

The Preparation and Stereochemistry of Optically Active Cobalt(III) Complexes with 3,3'-Dimethyl-2,2'-bipyridine and Bis(diamines) or Tetramines

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Bis(en), trien, tren and bis(*R,R*-chxn) cobalt(III) complexes of 3,3'-dimethyl-2,2'-bipyridine (dmbpy) have been prepared and resolved. The dissymmetric conformation of dmbpy arising from the non-coplanarity of the two pyridine rings is maintained in the inert complexes. 3,3'-Dimethyl-2,2'-bipyridine coordinates to the cobalt(III) ion with a stereospecific conformation depending on the configuration. The absorption and circular dichroism (CD) spectra of the dmbpy complexes were compared with those of the corresponding 2,2'-bipyridine (bpy) complexes.

Although bpy is one of the most extensively studied chelating agents,¹⁾ little work has been done on its 3,3'-dimethyl derivative. On the basis of molecular models, it seems that metal chelate of the dmbpy has considerable strain caused by its puckered conformation. Cagle Jr. and Smith²⁾ reported that dmbpy forms an iron(II) complex in an aqueous solution, but its absorption intensity of 526 nm is only one-fifth of that of the bpy complex. They explained this by considering a twisted conformation of the dmbpy moiety in contrast with the planar chelate ring of bpy. So far no metal complex of dmbpy has been isolated. We have been succeeded in preparing several cobalt(III) complexes containing this ligand. A part of the study has been reported briefly.³⁾

Twisted conformation of dmbpy can give atropisomerism such as biphenyl derivatives,⁴⁾ but the isomers were not isolated presumably because of its rapid racemization. The conformation of the ligand might be fixed by an inert metal complex formation. Only a limited number of metal chelates involving such an isomerism are known.^{5,6)}

This paper deals with the preparation and resolution of several cobalt(III) complexes of dmbpy. The stereochemistry of the complexes is discussed.

Experimental

Materials. 3,3'-Dimethyl-2,2'-bipyridine: 3-Methylpyridine was refluxed with sodium amide in xylene⁷⁾ and the resulting 2-amino-3-methylpyridine was converted into 2-bromo-3-methylpyridine by means of the Sandmeyer reaction.⁸⁾ Condensation of the bromo compound by Ullmann reaction yielded 3,3'-dimethyl-2,2'-bipyridine.⁹⁾ Found: C, 78.42; H, 6.65; N, 15.09%. Calcd for C₁₂H₁₂N₂: C, 78.23; H, 6.75; N, 15.21%.

2,2',2''-Triaminotriethylamine (tren). This was prepared according to the method given in literatures.^{10,11)}

[Co(dmbpy)₃](ClO₄)₃. Air was bubbled through a mixture of CoCl₂·6H₂O (2.38 g in 50 ml of water), dmbpy (5.52 g in 10 ml of ethanol) and activated charcoal (1.0 g) for 12 h. The solution was filtered and the filtrate was warmed at 60 °C for 30 min with 10 ml of concentrated hydrochloric acid. Sodium perchlorate (4.0 g in 10 ml of water) was added to the cooled solution. The resulting yellow precipitate was filtered off, washed with a small amount of water, ethanol and ether, and recrystallized from hot water. Found: C, 47.22; H, 3.95; N, 8.94%. Calcd for C₃₆H₃₆N₆O₁₂CoCl₃: C, 47.50; H, 3.96; N, 9.24%.

[Co(tren)(dmbpy)](ClO₄)₃·4H₂O. A mixture of [Co(dmbpy)₃](ClO₄)₃ (1.82 g in 50 ml of water), 0.3 g of 2,2',2''-

triaminotriethylamine (tren) and activated charcoal (0.5 g) was warmed at 60 °C for 10 min and filtered. A few drops of concentrated hydrochloric acid was added to the filtrate. The solution was diluted 20 times with water and poured onto a SP-Sephadex C-25 column (φ 2.5×25 cm). The adsorbed orange band was washed with water and eluted with 0.2 M hydrochloric acid. The eluate of the orange band was collected, evaporated to dryness, dissolved in 10 ml of water, treated with 1 g of sodium perchlorate in 5 ml of water and stored in a refrigerator overnight. Orange crystals were filtered off and washed with ethanol-water (1 : 1), ethanol and then ether.

