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Preparation and Resolution of a Complete Series of $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ Complexes

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A complete series of ten complexes, $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ (en=ethylenediamine; tn=trimethylenediamine; tmd=tetramethylenediamine) was obtained by preparing four new complexes, $[Co(en)(tmd)_2]^{3+}$, $[Co(tn)_2(tmd)]^{3+}$, $[Co(tn)(tmd)_2]^{3+}$, and $[Co(en)(tn)(tmd)]^{3+}$. The new complexes were resolved into optical isomers by SP-Sephadex column chromatography. The absorption and circular dichroism spectra of all the complexes were recorded and discussed.

Ten complexes are expected for a series of complexes of the type, $[M(AA)_x(BB)_y(CC)_z]^{n+}$ (x, y, z=0, 1, 2, or 3; $x+y+z=3$), where AA, BB, and CC denote different bidentate ligands. However, no example of such a complete series has been reported. In a series of ten complexes, $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ (en=ethylenediamine; tn=trimethylenediamine; tmd=tetramethylenediamine), there remain four unknown complexes, $[Co(en)(tmd)_2]^{3+}$, $[Co(tn)_2(tmd)]^{3+}$, $[Co(tn)(tmd)_2]^{3+}$, and $[Co(en)(tn)(tmd)]^{3+}$, all of which contain a seven membered chelate ring. Recently we prepared two tmd complexes, $[Co(en)_2(tmd)]^{3+}$ [1] and $[Co(tmd)_3]^{3+}$,[2] and resolved them into optical isomers. The en, tn, and tmd ligands are the most representative diamines which form a five-, six-, and seven-membered chelate ring, respectively. The collective data on a complete series of complexes of these diamines will be useful in elucidating such properties as the electronic state and the optical activity of a cobalt(III) complex. This paper is concerned with the preparation and resolution of the four unknown tmd complexes and with the comparison of absorption and circular dichroism spectra of all the complexes of the present series.

Experimental

Ligands. The ligands, en, tn, and tmd were obtained from Wako Pure Chemical Industries Co. and used without further purification.

$[Co(en)(tn)(tmd)]Cl_3\cdot 0.5H_2O$. To a solution of *trans*-$[CoCl_2(en)(tn)]ClO_4$[3] (2.0 g, 5.5 mmol) in *N*,*N*-dimethylformamide(DMF)(100 cm^3) was added a solution of tmd (0.5 g, 5.5 mmol) in DMF (100 cm^3), and the solution was stirred for 5 h at room temperature. The resultant reddish brown solution was diluted with a 10^{-2} M HCl solution, and passed through an SP-Sephadex column (ϕ 2.7×5 cm). A small portion of the Sephadex charged with the product was poured on the top of an SP-Sephadex column (ϕ 2.7×120 cm), and the adsorbed complexes were eluted with a 0.2 M Na_2SO_4 solution adjusted to pH 2 with HCl. The column showed six bands; pink (very small amount), pink, yellow, orange, violet, and red-violet bands from bottom to top of the column. The effluent of the fourth orange band was diluted with a 10^{-2} M HCl solution and poured again on an SP-Sephadex column (ϕ 1.5×3 cm). The adsorbed complex was eluted with a 1.0 M KBr solution adjusted to pH 2 with HBr, and the effluent was concentrated to dryness in a vacuum desiccator over P_2O_5–NaOH. The residue was extracted with methanol and the extract was mixed with diethyl ether to give an orange precipitate. The precipitate (crude complex bromide) was filtered off and dissolved in a small amount of 10^{-2} M HCl. To this solution was added a solution of $K_3[Co(CN)_6]$ in 10^{-2} M HCl to precipitate hardly soluble hexacyanocobaltate(III) salt of the complex. This salt was filtered off, washed with water, and mixed with the anion exchanger (BIORAD AG 1×8, 200—400 mesh, in the chloride form) in 10^{-2} M HCl. After the mixture had been stirred for several hours, the resin was filtered off, and the filtrate was passed through a column of the anion exchanger of the same type as the above to ensure the conversion into chloride. The effluent was evaporated to dryness under reduced pressure. Recrystallization from 10^{-2} M HCl by the addition of ethanol gave orange crystals. The yield depends on the purity of the starting material, *trans*-$[CoCl_2(en)(tn)]ClO_4$ which is usually contaminated with *trans*-$[CoCl_2(en)_2]ClO_4$ and *trans*-$[CoCl_2(tn)_2]ClO_4$.
Found: C, 27.24; H, 8.02; N, 20.92%. Calcd for $CoC_9H_{31}N_6O_{0.5}Cl_3=[Co(en)(tn)(tmd)]Cl_3\cdot 0.5H_2O$: C, 27.25; H, 7.88; N, 21.19%.

