Bull. Chem. Soc. Jpn., **69**, 665—671 (1996)

Isomerization and Racemization of the Tris(4,4′-dimethoxy- or 4,4′-diethoxy-2,2′-bipyridine 1,1′-dioxide)chromium(III) Complexes

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(Received October 9, 1995)

Two new chromium(III) complexes, $[\mathrm{Cr(4,4'\text{-}X_2bpdo)_3}]^{3+}$ (X = MeO or EtO; bpdo = 2,2′-bipyridine 1,1′-dioxide), were prepared. These complexes form two diastereomers, $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$ and $lel_2ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$, which were separated and resolved by an SP-Sephadex column chromatographic method using achiral eluting agents, such as Na_2SO_4 or NaCl. The isomers isomerized to each other ($lel_3 \rightleftarrows lel_2ob$) fairly rapidly in water along with changes in the absorption spectra, and then racemized very slowly ($\Delta \rightleftarrows \Lambda$). These reactions, including conformational ($\delta \rightleftarrows \lambda$) and configurational ($\Delta \rightleftarrows \Lambda$) changes, are independent of H^+ and free ligand concentrations, and are supposed to proceed by an intramolecular mechanism. For a series of $[\mathrm{Cr(4,4'\text{-}X_2bpdo)_3}]^{3+}$ (X = H, Me, MeO, EtO), both the rates of isomerization and racemization are remarkably reduced along with an increase in the electron-releasing ability of the 4,4′-X_2 substituents on bpdo.

2,2′-Bipyridine 1,1′-dioxide (bpdo) forms a skew seven-membered chelate ring upon coordination to a metal ion.[1—3] Since the skew conformation produces a pair of enantiomers, δ and λ, as shown in Fig. 1, a tris(bpdo) complex has four possible racemic pairs of diastereomers: $lel_3(\Delta(\lambda\lambda\lambda), \Lambda(\delta\delta\delta))$, $lel_2ob(\Delta(\lambda\lambda\delta), \Lambda(\delta\delta\lambda))$, $lelob_2(\Delta(\lambda\delta\delta), \Lambda(\delta\lambda\lambda))$, and $ob_3(\Delta(\delta\delta\delta), \Lambda(\lambda\lambda\lambda))$. In previous papers, we reported that the $[\mathrm{Cr(bpdo)_3}]X_3$ complexes ($X = ClO_4^-$ and NO_3^-) crystallized in the *lel₂ob* form, but spontaneously isomerized to the lel_3 one upon dissolution in water along with rapid changes in the absorption spectra, and then racemized ($\Delta \rightleftarrows \Lambda$) slowly.[4,5] Similar reactions were observed for $[\mathrm{Cr(L)(bpdo)_2}](ClO_4)_n$ (L = 2,4-pentanedionate, oxalate, and malonate ions); these complexes crystallized in the $lel_2(\Delta(\lambda\lambda), \Lambda(\delta\delta))$ form, isomerized to the $lelob(\Delta(\lambda\delta), \Lambda(\delta\lambda))$ one in water, and then racemized, where lel_2 and *lelob* denote the structures of the isomers viewed along the pseudo-C_3 axis of each bis(bpdo) complex.[6,7] These facts show that the skewed bpdo chelate ring is flexible and can change its conformation ($\delta \rightleftarrows \lambda$) rather easily. We recently reported that $[\mathrm{Cr(4,4'\text{-}Me_2bpdo)_3}](ClO_4)_3$ (4,4′-Me_2bpdo=4,4′-dimethyl-2,2′-bipyridine 1,1′-dioxide) also showed similar isomerization and racemization reactions.[5] However, these reactions were fairly slow compared with those of $[\mathrm{Cr(bpdo)_3}]^{3+}$, and the rate differences are supposed to result from an electronic effect of the methyl group on bpdo.

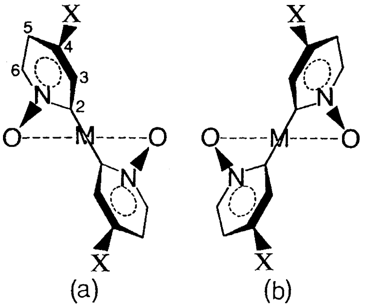

Fig. 1. Chiral conformations of 4,4′-X_2bpdo. (a) δ- and (b) λ-skew form.

This paper reports on the preparation of two new complexes, $[\mathrm{Cr\{4,4'\text{-}(MeO)_2bpdo\}_3}]^{3+}$ and $[\mathrm{Cr\{4,4'\text{-}(EtO)_2bpdo\}_3}]^{3+}$, where 4,4′-$(MeO)_2$bpdo and 4,4′-$(EtO)_2$bpdo denote 4,4′-dimethoxy and 4,4′-diethoxy derivatives of bpdo, respectively. These complexes yielded two racemic pairs of diastereomers (lel_3 and lel_2ob), which were separated and resolved by column chromatography. Although the isomers also isomerized and racemized in water, these reactions were much slower than those of $[\mathrm{Cr(4,4'\text{-}Me_2bpdo)_3}]^{3+}$. The differences in the rate are discussed concerning a series of $[\mathrm{Cr(4,4'\text{-}X_2bpdo)_3}]^{3+}$ (X = H, Me, MeO, EtO).

