May, 1992] © 1992 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 65, 1233—1239 (1992) 1233

Preparation, Stereochemistry, and Kinetics of Isomerization and Racemization of Bis(2,2′-bipyridine *N*,*N*′-dioxide)chromium(III) Complexes Containing an Oxalate or Malonate Ion

Hideaki Kanno,* Masanori Tomita, Shunji Utsuno,
and Junnosuke Fujita†
Department of Chemistry, Faculty of Science,
Shizuoka University, Oya, Shizuoka 422
† Department of Chemistry, Faculty of Science,
Nagoya University, Chikusa-ku, Nagoya 464-01

(Received January 9, 1992)

Two new chromium(III) complexes of the type, $[Cr(L)(bpdo)_2]^+$ (L=oxalate (ox^{2-}) or malonate (mal^{2-}) ion), where bpdo denotes 2,2′-bipyridine *N*,*N*′-dioxide, were prepared and resolved into a pair of enantiomers by use of $Ag_2[Sb_2\{(+)_{589}\text{-tartrate}\}_2]$. The perchlorates of these complexes were found to crystallize in the lel_2 ($\Delta(\lambda\lambda)$, $\Lambda(\delta\delta)$) form. Upon dissolution in water, the complexes isomerized to the *lel·ob* ($\Delta(\lambda\delta)$, $\Lambda(\delta\lambda)$) form with a rapid change in absorption spectra, and then racemized ($\Delta \rightleftarrows \Lambda$). Rates of the isomerization and racemization at 25 °C were 7.65×10^{-3} s^{-1} and 2.20×10^{-3} s^{-1}, respectively for the ox complex, and 4.95×10^{-3} s^{-1} and 6.42×10^{-5} s^{-1} for the mal one. These rates were independent of concentrations of H^+ and the free bpdo ligand, indicating an intramolecular mechanism for these reactions. The faster reactions of the ox complex than those of the mal one may be attributed to the steric effect due to the less crowded structure of the ox complex.

In previous papers,[1] we reported the isomerization arising from conformational inversion of the skew seven-memberd 2,2′-bipyridine *N*,*N*′-dioxide (bpdo) chelate ring ($\delta \rightleftarrows \lambda$) as shown in Fig. 1, and racemization ($\Delta \rightleftarrows \Lambda$) of $[Cr(acac)(bpdo)_2](ClO_4)_2$, where acac benotes an acetylacetonate ion. The $[Cr(acac)(bpdo)_2](ClO_4)_2$ complex crystallizes in the $lel_2(\Delta(\lambda\lambda)$, $\Lambda(\delta\delta))$ form, but upon dissolution in water it isomerizes to the *lel·ob*($\Delta(\lambda\delta)$, $\Lambda(\delta\lambda)$) one with a rapid absorption spectral change, and then racemizes slowly. A similar reaction is observed for $[Cr(bpdo)_3]X_3\cdot2H_2O$ ($X=ClO_4^-$, NO_3^-); the complexes crystallize in the $lel_2\cdot ob(\Delta(\lambda\lambda\delta)$, $\Lambda(\delta\delta\lambda))$ form, isomerize to the $lel_3(\Delta(\lambda\lambda\lambda)$, $\Lambda(\delta\delta\delta))$ one in water, and racemize.[2,3] Thus the skewed bpdo chelate ring[4] is flexible and can change its conformation rather easily.

In this paper, we have prepared two new related complexes, $[Cr(ox)(bpdo)_2]^+$ (ox=oxalate ion) and $[Cr(mal)(bpdo)_2]^+$ (mal=malonate ion), resolved into a pair of enantiomers, and studied the stereochemistry, and isomerization and racemization reactions. The results have been compared with those of $[Cr(acac)(bpdo)_2]^{2+}$ and $[Cr(bpdo)_3]^{3+}$ which are the same $[CrO_6]$-type complex.

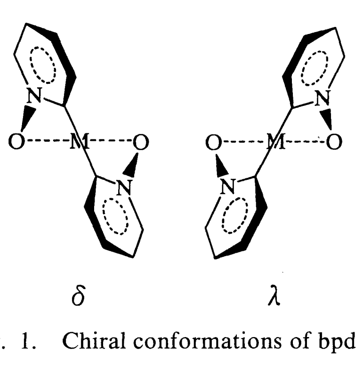

Fig. 1. Chiral conformations of bpdo.

Experimental

Preparation of $[CrCl_2(bpdo)_2]Cl\cdot3H_2O$. The complex was prepared by a method similar to that for the perchlorate of the complex.[5] Finely powdered $bpdo\cdot H_2O$[6] (4.2 g, 20 mmol) was suspended in an ethanol solution (50 cm^3) of $CrCl_3\cdot6H_2O$ (2.7 g, 10 mmol). The mixture was warmed at 70 °C with stirring for 1 h and evaporated under reduced pressure to dryness to give pink crystals. After stirring with 100 cm^3 of ethanol at 50 °C for 1 h, the crystals were collected by filtration, washed with 50% ethanol and then acetone, and air-dried. Yield: 3.8 g (65%). Found: C, 41.00; H, 3.65; N, 9.46%. Calcd for $C_{20}H_{22}N_4O_7Cl_3Cr$: C, 40.80; H, 3.77; N, 9.52%. The complex is insoluble in cold water and in common organic solvents, but soluble in hot water to give a green solution of $[Cr(bpdo)_2(H_2O)_2]^{3+}$ (vide post).

