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Preparation and Spectroscopic Studies of Cobalt(III) Complexes Containing Optically Active Seven-membered Chelate Ligands

Masaaki Kojima, Ken'ichi Morita, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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New cobalt(III) complexes of the types, *trans*-$[CoCl_2L_2]^+$, $[Co(NH_3)_4L]^{3+}$, *cis*-$[Co(NH_3)_2L_2]^{3+}$, and $[Co(en)_2L]^{3+}$, where L denotes a seven-membered chelate diamine ligand, (*R*)-2-methyl-1,4-butanediamine or *meso*- and (*R* or *S*)-2,5-hexanediamine, have been prepared. The dichloro complexes decompose gradually even in the solid state, and rapidly in methanol. The ammine and ethylenediamine complexes are stable in acidic water, but decompose gradually in neutral water. The absorption and circular dichroism spectra of all the complexes have been recorded in aqueous or acetone solutions. The circular dichroism spectra in the first absorption band region are changed by the addition of sulfate ions, and the variation has been discussed in terms of the structure of isomers and the conformational instability of the seven-membered chelate rings.

A six-membered chelate ring has been shown to be conformationally flexible and to interchange easily its conformation between two forms, the chair and the skew depending on environment. In the previous papers,[1—3] we reported that spectral changes in absorption and circular dichroism (CD) of some 1,3-diamine cobalt(III) complexes caused by the addition of sulfate ions can be interpreted in terms of such conformational instability of six-membered chelate rings.

Studies with molecular models suggest that a seven-membered diamine chelate ring is also conformationally labile and can interchange among some conformers (Fig. 1). In fact, two 1,4-butanediamine (tetramethylenediamine, tmd) chelate rings in *trans*-$[CoCl_2(tmd)_2]Cl\cdot H_2O$ have been shown by X-ray analysis to have different conformations, *skew(h)* and *skew(v)*,[4] while those in Δ-$[Co(tmd)_3]Br_3$ have the λ-*skew(h)* conformation.[5] In [Pd{(*S*)-ornithinato}$_2$], two seven-membered chelate (*N,N*) rings are in the *twist-chair* conformation, which can be regarded as the distorted *chair* form.[6] Thus, seven-membered chelate rings are stabilized in various conformations in crystals of metal complexes. In solution, however, these conformations might be changed by different factors such as solvation and ion-pair formation. In order to elucidate the conformation of seven-membered chelate rings in solution, we have prepared cobalt(III) complexes containing tmd, (*R*)-2-methyl-1,4-butanediamine (*R*-mtmd), and 2,5-hexanediamine (dmtmd), and measured their absorption and CD spectra in the absence and presence of sulfate ions.

Experimental

Measurements. Absorption spectra were recorded on a Hitachi 323 spectrophotometer, and CD spectra on JASCO model J-20 and J-40CS spectropolarimeters. Optical rotation at 589 nm were measured with a JASCO DIP-4 polarimeter. All the measurements were made at 25±1 °C.

Preparation. *2-Methyl-1,4-butanediamine (mtmd).* Dimethyl 2-methylbutanedioate prepared by the method of Jeffery and Vogel[7] was dissolved in methanol which had been saturated with ammonia. The solution was stirred for 6 days at room temperature to give 2-methyl-1,4-butanediamide. 2-Methyl-1,4-butanediamine (mtmd) was prepared by reducing the diamide with $LiAlH_4$ in dry tetrahydrofuran (THF). To a suspension of $LiAlH_4$ (11.4 g, 0.3 mol) in dry THF (280 cm^3) was added the diamide (7.6 g, 0.056 mol) in small portions. The mixture was refluxed for 27 h, and then cooled in an ice-bath. A mixture of water–THF (1: 1) was added dropwise with vigorous stirring. The slurry was filtered by suction, the residue was extracted with THF (*ca.* 100 cm^3) under reflux for 1 h, and filtered again. The extraction was repeated once more. The combined filtrate and extracts were mixed with hydrochloric acid to adjust the pH to *ca.* 2, and then evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water, and a concd sodium hydroxide solution was added. The separated amine layer was extracted three times with chloroform. The extracts were dried over potassium hydroxide pellets, and the chloroform was removed under atmospheric pressure. The remaining oily liquid was distilled under reduced pressure. Bp 88—91 °C/5.3 kPa (lit,[8] 172—173 °C/101 kPa). Yield: 10 g. The diamine was also prepared by reducing 1,2-dicyanopropane[9] in ethanol with sodium.[8] The *rac*-diamine thus obtained was resolved by the following method. To a hot ethanol solution (90 cm^3) of (*R,R*)-2,3-bis(benzoyloxy)succinic acid monohydrate (10 g, 0.027 mol) was slowly added an ethanol solution (27 cm^3) of *rac*-mtmd (2.8 g, 0.027 mol). White crystals (4.5 g, crude (*R,R*)-2,3-bis(benzoyloxy)-succinate) which formed were collected, washed with ethanol, recrystallized seven times from water, and then converted to the dihydrochloride ((+)-mtmd·2HCl) by a method similar to that for (*R,R*)-2,4-pentanediamine dihydrochloride.[10] Yield: *ca.* 30%. $[\alpha]=+5.6°$ (*c* 0.01, H_2O). The (+)-isomer is known to have the (*R*) configuration.[11]

2,5-Hexanediamine (dmtmd). This diamine was prepared by reducing 2,5-hexanedione dioxime[12] with sodium in ethanol according to the known method,[13] or with Raney-Ni in water. The dioxime (50 g, 0.35 mol) was dissolved in an aqueous solution (1 dm^3) of sodium hydroxide (150 g, 3.75 mol). To this solution was added Raney-Ni alloy (100 g) in small portions while the solution was vigorously stirred and cooled to keep the reaction temperature between 25 and 30 °C. After the addition had been completed (*ca.* 1.5 h), the mixture was allowed to stand overnight at room temperature. The residual nickel was filtered off and washed with water. The combined filtrate and washings were steam distilled until no further amine was detected. The distillate was acidified with hydrochloric acid (pH *ca.* 2) and evaporated to dryness to give the diamine hydrochloride. The free diamine was obtained from the hydrochloride by extracting and distilling according to a method similar to that for mtmd, for extraction ether being used instead of chloroform. Bp 80 °C/3.3 kPa (lit,[13] 175 °C/101 kPa). Yield: 12 g. The meso and active diamines were obtained by the following method. To a hot ethanol solution (240 cm^3) of (*R*,*R*)-2,3-bis(benzoyloxy)succinic acid monohydrate (24.3 g, 0.065 mol) was added an ethanol solution (70 cm^3) of the diamine (7.5 g, 0.065 mol). The solution was allowed to stand overnight at room temperature. Colorless crystals which formed were filtered, and recrystallized three times from water–ethanol (1:3). Yield: 6.7 g. $[\alpha]=-86.4°$ (*c* 0.033, H_2O). No change in the rotation was observed with further recrystallizations. This product was converted to the dihydrochloride ((+)-dmtmd·2HCl) by a method similar to that for (+)-mtmd·2HCl. Yield: 1.7 g. $[\alpha]=+11.4°$ (*c* 0.051, H_2O). The free diamine prepared from this dihydrochloride showed negative rotation. The *meso*-diamine dihydrochloride was obtained from the most soluble fraction of the (*R*,*R*)-2,3-bis(benzoyloxy)succinate salt by a method similar to that for the active diamine.

