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Preparation and Absorption and Circular Dichroism Spectra of Cobalt(III) Complexes with *N*,*N*,*N'*,*N'*-Tetrakis(2-aminoethyl)-1,2-ethanediamine, -1,3-propanediamine, -1,4-butanediamine, and -(*R*,*R*)- and -(*R*,*S*)- 2,4-pentanediamine

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Cobalt(III) complexes of new sexidentate ligands, *N*,*N*,*N'*,*N'*-tetrakis(2-aminoethyl)-1,3-propanediamine (ttn), -1,4-butanediamine (ttmd), and -(*R*,*R*)- and -(*R*,*S*)-2,4-pentanediamine (tptn) were prepared and resolved except the *RR*-tptn complex which formed the Δ-isomer stereoselectively. The monocyano complexes of *N*,*N*,*N'*,*N'*-tetrakis(2-aminoethyl)-1,2-ethanediamine (ten) and ttn, in which the ligands act as a quinquidentate, were also prepared. Absorption and CD spectra of these complexes and the known $[Co(ten)]^{3+}$ complex were compared with one another. The first d-d absorption bands of the sexidentate complexes, $[Co(A)]^{3+}$ are shifted to smaller wave numbers in the order, ttn>ten>ttmd for A, but those of $[Co(CN)(HA)]^{3+}$ are in the reverse order, ten>ttn. The d-d absorption bands of $[Co(\mathit{RS}\text{-tptn})]^{3+}$ which contains one axial methyl group show the remarkable red shift and the hyperchromic effect as compared with those of $[Co(\mathit{RR}\text{-tptn})]^{3+}$ with two equatorial methyl groups.

N,*N*,*N'*,*N'*-Tetrakis(2-aminoethyl)-1,2-ethanediamine (ten) can act as a sexidentate ligand to give metal complexes structurally similar to those of ethylenediaminetetraacetate (edta).1) Emmenegger and Schwarzenbach2) found that the first absorption band of $[Co(ten)]^{3+}$ shows a remarkable red shift (13 nm) as compared with that of $[Co(NH_3)_6]^{3+}$, and attributed it to the reduction of ligand field strength caused by a strained structure of the complex ion. Muto *et al.*3) found by the X-ray structure analysis that the coordination octahedron of this complex ion is largely distorted. Similar strain is involved in the structurally related $[Co(edta)]^-$ ion.4) The strain or distortion in such sexidentate complexes might be diminished or enhanced by changing ring members of the central diamine chelate rings. The strain would also be reduced by opening one chelate ring to form a complex of the type, $[Co(X)(Hten)]^{n+}$ (X=unidentate ligand).

This paper reports the preparation, resolution, and absorption and circular dichroism (CD) spectra of cobalt(III) complexes with sexidentate *N*,*N*,*N'*,*N'*-tetrakis(2-aminoethyl)-1,2-ethanediamine (ten), -1,3-propanediamine (ttn), -1,4-butanediamine (ttmd), and -2,4-pentanediamine (tptn) of (*R*,*R*) and (*R*,*S*) forms. When the last sexidentate (*RS*)-tptn ligand forms an octahedral complex, one methyl group of the ligand takes necessarily an axial disposition. The complexes of the type, $[Co(CN)(HA)]^{3+}$ (HA=$Hten^+$ and $Httn^+$) in which the hexamine ligands act as a quinquidentate with a free aminoethyl branch are also described in this paper.

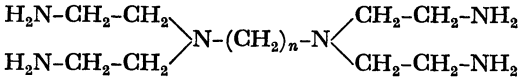
Experimental

Preparation of Ligands. All the hexamine ligands were prepared according to a method similar to that for ten reported by Moser and Schwarzenbach.1)

N-(Phenylsulfonyl)aziridine was prepared from aziridine5) and benzenesulfonyl chloride by the method of Moser and Schwarzenbach.1) (*R*,*R*)- and (*R*,*S*)-2,4-Pentanediamine (ptn) were obtained by the method of Bosnich and Harrowfield.6) Other diamines, 1,2-ethanediamine (en), 1,3-propanediamine (tn), and 1,4-butanediamine (tmd) were purchased (Tokyo Kasei) and used without further purification.

