 one from ^1H NMR studies. They also suggested that a rapid inversion of the bpdo chelate ring ($\delta \rightleftarrows \lambda$) seems unlikely because of the anticipated high barrier to interconversion of chelating bulky bpdo.

In a previous paper,[4] we reported that both racemic and optically active $[Cr(bpdo)_3](ClO_4)_3 \cdot 2H_2O$[5] crystallize in the $lel_2 \cdot ob$ form, but isomerize to the lel_3 one upon dissolution in water with a rapid change in absorption spectra, and then racemize ($\Delta \rightleftarrows \Lambda$) slowly. Similar isomerization and racemization were found to occur in $[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ (acac=acetylacetonate ion).[6] The complex forms the lel_2 isomer in the solid state and the $lel \cdot ob$ one in an aqueous solution. These facts indicate that the bpdo chelate ring is flexible and changes its conformation ($\delta \rightleftarrows \lambda$) easily. On the other hand, its conformation can be fixed when methyl groups are introduced in the 3- and 3′-positions. Thus, $[Cr(rac\text{-}3,3'\text{-}Me_2bpdo)_3]^{3+}$ (*rac*-3,3′-Me_2bpdo=racemic 3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide) yields three of four possible isomers, lel_3, $lel_2 \cdot ob$, and $lel \cdot ob_2$ in the formation ratio of 4, 1, and 1, respectively.[7]

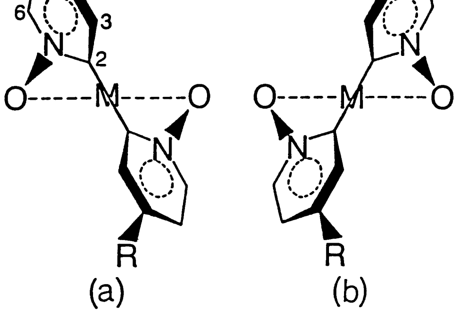

Fig. 1. Chiral conformations of bpdo (R=H) and 4,4′-Me_2bpdo ($R=CH_3$). (a) δ- and (b) λ-skew form.

In the present paper, we have studied the stereoisomerism of a new related complex, $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ (4,4′-Me_2bpdo = 4,4′-dimethyl-2,2′-bipyridine *N,N′*-dioxide). The complex also crystallizes in the $lel_2 \cdot ob$ isomer, isomerizes to the lel_3 one in water, and racemizes. However, these reactions are fairly slow compared with those of $[Cr(bpdo)_3]^{3+}$. The difference in rate between two complexes are discussed.

Experimental

Preparation of 4,4′-Dimethyl-2,2′-bipyridine *N,N′*-Dioxide (4,4′-Me_2bpdo). An acetic acid solution (150 cm^3) of 4,4′-dimethyl-2,2′-bipyridine (25 g; Tokyo Kasei Co.) was mixed with 30% aqueous hydrogen peroxide (100 cm^3). The solution was refluxed for 4 h, then mixed with another 80 cm^3 of 30% aqueous hydrogen peroxide and refluxed for 3 h. The resulting solution was evaporated under reduced pressure to give a pale yellow oil. The residue was mixed with water (ca. 100 cm^3) and the mixture was evaporated again. This procedure was repeated twice to remove acetic acid contained in the residue. To the oily residue, 100 cm^3 of acetone was added to give pale yellow crystals. The crystals were collected by filtration, washed with acetone, and air-dried. Recrystallization from a mixture of methanol and acetone (1 : 3) gave white needles. Yield: 21 g (72%). Found: C, 66.45; H, 5.64; N, 12.76%. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95%.

IR (nujol mull) 1258, 1239 (ν_{N-O}), and 839 cm^{-1} (δ_{N-O}). ^{13}C NMR (D_2O, TMS) δ=20.5 (CH_3), 129.5 and 129.9 (C_3 and C_5), 139.5 (C_6), 141.7 (C_2), 144.4 (C_4) (see Fig. 1). ^{1}H NMR (D_2O, TSP) δ=2.49 (s, 6H, CH_3). The ^{13}C NMR spectrum was assigned from a comparison with those of the related compounds.8)

Preparation and Resolution of Complexes. $[Cr(bpdo)_3](NO_3)_3\cdot 2H_2O$: The complex was prepared according to the literature method.9) Recrystallization from a mixture of methanol and diethyl ether (2:1) gave green crystals. The complex is very soluble in water. Yield: 80%. Found: C, 43.06; H, 3.41; N, 14.85%. Calcd for $C_{30}N_{28}N_9O_{17}Cr$: C, 42.97; H, 3.37; N, 15.03%.