trans-[CoCl$_2$(R-mtmd)$_2$]ClO$_4$. A mixture of *R*-mtmd·2HCl (2.0 g, 11.4 mmol) and sodium methoxide (1.08 g, 20 mmol) in methanol (15 cm^3) was stirred for *ca.* 1 h. Sodium chloride which deposited was filtered off and washed with a small amount of methanol. The combined filtrate and washings were diluted with dimethyl sulfoxide (DMSO, 200 cm^3). This solution of *R*-mtmd and a DMSO solution (200 cm^3) of $Co(NO_3)_2 \cdot 6H_2O$ (1.02 g, 3.5 mmol) were simultaneously added dropwise to vigorously stirred DMSO (500 cm^3). Air was bubbled through the resulting solution for 6 d in the presence of active charcoal (2 g). After removal of the active charcoal, the dark red solution was diluted with 4 dm^3 of 10^{-2} M HCl (1 M=1 mol/dm^3), and passed through a column (ϕ 2.7×7 cm) of SP-Sephadex. The Sephadex charged with the product was placed on the top of a column (ϕ 7×30 cm) of the same resin, and the adsorbed complexes were eluted with 0.2 M Na_2SO_4 adjusted to pH 2 with $HClO_4$. The effluent of the fastest moving violet band, which was presumed from the absorption spectrum to involve $[Co(R\text{-}mtmd)_2(H_2O)_2]^{3+}$, was collected, diluted with water, and passed again through an SP-Sephadex column (ϕ 2.7×5 cm). After the column had been washed with water, the adsorbed band was eluted with 1 M HCl. Perchloric acid (70%, 0.5 cm^3) was added to the eluate, and the solution was concentrated in a vacuum desiccator over P_2O_5 and NaOH to yield green needles. They were filtered and washed with water. Yield: 0.05 g. The complex is unstable even in the solid state, decomposing at room temperature in 2 months. It is much more unstable in solution; a methanol solution became turbid in 5 min, while an acetone solution was stable enough to record absorption and CD spectra, although it decomposed in a day.

trans-[CoCl$_2${(−)-dmtmd}$_2$]ClO$_4$·0.5H$_2$O. This complex was prepared from (+)-dmtmd·2HCl (dihydrochloride of (−)-dmtmd) and $Co(NO_3)_2 \cdot 6H_2O$ by a method similar to that for the corresponding *R*-mtmd complex. The complex is as unstable as the *R*-mtmd complex.

[Co(NH$_3$)$_4$(tmd)]Cl$_3$·1.5H$_2$O. This complex was prepared by a method similar to that reported.[14] To a DMSO solution (380 cm^3) of tmd (1.0 g, 11 mmol) was slowly added a DMSO solution (380 cm^3) of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ (5.3 g, 11 mmol). The solution was stirred for 2 days at room temperature. The resulting orange-red solution was diluted with water, adjusted to pH 2 with HCl, and poured onto a column (ϕ 2.7×4 cm) of SP-Sephadex. A small portion of the Sephadex charged with the product was placed on the top of a column (ϕ 2.7×120 cm) of SP-Sephadex, and the adsorbed complexes were eluted with 0.2 M Na_2SO_4 adjusted the pH to 2 with HCl. The column showed several bands. The effluent of the third orange band was diluted ten times with 10^{-2} M HCl and passed again through an SP-Sephadex column (ϕ 2×3 cm). After the column had been washed with 10^{-2} M HCl (10 dm^3), the adsorbed band was eluted with 1 M HCl. The effluent was evaporated to almost dryness in a vacuum desiccator over P_2O_5 and NaOH. Orange crystals which formed by the addition of ethanol were filtered and washed with ethanol. Yield: 0.5 g.

[Co(NH$_3$)$_4$(R- or S-mtmd)](ClO$_4$)$_3$. This complex was prepared from *rac*-mtmd and $[Co(NH_3)_5(H_2O)](ClO_4)_3$ by a method similar to that for the corresponding tmd complex. The effluent containing $[Co(NH_3)_4(mtmd)]^{3+}$ was diluted with 10^{-2} M HCl, and passed through a column (ϕ 2×3 cm) of SP-Sephadex. The adsorbed band was eluted with 1.5 M $NaClO_4$ adjusted to pH 2 with $HClO_4$. On concentration with a rotary evaporator, the effluent yielded orange crystals, which were collected and washed with ethanol. Yield: 10%. This racemate was resolved by SP-Sephadex column chromatography. The complex (*ca.* 50 mg) adsorbed on a column of SP-Sephadex (ϕ 2.7×120 cm) was eluted with 0.15 M sodium (+)-tartratoantimonate(III). A good separation between the enantiomers was observed. From the fast and the slowly eluted fractions, $[Co(NH_3)_4(S\text{-}mtmd)](ClO_4)_3$ and $[Co(NH_3)_4(R\text{-}mtmd)](ClO_4)_3$ were isolated, respectively, by a method similar to that for the racemate. The assignment of the isomers was made by comparing the CD spectra with that of the complex prepared from the active *R*-mtmd and $[Co(NH_3)_5(H_2O)](ClO_4)_3$.

[Co(NH$_3$)$_4$(meso-dmtmd)]Cl$_3$·2.5H$_2$O, [Co(NH$_3$)$_4${(+)-dmtmd}](ClO$_4$)$_3$·H$_2$O, and [Co(NH$_3$)$_4${(−)-dmtmd}](ClO$_4$)$_3$·H$_2$O. These complexes were prepared from a mixture of *meso*- and *rac*-dmtmd and $[Co(NH_3)_5(H_2O)](ClO_4)_3$ by a method similar to that for $[Co(NH_3)_4(tmd)]^{3+}$. By elution with 0.2 M Na_2SO_4 adjusted to pH 2 with HCl, the column showed five bands; orange-red ($[Co(NH_3)_5(H_2O)]^{3+}$), purple ($[Co(NH_3)_5(DMSO)]^{3+}$), yellow-orange ($[Co(NH_3)_6]^{3+}$) and two orange ($[Co(NH_3)_4(dmtmd)]^{3+}$) bands in the order of elution. From the fourth band, $[Co(NH_3)_4(meso\text{-}dmtmd)]Cl_3 \cdot 2.5H_2O$ was obtained by the same method as that for the corresponding tmd complex. The complex corresponding to the fifth band ($[Co(NH_3)_4(rac\text{-}dmtmd)]^{3+}$) was resolved into a pair of enantiomers by the same method as that for $[Co(NH_3)_4(mtmd)]^{3+}$. The fast and the slowly moving bands were assigned to the (−)-dmtmd and the (+)-dmtmd complexes, respectively, by comparing their CD spectra with that of the complex prepared by use of (+)-dmtmd·2HCl ((−)-dmtmd). The enantiomers were isolated as perchlorates by a method similar to that for $[Co(NH_3)_4(mtmd)](ClO_4)_3$ using an eluent of 1 M $HClO_4$ instead of 1.5 M $NaClO_4$. Attempts to obtain the crystalline chlorides were unsuccessful.

Λ-[Co(en)$_2$(R-mtmd)](ClO$_4$)$_3$·0.5H$_2$O and Δ-[Co(en)$_2$(R-mtmd)](ClO$_4$)$_3$·2H$_2$O. To a DMSOsolution (200 cm^3) of *trans*-$[CoCl_2(en)_2]ClO_4$ (0.7 g, 2 mmol) was slowly added a DMSO solution (50 cm^3) of *rac*-mtmd (0.2 g, 2 mmol). The solution was stirred for 2 d at room temperature. The resulting solution was subjected to SP-Sephadex column chromatography by a method similar to that for the corresponding tetraammine complex. By elution with 0.2 M Na_2SO_4 adjusted to pH 2 with HCl, the column showed four bands; two pink (small amount) and two orange (nearly the same amount) bands; M-I and M-II, in the order of elution. M-I and M-II are racemates of a pair of diastereomers, $\Lambda(R)$ and $\Delta(S)$, and $\Lambda(S)$ and $\Delta(R)$, respectively. The racemates were resolved without isolation by the same method as that for $[Co(NH_3)_4(mtmd)]^{3+}$. The faster eluted enantiomers of M-I and M-II are Λ-$[Co(en)_2(R\text{-}mtmd)]^{3+}$ (M-I-1) and Λ-$[Co(en)_2(S\text{-}mtmd)]^{3+}$(M-II-1). respectively. The isomers obtained from the slower eluted bands are thus Δ-$[Co(en)_2(S\text{-}mtmd)]^{3+}$ (M-I-2) and Δ-$[Co(en)_2(R\text{-}mtmd)]^{3+}$ (M-II-2).

