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Preparation and Resolution of a Series of Chromium(III) Complexes Containing 2,2′-Bipyridyl *N,N′*-Dioxide and Ethylenediamine

Hideaki Kanno, Kazuo Kashiwabara, and Junnosuke Fujita*

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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A series of chromium(III) complexes of the type, $[Cr(bpdo)_n(en)_{3-n}]^{3+}$ was obtained by preparing two new complexes, $n=1$ and 2, where bpdo denotes 2,2′-bipyridyl *N,N′*-dioxide. Each of the bpdo complexes gave only one pair of enantiomers, which were resolved by an SP-Sephadex column chromatographic or a chemical method. The circular dichroism spectra of the resolved complexes were compared with those of the related complexes of the known absolute configuration. The $[Cr(bpdo)_3]^{3+}$ complex in water racemizes spontaneously in dark. The rate is independent of the concentrations of the complex, acid, and the free ligand, and an intramolecular racemization mechanism is suggested.

Although a number of metal complexes with 2,2′-bipyridyl *N,N′*-dioxide(bpdo) have been known,[1] no optically active complexes have ever been obtained. This paper is concerned with the preparation and properties of optically active chromium(III) complexes containing bpdo.

The ligand bpdo forms a skew seven-membered chelate ring upon coordination. The skew conformer can exist in a pair of enantiomers which can be designated by δ and λ, as shown in Fig. 1. Simpson *et al.*[2] and Vinciguerra *et al.*[3] prepared first bpdo complexes with a variety of metal ions including chromium(III) and suggested that the bpdo moiety in metal complexes takes the skew conformation on the basis of IR spectra. ^{1}H-NMR spectra of $[M(bpdo)_3]^{2+}$ ($M=Co^{2+}$ and Ni^{2+}) were also best interpreted by assuming the skew conformation of the ligand.[4] A tris-type complex with the chiral conformers of bpdo results theoretically in four diastereomers, each of which has a pair of enantiomers. In this paper, we describe such optical isomerism in the chromium(III) complexes on the basis of the circular dichroism (CD) spectra.

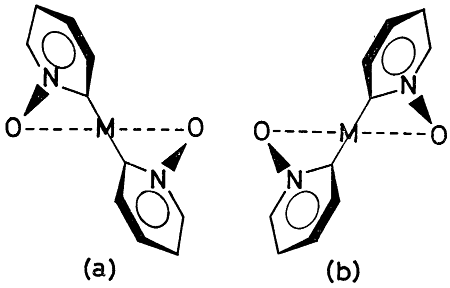

Fig. 1. The conformation of bpdo, (a) δ- and (b) λ-skew form.

Experimental

Preparation and Resolution of the Complexes. The chromium(III) complexes containing ethylenediamine (en) are photo-sensitive to occur hydrolysis. The $[Cr(bpdo)_3]^{3+}$ complex in solution does not hydrolyze in light, but its active isomer racemizes by exposure of ultraviolet light. Hence the following procedures should be done in dark, if necessary.

(1) $[Cr(bpdo)_3]^{3+}$: The racemic complex was prepared by a method similar to those of Simpson *et al.*[2] and Madan and Bull.[5] The solid of $bpdo\cdot H_2O$[6] (3.5 g, 17 mmol) was dissolved in an aqueous solution (20 cm^3) of $Cr(NO_3)_3\cdot 9H_2O$ (2.0 g, 5 mmol). The solution was adjusted to pH *ca.* 2 with hydrochloric acid to avoid the formation of hydroxo complexes, kept at 90 °C for 1 h, and cooled to room temperature. Sodium perchlorate was then added to the solution to yield green precipitate, which was recrystallized from hot water and air-dried. Yield: 4 g (88%). Found: C, 37.78; H, 2.73; N, 9.53%. Calcd for $C_{30}H_{27}N_6O_{19.5}Cl_3Cr=[Cr(bpdo)_3](ClO_4)_3\cdot 1.5H_2O$: C, 38.25; H, 2.89; N, 8.92%.