Found: C, 28.11; H, 5.03; N, 11.02%. Calcd for C₁₈H₁₈N₆O₁₆CoCl₃: C, 28.43; H, 5.00; N, 11.05%.

Partial Resolution of [Co(tren)(dmbpy)](ClO₄)₃·4H₂O.

About 200 mg of [Co(tren)(dmbpy)](ClO₄)₃·4H₂O was adsorbed on a column containing SP-Sephadex C-25 (φ 2.5×75 cm), and the band was eluted with 0.1 M aqueous solution of potassium (+)_D-tartratoantimonate (III) for fractionation into thirteen portions. The last fraction was adsorbed again on a SP-Sephadex C-25 column (φ 2.5×20 cm) and eluted with 0.2 M hydrochloric acid. The eluate was evaporated to dryness and dissolved in a small amount of water, the circular dichroism spectrum being recorded (Fig. 5). The concentration of the complex ion was determined by visible absorbance of the solution. The circular dichroism curve of the first part of the fractions showed a pattern enantiomeric to that of the last fraction.

[Co(en)₂(dmbpy)]Cl(ClO₄)₂·H₂O. A mixture of *trans*-[CoCl₂(en)₂]Cl (4.0 g in 40 ml of water), dmbpy (2.0 g in 10 ml of ethanol) and activated charcoal (0.5 g) was warmed at 60 °C for 1 h, then filtered. To the filtrate was added 20 ml of 1 M hydrochloric acid. The solution was diluted with water and poured onto the SP-Sephadex C-25 column (φ 5.5×30 cm). The adsorbed band was washed with water, then eluted with 0.2 M hydrochloric acid. The orange band was eluted off and the eluate was evaporated to dryness. The dried residue was dissolved in 40 ml of water and the solution was filtered. After the addition of sodium perchlorate (5 g in 10 ml of water), the solution was allowed to stand for 1 h at room temperature. Orange crystals obtained were collected, washed with cold water, ethanol and ether, and recrystallized from hot water. Found: C, 31.25; H, 4.94; N, 13.62%. Calcd for C₁₆H₂₂N₆O₉CoCl₃: C, 31.17; H, 4.87; N, 13.64%.

Resolution of [Co(en)₂(dmbpy)]Cl(ClO₄)₂·H₂O. **Method I:** A mixture of [Co(en)₂(dmbpy)]Cl(ClO₄)₂·H₂O (3.0 g in 50 ml of water) and K₃[Co(L-cysu)₃]¹²⁾ (cysu=cysteinsulfinate) (1.4 g in 20 ml of water) was heated at 80 °C on a water bath for 10 min, filtered, and left to stand for 3 h at room temperature. Needlelike yellow crystals of (+)_D-diastereomer which appeared were filtered and washed with water, ethanol and then ether. Yield 2.0 g. (The filtrate free from the (+)_D-

isomer was stored in order to obtain $(-)_D$ -isomer.) The $(+)_D$ -diastereomer was recrystallized twice from hot water. The CD strength at 485 nm did not change on repeated recrystallization. Pure $(+)_D$ -diastereomer in 20 ml of water was treated with 10 ml of 2 M hydrochloric acid. Yellow precipitate of $H_3[Co(L-cysu)_3]$ was filtered off, and the solution was treated with 2.0 g of sodium perchlorate in 5 ml of water, and stored in a refrigerator overnight. Needlelike orange crystals were collected and recrystallized from water. Yield 0.8 g. Found: C, 31.24; H, 4.98; N, 13.77%. Calcd for $C_{16}H_{22}N_6O_9CoCl_3$: C, 31.17; H, 4.87; N, 13.64%.

The filtrate free from the $(+)_D$ -isomer was evaporated to 10 ml. The precipitate was filtered off, and 2 ml of 6 M hydrochloric acid was added to the filtrate. Yellow precipitate of $H_3[Co(L-cysu)_3]$ was filtered off. The filtrate was treated with sodium perchlorate (2.0 g in 5 ml of water), and stored in a refrigerator. Needlelike orange crystals were collected and recrystallized twice from hot water. Yield 0.3 g.

