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CD Spectra and Absolute Configurations of *fac(a,b,c)*-$[Co(a)(b)(c)(1,4,7\text{-Triazacyclononane})]^{n+}$ Complexes

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Seventeen kinds of *fac(a,b,NH₃)*-$[Co(a)(b)(NH_3)(tacn)]^{n+}$ complexes (a, b=CN^-, NO_2^-, SO_3^{2-}, NCS^-, N_3^-, CH_3COO^-, H_2O, OH^-, Cl^-, or Br^-; tacn=1,4,7-triazacyclononane) have been prepared and optically resolved by column chromatography. The absolute configurations of these complexes have been determined by referring to the CD spectra of the related $[Co(a)(gly)(tacn)]^{n+}$ complexes (a=CN^-, NO_2^-, NCS^-, N_3^-, or Cl^-). It has been found that the signs of the Cotton peaks observed in the first absorption band region are closely related to the ligand field strengths of the unidentate ligands, and that the dominant Cotton peak is associated with the electronic transition which arises in the plane containing no ammonia molecule.

There are some reports on optically active cobalt(III) complexes with a chiral arrangement of donor atoms around a central metal ion. These complexes can be classified into two groups. One includes *cis-cis*-$[Co(a)_2(b)_2(CC)]$- and *all-cis*-$[Co(a)_2(b)_2(c)_2]$-type complexes in which the central metal ions are surrounded with three kinds of donor atoms.[1–4] A typical instance is an *all-cis*-$[Co(CN)_2(NH_3)_2(H_2O)_2]^+$ complex, and Mason[5] has attempted to explain the optical activity of the complex in terms of a dynamic coupling model

The other group represents a *fac(D)*-[Co(a)(BC)-(DDD)]-type complexes where one octahedral face of the complex is coordinated with a symmetrical terdentate ligand such as 1,4,7-triazacyclononane (=tacn) and the opposite face is occupied by three kinds of donor atoms.[6–9] In spite of the existence of two ring-pairs in this type of complex, the optical activity is considered to be mainly derived from a chiral arrangement of donor atoms.[8,9] However, the bidentate ligand (BC) used is limited to an amino acidate ion, and there is little information on the relation between the CD spectrum and the absolute configuration of the complex.

Recently, we reported the preparations and optical resolutions of $[Co(CN)(Br)(NH_3)(tacn)]^+$ [10] and *fac*-(*NH₃*)-$[Co(NO_2)(gly)(NH_3)_3]^+$.[11] No ring-pair is contained in these complexes, and these types of complexes are adequate to allow a study of the optical activity of the complexes with a chiral arrangement of donor atoms.

This paper will deal with further syntheses and optical resolutions of the complexes with a series of $[Co(a)(b)(NH_3)(tacn)]^{n+}$ (a, b=CN^-, NO_2^-, SO_3^{2-}, NCS^-, N_3^-, H_2O, OH^-, CH_3COO^-, Cl^-, or Br^-). The absolute configurations are determined by referring to the CD spectra of $[Co(a)(gly)(tacn)]^{n+}$ (a=CN^-, NO_2^-, NCS^-, N_3^-, or Cl^-)[8] and by chemical derivations from optically active complexes. The signs of the Cotton peaks in the first absorption band region are discussed on the basis of the absolute configurations of the complexes.

Experimental

Ligand. 1,4,7-Triazacyclononane trihydrochloride (tacn·3HCl) was prepared by the literature method.[12]

