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

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Both racemic and optically active $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ (bpdo=2,2′-bipyridine *N,N′*-dioxide) were found to crystallize in the $lel_2 \cdot ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$ isomer. The complexes isomerized spontaneously to the $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$ isomer upon dissolution in water with a rapid absorption spectral change, and then racemized ($\Delta \rightleftarrows \Lambda$) slowly. The rate constant for isomerization was 5.33×10^{-3} s^{-1} at 303.2 K, and that for racemization 1.93×10^{-4} s^{-1} at the same temperature. An intramolecular conformational inversion of the bpdo chelate ring ($\delta \rightleftarrows \lambda$) and an intramolecular twist mechanism were proposed for the isomerization and the racemization of the complex, respectively. Neither isomerization nor racemization was observed for $[Cr(en)(bpdo)_2]^{3+}$ in aqueous solution.

2,2′-Bipyridine *N,N′*-dioxide (bpdo) forms a skew seven-membered chelate ring upon coordination to a metal ion.[1,2] The skew chelate ring of bpdo was confirmed by X-ray analysis of $[La(bpdo)_4](ClO_4)_3$.[3] Since the skew conformation can exist in a pair of enantiomers, δ and λ as shown in Fig. 1, a tris-bpdo complex has four possible racemic pairs of diastereomers. By analogy with the stereoisomerism in $[M(en)_3]^{n+}$ (en= ethylenediamine),[4] these diastereomers can be designated as 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. reported that the dominant isomer 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.[5] They also suggested that a rapid chelate ring interconversion ($\delta \rightleftarrows \lambda$) seems unlikely because of the anticipated high barrier to chelated bpdo interconversion.[5]

In previous papers, we reported that $[Cr(bpdo)_3]^{3+}$ [6] and $[Cr(mbdo)_3]^{3+}$ [7] (mbdo=3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide) give one and three racemic pairs of diastereomers, respectively, and that the former complex racemizes spontaneously in aqueous solution. These results indicate that the bpdo chelate ring is flexible and changes its conformation ($\delta \rightleftarrows \lambda$) 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.[7] Recently, we also found that both racemic and $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ (acac=acetylacetonate(1−)) crystallize in the lel_2 ($\Delta(\lambda\lambda)$, $\Lambda(\delta\delta)$) isomer, but isomerize spontaneously to the $lel \cdot ob(\Delta(\lambda\delta), \Lambda(\delta\lambda))$ isomer and racemize in aqueous solution.[8] From kinetic studies, the isomerization of $[Cr(acac)(bpdo)_2]^{2+}$ was suggested to occur by intramolecular conformational inversion ($\delta \rightleftarrows \lambda$) of the bpdo chelate ring.[8] This result indicates that in some metal complexes, a favorable bpdo chelate ring conformation in a crystal is different from that in solution. Such a conformational change due to environment is known for $[Cr(en)_3]^{3+}$,[9] but the kinetics of conformational inversion of the en chelate ring can not be studied because of the very rapid interconversion in solution. This paper reports spontaneous isomerization of the tris-bpdo chromium(III) complex in aqueous solution sudied by absorption and circular dichroism (CD) spectroscopy. This paper also reports the results of reinvestigation on racemization of this complex.[6]

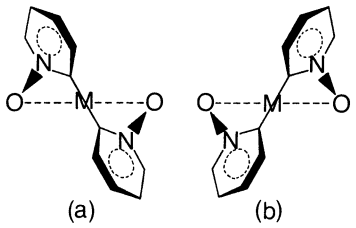

Fig. 1. The conformation of bpdo, (a) δ- and (b) λ-skew form.

Experimental

Materials. The bpdo ligand was prepared according to the literature.[10] The complexes, $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ and $[Cr(en)(bpdo)_2](ClO_4)_3 \cdot 1.5H_2O$ were prepared and resolved by the method reported previously.[6]

