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Preparation and Optical Resolution of $[Co(en)_x(dmbpy)_{3-x}]^{3+}$ ($x=0, 1$) and Related Complexes

Toshishige M. SUZUKI

Government Industrial Research Institute, Tohoku, Nigatake, Haranomachi, Sendai 983

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The optical resolution of $[Co(dmpy)_3]^{3+}$, $[Co(en)(dmbpy)_2]^{3+}$, $[Co(en)(bpy)_2]^{3+}$, and $[Rh(dmbpy)_3]^{3+}$(dmbpy =3,3′-dimethyl-2,2′-bipyridine) has been achieved using $(-)_\mathrm{D}$ tris(L-cysteinsulfinato)cobaltate(III). The dmbpy complexes consist of a pair of stereo-selective enantiomers. The absorption and CD spectra of two series of complexes, $[Co(en)_x(dmbpy)_{3-x}]^{3+}$ and $[Co(en)_x(bpy)_{3-x}]^{3+}$ ($x=0$, 1, 2, 3) and also $[Rh(dmbpy)_3]^{3+}$ have been investigated. The complexes containing more than two aromatic ligands showed an exciton CD in the ligand π-π^* transition region and the band has been related to the absolute configuration of the complexes. The spectral features of dmbpy complexes are different from those of the bpy complexes and such differences have been discussed with reference to the twisting nature of dmbpy chelates.

The metal chelates of 3,3′-dimethyl-2,2′-bipyridine (dmbpy) are expected to take a non-coplanar conformation owing to the steric interactions of the substituted methyl groups. Some bis(diamine) and tetramine cobalt(III) complexes with dmbpy have been prepared and resolved.[1] It has been found that dmbpy coordinates to the cobalt(III) ion with a stereospecific conformation depending on the given configuration.[1] The absolute configurations of $(+)_\mathrm{D}[Co(en)_2(dmbpy)]Cl(ClO_4)_2\cdot H_2O$[2] and $(-)_\mathrm{D}[Co(R,R\text{-}chxn)_2(dmbpy)]Br(ClO_4)_2\cdot H_2O$[3] (en=enthylenediamine, chxn=1,2-cyclohexanediamine) have been determined by an X-ray method to be $\Lambda(\delta$-dmbpy) and $\Delta(\lambda$-dmbpy),[4] respectively. The empirical assignments of the absolute configurations on the basis of the Cotton effects in the first d-d absorption band region[5] are consistent with the X-ray results.

Recently, $[Co(dmbpy)_3]^{3+}$, $[Co(en)(dmbpy)_2]^{3+}$, $[Co(en)(bpy)_2]^{3+}$, and $[Rh(dmbpy)_3]^{3+}$ (bpy=2,2′-bipyridine) have been prepared and resolved. The resolution of the series of complexes, $[Co(en)_x(dmbpy)_{3-x}]^{3+}$ and $[Co(en)_x(bpy)_{3-x}]^{3+}$ where $x=0$, 1, 2, 3 has now been completed. The absolute configuration of the bis and tris(diimine) cobalt(III) complexes can be estimated from the sign of the CD bands in the d-d absorption region[5] as well as in the ligand π-π^* transition region.[6] Data for the complete series of mixed complexes is necessary to elucidate the electronic state, optical activity and absolute configuration of the complexes.

In order to understand the twisted effects of dmbpy chelates, the absorption and CD spectra of dmbpy complexes have been compared with the corresponding bpy complexes, in which chelate conformation is believed to be planar.

Experimental

Materials. 3,3′-Dimethyl-2,2′-bipyridine was prepared as stated previously.[1]

$[Co(dmbpy)_3](ClO_4)_3$. This was prepared by air oxidation as described in a previous paper.[1] Oxidation with PbO_2 in place of bubbling air improved the yield. Approximately 50 mg of the complex was adsorbed on a SP-Sephadex column (ϕ2.5×50 cm) and eluted with 0.15 mol·dm^{-3} potassium $(+)_\mathrm{D}$-tartratoantimoniate(III). The eluate was fractionated and the visible absorption spectra measured. All the fractions showed very similar spectra, indicating the absence of geometrical isomers.