Resolution of $[Cr(bpdo)_3]^{3+}$: The resolution of$[Cr(bpdo)_3](ClO_4)_3$ with $(+)_{589}$-$Ag_3[Co(\text{L-cysu})_3]$ (L-cysu=L-cysteinesulfinato(2−)-*S,N*)10) was reported previously.11) The nitrate was resolved in a similar manner using $(+)_{589}$-$K_3[Co(\text{L-cysu})_3]$.10) The resolving agent (1.9 g, 2.6 mmol) was dissolved in an aqueous solution (20 cm^3) of $[Cr(bpdo)_3]$ $(NO_3)_3\cdot 2H_2O$ (4.2 g, 5.1 mmol). The solution was cooled in an ice-bath to give yellowish green crystals, which were collected by filtration, washed with 50% ethanol and then ethanol, and air-dried. The diastereomeric salt (2.0 g) was dissolved in ice cold water (30 cm^3) and immediately $NaClO_4$ (1.0 g) was added to the solution with stirring to yield green crystals. They were collected by filtration, washed thoroughly with a 1 mol dm^{-3} $NaClO_4$ solution to remove the resolving agent, then with a small amount of cold water, finally with ethanol, and dried over P_4O_{10}. Yield: 1.6 g. The complex showed a negative rotation at 589 nm in water but rapidly lost its activity.4,11) Found: C, 37.83; H, 2.93; N, 9.11%. Calcd for $(-)_{589}$-$[Cr(bpdo)_3](ClO_4)_3\cdot 2H_2O$=$C_{30}H_{28}N_6O_{20}Cl_3Cr$: C, 37.89; H, 2.97; N, 8.84%.

$[Cr(4,4'\text{-}Me_2bpdo)_3](ClO_4)_3\cdot 2H_2O$: An aqueous solution (50 cm^3) containing $Cr(NO_3)_3\cdot 9H_2O$ (2.0 g, 5 mmol) and 4,4'-Me_2bpdo (3.5 g, 16 mmol) was warmed at 80 °C for 2 h and then cooled to room temperature. Sodium perchlorate (3 g) was added to the resulting solution to yield green crystals, which were collected by filtration, washed with ice cold water, recrystallized from hot water, and dried over P_4O_{10}. Yield: 4 g (80%). Found: C, 41.98; H, 3.77; N, 8.21%. Calcd for $C_{36}H_{40}N_6O_{20}Cl_3Cr$: C, 41.77; H, 3.90; N, 8.12%.

$[Cr(4,4'\text{-}Me_2bpdo)_3](NO_3)_3\cdot 2H_2O$: The complex was prepared by a method similar to that for $[Cr(bpdo)_3](NO_3)_3\cdot 2H_2O$.9) A methanol solution (50 cm^3) containing $Cr(NO_3)_3\cdot 9H_2O$ (2.0 g, 5 mmol) and 4,4'-Me_2bpdo (3.5 g, 16 mmol) was refluxed for 4 h, cooled to room temperature, and mixed with 40 cm^3 of diethyl ether. On standing the mixture in a refrigerator for 24 h, green needles were formed, collected by filtration, washed with acetone, and dried over P_4O_{10}. The complex was recrystallized from a mixture of methanol and diethyl ether (2:1). The nitrate is much more soluble in water than the perchlorate. Yield: 3.6 g (85%). Found: C, 46.93; H, 4.26; N, 13.62%. Calcd for $C_{36}H_{40}N_9O_{17}Cr$: C, 46.86; H, 4.37; N, 13.66%.

Resolution of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$: The resolution of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ was achieved by SP-Sephadex column chromatography. All the procedures were carried out in a cold room (at ca. 5 °C) because of racemization of the complex in water at ordinary temperature. An aqueous solution of the perchlorate or nitrate (0.2 g) of the complex was applied on a column (ϕ 2.2×130 cm) of SP-Sephadex C-25. By elution with a 0.3 mol dm^{-3} Na_2SO_4 solution, the column gave two completely separate bands. The faster moving band contained the $(+)_{589}$-isomer. Each eluate of the bands was collected and mixed with $NaClO_4$ to give green crystals. They were collected by filtration, washed with a small amount of ice cold water and then ethanol, and dried over P_4O_{10}. Found for the $(-)_{589}$-isomer: C, 40.52; H, 3.94; N, 7.83%. Found for the $(+)_{589}$-isomer: C, 40.44; H, 4.03; N, 7.76%. Calcd for $[Cr(4,4'\text{-}Me_2bpdo)_3](ClO_4)_3\cdot 4H_2O$=$C_{36}H_{44}N_6O_{22}Cl_3Cr$: C, 40.37; H, 4.14; N, 7.85%. Resolution of the complex by elution with a 0.3 mol dm^{-3} $Na_2[Sb_2\{(+)_{589}\text{-tartrate}\}_2]$ solution was unsuccessful to give only one band. Very small negative and positive rotations were observed at 589 nm only for the front and rear fractions of the band, respectively. In contrast to the elution with Na_2SO_4, the $(-)_{589}$-isomer was eluted faster.