Preparation of $[Cr(ox)(bpdo)_2]ClO_4\cdot H_2O$ and $[Cr(mal)(bpdo)_2]ClO_4\cdot2H_2O$. A suspension of $[CrCl_2(bpdo)_2]Cl\cdot3H_2O$ (5.9 g, 10 mmol) in water (200 cm^3) was warmed at 60 °C with stirring for 3 h to give a green solution. Then, the solution was mixed with sodium oxalate (2.0 g, 15 mmol) or sodium malonate (2.0 g, 14 mmol) and kept at 60 °C for 3 h. The resulting solution was diluted with water (1 dm^3) and applied on a column (ϕ 3.5×50 cm) of SP-Sephadex C-25. By elution with a 0.8 mol dm^{-3} NaCl solution, the column gave two separate bands. The slower moving green band was found to contain $[Cr(bpdo)_2(H_2O)_2]^{3+}$. The eluate of the faster moving band was collected and mixed with $NaClO_4$ (1.2 g, 10 mmol) to give dark green crystals. They were collected by filtration, washed with a small amount of cold water and then ethanol, and air-dried. Recrystallization from hot water (ca. 70 °C) gave dark green needles ($[Cr(ox)(bpdo)_2]ClO_4\cdot H_2O$) or cubic crystals ($[Cr(mal)(bpdo)_2]ClO_4\cdot2H_2O$). Yield: The ox complex, 1.3 g (21%); the mal complex, 2.1 g (32%). Found for the ox complex: C, 41.97; H, 2.81; N, 8.66%. Calcd for $C_{22}H_{18}N_4O_{13}ClCr$: C, 41.69; H, 2.86; N, 8.84%. Found for the mal complex: C, 41.70; H, 3.19; N, 8.33%. Calcd for $C_{23}H_{22}N_4O_{14}ClCr$: C, 41.49; H, 3.33; N, 8.41%.

Resolution of $[Cr(ox)(bpdo)_2]^+$ and $[Cr(mal)(bpdo)_2]^+$. The perchlorate of the ox complex (2.0 g, 3.2 mmol) was stirred with a Dowex 1×8 anion exchanger (Cl^- from, 10 g) in water (50 cm^3) for a while, and the exchanger was filtered off. To the filtrate was added the resolving agent, $Ag_2[Sb_2\{(+)_{589}\text{-tartrate}\}_2]$ (1.6 mmol). After stirring for 30 min, the precipitated AgCl was filtered off. The filtrate was evaporated to ca. 20 cm^3 under reduced pressure at 50 °C. On storing the solution in a refrigerator for 24 h, dark green crystals were formed, collected by filtration, washed with 80% ethanol and then ethanol, and dried over P_4O_{10}. The crystals showed a positive rotation at 589 nm in water, but rapidly lost the activity. Yield: 0.96 g. Found: C, 34.30; H, 3.48; N, 5.98%. Calcd for $(+)_{589}$-$[Cr(ox)(bpdo)_2][Sb_2\{(+)_{589}\text{-tartrate}\}_2]_{0.5}\cdot 7H_2O=C_{26}H_{32}N_4O_{21}CrSb$: C, 34.31; H, 3.54; N, 6.15%.

The mal complex was resolved by a method similar to that for the ox complex using the resolving agent (1.5 mmol) and an aqueous solution of $[Cr(mal)(bpdo)_2]Cl$, which was prepared from the perchlorate (2.0 g, 3.0 mmol). After removing AgCl, the filtrate was evaporated to ca. 20 cm^3 and then mixed with 60 cm^3 of ethanol with stirring to yield green crystals. After standing the mixture in an ice-bath for 10 min, the crystals formed were collected by filtration. The crystals showed a positive rotation at 589 nm, but gradually lost its activity. Yield: 0.9 g. Found: C, 34.71; H, 3.69; N, 5.78%. Calcd for $(+)_{589}$-$[Cr(mal)(bpdo)_2][Sb_2\{(+)_{589}\text{-tartrate}\}_2]_{0.5}\cdot 8H_2O=C_{27}H_{36}N_4O_{22}CrSb$: C, 34.41; H, 3.85; N, 5.95%.

The optically active complexes with other achiral anions such as ClO_4^- were very soluble in water and could not be isolated. An aqueous solution of the chloride of each active complex was prepared from the above diastereomeric salt using a small column of Dowex 1×8 (Cl^- form) at ca. 0 °C. The solution showed a positve rotation at 589 nm, but gradually lost the activity at room temperature.

Kinetic Measurements. Isomerization of the Complexes: Upon dissolution in water, both $[Cr(ox)(bpdo)_2]ClO_4\cdot H_2O$ and $[Cr(mal)(bpdo)_2]ClO_4\cdot 2H_2O$ show a rapid change in absorption spectra. The change in absorbance at 450 nm was followed using a JASCO UVIDEC-320 spectrophotometer in the temperature range of 5.0—25.0 °C (±0.1 °C). Ionic strengths (I=0.1) of the solutions were adjusted with an aqueous solution of NaCl. Because of insufficient solubility of the racemic perchlorates in water, the complexes were converted into the chloride by the following method. A mixture of a Dowex 1×8 (Cl^- form, 2 g) and a 0.1 mol dm^{-3} NaCl solution (10 cm^3) was kept at a constant temperature in a water bath. To the mixture, the finely ground complex (ca. 40 mg) was added. After being stirred for 1 min, the Dowex anion exchanger was filtered off using a glass filter immersed in the same water bath using a polyethylene bag. The filtrate was applied for the measurement. The complex concentrations were in the range of 4.5—6.0 mmol dm^{-3}. In each kinetic run, the rate of change obeyed the first-order kinetic law. The observed rate constant ($k^{\mathrm{i}}_{\mathrm{obsd}}$) is expressed as $k^{\mathrm{i}}_{\mathrm{obsd}}=-\ln\,[(A_t-A_\infty)/(A_0-A_\infty)]/t$, where A's are absorbances at the time denoted by suffixes.