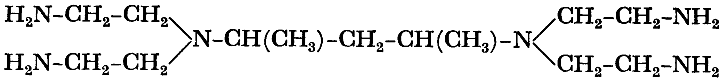
Benzene solutions of *N*-(phenylsulfonyl)aziridine (0.33 mol in 100 cm^3) and a diamine (0.058 mol in 10 cm^3) were dried with Na_2SO_4 (4 °C) and molecular sieves 4A 1/16 (room temperature), respectively, for 1 d. To the former solution was carefully added the latter solution dropwise with stirring, the solution being kept at *ca.* 20 °C. The resulting solution was stirred at *ca.* 30 °C for 2 d to give the tetrakis(phenylsulfonyl)derivative. The derivatives from en, tmd, and *RR*-ptn were fine white crystalline products, which were filtered, washed three times with benzene, and dried *in vacuo*, but those from the other diamines were faintly brown colored oily products, and the benzene was removed by evaporating under reduced pressure.

The tetrakis(phenylsulfonyl)derivatives (0.05 mol) were hydrolyzed by heating at 150 °C in a mixture of concd H_2SO_4 (60 g) and water (15 g) for 17 h. Each of the resulting brown solutions was cooled to room temperature, mixed with water (*ca.* 50 cm^3), and adjusted the pH to *ca.* 8 with a concd aqueous KOH solution. After cooling, K_2SO_4



$$\begin{array}{l}H_2N\text{-}CH_2\text{-}CH_2\\ H_2N\text{-}CH_2\text{-}CH_2\end{array}\!\!>\!N\text{-}(CH_2)_n\text{-}N\!<\!\!\begin{array}{l}CH_2\text{-}CH_2\text{-}NH_2\\ CH_2\text{-}CH_2\text{-}NH_2\end{array}$$

n=2(ten), 3(ttn), and 4(ttmd)



$$\begin{array}{l}H_2N\text{-}CH_2\text{-}CH_2\\ H_2N\text{-}CH_2\text{-}CH_2\end{array}\!\!>\!N\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}N\!<\!\!\begin{array}{l}CH_2\text{-}CH_2\text{-}NH_2\\ CH_2\text{-}CH_2\text{-}NH_2\end{array}$$

R,*R*- and *R*,*S*-tptn

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and potassium benzenesulfonate precipitated were filtered off and the precipitate was washed well with ethanol. The filtrate and washings were combined and evaporated under reduced pressure. From the residue the free ligand was extracted with ethanol and the extract was evaporated. This procedure was repeated until the oily ligand was free from potassium benzenesulfonate. All the ligands thus prepared were used for the preparation of complexes without distillation because of their high boiling points. However, all the ligands showed satisfactory ^{1}H NMR spectra in $CDCl_3$ and their metal complexes gave good analytical results.

Preparation of Complexes. *[Co(ten)]Br$_3$·2H$_2$O*: Emmenegger and Schwarzenbach[2] first prepared this complex by heating a mixture of ten and $[CoBr(NH_3)_5]Br_2$ over a flame. Yoshikawa *et al.*[7] obtained the complex by stirring an aqueous solution containing the same reactants with active charcoal at room temperature. In the present study, the complex was prepared from *trans*-$[CoCl_2py_4]Cl\cdot 6H_2O$ (py=pyridine)[8] and ten in methanol in the absence of active charcoal.

A methanol solution (50 cm^3) of ten (1 g, 4.3 mmol) was added to a methanol solution (200 cm^3) of *trans*-$[CoCl_2py_4]Cl\cdot 6H_2O$ (3 g, 5.1 mmol). The solution was stirred for several hours at room temperature and then the methanol was evaporated under reduced pressure. The residue was dissolved in 2 dm^3 of water and the pH of the solution was adjusted to *ca.* 3 with hydrochloric acid. This was poured on a column (ϕ5 cm × 40 cm) of SP-Sephadex C-25 resin and the product adsorbed was chromatographed with a 0.2 mol/dm^3 Na_2SO_4 solution. To the main red orange eluate was added an aqueous solution of $K_3[Co(CN)_6]$ (*ca.* 2 g). After 1 d, hardly soluble red orange crystals of [Co(ten)]-$[Co(CN)_6]$ formed were filtered, washed with cold water, and then mixed with Dowex 1×8 resin in the bromide form in water in order to convert into bromide. The resin was filtered off and the filtrate was evaporated to *ca.* 3 cm^3 under reduced pressure. The concentrate was mixed with ethanol and stored in a refrigerator for several days to give red orange crystals which were filtered, washed with ethanol and then ether, and air dried.

*[Co(ttn)]Br$_3$·H$_2$O, [Co(*RR*-tptn)]Cl$_3$·2H$_2$O, and [Co(*RS*-tptn)]Cl$_3$·2H$_2$O*: These complexes were obtained as orange, orange, and red crystals, respectively, by a method similar to that for the ten complex. The *RR*-tptn complex was crystallized by adding acetone instead of ethanol, since the complex is soluble in a mixture of ethanol and water.