$(-)_\mathrm{D}[Co(dmbpy)_3](ClO_4)_3\cdot H_2O$. The complex perchlorate (3.6 g) was converted into the bromide by treatment with an anion exchanger, Dowex 1-X8 in the bromide form. A mixture of the solution of the bromide (50 cm^3) and $K_3[Co(L\text{-}cysu)_3]$(cysu=cysteinsulfinato)[7](1.0 g) was stored in a refrigerator overnight. Needlelike crystals of the $(-)_\mathrm{D}$-diastereoisomer were filtered, washed with water and acetone (1.4 g). The second crop of crystals (0.3 g) was obtained by concentrating the filtrate to half volume. The first and the second crystal crops were combined, recrystallized twice from hot water to give a reproducible CD spectrum. The $(-)_\mathrm{D}$-diastereoisomer in water (20 cm^3) was treated with concentrated hydrochloric acid (1 cm^3). Yellow precipitate of $H_3[Co(L\text{-}cysu)_3]$ was filtered off. The filtrate was treated with 70% perchloric acid (2 cm^3) and the yellow crystals of the perchlorate salt were collected and recrystallized from hot water. Found: C, 46.38; H, 4.25; N, 8.84%. Calcd for $C_{36}H_{36}N_6Cl_3O_{12}Co\cdot H_2O$: C, 46.59; H, 4.13; N, 9.06%.

Preparation of $[Co(en)(dmbpy)_2](ClO_4)_3$. To a solution of $[Co(dmbpy)_3](ClO_4)_3$(1.83 g in 400 cm^3 of water) was added a 10% solution of ethylenediamine (1.2 g) and activated charcoal (0.5 g). The solution was stirred at room temperature for 15 min and then filtered. The filtrate was acidified with a few drops of concentrated hydrochloric acid and poured onto a column of SP-Sephadex (ϕ3.0×40 cm). The adsorbed band was washed with water and eluted with 0.15 mol·dm^{-3} sodium sulfate solution. The column gave four separate bands in the order of elution, I, II, III, and IV, which were $[Co(en)_3]^{3+}$, $[Co(en)_2(dmbpy)]^{3+}$, $[Co(dmbpy)_3]^{3+}$, and $[Co(en)(dmbpy)_2]^{3+}$, respectively. The eluatant of band IV was fractionated and the absorption spectra recorded. No indication for the presence of the geometrical isomer was found. The fractions were collected, evaporated to dryness and the yellow residue extracted with methanol (50 cm^3) and the extract was evaporated to dryness. The residual solid was dissolved in water (20 cm^3) and 70% perchloric acid was added (1 cm^3). The orange-yellow precipitate was filtered off and recrystallized from hot water (300 mg) Found: C, 39.52; H, 4.41; N, 10.34%. Calcd for $C_{26}H_{32}N_6Cl_3O_{12}Co$: C, 39.74; H, 4.10; N, 10.69%.

$(+)_\mathrm{D}[Co(en)(dmbpy)_2](ClO_4)_3$. 1.2 g of perchlorate was converted into the bromide using the anion exchanger Dowex 1-X8 in the bromide form. To the solution of the bromide (50 cm^3) was added $K_3[Co(L\text{-}cysu)_3]$(0.64 g in 10 cm^3 of water) and the solution stored in a refrigerator for 3 h. The yellow crystals of the $(-)_\mathrm{D}$-diastereoisomer were

filtered off, washed with a small amount of ethanol and finally ether, (400 mg). The filtrate was evaporated to half volume and stored in a refrigerator overnight and a second crop of crystals (60 mg) were obtained. The crystals were combined and recrystallized from hot water (300 mg). The $(+)_D$-diastereoisomer was suspended in water (5 cm^3) and stirred for 1 h with 3 mol·dm^{-3} hydrochloric acid (1 cm^3). The yellow precipitate was filtered off and the filtrate was treated with 70% perchloric acid (0.5 cm^3). The orange crystals of $(+)_D$[Co(en)(dmbpy)$_2$](ClO$_4$)$_3$ were collected and recrystallized from hot water. Found: C, 39.74; H, 4.34; N, 10.71%. Calcd for $C_{26}H_{32}N_6Cl_3O_{12}Co$: C, 39.74; H, 4.10; N, 10.69%.