Experimental

Preparation of Ligands. The ligands, 4,4′-$(MeO)_2$bpdo and 4,4′-$(EtO)_2$bpdo, were prepared from 4,4′-$(NO_2)_2$bpdo[8] according to the literature methods.[9] Each ligand was recrystallized from a mixture of water and acetone (1 : 10) to give colorless crystals, which were collected by filtration, washed with acetone, and air-dried. Found for 4,4′-$(MeO)_2$bpdo: C, 54.10; H, 5.30; N, 10.41%. Calcd for $C_{12}H_{12}N_2O_4 \cdot H_2O$: C, 54.13; H, 5.30; N, 10.52%. ^{13}C NMR (D_2O, TMS) $\delta = 57.6$ (CH_3O), 114.7 and 114.9 (C_3 and C_5), 141.5 (C_6), 143.0 (C_2), 161.9 (C_4) (see Fig. 1). ^{1}H NMR (D_2O, TSP) $\delta = 3.99$ (s, 6H, CH_3O), 7.35 (m, 4H, H-C_3 and H-C_5), 8.35 (d, 2H, H-C_6). Found for 4,4′-$(EtO)_2$bpdo:

C, 60.55; H, 5.79; N, 10.13%. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14%. ^{13}C NMR (D_2O, TMS) $\delta = 14.3$ ($\underline{C}H_3CH_2O$), 66.9 ($CH_3\underline{C}H_2O$), 115.0 and 115.2 (C_3 and C_5), 141.5 (C_6), 143.1 (C_2), 161.0 (C_4). ^{1}H NMR (D_2O, TSP) $\delta = 1.44$ (t, 6H, $C\underline{H}_3CH_2O$), 4.27 (q, 4H, $CH_3C\underline{H}_2O$), 7.31 (m, 4H, H-C_3 and H-C_5), 8.33 (d, 2H, H-C_6). The NMR spectra were assigned by reference to those reported for the related compounds.[10]

Preparation of Complexes. An aqueous solution (50 cm^3) containing $Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g, 5 mmol) and $4,4'\text{-}(MeO)_2bpdo \cdot H_2O$ (4.3 g, 16 mmol) or $4,4'\text{-}(EtO)_2bpdo$ (4.4 g, 16 mmol) was warmed at 80 °C for 3 h, and then cooled to room temperature. The resulting solution was mixed with $NaClO_4$ (3 g) to give green crystals, which were collected by filtration, washed with ice-cold water, and dried over P_4O_{10}. Yield: the $4,4'\text{-}(MeO)_2bpdo$ complex, 5.0 g (88%); the $4,4'\text{-}(EtO)_2bpdo$ complex, 5.5 g (90%). Found for the $4,4'\text{-}(MeO)_2bpdo$ complex: C, 38.03; H, 3.47; N, 7.28%. Calcd for $[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O = C_{36}H_{40}N_6O_{26}Cl_3Cr$: C, 38.23; H, 3.56; N, 7.43%. Found for the $4,4'\text{-}(EtO)_2bpdo$ complex: C, 41.25; H, 4.15; N, 6.89%. Calcd for $[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O = C_{42}H_{52}N_6O_{26}Cl_3Cr$: C, 41.51; H, 4.31; N, 6.92%.

Separation of Diastereomers of the Complexes. Each of the $[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$ and $[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3]^{3+}$ complexes yielded two racemic pairs of diastereomers ($\Delta(\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta)$, and $\Delta(\lambda\lambda\delta)$ and $\Lambda(\delta\delta\lambda)$), which were separated and resolved by SP-Sephadex column chromatography. All of the operations for chromatography were carried out in a cold room (at ca. 5 °C) in order to reduce any isomerization and racemization of the complexes in water (vide post). An aqueous solution of $[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O$ (0.4 g) was applied on a column (ϕ 3×130 cm) of SP-Sephadex C-25. Elution with a 0.35 mol dm^{-3} Na_2SO_4 solution gave three completely separate bands: $(+)_{589}$-**I**, $(+)_{589}$-**II**, and **III** in the order of elution. The fractions of **III** were collected and rechromatographed by an SP-Sephadex column (ϕ 3×130 cm) and a 0.6 mol dm^{-3} NaCl solution to give two separate bands: $(-)_{589}$-**I** and $(-)_{589}$-**II** in the order of elution. The optically active complexes were isolated as perchlorate by mixing the eluate with $NaClO_4$. The precipitate was collected by filtration, washed with ice-cold water and then ethanol, and dried over P_4O_{10}. As shown later, **I** and **II** were assigned to the *lel*$_3$ and *lel*$_2$*ob* isomers, respectively. Found for $(+)_{589}$-**I**: C, 38.15; H, 3.42; N, 7.50%. Calcd for $(+)_{589}$-*lel*$_3$-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O$: C, 38.23; H, 3.56; N, 7.43%. Found for $(+)_{589}$-**II**: C, 38.31; H, 3.48; N, 7.39%. Calcd for $(+)_{589}$-*lel*$_2$*ob*-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O$: C, 38.23; H, 3.56; N, 7.43%.

A quite similar behavior in chromatographic separation was observed for the $4,4'\text{-}(EtO)_2bpdo$ complex. This complex also gave two pairs of enantiomers, *lel*$_3$($(+)_{589}$- and $(-)_{589}$-**I**) and *lel*$_2$*ob*($(+)_{589}$- and $(-)_{589}$-**II**), which were isolated as perchlorate. Found for $(+)_{589}$-**I**: C, 41.49; H, 4.33; N, 6.88%. Calcd for $(+)_{589}$-*lel*$_3$-$[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O$: C, 41.51; H, 4.31; N, 6.92%. Found for $(+)_{589}$-**II**: C, 41.61; H, 4.28; N, 6.97%. Calcd for $(+)_{589}$-*lel*$_2$*ob*-$[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O$: C, 41.51; H, 4.31; N, 6.92%.

Kinetic Measurements. **Isomerization of the Complexes:** Upon dissolution in water at ordinary temperature, the optically active isomers of the $4,4'\text{-}(MeO)_2bpdo$ and $4,4'\text{-}(EtO)_2bpdo$ complexes showed changes in the absorption spectra. The changes in the absorbance at 620 nm were followed by a JASCO UVIDEC-320 spectrophotometer in the temperature range of 30.0—50.0 °C (±0.1 °C). The pH and ionic strength ($I = 0.1$) of the solutions were adjusted with aqueous solutions of HCl and NaCl. Because of insufficient solubility of the perchlorates in water, the complexes were converted into the chlorides using a Dowex 1×8 anion exchanger (Cl^- form) by a similar procedure to that for $[Cr(ox)(bpdo)_2]ClO_4 \cdot 2H_2O$.[7] The complex concentrations of solutions were in the range of 3.4—5.0 mmol dm^{-3}. In each kinetic run, the rate of change obeyed the first-order kinetic law, and the observed rate constant (k^{i}_{obs}) is expressed as $k^{i}_{obs} = -\ln[(A_t - A_\infty)/(A_0 - A_\infty)]/t$, where A's are absorbances at the time denoted by the suffixes.