Kinetic Runs. Both racemic and optically active $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution show a rapid absorption spectral change. The change in absorbance at 620 nm was continuously recorded on a Shimadzu MPS-50L spectrophotometer in the temperature range of 15.0 to 35.0 °C using a 1 cm quartz cell with a cell jacket to maintain the temperature constant within ±0.1 °C. The pH and ionic strength (I=0.1) of solutions were adjusted with an aqueous solution of NaCl-HCl. Because of insufficient solubility of $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in water for the measurement (ca. 1.5 mmol dm^{-3} at 20 °C), the complex was converted into the chloride by the following method. A mixture of a Dowex 1-x8 anion exchanger in the chloride form (1 g) and an aqueous solution of NaCl (0.1 mol dm^{-3}, 20 cm^3) was kept at a constant temperature in a water bath. To the mixture, the finely ground complex (ca. 0.13 g) 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. The complex concentrations were in the range of 5.0 to 7.6 mmol dm^{-3}. The rate of spectral change obeyed the first order kinetic law and the observed rate constant (k_{obsd}) is expressed as follows:

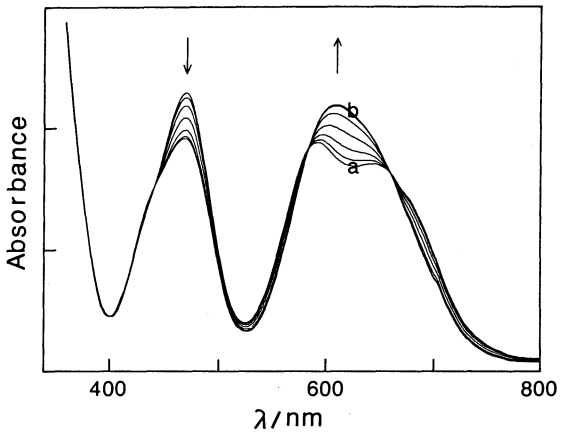

Fig. 2. Absorption spectral change in the visible region of $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution at 15.0°C. Trends of the spectral change with time are shown by arrows. Reaction time (min): 2.5(a), 4, 8, 16, 32, 64, ∞(b).

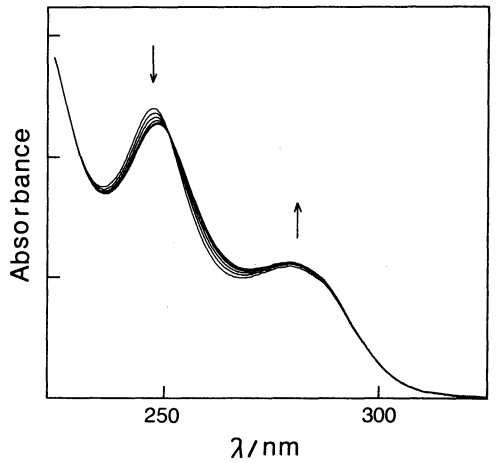

Fig. 3. Absorption spectral change in the ultraviolet region of $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution at 18.0°C. Reaction time (min): 2, 4, 8, 16, 32, ∞.

$$k_{obsd} = -\ln[(A_t - A_\infty)/(A_0 - A_\infty)]/t,$$

where A's are absorbances at the time denoted by suffixes. For a comparison, the measurements were also carried out for the perchlorate of the complex without exchanging it into the chloride. The rate observed for the perchlorate agreed with that for the chloride within the experimental error.

A decrease in optical activity at 589 nm of $(-)_{589}$-$[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution was observed by similar procedures as described above using a Union PM-101 digital polarimeter and a 5 cm quartz cell. The perchlorate of the complex was used for the measurements. The temperatures and the complex concentrations were in the range of 25.0 to 45.0 °C and 1.0 to 1.5 mmol 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). 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.

For $[Cr(en)(bpdo)_2](ClO_4)_3$, the same experiments were carried out as those for $[Cr(bpdo)_3]^{3+}$ in the dark so as to avoid photoinduced reactions.[6] Neither absorption spectral change nor loss of optical activity was observed in acidic solution. However, the complex in neutral aqueous solution showed a slight decrease in absorbance (<1% at 530 nm) after 2 h. The resulting solution contained a very small amount of a hydrolyzed product as detected by column chromatography.