Resolution of $[Co(en)(tn)(tmd)]^{3+}$. A solution containing about 120 mg (0.3 mmol) of $[Co(en)(tn)(tmd)]Cl_3\cdot 0.5H_2O$ was poured on an SP-Sephadex column (ϕ 2.7×120 cm) and the adsorbed band was eluted with a 0.18 M sodium $(+)_{589}$-tartratoantimonate(III) solution. Two bands, the $(-)_{589}$- and $(+)_{589}$-isomers, were eluted in this order. Each isomer was isolated as bromide by the same method as that for the racemic complex chloride except that the anion exchanger was used in the bromide form. The complex was recrystallized from 10^{-2} M HBr by the addition of methanol. The complex chloride was hygroscopic. Found: C, 19.68; H, 5.79; N, 15.22%. Calcd for $CoC_9H_{34}N_6O_2Br_3=(+)_{589}$-$[Co(en)(tn)(tmd)]Br_3\cdot 2H_2O$: C, 19.41; H, 6.15; N, 15.09%.

$[Co(tn)_2(tmd)]Br_3\cdot 3.5H_2O$. To a solution of *trans*-$[CoCl_2(tn)_2]ClO_4$[4] (4.2 g, 11 mmol) in DMF (300 cm^3) was added a solution of tmd (1 g, 11 mmol) in DMF (200 cm^3) with stirring. The solution was stirred for 1 h at room temperature, and the product was chromatographed by a method similar to that for $[Co(en)(tn)(tmd)]^{3+}$. By developing the adsorbed band with a 0.2 M Na_2SO_4 solution adjusted to pH 2 with HCl, the column gave five bands, blue-violet, violet, reddish orange, violet, and pink in the order of elution. The effluent of the third reddish orange band was reloaded on an SP-Sephadex column (ϕ2.7×5 cm) after dilution with 10^{-2} M HCl. The adsorbed complex was eluted with a 1.0 M KBr solution adjusted to pH 2 with HBr. The eluate was concentrated to a small volume in a rotary evaporator, and the concentrate was kept in a refrigerator to give reddish orange crystals. These were filtered off, and recrystallized from 10^{-2} M HBr. Yield: about 50%. Found: C, 20.02; H, 6.17; N, 14.10%. Calcd for $CoC_{10}H_{39}N_6O_{3.5}Br_3=[Co(tn)_2(tmd)]Br_3\cdot 3.5H_2O$: C, 20.08; H, 6.57; N, 14.05%.

Resolution of $[Co(tn)_2(tmd)]^{3+}$. The resolution was achieved by a method similar to that for $[Co(en)(tn)(tmd)]^{3+}$. The separation of optical isomers was incomplete, but the initial and the final fractions of the eluted complex showed negative and positive CD bands, respectively in the region of the first absorption band. The initial fractions of the effluent were collected, and chromatographed repeatedly until no further increase in dissymmetry factor ($\Delta\varepsilon/\varepsilon$) was observed. The isolation of the optical pure isomer was not attained, because of its small amounts. The quantitative CD curve of the complex was determined with the aid of the ε value of the racemate.

Preparation and Resolution of $[Co(en)(tmd)_2]^{3+}$. A solution of tmd (5.28 g, 60 mmol) and en (1.8 g, 30 mmol) in dimethyl sulfoxide (DMSO) (400 cm^3) was added to a solution of $Co(NO_3)_2\cdot 6H_2O$ (8.8 g, 30 mmol) and tmd·2HBr (3.75 g, 15 mmol) in DMSO (400 cm^3) with stirring. The cobalt ions were oxidized by bubbling a stream of air through the solution for 9 h at room temperature. The resultant dark red solution was diluted with 10^{-2} M HCl and poured on SP-Sephadex. The adsorbed complexes were chromatographed by a method similar to that for $[Co(en)(tn)(tmd)]^{3+}$ with a 0.2 M Na_2SO_4 solution adjusted to pH 2 with HCl. The column gave nine bands; blue-violet, red, yellow, orange, pink, orange, pink, orange, and red-violet bands from bottom to top of the column. The effluent of the fourth orange band was a mixture of $[Co(en)(tmd)_2]^{3+}$ and other tris-diamine complexes as described below, and it was used for optical resolution without isolating the complex racemate. The effluent was reloaded on an SP-Sephadex column ($\phi 2.7\times$ 120 cm) after dilution with 10^{-2} M HCl, and the adsorbed band was eluted with a 0.15 M sodium $(+)_{589}$-tartratoantimonate(III) solution. The column gave four pairs of bands (Δ and Λ), yellow ($[Co(en)_3]^{3+}$), yellowish orange ($[Co(en)_2(tmd)]^{3+}$), orange ($[Co(en)(tmd)_2]^{3+}$), and orange (not characterized) bands in the order of elution. Each eluate of the third pair of the orange bands was passed through an SP-Sephadex column ($\phi 1.5\times 3$ cm) after dilution with 10^{-2} M HCl and the adsorbed complex was eluted with a 1.0 M NaCl solution adjusted to pH 2 with HCl. The isomers were precipitated as hexacyanocobaltate(III) by the addition of $K_3[Co(CN)_6]$ in 10^{-2} M HCl. These salts were converted into chlorides by the use of the anion exchanger as described for $[Co(en)(tn)(tmd)]^{3+}$. Orange crystals were obtained by recrystallizing from 10^{-2} M HCl and methanol. Yield: about 1%. Found: C, 28.62; H, 8.16; N, 19.94%. Calcd for $CoC_{10}H_{34}N_6OCl_3=(-)_{589}$-$[Co(en)(tmd)_2]Cl_3\cdot H_2O$: C, 28.61; H, 8.11; N, 20.03%.