Kinetic Measurements. Isomerization of the Complexes: In aqueous solutions, both perchlorate and nitrate of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ show a rapid change in absorption spectra. The change in absorbance at 620 nm was followed using a JASCO UVIDEC-320 spectrophotometer in the temperature range of 20.0—40.0 °C (±0.1 °C). The pH and ionic strength (I=0.1) of solutions were adjusted with aqueous solutions of NaCl and HCl. The complex concentrations were in the range of 8.2—12 mmol dm^{-3} for the nitrate and 2.0—2.3 mmol dm^{-3} for the perchlorate which is hardly soluble in water. In each kinetic run, the rate of change obeyed the first-order kinetic law. The observed rate constant (k_{obsd}) is expressed as $k_{obsd}=-\ln[(A_t-A_\infty)/(A_0-A_\infty)]/t$, where A's are absorbances at the time denoted by suffixes.

The rate for isomerization of the chloride and perchlorate of $[Cr(bpdo)_3]^{3+}$ in water has been reported in our previous paper.4) In this work, the kinetic measurements for isomerization of $[Cr(bpdo)_3](NO_3)_3\cdot 2H_2O$ were carried out by a method described above in the temperature and the complex concentration ranges of 22.0—35.0 °C and 7.0—12 mmol dm^{-3}, respectively. The rate for the nitrate agreed with those for the chloride and perchlorate.

Racemization of the Complex: The decrease in optical rotation at 589 nm of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ in water was followed using a Union PM-101 digital polarimeter. The temperatures and the complex concentrations were in the range of 40.0—55.0 °C (±0.1 °C) and 1.1—2.9 mmol dm^{-3}, respectively. The complex lost the activity in two steps with different rates, the first rapid and the subsequent slow steps (vide post). 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.

Other Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Shimadzu UV-3100 spectrophotometer and a JASCO J-500 spectropolarimeter, respectively, using a cell jacket to maintain the temperature constant. ^{13}C and ^{1}H NMR and IR spectra were recorded on a JEOL JNM-PFT60 and a VARIAN EM-390 spectrometer, and a JASCO IR REPORT-100 spectrophotometer, respectively.

Results and Discussion

Preparation and Properties of the Complex. White crystalline 4,4'-Me_2bpdo was obtained by a method similar to that for bpdo12) from 4,4'-dimethyl-2,2'-bipyridine and hydrogen peroxide. The $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ complex was prepared by a method similar to that for $[Cr(bpdo)_3]^{3+}$ 9,11,13) from $Cr(NO_3)_3\cdot 9H_2O$ and the ligand. As shown later, both perchlorate and nitrate of the complex crystallized in the $lel_2 \cdot ob$ isomer. This isomer isomerized fairly rapidly to the lel_3 form upon dissolution in water. The complex was completely resolved into a pair of enantiomers by SP-Sephadex column chromatography carried out at 5 °C using an achiral eluting reagent, an aqueous Na_2SO_4 solution. The same chromatography at 20 °C was unsuccessful to give only one band on the column because of racemization of the complex. The $[Cr(bpdo)_3]^{3+}$ complex racemizes too fast to be resolved by a column chromatographic method.[4,11]

The achievement in resolution using Na_2SO_4 indicates that the enantiomers of the complex are discriminated