Racemization of the Complexes: All of the active isomers in water at ordinary temperature also showed changes in optical rotation. The change at 589 nm was followed by similar procedures as described above using a Union PM-101 digital polarimeter. The temperatures and complex concentrations were in the range of 35.0—55.0 °C (±0.1 °C) and 2.0—5.1 mmol dm^{-3}, respectively. The rotation of the $(+)_{589}$-**II** isomer decreased in two different steps, the change in the first step being about 100-times faster than that in the second step. In the second step, the rate of decrease in rotation obeyed the first-order kinetic law; the observed rate constant (k^{r}_{obs}) is also expressed by the same equation as that for the isomerization (k^{i}_{obs}), where the A's are the optical rotations in degrees. A similar change was observed for the $(+)_{589}$-**I** isomer, excepting that its rotation increased in the first step.

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 spectra were measured with a Bruker AC300 spectrometer.

Results and Discussion

Preparation and Properties of the Complexes. Two new chromium(III) complexes of $4,4'\text{-}(MeO)_2bpdo$ and $4,4'\text{-}(EtO)_2bpdo$, $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ (X=MeO, EtO) were prepared by a method similar to that for $[Cr(bpdo)_3]^{3+}$.[1,5,11] Both complexes formed two of four possible racemic pairs of diastereomers, **I** and **II**. The diastereomers were separated and completely resolved into a pair of enantiomers by SP-Sephadex column chromatography carried out at 5 °C using achiral eluting reagents, aqueous solutions of Na_2SO_4 or NaCl. The low-temperature chromatography was essential to reduce isomerization and racemization of the complexes in water. The achievement in resolution using achiral eluting reagents indicates that the enantiomers of these complexes are discriminated by chiral SP-Sephadex comprising D-glucose.[12,13] A similar behavior in chromatographic resolution was observed for the following complexes: $[Cr(acac)(bpy)(bpdo\ \text{or}\ 3,3'\text{-}Me_2bpdo)]^{2+}$ (bpy = 2,2'-bipyridine; $3,3'\text{-}Me_2bpdo$ = 3,3'-dimethyl-2,2'bipyridine 1,1-dioxide)[14] and $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$.[5]

Figure 2 shows the absorption spectra of isomers **I** and **II** of $[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3](ClO_4)_3 \cdot 2H_2O$ in water. The spectra of both isomers gradually changed, showing isosbestic points at the same wavelengths. After attaining equilibrium, the isomers showed the same spectrum over the whole region. The $4,4'\text{-}(EtO)_2bpdo$ complex also showed a similar spectral change to that of the $4,4'\text{-}(MeO)_2bpdo$ complex. Since these complexes were not hydrolyzed during the changes, as confirmed by column chromatography of the reaction products, the spectral changes are attributable to isomerization between two isomers of the complex. The structures of the isomers were assigned from comparisons of the absorp-

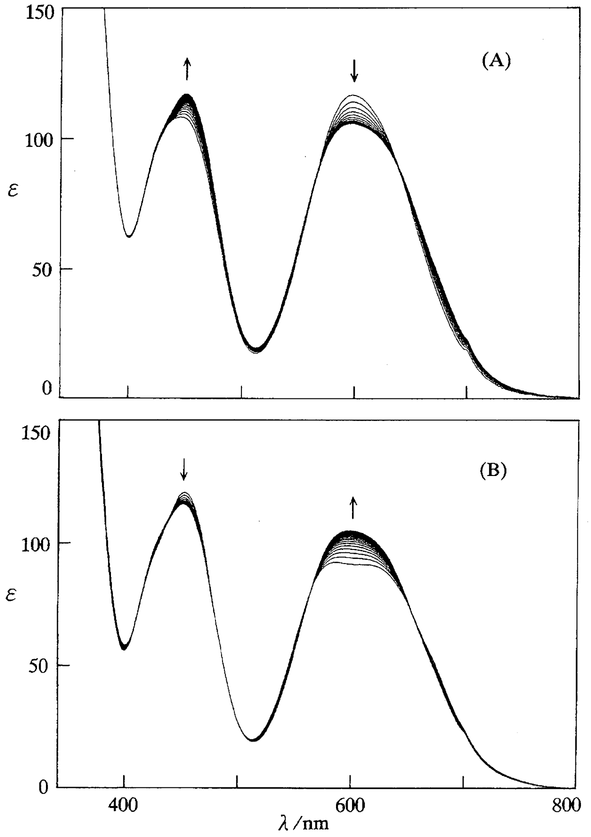

Fig. 2. Changes in absorption spectra of $[Cr\{4,4'-(MeO)_2bpdo\}_3](ClO_4)_3\cdot 2H_2O$ in water at 30.0 °C. The spectra were recorded at 10—250 min after dissolution at regular time intervals (10 min). (A) Isomer **I** (lel_3), (B) isomer **II** (lel_2ob).