The complex was resolved with $(+)_{589}$-$Ag_3[Co(\text{L-cysteinesulfinato}(2-)\text{-}SN)_3]$.[7] The resolving agent (0.9 g, 1.1 mmol) was added to an aqueous solution (20 cm^3) of $[Cr(bpdo)_3]Cl_3$ which was prepared from the perchlorate (1.0 g, 1.1 mmol) and the anion exchanger, Dowex 1X8 in the chloride form. White precipitate of AgCl was filtered off and a small amount of ethanol was added to the filtrate to yield greenish orange precipitate, which was recyrstallized from water by adding ethanol. The product was dissolved in water and sodium perchlorate was added to the solution to give green crystals, which were filtered, washed with cold water and then ethanol, and air-dried. The crystals showed positive rotation at 589 nm in water. This complex loses gradually its optical activity in water. Found: C, 37.69; H, 2.58; N, 9.55%. Calcd for $C_{30}H_{27}N_6O_{19.5}Cl_3Cr=(+)_{589}$-$[Cr(bpdo)_3](ClO_4)_3\cdot 1.5H_2O$: C, 38.25; H, 2.89; N, 8.92%.

Attempts to separate possible diastereomers were all unsuccessfull by SP-Sephadex column chromatography. The column gave only one band of $[Cr(bpdo)_3]^{3+}$, all fractions of which showed the same pattern in the absorption spectra. The resolution was not achieved by the column chromatography because of racemization of the complex (*vide infra*).

(2) $[Cr(bpdo)_2en]^{3+}$: To an aqueous solution (10 cm^3, pH *ca.* 2) of $[CrCl_2(H_2O)_2(en)]Cl$[8] (1.1 g, 4 mmol) was added $bpdo\cdot H_2O$ (1.7 g, 8.2 mmol) and the solution was stirred at 50 °C for 4 h. Sodium perchlorate was then added to the solution to yield violet crystals, which were filtered. Yield: 1.1 g (34%). The product was contaminated with a small amount of $[Cr(bpdo)_3](ClO_4)_3$, and purified by SP-Sephadex column chromatography. The crude product dissolved in water was poured on an SP-Sephadex column, and the adsorbed band was eluted with a 0.3 mol dm^{-3} Na_2SO_4 solution. The violet fractions were collected, concentrated under reduced pressure to a small volume, and mixed with sodium perchlorate to yield violet crystals. They were washed with a mixture of water and ethanol (1:1), then ethanol and air-dried. Yield: 0.7 g (20%). Found: C, 32.46; H, 2.89; N, 10.11%. Calcd for $C_{22}H_{27}N_6O_{17.5}Cl_3Cr=[Cr(bpdo)_2en](ClO_4)_3\cdot 1.5H_2O$: C, 32.46; H, 3.35; N, 10.33%.

The resolution was achieved by use of the complex chloride and $(-)_{589}$-$K[As(cat)_3]$[9] (cat=1,2-benzenediolate ion). An aqueous solution (20 cm^3) of the chloride which was prepared from the perchlorate (1.2 g, 1.5 mmol) and a Dowex 1X8 anion exchanger in the chloride form was adjusted to pH 7—8 with potassium carbonate. To this solution was added an aqueous solution (30 cm^3) of the resolving agent (0.66 g, 1.5 mmol) to yield violet precipitate, which was filtered off. The filtrate was stirred for a while with a Dowex 1X8 anion exchanger in the chloride form to remove the resolving agent remained. The resulting solution gave positive rotation at 589 nm and was used for the CD measurement. The absorption spectrum of the solution was identical with that of the racemic complex and remained constant, but the optical activity was lost gradually at room temperature. Hence the procedure of resolution was carried out at a temperature as low as possible. The violet precipitate obtained above by the addition of the resolving agent was quite insoluble in water and the resolving agent could not be removed by usual methods. The optically active complex was isolated as perchlorate by the addition of sodium perchlorate to the filtrate obtained above. Found: C, 32.95; H, 2.94; N, 10.51%. Calcd for $C_{22}H_{26}N_6O_{17}Cl_3Cr$=$(+)_{589}$-$[Cr(bpdo)_2en](ClO_4)_3 \cdot H_2O$: C, 32.83; H, 3.26; N, 10.44%. The resolution by SP-Sephadex column chromatography was not achieved and the column showed only one band of racemic $[Cr(bpdo)_2en]^{3+}$.