Racemization of the Complexes: Decreases in optical activity at 589 nm for $(+)_{589}$-isomers of the ox and mal complexes in water were followed using a Union PM-101 digital polarimeter. As described above, the $(+)_{589}$-isomers could not be isolated with achiral counter anions. Hence, each diastereomeric salt of the $(+)_{589}$-isomers was converted into the chloride by the following method. The diastereomeric salt (ca. 0.1 g) was added to an aqueous solution of NaCl (0.1 mol dm^{-3}, 20 cm^3) which had been kept at a constant temperature in a water bath. The solution was passed through a small column of Dowex 1×8 (Cl^- form, ϕ 2.2×5 cm) which had been immersed in the same water bath using a polyethylene bag. The eluate was applied for the measurement. The temperatures of solutions were in the range of 10.0—25.0 °C and 25.0—40.0 °C for the ox and mal complexes, respectively. The complex concentrations were in the range of 5.0—7.5 mmol dm^{-3}. Both ox and mal complexes 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 ($k^{\mathrm{r}}_{\mathrm{obsd}}$) is also expressed by the above equation, where A's are optical rotations in degree.

Other Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Shimadzu UV-3100 spectrophotometer and a JASCO J-500 spectropolarimeter, respectively.

Results and Discussion

Preparation and Properties of the Complexes. A bis-bpdo chromium(III) complex, $[CrCl_2(bpdo)_2]Cl\cdot 3H_2O$ was obtained from $CrCl_3\cdot 6H_2O$ and bpdo in ethanol by a method similar to that for $[CrCl_2(bpdo)_2]ClO_4\cdot H_2O$.[5] The chloride which forms pink crystals is hardly soluble in cold water, but is gradually dissolved in hot water to give a green solution. The absorption spectrum of the green solution indicates $[Cr(bpdo)_2(H_2O)_2]^{3+}$ yielded by hydrolysis (vide post). The diaqua complex could not be isolated.

Two new complexes, [Cr(ox or mal)$(bpdo)_2]^+$ were prepared from $[CrCl_2(bpdo)_2]Cl\cdot 3H_2O$ and Na_2ox Na_2mal in water. The complexes were purified by SP-Sephadex column chromatography and isolated as the perchlorate. The complexes are stable in neutral or acidic aqueous solutions, but gradually decompose in basic solutions. As shown later, these perchlorates crystallize in the *lel*₂ form, but isomerize rapidly to the *lel·ob* one upon dissolution in water. The complexes were resolved with $[Sb_2\{(+)_{589}\text{-tartrate}\}_2]^{2-}$. The $(+)_{589}$-isomers formed a less soluble diastereomeric salt with this resolving agent. The isomer with other achiral anions such as ClO_4^- was very soluble in water and could not be isolated. Aqueous solutions of the optically active chloride gradually lost the activity at room temperature.

Figures 2 and 3 show the absorption spectra of racemic $[Cr(ox)(bpdo)_2]ClO_4\cdot H_2O$ and $[Cr(mal)(bpdo)_2]ClO_4\cdot 2H_2O$ in water, respectively. The spectra change rapidly with an isosbestic point at 435 nm for the former and 432 nm for the latter. The same spectral changes are observed for optically active isomers of these complexes. Since the complexes are stable in water as confirmed by column chromatography of the reaction products, the spectral changes are attributable to the isomerization between two isomers of the complex. A very similar

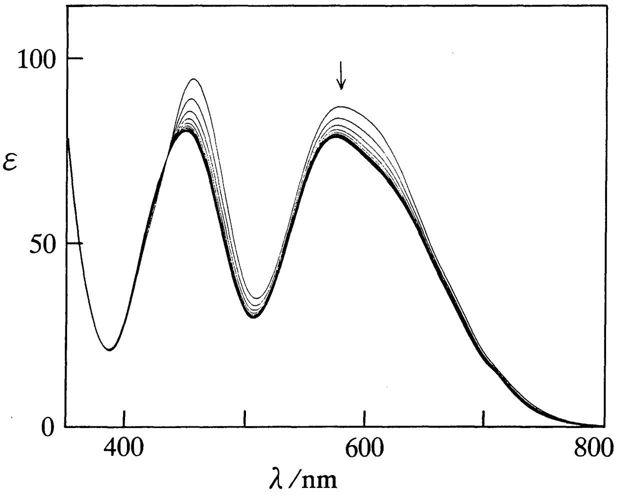

Fig. 2. Absorption spectral change with time of $[Cr(ox)(bpdo)_2]ClO_4{\cdot}H_2O$ in water at 18.0 °C. The spectrum was recorded at 2—60 min after dissolution in water at regular time intervals (2 min). Trend of the change is shown by an arrow.

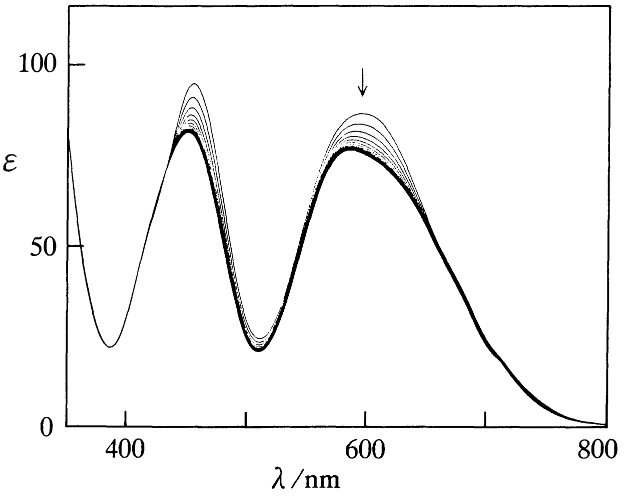

Fig. 3. Absorption spectral change with time of $[Cr(mal)(bpdo)_2]ClO_4{\cdot}2H_2O$ in water at 18.0 °C. The spectrum was recorded at 2—60 min after dissolution in water at regular time intervals (2 min).