The absolute configurations of these isomers were assigned by comparing the CD spectra with those of the isomers prepared by use of active *R*-mtmd which was obtained by neutralizing *R*-mtmd·2HCl with sodium methoxide in methanol. When excess sodium methoxide was used to neutralize the (*R*)-dihydrochloride, Δ-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ (M-II-2) was not yielded, giving only Λ-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ (M-I-1) stereoselectively. All the isomers were isolated as perchlorates by the same method as that for $[\mathrm{Co(NH_3)_4(mtmd)}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$.

Preparation and Resolution of $[\mathrm{Co(en)_2(dmtmd)}]^{3+}$. The isomers of this complex were prepared from dmtmd·2HCl (a mixture of *meso* and *rac* forms)and *trans*-$[\mathrm{CoCl_2(en)_2}]\mathrm{ClO_4}$ in *N,N*-dimethylformamide (DMF) by a method similar to that for the corresponding mtmd complex. By elution with 0.2 M $\mathrm{Na_2SO_4}$ adjusted to pH 2 with HCl, the column gave four bands; orange-yellow ($[\mathrm{Co(en)_3}]^{3+}$) and three orange bands, D-I, D-II, and D-III named in the order of elution. From the effluent of D-II, *rac*-$[\mathrm{Co(en)_2}(meso\text{-dmtmd})]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$ was isolated by the same method as that for $[\mathrm{Co(NH_3)_4(tmd)}]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$. In a similar way one racemate (Λ-$[\mathrm{Co(en)_2}\{(+)\text{-dmtmd}\}]^{3+}$ and Δ-$[\mathrm{Co(en)_2}\{(-)\text{-dmtmd}\}]^{3+}$) was isolated as perchlorate from the effluent of D-III. The racemate in D-I (Λ-$[\mathrm{Co(en)_2}\{(-)\text{-dmtmd}\}]^{3+}$ and Δ-$[\mathrm{Co(en)_2}\{(+)\text{-dmtmd}\}]^{3+}$) was not isolated because of a small amount. The formation ratio of the racemates, D-I: D-II: D-III was 1 : 4 : 2. Each of the racemates was resolved into a pair of enantiomers by the same method as that for $[\mathrm{Co(NH_3)_4(mtmd)}]^{3+}$. In all cases, the column showed two separate bands (D-I-1, D-I-2, *etc.*), the Λ isomer (D-I-1, *etc.*) being eluted faster. The optically active chlorides were obtained by the same method as that for $[\mathrm{Co(NH_3)_4(tmd)}]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$. To assign the isomers, the (−)-dmtmd complex was prepared from (+)-dmtmd·2HCl ((−)-dmtmd). A pair of diastereomers, $\Lambda(-)$ and $\Delta(-)$ corresponding to D-I-1 and D-III-2, respectively, were obtained.

Preparation and Resolution of cis-$[\mathrm{Co(NH_3)_2(tmd)_2}]^{3+}$. The *trans*-$[\mathrm{CoCl_2(tmd)_2}]\mathrm{ClO_4}$[15] complex was dissolved in liquid ammonia to give an orange solution. After evaporation of ammonia, the crude complex remained was dissolved in 10^{-2} M HCl and column-chromatographed by the same method as that for $[\mathrm{Co(NH_3)_4(tmd)}]^{3+}$. The column showed two orange bands. From the slower moving band, *cis*-$[\mathrm{Co(NH_3)_2(tmd)_2}](\mathrm{ClO_4})_3$ was obtained by the same method as that for $[\mathrm{Co(NH_3)_4(mtmd)}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$. Yield: 70%. The trans isomer (the faster moving band) was not isolated because of the very small amount. The cis isomer was resolved by the same method as that for $[\mathrm{Co(NH_3)_4(mtmd)}]^{3+}$, the (+)-$\Delta$ isomer being eluted first. The enatiomers were isolated as perchlorates by the method described.

cis-Δ-$[\mathrm{Co(NH_3)_2}\{(-)\text{-dmtmd}\}_2]\mathrm{Cl_3}\cdot2\mathrm{H_2O}$. This complex was prepared from *trans*-$[\mathrm{CoCl_2}\{(-)\text{-dmtmd}\}_2]\mathrm{ClO_4}\cdot\mathrm{H_2O}$ and liquid ammonia by the same method as that for the corresponding tmd complex, and isolated as chloride by the method described. Yield: 10%. The other diastereomer was not yielded under the conditions given.

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

Results and Discussion

Preparation and Stability of the Complexes. The *trans*-$[\mathrm{CoCl_2}(R\text{-mtmd})_2]^{+}$ and $[\mathrm{CoCl_2}\{(-)\text{-dmtmd}\}_2]^{+}$ complexes were prepared by oxidizing a DMSO solution of the diamine and cobalt(II) ions with air and by treating with hydrochloric acid. The air-oxidation in aqueous solution resulted in only the formation of insoluble cobalt hydroxide. The DMSO solution was prepared by slowly mixing fairly dilute solutions of the reactants in order to avoid the formation of polymeric complexes.[16] The yields are still very poor, *ca.* 3%. The complexes isolated as perchlorate decompose gradually even in the solid state, and rapidly in methanol (Experimental). The *trans*-$[\mathrm{CoCl_2}(R\text{-mtmd})_2]^{+}$ complex can have two geometrical isomers, *trans-trans* and *trans-cis*, by the alignment of the two methyl groups. However, no attempt to separate them was made because of instability of the complex. The tetraammine and bis(ethylenediamine) complexes of the diamines were prepared from $[\mathrm{Co(NH_3)_5(H_2O)}]^{3+}$ and *trans*-$[\mathrm{CoCl_2(en)_2}]^{+}$, respectively by mixing with the diamine in a large amount of DMSO or DMF. Such reactions are