$[Co(tn)(tmd)_2]Cl_3$. To a solution of $Co(NO_3)_2\cdot 6H_2O$ (8.8 g, 30 mmol) and tmd·2HBr (7.6 g, 30 mmol) in DMSO (800 cm^3) were added a solution of tmd (6.68 g, 76 mmol) and tn (1.12 g, 15 mmol) in DMSO (1200 cm^3) and active charcoal (1 g). The air oxidation of the cobalt ions was carried out for 50 h at room temperature. The reaction mixture was filtered to remove the charcoal. The filtrate was diluted with 10^{-2} M HCl and passed through an SP-Sephadex column ($\phi 7\times 30$ cm). By developing the adsorbed band with a 0.5 M HCl solution, the column showed seven bands; violet, orange, blue-violet, red, blue-violet, reddish orange, and red-violet in the order of elution. The effluents of the first violet and the second orange bands were collected and reloaded on an SP-Sephadex column ($\phi 5.5\times 30$ cm) after dilution with 10^{-2} M HCl, and the adsorbed band was eluted with a 0.2 M Na_2SO_4 solution adjusted to pH 2 with HCl. Five bands, violet, violet, orange, brown, and reddish brown were eluted in this order. The effluent of the third band was further loaded on an SP-Sephadex column ($\phi 2.7\times$ 120 cm) after dilution with 10^{-2} M HCl, and the adsorbed complexes were eluted with a 0.15 M sodium $(+)_{589}$-tartratoantimonate(III) solution. The column showed five separate bands; orange ($[Co(tn)_3]^{3+}$), reddish orange ($[Co(tn)_2(tmd)]^{3+}$), red ($[Co(tn)(tmd)_2]^{3+}$), and two purplish red ($(+)_{589}$- and $(-)_{589}$-$[Co(tmd)_3]^{3+}$) bands in the order of elution. The red crystals of $[Co(tn)(tmd)_2]Cl_3$ were obtained from the effluent of the third red band by a method similar to that for $[Co(en)(tn)(tmd)]^{3+}$. Yield: about 0.3%. Found: C, 31.38; H, 8.02; N, 20.22%. Calcd for $CoC_{11}H_{34}N_6Cl_3=$ $[Co(tn)(tmd)_2]Cl_3$: C, 31.78; H, 8.24; N, 20.22%.

Resolution of $[Co(tn)(tmd)_2]^{3+}$. The resolution was achieved by a method similar to that for $[Co(tn)_2(tmd)]^{3+}$. The bands of enantiomers were separated incompletely, so that the chromatography was repeated until no further increase in dissymmetry factor ($\Delta\varepsilon/\varepsilon$) was observed. No isolation of the isomer was made.

Resolution of $[Co(en)_2(tn)]^{3+}$ *and* $[Co(en)(tn)_2]^{3+}$. The racemic complexes were prepared by the method of Ogino and Fujita[5] and resolved by a method similar to that for $[Co(en)(tn)(tmd)]^{3+}$. The separation of bands of Δ- and Λ-$[Co(en)_2(tn)]^{3+}$ was complete, but that of Δ- and Λ-$[Co(en)(tn)_2]^{3+}$ was not, and the chromatography was repeated to obtain the optically pure isomer. Each isomer adsorbed on SP-Sephadex was eluted with a 1.5 M $NaClO_4$ solution and the effluent was evaporated in a vacuum desiccator over P_2O_5 to give orange crystals. These were recrystallized from a small amount of water by the addition of ethanol. Found: C, 14.32; H, 4.88; N, 14.31%. Calcd for $CoC_7H_{30}N_6O_{14}Cl_3$ $=(+)_{589}$-$[Co(en)_2(tn)](ClO_4)_3\cdot 2H_2O$: C, 14.31; H, 5.15; N, 14.30%. Found: C, 17.13; H, 5.06; N, 14.93%. Calcd for $CoC_8H_{28}N_6O_{12}Cl_3=(+)_{589}$-$[Co(en)(tn)_2](ClO_4)_3$: C, 16.99; H, 4.99; N, 14.86%.