spectral change was observed for $[Cr(acac)(bpdo)_2]^{2+}$ in water, and the change was attributed to the isomerization from the *lel*$_2$ to *lel·ob* isomers of the complex.[1] The *lel*$_2$ and *lel·ob* structures were assigned from a comparison of absorption spectra with those of $[Cr(acac)\{(R\ \text{or}\ S)\text{-}3,3'\text{-}Me_2bpdo\}_2]^{2+}$, where (*R*)- or (*S*)-3,3′-Me$_2$bpdo denotes (*R*)- or (*S*)-3,3′-dimethyl-2,2′-bipyridine *N*,*N*′-dioxide, and forms a conformationally fixed chelate ring in a λ or δ form, respectively.[7] The spectral patterns of $[Cr(ox\ or\ mal)(bpdo)_2]^+$ are also similar to that of $[Cr(acac)(bpdo)_2]^{2+}$. Thus $[Cr(ox\ or\ mal)(bpdo)_2]^+$ with ClO_4^- or $[Sb_2\{(+)_{589}\text{-tartrate}\}_2]^{2-}$ crystallizes in the *lel*$_2$ form and isomerizes to the *lel·ob* one in water. The *ob*$_2$ isomer will not be formed because of its extremely crowded structure. Figure 4 shows schematic structures of the *lel*$_2$ and *lel·ob* isomers of Λ-$[Cr(ox)(bpdo)_2]^+$. The models indicate that the *lel*$_2$ isomer seems to isomerize easily to the *lel·ob* one and vice versa. The conformation of the larger mal chelate ring in $[Cr(mal)(bpdo)_2]^+$ is unknown, although the mal chelate rings in $[Cr(mal)_3]^{3-}$ [8] and $[Co(mal)_2(en)]^-$ [9] are nearly planar. When the mal chelate ring forms a planar conformation, the models indicate that the conformational inversion of bpdo in $[Cr(mal)(bpdo)_2]^+$ occurs easily and that the steric condition among the ligands is very similar to that in $[Cr(acac)(bpdo)_2]^{2+}$.[1]

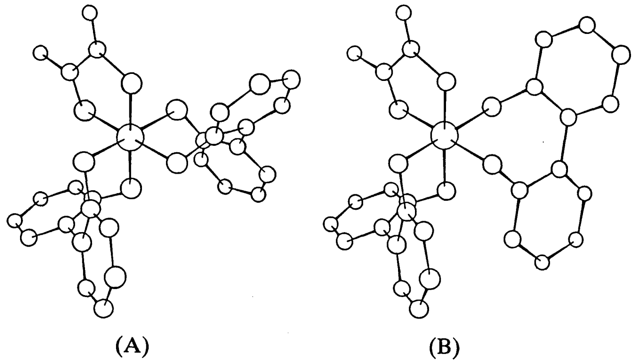
(A) (B)

Fig. 4. Schematic drawings of two conformational isomers of Λ-$[Cr(ox)(bpdo)_2]^+$; (A) Λ(δδ)(*lel*$_2$), (B) Λ(δλ)(*lel·ob*).

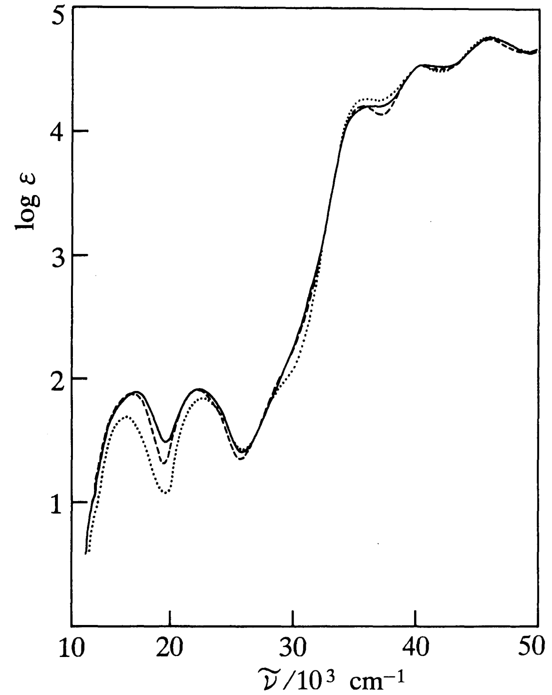

Fig. 5. Absorption spectra of $[Cr(ox)(bpdo)_2]^+$ (——), $[Cr(mal)(bpdo)_2]^+$ (----), and $[Cr(bpdo)_2(H_2O)_2]^{3+}$ (····) in water at 25.0 °C. The spectra of the ox and mal complexes were recorded after an equilibrium of *lel*$_2$ $\rightleftarrows$ *lel·ob* had been reached.

Figure 5 shows the absorption spectra of [Cr(ox)-

(bpdo)$_2$]$^+$ and [Cr(mal)(bpdo)$_2$]$^+$ in water at 25 °C after an equilibrium was reached between the two isomers, $lel_2 \rightleftarrows lel\cdot ob$. The spectrum of [Cr(bpdo)$_2$(H$_2$O)$_2$]$^{3+}$ prepared from [CrCl$_2$(bpdo)$_2$]Cl·3H$_2$O in 0.01 mol dm^{-3} hydrochloric acid is also given in Fig. 5. The spectral data are listed in Table 1. Both spectra of the ox and mal complexes are nearly the same over the whole region. The first d–d absorption bands ($^4T_{2g} \leftarrow {}^4A_{2g}$) of the ox and mal complexes are slightly sifted to lower wave numbers, respectively, from those of [Cr(ox)$_3$]$^{3-}$ [10] and [Cr(mal)$_3$]$^{3-}$,[11] but to higher wave numbers by ca. 800 cm^{-1} from that of [Cr(bpdo)$_3$]$^{3+}$.[12] The diaqua complex shows the first d–d band at lower wave numbers than those of the ox and mal complexes, the band position being similar to that of [Cr(bpdo)$_3$]$^{3+}$. In the ultraviolet region, [Cr(ox)(bpdo)$_2$]$^+$ and [Cr(mal)(bpdo)$_2$]$^+$ as well as [Cr(bpdo)$_2$(H$_2$O)$_2$]$^{3+}$ exhibit three strong absorption bands characteristic of the chelated bpdo ligand.[1,12]