Preparation of Complexes. *1)* *[Co(CN)(Br)(NH₃)(tacn)]Cl*: The preparation of this complex has been described in an earlier paper.[10] The description will be given here again with a few modifications. To an aqueous suspension of the complex, $[Co(CN)(SO_3)(NH_3)(tacn)]$[10] (1 g, 3 mmol in 2 cm³ H_2O), which had been prepared from $[Co(CN)(SO_3)(NH_3)_4]$,[13] was added 10 cm³ of 47% HBr little by little, and the mixed solution was stirred at 50 °C for 6 h, whereupon the color of the solution turned red. After cooling to room temperature, large amounts of ethanol and ether were successively added to the solution. The precipitated material was filtered and dissolved in water (500 cm³). The solution was chromatographed on a column of Dowex 50W-X8 (3 cm×10 cm, Na^+ form). By elution with a 0.3 mol/dm³ NaCl solution, a red band was discharged from the column. The effluent was concentrated by a rotary evaporator below 35 °C, with simultaneous removal of the precipitated salt used as the eluting agent. After addition of a small amount of ethanol to the final filtrate, reddish crystals deposited on standing the mixture in a refrigerator. This crude product was recrystallized from warm water (*ca.* 40 °C). The yield was *ca.* 0.5 g. Found: C, 24.16; H, 5.35; N, 19.96%. Calcd for $[Co(CN)(Br)(NH_3)(tacn)]Cl$: C, 24.26; H, 5.25; N, 20.21%.

2) *[Co(CN)(H₂O)(NH₃)(tacn)](ClO₄)₂·H₂O*: An aqueous solution (10 cm³) of the complex, $[Co(CN)(Br)(NH_3)(tacn)]Cl$ (0.7 g, 2 mmol), was adjusted to pH 9 with 5 mol/dm³ KOH, and stirred until its color changed from red to orange, whereupon the corresponding hydroxo complex, $[Co(CN)(OH)(NH_3)(tacn)]^+$, formed. After the solution had been acidified with 1 mol/dm³ $HClO_4$ until pH 5, the resulting solution was once filtered and diluted to 500 cm³ with water. This solution was poured onto a column of SP-Sephadex C-25 (4.5 cm×20.0 cm, Na^+ form). By elution with 0.1 mol/dm³ $HClO_4$, a yellow band was discharged from the column. The eluate was treated in a similar way to that in 1). The yield was *ca.* 0.4 g. Found: C, 18.17; H, 4.60; N, 15.11%. Calcd for $[Co(CN)(H_2O)(NH_3)(tacn)](ClO_4)_2\cdot H_2O$: C, 18.03; H, 4.77; N, 15.03%.

3) *[Co(CN)(Cl)(NH₃)(tacn)]Cl*: For the preparation of the $[Co(CN)(H_2O)(NH_3)(tacn)]^{2+}$ complex, the elution was carried out with 0.1 mol/dm³ HCl. When the eluate was concentrated to a small volume, the solution turned red. The solution was stirred at 40 °C for 2 h, and poured onto a column of Dowex 50W-X8 (4 cm×10 cm, H^+ form). The eluate obtained by the elution with 0.3 mol/dm³ HCl was concentrated to a small volume by a rotary evaporator at 35 °C, and a small amount of ethanol was added to the concentrate. This solution was kept in a refrigerator until red crystals of the desired complex deposited. The crude product was recrystallized from 6 mol/dm³ HCl. The yield was *ca.* 0.5 g. Found: C, 27.70; H, 6.13; N, 23.21%

Calcd for $[Co(CN)(Cl)(NH_3)(tacn)]Cl$: C, 27.83; H, 6.01; N, 23.18%.

4) $[Co(CN)(NO_2)(NH_3)(tacn)]Cl\cdot 1.3H_2O$: To a solution of $[Co(CN)(H_2O)(NH_3)(tacn)](ClO_4)_2\cdot H_2O$ (1 g, in 50 cm^3 H_2O), was added $NaNO_2$ (1 g, 14 mmol). The solution was stirred at room temperature until its color changed from orange to lemon yellow. The reacted solution was diluted to 500 cm^3 and charged on a column of Dowex 50W-X8 (3 cm × 5.0 cm, Na^+ form). By elution with a 0.3 mol/dm^3 NaCl solution, a lemon yellow band was discharged from the column. The effluent was treated in a similar way to that in 1). The yield was *ca.* 0.7 g. Found: C, 25.29; H, 6.14; N, 24.83%. Calcd for $[Co(CN)(NO_2)(NH_3)(tacn)]Cl\cdot 1.3H_2O$: C, 25.02; H, 6.18; N, 25.01%.