Other complexes, $[Co(en)_3]^{3+}$, $[Co(en)_2(tmd)]^{3+}$, $[Co(tn)_3]^{3+}$, and $[Co(tmd)_3]^{3+}$ were prepared and resolved by the methods given in Table 1.

Measurements. Absorption and circular dichroism spectra were obtained on a Hitachi 323 spectrophotometer and a JASCO J-20 spectropolarimeter, respectively.

Results and Discussion

Preparation and Resolution of the Complexes. All of the new complexes contain the seven-membered chelate ligand. Since such large chelate ligands as tmd tend to coordinate to two metal ions to form polymeric complexes,[5] the reactions were carried out in dilute solutions as described in the Experimental part. Nonaqueous solvents such as DMSO are known to be useful for preparing complexes containing large chelate rings.[5] However, in the reactions of *trans*-$[CoCl_2(en)(tn)]^+$ or of *trans*-$[CoCl_2(tn)_2]^+$ with tmd in DMSO, a partial reduction of Co(III) to Co(II) takes place and disproportionation occurs to yield all possible complexes. Such a reduction may be avoided by use of DMF instead of DMSO, and no disproportionation is observed in the reactions. The perchlorates of the above dichloro complexes as well as the corresponding bis-en complex are fairly soluble in DMF and will be good starting materials for preparing mixed tris-diamine complexes. However, the reactions between *trans*-$[CoCl_2(en)_2]ClO_4$ and tn, and between *trans*-$[CoCl_2(tn)_2]ClO_4$ and en in DMF are accompanied by disproportionation, although no reduction seems to occur. For the preparation of both $[Co(en)(tmd)_2]^{3+}$ and $[Co(tn)(tmd)_2]^{3+}$, *trans*-$[CoCl_2(tmd)_2]^+$ should be useful as a starting material.

Table 1. Data on optical resolution of $[Co(en)_x(tn)_y(tmd)_z]^{3+}$

Complex	SP-Sephadex column chromatography			Chemical resolution			X-Ray analysis	
	Faster moving isomer	Eluent	Ref.	Less soluble isomer	Resolv. agent	Ref.	Absolute config.	Ref.
$[Co(en)_3]^{3+}$	(+)*(Λ)	a	8)	(+)	d	9)	(+)-Λ	10)
$[Co(en)_2(tn)]^{3+}$	(+) (Λ)	b	This work	(+)	e	11)	(+)-Λ	12)
$[Co(en)(tn)_2]^{3+}$	(+) (Λ)	b	This work	(+)	e	11)		
$[Co(en)_2(tmd)]^{3+}$	(−) (Λ)	b	1)					
$[Co(tn)_3]^{3+}$	(−) (Λ)	c	6)	(−) (+)	e f	13) 14)	(−)-Λ	15)
$[Co(en)(tn)(tmd)]^{3+}$	(−) (Λ)	b	This work				(+)-Δ	16)
$[Co(en)(tmd)_2]^{3+}$	(−) (Λ)	b	This work					
$[Co(tn)_2(tmd)]^{3+}$	(+) (Δ)	b	This work					
$[Co(tn)(tmd)_2]^{3+}$	(+) (Δ)	b	This work					
$[Co(tmd)_3]^{3+}$	(+) (Δ)	b	2)	(−)	g	2)	(+)-Δ	17)

*: (+) or (−) at NaD line (589 nm); a: sodium $(+)_{589}$-tartrate; b: sodium $(+)_{589}$-tartratoantimonate(III); c: see the text; d: barium $(+)_{589}$-tartrate; e: sodium nitro-$(+)_{589}$-camphorate; f: $(-)_{589}$-$K[As(cat)_3]$ (cat = catecholate ion = 1,2-benzenediolate ion); g: silver $(+)_{589}$-tartratoantimonate(III).

However, this complex may be obtained only a little as a by-product in the preparation of $[Co(tmd)_3]^{3+}$.[2)] Attempts to obtain this dichloro complex enough for reactions have all been unsuccessful. Hence, the two bis-tmd complexes of en or tn were prepared by oxidizing mixtures of Co(II) and the corresponding diamines in DMSO and isolated by the aid of SP-Sephadex column chromatography. The yields were extremely low, less than 1%. The same reactions in DMF result in the formation of hardly soluble black precipitates which appear to be a peroxo complex, and the reactions do not proceed further.