Found: C, 31.22; H, 4.87; N, 13.66%. Calcd for $C_{16}H_{22}N_6O_9CoCl_3$: C, 31.17; H, 4.87; N, 13.64%.

Method II: An aqueous solution of the racemic complex (about 8 mg) was poured on a SP-Sephadex C-25 column (ϕ 1.3 \times 110 cm) and the adsorbed orange band was eluted with 0.15 M aqueous solution of potassium $(+)_D$ -tartratoantimonate(III) at a rate of 0.47 ml per min. The eluate was fractionated into 5 ml portions and the absorption spectrum of each fraction was checked (330 nm). Only two isomers were obtained (Fig. 2a). The $(+)_D$ -isomer was eluted faster than the $(-)_D$ -isomer.

cis- α -[Co(trien)(dmbpy)]Cl(ClO₄)₂. This complex was prepared according to a method similar to that for [Co(en)₂(dmbpy)]Cl(ClO₄)₂·H₂O. A mixture of *cis*- α -[CoCl₂(trien)]Cl¹³ (4.4 g in 30 ml of water), dmbpy (2.0 g in 5 ml of ethanol) and activated charcoal (1 g) was warmed at 70 °C for 20 min, and filtered. The filtrate was acidified with 1 M hydrochloric acid and treated with 5 g of sodium perchlorate in 10 ml of water. Orange crystals appeared within a minute. They were filtered off after 30 min and washed with a small amount of ice-water, ethanol and then ether, and recrystallized from hot water. Yield 4.8 g.

Found: C, 34.43; H, 4.84; N, 13.03%. Calcd for $C_{18}H_{30}N_6O_8CoCl_3$: C, 34.64; H, 4.85; N, 13.47%.

Resolution of cis- α -[Co(trien)(dmbpy)]Cl(ClO₄)₂. This complex was resolved by a method similar to that for [Co(en)₂(dmbpy)]Cl(ClO₄)₂·H₂O with K₃[Co(L-cysu)₃] as resolving agent. Two optical isomers were obtained. The CD curve showed that they are enantiomeric to each other. A chromatographic method similar to that for [Co(en)₂(dmbpy)]³⁺ was also employed. An aqueous solution of 18 mg of the complex was poured on a SP-Sephadex C-25 column (ϕ 1.3 \times 110 cm) and the adsorbed band was eluted with a 0.15 M potassium $(+)_D$ -tartratoantimonate(III) as the eluent. The eluate was fractionated into 5 ml portions and their absorption spectra (280 nm) was checked. Figure 2b shows that two well separated bands were obtained. The $(+)_D$ -isomer was eluted faster than the $(-)_D$ -isomer. The CD curves show that these isomers are enantiomeric to each other.

$(-)_D[Co(R,R\text{-chxn})_2(dmbpy)](ClO_4)_3$. This complex was prepared by a method similar to that for [Co(en)₂(dmbpy)]Cl(ClO₄)₂·H₂O. A mixture of *trans*-[CoCl₂(*R,R*-chxn)₂]ClO₄ (chxn = cyclohexanediamine) (1.0 g in 20 ml of water), dmbpy (0.5 g in 10 ml of ethanol) and activated charcoal (0.5 g) was warmed at 70 °C for 15 min, filtered and treated with 10 ml of 1 M hydrochloric acid. The

solution was diluted with water 10 times in volume and poured on a column of SP-Sephadex C-25 (ϕ 3.0 \times 30 cm). The adsorbed band was eluted with 0.2 M hydrochloric acid. All the fractions showed equal absorption and CD patterns. They were collected and evaporated to dryness. The residue was dissolved in 20 ml of water, filtered, treated with 1.5 g of sodium perchlorate in 10 ml of water and stored in a refrigerator overnight. Orange crystals were filtered off and washed with a small volume of water, ethanol and ether and then air dried.

Found: C, 37.35; H, 5.54; N, 10.97%. Calcd for $C_{24}H_{40}N_6O_{12}CoCl_3$: C, 37.47; H, 5.20; N, 10.97%.