5) $[Co(CN)(NCS)(NH_3)(tacn)]Cl\cdot 2H_2O$: An aqueous solution (50 cm^3) containing $[Co(CN)(H_2O)(NH_3)(tacn)](ClO_4)_2\cdot H_2O$ (0.5 g) and KSCN (1 g, 10 mmol) was adjusted to pH 3 with $HClO_4$, and then stirred at 50 °C for 4—5 h. The resulting orange solution was chromatographed in the same manner as 1). The yield was *ca.* 0.3 g. Found: C, 26.81; H, 6.05; N, 26.62%. Calcd for $[Co(CN)(NCS)(NH_3)(tacn)]Cl\cdot 2H_2O$: C, 26.64; H, 6.15; N, 23.30%.

6) $[Co(CN)(N_3)(NH_3)(tacn)]Cl$: This complex was prepared in the same manner as the isothiocyanato complex, except for the use of NaN_3 (1.0 g, 15 mmol) in place of KSCN. The crystals of the desired complex could not be obtained from the orange effluent, because the desired complex decomposed in the concentrated solution. Therefore, the ε value of the desired complex was determined by atomic absorption analysis with the freshly eluted solution.

7) $[Co(CN)(SO_3)(NH_3)(tacn)]\cdot 0.5H_2O$: This complex has been prepared from the reaction of $[Co(CN)(SO_3)(NH_3)_4]$ with tacn·3HCl.[10] In this work, the complex was derived from the $[Co(CN)(H_2O)(NH_3)(tacn)]^{2+}$ complex. To a solution of the aqua complex salt (0.3 g, in 20 cm^3 H_2O) was added $NaHSO_3$ (0.5 g, 5 mmol), and the solution was adjusted to pH 4 with $HClO_4$. The solution was then stirred at room temperature until its color changed from orange to lemon yellow. The resulting solution was poured onto a column of Dowex 50W-X8 (3 cm × 30 cm, Na^+ form) and the adsorbed species on the column was eluted with water. Two components of noncharged species were collected. The first eluted species was unknown. The fraction of the second component was concentrated by a rotary evaporator at *ca.* 35 °C. This fraction was identified with the desired complex by absorption spectrum. The yield was *ca.* 0.1 g.

8) $[Co(CN)(CH_3COO)(NH_3)(tacn)]Cl$: An aqueous solution (20 cm^3) containing the aqua complex salt (0.5 g) and potassium acetate (1 g, 10 mmol) was adjusted to pH 4 with acetic acid, and then stirred at 40 °C for 3 h. The resulting solution was concentrated to a small volume by a rotary evaporator at 40 °C, filtered once, and diluted to 1 dm^3 with water. This solution was poured onto a column of Dowex 50W-X8 (3.0 cm × 20 cm, Na^+ form). By elution with a 0.3 mol/dm^3 NaCl solution, three components corresponding to univalent cationic species were collected. The optical resolution of each species was attempted by means of column chromatography (Dowex 50W-X8, 200—400 mesh, 2.5 cm × 60 cm) by use of a 0.3 mol/dm^3 $Na_2[Sb_2(d\text{-tart})_2]$ solution as eluent. The absorption and CD spectra of the second species agreed with those of the $[Co(CN)(Cl)(NH_3)(tacn)]^+$ complex. The optical resolution of the third species was unsuccessful and this fact indicated that the third species was not the desired complex. On the other hand, the first species could be resolved into the optical antipodes, and by comparison with the spectra of $[Co(CN)(H_2O)(NH_3)(tacn)]^{2+}$ and $[Co(CN)(OH)(NH_3)(tacn)]^+$, it was considered that this species had a $[Co(C)(O)(N)_4]$ chromophore. Therefore, the first species was assigned to the desired complex, $[Co(CN)(CH_3COO)(NH_3)(tacn)]^+$. The fact that the first species was converted to the $[Co(CN)(Cl)(NH_3)(tacn)]^+$ complex by treatment with 6 mol/dm^3 HCl at 40 °C also supported the assignment. The ε value of the desired complex was evaluated in the same manner as in 6), because the yield was very poor.