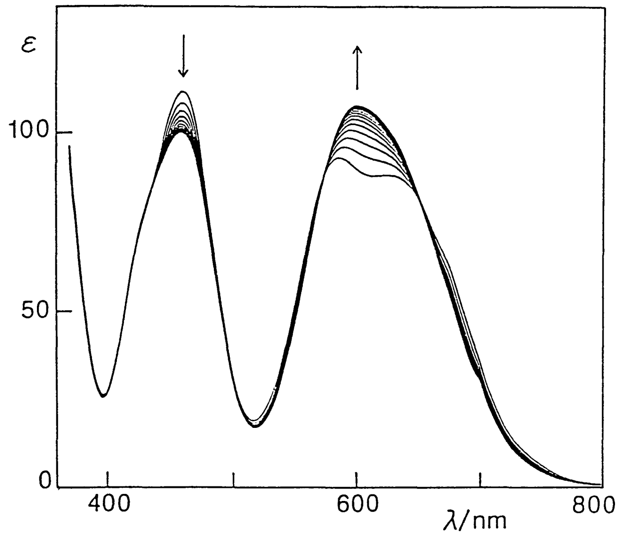

Fig. 2. Absorption spectral change with time of $[Cr(4,4'\text{-}Me_2bpdo)_3](NO_3)_3 \cdot 2H_2O$ in water at 25.0 °C. Spectra were recorded at 1—156 min after dissolution in water at regular time intervals (5 min). Trends of the spectral change are shown by arrows.

by chiral SP-Sephadex resin composed of D-glucose.[14] On the contrary, elution with $Na_2[Sb_2\{(+)_{589}\text{-tartrate}\}_2]$, which is known as an effective eluting reagent for chromatographic resolution of metal complexes,[14,15] resulted in very poor resolution. The $(-)_{589}$-isomer was eluted faster in the chromatography with this chiral eluent, while the $(+)_{589}$-isomer was eluted faster with Na_2SO_4. That is to say, opposed effects were observed between the discrimination by the resin and that by $[Sb_2\{(+)_{589}\text{-tartrate}\}_2]^{2-}$. A similar behavior in chromatographic resolution was observed for the complexes, $[Cr(acac)(bpy)(bpdo \text{ and } 3,3'\text{-}Me_2bpdo)]^{2+}$ (bpy=2,2'-bipyridine).[16]

Figure 2 shows the absorption spectra of racemic $[Cr(4,4'\text{-}Me_2bpdo)_3]X_3$ ($X=NO_3^-$, ClO_4^-) in water which change rapidly with isosbestic points at 653, 575, and 437 nm. The optically active isomer behaves in the same way. Since the complex is stable in water as confirmed by column chromatography of the reaction product, the spectral change is attributable to the isomerization between two isomers of the complex. The spectrum immediately after dissolution in water closely resembles that of the $lel_2 \cdot ob$ isomer of $[Cr\{(R \text{ or } S)\text{-}3,3'\text{-}Me_2bpdo\}_3]^{3+}$, while the final spectrum resembles that of the lel_3 isomer of the same complex.[7] Thus it is concluded that the nitrate and perchlorate of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ crystallize in the $lel_2 \cdot ob$ isomer, but isomerize to the lel_3 one in water, and the complex exists in an equilibrium, $lel_2 \cdot ob \rightleftarrows lel_3$ with a great preference for the latter (vide post). The same isomerization from $lel_2 \cdot ob$ to lel_3 was observed for $[Cr(bpdo)_3]^{3+}$,[4] of which the spectral change was faster than that of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$. Figure 3 shows the structures by Dreiding molecular models of the lel_3 and $lel_2 \cdot ob$ isomers of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$. The complex has a crowded structure, but the isomerization between the lel_3 and $lel_2 \cdot ob$ isomers, a conformational inversion of one che-

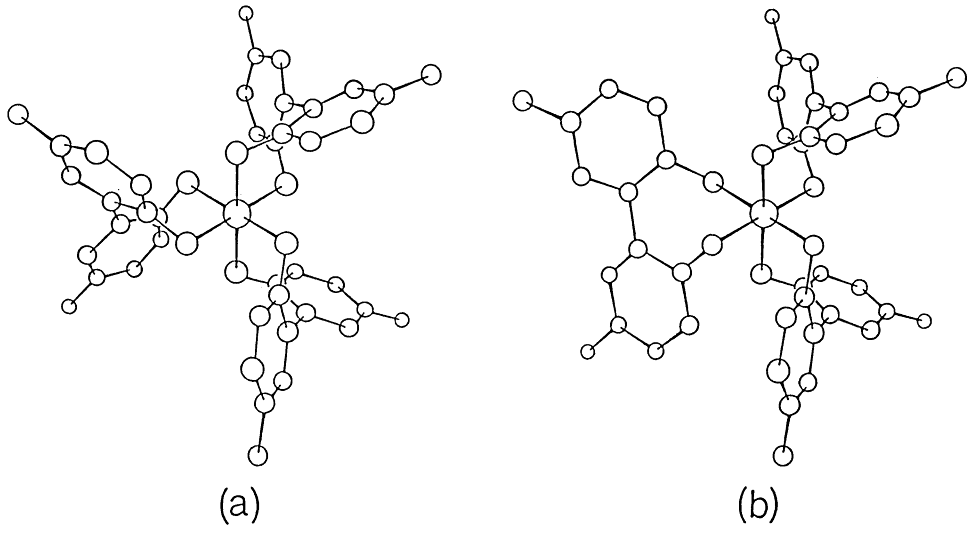
(a)
(b)