$(-)_D[Co(R,R\text{-chxn})_2(bpy)](ClO_4)_3$. The procedure was similar to that for the $(-)_D[Co(R,R\text{-chxn})_2(dmbpy)](ClO_4)_3$ using bpy instead of dmbpy. A mixture of 1.2 g of *trans*-[CoCl₂(*R,R*-chxn)₂]ClO₄ in 25 ml of water, 0.5 g of bpy in 10 ml of ethanol and 0.5 g of activated charcoal was heated at 60 °C for 15 min, filtered, acidified with 10 ml of 1 M hydrochloric acid, diluted with water and poured onto a column containing SP-Sephadex C-25. The adsorbed orange band was eluted with 0.2 M hydrochloric acid. Absorption and CD spectra of the fractions were checked. Fractions giving similar spectral data were collected and evaporated to dryness. The residue was dissolved in 20 ml of water. The solution was filtered, and treated with 1.5 g of sodium perchlorate in 10 ml of water. The orange crystals were filtered off and washed with a small volume of ice-water, ethanol and ether, and recrystallized from water. Yield 0.65 g.

Found: C, 35.59; H, 4.93; N, 11.31%. Calcd for $C_{22}H_{36}N_6O_{12}CoCl_3$: C, 35.62; H, 4.89; N, 11.33%.

Measurements. Absorption and CD spectra were recorded on a Shimadzu Double 40-R spectrophotometer and a Jasco J-20 spectropolarimeter, respectively, at room temperature. PMR spectra were recorded with a JNM-PMX 60 spectrometer using DSS as an internal standard. Infrared spectra were recorded over the NaCl region with a Hitachi Model 285 infrared spectrometer. The complexes, $(+)_D[Co(en)_2(dmbpy)]Cl(ClO_4)_2 \cdot H_2O$, $(+)_D[Co(trien)(dmbpy)]Cl(ClO_4)_2$ and $(-)_D[Co(R,R\text{-chxn})_2(dmbpy)](ClO_4)_3$ were converted into their bromide by use of the anion exchanger Dowex 1-X8 in bromide form, for the measurement of PMR and infrared spectra. Most of the measurements were made at 25 °C.

Results and Discussion

Preparation and Stereochemistry. The cobalt(III) complexes, [Co(dmbpy)₃]³⁺, [Co(trien)(dmbpy)]³⁺, [Co(en)₂(dmbpy)]³⁺, [Co(trien)(dmbpy)]³⁺, and [Co(*R,R*-chxn)₂(dmbpy)]³⁺ were characterized by elemental analysis, absorption, CD and PMR spectra. Among these complexes, the *tren* complex has no chiral configuration around the cobalt(III) ion and the optical activity in this complex arises exclusively from the twisted conformation of the dmbpy chelate. [Co(*tren*)(dmbpy)]³⁺ was partially resolved by column chromatography, and the CD spectrum in the visible region remained unchanged at room temperature for several days. This indicates that the dmbpy chelate of this complex is twisted and takes a nonconvertible conformation.

The bis(en), *tren*, bis(*R,R*-chxn) complexes have two kinds of dissymmetry; the configurational dissymmetry, Δ and Λ , and conformational dissymmetry, δ and λ (Fig. 1). Consequently, four optical isomers

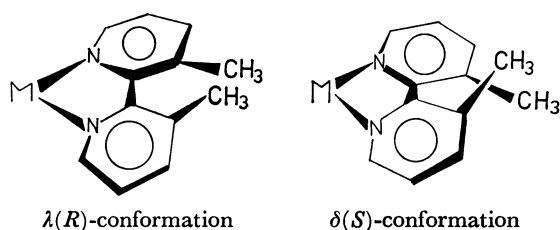


Fig. 1. Two conformations of dmbpy chelates.