[Co(en)(bpy)$_2$](ClO$_4$)$_3$·4H$_2$O. To a solution of [CoCl$_2$(bpy)$_2$]Cl (3.8 g in 100 cm^3 of water) was added 10% ethylenediamine solution (4.8 g) and the mixture warmed at 60 °C for 3 h. Concentrated hydrochloric acid (0.5 cm^3) was added to the solution and resulting solution diluted to 1000 cm^3 and poured onto a column of SP-Sephadex (ϕ 3.5 × 80 cm). The adsorbed band was washed with water and eluted with 0.2 mol·dm^{-3} hydrochloric acid. The column gave three separate bands, I, II, III, in the order of elution, which were [Co(bpy)$_3$]$^{3+}$, [Co(en)(bpy)$_2$]$^{3+}$, and [Co(en)$_2$(bpy)]$^{3+}$, respectively. The effluent of band II was evaporated to dryness, the residue dissolved in water (10 cm^3) and filtered. After the addition of 70% perchloric acid (2 cm^3), the solution was placed in a refrigerator overnight and the yellow crystals were collected and recrystallized from hot water (1.3 g). Found: C, 33.16; H, 3.74; N, 10.59%. Calcd for $C_{22}H_{24}N_6Cl_3O_{12}Co\cdot 4H_2O$: C, 32.96; H, 3.99; N, 10.47%.

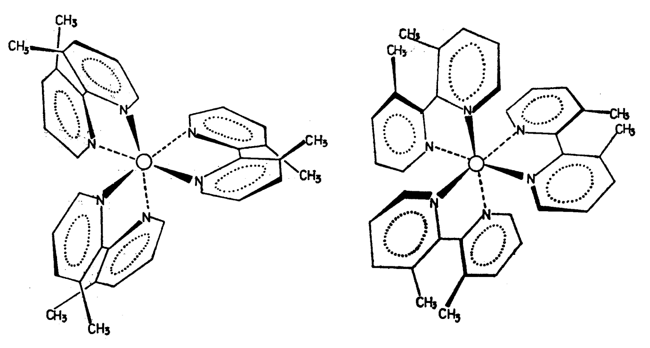
$(+)_D$[Co(en)(bpy)$_2$](ClO$_4$)$_3$. This complex was resolved by a similar method as that for [Co(en)(dmbpy)$_2$]$^{3+}$ using K$_3$[Co(L-cysu)$_3$]. Found: C, 35.20, H, 3.28; N, 11.36%. Calcd for $C_{22}H_{24}N_6Cl_3O_{12}\cdot H_2O$: C, 35.34; H, 3.47; N, 11.23%.

$(-)_D$[Rh(dmbpy)$_3$](ClO$_4$)$_3$. This complex was prepared by a similar method to that for [Rh(bpy)$_3$](ClO$_4$)$_3$ using dmbpy instead of bpy.[8] Optical resolution was achieved using K$_3$[Co(L-cysu)$_3$]. Found: C, 45.29; H, 3.75; N, 8.92%. Calcd for $C_{36}H_{36}N_6Cl_3O_{12}Rh$: C, 45.33; H, 3.68; N, 8.81%.

Measurements. Absorption and CD spectra were recorded at room temperature on a Shimadzu Double 40-R spectrometer and a JASCO J-20 spectropolarimeter, respectively. PMR spectra were measured with a JNM-PMX60 and a JEOL Model 4H-100 spectrometer using DSS as the internal standard.