The complexes containing the tmd chelate ligand decompose gradually in neutral water, but stable in acidic solutions. The four new tmd complexes behave as monomeric tripositive ions in SP-Sephadex column chromatography; these complexes adsorbed on SP-Sephadex are easily eluted with 0.1—0.2 M Na_2SO_4 solutions.[5)]

All the complexes, $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ except $[Co(tn)_3]^{3+}$ can be resolved into their antipodes by SP-Sephadex column chromatography. By elution with sodium $(+)_{589}$-tartratoantimonate(III), the complexes containing the en ligand give Λ isomers first, while those of the series, $[Co(tn)_y(tmd)_z]^{3+}$, Δ isomers reversely. For $[Co(tn)_2(tmd)]^{3+}$ and $[Co(tn)(tmd)_2]^{3+}$, the separation of enantiomers on a column is insufficient, and repeated chromatography is necessary to obtain optically pure isomers. The $[Co(tn)_3]^{3+}$ complex cannot be resolved by SP-Sephadex column chromatography, but done completely by a modified Sephadex(D-$(-)_{589}$-tartrate form) column chromatography using a sodium L-$(+)_{589}$-tartrate solution as the eluent.[6)] The data on optical resolution for all the complexes are given in Table 1.

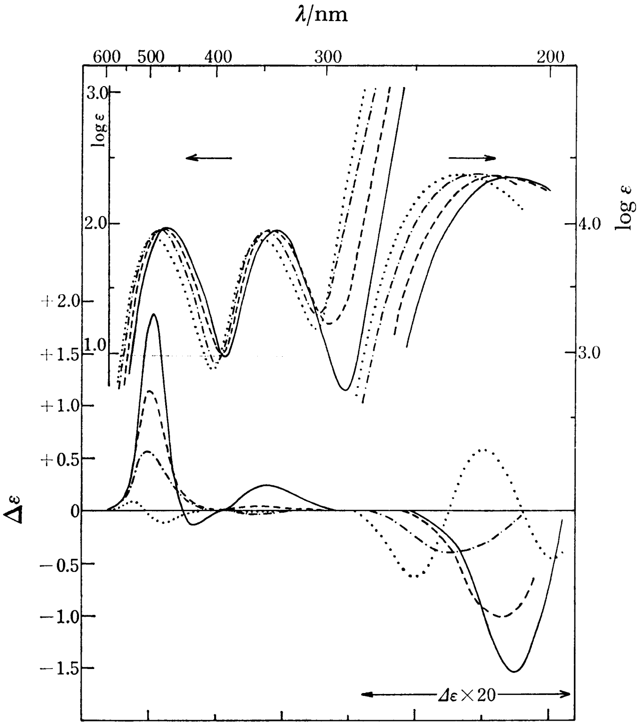

Fig. 1. Absorption and CD spectra of a series of Λ-$[Co(en)_x(tn)_y]^{3+}$ complexes; $(+)_{589}$-$[Co(en)_3]^{3+}$ (——), $(+)_{589}$-$[Co(en)_2(tn)]^{3+}$ (----), $(+)_{589}$-$[Co(en)(tn)_2]^{3+}$ (—·—), and $(-)_{589}$-$[Co(tn)_3]^{3+}$ (······).

Absorption and Circular Dichroism Spectra. Figures 1 to 4 show the absorption and circular dichroism spectra of the present series of complexes, $[Co(en)_x(tn)_y(tmd)_z]^{3+}$, and Table 2 lists the numerical data. Both the d-d and the charge-transfer absorption bands shift to longer wavelengths as the number of ring members of the ligands increases. In Fig. 5 are plotted the maximum positions of these absorption bands against the number of ring members. The magnitude of shifts becomes smaller with increase in the number of ring members. In particular, the charge-transfer band of $[Co(tmd)_3]^{3+}$ shifts very little as compared with that of $[Co(tn)_3]^{3+}$, and those bands in the complexes, $[Co(tn)_y(tmd)_z]^{3+}$, are at nearly the same wavelengths. A similar shift of absorption bands due to the increase