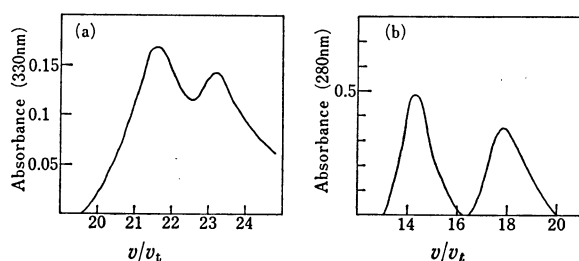


Fig. 2. a) Elution curve of $[\text{Co}(\text{en})_2(\text{dmbpy})]^{3+}$ ion. Plots of absorbance at 330 nm (path length = 1.0 cm) vs. the ratio of the eluate volume (v) to the bed volume ($v_t = 146$ ml). b) Elution curve of $\text{cis-}\alpha$ - $[\text{Co}(\text{trien})(\text{dmbpy})]^{3+}$ ion. Plots of absorbance at 280 nm (path length = 1.0 cm) vs. the ratio of the eluate volume (v) to the bed volume ($v_t = 146$ ml).

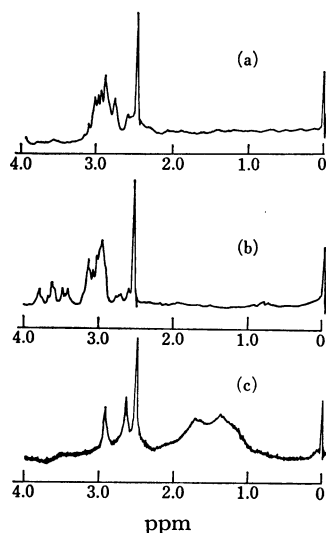


Fig. 3. The PMR spectra of a) $[\text{Co}(\text{en})_2(\text{dmbpy})]\text{Br}_3$ b) $\text{cis-}\alpha$ - $[\text{Co}(\text{trien})(\text{dmbpy})]\text{Br}_3$ c) $(-)\text{-D}[\text{Co}(\text{R,R-chxn})_2(\text{dmbpy})]\text{Br}_3$ in D_2O .

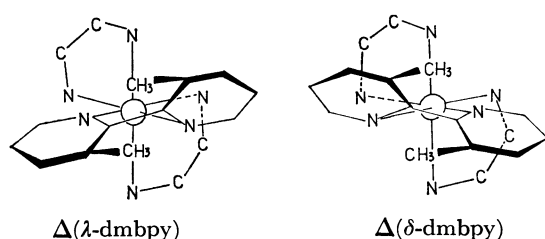


Fig. 4. Schematic structures of Δ - $[\text{Co}(\text{en})_2(\lambda\text{-dmbpy})]^{3+}$ and Δ - $[\text{Co}(\text{en})_2(\delta\text{-dmbpy})]^{3+}$ ions.

TABLE 1. ABSORPTION (AB) AND CIRCULAR DICHROISM (CD) SPECTRAL DATA IN 10^3 cm^{-1} , ($\log \epsilon$) AND ($\epsilon_l - \epsilon_r$)

Complex	AB	CD
$(+)\text{-D}[\text{Co}(\text{tren})\text{-}(\text{dmbpy})]^{3+}$	20.83(2.23)	19.80(+ 0.022)
	31.75(3.99)	22.22(- 0.018)
	43.86(4.58)	28.57(+ 0.58)
		31.25(+ 0.20)
$(+)\text{-D}[\text{Co}(\text{en})_2\text{-}(\text{bpy})]^{3+}$	21.74(1.99)	20.70(+ 3.02)
	ca. 31.25(4.03)	32.47(- 6.64)
	32.46(4.12)	ca. 45.87(- 24.83)
	45.87(4.68)	49.50(+ 28.87)
$(+)\text{-D}[\text{Co}(\text{en})_2\text{-}(\text{dmbpy})]^{3+}$	21.28(2.21)	21.05(+ 7.45)
	30.30(3.77)	28.17(- 5.84)
	33.67(3.91)	33.78(- 4.72)
	44.24(4.73)	39.37(- 21.11)
		47.17(+ 35.70)
$(+)\text{-D-cis-}\alpha$ - $[\text{Co}(\text{trien})\text{-}(\text{dmbpy})]^{3+}$	21.05(2.29)	20.74(+ 7.23)
	30.30(3.67)	28.17(- 4.14)
	34.01(3.91)	30.12(- 6.02)
		31.55(- 6.20)
		40.81(- 18.53)
	43.48(4.76)	48.08(+ 46.30)
$(-)\text{-D}[\text{Co}(\text{R,R-chxn})_2\text{-}(\text{bpy})]^{3+}$	21.28(2.07)	20.53(- 3.31)
	32.26(4.11)	32.26(+ 9.29)
		40.98(+ 42.72)
	45.05(4.64)	48.54(- 34.49)
$(-)\text{-D}[\text{Co}(\text{R,R-chxn})_2\text{-}(\text{dmbpy})]^{3+}$	21.10(2.17)	20.83(- 7.12)
	ca. 30.49(3.82)	27.78(+ 5.41)
	31.75(3.88)	30.03(+ 5.41)
	32.79(3.90)	33.78(+ 7.33)
		40.48(+ 51.80)
	44.14(4.72)	46.72(- 61.50)