Results and Discussion

A 3,3′-dimethyl-2,2′-bipyridine chelate can assume dissymmetric conformations (δ and λ) and consequently eight optical isomers arise from the conformational and configurational dissymmetry are possible for a tris complex. The PMR spectra of [Co(dmbpy)$_3$]$^{3+}$ and [Rh(dmbpy)$_3$]$^{3+}$ in D$_2$O gave a single methyl signals at 2.55 and 2.67 ppm, respectively, indicating all the methyl groups in the complex are equivalent. Chromatographic separation of the isomers of [Co(dmbpy)$_3$]$^{3+}$ suggests that the complex consists of only one geometrical isomer; *i.e.*, a pair of enantiomers. Four of the eight possible isomers, $\Delta(\lambda\lambda\lambda)$, $\Lambda(\delta\delta\delta)$, $\Delta(\delta\delta\delta)$, and $\Lambda(\lambda\lambda\lambda)$, two pairs of enantiomers have D$_3$ symmetry in which all the methyl groups are equivalent. Figure 1 shows a schematic drawing of the two isomers, (a) $\Lambda(\delta\delta\delta)$ (*lel*) and (b) $\Lambda(\lambda\lambda\lambda)$ (*ob*). The 2C–2C′ bond of each dmbpy chelate in (a) is pseudo-parallel (*lel*) to the three-fold axis whereas in (b) it is oblique. A molecular model examination suggests that the (b) configuration has appreciable non-bonded atomic interactions between dmbpy chelates in contrast to the (a) configuration. Clearly the same relationship holds for $\Delta(\delta\delta\delta)$ and $\Lambda(\delta\delta\delta)$. Thus the tris complexes are most likely to consist of a pair of enantiomeric forms, $\Delta(\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta)$.



(a) (b)

Fig. 1. Schematic drawings of the two isomers of [Co(dmbpy)$_3$]$^{3+}$; (a) $\Lambda(\delta\delta\delta)$(*lel*), (b) $\Lambda(\lambda\lambda\lambda)$(*ob*).

The bis(dmbpy) complex, [Co(en)(dmbpy)$_2$]$^{3+}$ was obtained by treating the tris complex in aqueous solution with ethylenediamine in the presence of activated charcoal. Other species, such as [Co(en)$_2$(dmbpy)]$^{3+}$, [Co(en)$_3$]$^{3+}$ formed by disproportionation were separated on a Sephadex column. No indication for the presence of more than a pair of enantiomers was found for the bis(dmbpy) complex. Two dmbpy chelates in [Co(en)(dmbpy)$_2$]$^{3+}$ are expected to take the (*lel*, *lel*) form exclusively owing to similar steric requirements as described for the tris complexes.

In addition to the series of dmbpy complexes, the optical resolution of the bpy complex series, [Co(en)$_x$(bpy)$_{3-x}$]$^{3+}$ was completed by the resolution of [Co(en)(bpy)$_2$]$^{3+}$. Figures 2 and 3 show the absorption and CD spectra of the series where [Co(en)$_3$]$^{3+}$ has been excluded to avoid complications. The numerical data is listed in Table 1. The first absorption maximum for the dmbpy complex appears always at longer wavelengths than that of the corresponding bpy complex. Since the first d-d peak positions for the dmbpy complex series do not significantly vary with x (see Table), except for the [Co(dmbpy)$_3$]$^{3+}$ ion, dmbpy appears to lie close to ethylenediamine in the spectrochemical series. The torsional strain of the dmbpy chelate induced by twisting about the 2C–2C′ bond should more or less affect the strength of the coordination bond.

For the dmbpy complexes, strong bands have been observed in the region, 27000—31000 cm^{-1}, In the case of [Co(dmbpy)$_3$]$^{3+}$, the first absorption band is obscured by overlapping. The nature of the band should be a charge transfer transition, since the free ligand does not have a band in this region.[9] The peak maxima shifts to lower energy and the intensities decrease in the order, [Co(en)$_2$(dmbpy)]$^{3+}$, [Co(en)(dmbpy)$_2$]$^{3+}$, and [Co(dmbpy)$_3$]$^{3+}$. This is also the