[Co(ttmd)]Br$_3$·H$_2$O: Since the complex contains a seven-membered chelate ring, the reaction was carried out in a dilute solution in order to avoid the formation of polynuclear complexes.[9]

Methanol solutions of *trans*-$[CoCl_2py_4]Cl\cdot 6H_2O$ (1 g in 500 cm^3) and ttmd (0.4 g in 500 cm^3) were simultaneously added to 500 cm^3 of methanol dropwise with stirring over a few hours at room temperature. The resulting solution was stirred for 1 d at room temperature. The methanol was evaporated to dryness under reduced pressure and the residue was dissolved in 2 dm^3 of water. The solution was adjusted to pH *ca.* 3 with hydrochloric acid and poured on a column (ϕ5 × 40 cm) of SP-Sephadex C-25 resin. By elution with 0.25 mol/dm^3 Na_2SO_4, several bands were eluted from the column, a small amount of high charged species remaining on the top of the column. The red main eluate was rechromatographed by the same method after dilution with water. From the eluate, red crystals of [Co(ttmd)]-$[Co(CN)_6]$ were obtained and converted into bromide by the same method as that for the ten complex.

[Co(CN)(Hten)]Br$_3$·2H$_2$O: To a cold (*ca.* 4 °C) aqueous solution (100 cm^3) containing $[Co(ten)]Br_3\cdot 2H_2O$ (0.5 g) and KCN (0.07 g) was added a small amount of active charcoal and the mixture was allowed to stand at *ca.* 4 °C for 5 h with occasional shaking. The active charcoal was filtered off and the filtrate was diluted to 2 dm^3 with water. This was poured on a column (ϕ2.7 × 60 cm) of SP-Sephadex C-25 resin. The column was thoroughly washed with water and the product adsorbed was eluted with a 0.2 mol/dm^3 Na_2SO_4 solution adjusted the pH to *ca.* 9 with Na_2CO_3. Three bands, yellow, orange, and red orange were eluted in succession, the second orange band being the largest amount. The first yellow and the third red orange bands were presumed from the absorption spectra to involve a dicyano and the starting complexes, respectively. The second orange eluate was diluted ten times with water and the solution was poured again on a small column (ϕ2.7 × 5 cm) of SP-Sephadex C-25 resin. After the column had been washed with 0.01 mol/dm^3 hydrobromic acid in order to remove Na^+ ions, the complex was eluted with 2 mol/dm^3 hydrobromic acid. The eluate was mixed with acetone and allowed to stand for several days at room temperature to give orange crystals of $[Co(CN)(Hten)]Br_3\cdot 2H_2O$.

[Co(CN)(Httn)]Br$_3$·nH$_2$O: An aqueous solution (150 cm^3) containing $[Co(ttn)]Br_3\cdot H_2O$ (0.95 g), KCN (0.13 g), and a small amount of active charcoal was stored in a refrigerator (*ca.* 4 °C) for 3 d with occasional shaking. After filtering off the active charcoal, the filtrate was diluted with water to 3 dm^3 and the solution was poured on a column (ϕ2.7 × 120 cm) of SP-Sephadex C-25 resin. The column was washed with water and the product adsorbed was then eluted with a 0.2 mol/dm^3 Na_2SO_4 solution adjusted the pH to *ca.* 3 with hydrochloric acid. Three orange bands, I, II, and III were eluted in succession. Band I was found to be contaminated with a small amount of the starting complex, so that the eluate was rechromatographed by use of a 0.2 mol/dm^3 Na_2SO_4 solution adjusted the pH to *ca.* 9 with Na_2CO_3 as an eluent, the starting complex being eluted much slower. From bands I and III, orange crystals of $[Co(CN)(Httn)]Br_3\cdot H_2O$ (A) and $[Co(CN)(Httn)]Br_3\cdot 2H_2O$ (B) were obtained, respectively, by the same method as that for the corresponding ten complex. The amount of band II was too small to isolate the complex.

No reaction took place between [Co(*RR*-tptn)]Cl$_3$·2H$_2$O and KCN even at a higher temperature. Reactions of [Co(*RS*-tptn)]Cl$_3$·2H$_2$O or $[Co(ttmd)]Br_3\cdot H_2O$ with KCN resulted in decomposition of the complexes to yield cobalt(II) species and other unknown complexes, no mono cyano complexes being found in both reaction products.