9) $[Co(NO_2)_2(NH_3)(tacn)]Cl\cdot 2H_2O$: The ligand, tacn·3HCl (1.0 g, 4.2 mmol), was dissolved in a minimum amount of water and neutralized with aqueous KOH. The resulting solution was added dropwise to a solution containing *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$[14] (1.5 g, 5.3 mmol in 50 cm^3 H_2O). The mixed solution was adjusted to pH 9—10 with a 5 mol/dm^3 KOH solution and stirred at 55 °C for 12 h. Then, the color of the solution changed from orange to wine-red. After cooling to room temperature, the solution was diluted to 2 dm^3 with water, and poured onto a column of Dowex 50W-X8 (4 cm × 25 cm, Na^+ form). The adsorbed species was washed with water and eluted with a 0.3 mol/dm^3 NaCl solution. Three components of univalent cationic species were collected in each fraction. The second and third species were identified with *trans*- and *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ respectively.[14] The first lemon-yellow fraction was treated in a similar way to that in 1). The yield was *ca.* 0.5 g. Found: C, 19.70; H, 6.20; N, 23.14%. Calcd for $[Co(NO_2)_2(NH_3)(tacn)]Cl\cdot 2H_2O$: C, 19.55; H, 6.01; N, 22.80%.

10) $[Co(Cl)(H_2O)(NH_3)(tacn)]Cl_2\cdot NaCl$: This complex was prepared by an acid-hydrolysis of $[Co(NO_2)_2(NH_3)(tacn)]Cl\cdot 2H_2O$. The dinitro complex salt (1.0 g) was dissolved in 1 mol/dm^3 HCl (20 cm^3) and the solution was stirred at 60 °C for 2 h. After cooling to room temperature, the solution was neutralized with 5 mol/dm^3 NaOH and concentrated to a small volume by a rotary evaporator with simultaneous removal of deposited NaCl. The concentrate was adjusted to pH 10 with 5 mol/dm^3 NaOH and stirred at room temperature for a while. Then, the solution was diluted to 2 dm^3 with water and adjusted to pH 5 with 5 mol/dm^3 $HClO_4$. The solution was poured onto a column of SP-Sephadex C-25 (4.0 cm × 25 cm, Na^+ form). The adsorbed species were eluted with 0.1 mol/dm^3 NaCl, and three bands were discharged from the column. The eluate for each band was collected in a fraction and submitted to the measurement of the absorption spectrum. The first eluted species was identified with the dinitro complex. The second species, which contained a bivalent cation, was assumed to be the mixture of the $[Co(NO_2)(H_2O)(NH_3)(tacn)]^{2+}$ and $[Co(Cl)(H_2O)(NH_3)(tacn)]^{2+}$ complex. The last red species, which contained a tervalent cation, was assumed to be $[Co(H_2O)_2(NH_3)(tacn)]^{3+}$ complex. This last fraction was treated in a similar way to that in 1). The fact that the color changed from red to purple by concentrating the effluent indicated the formation of $[Co(Cl)(H_2O)(NH_3)(tacn)]^{2+}$ species. The yield was *ca.* 0.5 g. Found: C, 19.11; H, 5.21; N, 13.46%. Calcd for $[Co(Cl)(H_2O)(NH_3)(tacn)]Cl_2\cdot NaCl$: C, 18.57; H, 5.20; N, 14.44%.

11) $[Co(NCS)(H_2O)(NH_3)(tacn)](ClO_4)_2\cdot H_2O$: An aqueous solution (20 cm^3) containing $[Co(Cl)(H_2O)(NH_3)(tacn)]Cl_2\cdot NaCl$ (1.0 g, 3 mmol) and an equimolar amount of KSCN (0.4 g) was adjusted to pH 3 with 5 mol/dm^3 $HClO_4$ and stirred at *ca.* 40 °C for 1 h. After cooling to room temperature, the solution was adjusted to pH 10 with 5 mol/dm^3 KOH, and stirred for a while. After dilution to 2 dm^3 with water, the diluted solution was neutralized with 5 mol/dm^3 $HClO_4$ and poured onto a column of SP-Sephadex

C-25 (4 cm×25 cm, Na$^+$ form). At first, by elution with 0.03 mol/dm^3 NaCl, a red band corresponding to an univalent cation was discharged. This species was assigned to a [Co(NCS)$_2$(NH$_3$)(tacn)]$^+$ complex by elemental analysis. Found: C, 25.34; H, 4.33; N, 21.35%. Calcd for [Co(NCS)$_2$(NH$_3$)(tacn)]Cl·0.5H$_2$O: C, 24.89; H, 4.70; N, 21.27%. A red band corresponding to the bivalent cation of the desired complex was eluted with 0.1 mol/dm^3 HClO$_4$. The solution was treated in a similar way to that in 1). The yield was *ca.* 0.5 g. Found: C, 16.52; H, 4.03; N, 14.37%. Calcd for [Co(NCS)(H$_2$O)(NH$_3$)(tacn)](ClO$_4$)$_2$·H$_2$O: C, 16.87; H, 4.46; N, 14.06%.