An aqueous solution of the chloride of (+)$_{589}$-[Cr(mal)(bpdo)$_2$]$^+$ loses optical activity in two steps with different rates as shown in Fig. 6. In the first rapid step (A), the decrease in activity accompanied the change of the absorption spectrum shown in Fig. 3, while no change in the spectrum was observed in the subsequent slow step (B). A quite similar change in activity was observed for an aqueous solution of the chloride of (+)$_{589}$-[Cr(ox)(bpdo)$_2$]$^+$. Figures 7 and 8 show the change in CD spectra of these (+)$_{589}$-isomers. In the first rapid step (Figs. 7(A) and 8(A)), the spectrum changes with isodichroic points at 586, 502, and 385 nm for the ox complex and at 598, 501, and 378 nm for the mal one. On the other hand, the spectrum simply decreases the magnitude in the second slow step (Figs. 7(B) and 8(B)). Thus it is concluded that the first rapid step (A) involves the isomerization of the complex, $lel_2 \rightleftarrows lel\cdot ob$, and the second slow step (B) the racemization of the complex between the enantiomers, $\Lambda \rightleftarrows \Delta$. For (−)$_{589}$-[Cr(acac)(bpdo)$_2$](ClO$_4$)$_2$·H$_2$O, which shows a very similar change in CD spectrum in water, we reported that the complex

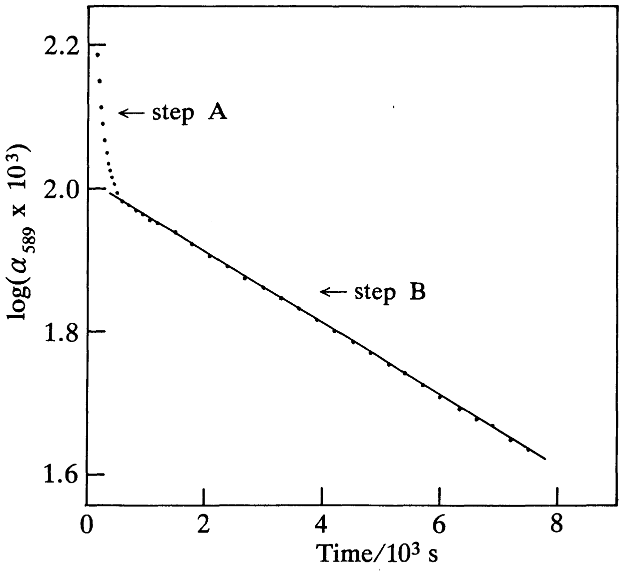

Fig. 6. Decrease in optical rotation with time of (+)$_{589}$-[Cr(mal)(bpdo)$_2$]Cl in water at 30.0 °C. [Complex]= 7.50 mmol dm^{-3}; I=0.1 (NaCl).

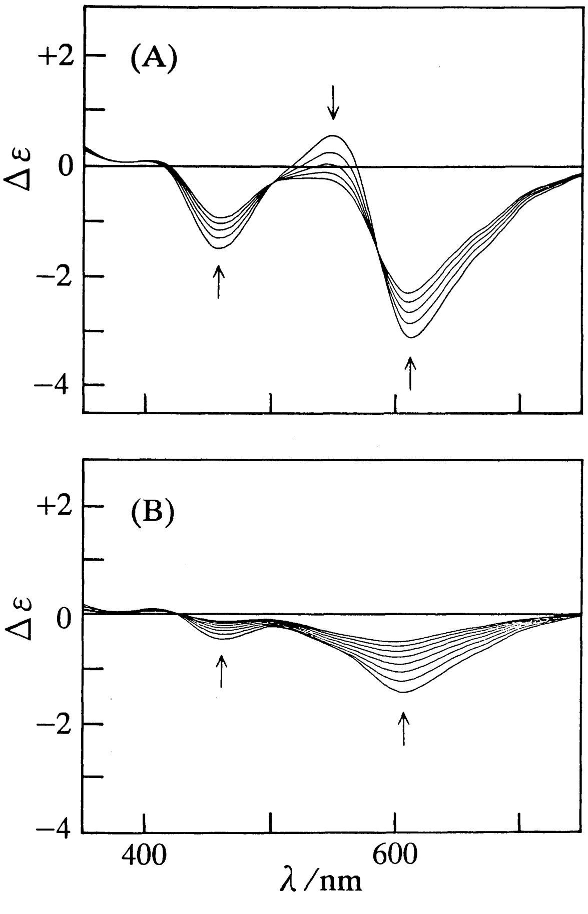

Fig. 7. CD spectral change with time of (+)$_{589}$-[Cr(ox)(bpdo)$_2$]Cl in water at 10.0 °C. Reaction time (min): (A): 2, 4, 6, 8, 10; (B): 25, 30, 35, 40, 45, 50, 55, 60 after dissolution in water.