tion spectra with those of $[Cr\{(R \text{ or } S)\text{-}3,3'\text{-}Me_2bpdo\}_3]^{3+}$, where ($R$ or S)-3,3'-Me_2bpdo forms a conformationally fixed chelate ring in a λ and δ form, respectively, because of the steric hindrance due to the two methyl groups.[15] The spectra of isomers **I** and **II** immediately after dissolution in water closely resemble those of the lel_3 and lel_2ob isomers of $[Cr\{(R \text{ or } S)\text{-}3,3'\text{-}Me_2bpdo\}_3]^{3+}$, respectively. It is thus concluded that **I** and **II** are the lel_3 and lel_2ob isomers, respectively, and isomerize to each other, $lel_3 \rightleftarrows lel_2ob$ in water. These results support the previous conclusion that $[Cr(bpdo)_3]X_3\cdot 2H_2O$[4,5] and $[Cr(4,4'\text{-}Me_2bpdo)_3]X_3\cdot 2H_2O$[5] ($X = ClO_4^-$, NO_3^-) crystallize in the lel_2ob form, but isomerize to the lel_3 one in water. Figure 3 shows the structures by Dreiding molecular models of the lel_3 and lel_2ob isomers of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$. The models indicate that they isomerize easily to each other. The isomerization corresponds to a conformational inversion ($\delta \rightleftarrows \lambda$) of one chelate ring in the complex. An examination with molecular models indicates that the $lelob_2$ and ob_3 isomers do not form because of their extremely crowded structures.[4,5]

Figure 4 compares the absorption spectra of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ (X = H, Me, MeO, EtO) in water at 35.0 °C, after an equilibrium of $lel_3 \rightleftarrows lel_2ob$ was reached. The spectral data are listed in Table 1. The spectral patterns of the complexes were very similar in the region of the first ligand field band (${}^4T_{2g} \leftarrow {}^4A_{2g}$), and were almost unchanged in the 30—55 °C range. An examination with molecular models indicates that the distribution of the lel_3 and lel_2ob isomers at equilibrium will be independent of the 4,4'-X_2 substituents. These results suggest that the distribution of the two isomers at equilibrium would be nearly the same for all of the complexes, and would be little dependent on the temperature in this temperature range. From the spectra at the equilibrium and the spectra of the pure lel_3 and lel_2ob isomers, the isomer distributions ($lel_3 : lel_2ob$) at the equilibrium were estimated to be 1.6 : 1 for the 4,4'-$(MeO)_2$bpdo complex and 1.5 : 1 for the 4,4'-$(EtO)_2$bpdo one. The spectra of the pure lel_3

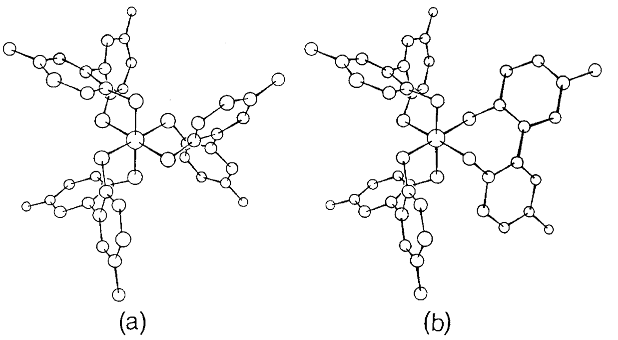

Fig. 3. Schematic drawings of two conformational isomers of Λ-$[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$; (a) $\Lambda(\delta\delta\delta)$ (lel_3), (b) $\Lambda(\delta\delta\lambda)$ (lel_2ob).

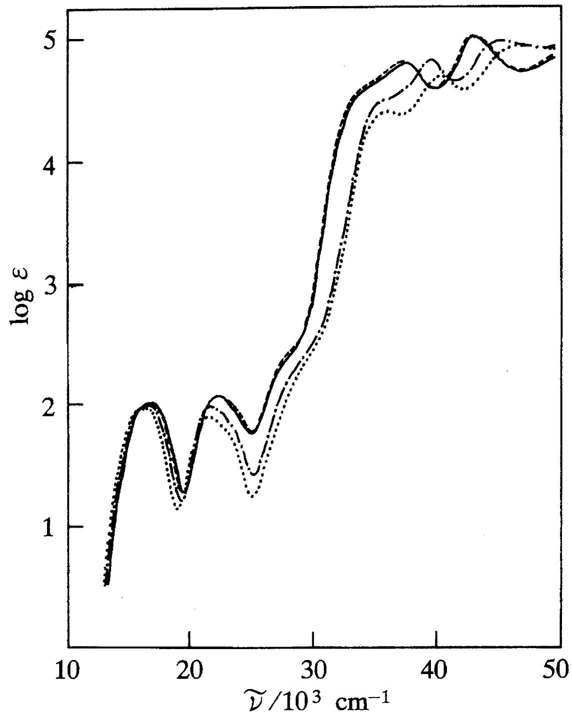

Fig. 4. Absorption spectra of $[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$ (——), $[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3]^{3+}$ (- - -), $[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ (- • -), and $[Cr(bpdo)_3]^{3+}$ (••••) in water at 35.0 °C. The spectra were recorded after an equilibrium of $lel_3 \rightleftarrows lel_2ob$ had been reached.

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

Compounds	$\tilde{\nu}/10^3$ cm^{-1} (log ε)
bpdo[b)]	38.55(4.32), 46.08(4.48)
4,4'-Me_2bpdo[b)]	38.20(4.35), 46.04(4.47)
4,4'-$(MeO)_2$bpdo	37.33(4.38), 46.64(4.48)
4,4'-$(EtO)_2$bpdo	37.23(4.40), 46.62(4.48)
$[Cr(bpdo)_3]^{3+}$ [b)]	14.3(1.5)sh,[c)] 16.41(1.97), 21.39(1.90), 22.7(1.8)sh, 30.3(2.5)sh, 35.96(4.40), 40.26(4.96), 46.73(4.94)
$[Cr(4,4'\text{-}Me_2bpdo)_3]^{3+}$ [b)]	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)
$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$	14.3(1.4)sh, 16.72(2.02), 22.12(2.06), 23.3(2.0)sh, 28.6(2.5)sh, 34.5(4.6)sh, 37.44(4.79), 43.05(5.01)
$[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3]^{3+}$	14.3(1.3)sh, 16.69(2.03), 22.22(2.07), 23.3(2.0)sh, 28.6(2.5)sh, 34.5(4.7)sh, 37.20(4.82), 42.88(5.03)

a) The data for the complexes correspond to the spectrum of an equilibrium mixture of the *lel*$_3$ and *lel*$_2$*ob* isomers at 35.0 °C.
b) From Ref. 5. c) sh: Shoulder.