(3) $[Cr(bpdo)(en)_2]^{3+}$: To an aqueous solution (30 cm^3) of *cis*-$[CrCl_2(en)_2]Cl$[10] (1.5 g, 5 mmol) was added bpdo·H_2O (1.7 g, 8.2 mmol) and the solution was stirred at 50 °C for 1 h. Sodium perchlorate was then added to the solution to yield red orange crystals, which were filtered and recrystallized from warm water (50 °C). Yield: 1.7 g (50%). Found: C, 24.21; H, 3.88; N, 12.39%. Calcd for $C_{14}H_{28}N_6O_{16}Cl_3Cr$=$[Cr(bpdo)(en)_2](ClO_4)_3 \cdot 2H_2O$: C, 24.20; H, 4.07; N, 12.10%.

The complex was resolved completely by SP-Sephadex column chromatography. The complex perchlorate (*ca.* 0.35 g) was loaded on a column (ϕ 2.7×80 cm) of SP-Sephadex C-25 in the sodium form and the adsorbed red orange band was eluted with a 0.2 mol dm^{-3} sodium $(+)_{589}$-tartratoantimonate(III) solution. When the band was separated into two, the column was washed with water to remove the eluent. Two parts of the resin adsorbed the complex were separately taken out from the column and poured into small columns (ϕ 2.7×30 cm). Each of the adsorbed complexes (a pair of enantiomers) was eluted with a 3 mol dm^{-3} lithium chloride solution and the eluate was mixed with sodium perchlorate to give red orange precipitate. The isomer obtained from the fast eluted band showed positive rotation at 589 nm. The optical activity of this complex remains unchanged in dark at room temperature. Found: C, 24.37; H, 3.51; N, 12.01%. Calcd for $C_{14}H_{28}N_6O_{16}Cl_3Cr$=$[Cr(bpdo)(en)_2](ClO_4)_3 \cdot 2H_2O$: C, 24.20; H, 4.07; N, 12.10%.

(4) $[Cr(en)_3]^{3+}$: This complex was prepared by the method described previously[11] and resolved by an SP-Sephadex column chromatographic method similar to that for $[Co(en)_3]^{3+}$.[12] The complex chloride (*ca.* 0.5 g) was loaded on a column (ϕ 2.7×50 cm) of SP-Sephadex C-25 resin in the sodium form and the complex was eluted with a 0.3 mol dm^{-3} sodium $(+)_{589}$-tartratoantimonate(III) solution. Each eluate of the two separate bands was collected and diluted with water. The solution was poured on a small column of SP-Sephadex C-25 in the hydrogen form. The adsorbed complex was eluted with a 3 mol dm^{-3} lithium chloride solution and the eluate was concentrated under reduced pressure to yield orange crystals of the active chloride. The isomer obtained from the fast moved band showed positive rotation at 589 nm.

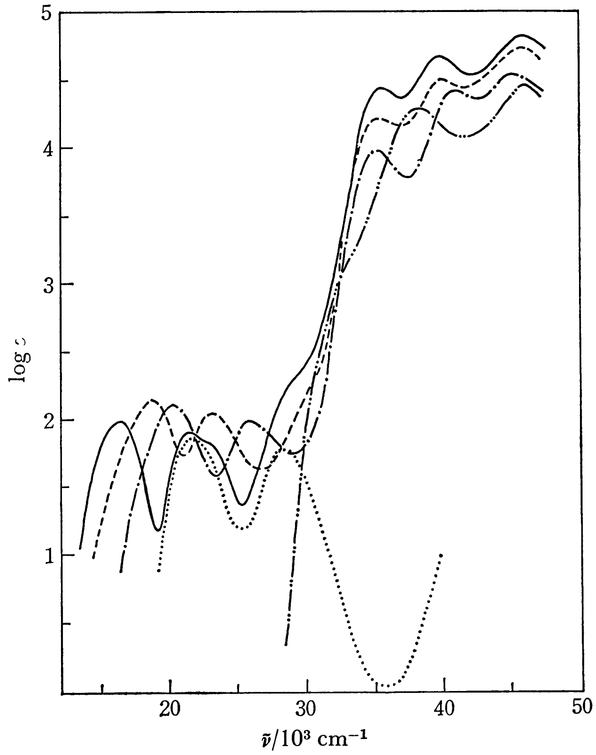

Fig. 2. Absorption spectra of $[Cr(bpdo)_3]^{3+}$ (——), $[Cr(bpdo)_2en]^{3+}$ (----), $[Cr(bpdo)(en)_2]^{3+}$ (—·—), $[Cr(en)_3]^{3+}$ (······), and bpdo (—··—) in water.