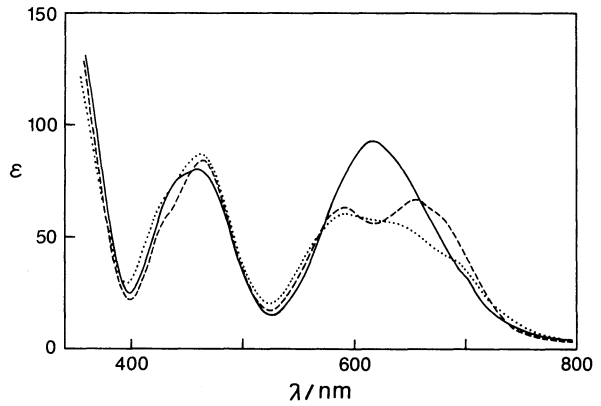

Fig. 4. Absorption spectra of three diastereomers of $[Cr(rac\text{-}mbdo)_3]^{3+}$ in the visible region in aqueous solution; *lel*$_3$ (——), *lel*$_2$·*ob* (----), and *lel*·*ob*$_2$ (·····).[7]

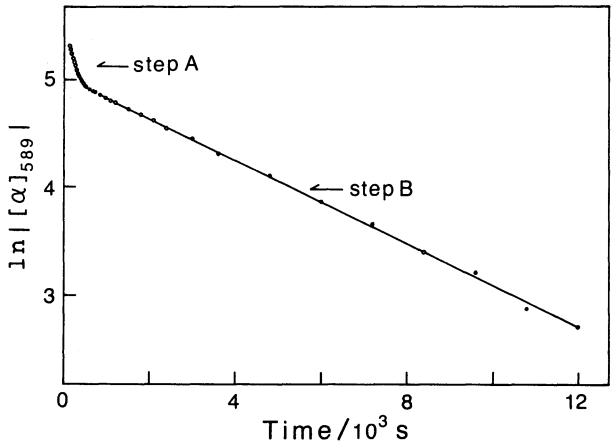

Fig. 5. Decrease in optical rotation (at 589 nm) of $(-)_{589}$-$[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ with time in aqueous solution at 30.0°C. [Complex]=1.17×10^{-3} mol dm^{-3}; I=0.1.

Other Measurements. Absorption and circular dichroism spectra were recorded on a Shimadzu MPS-50L spectrophotometer and a Jasco J-500 spectropolarimeter, respectively. Optical rotations were measured with a Union PM-101 digital polarimeter.

Results and Discussion

Properties of the Complexes. Quagliano et al. first prepared bpdo complexes with a variety of metal ions including chromium(III).[2] As we reported previously,[6] $[Cr(bpdo)_3]^{3+}$ gives only one racemic pair of diastereomers of four possible ones. No indication for the formation of the other isomers was found by SP-Sephadex column chromatography. The optical resolution of the complex[6] was achieved by a chemical

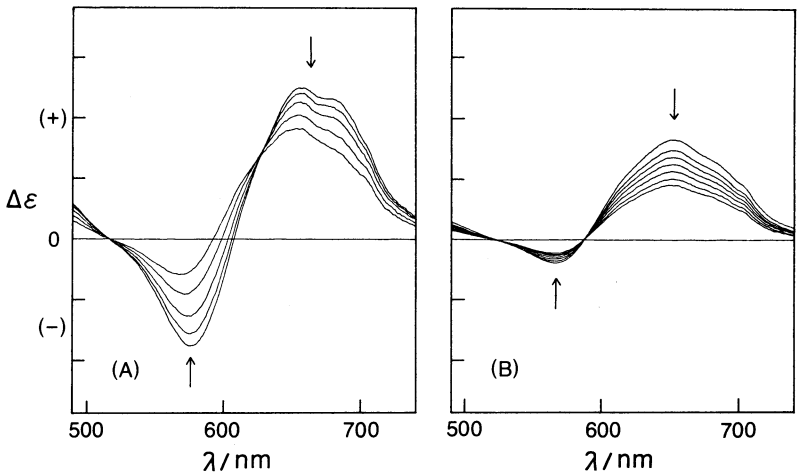

Fig. 6. CD spectral change in the region of the first absorption band of $(-)_{589}$-$[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution at 15.0°C. Trends of the spectral change with time are shown by arrows. Reaction time (min): (A): 2.5, 4, 7, 13, 25; (B): 50, 80, 110, 140, 170, 200, 230.

method using $(+)_{589}$-[Co(L-cysteinesulfinato(2−)-$S,N)_3]^{3-}$.[11] The optically active complex loses gradually its activity in aqueous solution at room temperature.