Fig. 3. Schematic drawing of the two conformational isomers of Δ-$[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$; (a) $\Delta(\lambda\lambda\lambda)(lel_3)$, (b) $\Delta(\lambda\lambda\delta)(lel_2 \cdot ob)$.

late ring, seems to occur easily. However, the inversion is much slower than those of diamine chelate rings in $[Fe(CN)_4(1,2\text{- or }1,3\text{-diamine})]^-$ (10^4—10^8 s^{-1} at 25 °C), the kinetics of which were studied by ^1H NMR spectroscopy.17)

The two absorption bands in Fig. 2 correspond to the two d-d transitions of Cr(III), $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$. The $lel_2 \cdot ob$ isomer has lower symmetry (C_2) than the lel_3 isomer (D_3) and shows the split band due to the first spin-allowed transition around 600 nm. The splitting disappears and the band becomes single and sharp with passage of time. Figure 4 shows the absorption spectra of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ and $[Cr(bpdo)_3]^{3+}$ in water at 25 °C after an equilibrium was reached between the two isomers. The spectra of free 4,4'-Me_2bpdo and bpdo ligands are also given in Fig. 4. The spectral data are listed in Table 1. The spectra of these two complexes are very similar over the whole region. The first d-d band of the 4,4'-Me_2bpdo complex (16560 cm^{-1}) is at higher energy by 150 cm^{-1} than that of the bpdo complex (16410 cm^{-1}). Whyman et al.18) reported that the ligand field strength (10 Dq) of $[Cr(4\text{-}Rpyo)_6]^{3+}$ (4-Rpyo=4-substituted pyridine *N*-oxide) increases in the order of R=Cl<H<CH_3<CH_3O, and the Dq value increases with an increase in electron-releasing ability of the substituent at the 4-position of pyridine. The 10 Dq value of $[Cr(4\text{-}CH_3pyo)_6]^{3+}$ (16000 cm^{-1}) is larger by 130 cm^{-1} than that of $[Cr(pyo)_6]^{3+}$ (15870 cm^{-1}).18) The shift of the band of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ to higher energy from that of $[Cr(bpdo)_3]^{3+}$ is attributable to the same electron-releasing effect of two 4-methyl groups on bpdo. The $[Cr(4,4'\text{-}(MeO)_2bpdo)_3]^{3+}$ (4,4'-$(MeO)_2$bpdo=4,4'-dimethoxy-2,2'-bipyridine *N,N'*-dioxide) complex shows the first d-d band at 16720 cm^{-1} higher in energy by 160 cm^{-1} than that of the 4,4'-Me_2bpdo complex.19)

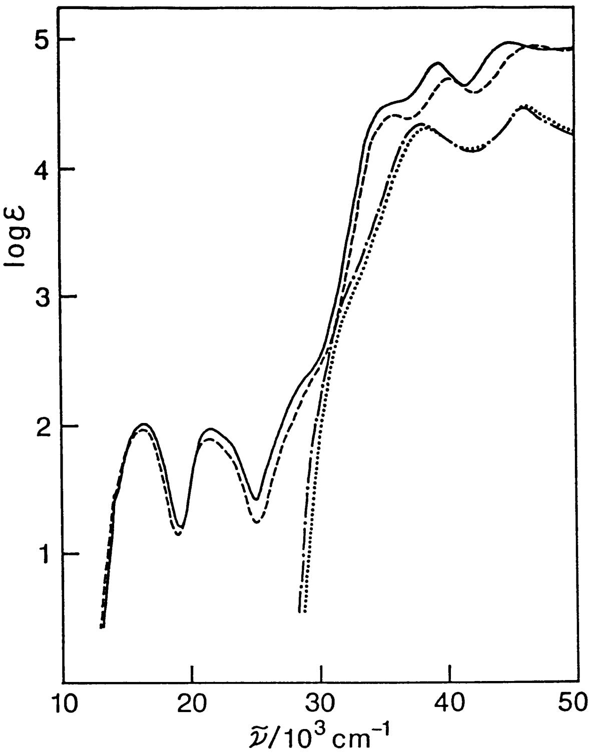

Fig. 4. Absorption spectra of $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ (——), $[Cr(bpdo)_3]^{3+}$ (– – –), 4,4'-Me_2bpdo (—·—), and bpdo (······) in water. The spectra were recorded after an equilibrium of $lel_2 \cdot ob \rightleftarrows lel_3$ had been reached.