Kinetic Runs. Decrease in the CD strength of $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ at the CD peak (485 or 575 nm) was continuously recorded on a JASCO model J-20 spectropolarimeter with a cell jacket to keep the temperature constant within ±0.1 °C using a Haake thermostat Type FSe. A Takara Thermister Type SPD-10 thermometer was placed inside the CD cell. The pH and ionic strength of the solution were adjusted with an aqueous solution of $NaClO_4$–$HClO_4$. The rate of decrease obeyed the first order kinetic law and the observed rate constant (k_{obsd}) is expressed as follows: $k_{obsd} = -\ln[(\alpha_t - \alpha_\infty)/(\alpha_0 - \alpha_\infty)]/t$ where α's are CD strengths at the time denoted by the suffixes.

Absorption and circular dichroism spectra were recorded on a HITACHI 323 spectrophotometer and a JASCO model J-20 spectropolarimeter, respectively.

Results and Discussion

Two new complexes, $[Cr(bpdo)_n(en)_{3-n}]^{3+}$ (n=1 and 2) were prepared from *cis*-$[CrCl_2(en)_2]^+$ and $[CrCl_2(H_2O)_2en]^+$, respectively, by replacing the chloride ions and water molecules with bpdo. The reactions should be carried out at below *ca.* 50 °C to reduce the formation of $[Cr(bpdo)_3]^{3+}$. The pure complexes were easily isolated from the crude products by SP-Sephadex column chromatography using a 0.3 mol dm^{-3} Na_2SO_4 solution as an eluent. The tris- and bis-en complexes were resolved by SP-Sephadex column chromatography, while the tris- and bis-bpdo complexes were not done by this method, but achieved by the chemical method with $(+)_{589}$-[Co(L-cysteinesulfinato-(2−)-SN)$_3$]$^{3-}$ and $(-)_{589}$-$[As(cat)_3]^-$, respectively. The former two complexes are optically stable in water at room temperature in dark, while the latter two complexes lose slowly the optical activity under

TABLE 1. ABSORPTION AND CD SPECTRAL DATA

	Absorption $\tilde{\nu}/10^3\ cm^{-1}$ (log ε)	CD $\tilde{\nu}/10^3\ cm^{-1}$ ($\Delta\varepsilon$)
bpdo	38.4 (4.30)	
	46.0 (4.45)	
$(+)_{589}$-$[Cr(en)_3]^{3+}$	21.8 (1.89)	21.9 (+1.64)
	28.6 (1.80)	26.5 (+0.07)
		30.4 (+0.08)
$(+)_{589}$-$[Cr(bpdo)(en)_2]^{3+}$	20.4 (2.11)	18.9 (+3.25)
	26.0 (1.99)	24.7 (+0.43)
	35.2 (3.96)	27.0 (+0.43)
	40.8 (4.43)	31.6 (+0.20)
	45.1 (4.55)	34.4 (−7.76)
		37.8 (+24.8)
		40.9 (−86.3)
		45.0 (+77.7)
$(-)_{589}$-$[Cr(bpdo)_2(en)]^{3+}$	18.8 (2.15)	17.5 (+3.75)
	23.2 (2.06)	22.9 (+2.08)
	35.5 (4.21)	29.4 (−0.72)
	40.0 (4.52)	34.5 (−46.5)
	45.5 (4.73)	37.5 (+13.4)
		40.0 (−81.0)
		43.5 (+67.4)
$(+)_{589}$-$[Cr(bpdo)_3]^{3+}$	16.3 (2.01)	15.2 (−2.66)
	21.4 (1.94)	17.6 (+0.46)
	22.5^{sh} (1.88)	20.6 (−0.52)
	35.7 (4.46)	23.3 (+0.08)
	40.0 (4.67)	29.0 (+0.62)
	45.8 (4.83)	34.7 (+56.5)
		38.0 (+59.3)
		40.8 (−80.0)