TABLE 1. ANALYTICAL DATA OF THE NEW COMPLEXES

Complex	C (%) Found(Calcd)	H (%) Found(Calcd)	N (%) Found(Calcd)
trans-$[\mathrm{CoCl_2}(rac\text{-mtmd})_2]\mathrm{ClO_4}$	27.49(27.70)	6.45(6.51)	12.84(12.92)
trans-$[\mathrm{CoCl_2}(R\text{-mtmd})_2]\mathrm{ClO_4}$	27.46(27.70)	6.34(6.51)	12.67(12.92)
trans-$[\mathrm{CoCl_2}\{(-)\text{-dmtmd}\}_2]\mathrm{ClO_4}\cdot0.5\mathrm{H_2O}$	30.75(30.62)	7.04(7.07)	11.90(11.90)
$[\mathrm{Co(NH_3)_4(tmd)}]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$	13.74(13.78)	7.81(7.81)	24.49(24.11)
$[\mathrm{Co(NH_3)_4}(rac\text{-mtmd})](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$	11.08(11.01)	5.16(5.17)	15.47(15.40)
$[\mathrm{Co(NH_3)_4}(R\text{-mtmd})](\mathrm{ClO_4})_3$	11.55(11.38)	4.84(4.97)	15.60(15.93)
$[\mathrm{Co(NH_3)_4}(meso\text{-dmtmd})]\mathrm{Cl_3}\cdot2.5\mathrm{H_2O}$	18.35(18.26)	8.30(8.43)	21.20(21.29)
$[\mathrm{Co(NH_3)_4}\{(+)\text{-dmtmd}\}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$	13.29(12.88)	5.09(5.40)	15.01(15.02)
$[\mathrm{Co(NH_3)_4}\{(-)\text{-dmtmd}\}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$	12.91(12.88)	5.13(5.40)	14.85(15.02)
Λ-$[\mathrm{Co(en)_2}(R\text{-mtmd})](\mathrm{ClO_4})_3\cdot0.5\mathrm{H_2O}$	18.60(18.36)	5.33(5.31)	13.61(14.28)
Δ-$[\mathrm{Co(en)_2}(R\text{-mtmd})](\mathrm{ClO_4})_3\cdot2\mathrm{H_2O}$	17.88(17.56)	5.51(5.57)	13.16(13.65)
$[\mathrm{Co(en)_2}(meso\text{- dmtmd})]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$	28.28(28.02)	8.37(8.23)	19.49(19.60)
Δ-$[\mathrm{Co(en)_2}(meso\text{-dmtmd})]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$	28.32(28.02)	8.55(8.23)	19.52(19.60)
Λ-$[\mathrm{Co(en)_2}\{(-)\text{-dmtmd}\}]\mathrm{Cl_3}\cdot0.5\mathrm{H_2O}$	29.24(29.25)	8.28(8.10)	20.11(20.46)
$[\mathrm{Co(en)_2}(rac\text{-dmtmd})](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$(D-III)	19.75(19.64)	5.80(5.60)	13.85(13.74)
Δ-$[\mathrm{Co(en)_2}\{(-)\text{-dmtmd}\}]\mathrm{Cl_3}\cdot1.5\mathrm{H_2O}$	28.14(28.02)	8.38(8.23)	20.21(19.60)
cis-$[\mathrm{Co(NH_3)_2(tmd)_2}](\mathrm{ClO_4})_3\mathrm{H_2O}$	16.43(16.41)	5.24(5.51)	14.58(14.35)
cis-Δ-$[\mathrm{Co(NH_3)_2(tmd)_2}](\mathrm{ClO_4})_3$	16.71(16.93)	5.42(5.33)	14.81(14.80)
cis-Δ-$[\mathrm{Co(NH_3)_2}\{(-)\text{-dmtmd}\}_2]\mathrm{Cl_3}\cdot2\mathrm{H_2O}$	30.81(31.23)	9.05(9.09)	17.97(17.57)

known to be useful in obtaining complexes containing a large chelate ring.[16] Similar reactions with 1,2- or 1,3-diamines are usually accompanied by disproportionation to yield complexes of other bis- and tris-diamine than the desired mono-diamine. In the present study, however, the formation of bis or tris(1,4-diamine) complexes are *seldom* observed. These complexes would be unstable because of crowding due to the bulky seven-membered chelate rings. The $[Co(en)_2(R\text{-}mtmd)]^{3+}$ complex yielded only the Λ isomer when excess sodium methoxide was used for neutralizing *R*-mtmd·2HCl. However, when distilled free *R*-mtmd was used, such selectivity was not observed, forming the Λ and Δ isomers in nearly the same amount. The di- and tetraammine and bis(ethylenediamine) complexes with the 1,4-diamines are stable in acidic water, but decom-

Table 2. Absorption(AB) and CD spectral data

Complex	$\tilde{\nu}^{AB}/10^{-3}$ cm^{-1} (log ε)	$\tilde{\nu}^{CD}/10^{-3}$ cm^{-1} (Δε)
$[Co(NH_3)_4(tmd)]^{3+}$	20.70(1.83)	
	29.00(1.76)	
	48.20(4.32)	
$[Co(NH_3)_4(R\text{-}mtmd)]^{3+}$	20.72(1.83)	21.00(−0.34)
	29.03(1.76)	28.30(+0.014)
	48.20(4.32)	47.50(−8.2)
$[Co(NH_3)_4\{(-)\text{-}dmtmd\}]^{3+}$	20.62(1.90)	20.41(−0.25)
	28.82(1.83)	
	47.62(4.37)	40.50(−0.76)
		46.30(+6.2)
$[Co(NH_3)_4(meso\text{-}dmtmd)]^{3+}$	20.45(1.88)	
	28.74(1.83)	
	46.1 (4.3)sh	
	49.50(4.38)	
Λ-$[Co(en)_2(R\text{-}mtmd)]^{3+}$	20.96(1.93)	19.75(+1.07)
		22.10(−0.58)
	29.00(1.90)	28.00(+0.15)
	45.70(4.33)	46.30(−30)
Δ-$[Co(en)_2(R\text{-}mtmd)]^{3+}$	20.88(1.99)	20.58(−1.22)
	28.99(1.96)	29.20(+0.070)
	45.70(4.40)	45.90(+20)
Δ-$[Co(en)_2\{(-)\text{-}dmtmd\}]^{3+}$	20.83(1.96)	19.88(−1.11)
		22.73(+0.06)
	28.99(1.93)	27.70(−0.12)
	45.20(4.37)	45.90(+24)
Λ-$[Co(en)_2\{(-)\text{-}dmtmd\}]^{3+}$	20.79(2.02)	21.14(+1.09)
	28.90(1.99)	28.74(−0.17)
	45.20(4.36)	46.10(−15)
Δ-$[Co(en)_2(meso\text{-}dmtmd)]^{3+}$	20.62(2.03)	20.24(−0.79)
		26.39(−0.022)
	28.65(2.00)	29.50(+0.037)
	45.10(4.39)	45.50(+18)
cis-Δ-$[Co(NH_3)_2(tmd)_2]^{3+}$		18.32(−0.034)
	20.33(1.85)	20.88(+0.52)
	28.49(1.81)	27.78(−0.040)
	45.00(4.33)	45.50(+17)
cis-Δ-$[Co(NH_3)_2\{(-)\text{-}dmtmd\}_2]^{3+}$		18.87(−0.29)
	20.12(1.93)	21.41(+0.088)
	28.21(1.89)	27.55(−0.067)
	44.10(4.40)	42.00(+3.6)
trans-$[CoCl_2(R\text{-}mtmd)_2]^{+}$ [a]	15.58(1.64)	15.67(−1.27)
	20.12(1.49)	20.00(+0.58)
	24.69(1.81)	23.81(+0.21)
trans-$[CoCl_2\{(-)\text{-}dmtmd\}_2]^{+}$ [a]	15.43(1.71)	15.58(+1.43)
	19.80(1.57)	19.69(−1.45)
	24.45(1.89)	25.40(+0.10)
trans-$[CoCl_2(tmd)_2]^{+}$ [a]	15.55(1.67)	
	20.04(1.50)	
	24.57(1.83)	

a) Solvent: acetone, sh: shoulder.

pose gradually in neutral water. Thus, care was taken to maintain solutions acidic in the course of preparation. The chelate coordination of 1,4-diamines in all the complexes is supported by elution behavior in column chromatography.[16]