Table 1. Absorption Spectral Data

Complexes	$\tilde{\nu}$/10^3 cm^{-1} (log ε)
[Cr(bpdo)$_2$(H$_2$O)$_2$]$^{3+}$[a]	16.50 (1.69), 22.68 (1.85), 35.71 (4.29), 40.08 (4.55), 45.87 (4.78)
[Cr(ox)(bpdo)$_2$]$^+$[b]	14.1 (1.2) sh, 17.39 (1.89), 22.36 (1.91), 36.23 (4.21), 40.72 (4.54), 45.91 (4.76)
[Cr(mal)(bpdo)$_2$]$^+$[b]	14.1 (1.3) sh, 17.12 (1.88), 22.16 (1.91), 35.71 (4.21), 40.40 (4.53), 45.75 (4.75)

a) The complex was prepared by aquation of [CrCl$_2$(bpdo)$_2$]Cl·3H$_2$O in 0.01 mol dm^{-3} HCl. b) The data correspond to the spectrum of an equilibrium mixture of lel_2 and $lel\cdot ob$ isomers. sh: Shoulder.

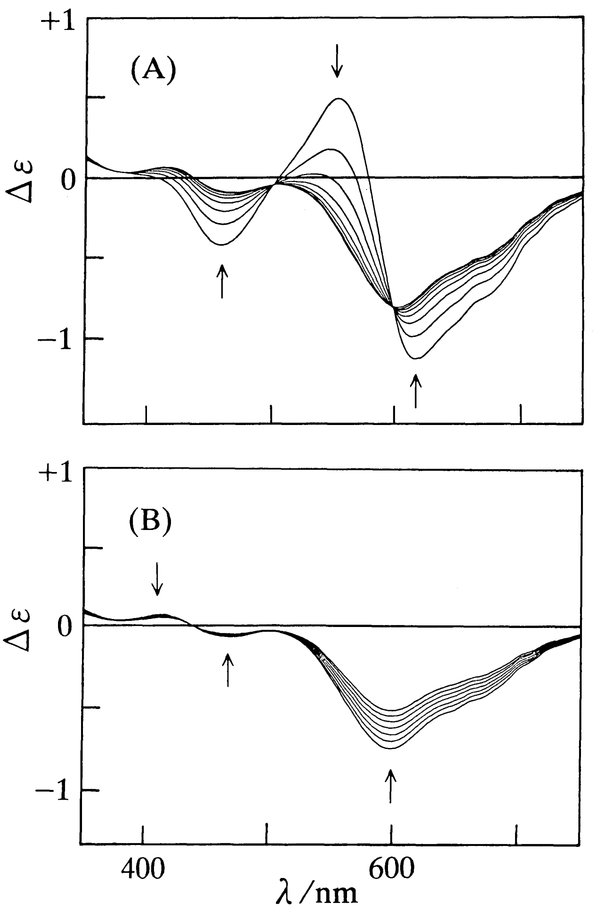

Fig. 8. CD spectral change with time of $(+)_{589}$-$[Cr(mal)(bpdo)_2]Cl$ in water at 17.0 °C. Reaction time (min): (A): 2, 5, 8, 11, 14, 17, 20, 23; (B): 50, 80, 110, 140, 170, 200, 230 after dissolution in water.

crystallizes in the $\Delta(\lambda\lambda)(lel_2)$ form, but isomerizes rapidly to the $\Delta(\lambda\delta)(lel{\cdot}ob)$ one in water, and then racemizes slowly.[1] The CD spectrum of the acac complex is nearly enantiomeric to those of the $(+)_{589}$-isomers of ox and mal complexes. Thus it is concluded that $[Sb_2\{(+)_{589}\text{-tartrate}\}_2]^{2-}$ salts of $(+)_{589}$-$[Cr(ox)(bpdo)_2]^+$ and $(+)_{589}$-$[Cr(mal)(bpdo)_2]^+$ crystallize in the $\Lambda(\delta\delta)(lel_2)$ form, isomerize to the $\Lambda(\delta\lambda)(lel{\cdot}ob)$ one upon dissolution in water, and then racemize, $\Lambda(\delta\lambda)\rightleftarrows\Delta(\lambda\delta)$.

While the bpdo chelate rings in $[Cr(L)(bpdo)_2]^{n+}$ (L$=$$ox^{2-}$, mal^{2-}, $acac^-$, bpdo) invert the conformation easily in aqueous solutions, $[Cr(en)(bpdo)_2]^{3+}$ (en=ethylenediamine) forms only the lel_2 isomer and shows no isomerization due to the inversion of bpdo.[2,12] Studies with molecular models indicate that in the $lel{\cdot}ob$ form of the en complex, the amino or methylene protons of the puckered en chelate ring come very close to the pyridine ring of the *ob*-form bpdo chelate ring, whereas there is no such proximity among the ligands in the lel_2 form. Hence $[Cr(en)(bpdo)_2]^{3+}$ is supposed to be stabilized in the lel_2 form and shows no inversion of bpdo chelate ring, $\delta\rightleftarrows\lambda$. Furthermore, $[Cr(en)(bpdo)_2]^{3+}$ is also stable to racemization.[2] This fact suggests that racemization of bis- and tris-bpdo complexes occurs easily only when the bpdo chelate ring can invert the chiral conformation. Stability of bpdo complexes toward racemization seems to depend largely on conformational stability of the bpdo chelate ring resulting from steric conditions in a complex.