12) [Co(NCS)(NO$_2$)(NH$_3$)(tacn)]Cl·H$_2$O: To a solution of [Co(NCS)(H$_2$O)(NH$_3$)(tacn)](ClO$_4$)$_2$·H$_2$O (0.5 g in 20 cm^3 H$_2$O), was added NaNO$_2$ (1.0 g, 14 mmol). The solution was adjusted to pH 3 with HClO$_4$, and stirred at room temperature until the color changed from red to orange. The resulting solution was treated in the same manner as in 4). The yield was *ca.* 0.3 g. Found: C, 23.20; H, 5.33; N, 22.85%. Calcd for [Co(NCS)(NO$_2$)(NH$_3$)(tacn)]Cl·H$_2$O: C, 23.18; H, 5.56; N, 23.17%.

13) [Co(NCS)(N$_3$)(NH$_3$)(tacn)]Cl·0.5H$_2$O: An aqueous solution (20 cm^3) containing [Co(NCS)(H$_2$O)(NH$_3$)(tacn)](ClO$_4$)$_2$·H$_2$O (0.5 g) and NaN$_3$ (1 g, 15 mmol) was adjusted to pH 3 with HClO$_4$, and then stirred at 50 °C for 4—5 h. The resulting red solution was treated in a way similar to that in 4). The yield was *ca.* 0.3 g. Found: C, 23.63; H, 5.28; N, 32.05%. Calcd for [Co(NCS)(NO$_2$)(NH$_3$)(tacn)]Cl·0.5H$_2$O: C, 24.04; H, 5.48; N, 32.04%.

14) [Co(N$_3$)(H$_2$O)(NH$_3$)(tacn)](ClO$_4$)$_2$: This complex was prepared in the same manner as the [Co(NCS)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complex, except for the use of NaN$_3$ (0.4 g, 6 mmol) in place of KSCN. Since the yield was very poor, the crystals of the desired complex could not be obtained. The ε value of the complex was evaluated in the same manner as in 6). This complex was also prepared from [Co(NCS)(N$_3$)(NH$_3$)(tacn)]$^+$ by treatment of H$_2$O$_2$ in an acidic solution.

15) [Co(NO$_2$)(H$_2$O)(NH$_3$)(tacn)](ClO$_4$)$_2$: This complex was prepared by the reaction of the [Co(NCS)(NO$_2$)(NH$_3$)(tacn)]$^+$ complex with H$_2$O$_2$, or by acid-hydrolysis of the [Co(NO$_2$)$_2$(NH$_3$)(tacn)]$^+$ complex.

Method 1: A solution containing [Co(NCS)(NO$_2$)(NH$_3$)(tacn)]Cl·0.5H$_2$O (0.2 g in 50 cm^3 30% H$_2$O$_2$) was adjusted to pH 3 with 5 mol/dm^3 HClO$_4$ and stirred for 5—6 h. The resulting solution was diluted to 3 dm^3 and poured onto a column of Dowex 50W-X8 (2.5 cm×20 cm, Na$^+$ form). By elution with 0.3 mol/dm^3 NaCl, a lemon-yellow band corresponding to univalent cation was discharged. This species was identified with [Co(CN)(NO$_2$)(NH$_3$)(tacn)]$^+$. After this, two yellow bands corresponding to bivalent cations were eluted with 1 mol/dm^3 HClO$_4$. The earlier eluate was assigned to the desired complex by its absorption spectrum and the later eluate was assumed to be [Co(NO$_2$)(NH$_3$)$_2$(tacn)]$^{2+}$ species. After neutralizing the earlier eluate, the solution was treated in a similar way to that in 14).