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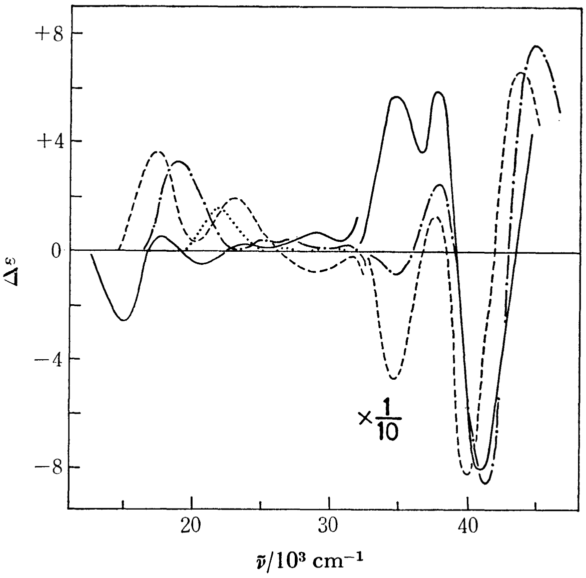

Fig. 3. CD spectra of $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ (——), $(-)_{589}$-$[Cr(bpdo)_2en]^{3+}$ (----), $(+)_{589}$-$[Cr(bpdo)(en)_2]^{3+}$ (—·—), and $(+)_{589}$-$[Cr(en)_3]^{3+}$ (······) in water.

the same conditions (*vide infra*).

The bpdo ligand forms a skew seven-membered chelate ring upon coordination. The skew conformation is chiral and can exist in a pair of enantiomers which are designated by δ and λ, as shown in Fig. 1. The δ-(or λ-)skew conformers in the Λ- and Δ-configurations form the *lel*(or *ob*) and *ob*(or *lel*) structures, respectively, as seen in $[Co(en)_3]^{3+}$ which is constituted by the gauche conformers of en.[13] For $[Cr(bpdo)_3]^{3+}$, therefore, there are four possible diastereomers, each of which has a pair of enantiomers ($lel_3 : \Lambda(\delta\delta\delta)=\Delta(\lambda\lambda\lambda)$, $lel_2ob : \Lambda(\delta\delta\lambda)=\Delta(\lambda\lambda\delta)$, $lelob_2 : \Lambda(\delta\lambda\lambda)=\Delta(\lambda\delta\delta)$, and $ob_3 : \Lambda(\lambda\lambda\lambda)=\Delta(\delta\delta\delta)$). Similarly, $[Cr(bpdo)_2en]^{3+}$ and $[Cr(bpdo)(en)_2]^{3+}$ have three ($lel_2 : \Lambda(\delta\delta)=\Delta(\lambda\lambda)$, $lelob : \Lambda(\delta\lambda)=\Delta(\lambda\delta)$, and $ob_2 : \Lambda(\lambda\lambda)=\Delta(\delta\delta)$) and two ($lel : \Lambda(\delta)=\Delta(\lambda)$ and $ob : \Lambda(\lambda)=\Delta(\delta)$) diastereomers, respectively. However, each of the bpdo complexes gave only one diastereomer. These results suggest that the bpdo chelate ring changes easily its conformation ($\delta \rightleftharpoons \lambda$) in solution, and that each complex crystallizes in a particular diastereomer. The structures of the diastereomers are not certain at present. However, molecular models indicate that the *lel* isomers are always less crowded than the *ob* isomers. The tris-, bis- and mono-bpdo complexes isolated will have the lel_3, lel_2 and *lel* structures, respectively in the solid state, but will be in equilibrium among the isomers involving the *ob* conformation in solution. The bis(ethylenediamine)cobalt(III) complex containing 2,2′-diaminobiphenyl which forms a similar seven-membered chelate ring is also known to yield only one pair of enantiomers, $\Lambda(\delta)$ and $\Delta(\lambda)$.[14,15]