Kinetics of Isomerization and Racemization of the Complexes. The values of the observed rate constant (k^{i}_{obsd}) for isomerization are listed in Table 2. The rate for the optically active complex agreed with that for the racemate within the experimental error. The activation parameters are given in Table 3 together with those of the related bpdo complexes. The isomerizations of both ox and mal complexes were independent of concentrations of H^+ and the free bpdo ligand, indicating an intra-

Table 2. Rate Constants for the Isomerization of $[Cr(L)(bpdo)_2]^+$ in Water (I=0.1)

t/°C	$k^{i}_{obsd}/10^{-3}\ s^{-1}$	t/°C	$k^{i}_{obsd}/10^{-3}\ s^{-1}$
	L=ox^{2-}		
5.0	0.660±0.001[a]	15.0[d]	2.31±0.03
10.0	1.26 ±0.01	20.0	4.28±0.03
10.0[b]	1.29 ±0.02	20.0[b]	4.24±0.04
15.0	2.34 ±0.02	20.0[c]	4.20±0.05
15.0[b]	2.33 ±0.02	20.0[d]	4.21±0.04
15.0[c]	2.35 ±0.02	25.0	7.65±0.09
	L=mal^{2-}		
5.0	0.408±0.002	20.0[d]	2.68±0.03
10.0	0.793±0.002	25.0	4.95±0.03
15.0	1.46 ±0.02	25.0[b]	4.91±0.05
15.0[b]	1.50 ±0.02	25.0[c]	4.96±0.04
15.0[c]	1.48 ±0.02	25.0[d]	5.01±0.05
20.0	2.72 ±0.02		

a) Errors are standard deviations estimated by least squares. b) In 0.1 mol dm^{-3} HCl. c) In 0.05 mol dm^{-3} bpdo. d) For the $(+)_{589}$-isomer.

Table 3. Isomerization Rate Constants at 25.0 °C and Activation Parameters for $[Cr(L)(bpdo)_2]^{n+}$ in Water

L	k^{i}_{obsd}	$\Delta H^{\ne}$	$\Delta S^{\ne}$	$\Delta G^{\ne}_{298.2}$
	$10^{-3}\ s^{-1}$	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
ox^{2-}	7.65±0.09	82.1±0.4	−10.2 ±1.1	85.1±0.8
mal^{2-}	4.95±0.03	83.5±0.4	−9.17±1.40	86.2±0.9
$acac^-$[a]	4.54±0.03[b]	74.9	−38.5	86.4
bpdo[c]	3.06±0.03[b]	79.6	−26.1	87.4

a) From Ref. 1. b) This work. c) From Ref. 2.

molecular mechanism. In the presence of Na_2ox or Na_2mal, the spectral changes were slightly accelerated by formation of a small amount of $[Cr(ox\ or\ mal)_2(bpdo)]^-$ as confirmed by column chromatography of the reaction products. The rates for the ox and mal complexes differ little from those for $[Cr(acac)(bpdo)_2]^{2+}$ and $[Cr(bpdo)_3]^{3+}$ as Table 3 shows. The rate seems to be independent of the charge of complex, but depend on the steric factor. The ox complex, where both *lel*$_2$ and *lel·ob* forms have the least crowded structure of these four complexes, has the largest k^{i}_{obsd}, although the difference in rate is rather small.

As Fig. 9 shows, there is a good linear relationship between the activation enthalpies and entropies for the isomerization of $[Cr(L)(bpdo)_2]^{n+}$. It has been proposed that a set of related reactions should proceed via the same mechanism when there is a linear relationship between the activation enthalpies and entropies.[13,14] Thus the isomerizations ($\delta \rightleftarrows \lambda$) of $[Cr(L)(bpdo)_2]^{n+}$ will be isokinetic and proceed by the same intramolecular mechanism.

The values of k^{r}_{obsd} for racemization are given in Table 4, and the activation parameters in Table 5 together with those of the related bpdo complexes. The racemizations of the present complexes were also independent of concentrations of H^+ and the free bpdo ligand, suggesting an intramolecular mechanism too. The small negative values for the activation entropy will also indicate such a mechanism. The rate and the activation parameters for the mal complex are similar to those for the racemization of $[Cr(acac)(bpdo)_2]^{2+}$ [1] and $[Cr(bpdo)_3]^{3+}$.[2,3] In our previous studies, the racemizations of $[Cr(acac)(bpdo)_2]^{2+}$ and $[Cr(bpdo)_3]^{3+}$ were proposed to proceed by an intramolecular twist mechanism from a comparison of the activation parameters with those for other complexes such as $[Cr(phen)_3]^{3+}$ (phen=1,10-phenanthroline).[15,16] Thus the mal complex is supposed to racemize by the same mechanism. On the other hand, the racemization of $[Cr(ox)(bpdo)_2]^+$ is very rapid compared to those of the other bpdo complexes. Extensive studies have been reported on racemizations of oxalato complexes of chromium(III).[17] For example, $[Cr(ox)_3]^{3-}$ racemizes via a one-ended dissociation (bond-rupture) of oxalate chelate rings,[16,17] and $[Cr(ox)(phen)_2]^+$ does via a twist mechanism.[16,18] The activation parameters for $[Cr(ox)(bpdo)_2]^+$ are similar to those for $[Cr(ox)_3]^{3-}$ ($\Delta H^{\neq}$=66.5 kJ mol^{-1}, $\Delta S^{\neq}$=−76 J K^{-1} mol^{-1})[16] rather than those for $[Cr(ox)(phen)_2]^+$ ($\Delta H^{\neq}$=72.9 kJ mol^{-1}, $\Delta S^{\neq}$=−69 J K^{-1} mol^{-1}),[16] indicating a mechanism via bond-rupture of the ox chelate ring for the present ox complex. However, the racemizations of $[Cr(ox)(bpdo)_2]^+$ as well as $[Cr(ox)(phen)_2]^+$ are