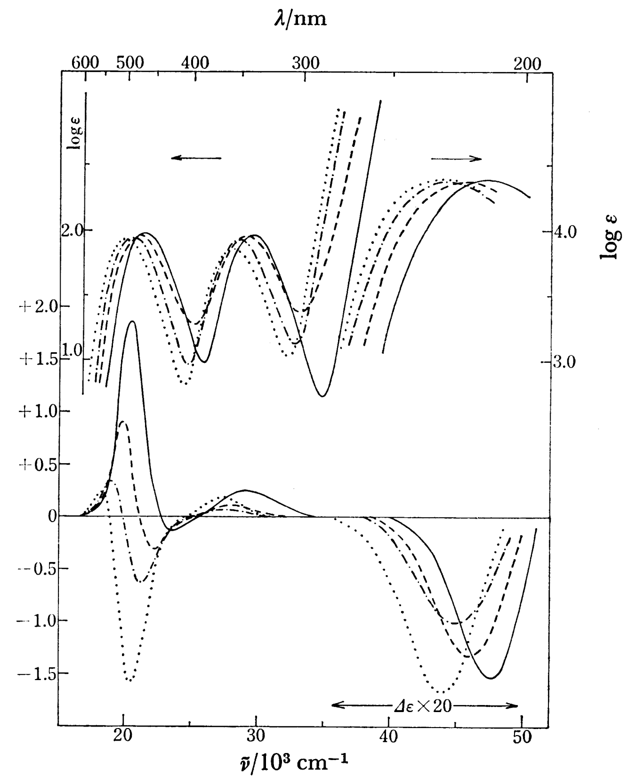

Fig. 2. Absorption and CD spectra of a series of Λ-$[Co(en)_x(tmd)_z]^{3+}$ complexes; $(+)_{589}$-$[Co(en)_3]^{3+}$ (——), $(-)_{589}$-$[Co(en)_2(tmd)]^{3+}$ (----), $(-)_{589}$-$[Co(en)(tmd)_2]^{3+}$ (—·—), and $(-)_{589}$-$[Co(tmd)_3]^{3+}$ (······).

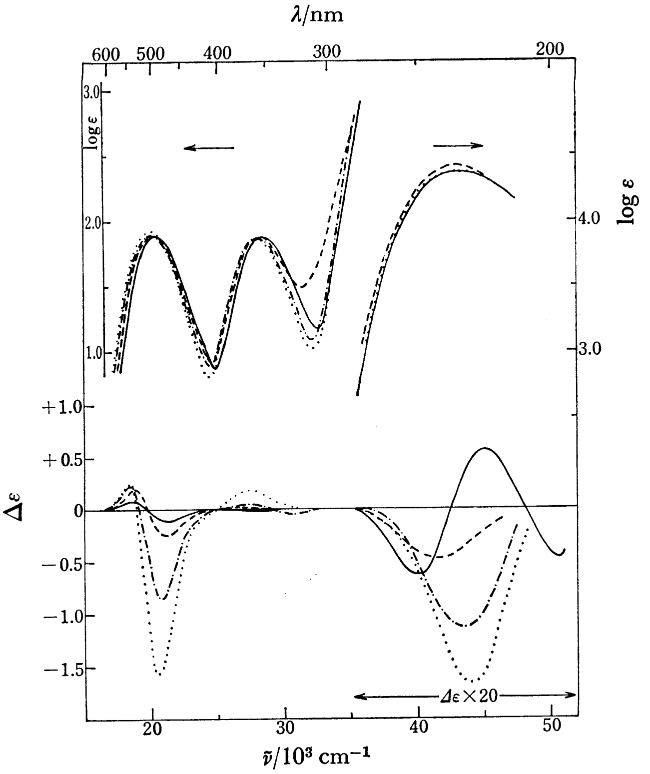

Fig. 3. Absorption and CD spectra of a series of Λ-$[Co(tn)_y(tmd)_z]^{3+}$ complexes; $(-)_{589}$-$[Co(tn)_3]^{3+}$ (——), $(-)_{589}$-$[Co(tn)_2(tmd)]^{3+}$ (----), $(-)_{589}$-$[Co(tn)(tmd)_2]^{3+}$ (—·—), and $(-)_{589}$-$[Co(tmd)_3]^{3+}$ (······).

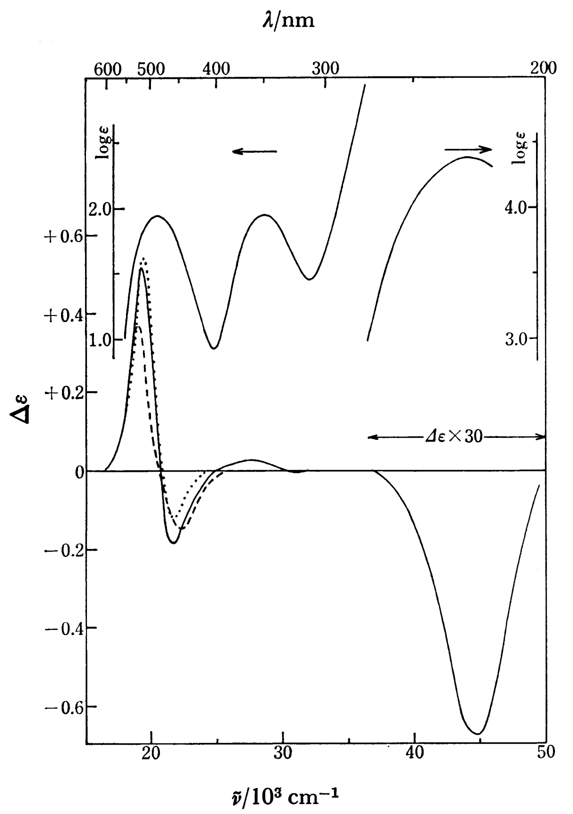

Fig. 4. Absorption and CD spectra of Λ-$(-)_{589}$-$[Co(en)(tn)(tmd)]^{3+}$ (——). Calculated CD curves of Λ-$[Co(en)(tn)(tmd)]^{3+}$ from 1/2{Λ-$[Co(en)_2(tn)]^{3+}$ + Λ-$[Co(tn)_2(tmd)]^{3+}$ + Λ-$[Co(en)(tmd)_2]^{3+}$} − 1/6{Λ-$[Co(en)_3]^{3+}$ + Λ-$[Co(tn)_3]^{3+}$ + Λ-$[Co(tmd)_3]^{3+}$} (······) and 1/3{Λ-$[Co(en)_3]^{3+}$ + Λ-$[Co(tn)_3]^{3+}$ + Λ-$[Co(tmd)_3]^{3+}$} (----).