Figure 2 shows the absorption spectra of the complexes and the free ligand. Table 1 gives the spectral data. The first and the second absorption bands shift to lower wave numbers by replacing en with bpdo, but the magnitudes of the shift are not proportional to the number of the bpdo ligand, the first absorption

TABLE 2. KINETIC DATA FOR RACEMIZATION

Complex	Temp (°C)	pH (Ionic strength)	$\frac{k}{10^{-4}\ \mathrm{s}^{-1}}$	$\frac{E_a}{\mathrm{kJ\ mol}^{-1}}$	$\frac{\Delta S^*}{\mathrm{J\ K\ mol}^{-1}}$	Ref.
$(+)_{589}$-$[Cr(bpdo)_3]^{3+}$	26.9	7 (2.1×10^{-2})	1.40±0.04	81.3±4.4	−49±14	
	36.3	7 (2.3×10^{-2})	3.72±0.12			
	47.5	7 (2.4×10^{-2})	10.6±0.1			
	28.0	2 (2.1×10^{-2})	1.54±0.06	80.2±5.0	−51±17	
	36.5	2 (2.1×10^{-2})	3.54±0.09			
	47.5	2 (2.0×10^{-2})	10.0±0.1			
$[Cr(phen)_3]^{3+}$	25	6	0.005	98.7	−46	22)
$[Cr(ox)_3]^{3-}$	18.2	7	1.75	66.2	−100	23)

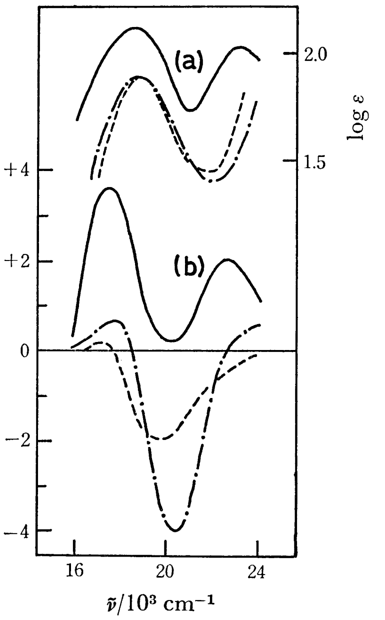

Fig. 4. Absorption (a) and CD (b) spectra of $[CrO_4N_2]$ complexes in the region of the first absorption band, $(-)_{589}$-$[Cr(bpdo)_2en]^{3+}$ (——), Λ-$[Cr(acac)_2en]^+$ (—·—), and Λ-$[Cr(ox)_2en]^-$ (----).

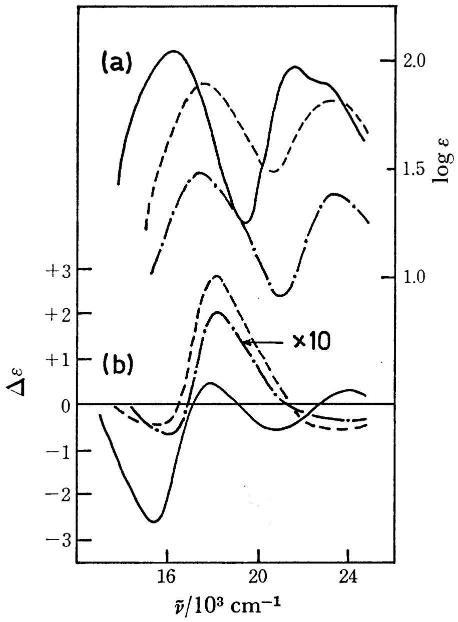

Fig. 5. Absorption (a) and CD (b) spectra of $[CrO_6]$ complexes in the region of the first absorption band, $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ (——), Λ-$[Cr(mal)_3]^{3-}$ (—·—), and Λ-$[Cr(ox)_3]^{3-}$ (----).

band of $[Cr(bpdo)_3]^{3+}$ being at lower wave numbers by 1000 cm^{-1} than those expected from other complexes of the present series. In a series of complexes, $[Cr(ox)_{3-n}(en)_n]^{2n-3}$ (ox=oxalate ion),16,17) the first absorption bands shift regularly with nearly the same interval. In the ultraviolet region, the bpdo complexes exhibit three strong absorption bands, while the free ligand two bands, the lower wave number band of which seems to split into two in the complexes. The intensities of the bands in the complexes are nearly proportional to the number of the bpdo ligand.