Absorption and CD Spectra. As seen in Table 2, the first absorption maxima of $[Co(NH_3)_4(R\text{-mtmd})]^{3+}$, $[Co(NH_3)_4(tmd)]^{3+}$, $[Co(NH_3)_4\{(-)\text{-dmtmd}\}]^{3+}$, and $[Co(NH_3)_4(\textit{meso}\text{-dmtmd})]^{3+}$ appear at 20720, 20700, 20620, and 20450 cm^{-1}, respectively. Thus the order of these 1,4-diamines in the spectrochemical series can be determined as R-mtmd$\gtrsim$tmd$>$(−)-dmtmd$>$*meso*-dmtmd. Since the basicities of (−)-dmtmd and *meso*-dmtmd ligands will be similar, the red shift of the first absorption band of the *meso*-dmtmd complex can be attributed to the strained structure of the complex (*vide infra*). It is reported that cobalt(III) complexes with a strained structure show the red shift in the first absorption band.[17] In the ultraviolet region, the *meso*-dmtmd complex shows a shoulder (46100 cm^{-1}) and a strong band (49500 cm^{-1}), which can be assigned to charge transfer transitions from the *meso*-dmtmd and ammonia ligands, respectively to the cobalt(III) ion. No shoulders are observed for the other tetraammine complexes. The appearance of the shoulder in the *meso*-dmtmd complex indicates that there is a fairly large energy difference between those two kinds of charge transfer transitions. For the other complexes, the charge transfer bands from the 1,4-diamines to the cobalt(III) ion might be hidden by that from the ammonia to the cobalt(III) ion owing to small energy differences between them. The $[Co(NH_3)_6]^{3+}$ complex gives the charge transfer band at 51150 cm^{-1}.[18] Thus the strained $[Co(NH_3)_4(\textit{meso}\text{-dmtmd})]^{3+}$ complex shows the red shift in both the d-d and charge transfer bands.

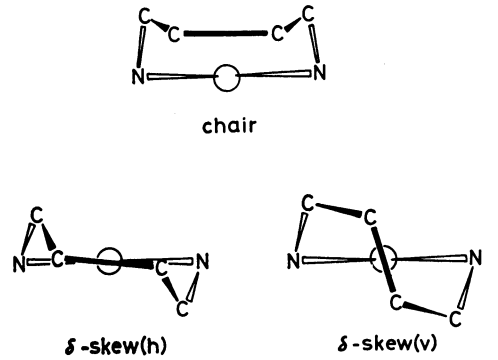
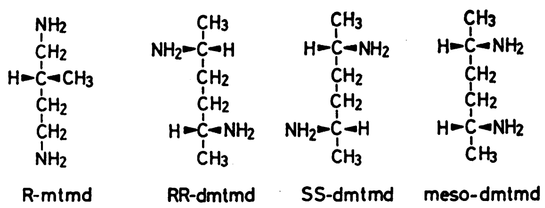


Fig. 1. Possible conformations of a seven-membered 1,4-diamine chelate ring.

Figure 1 shows three typical conformations of a 1,4-diamine chelate ring. Each of the skew conformations is chiral and has its antipode. The chair conformation seems to be unstable because big steric hindrance is involved among the axial hydrogens of 1- and 4-carbon atoms of the 1,4-diamine chelate ring and an apical ligand. However, the *meso*-dmtmd chelate ring might take the chair conformation, since both methyl groups can have equatorial positions in only this form. In any skew conformation one of the two methyl groups is forced to take the axial position. Molecular models indicate that for 1,4-diamine chelate rings, conformations with an axial methyl group do not seem to be plausible. Thus the $[Co(NH_3)_4(\textit{meso}\text{-dmtmd})]^{3+}$ complex would be strained and shows the red shift in the absorption spectrum. The conformations of the R-mtmd and RR-dmtmd chelate rings with the equatorial methyl group(s) are either *δ-skew*(*h*) or *λ-skew*(*v*), and *λ-skew*(*h*) or *λ-skew*(*v*), respectively (Figs. 1 and 2).



Conformation

Ligand	δ-skew(h)	λ-skew(h)	δ-skew(v)	λ-skew(v)	chair
R-mtmd	e	a	a	e	e(a)
RR-dmtmd	aa	ee	aa	ee	ae
SS-dmtmd	ee	aa	ee	aa	ae
meso-dmtmd	ae	ae	ae	ae	ee(aa)

e: methyl equatorial a: methyl axial

Fig. 2. Absolute configurations of R-mtmd and three isomers of dmtmd, and their conformations in chelates.

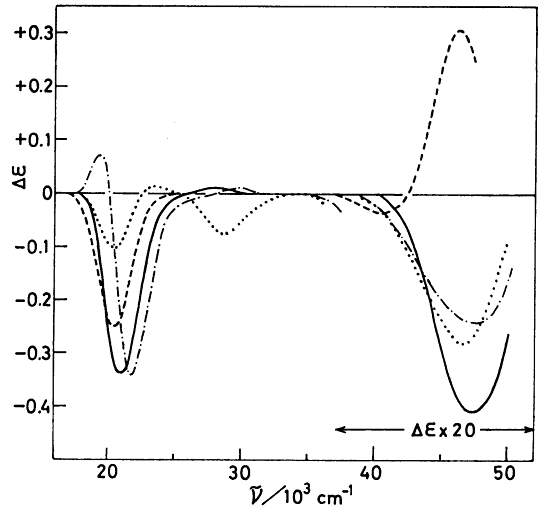


Fig. 3. CD spectra of $[Co(NH_3)_4(diamine)]^{3+}$ in water. Diamine: R-mtmd (——), (−)-dmtmd (------), SS-2,3-bn (-·-·-·), and SS-ptn (······).

Figure 3 compares CD spectra of some tetraamine complexes of a chiral diamine. Except for the (−)-dmtmd complex, all the complexes show negative CD in both the first and the charge transfer absorption band regions. Since the (S,S)-2,3-butanediamine (SS-2,3-bn)[18] and (S,S)-2,4-pentanediamine (SS-ptn)[1] chelate rings are stabilized in the *δ-gauche* and *δ-skew* forms, respectively, the R-mtmd chelate ring can also be assigned to have the same chirality, *δ-skew*(*h*). The R-mtmd complex increases the CD strength in the first absorption band region in DMSO ($\Delta\varepsilon = -0.48$ at

21000 cm^{-1}). The same trend is observed for the *SS*-2,3-bn and *SS*-ptn complexes. In the (−)-dmtmd complex, on the other hand, the CD sign in the first absorption band region differs from that in the charge transfer absorption band region. In addition, the complex decreases the CD strength in the first absorption band region in DMSO ($\Delta\varepsilon = -0.18$ at 20300 cm^{-1}), which is opposite to those of the other tetraammine complexes. The results make the assignment for the chirality of the (−)-dmtmd chelate ring difficult. Thus the *trans*-$[\mathrm{CoCl_2}\{(-)\text{-dmtmd}\}_2]^+$ complex was prepared and the CD spectrum was compared with those of the related complexes. The relationship between CD patterns and conformational chirality in complexes of this type has also been studied extensively.[10,19]

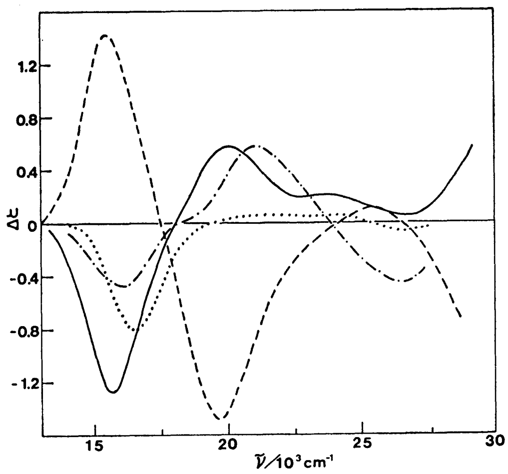


Fig. 4. CD spectra of *trans*-$[\mathrm{CoCl_2(diamine)_2}]^+$. Diamine: *R*-mtmd(——, in acetone), (−)-dmtmd (------, in acetone), *SS*-2,3-bn (······, in methanol), and *SS*-ptn (-·-·-, in methanol).