Optical Resolution. The $[Co(ttn)]^{3+}$, $[Co(ttmd)]^{3+}$, and [Co(*RS*-tptn)]$^{3+}$ complexes were resolved by the same SP-Sephadex column chromatographic method as that for [Co(ten)]$^{3+}$ reported by Yoshikawa *et al.*[7]

By elution with 0.2 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III), each of $[Co(ten)]^{3+}$, $[Co(ttmd)]^{3+}$, and [Co(*RS*-tptn)]$^{3+}$ was completely resolved giving two well separated bands of enantiomers. In the case of $[Co(ttn)]^{3+}$, however, the separation of bands was poor, so that the eluate was fractionated into 10 cm^3 and optical purity of each fraction was examined by taking a ratio of CD strength to optical density at 505 nm, the fractions with the ratio of a constant value being collected. The enantiomers eluted faster are $(-)_{589}$-$[Co(ten)]^{3+}$, $(+)_{589}$-$[Co(ttn)]^{3+}$, $(-)_{589}$-$[Co(ttmd)]^{3+}$, and $(-)_{589}$-[Co(*RS*-tptn)]$^{3+}$. For each complex, the optically pure fractions were collected, diluted about ten times with water, and poured on a small column of SP-Sephadex C-25 resin. After washing the column with 0.01 mol/dm^3 hydrochloric acid, the complex was eluted with

TABLE 1. ANALYTICAL DATA OF THE NEW COMPLEXES

Complexes	C(%)		H(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
$[Co(ttn)]Br_3 \cdot H_2O$	23.44	23.46	5.64	5.73	14.90	14.93
$[Co(ttmd)]Br_3 \cdot H_2O$	24.91	24.98	5.82	5.94	14.36	14.56
$[Co(RR\text{-tptn})]Cl_3 \cdot 2H_2O$	32.64	32.82	7.85	8.05	17.72	17.66
$[Co(RS\text{-tptn})]Cl_3 \cdot 2H_2O$	33.13	32.82	7.88	8.05	17.85	17.66
$[Co(CN)(Hten)]Br_3 \cdot 2H_2O$	22.28	22.24	5.81	5.60	16.28	16.50
$[Co(CN)(Httn)]Br_3 \cdot H_2O$(A)	24.51	24.42	5.63	5.64	16.66	16.62
$[Co(CN)(Httn)]Br_3 \cdot 2H_2O$(B)	24.12	23.70	5.83	5.80	15.63	16.12

ten$=C_{10}H_{28}N_6$, ttn$=C_{11}H_{30}N_6$, ttmd$=C_{12}H_{32}N_6$, tptn$=C_{13}H_{34}N_6$.

2 mol/dm^3 hydrochloric acid and the eluate was used for the measurement of CD spectra. The optically active complexes were not isolated because of small amounts. The $\Delta\varepsilon$ values were determined with the aid of ε values of the racemates.

Analytical data of the new complexes are given in Table 1.

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40 CS spectropolarimeter, respectively. ^{1}H NMR (D_2O, TMS) and ^{13}C NMR (D_2O, dioxane) were obtained with a JEOL JNM-PMX 60 and a JEOL FX-100 spectrometer, respectively.

Results and Discussion

Absorption Spectra. *The ten, ttn, and ttmd Complexes*: The $[Co(ten)]^{3+}$, $[Co(ttn)]^{3+}$, and $[Co(ttmd)]^{3+}$ complexes contain a five-, six-, and seven-membered chelate ring, respectively, for the central ditertiary diamine chelate ring. In general, the first absorption band of a tris(diamine)cobalt(III) complex is shifted to smaller wavenumbers as the number of ring members increases. For example, $[Co(en)_3]^{3+}$, $[Co(tn)_3]^{3+}$, and $[Co(tmd)_3]^{3+}$ give the first absorption band at 21400, 20400, and 19900 cm^{-1}, respectively.[10] However, those of the ten-type complexes are shifted to smaller wavenumbers in the order of $[Co(ttn)]^{3+}$, $[Co(ten)]^{3+}$, and $[Co(ttmd)]^{3+}$, the order of the first two complexes being opposite to that expected from the tris(diamine) complexes (Table 2 and Fig. 1). Emmenegger and Schwarzenbach[2] first found the red shift of the first absorption band for $[Co(ten)]^{3+}$ from a comparison with $[Co(NH_3)_6]^{3+}$ (21000 cm^{-1}) and attributed it to a strained structure of the complex ion. The strained structure was confirmed by the X-ray structure analysis on $(+)_{589}$-$[Co(ten)][Co(CN)_6] \cdot 2H_2O$;[3] the six nitrogen donor atoms forms a distorted octahedron, the N–Co–N angles (83.3—102.2°) largely deviating from that of the regular octahedron (90°), and the distortion of the two chelate rings linked meridionally with the central ethylenediamine chelate ring is particularly noticeable. Such a distortion might weaken the ligand field strength to cause the red shift of the first absorption band in $[Co(ten)]^{3+}$. The strain or distortion in $[Co(ttn)]^{3+}$ would be much reduced as compared with that in $[Co(ten)]^{3+}$, since $[Co(ttn)]^{3+}$ containing a six-membered chelate ring gives the first absorption band at a higher wavenumber than that of $[Co(ten)]^{3+}$. Dreiding molecular models clearly indicate that $[Co(ttn)]^{3+}$ is much less strained than $[Co(ten)]^{3+}$. In the model of $[Co(ten)]^{3+}$, considerable strains are involved in the three five-membered chelate rings fused in a plane with the cobalt(III) ion as confirmed