Both racemic and optically active $[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution show a rapid absorption spectral change with isosbestic points at 660, 584, 442, and 251 nm as shown in Figs. 2 and 3. The complexes are not hydrolyzed during the spectral change, no hydrolyzed product such as $[Cr(bpdo)_2(H_2O)_2]^{3+}$ [12] being detected on column chromatograms. These results suggest that the spectral change is caused by isomerization between two isomers of four possible ones of the complex. As Fig. 2 shows, the splitting first absorption band ($^4T_{2g} \leftarrow {}^4A_{2g}$) around 610 nm becomes a single peak with passage of time. All of the possible isomers of the complex have a $[CrO_6]$ chromophore in which the coordinated oxygen atoms are the same kind. However, actual symmetries of the lel_3 and ob_3 isomers will be D_3, and those of the $lel_2 \cdot ob$ and $lel \cdot ob_2$ isomers will lower to C_2. In the fields of D_3 and C_2 symmetries, the first absorption band of an octahedral parentage ($^4T_{2g}$) will split into two ($^4A_1$, ^4E) and three (2^4A, ^4B) components, respectively.[13] Figure 4 shows the absorption spectra of the isomers of $[Cr(rac\text{-mbdo})_3]^{3+}$.[7] The complex gives three racemic pairs of diastereomers, the lel_3, $lel_2 \cdot ob$, and $lel \cdot ob_2$ isomers. The ob_3 isomer will not be formed because of its extremely crowded structure.[6,7] By comparing the spectra in Figs. 2 and 4, it is seen that spectra a and b of the bpdo complex quite resemble those of the $lel_2 \cdot ob$ and lel_3 isomers of the mbdo complex, respectively. Thus the isomers corresponding to spectra a and b in Fig. 2 can be assigned to have the $lel_2 \cdot ob$ and lel_3 structures, respectively, and it is concluded that the spectral change in the bpdo complex is caused by isomerization of the complex, $lel_2 \cdot ob \rightleftarrows lel_3$. In the ultraviolet region, the spectra of the

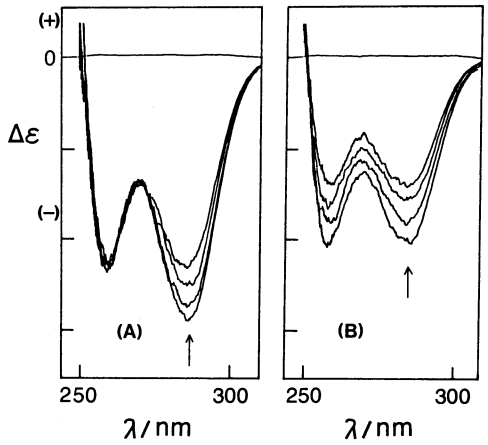

Fig. 7. CD spectral change in the ultraviolet region of $(-)_{589}$-$[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ in aqueous solution at 18.0°C. Reaction time (min): (A): 2, 5, 11, 23; (B): 50, 80, 110, 140.

three isomers of the mbdo complex are similar.[7] The spectral change in the bpdo complex is also very small as shown in Fig. 3. Molecular models indicate that the $lel_2 \cdot ob$ isomer of the bpdo complex isomerizes to the lel_3 one without difficulty and vice versa, since the bpdo chelate ring is flexible and changes its comformation, $\delta \rightleftarrows \lambda$, very easily.[6-8]

As shown in Fig. 5, an aqueous solution of $(-)_{589}$-$[Cr(bpdo)_3](ClO_4)_3 \cdot 1.5H_2O$ loses the optical activity in two steps with different rates, the first rapid (step A) and the subsequent slow (step B) steps. In the former step, the decrease in activity accompanies the absorption spectral change stated above, while no spectral change was observed in the latter step. These results suggest that step A involves the isomerization reaction between the diastereomers, $lel_2 \cdot ob \rightleftarrows lel_3$, and step B the racemization reaction between the enantiomers, $\Delta \rightleftarrows \Lambda$, of the complex. Figures 6 and 7 show the CD