The *R*-mtmd complex shows a CD pattern similar to those of the *SS*-2,3-bn[10,18] and *SS*-ptn[20] complexes; negative and positive CD bands corresponding to the Ia ($^1\mathrm{E_g}\leftarrow{}^1\mathrm{A_{1g}}$) and Ib ($^1\mathrm{A_{2g}}\leftarrow{}^1\mathrm{A_{1g}}$) bands,[21] respectively (Fig. 4). Thus the R-mtmd chelate ring can be assigned to have the *δ-skew*(*h*) conformation. This assignment agrees with that based on the CD spectrum of the tetraammine complex. On the other hand, the CD pattern of the (−)-dmtmd complex is opposite to those of the other dichloro complexes, indicating the conformation of *λ* chirality. When the *λ*-(−)-dmtmd chelate ring has two equatorial methyl groups, the two chiral carbon atoms are determined to have the (*R*,*R*) configuration, regardless of two kinds of conformations, *skew*(*h*) or *skew*(*v*). This assignment is supported by CD spectra of a pair of diastereomers of $[\mathrm{Co(en)_2}\{(-)\text{-dmtmd}\}]^{3+}$ discussed later. The reason why the $[\mathrm{Co(NH_3)_4}\{(-)\text{-dmtmd}\}]^{3+}$ complex, in which the chelate ring has *λ* chirality, shows the negative CD band in the first absorption band region is unknown. Similar anomalous CD has been reported for the tetraammine complexes of (*S*,*S*)-1,3-diphenyl-1,3-propanediamine[22] and (*S*)-1,3-butanediamine.[2]

In Fig. 5 are shown CD spectra of M-I-1 and M-II-2

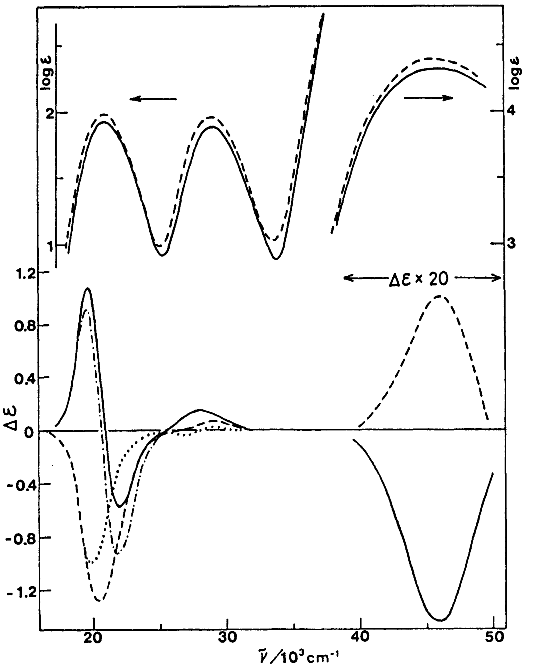


Fig. 5. Absorption and CD spectra of *Λ*-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ (M-I-1) in water (——) and in 0.2 mol/dm^3 $\mathrm{Na_2SO_4}$ (-·-·-), and *Δ*-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ (M-II-2) in water (------) and in 0.2 mol/dm^3 $\mathrm{Na_2SO_4}$ (······).

isomers of the $[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ complex in aqueous solutions in the absence or the presence of sulfate ions. The complexes give a typical CD pattern for a tris(diamine) complex, and their absolute configurations can be assigned on the basis of the CD spectra in the first absorption band region; M-I-1 and M-II-2 are assigned to the *Λ*(*R*) and *Δ*(*R*) isomers, respectively. The line connecting 1- and 4-carbon atoms of the *R*-mtmd chelate ring in the *δ-skew*(*h*) (or *λ-skew*(*v*)) or *λ-skew*(*v*) (or *δ-skew*(*h*)) form is nearly parallel or oblique to the pseudo $\mathrm{C_3}$ axis of the *Λ* (or *Δ*)-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ complex, respectively. Thus *Λ* and *Δ* isomers of the *R*-mtmd complex in the *δ-skew*(*h*) conformation are designated as "*lel*" and "*ob*" isomers, respectively, as in the case of $[\mathrm{Co(en)_3}]^{3+}$.[23] The CD patterns of *Λ*- and *Δ*-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ in aqueous solutions are characteristic of the "*lel*" and "*ob*" isomers, respectively; the former gives two CD bands with different signs in the first absorption band region, while the latter only one band in this region. Thus the *R*-mtmd chelate rings in these complexes are also stabilized in the *δ-skew*(*h*) conformation. In the presence of sulfate ions, the *Λ*(*R*) isomer diminishes the CD strength of the major positive component, and complementarily enhances that of the minor component. Such a phenomenon is known to be brought about by an increase in the amount of the *lel*$_3$ conformer of a tris(diamine) complex stabilized by ion-association with a sulfate ion.[24] The ion-pair is formed through hydrogen bonding between the three amino protons nearly parallel to the $\mathrm{C_3}$ axis of a tris(diamine) complex and a sulfate ion, and the *lel*$_3$ structure affords such amino protons. Thus the *Λ*-$[\mathrm{Co(en)_2}(R\text{-mtmd})]^{3+}$ complex will be stabilized in the *Λ*(*δ-gauche*$_2$, *δ-skew*(*h*))(*lel*$_3$) conformer to increase the amount of δ-diamines in the presence of sulfate ions, and increases the negative CD strength in the first absorption band region. It is known that the vicinal effect of a δ-diamine chelate ring in the $[CoN_6]$-type complex is negative in this region.[25] The Δ-$[Co(en)_2(R\text{-mtmd})]^{3+}$ complex also shows a CD change on addition of sulfate ions, decreasing considerably the negative strength. According to the previous discussion, the decrease in the negative CD strength indicates an increase in the amount of λ-diamines in order to form the Δ(*lel*$_3$) conformer. The complex can afford the *lel*$_3$ conformer when the *R*-mtmd chelate ring forms the *λ-skew(v)* structure, in which the methyl group is disposed equatorially.

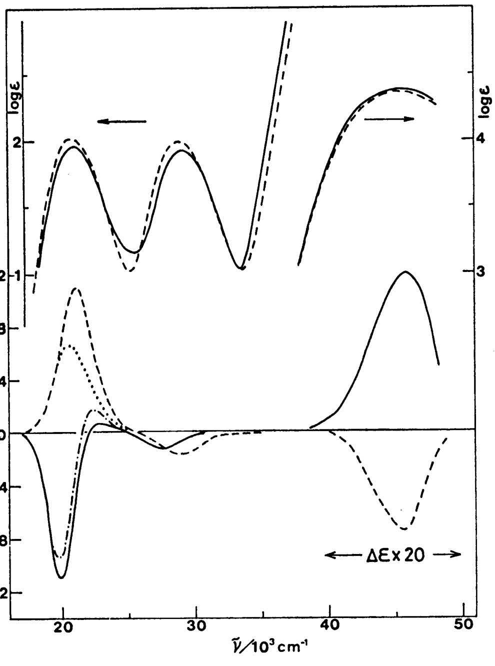


Fig. 6. Absorption and CD spectra of Δ-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ (D-III-2) in water (——) and in 0.2 mol/dm^3 Na_2SO_4 (-·-·-·), and Λ-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ (D-I-1) in water (------) and in 0.2 mol/dm^3 Na_2SO_4 (······).