TABLE 2. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption $\tilde{\nu}/10^3$ cm^{-1}(log ε)	CD $\tilde{\nu}/10^3$ cm^{-1}($\Delta\varepsilon$)
$(-)_{589}$-$[Co(ten)]^{3+}$	20.5(2.35)	19.6(−3.63)
		22.1(+0.58)
	29.2(2.25)	29.8(−1.04)
	43.7(4.30)	44.0(+11.0)
$(+)_{589}$-$[Co(ttn)]^{3+}$	21·0(1.96)	19.8(+1.62)
		22.1(−0.59)
	29.0(1.95)	27.8(+0.50)
		ca. 35.5(*ca.* +0.3)
	44.0(4.27)	43.3(− 7.0)
$(-)_{589}$-$[Co(ttmd)]^{3+}$	20.0(2.23)	19.2(−1.20)
		21.7(+0.11)
		26.0(−0.25)
	28.3(2.11)	*ca.* 29 (*ca.* −0.1)
		36.6(+1.11)
	46.0(4.16)	40.5(−0.67)
		46.5(−4.52)
$(-)_{589}$-$[Co(RR\text{-tptn})]^{3+}$	20.8(2.07)	19·8(−2.14)
		22.1(+0.56)
	28.7(1.98)	27.5(−0.76)
		37.9(−1.55)
	43.0(4.25)	42.2(+1.55)
		44.8(−0.80)
$(-)_{589}$-$[Co(RS\text{-tptn})]^{3+}$	20.0(2.32)	19.3(−3.38)
		22.0(+0.25)
	28.1(2.20)	26.5(−0.95)
		ca. 29 (*ca.* −0.6)
		37.3(−1.00)
	42.0(4.26)	44.5(−3.10)
$[Co(CN)(Hten))]^{3+}$	22.2(2.13)	
	30.5(2.09)	
	43.9(3.85)	
$[Co(CN)(Httn)]^{3+}$ (A)	21.9(1.98)	
	30.2(1.96)	
	43.7(4.03)	
(B)	21.6(2.10)	
	29.7(2.13)	
	43.5(4.03)	

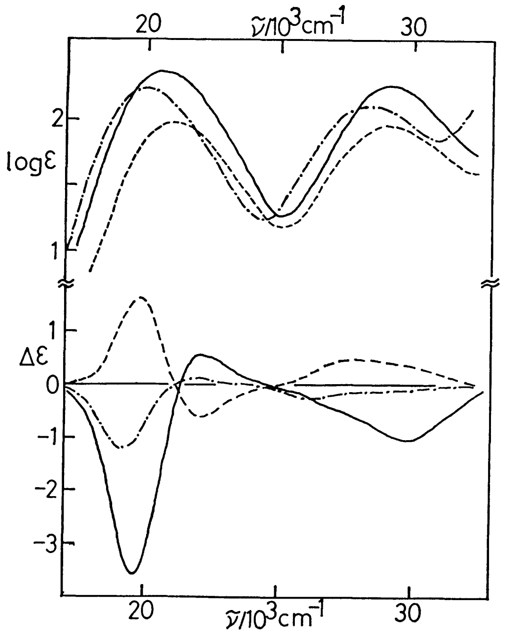

Fig. 1. Absorption and CD spectra of $(-)_{589}$-[Co(ten)]$^{3+}$ (——), $(+)_{589}$-[Co(ttn)]$^{3+}$ (- - -), and $(-)_{589}$-[Co(ttmd)]$^{3+}$ (—·—).