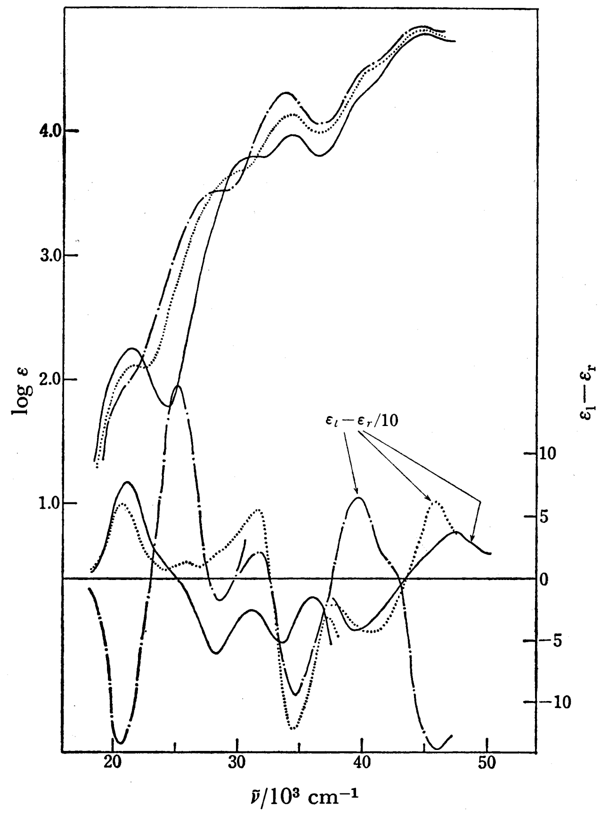


Fig. 2. Absorption and CD spectra of (——)Δ$[Co(en)_2(dmbpy)]^{3+}$, (······) $(+)_D[Co(en)(dmbpy)_2]^{3+}$, and (-··-)$(-)_D[Co(dmbpy)_3]^{3+}$ in water.

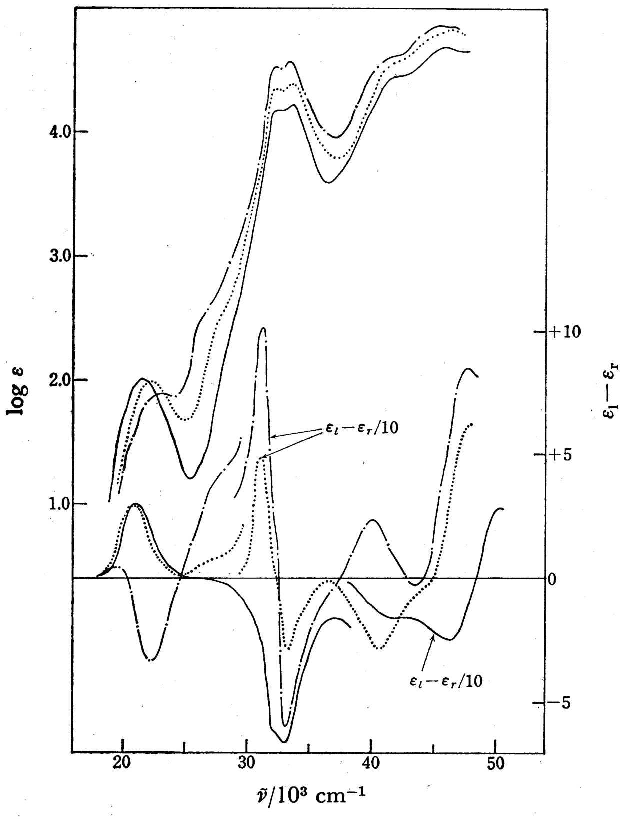


Fig. 3. Absorption and CD spectra of (——) $(+)_D[Co(en)_2(bpy)]^{3+}$, (······) $(+)_D[Co(en)(bpy)_2]^{3+}$, and (-··-) $(+)_D[Co(bpy)_3]^{3+}$ in water.