in the ring members was observed for the complexes of the type, $[Co(am)(en)_2]^{2+}$ (am=amino acidate ion); the first absorption bands of $[Co(gly)(en)_2]^{2+}$, $[Co(\beta\text{-}ala)(en)_2]^{2+}$, and $[Co(amb)(en)_2]^{2+}$ (amb=4-aminobutanoic acidate ion) are at 20.5, 20.2, and 19.8×10^3 cm^{-1}, respectively.[7)]

Although accurate intensity of absorption bands may be determined with difficulty, the apparent intensities (not band area) of the first absorption bands decrease in the order of the complexes of the ligands, en>tmd>tn; the intensities are not proportional to the number of ring members. Such a regular trend is not seen for the second and the charge-transfer absorption bands.

Figures 1—3 show the circular dichroism spectra of three series of complexes, $[Co(en)_x(tn)_y]^{3+}$, $[Co(en)_x(tmd)_z]^{3+}$, and $[Co(tn)_y(tmd)_z]^{3+}$, respectively. Of these complexes, the absolute configurations of $(+)_{589}$-$[Co(en)_3]^{3+}$, $(-)_{589}$-$[Co(tn)_3]^{3+}$, $(+)_{589}$-$[Co(en)_2(tn)]^{3+}$, and $(+)_{589}$-$[Co(tmd)_3]^{3+}$ have been determined by X-ray work to be Λ, Λ, Λ, and Δ, respectively (Table 1). Since the CD spectra of each series show a gradual change in the region of the first absorption band, the configurations of the other complexes shown in Figs. 1—3 can be assigned to Λ. The signs of the main CD bands in this region depend on the number of ring members. However, these nine complexes exhibit all positive CD components at a longer wavelength side

TABLE 2. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption		CD			
			in water		in 0.2 M Na_2SO_4	
	$\tilde{\nu}/10^3$ cm^{-1}	log ε	$\tilde{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$	$\tilde{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$
$(+)_{589}$-$[Co(en)_3]^{3+}$	21.4	1.97	20.4	+1.89	20.3	+1.84
			23.3	−0.12	23.0	−0.36
	29.5	1.93	28.6	+0.25		
	47.1	4.36	47.4	−31		
$(+)_{589}$-$[Co(en)_2(tn)]^{3+}$	21·1	1.96	20.2	+1.14	20.0	+0.98
					22.8	−0.084
	29.2	1.95	27.6	+0.038		
	45.7	4.35	46.5	−20		
$(+)_{589}$-$[Co(en)(tn)_2]^{3+}$	20.7	1.94	19.9	+0.57	19.6	+0.38
					22.9	−0.010
	28.7	1.94	28.2	−0.038		
	44.4	4.37	42.6	−7.9		
$(-)_{589}$-$[Co(en)_2(tmd)]^{3+}$	21.0	1.95	19.7	+0.88	19.6	+0.66
			22.2	−0.33	21.8	−0.65
	29.1	1.94	27.8	+0.11		
	45.5	4.35	46.1	−27		
$(-)_{589}$-$[Co(tn)_3]^{3+}$	20.4	1.88	18.8	+0.083	18.1	+0.023
			21.1	−0.11	20.7	−0.31
	28.5	1.88	28.4	−0.018		
	43.3	4.38	40.0	−13		
			45.3	+12		
			50.5	−9.1		
$(-)_{589}$-$[Co(en)(tn)(tmd)]^{3+}$	20.6	1.95	19.3	+0.51	19.1	+0.35
			21.9	−0.19	21.4	−0.56
	28.6	1.94	27.4	+0.026		
	44.2	4.38	44.8	−20		
$(-)_{589}$-$[Co(en)(tmd)_2]^{3+}$	20.4	1.94	19.0	+0.34	18.7	+0.18
			21.2	−0.64	21.0	−0.94
	28.4	1.91	27.4	+0.061		
	44.1	4.37	45.0	−20		
$(-)_{589}$-$[Co(tn)_2(tmd)]^{3+}$	20.2	1.89	18.8	+0.19	19.5	+0.099
			21.1	−0.24	20.8	−0.44
	28.2	1.87	27.0	+0.01		
			30.3	−0.044		
	43.1	4.41	41.8	−9.4		
$(-)_{589}$-$[Co(tn)(tmd)_2]^{3+}$	20.1	1.90	18.5	+0.22	18.1	+0.050
			20.7	−0.87	20.6	−0.94
	28.2	1.86	27.0	+0.04		
			31.3	−0.04		
	43.1	4.40	43.3	−23		
$(-)_{589}$-$[Co(tmd)_3]^{3+}$	19.9	1.92	18.4	+0.24	17.8	+0.03
			20.5	−1.56	20.3	−2.20
	28.0	1.87	27.4	+0.18		
	43.1	4.38	43.9	−33		