are possible for each complex. In addition to the optical isomers, the trien complex has geometric isomers, *i.e.* *cis-α* and *cis-β*. They can usually be distinguished by their IR spectra in the 990–1090 cm^{-1} region; while *cis-α* complexes show two strong absorption bands in this region, *cis-β* complexes give four bands.¹⁵⁾ The IR spectrum of $[\text{Co}(\text{trien})(\text{dmbpy})]\text{Br}_3$ shows two strong band in this region and hence the complex can be assigned to *cis-α* isomer.

The en and trien complexes were resolved by chemical and chromatographic methods. The CD spectra of the two isomers of the chemically resolved en (or trien) complex showed symmetrical curves to each other over all the wavelengths, indicating that they are a pair of enantiomers. The en and trien complexes were adsorbed on a column of SP-Sephadex C-25 and eluted with 0.15 M potassium $(+)\text{-D}$ -tartaratoimionate(III) solution. Figure 2 shows their elution curves. No indication for the presence of more than two isomers was found in both chemical and chromatographic resolution. On the other hand, $[\text{Co}(\text{R,R-chxn})_2(\text{dmbpy})](\text{ClO}_4)_3$ yielded only $(-)\text{-D}$ -isomer stereospecifically (see Experimental). The PMR spectra

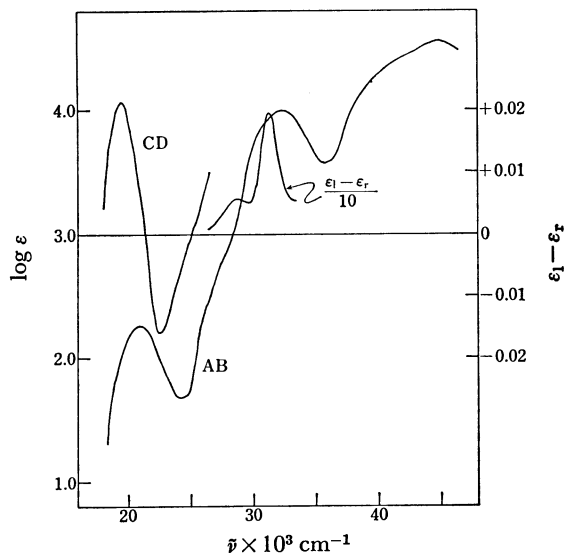


Fig. 5. Absorption (AB) and CD spectra of (+)_D-[Co(trien)(dmbpy)]³⁺.

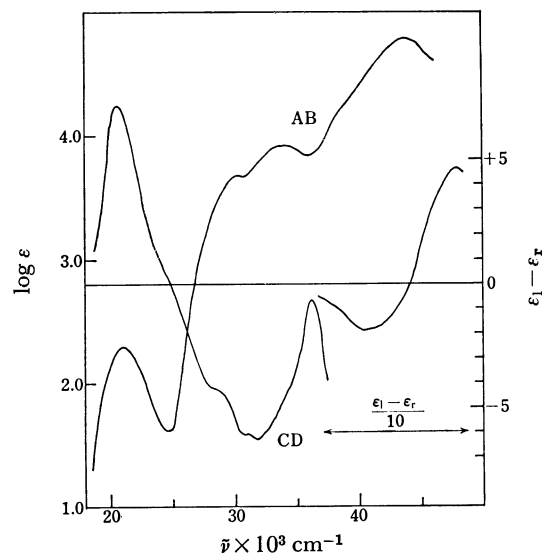


Fig. 7. AB and CD spectra of (+)_D-cis-α-[Co(trien)(dmbpy)]³⁺.