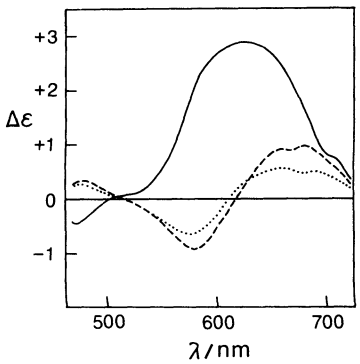

Fig. 8. CD spectra of three diastereomers of $(-)_{589}$-[Cr(rac-mbdo)$_3$]$^{3+}$ in the region of the first absorption band in aqueous solution; $lel_3(\Lambda(\lambda\lambda\lambda))$ (——), $lel_2\cdot ob(\Lambda(\lambda\lambda\delta))$ (----), and $lel\cdot ob_2(\Lambda(\delta\lambda\lambda))$ (·····).[7]

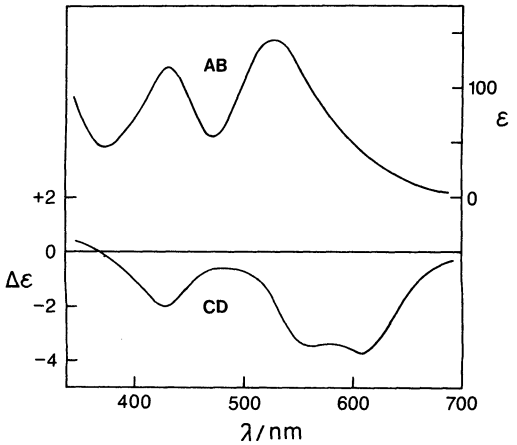

Fig. 9. Absorption and CD spectra in the visible region of $(+)_{589}$-[Cr(en)(bpdo)$_2$](ClO$_4$)$_3\cdot$H$_2$O in 10^{-2} mol dm^{-3} hydrochloric acid.

spectral change of the $(-)_{589}$-isomer in the region of the first absorption band and in the ultraviolet region, respectively. In both regions, the spectrum varies in two steps. In the first rapid step (Figs. 6 (A) and 7 (A)), the spectrum shows a change in both magnitude and pattern and accompanies the absorption spectral change, while in the subsequent slow step (Figs. 6 (B) and 7 (B)), it only shows a decrease in magnitude and neither change in CD pattern nor in absorption spectrum was observed. In the region of the first absorption band, the complex exhibits two CD components of similar strength with opposite signs at the beginning of the reaction, but the negative component diminishes more rapidly than the positive component does. Figure 8 shows the CD spectra of the three isomers of $(-)_{589}$-[Cr(*rac*-mbdo)$_3$]$^{3+}$, $lel_3(\Lambda(\lambda\lambda\lambda))$, $lel_2\cdot ob(\Lambda(\lambda\lambda\delta))$, and $lel\cdot ob_2(\Lambda(\delta\lambda\lambda))$, in the region of the first absorption band.[7] Both isomers of the $lel_2\cdot ob$ and $lel\cdot ob_2$ show two CD components of similar strength with opposite signs, while the lel_3 one exhibits only one positive CD component. The CD spectra of these isomers suggest that the CD spectral change of the bpdo complex in the first rapid step is caused by isomerization of the complex, $lel_2\cdot ob(\Lambda(\lambda\lambda\delta))\rightleftarrows lel_3(\Lambda(\lambda\lambda\lambda))$. Although it is not clear from the CD spectra whether the initial isomer of the bpdo complex is $lel_2\cdot ob$ or $lel\cdot ob_2$, it is assigned to the $lel_2\cdot ob$ isomer from the previous absorption spectral and kinetic studies (vide post). Thus it is concluded that $(-)_{589}$-[Cr(bpdo)$_3$](ClO$_4$)$_3\cdot$1.5H$_2$O crystallizes in the $\Lambda(\lambda\lambda\delta)(lel_2\cdot ob)$ structure and rapidly isomerizes in aqueous solution to the $\Lambda(\lambda\lambda\lambda)(lel_3)$ structure and then slowly racemizes, $\Lambda\rightleftarrows\Lambda$.