Table 1. Absorption (AB) and circular dichroism (CD) spectral data in 10 cm^{-1}, (log ε) and ($\varepsilon_l-\varepsilon_r$)

Complex	AB	CD
$(+)_D[Co(en)_3]^{3+}$ a)	21.40(1.97)	20.40(+1.89)
		23.30(−0.12)
	29.50(1.93)	28.60(+0.25)
	47.10(4.36)	47.40(−31.0)
$(+)_D[Co(en)_2$-$(dmbpy)]^{3+}$ b)	21.28(2.21)	21.05(+7.45)
	30.30(3.77)	28.17(−5.84)
	33.67(3.91)	33.78(−4.72)
		39.37(−21.1)
	44.24(4.73)	47.17(+35.7)
$(+)_D[Co(en)$-$(dmbpy)_2]^{3+}$	21.28(2.12)	20.41(+5.81)
	sh 28.57(3.63)	25.97(+1.10)
	33.33(4.15)	31.75(+5.40)
		34.48(−12.4)
	sh 40.32(4.49)	40.98(−23.1)
	43.48(4.77)	45.87(+36.2)
$(-)_D[Co$-$(dmbpy)_3]^{3+}$	sh 20.62(1.95)	20.83(−12.9)
	27.78(3.55)	25.12(+15.6)
	32.89(4.33)	32.05(+27.2)
		34.84(−90.2)
		39.37(+71.0)
	42.74(4.89)	sh 42.02(+16.9)
		46.30(−137.0)
$(+)_D[Co(en)_2$-$(bpy)]^{+}$ b)	21.74(1.99)	20.70(+3.02)
	sh 31.25(4.03)	32.47(−6.64)
	32.46(4.12)	sh 45.87(−24.8)
	45.87(4.68)	49.50(+28.9)
$(+)_D[Co(en)$-$(bpy)_2]^{3+}$	21.83(1.96)	20.62(+3.04)
	31.44(4.34)	30.96(+48.7)
	32.57(4.41)	33.00(−27.2)
	sh 40.82(4.60)	40.48(−28.1)
	45.45(4.88)	47.62(+64.4)
$(+)_D[Co$-$(bpy)_3]^{3+}$ c)		19.80(+0.35)
	22.22(1.89)	22.22(−3.33)
	31.45(4.49)	31.15(+104)
	32.68(4.53)	33.44(−59.2)
		39.68(+23.6)
	45.05(4.84)	43.10(−4.22)
		46.51(+84.3)
$(-)_D[Rh$-$(dmbpy)_3]^{3+}$	sh 30.49(4.41)	29.85(+19.7)
	31.45(4.46)	32.68(−35.6)
		36.50(−14.3)
	sh 42.37(4.73)	40.98(+59.8)
	sh 47.62(4.99)	46.51(−62.1)
$(+)_D[Rh$-$(bpy)_3]^{3+}$ c)	31.45(4.56)	31.15(+145)
	32.79(4.54)	32.36(+52.1)
		sh 33.33(−37.7)
		34.38(−57.9)
	41.67(4.60)	41.67(+15.0)
		45.45(−72.5)

a) Ref. 17. b) Ref. 1. c) Ref. 7.

order of increasing steric interaction. In the case of the bpy complexes, such bands are less marked than for dmbpy complexes.

The intense absorption at about 32000—33000 cm^{-1} for all complexes is ascribed to the ligand π-π* transition.[9,10] The band maxima for the dmbpy complexes always have lower intensities and appear at shorter wavelengths compared with those of the bpy complexes. Single bond twisting in a conjugated system away from coplanarity is known to affect the position and/or the intensities of the π-π^* absorption bands.[11] Therefore, the spectral differences between the bpy and dmbpy series are mainly attributable to the differences in conformation of the chelate rings.