and *lel*$_2$*ob* isomers were obtained from the changes in the spectra of the **I** and **II** isomers by extrapolating the spectra back to zero time, respectively. The *lel*$_3$ isomer of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ is somewhat more stable than the *lel*$_2$*ob* one in water.[4,5)]

As Fig. 4 shows, the first ligand field band of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ at equilibrium shifts to the higher energy side in the order $X = H$ (16410 cm^{-1}) < Me (16560 cm^{-1}) < EtO (16690 cm^{-1}) < MeO (16720 cm^{-1}). Whyman et al.[16)] reported that the ligand field strength (10 *Dq*) of $[Cr(4\text{-}Xpyo)_6]^{3+}$ (4-Xpyo = 4-substituted pyridine 1-oxide) increases in the order X = Cl (15750 cm^{-1}) < H (15870 cm^{-1}) < Me (16000 cm^{-1}) < MeO (16130 cm^{-1}), and that the *Dq* value increases with an increase in electron-releasing ability of the substituent at the 4-position of pyridine. For the series of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$, the shift of the first ligand field band is also attributable to the same electron-releasing effect of two substituents (X) on bpdo.[5)] As shown in Fig. 5, a good linear relationship was observed between the 10 *Dq* value of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ and the Hammett substituent constant (σ_p) for the X group.

An aqueous solution of $(+)_{589}$-**II**-isomer lost activity in two different steps, as Fig. 6 shows. In the first step (A), a decrease in rotation accompanied a change in the absorption spectrum (in Fig. 2). In the subsequent slow step (B), no change in the absorption spectrum was observed. A similar change in rotation was observed for the $(+)_{589}$-**I** isomer, except that its rotation increased in the first step. Figure 7 shows the changes in the CD spectra of isomers **I** and **II** of $(+)_{589}$-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$ in step (A). In this step, the CD spectra of the isomers change with isodichroic points at the same wavelengths. After an equilibrium of isomerization (*lel*$_3$$\rightleftarrows$*lel*$_2$*ob*), both isomers show the same CD spectrum, which simply decreases the magnitude very slowly (step (B)). The results indicate that the complex isomerizes in the first step (A) and racemizes in the second step (B). The CD patterns of isomers $(+)_{589}$-**I** and $(+)_{589}$-**II** immediately after dissolution resemble those of $\Lambda(\delta\delta\delta)$-*lel*$_3$-$[Cr\{(S)\text{-}3,3'\text{-}Me_2bpdo\}_3]^{3+}$ and $\Lambda(\delta\delta\lambda)$-*lel*$_2$*ob*-$[Cr\{(S)\text{-}3,3'\text{-}Me_2bpdo\}_2\{(R)\text{-}3,3'\text{-}Me_2bpdo\}]^{3+}$, respectively.[15)] Thus, $(+)_{589}$-**I**- and $(+)_{589}$-**II**-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$ can be assigned to the $\Lambda(\delta\delta\delta)$ (*lel*$_3$) and $\Lambda(\delta\delta\lambda)$ (*lel*$_2$*ob*) isomers, respectively. A very similar behavior in the CD spectrum was observed for the 4,4'-$(EtO)_2$bpdo complex, as shown in Fig. 8.

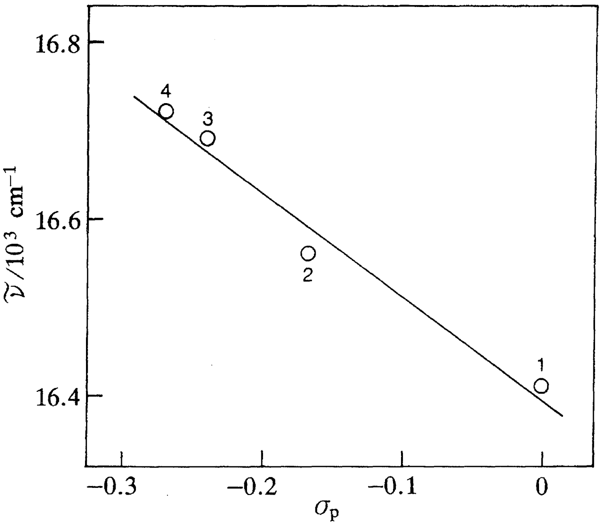

Fig. 5. The correlation between the peak positions of the first ligand field band (10 *Dq*) of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ at equilibrium in water and the Hammett substituent constant (σ_p) for the X group; X = H (1), Me (2), EtO (3), and MeO (4).

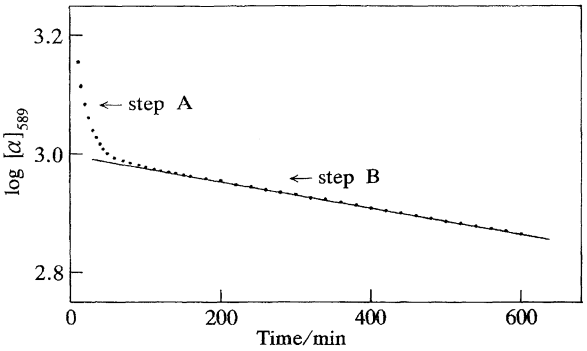

Fig. 6. Decrease in optical rotation (589 nm) with time of $(+)_{589}$-*lel*$_2$*ob*-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$ (isomer **II**) in water at 40.0 °C. [Complex]=4.71 mmol dm^{-3}; I=0.1 (NaCl).