The [Cr(en)(bpdo)$_2$]$^{3+}$ complex[6] gives only one pair of diastereomers which was resolved by a chemical method using $(-)_{589}$-[As(1,2-benzenediolate(2−))$_3$]$^-$,[14] although the complex can have three possible racemic pairs of diastereomers, lel_2, $lel\cdot ob$, and ob_2. Both racemic and $(+)_{589}$-[Cr(en)(bpdo)$_2$](ClO$_4$)$_3$ show no absorption and CD spectral changes in acidic solution (pH ca. 2) at room temperature, but they are slowly hydrolyzed in neutral aqueous solution (see Experimental). The slow loss of optical activity of the complex described in our previous paper[6] is attributable to the hydrolysis of the complex. Figure 9 shows the absorption and CD spectra of $(+)_{589}$-[Cr(en)(bpdo)$_2$]$^{3+}$ in the visible region recorded in this work. In the region of the first absorption band, the complex exhibits two positive CD components. In our previous work, the CD component on the low energy side could not be observed because it lies outside the region measurable by our instrument.[6] The corrected CD spectral data of the $(+)_{589}$-isomer in the visible region are as follows in $\tilde{\nu}$/cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1}); 16500 (−3.72), 17860 (−3.49), and 23360 (−1.99). The absolute configuration of the complex including chirality of bpdo could not be assigned from the CD spectrum, because its pattern is quite different from those of analogous complexes.[6] However, examination with molecular models indicates that in the $lel\cdot ob$ structure of the complex, the amino or methylene protons of the puckered en chelate ring comes very close to the pyridine ring of the *ob*-form bpdo ligand, whereas there is no such proximity among the ligands in the lel_2 structure. The ob_2 isomer will not be formed because of its extremely crowded structure. Thus [Cr(en)(bpdo)$_2$](ClO$_4$)$_3$ will be stabilized in the lel_2 structure and shows no isomerization in solution. The complex does not racemize either under the same conditions as for [Cr(bpdo)$_3$]$^{3+}$ and [Cr(acac)(bpdo)$_2$]$^{2+}$ described below. Although the reason for this remains unknown at the moment, racemization of the bpdo complex seems to take place with conformational inversion of the bpdo chelate ring, i.e. the isomerization of the complex. The stereoselective formation of lel_2-[Cr(en)(bpdo)$_2$]$^{3+}$ is in contrast to that of [Cr(acac)(bpdo)$_2$](ClO$_4$)$_2$ which was found to crystallize in the lel_2 isomer but isomerize to the $lel\cdot ob$ one and racemize in aqueous solution.[8] Molecular models indicate that

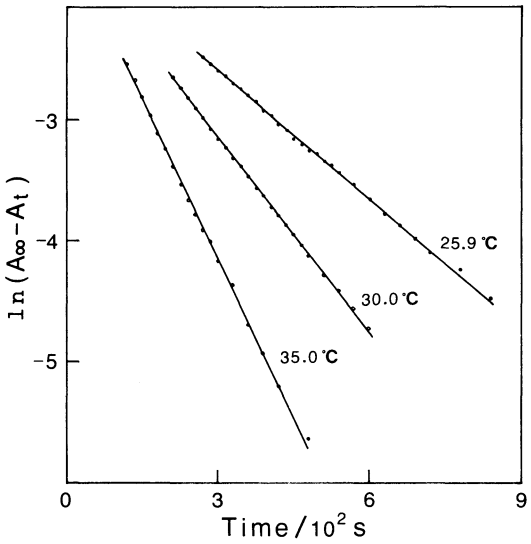

Fig. 10. Plots of $\ln(A_\infty - A_t)$ vs. time for change of absorbance (at 620 nm) of $[Cr(bpdo)_3]^{3+}$ in aqueous solution. [complex]=6.45×10^{-3} mol dm^{-3}; I=0.1.

there is no extreme proximity between the acac and bpdo ligands in these isomers. The difference in reactivity between the en and acac bis-bpdo complexes will be also attributable to such steric conditions. Recently, we found that the conformations of bpdo in mixed-ligand chromium(III) complexes are greatly influenced by other ligands in the complex.[6,8,15] For example, $[Cr(acac)_2(bpdo)]^+$ gives only a $lel(\Delta(\lambda), \Lambda(\delta))$ isomer,[8] whereas $[Cr(bpy)_2(bpdo)]^{3+}$ (bpy=2,2′-bipyridine) only an $ob(\Delta(\delta), \Lambda(\lambda))$ isomer.[15] Thus the bpdo chelate ligand changes its conformation very easily depending upon steric conditions in a complex.