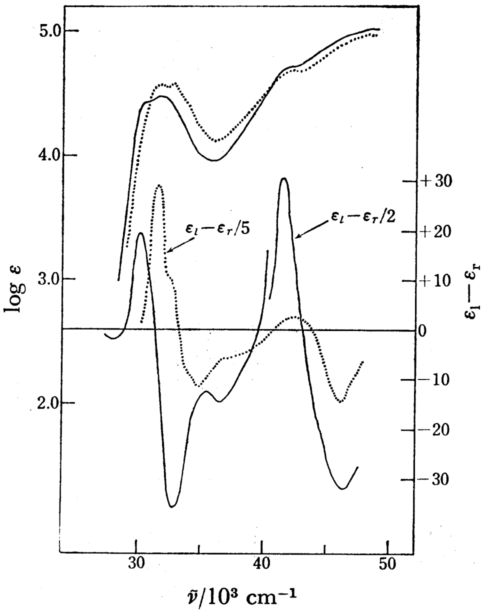


Fig. 4. Absorption and CD spectra of (——) $(-)_D$-$[Rh(dmbpy)_3]^{3+}$, and (······) $(+)_D[Rh(bpy)_3]^{3+}$ in water.

All the CD spectral data given in Table 1 and Figs. 2—4 are for isomers derived from the less soluble diastereoisomeric salt with $[Co(\text{L-cysu})_3]^{3-}$ ion. Of these, the absolute configuration of $(+)_D[Co(en)_3]^{3+}$ [12] and $(+)_D[Co(en)_2(dmbpy)]^{3+}$ [2] have been assigned Λ by X-ray method. The empirical assignment of the absolute configuration on the basis of the dominant CD peaks in the first d-d region are consistent with Λ. The complexes containing two or three bpy or dmbpy units always give a positive-negative CD couplet from the longer wavelength side in the ligand π-π^* region. The exciton couplet CD of the π-π^* transition has been related nonempirically to the absolute configurations of the complexes; when the configuration is Λ, the negative component of the π-π^* couplet lies at a higher energy, while it lies at lower energy when the chirality is Δ.[6] From this rule, the present complexes have been assigned the Λ-configuration.

The bis complexes, $(+)_D[Co(en)(bpy)_2]^{3+}$ and $(+)_D$-$[Co(en)(dmbpy)_2]^{3+}$ exibit one positive CD band in the first d-d absorption band region, giving an assignment of Λ-configuration which is consistent with that predicted from the π-π^* exciton CD bands. On the contrary, $(+)_D[Co(bpy)_3]^{3+}$ [13] and $(-)_D[Co(dmbpy)_3]^{3+}$ gave the negative CD in the first absorption band region, which contradicts the configuration predicted from the exciton CD. The charge-transfer bands have however been located close to or overlapping the first absorption band region for the present tris complexes leading that the CD bands in this region would be complicated by the CD components associated with the charge-transfer bands. The d-d absorption bands of the bis and mono (bpy or dmbpy) complexes are relatively clear compared with those of the tris complexes and the CD bands beneath the d-d absorption appear less affected by adjacent transitions. Many bis(bpy or 1,10-phenanthroline) complexes of cobalt(III),[13–16] whose d-d absorption bands are rather isolated from adjacent bands give CD consistent with the ligang exciton CD for assigning the absolute configuration. The CD in the first absorption band region is at times greately affected by the steric and electronic circumstances of surrounding ligands,[17,18] whereas the exciton CD of tris complexes is usually very intense and not significantly affected by other transitions.[6c] Comparing the exciton CD of the present tris and bis pairs, the absolute configurations of $(+)_D[Co(bpy)_3]^{3+}$, $(+)_D[Co(en)(bpy)_2]^{3+}$, $(-)_D$-$[Co(dmbpy)_3]^{3+}$, and $(+)_D[Co(en)(dmbpy)_2]^{3+}$ have been assigned as Λ

The absorption and CD spectra of $(-)_D$[Rh-dmbpy)$_3]^{3+}$ are shown in Fig. 4 along together those of $(+)_D[Rh(bpy)_3]^{3+}$.[7] The CD patterns of the two complexes are quite similar over all the wavelength region. The intense exciton couplet CD is centered at about 33000 cm^{-1} for the bpy complex and 32000 cm^{-1} for the dmbpy complex. The patterns indicate that the absolute configuration of the complexes are assignable to Λ.

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