Kinetics of Isomerization and Racemization of the Complexes. The isomerization of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ (X=MeO, EtO) in water, *lel*$_3$$\rightleftarrows$*lel*$_2$*ob*, was followed by monitoring the change in absorbance at 620 nm. It gave the first-order rate constant. Each kinetic run, starting from either the *lel*$_3$ isomer or *lel*$_2$*ob* one, gave the same rate constant within

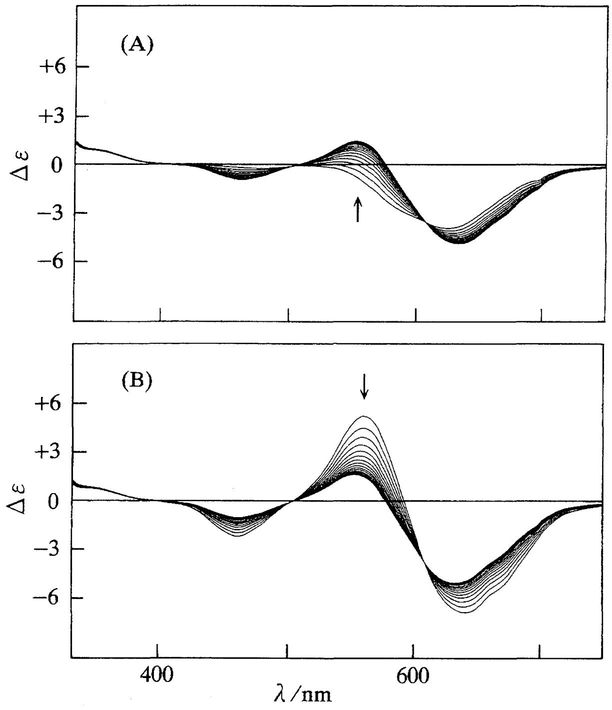

Fig. 7. Changes in CD spectra of $(+)_{589}$-$[\mathrm{Cr}\{4,4'\text{-}(\mathrm{MeO})_2\mathrm{bpdo}\}_3]^{3+}$ in water at 30.0 °C. The spectra were recorded at 10—180 min after dissolution at regular time intervals (10 min). (A) Isomer **I** (*lel*$_3$), (B) isomer **II** (*lel*$_2$*ob*).

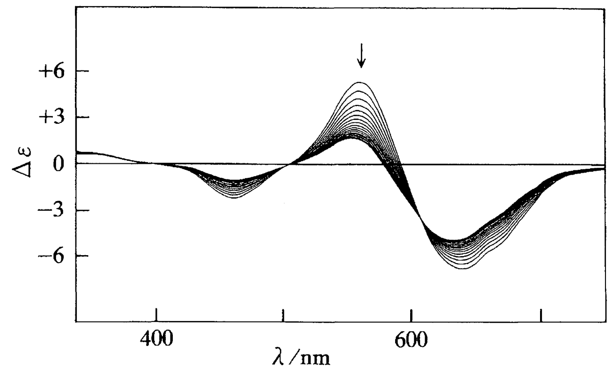

Fig. 8. Change in CD spectrum of $(+)_{589}$-**II**-*lel*$_2$*ob*-$[\mathrm{Cr}\{4,4'\text{-}(\mathrm{EtO})_2\mathrm{bpdo}\}_3]^{3+}$ in water at 30.0 °C. The spectra were recorded at 10—180 min after dissolution at regular time intervals (10 min).

Table 2. Observed Rate Constants for Isomerization of $[\mathrm{Cr}(4,4'\text{-}\mathrm{X}_2\mathrm{bpdo})_3]^{3+}$ in Water ($I=0.1$)

$t/°\mathrm{C}$	$k^{\mathrm{i}}_{\mathrm{obs}}/10^{-3}\ \mathrm{s}^{-1}$	$t/°\mathrm{C}$	$k^{\mathrm{i}}_{\mathrm{obs}}/10^{-3}\ \mathrm{s}^{-1}$
	$(+)_{589}$-**I**-*lel*$_3$-$[\mathrm{Cr}\{4,4'\text{-}(\mathrm{MeO})_2\mathrm{bpdo}\}_3]^{3+}$		
30.0	0.345±0.003[a]	35.0[d]	0.644±0.003
30.0[b]	0.348±0.003	40.0	1.10 ±0.02
35.0	0.647±0.004	45.0	1.85 ±0.02
35.0[b]	0.642±0.004	45.0[c]	1.83 ±0.03
35.0[c]	0.646±0.003	50.0	3.11 ±0.03
	$(+)_{589}$-**II**-*lel*$_2$*ob*-$[\mathrm{Cr}\{4,4'\text{-}(\mathrm{MeO})_2\mathrm{bpdo}\}_3]^{3+}$		
30.0	0.347±0.003	40.0[b]	1.09±0.02
30.0[b]	0.344±0.003	40.0[d]	1.08±0.02
35.0	0.647±0.003	45.0	1.86±0.02
35.0[b]	0.641±0.003	45.0[c]	1.87±0.03
35.0[c]	0.648±0.004	50.0	3.13±0.03
40.0	1.11 ±0.02		
	$(+)_{589}$-**I**-*lel*$_3$-$[\mathrm{Cr}\{4,4'\text{-}(\mathrm{EtO})_2\mathrm{bpdo}\}_3]^{3+}$		
30.0	0.315±0.002	40.0[d]	1.02±0.03
30.0[b]	0.311±0.003	45.0	1.70±0.01
35.0	0.578±0.003	45.0[b]	1.69±0.02
35.0[c]	0.581±0.004	45.0[c]	1.67±0.02
40.0	1.01 ±0.01	50.0	2.83±0.02
	$(+)_{589}$-**II**-*lel*$_2$*ob*-$[\mathrm{Cr}\{4,4'\text{-}(\mathrm{EtO})_2\mathrm{bpdo}\}_3]^{3+}$		
30.0	0.318±0.002	40.0[d]	1.02±0.01
30.0[b]	0.313±0.004	45.0	1.68±0.02
35.0	0.581±0.003	45.0[b]	1.67±0.02
35.0[c]	0.577±0.004	45.0[c]	1.71±0.03
40.0	1.04 ±0.02	50.0	2.85±0.02

a) Errors are standard deviations estimated by least squares. b) In 0.1 mol dm^{-3} HCl. c) For $(-)_{589}$-isomer. d) In 0.05 mol dm^{-3} $4,4'\text{-}(\mathrm{MeO})_2\mathrm{bpdo}$ or $4,4'\text{-}(\mathrm{EtO})_2\mathrm{bpdo}$.