Kinetics of Isomerization and Racemization of $[Cr(bpdo)_3]^{3+}$. The rate of isomerization of $[Cr(bpdo)_3]^{3+}$ in aqueous solution, $lel_2 \cdot ob \rightleftarrows lel_3$, was followed by monitoring the change in absorbance at 620 nm with time under the conditions described in Experimental part. As Fig. 10 shows, the rate of the spectral change obeyed the first order kinetic law for at least four half-lives, 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 rate for the optically active complex agreed with that for the racemate within the experimental error. The values of k_{obsd} are listed in Table 1. Arrhenius treatment of log(k_{obsd}) vs. T^{-1} yielded an activation energy of (82.1±1.3) kJ mol^{-1} and Eyring treatment of log(k_{obsd}/T) vs. T^{-1} gave an activation enthalpy of (79.6±1.3) kJ mol^{-1} and an activation entropy of (−26.1± 4.3) J K^{-1} mol^{-1}. The rate was independent of concentrations of H^+ and the free ligand (bpdo). Hence it is suggested that the isomerization proceeds by an intramolecular mechanism. In a previous paper,[8] we have reported that $\Delta(\lambda\lambda)(lel_2)$-$[Cr(acac)(bpdo)_2]^{2+}$ isomerized to the $\Delta(\lambda\delta)(lel \cdot ob)$ isomer at a rate 3.31×10^{-3} s^{-1} (22.0 °C), and that the activation energy, enthalpy, and entropy values were 77.3 kJ mol^{-1}, 74.9 kJ mol^{-1}, and −38.5 J K^{-1} mol^{-1}, respectively. The rate and kinetic parameters of $[Cr(bpdo)_3]^{3+}$ are similar to those of $[Cr(acac)(bpdo)_2]^{2+}$ ($\lambda\lambda \rightleftarrows \lambda\delta$). Thus the isomerization reactions of these two complexes would proceed by the same mechanism, and the isomerization of $[Cr(bpdo)_3]^{3+}$ will not involve the reaction, $lel \cdot ob_2(\Delta(\lambda\delta\delta)) \rightleftarrows lel_3(\Delta(\lambda\lambda\lambda))$, in which simultaneous inversion of two bpdo chelate rings $\delta\delta \rightleftarrows \lambda\lambda$ takes place.

Table 1. Rate Constants for the Isomerization of $[Cr(bpdo)_3]^{3+}$ in Aqueous Solutions (I=0.1[a])

t/°C	$k_{obsd}\times10^3$/s^{-1}	t/°C	$k_{obsd}\times10^3$/s^{-1}
15.0	0.962±0.004[b]	30.0	5.33±0.03
18.5	1.43±0.01	30.0[c]	5.37±0.05
22.0	2.16±0.01	30.0[d]	5.30±0.04
22.0[c]	2.15±0.01	30.0[e]	5.34±0.06
22.0[d]	2.13±0.02	30.0[f]	5.36±0.06
22.0[e]	2.15±0.01	30.0[g]	5.36±0.05
22.0[f]	2.13±0.03	35.0	8.66±0.09
25.9	3.51±0.03		

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} dpdo. e) For $(-)_{589}$-isomer. f) For the perchlorate of the complex (see Experimental). g) For $(+)_{589}$-isomer.

Table 2. Rate Constants for the Racemization of $(-)_{589}$-$[Cr(bpdo)_3]^{3+}$ in Aqueous Solutions (I=0.1[a])

t/°C	$k_{obsd}\times10^4$/s^{-1}	t/°C	$k_{obsd}\times10^4$/s^{-1}
25.0	1.13±0.02[b]	35.0	3.20±0.02
29.8[c]	1.90±0.01	39.8[d]	5.23±0.04
30.0	1.93±0.02	40.0	5.25±0.03
30.0[d]	1.93±0.03	40.0[c]	5.21±0.03
30.0[e]	1.91±0.02	45.0	8.38±0.06
30.0[f]	1.93±0.03	45.0[d]	8.41±0.05

a) Ionic strength adjusted with NaCl. b) Errors are standard deviations estimated by least squares. c) In 0.05 mol dm^{-3} dpdo. d) In 0.1 mol dm^{-3} HCl. e) For $(+)_{589}$-isomer. f) For the chloride of the complex prepared with a Dowex anion exchanger (see Experimental).