by the X-ray structure analysis. For [Co(ttn)]$^{3+}$, however, neither the corresponding five-six-five-membered chelate rings nor the other chelate rings appear to involve remarkable strain. Thus it is presumed that the reverse order in the first absorption maxima of the two complexes is caused by the strained structure of [Co(ten)]$^{3+}$. On the other hand, [Co(ttmd)]$^{3+}$ shows the first absorption band at the smallest wavenumbers among the three complexes. A molecular model indicates that this complex ion involves no remarkable strain for the skeleton of all the chelate rings, but forms a very crowded structure, some methylene protons coming very close to one another. A crowded complex would expand the molecular volume in order to reduce non-bonded interactions among atoms. The expansion might lengthen the metal-ligand distances to weaken the ligand field strength. In fact, the Co–N distances of [Co(en)$_3$]$^{3+}$,[11] [Co(tn)$_3$]$^{3+}$,[12] and [Co(tmd)$_3$]$^{3+}$ [13] are 1.959—1.979, 1.966—1.999, and 1.986—2.000 Å, respectively, and with an increase in the Co–N distance the absorption maxima are shifted to smaller wavenumbers (*vide infra*).

In contrast with the first absorption band, the second absorption bands are in the usual order of [Co(ten)]$^{3+}$, [Co(ttn)]$^{3+}$, and [Co(ttmd)]$^{3+}$. Accordingly, the energy difference between the first and the second bands becomes larger in [Co(ten)]$^{3+}$ (8700 cm^{-1}) than in [Co(ttn)]$^{3+}$ (8000 cm^{-1}). For a low-spin, octahedral cobalt(III) complex, the energy difference between the first ($^1T_{1g}\leftarrow{}^1A_{1g}$, 10Dq−C) and the second ($^1T_{2g}\leftarrow{}^1A_{1g}$, 10Dq+16B−C) absorption bands is expressed by 16B, where Dq is the parameter of ligand field strength and B and C those of Racah of interelectronic repulsion.[14] The B value is known to be a measure for representing covalent character of the bond between a ligand and a metal ion, the smaller the value the more the covalent character.[15] The B values for the ten and ttn complexes are 544 and 500 cm^{-1}, respectively. Since the values for a series of complexes, [Co(en)$_x$(tn)$_y$(tmd)$_z$]$^{3+}$ [10] are almost constant, 500—506 cm^{-1}, the value of 544 cm^{-1} for [Co(ten)]$^{3+}$ appears to be fairly large and to have relations with the strained structure. Donor atoms in a strained complex would deviate from the regular octahedral coordination sites. The deviation might cause misalignment of the lone-pair orbital of the donor atom to orbitals of the metal ion to decrease the overlap of orbitals between them. The decrease in overlap, or the decrease in covalent character would correspond to an increase in the B value. The [Co(ttmd)]$^{3+}$ complex shows the B value of 519 cm^{-1}. This value indicates that the complex is not so strained as [Co(ten)]$^{3+}$ as the molecular model suggested.

The strain in [Co(ten)]$^{3+}$ would be reduced by forming a quinquidentate complex, [Co(X)(Hten)]$^{n+}$ (X=unidentate ligand), liberating one chelate ring. Emmenegger and Schwarzenbach[2] prepared such complexes with various unidentate ligands. In this study, [Co(CN)(Hten)]$^{3+}$ was newly prepared, since the ttn ligand gave a quinquidentate complex only with a cyanide ion. Although quinquidentate complexes of ten and ttn have two and three possible geometrical isomers, respectively, the cyanide complexes obtained are one and two isomers for ten and ttn, respectively. The structures of the isomers could not be assigned. The structurally related [Co(X)(Hedta)]$^{n-}$ complexes always give only one isomer in which the X ligand occupies the coordination site meridional to the nitrogen atoms of ethylenediamine.[16,17] No corresponding 1,3-propanediaminetetraacetato complex is known, but similar triacetato complexes with H_2O or Cl^- give all of the possible three isomers.[18] In the present quinquidentate complexes, the first absorption band of [Co(CN)(Hten)]$^{3+}$ is observed at a higher wavenumber than those of either isomer of [Co(CN)(Httn)]$^{3+}$ (Table 2 and Fig. 2). The result supports that [Co(ten)]$^{3+}$ is strained and the strain is reduced to a great extent by releasing one chelate ring from the coordination sphere. The ttmd complex gave no monocyano complex.