Table 1. Absorption Spectral Data in Water[a)]

Compound	$\tilde{\nu}$ / 10^3 cm^{-1} (log ε)
bpdo[b)]	38.55 (4.32), 46.08 (4.48)
4,4'-Me_2bpdo	38.20 (4.35), 46.04 (4.47)
$[Cr(bpdo)_3]^{3+}$ [b)]	14.3 (1.5)sh, 16.41 (1.97), 21.39 (1.90), 22.7 (1.8)sh, 30.3 (2.5)sh, 35.96 (4.40), 40.26 (4.69), 46.73 (4.94)
$[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$	14.3 (1.5)sh, 16.56 (2.01), 21.72 (1.98), 22.7 (1.9)sh, 29.4 (2.4)sh, 36.4 (4.5)sh, 39.39 (4.81), 45.23 (4.97)

a) The data for the complexes are those for an equilibrium mixture of lel_3 and $lel_2 \cdot ob$ isomers. b) This work. sh: Shoulder.

Figure 5 shows that $(-)_{589}$-$[Cr(4,4'\text{-}Me_2bpdo)_3](ClO_4)_3 \cdot 4H_2O$ in aqueous solution loses optical activity in two steps with different rates. In the first rapid step (A), the decrease in activity accompanied the change of absorption spectra shown in Fig. 2, while no change of the spectra was observed in the subsequent slow step (B). Figure 6 shows the CD spectral change of the same $(-)_{589}$-isomer. In the first rapid step (Fig. 6(A)), the spectra change with isodichroic points at 596 and 510 nm, while in the second slow step (Fig. 6(B)), the spectra simply decrease the magnitude. These results support the previous conclusion that the first rapid step

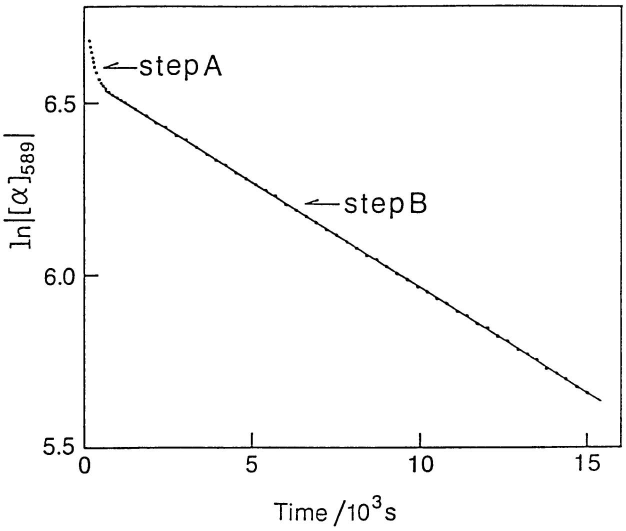

Fig. 5. Decrease in optical rotation with time of $(-)_{589}$-$[Cr(4,4'\text{-}Me_2bpdo)_3](ClO_4)_3 \cdot 4H_2O$ in water at 40.0 °C. [Complex]=1.09 mmol dm^{-3}; *I*=0.1.

involves the isomerization of the *lel*$_2$·*ob* to *lel*$_3$ isomers, and the second slow step the racemization of the complex. The CD pattern of the $(-)_{589}$-isomer in the slow step (B) resembles that of $\Delta(\lambda\lambda\lambda)$-*lel*$_3$-[Cr{(*R*)-3,3′-Me$_2$bpdo}$_3$]$^{3+}$,[7] and the complex can be assigned to the Δ configuration. Thus it is concluded that $(-)_{589}$-[Cr(4,4′-Me$_2$bpdo)$_3$](ClO$_4$)$_3$·4H$_2$O crystallizes in the $\Delta(\lambda\lambda\delta)$ (*lel*$_2$·*ob*) isomer, but upon dissolution in water it isomerizes rapidly to the $\Delta(\lambda\lambda\lambda)$ (*lel*$_3$) isomer and then racemizes slowly, $\Delta(\lambda\lambda\lambda)$ (*lel*$_3$)$\rightleftarrows$ $\Lambda(\delta\delta\delta)$ (*lel*$_3$).