Figure 3 compares the CD spectra of $(+)_{589}$-$[Cr(bpdo)_{3-n}(en)_n]^{3+}$ (n=0, 2, and 3) and $(-)_{589}$-$[Cr(bpdo)_2en]^{3+}$. The last isomer is opposite to that used for the measurement. The tris- and bis-bpdo complexes racemize spontaneously in solution so that the spectral variations with time are corrected at each wave number (*vide infra*). Since $(+)_{589}$-$[Cr(en)_3]^{3+}$ has been assigned to the Λ-configuration,18) $(+)_{589}$-$[Cr(bpdo)(en)_2]^{3+}$ which gives a similar positive CD band in the region of the first absorption band can be assigned to the same Λ-configuration. The analogous complexes of the type, $[CrO_2N_4]$ such as Λ-$(+)_{589}$-$[Cr(acac)(en)_2]^{2+}$ 19) (acac=acetylacetonate ion) or Λ-$(+)_{589}$-$[Cr(ox)(en)_2]^{+}$ 20) also give a positive CD band in this region. The CD patterns of $(-)_{589}$-$[Cr(bpdo)_2en]^{3+}$ and $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ isomers in the region of the first absorption band are quite different from those of complexes of the type, $[CrO_4N_2]$ and $[CrO_6]$, respectively, whose absolute configurations have been known, as shown in Figs. 4 and 5. However, these isomers show the same CD pattern in the ultraviolet region as that of $(+)_{589}$-[Cr(bpdo)-

$(en)_2]^{3+}$ except the positive band at 34700 cm^{-1} of $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$. Therefore, both $(-)_{589}$-$[Cr(bpdo)_2en]^{3+}$ and $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ may be assigned to the Λ-configuration. In Fig. 5 is compared the CD spectrum of $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ in the region of the first absorption band with those of Λ-$[Cr(ox)_3]^{3-}$[17,20] and Λ-$[Cr(mal)_3]^{3-}$[17,20] (mal=malonate ion). All of the isomers show a negative and a positive CD band from the smaller wave number side. The CD strength of the malonato complex is extremely weak and the sign of the main CD band of the bpdo complex is negative and opposite to that of the oxalato complex. Such a change in the CD spectra among the complexes of five-, six-, and seven-membered chelate rings is very similar to that observed for a series of complexes, $[Co(NH_2(CH_2)_nNH_2)_3]^{3+}$ (n=2, 3, and 4).[21] On the other hand, the CD pattern of $(-)_{589}$-$[Cr(bpdo)_2en]^{3+}$ is quite different from those of analogous complexes and is not given any plausible discussion at present.

As stated previously, the optically active $[Cr(bpdo)_3]^{3+}$ and $[Cr(bpdo)_2en]^{3+}$ lose their activity in solution. The rates of decrease in the optical activity for $(+)_{589}$-$[Cr(bpdo)_3]^{3+}$ were obtained under the conditions described in Experimental part in dark so as to avoid photo-induced reactions. During the loss of optical activity, the absorption spectrum of the complex was unchanged. The rates obeyed the first order kinetic law and the rate constants (k_{obsd}) were calculated from the slopes of time *vs.* $\Delta\varepsilon$. The data are given in Table 2 together with the activation parameters, and with data for other chromium(III) complexes for comparison. The loss of optical activity should be caused by racemization of the complex, and the racemization will involve both inversions of the complex ion and the ligand, $\Delta \rightleftharpoons \Lambda$ and $\delta \rightleftharpoons \lambda$. The rates were independent of the concentrations of the complex, acid, and the free ligand. Hence, the racemization is suggested to proceed by an intramolecular twist mechanism.[22] The activation parameters are similar to those of other complexes given in Table 2, for which intramolecular mechanisms have been postulated.[23]

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