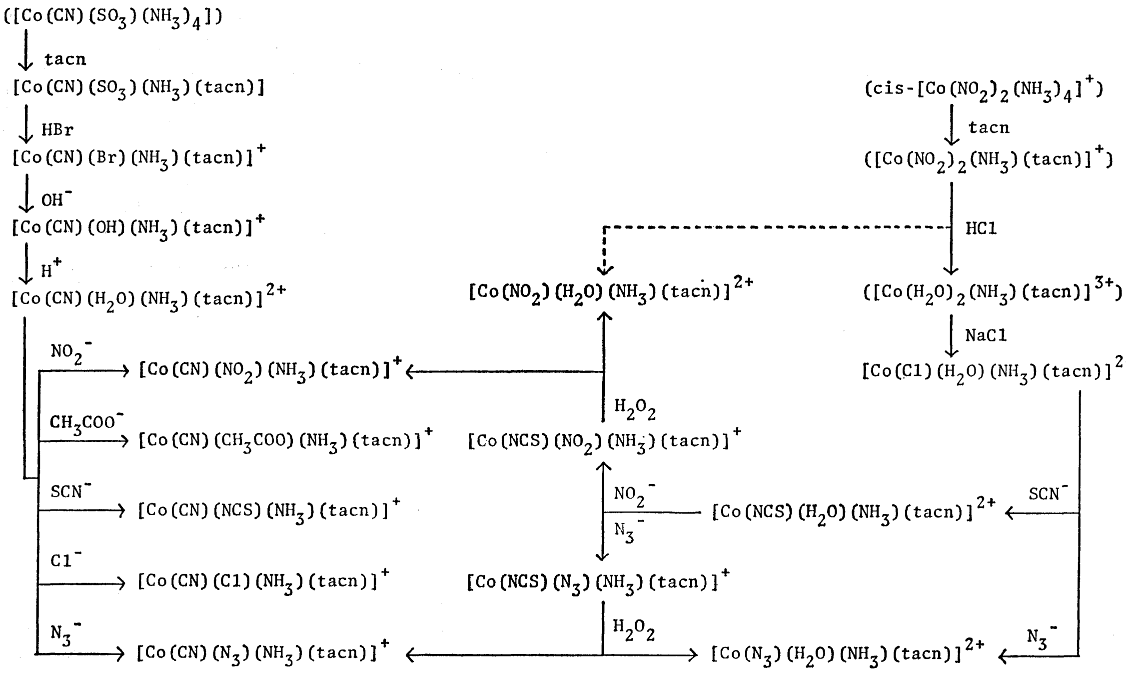
Method 2: On the synthesis of [Co(Cl)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$, the orange band corresponding to the bivalent cation was rechromatographed on a column of Dowex 50W-X8 (2.5 cm×20 cm). The orange and red bands were eluted with 1 mol/dm^3 HClO$_4$. The orange band was assigned to [Co(NO$_2$)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ and the red band to [Co(Cl)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$.

Optical Resolution. Except for the [Co(NO$_2$)$_2$(NH$_3$)(tacn)]$^+$ and [Co(CN)(SO$_3$)(NH$_3$)(tacn)] complexes all complexes prepared in this study were partially resolved into the optical antipodes by means of column chromatography. In the cases of bivalent cations, the optical resolutions were carried out on a column of SP-Sephadex C-25 (2.5 cm×120 cm, Na$^+$ form) using 0.1 mol/dm^3 K$_2$[Sb$_2$(*d*-tart)$_2$] solution as eluent. On the other hand, since the [Co(CN)(NO$_2$)(NH$_3$)(tacn)]$^+$ and [Co(CN)(NCS)(NH$_3$)(tacn)]$^+$ complexes were yellowish univalent cations, a column of SP-Sephadex C-25 (2.5 cm×120 cm, Na$^+$ form) and 0.03 mol/dm^3 K$_2$[Sb$_2$(*d*-tart)$_2$] solution as eluent were used. For the remaining complexes, the optical resolutions were performed on a column of Dowex 50W-X8 (200—400 mesh, 2.5 cm×60 cm, Na$^+$ form) using 0.3 mol/dm^3 Na$_2$[Sb$_2$(*d*-tart)$_2$] solution as eluent. When the adsorbed band had descended to one tenth of the column height, the band was washed with water and eluted with 0.1 mol/dm^3 HClO$_4$, 0.03 mol/dm^3 NaCl or 0.3 mol/dm^3 NaCl. The eluates thus concentrated were submitted to the measurements of the CD spectra, while the concentrations of the complex species were evaluated from the absorption spectral data. The isomers are stable enough to measure the spectra in a solution.