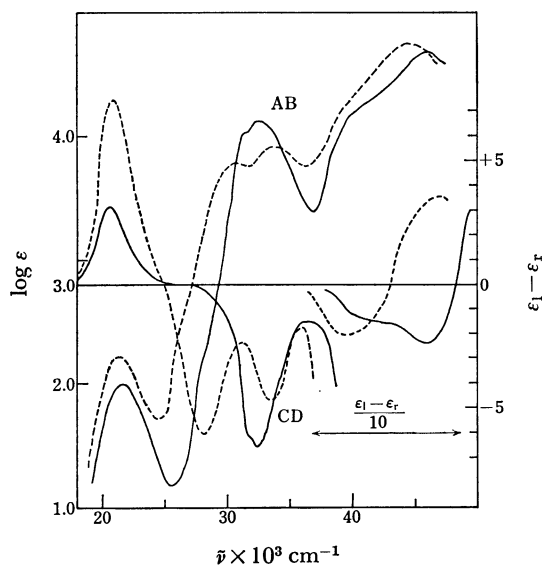


Fig. 6. AB and CD spectra of (+)_D[Co(en)₂(bpy)]³⁺ (—) and (+)_D[Co(en)₂(dmbpy)]³⁺ (---).

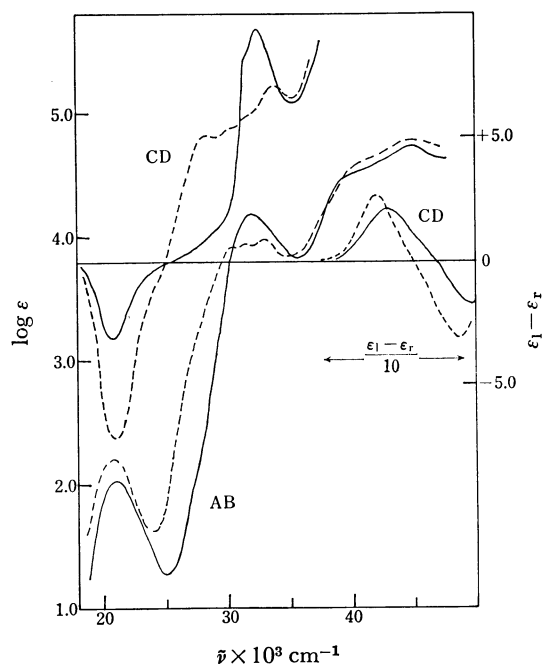


Fig. 8. AB and CD spectra of (-)_D[Co(*R,R*-chxn)₂(bpy)]³⁺ (—) and (-)_D[Co(*R,R*-chxn)₂(dmbpy)]³⁺ (---).

of en, trien and *R,R*-chxn complexes show only one methyl signal at *ca.* 2.5 ppm (Fig. 3). The results also support the view that the dmbpy coordinates stereospecifically to the central cobalt(III) ion in the given configuration.

Recently, Douglas *et al.*⁵⁾ and Tanimura *et al.*⁶⁾ prepared and resolved a series of cobalt(III) complexes of 2,2'-diaminobiphenyl (dabp). The bidentate ligand dabp also takes a non-coplanar conformation upon coordination as dmbpy does. They reported that the conformation of the dabp chelates depends on the configuration of the complexes. The crystal structure of Δ -[Co(*R*-pn)₂(dabp)]Cl₃ has been determined by X-ray analysis, the conformation of the dabp chelate being found to be λ .⁶⁾

Figure 4 gives a schematic representation of the two possible structures of Δ -[Co(en)₂(dmbpy)]³⁺. In the Δ (λ -dmbpy) arrangements, the pyridine rings are twist-

ed into open faces of the octahedron, *i.e.*, the faces are not occupied by en chelates. The interaction between π -electron cloud of bipyridine rings and ethylenediamine protons of Δ (λ -dmbpy) seems to be less than Δ (δ -dmbpy). The same relationship holds for Λ (δ -dmbpy) and Λ (λ -dmbpy).