Our previous study on racemization of $[Cr(bpdo)_3]^{3+}$ in aqueous solution[6] was reinvestigated in this paper. The rate of loss of activity of $(-)_{589}$-$[Cr(bpdo)_3]^{3+}$ was followed by monitoring the change in optical rotation at 589 nm with time under the conditions described in Experimental part. As Fig. 5 shows, the rate in step B obeyed the first order kinetic law 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. The values of k_{obsd} are given in Table 2. The rate of racemization was independent of concentrations of H^+ and the free ligand (bpdo). Hence the racemization ($\Delta \rightleftarrows \Lambda$) will also proceed by an intramolecular mechanism. The estimated values of activation energy, enthalpy, and entropy are (79.0±0.3)

kJ mol^{-1}, (76.5±0.3) kJ mol^{-1}, and (−64.0±1.0) J K^{-1} mol^{-1}, respectively, which agree with those estimated in our previous work.[6] From a comparison of these kinetic parameters with those of other complexes such as $[Cr(phen)_3]^{3+}$,[16] the racemization of $[Cr(bpdo)_3]^{3+}$ is suggested to proceed via an intramolecular twist mechanism. The small negative activation entropy value for the racemization of $[Cr(bpdo)_3]^{3+}$ seems to be consistent with such a mechanism.[17] In our previous work,[8] the rate of racemization of $(-)_{589}$-$[Cr(acac)(bpdo)_2]^{2+}$ in aqueous solution was found to be 1.51×10^{-4} s^{-1} at 25.0 °C with the activation energy, enthalpy, and entropy of 84.8 kJ mol^{-1}, 82.4 kJ mol^{-1}, and −41.7 J K^{-1} mol^{-1}, respectively. The rate and kinetic parameters of $[Cr(bpdo)_3]^{3+}$ are very similar to those of $[Cr(acac)(bpdo)_2]^{2+}$, and the racemization reactions of these two complexes would proceed by the same mechanism. For the intramolecular racemization of a tris(chelate)-type complex, several different twist mechanisms have been proposed.[18] However, it is difficult to determine which mechanism is the most probable for the present complexes.

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References

1) R. G. Garvey, J. N. Nelson, and R. O. Ragsdale, *Coord. Chem. Rev.*, **3**, 375 (1968); N. M. Karayannis, L. L. Pytlewski, and C. M. Mikulski, *ibid.*, **11**, 93 (1973); N. M. Karayannis, A. N. Speca, D. E. Chasan, and L. L. Pytlewski, *ibid.*, **20**, 37 (1976).

2) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963); A. Vinciguerra, P. G. Simpson, Y. Kakiuti, and J. V. Quagliano, *ibid.*, **2**, 286 (1963).

3) A. R. Al-Karaghouli, R. O. Day, and J. S. Wood, *Inorg. Chem.*, **17**, 3702 (1978).

4) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

5) I. Bertini, D. Gatteschi, and L. J. Wilson, *Inorg. Chim. Acta*, **4**, 629 (1970).

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

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

8) 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).

9) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842, 1362 (1968); K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

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

11) L. S. Dollimore and R. D. Gillard, *J. Chem. Soc., Dalton Trans.*, **1973**, 933.

12) H. Kanno, unpublished work; absorption spectral data of $[Cr(bpdo)_2(H_2O)_2]^{3+}$ prepared by aquation of $[CrCl_2(bpdo)_2]Cl\cdot 3H_2O$ in 0.01 mol dm^{-3} hydrochloric acid λ/nm (ε/mol^{-1} dm^3 cm^{-1}); 606 (48.7), 441 (70.0), 280 (19500), 250 (35300), and 218 (60400). The preparation of the dichloro complex will be described elsewhere.

13) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley-Interscience, New York (1971).

14) R. F. Weinland and J. Heinzler, *Chem. Ber.*, **52**, 1316 (1919); G. E. Ryschkewitsch and J. M. Garrett, *J. Am. Chem. Soc.*, **90**, 7234 (1968).

15) H. Kanno, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **53**, 2881 (1980); H. Kanno, S. Utsuno, and J. Fujita, *ibid.*, **59**, 1293 (1986).

16) N. A. P. Kane-Maguire and S. A. Edwards, *J. Inorg. Nucl. Chem.*, **38**, 1037 (1976); G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, **16**, 929 (1977).

17) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 6411 (1972); M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *ibid.*, **95**, 4537 (1973).

18) See for example: F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley-Interscience, New York (1967); J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971); N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).