Kinetics of Isomerization and Racemization of [Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$. The isomerization of [Cr(4,4′-Me$_2$bpdo)$_3$] (NO$_3$)$_3$·2H$_2$O in water, *lel*$_2$·*ob*$\rightleftarrows$*lel*$_3$, was followed by monitoring the change in absorbance at 620 nm under the conditions described in Experimental part. The rate of spectral change obeyed the first-order kinetic law and the observed rate constant (k_{obsd}) was obtained from the slope of log ($A_\infty - A_t$) vs. time, where A's are absorbances at the time denoted by suffixes. The values of k_{obsd} are listed in Table 2, and the activation parameters in Table 3. The values for [Cr(bpdo)$_3$](NO$_3$)$_3$·2H$_2$O studied in this work are also given in the tables for comparison. The data of the nitrate of bpdo complex agreed well with those of the chloride and perchlorate reported previously.[4] The rates of both 4,4′-Me$_2$bpdo and bpdo complexes were independent of concentrations of H$^+$ and the free ligand, indicating an intramolecular reaction. The small nega-

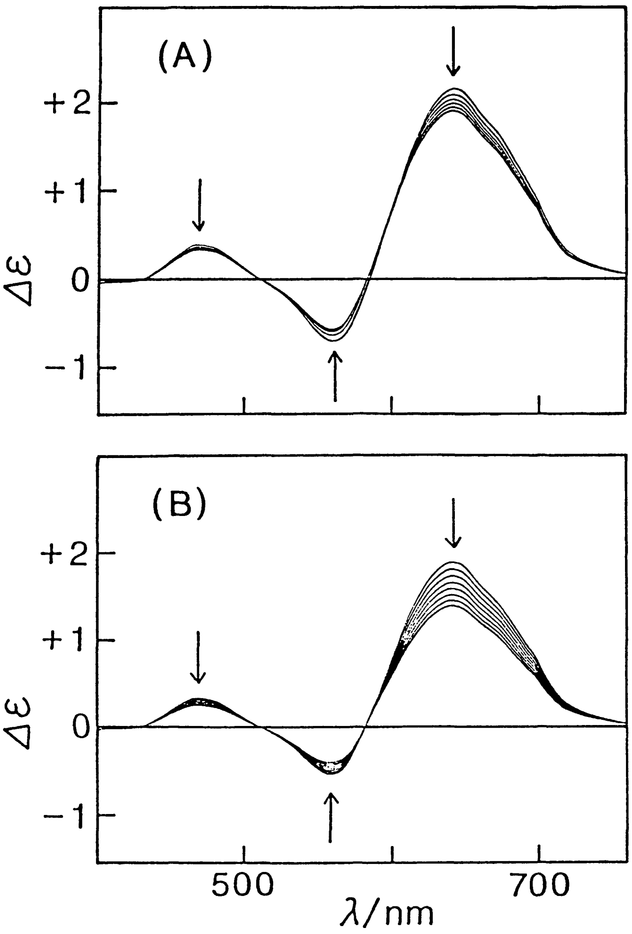

Fig. 6. CD spectral change with time of $(-)_{589}$-[Cr(4,4′-Me$_2$bpdo)$_3$](ClO$_4$)$_3$·4H$_2$O in water at 35.0 °C. Trends of the spectral change are shown by arrows. Reaction time (min): (A): 5, 10, 20, 30, 40, 50; (B): 60, 80, 100, 120, 140, 160, 180, 200 after dissolution in water.

Table 2. Rate Constants for the Isomerization of [Cr(L)$_3$](NO$_3$)$_3$ in Water (I=0.1)

t/°C	k_{obsd}/ 10^{-3} s^{-1}	t/°C	k_{obsd}/ 10^{-3} s^{-1}
	L=bpdo		
22.0	2.14±0.01$^{a)}$	30.0$^{b)}$	5.33±0.05
24.0	2.75±0.02	30.0$^{c)}$	5.36±0.04
30.0	5.35±0.04	35.0	8.69±0.08
	L=4,4′-Me$_2$bpdo		
20.0	0.755±0.002	30.0$^{e)}$	2.55±0.02
20.0$^{d)}$	0.753±0.003	35.0	4.39±0.03
25.0	1.39±0.01	35.0$^{b)}$	4.42±0.02
25.0$^{b)}$	1.38±0.01	35.0$^{d)}$	4.41±0.03
30.0	2.52±0.01	35.0$^{e)}$	4.38±0.04
30.0$^{b)}$	2.53±0.01	35.0$^{c,e)}$	4.39±0.03
30.0$^{c)}$	2.52±0.02	40.0	7.69±0.04
30.0$^{d)}$	2.53±0.02	40.0$^{b)}$	7.63±0.06

a) Errors are standard deviations estimated by least squares. b) In 0.1 mol dm^{-3} HCl. c) In 0.05 mol dm^{-3} free ligand (bpdo or 4,4′-Me$_2$bpdo). d) For the perchlorate of the complex. e) For the $(-)_{589}$-isomer.