R-Diamine such as *R*-pn or *R,R*-chxn takes the λ -gauche conformation upon coordination.^{15,16)} Thus, the structure of the stereospecifically formed (-)_D[Co(*R,R*-chxn)₂(dmbpy)]³⁺ should be either Δ ($\lambda\lambda,\delta$ -dmbpy) or Δ ($\lambda\lambda,\lambda$ -dmbpy). The absolute configuration was assigned to Δ from the CD sign of the first d-d region.¹⁷⁾ Molecular model studies suggest that the 2C-2C' bond

in λ -dmbpy chelate is parallel to the pseudo-three fold axis whereas it is oblique in δ -dmbpy. The stability of these two isomers might differ. The tris(*R*-diamine) cobalt(III) complexes have two optical isomers Δ -($\lambda\lambda\lambda$)(*lcl*) and Λ ($\lambda\lambda\lambda$)(*ob*) in which the *lcl* isomer of $[\text{Co}(\text{R-pn})_3]^{3+}$ is known to be more stable than the *ob* isomer.¹⁵⁾ It is likely that the dmbpy chelate takes λ conformation in $(-)_D[\text{Co}(\text{R,R-chxn})_2(\text{dmbpy})]^{3+}$. This agrees with the molecular model consideration for the $[\text{Co}(\text{en})_2(\text{dmbpy})]^{3+}$ (Fig. 4).

Absorption Spectra. The absorption and CD spectra of all the $[\text{Co}(\text{N})_6]^{3+}$ type complexes are shown in Figs. 5–8. Their band locations and intensities are given in Table 1. The first absorption band maxima of the dmbpy complexes have higher intensities and appear at longer wavelength as compared with $(+)_D[\text{Co}(\text{en})_2(\text{bpy})]^{3+}$ or $(-)_D[\text{Co}(\text{R,R-chxn})_2(\text{bpy})]^{3+}$. The absorption peaks in 25000–35000 cm^{-1} region might be related to the electronic transitions of the coordinated dmbpy or bpy.¹⁸⁾ The intensities of these bands of the dmbpy complexes are always lower and the band patterns are broader as compared with those of the bpy complexes. These effects are presumably due to a torsional strain and inhibition of resonance of the dmbpy chelate.¹⁹⁾

CD Spectra. Two component Cotton effects, a positive and a negative peaks from longer to shorter wavelength are observed in the visible region of the $(+)_D[\text{Co}(\text{tren})(\text{dmbpy})]^{3+}$ (Fig. 5). Two positive Cotton effects are observed in the region 28000–35000 cm^{-1} . The origin of the optical activity of this complex is due to the twisted conformation of the dmbpy chelate. The absolute conformation of the ligand cannot be assigned from the CD spectra at present.

A strong CD band is observed for each $(+)_D[\text{Co}(\text{en})_2(\text{dmbpy})]^{3+}$, *cis* α - $(+)_D[\text{Co}(\text{trien})(\text{dmbpy})]^{3+}$ and $(-)_D[\text{Co}(\text{R,R-chxn})_2(\text{dmbpy})]^{3+}$ in the first absorption region (Figs. 6–8). Their CD magnitudes are greater than those of the bpy complexes. The CD sign of a cobalt(III) complex in the first absorption band is known to depend on the absolute configuration of the complex.¹⁷⁾ Thus, the absolute configurations of $(+)_D[\text{Co}(\text{en})_2(\text{dmbpy})]^{3+}$, $(+)_D[\text{Co}(\text{trien})(\text{dmbpy})]^{3+}$, and $(-)_D[\text{Co}(\text{R,R-chxn})_2(\text{dmbpy})]^{3+}$ are assigned to Λ , Λ and Δ , respectively. While the CD spectra of bpy complexes gave one component Cotton effect in the region 25000–35000 cm^{-1} , the dmbpy complexes showed broad and split peaks. The absolute conforma-

tion of the twisted dmbpy can not be assigned at present from the CD patterns in these region.

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Note added in proof

The structure of $(+)_D[\text{Co}(\text{en})_2(\text{dmbpy})]\text{Cl}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was determined recently by X-ray crystal analysis. The configuration of the complex and the conformation of dmbpy were found to be Λ and δ , respectively. (S. Sato and Y. Saito, private communication)

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