The D-I-1 and D-III-2 isomers of $[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ can be assigned to the Λ and Δ configurations, respectively from the sign of the main CD band in the first absorption band region (Fig. 6). The Λ and Δ isomers show CD patterns characteristic of the "*ob*" and "*lel*" isomers, respectively. This indicates that the (−)-dmtmd ligand has the (*R*,*R*) carbon atoms, forming the *λ-skew(h)* or *λ-skew(v)* conformation with the two equatorial methyl groups. The assignment for (−)-dmtmd agrees with that given previously from the CD spectrum of *trans*-$[CoCl_2\{(-)\text{-dmtmd}\}_2]^+$. The CD change for the Δ(*lel*) isomer caused by the addition of sulfate ions is characteristic of the "*lel*" isomer, but the magnitude of the change is fairly small as compared with that of Λ(*lel*)-$[Co(en)_2(R\text{-mtmd})]^{3+}$. The smaller CD change in the (−)-dmtmd complex seems to be related with difficulty in forming an ion-pair with a sulfate ion. The Δ-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ complex can form the *lel*$_3$ conformer (*λ-gauche*$_2$, *λ-skew(h)* or *λ-skew(v)*), and provides two sets of three N–H bonds for the ion-pair formation with a sulfate ion. In the *lel*$_3$ conformer, however, the two methyl groups on 1- and 4-carbons of the (−)-dmtmd ligand stick out in nearly parallel with the pseudo C_3 axis of the complex ion, and hinder a sulfate ion from approaching the complex ion along this axis. On the other hand, the methyl group on 2-carbon of the *R*-mtmd complex is disposed far from the pseudo C_3 axis to involve no such hindrance to a sulfate ion. Thus Δ(*lel*)-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ might have weaker affinity in ion-association with sulfate ions than the *R*-mtmd complex, and shows the smaller CD change in the presence of sulfate ions. On the other hand, the CD change of Λ(*ob*)-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ in the presence of sulfate ions is as large as that of Δ(*ob*)-$[Co(en)_2(R\text{-mtmd})]^{3+}$ (Fig. 6). The two methyl groups in Λ(*ob*)-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ are disposed far from the pseudo C_3 axis, differing from those in the Δ(*lel*)-(−)-dmtmd complex. However, the complex should not form the *lel*$_3$ conformer, since the conversion of the (−)-dmtmd chelate ring to the *lel* form (*δ-skew(h* or *v)*) with the two axial methyl groups is very unlikely. The reason for the large CD change is not clear. However, molecular models indicate that the large and flexible (−)-dmtmd chelate ring can form rather easily an intermediate conformation suitable for ion-association with a sulfate ion by a slight distortion from the typical skew form. The Λ(*ob*) isomer comprising such a conformer might form an ion-pair with a sulfate ion to cause the large CD change. The suggestion that the Λ(*ob*) isomer has stronger affinity for a sulfate ion than the Δ(*lel*) isomer is supported by the elution order in column chromatography. By elution with 0.2 M Na_2SO_4, the former is eluted faster than the latter (Experimental). In similar column chromatographic separation for a pair of diastereomers, it has been observed that a *lel* isomer is always eluted faster than an *ob* isomer.[26] The $[Co(en)_2(R\text{-mtmd})]^{3+}$ complex in this study is the case. The elution order of such a pair of diastereomeric complexes is reported to depend on the ion-association constant between a complex ion and an anion;[27] a complex with the larger value is eluted faster. In the ion-association between $[Co(R\text{-pn})_3]^{3+}$ (*R*-pn=(*R*)-1,2-propanediamine) and a sulfate ion, the constant for the Δ(*lel*$_3$) isomer is larger than that for the Λ(*ob*$_3$) isomer.[28] Thus the Λ(*ob*) isomer of $[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$ which is eluted faster than the other Δ(*lel*) isomer should have a larger constant in association with a sulfate ion, and causes a larger CD change than the other isomer does in the presence of sulfate ions.

In Fig. 7 are shown the CD spectra of Δ-$[Co(en)_2(meso\text{-dmtmd})]^{3+}$ (D-II-2) in the absence and presence of sulfate ions, the absolute configuration of which is assigned on the basis of the CD sign in the first absorption band region. In the presence of sulfate ions, the complex shows a CD change as small as that in Δ(*lel*)-$[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$. The small CD change of the *meso*-dmtmd complex would also be attributable to weak association with a sulfate ion as stated for the

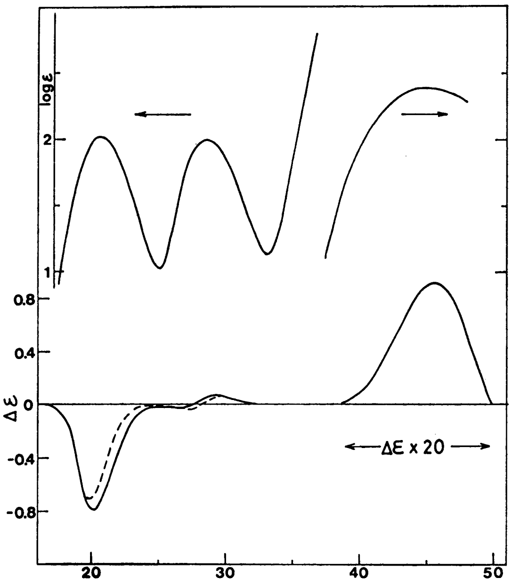


Fig. 7. Absorption and CD spectra of Δ-[Co(en)$_2$(*meso*-dmtmd)]$^{3+}$ (D-II-2) in water (——) and in 0.2 mol/dm^3 Na$_2$SO$_4$ (------).

Δ(*lel*)-(−)-dmtmd complex. When the *meso*-dmtmd chelate ring is in the same chair form as that in the tetraammine complex, one methyl group is disposed near one set of three N–H bonds to hinder the ion-association, but the other methyl group is located away from the other set of three N–H bonds, a sulfate ion being able to approach the complex ion. However, the amino protons of the *meso*-dmtmd ligand are oblique to the C_3 axis of the complex ion, and unfavorable for association of the *lel*$_3$-SO$_4{}^{2-}$ type. The *meso*-dmtmd chelate ring would be less flexible than the (−)-dmtmd chelate one because of the strained structure as stated previously. Thus the [Co(en)$_2$(*meso*-dmtmd)]$^{3+}$ complex would have weak affinity for a sulfate ion to cause the small CD change.

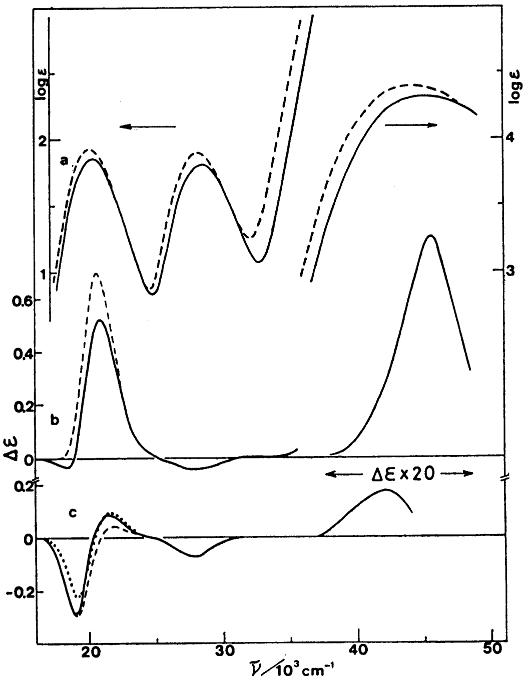


Fig. 8. a. Absorption spectra of *cis*-Δ-[Co(NH$_3$)$_2$(tmd)$_2$]$^{3+}$ (——) and *cis*-Δ-[Co(NH$_3$)$_2${(−)-dmtmd}$_2$]$^{3+}$ (------) in water.
b. CD spectra of *cis*-Δ-[Co(NH$_3$)$_2$(tmd)$_2$]$^{3+}$ in water (——) and in 0.2 mol/dm^3 Na$_2$SO$_4$ (------).
c. CD spectra of *cis*-Δ-[Co(NH$_3$)$_2${(−)-dmtmd}$_2$]$^{3+}$ in water (——) and in 0.2 mol/dm^3 Na$_2$SO$_4$ (------), and the calculate dCD curve, $2\times\Delta\varepsilon$([Co(NH$_3$)$_4${(−)-dmtmd}]$^{3+}$)$+\Delta\varepsilon$(*cis*-Δ-[Co(NH$_3$)$_2$(tmd)$_2$]$^{3+}$) (······).