Reactivity of the sexidentate complexes toward strong bases such as OH^- or CN^- seems to be related with the stability of these complexes expected from the maximum wavenumbers of the first absorption bands. The [Co(ten)]$^{3+}$ complex readily reacts with OH^- [2] or CN^- to yield quinquidentate complexes, opening

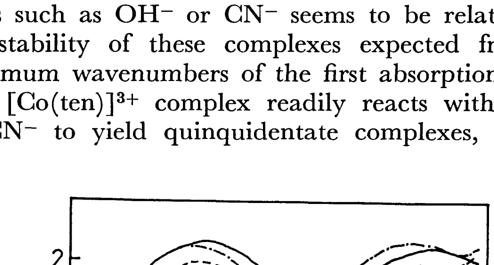

Fig. 2. Absorption spectra of [Co(CN)(Hten)]$^{3+}$ (——), and the two isomers of [Co(CN)(Httn)]$^{3+}$, (A) (- - -) and (B) (—·—).

one chelate ring. The $[Co(ttn)]^{3+}$ complex also gives the mono cyano complex, but the reaction is rather slow as compared with the case of $[Co(ten)]^{3+}$ (Experimental). The ttn complex does not react with OH^-. The $[Co(ttmd)]^{3+}$ complex affords no quinquidentate complex by the reaction with CN^- or OH^-, but gives cobalt(II) species and a small amount of unknown cobalt(III) complexes.

The RR- *and* RS-*tptn Complexes*: The two methyl groups in each *RR*(or *SS*)- and *RS*-ptn chelate ring become equatorial in a λ(or δ)-skew and a chair conformation, respectively.[19] The skeletons of *RR*- and *RS*-tptn ligands in sexidentate complexes should be similar to that of ttn in $[Co(ttn)]^{3+}$, the conformation of the six-membered 1,3-diamine part being in a skew form. When this part forms a chair conformation, both *RR*- and *RS*-tptn ligands can not act as a sexidentate in an octahedral complex. Accordingly, one methyl group in the sexidentate $[Co(RS\text{-tptn})]^{3+}$ complex adopts necessarily an axial disposition. The axial methyl group comes very close to one of the two five-membered chelate rings apical to the six-membered ring and hence $[Co(RS\text{-tptn})]^{3+}$ would be less stable than $[Co(RR\text{-tptn})]^{3+}$. The structurally related ligands, (*R*,*R*(or *S*,*S*))- and (*R*,*S*)-2,4-pentanediaminetetraacetate (ptnta) form stereoselectively Δ(or Λ)-$[Co(RR(\text{or } SS)\text{-ptnta})]^-$ and $[Co(Cl)(RS\text{-Hptnta})]^-$, respectively.[20] The *RS*-ptnta in the latter complex functions as a quinquidentate, leaving a free acetate branch, and the six-membered chelate ring forms a chair conformation with two methyl groups disposed equatorially. This indicates that ptnta is not a so strong ligand as it forms a sexidentate complex by overcoming the unstabilization caused by the axial methyl group.

The orange $[Co(RR\text{-tptn})]^{3+}$ and red $[Co(RS\text{-tptn})]^{3+}$ complexes show the first absorption band at 20800 and 20000 cm^{-1}, respectively (Table 2 and Fig. 3). While the maximum wavenumber of the former is nearly the same as that of $[Co(ttn)]^{3+}$, the wavenumber of the latter is as small as that of the crowded $[Co(ttmd)]^{3+}$ complex. Both tptn complexes lose the water of crystallization by heating *in vacuo* without the change of color. Absorption spectra of the complexes do not depend on pH of the solutions. ^{13}C NMR spectra (100 MHz) of the *RR*- and *RS*-tptn complexes in D_2O solutions exhibit seven and twelve (one strong peak due to accidental degeneracy) signals in accordance with the symmetry argument. All the facts lead to the conclusion that both *RR*- and *RS*-tptn ligands act as a sexidentate in the complexes. Thus the red shift of the first absorption band in $[Co(RS\text{-tptn})]^{3+}$ can be attributed to the crowded structure due to the presence of the axial methyl group. On the other hand, the B value (506 cm^{-1}) of this complex is nearly the same as those of $[Co(RR\text{-tptn})]^{3+}$ (493 cm^{-1}) and $[Co(ttn)]^{3+}$ (500 cm^{-1}). This suggests that the red $[Co(RS\text{-tptn})]^{3+}$ complex is not distorted like $[Co(ten)]^{3+}$ and the red shift of the first absorption band is caused by the crowded structure as described for $[Co(ttmd)]^{3+}$. A complex which contains an axial methyl group is known for Λ-β-$[Co(ox)(R,R\text{-}2,3'',2\text{-tet})]^+$ (ox=oxalate ion, *R*,*R*-2,3″,2-tet=(4*R*,6*R*)-4,6-dimethyl-3,7-diazanonane-1,9-diamine), in which the central six-membered chelate ring adopts a chair conformation with one methyl group axial and the other equatorial.[21] This complex, however, shows the first absorption band (19800 cm^{-1}) at a little smaller wavenumber than that of the corresponding *R*,*S*-2,3″,2-tet complex (19920 cm^{-1}), in which the six-membered chelate ring is also in a chair form, but both methyl groups are disposed equatorially.[22] For the *RR*- and *RS*-tptn complexes which contain a skew six-membered chelate ring, the wavenumber difference in the first absorption bands amounts to 800 cm^{-1}.