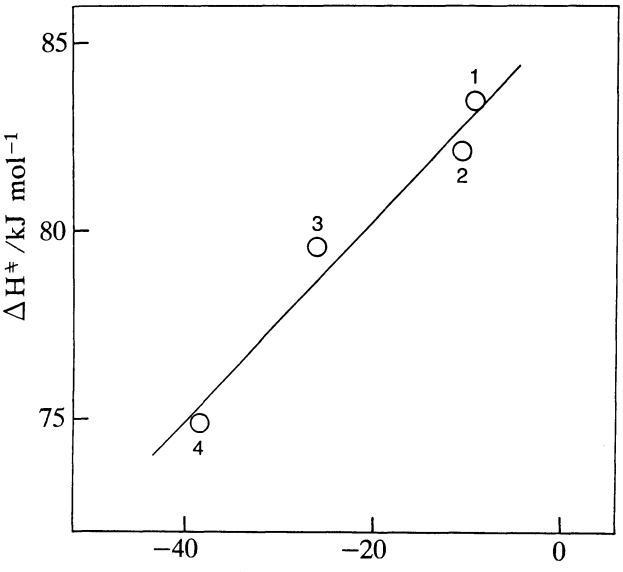

Fig. 9. The correlation between the activation enthalpy and entropy for the isomerization of $[Cr(L)(bpdo)_2]^{n+}$ in water; L=mal^{2-} (1), ox^{2-} (2), bpdo (3), and acac$^-$ (4).

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

t/°C	k^{r}_{obsd}/10^{-4} s^{-1}	t/°C	k^{r}_{obsd}/10^{-4} s^{-1}
	L=ox^{2-}		
10.0	4.80±0.03	20.0$^{b)}$	13.0±0.2
15.0	8.12±0.05	25.0	22.0±0.3
20.0	13.2±0.2	25.0$^{a)}$	22.1±0.2
20.0$^{a)}$	13.3±0.2	25.0$^{b)}$	21.9±0.2
	L=mal^{2-}		
20.0	0.372±0.003	35.0	1.84±0.02
25.0	0.642±0.002	35.0$^{a)}$	1.87±0.02
30.0	1.14 ±0.01	35.0$^{b)}$	1.84±0.02
30.0$^{a)}$	1.17 ±0.02	40.0	3.17±0.03
30.0$^{b)}$	1.12 ±0.02		

a) In 0.1 mol dm^{-3} HCl. b) In 0.05 mol cm^{-3} bpdo.

Table 5. Racemization Rate Constants at 25.0 °C and Activation Parameters for $[Cr(L)(bpdo)_2]^{n+}$ in Water

L	k^{r}_{obsd}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{298.2}$
	10^{-4} s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
ox^{2-}	22.0 ±0.3	68.2±0.9	−67.0±3.0	88.2±1.8
mal^{2-}	0.642±0.002	79.0±1.1	−60.2±3.4	97.0±2.5
acac$^{-a)}$	1.51	82.4	−41.7	94.8
bpdo$^{b)}$	1.13	76.5	−64.0	95.6

a) From Ref. 1. b) From Ref. 2.

independent of concentration of H^+, while that of $[Cr(ox)_3]^{3-}$ is dependent.[17] The racemization of $[Cr(ox)_2(phen)]^-$ depends on concentration of H^+.[19] Broomhead et al. proposed that its mechanism involves two intramolecular processes, twist and bond-rupture of ox chelate rings, and that the former process is independent of concentration of H^+.[20] Thus monooxalato complexes of chromium(III) such as $[Cr(ox)(bpdo)_2]^+$ or $[Cr(ox)(phen)_2]^+$ would racemize by a twist mechanism without rupture of the Cr–ox bond. Studies with molecular models suggest that the *lel·ob* form of the present ox complex racemizes very easily by twisting around the pseudo-C_3 axis of the complex. The rapid racemization of $[Cr(ox)(bpdo)_2]^+$ will be attributable to the less crowded structure than those of the other bpdo complexes containing a larger chelate ring than the planar five-membered ox chelate one.

References

1) H. Kanno, T. Shimotori, S. Utsuno, and J. Fujita, *Chem. Lett.*, **1983**, 939; H. Kanno, S. Utsuno, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3443 (1984).

2) H. Kanno and J. Fujita, *Bull. Chem. Soc. Jpn.*, **60**, 589 (1987).

3) H. Kanno, J. Yamamoto, S. Murahashi, S. Utsuno, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **64**, 2936 (1991).

4) A. R. Al-Karaghouli, R. O. Day, and J. S. Wood, *Inorg. Chem.*, **17**, 3702 (1978); N. W. Alcock and M. M. Roberts, *Acta Crystallogr., Sect. C*, **43**, 476 (1987).

5) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).

6) I. Murase, *Nippon Kagaku Zasshi*, **77**, 682 (1956).

7) H. Kanno, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **52**, 1408 (1979).

8) K. R. Butler and M. R. Snow, *J. Chem. Soc., Chem. Commun.*, **1971**, 550; *J. Chem. Soc., Dalton Trans.*, **1976**, 251.

9) K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **45**, 1755 (1972).

10) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883.

11) J. C. Chang, *J. Inorg. Nucl. Chem.*, **30**, 945 (1968).

12) H. Kanno, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **52**, 761 (1979).

13) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); J. E. Leffler and W. H. Graham, *J. Phys. Chem.*, **63**, 687 (1959); B. M. Graybill and J. E. Leffler, *ibid.*, **63**, 1461 (1959).

14) J. A. Broomhead and F. P. Dwyer, *Aust. J. Chem.*, **16**, 51 (1963); J. A. Broomhead, *ibid.*, **16**, 186 (1963).

15) N. A. P. Kane-Maguire and S. A. Edwards, *J. Inorg. Nucl. Chem.*, **38**, 1037 (1976).

16) G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, **16**, 929 (1977); G. A. Lawrance and S. Suvachittanont, *Inorg. Chim. Acta*, **32**, L13 (1979).

17) K. V. Krishnanurty and G. M. Harris, *Chem. Rev.*, **61**, 213 (1961); N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).

18) J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, **5**, 955 (1971).

19) J. A. Broomhead, *J. Inorg. Nucl. Chem.*, **27**, 2049 (1965).

20) J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, **9**, 1243 (1970).