In Fig. 8 are compared CD spectra of the Δ isomers of $(+)_{589}$-[Co(NH$_3$)$_2$(tmd)$_2$]$^{3+}$ and $(-)_{589}$-[Co(NH$_3$)$_2${(−)-dmtmd}$_2$]$^{3+}$ in the absence and presence of sulfate ions. The main CD bands of these complexes exhibit different signs in the first absorption band region. The absolute configuration of the tmd complex was assigned from a comparison of CD patterns of Δ-[Co(en)(tmd)$_2$]$^{3+}$[29] and Δ-[Co(tmd)$_3$]$^{3+}$,[29] and that of the(−)-dmtmd complex was done on the basis of the stereoselective complex formation {Δ(*lel*$_2$)}brought about by the ligand of *R*,*R*-configuration. The Δ(*ob*$_2$) isomer involves severe steric hindrance between the two chelate ligands. Both Δ isomers of the tmd and (−)-dmtmd complexes show a negative CD component in the small wavenumber side in the first absorption band region, and a strong positive CD band in the ultraviolet region. The features agree with those observed for other related complexes of the Δ configuration. The Δ-[Co(NH$_3$)$_2${(−)-dmtmd}$_2$]$^{3+}$ complex involves two chiral sources, the Δ configuration and the *RR*-dmtmd chelate ligand of λ-*skew*(*h* or *v*). When the additive law[25,30] for the configurational and vicinal CD effects holds in the CD spectrum of Δ-[Co(NH$_3$)$_2${(−)-dmtmd}$_2$]$^{3+}$, it can be approximated by the sum of the CD spectrum of Δ-[Co(NH$_3$)$_2$(tmd)$_2$]$^{3+}$ and the curve doubled the CD strength of [Co(NH$_3$)$_4${(−)-dmtmd}]$^{3+}$. The CD curve calculated in the first absorption band region resembles

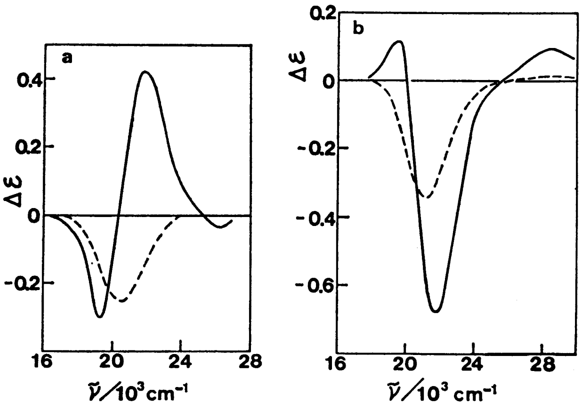


Fig. 9. a. Vicinal effect CD of the (−)-dmtmd ligand. The calculated CD curve, $1/2\{\Delta\varepsilon(\Lambda$-[Co(en)$_2${(−)-dmtmd}]$^{3+})+\Delta\varepsilon(\Delta$-[Co(en)$_2${(−)-dmtmd}]$^{3+})\}$, (——). The observed CD spectrum of [Co(NH$_3$)$_4${(−)-dmtmd}]$^{3+}$ (------).
b. Vicinal effect CD of the *R*-mtmd ligand. The calculated CD curve, $1/2\{\Delta\varepsilon(\Lambda$-[Co(en)$_2$(*R*-mtmd)]$^{3+})+\Delta\varepsilon(\Delta$-[Co(en)$_2$(*R*-mtmd)]$^{3+})\}$, (——). The observed CD spectrum of [Co(NH$_3$)$_4$(*R*-mtmd)]$^{3+}$ (------).

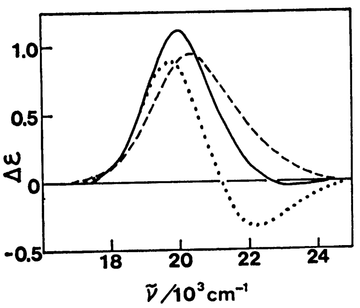


Fig. 10. Configurational effect CD ($\Delta\varepsilon(\Lambda)$) curves. The calculated CD curve, $1/2\{\Delta\varepsilon(\Lambda\text{-}[Co(en)_2(R\text{-mtmd})]^{3+}) - \Delta\varepsilon(\Delta\text{-}[Co(en)_2(R\text{-mtmd})]^{3+})\}$, (——). The calculated CD curve, $1/2\{\Delta\varepsilon(\Lambda\text{-}[Co(en)_2\{(-)\text{dmtmd}\}]^{3+}) - \Delta\varepsilon(\Delta\text{-}[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+})\}$, (----). The observed CD spectrum of $\Lambda\text{-}[Co(en)_2(tmd)]^{3+}$(······).

well the observed CD spectrum (Fig. 8). Thus the strong negative CD of $\Delta\text{-}[Co(NH_3)_2\{(-)\text{-dmtmd}\}_2]^{3+}$ in the first absorption band region can be attributed to the strong negative vicinal effect of the *RR*-dmtmd chelate ligand.

In the presence of sulfate ions, the tmd complex shows fairly large CD change, but the (−)-dmtmd complex a little change. Such a difference might also be related with a difference in the flexibility and structure of the chelate rings. The more flexible tmd chelate ring would be stabilized in a certain conformation by forming an ion-pair between the complex ion and a sulfate ion. On the other hand, the (−)-dmtmd complex has four methyl groups, which hinder a sulfate ion from approaching the N–H protons of the chelate ligands to cause little change in the conformation of the chelate rings. Thus the complex would show the small CD change in the presence of sulfate ions.

Figures 9 and 10 show the configurational and vicinal effect CD curves obtained by the usual way[30] from CD spectra of the diastereomers of $[Co(en)_2(R\text{-mtmd})]^{3+}$ and $[Co(en)_2\{(-)\text{-dmtmd}\}]^{3+}$. These curves are compared with CD spectra of the related complexes in the Figures. The additive law for the configurational and vicinal effects does not hold among these complexes, although it works among the ammine complexes of tmd and (−)-dmtmd. The lack of the additivity might be related with crowded structures of those tris-chelate-type complexes involving a large seven-membered chelate ring. Some six-membered diamine complexes have also been reported to show lack of the additivity, and it has been interpreted as the results of flexible conformation of a six-membered chelate ring; the conformation of a six-membered chelate ring in one complex would differ from that in the other.[1] The same interpretation can be made on the complexes concerned. The stable conformation of a seven-membered chelate ring in the crowded bis-en complex would differ from that in the much less crowded tetraammine complex, and this might cause the lack of the additivity.

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