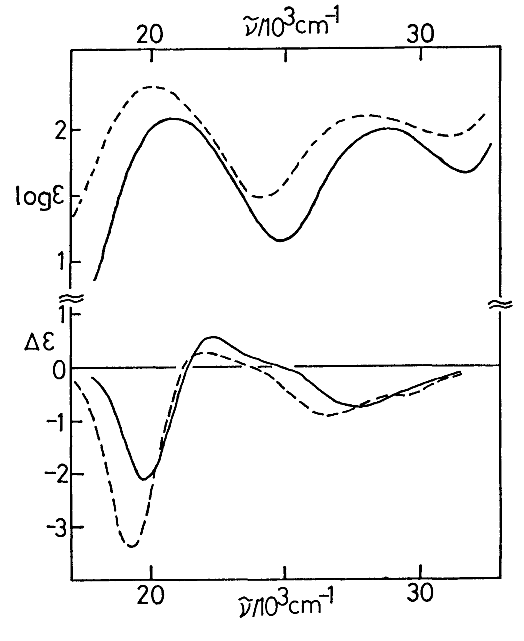

Fig. 3. Absorption and CD spectra of $(-)_{589}$-$[Co(RR\text{-tptn})]^{3+}$ (——) and $(-)_{589}$-$[Co(RS\text{-tptn})]^{3+}$ (- - -).

Circular Dichroism Spectra. The CD spectra of $(-)_{589}$-$[Co(ten)]^{3+}$, $(+)_{589}$-$[Co(ttn)]^{3+}$, and $(-)_{589}$-$[Co(ttmd)]^{3+}$, all of which were enantiomers eluted faster by SP-Sephadex column chromatography, are compared in Fig. 1. The absolute configuration of $(+)_{589}$-$[Co(ten)]^{3+}$ has been determined by the X-ray method to be Λ.[3] On the basis of the CD pattern in the region of the first absorption band of $(-)_{589}$-Δ-$[Co(ten)]^{3+}$, $(+)_{589}$-$[Co(ttn)]^{3+}$ and $(-)_{589}$-$[Co(ttmd)]^{3+}$ can be assigned to the Λ and Δ configurations, respectively. The strengths of main CD bands in this region decrease with an increase in ring members of the central chelate ring. In the Λ-$[Co(en)_x(tn)_y(tmd)_z]^{3+}$ complexes, the positive CD bands reduce the strength remarkably with an increase in the ring members, the main CD band of Λ-$[Co(tmd)_3]^{3+}$ showing strong negative.[10] The spectral changes in CD among the ten-type complexes appear to be the same case. The CD spectra in the other region are rather complicated and no discussion can be made.

The CD spectra of $(-)_{589}$-$[Co(RR\text{-tptn})]^{3+}$ and $(-)_{589}$-$[Co(RS\text{-tptn})]^{3+}$ are shown in Fig. 3. The $[Co(RR\text{-tptn})]^{3+}$ complex should have the Δ configuration stereoselectively owing to the equatorial preference of the methyl groups.[20] The CD spectrum of this complex is almost the mirror image of that of $(+)_{589}$-$[Co(ttn)]^{3+}$ in Fig. 1. The result supports the previous assignment for Δ-$(+)_{589}$-$[Co(ttn)]^{3+}$. The $(-)_{589}$-[Co(*RS*-tptn)]$^{3+}$ complex which was eluted faster in column chromatography shows a CD spectral pattern similar to that of $(-)_{589}$-Δ-[Co(*RR*-tptn)]$^{3+}$, indicating the same Δ configuration. The similarlity also supports that the *RS*-tptn ligand acts as a sexidentate in the complex. In the first absorption band, both CD strength and absorption intensity of the *RS*-tptn complex are stronger than those of the *RR*-tptn complex and the values of the dissymmetry factor g ($\Delta\varepsilon/\varepsilon$) are nearly the same (*ca.* 0.017). A similar, but smaller difference is seen in the CD and absorption spectra between Δ-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]$^{+}$ and -[Co(ox)(*R*,*S*-2,3″,2-tet)]$^{+}$.[22] The presence of an axial methyl group in a complex seems to cause the red shift and the hyperchromic effect on the absorption and CD spectra.

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