Table 4. Rate Constants for the Racemization of $(-)_{589}$-[Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$ in Water (I=0.1)

t/°C	k_{obsd}/ 10^{-5} s^{-1}	t/°C	k_{obsd}/ 10^{-5} s^{-1}
35.0	3.46±0.03	45.0$^{a)}$	10.0±0.02
40.0	6.09±0.02	45.0$^{b)}$	10.2±0.02
40.0$^{a)}$	6.12±0.01	45.0$^{b,c)}$	10.1±0.01
40.0$^{b)}$	6.09±0.02	50.0	17.8±0.02
40.0$^{c)}$	6.10±0.01	50.0$^{a)}$	17.6±0.03
45.0	10.2 ±0.01	55.0	29.5±0.02

a) In 0.1 mol dm^{-3} HCl. b) In 0.05 mol dm^{-3} 4,4′-Me$_2$bpdo. c) For the $(+)_{589}$-isomer.

Table 3. Isomerization Rate Constants at 35.0 °C and Activation Parameters for Complexes in Water

Complex	k_{obsd}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{308.2}$
	10^{-3} s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
[Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$	4.39	86.0±0.3	−11.3±0.8	89.5±0.5
[Cr(bpdo)$_3$]$^{3+\,a)}$	8.69	78.9±1.8	−28.4±5.9	87.7±3.6
[Cr(acac)(bpdo)$_2$]$^{2+\,b)}$	12.2$^{c)}$	74.9	−38.5	86.8

a) This work. b) From Ref. 6. c) At 34.6 °C.

Table 5. Racemization Rate Constants at 35.0 °C and Activation Parameters for Complexes in Water

Complex	k_{obsd}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{308.2}$
	10^{-5} s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
[Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$	3.46	87.5±0.6	−46.8±2.0	102±1
[Cr(bpdo)$_3$]$^{3+}$ [a]	32.0	76.5	−64.0	96.2
[Cr(acac)(bpdo)$_2$]$^{2+}$ [b]	47.6	82.4	−41.7	95.3

a) From Ref. 4. b) From Ref. 6.

tive values for the activation entropy would also indicate that the reactions proceed by an intramolecular mechanism. The activation enthalpy of 4,4′-Me$_2$bpdo complex is a little larger than that of the bpdo complex, and the complex isomerizes about two times slower than does the bpdo complex. The effect of two 4-methyl substituents is not clear on the conformational inversion of the 4,4′-Me$_2$bpdo chelate ring. The rate of racemization of the 4,4′-Me$_2$bpdo complex is also reduced by a factor of 10 compared with that of the bpdo complex as stated below.

Racemization of [Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$ in water was studied by monitoring the change in optical rotation at 589 nm under the conditions described in Experimental part. The rate in step (B) in Fig. 5 obeyed the first-order kinetic law and the rate constant (k_{obsd}) was obtained from the slope of log $|\alpha_t|$ vs. time, where α is degrees of optical rotation. The k_{obsd} values are given in Table 4, and the activation parameters in Table 5 together with those of the bpdo complexes. The rate was independent of concentrations of H$^+$ and the free ligand. The kinetic parameters for the 4,4′-Me$_2$bpdo and bpdo complexes in Table 5 are similar to those for the racemization of such complexes as [Cr(bpy)$_3$]$^{3+}$ or [Cr(1,10-phenanthroline)$_3$]$^{3+}$, for which the reactions are suggested to proceed via an intramolecular twist mechanism.[20] The present dioxide complexes are supposed to racemize by such a mechanism, but the details remain unknown.

As Table 5 shows, the racemization of [Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$ is about ten times as slow as that of [Cr(bpdo)$_3$]$^{3+}$. If it is assumed that these racemizations proceed by an intramolecular twist mechanism, the reactions involve both configurational ($\Delta\rightleftarrows\Lambda$) and conformational ($\delta\rightleftarrows\lambda$) inversions of three chelate rings in the complex. Studies with molecular models suggest that introduction of two methyl groups at the 4,4′-positions of bpdo scarcely exerts a steric effect on these inversions. As stated previously, the electron-releasing methyl groups on bpdo would increase the electron density of oxygen donor atoms and strengthen the Cr–O bonds to stabilize the complex. The rates of [Cr(4,4′-Me$_2$bpdo)$_3$]$^{3+}$ slower than those of [Cr(bpdo)$_3$]$^{3+}$ are supposed to result from such an electronic effect of the methyl substituent.

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