the experimental error. The rates of both $4,4'\text{-}(\mathrm{MeO})_2\mathrm{bpdo}$ and $4,4'\text{-}(\mathrm{EtO})_2\mathrm{bpdo}$ complexes were very similar. The values of the observed rate constant ($k^{\mathrm{i}}_{\mathrm{obs}}$) for isomerization are listed in Table 2. The rates were independent of the concentrations of both H^+ and the corresponding free $4,4'\text{-}\mathrm{X}_2\mathrm{bpdo}$ ligand. These results suggest that the isomerizations of both complexes proceed via a similar intramolecular mechanism. The isomerization can be expressed as

$$lel_3 \underset{k^{\mathrm{i}}_2}{\overset{k^{\mathrm{i}}_1}{\rightleftarrows}} lel_2ob$$

From the $k^{\mathrm{i}}_{\mathrm{obs}}$ $(=k^{\mathrm{i}}_1+k^{\mathrm{i}}_2)$ and the equilibrium constant ($K=[lel_3]/[lel_2ob]$), rate constants, k^{i}_1 and k^{i}_2 can be obtained. The values of the rate constant and the kinetic parameters for the forward and reverse reactions are listed in Table 3. For both complexes, the equilibrium constants are close to unity, and the parameter values are similar for the forward and reverse reactions. The small negative values for the activation entropy would indicate an intramolecular mechanism. These kinetic results are consistent with the previous conclusion that the isomerization occurs reversibly by a conformational inversion of the $4,4'\text{-}\mathrm{X}_2\mathrm{bpdo}$ chelate ring in the complex. Although the rates for isomerizations, $lel_3 \rightleftarrows lel_2ob$ of $[\mathrm{Cr}(\mathrm{bpdo})_3]^{3+}$ and $[\mathrm{Cr}(4,4'\text{-}\mathrm{Me}_2\mathrm{bpdo})_3]^{3+}$ in water, have been reported previously, their k^{i}_1 and k^{i}_2 could not be estimated, because of an unsuccessful separation of the isomers.[4,5] Hence, the values for the kinetic parameters estimated from $k^{\mathrm{i}}_{\mathrm{obs}}$ of the series of $[\mathrm{Cr}(4,4'\text{-}\mathrm{X}_2\mathrm{bpdo})_3]^{3+}$ (X=H, Me, EtO, MeO) are compared in Table 4. The values indicate that the isomerizations of all the complexes proceed by a similar mechanism. However, the isomerization of the bpdo complex is about 15-times as fast as that of the $4,4'\text{-}(\mathrm{EtO})_2\mathrm{bpdo}$ one. As shown in Table 4, the rate of isomerization tends to decrease along with an increase in the electron-releasing ability of the $4,4'\text{-}\mathrm{X}_2$ substituents on bpdo; that

Table 3. Equilibrium Constants and Kinetic Parameters for Isomerization of $[Cr(L)_3]^{+3}$ in Water at 35.0 °C

L	$K^{a)}$		k^i	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
			10^{-4} s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
$4,4'\text{-}(MeO)_2bpdo$	1.6±0.1	*lel*$_3$→*lel*$_2$*ob*	k^i_1 : 2.49	86.3±0.8	−34.5+2.4	96.1±1.1
		lel$_2$*ob*→*lel*$_3$	k^i_2 : 3.98	86.3±0.8	−30.6+2.4	95.7±1.1
$4,4'\text{-}(EtO)_2bpdo$	1.5±0.1	*lel*$_3$→*lel*$_2$*ob*	k^i_1 : 2.31	86.4±0.8	−34.6+2.5	97.0±1.2
		lel$_2$*ob*→*lel*$_3$	k^i_2 : 3.47	86.4±0.8	−31.2+2.5	96.0±1.2

a) $K=[lel_3]/[lel_2ob]=k^i_2/k^i_1$; $k^i_{obs}=k^i_1+k^i_2$.

Table 4. A Comparison of Rate Constants and Activation Parameters for Isomerization of $[Cr(L)_3]^{3+}$ in Water at 35.0 °C$^{a)}$

L	$\sigma_p$$^{b)}$	k^i_{obs}	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
		10^{-3} s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
bpdo$^{c)}$	0	8.69	78.9	−28.4	87.7
$4,4'\text{-}Me_2bpdo$$^{c)}$	−0.17	4.39	86.0	−11.3	89.5
$4,4'\text{-}(EtO)_2bpdo$	−0.24	0.578	86.4±0.8	−26.9±2.5	94.7±1.2
$4,4'\text{-}(MeO)_2bpdo$	−0.27	0.647	86.3±0.8	−26.6±2.4	94.5±1.1

a) Activation parameters were obtained from the observed rate constant, k^i_{obs} $(=k^i_1+k^i_2)$. b) Substituent parameter for the X group of $4,4'\text{-}X_2bpdo$. c) From Ref. 5.

is, the rate of conformational inversion of the $4,4'\text{-}X_2bpdo$ chelate ring seems to be dependent on the electronic effect of the substituent.

Table 5 lists the observed rates for the racemization (k^r_{obs}) of the $4,4'\text{-}(MeO)_2bpdo$ and $4,4'\text{-}(EtO)_2bpdo$ complexes in water, and Table 6 gives their kinetic parameters with those of the related complexes. Each kinetic run, starting from either isomers, gave the same result within the experimental error. The racemizations of the complexes were also independent of the concentrations of H^+ and the free ligand, suggesting an intramolecular mechanism. The kinetic parameters for all of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ are very similar to those for the racemization of $[Cr(bpy)_3]^{3+}$ [17] or $[Cr(1,10\text{-phenanthroline})_3]^{3+}$,[17,18] for which the reactions are suggested to proceed via an intramolecular twist mechanism.[19] The present tris(dioxide) complexes are supposed to racemize by the same mechanism.