of the first absorption band. The strengths of these components are diminished in the presence of Na_2SO_4, and complementarily the negative CD components are enhanced (Table 2). The signs of the CD bands at the longest wavelengths in the charge-transfer region are all negative. All these observations have been reported for some complexes of the present series (Table 1). The CD spectrum of $(-)_{589}$-$[Co(en)(tn)(tmd)]^{3+}$ shown in Fig. 4 satisfies the above observations, and can be assigned to the same absolute configuration, *Λ*. The gradual changes of the CD spectra shown in Figs. 1—3 indicate that the CD spectrum of a mixed tris-diamine complex in the region of the first absorption band can be approximated by a sum of the contributions from three pairs of the chelate rings in chiral configuration. For example, the CD curve of [Co(en)(tn)-

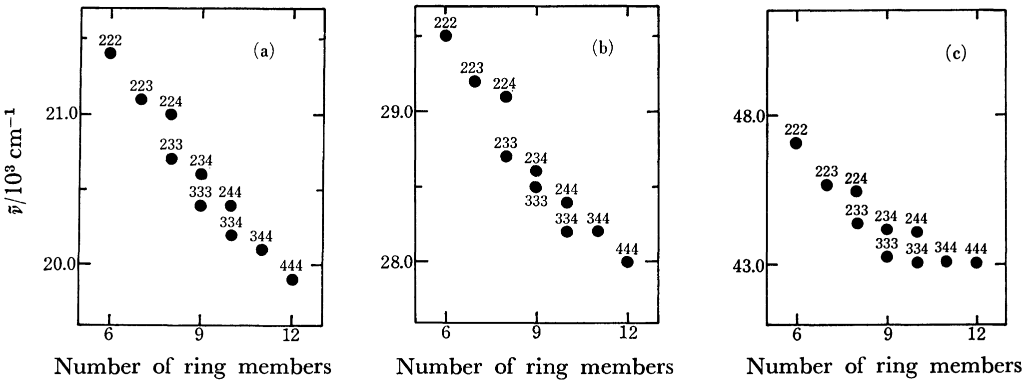

Fig. 5. Positions of (a) the first, (b) the second, and (c) the charge-transfer absorption bands of [Co(en)$_x$(tn)$_y$(tmd)$_z$]$^{3+}$. In the Figs. 2, 3, and 4 indicate en, tn, and tmd in the complex, respectively. For example, 234 denotes [Co(en)(tn)(tmd)]$^{3+}$.

(tmd)]$^{3+}$ which involves three pairs of chiral configurations, en-tn, en-tmd, and tn-tmd may be evaluated from the observed CD spectra of the following six complexes; $[\mathrm{Co(en)(tn)(tmd)}]^{3+} = 1/2\{[\mathrm{Co(en)_2(tn)}]^{3+} + [\mathrm{Co(tn)_2(tmd)}]^{3+} + [\mathrm{Co(en)(tmd)_2}]^{3+}\} - 1/6\{[\mathrm{Co(en)_3}]^{3+} + [\mathrm{Co(tn)_3}]^{3+} + [\mathrm{Co(tmd)_3}]^{3+}\}$. The calculated CD curve of [Co(en)(tn)(tmd)]$^{3+}$ shown in Fig. 4 agrees well with the observed one. If the CD spectrum of a tris-chelate complex can be approximated by a sum of the contributions from each chelate ring, the CD curve of [Co(en)(tn)(tmd)]$^{3+}$ is obtained by the following equation; $[\mathrm{Co(en)(tn)(tmd)}]^{3+} = 1/3\{[\mathrm{Co(en)_3}]^{3+} + [\mathrm{Co(tn)_3}]^{3+} + [\mathrm{Co(tmd)_3}]^{3+}\}$(or $1/3\{[\mathrm{Co(en)_2(tn)}]^{3+} + [\mathrm{Co(tn)_2(tmd)}]^{3+} + [\mathrm{Co(en)(tmd)_2}]^{3+}\}$). The calculated CD curve is also given in Fig. 4. This curve agrees less satisfactorily with the observed spectrum compared with that approximated by the sum of the contributions of three pairs of the chelate rings.

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