The rate of racemization of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ is also reduced along with an increase in the electron-releasing ability of the substituent, as shown in Table 6. The rate of the $4,4'\text{-}(MeO)_2bpdo$ complex is about 1/65 compared with that of the bpdo one. If it is assumed that the $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ complexes racemize 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. Molecular models suggest that the introduction of two substituents (Me, EtO, or MeO) at the 4,4′-positions of bpdo scarcely exerts a steric effect on both inversions. As Fig. 9 shows, a good linear relationship was observed between k^r_{obs} and σ_p. Thus, the rate of racemization of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ depends on an electronic effect of the substituent. As stated previously, the electron-releasing groups on bpdo would increase the electron density of oxygen donor atoms and strengthen the Cr–O bonds to stabilize the complex. The smaller rates of both the isomerization and racemization of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ compared with those of $[Cr(bpdo)_3]^{3+}$ are attributable to such an electronic effect of the 4,4′-substituents.

Table 5. Observed Rate Constants for Racemization of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ in Water (I=0.1)

t/°C	$k^r_{obs}/10^{-5}$ s^{-1}	t/°C	$k^r_{obs}/10^{-5}$ s^{-1}
$(+)_{589}$-**I**-*lel*$_3$-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$			
35.0	0.490±0.004	45.0$^{c)}$	1.51±0.02
40.0	0.872±0.007	50.0	2.60±0.04
40.0$^{a)}$	0.867±0.008	50.0$^{a)}$	2.61±0.03
45.0	1.53 ±0.02	55.0	4.41±0.05
45.0$^{b)}$	1.55 ±0.03	55.0$^{b)}$	4.43±0.05
$(+)_{589}$-**II**-*lel*$_2$*ob*-$[Cr\{4,4'\text{-}(MeO)_2bpdo\}_3]^{3+}$			
35.0	0.493±0.005	45.0$^{c)}$	1.56±0.03
40.0	0.873±0.009	50.0	2.59±0.03
40.0$^{a)}$	0.869±0.007	50.0$^{a)}$	2.58±0.04
45.0	1.51 ±0.02	55.0	4.45±0.05
45.0$^{b)}$	1.53 ±0.02	55.0$^{b)}$	4.39±0.06
$(+)_{589}$-**I**-*lel*$_3$-$[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3]^{3+}$			
35.0	0.611±0.005	45.0$^{c)}$	1.82±0.02
40.0	1.07 ±0.01	50.0	3.14±0.02
45.0	1.82 ±0.02	50.0$^{a)}$	3.12±0.03
45.0$^{a)}$	1.79 ±0.03	55.0	5.20±0.05
45.0$^{b)}$	1.78 ±0.03	55.0$^{b)}$	5.25±0.06
$(+)_{589}$-**II**-*lel*$_2$*ob*-$[Cr\{4,4'\text{-}(EtO)_2bpdo\}_3]^{3+}$			
35.0	0.608±0.006	45.0$^{c)}$	1.79±0.02
40.0	1.07 ±0.01	50.0	3.17±0.02
45.0	1.81 ±0.02	50.0$^{a)}$	3.15±0.02
45.0$^{a)}$	1.80 ±0.02	55.0	5.23±0.05
45.0$^{b)}$	1.83 ±0.03	55.0$^{b)}$	5.19±0.05

a) In 0.1 mol dm^{-3} HCl. b) For $(-)_{589}$-isomer. c) In 0.05 mol dm^{-3} $4,4'\text{-}(MeO)_2bpdo$ or $4,4'\text{-}(EtO)_2bpdo$.

Table 6. A Comparison of Rate Constants and Activation Parameters for Racemization of $[Cr(L)_3]^{3+}$ in Water at 35.0 °C

L	σ_p	k^r_{obs}	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
		$10^{-5}\ s^{-1}$	$kJ\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$	$kJ\ mol^{-1}$
bpdo[a)]	0	32.0	76.5	−64.0	96.2
4,4′-Me_2bpdo[b)]	−0.17	3.46	87.5	−46.8	102
4,4′-$(EtO)_2$bpdo	−0.24	0.611	87.8±0.4	−60.3±1.2	106±1
4,4′-$(MeO)_2$bpdo	−0.27	0.490	89.7±0.3	−55.9±0.8	107±1

a) From Ref. 4. b) From Ref. 5.

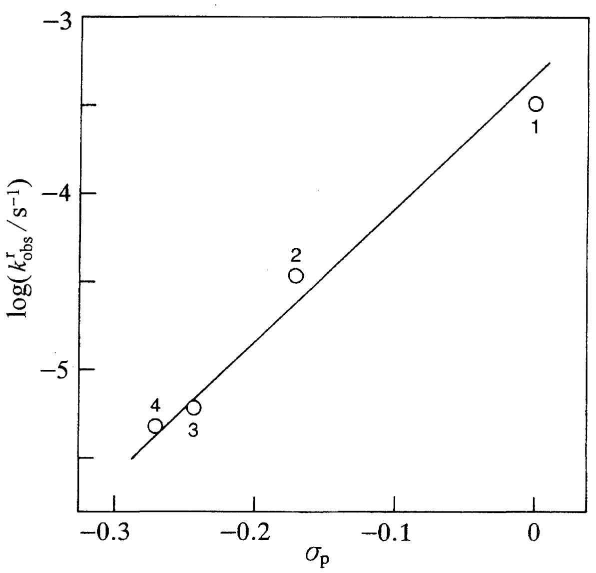

Fig. 9. The correlation between the observed rate constant for the racemization (k^r_{obs}) of $[Cr(4,4'\text{-}X_2bpdo)_3]^{3+}$ at 35.0 °C in water and the Hammett substituent constant (σ_p) for the X group; X=H (1), Me (2), EtO (3), and MeO (4).

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