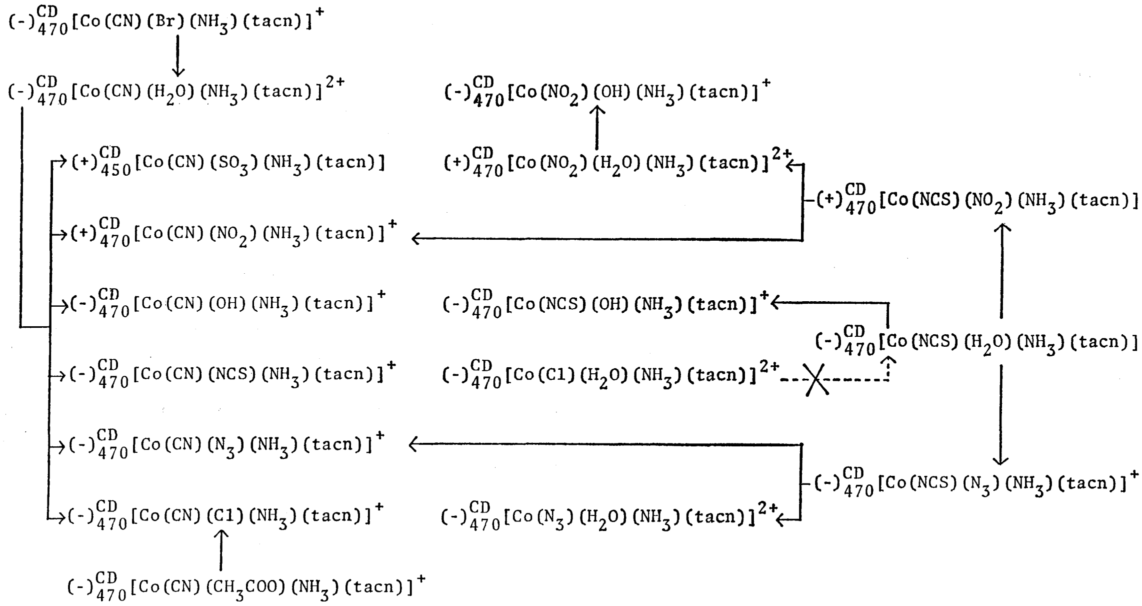
Derivation from Optically Active Complexes. The $(-)^{\mathrm{CD}}_{470}$-[Co(CN)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complex could be derived from the $(-)^{\mathrm{CD}}_{470}$[Co(CN)(Br)(NH$_3$)(tacn)]$^+$ complex, according to the procedure described in 2). Furthermore, the $(-)^{\mathrm{CD}}_{470}$[Co(CN)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complex could be converted to the $(-)^{\mathrm{CD}}_{470}$[Co(CN)(Cl)(NH$_3$)(tacn)]$^+$, $(-)^{\mathrm{CD}}_{470}$-[Co(CN)(OH)(NH$_3$)(tacn)]$^+$, $(-)^{\mathrm{CD}}_{470}$[Co(CN)(NCS)(NH$_3$)(tacn)]$^+$, $(-)^{\mathrm{CD}}_{470}$[Co(CN)(N$_3$)(NH$_3$)(tacn)]$^+$, $(+)^{\mathrm{CD}}_{470}$[Co(CN)(NO$_2$)(NH$_3$)(tacn)]$^+$, and $(+)^{\mathrm{CD}}_{450}$[Co(CN)(SO$_3$)(NH$_3$)(tacn)] by the methods described in 3)—7), respectively. The $(-)^{\mathrm{CD}}_{470}$[Co(CN)(CH$_3$COO)(NH$_3$)(tacn)]$^+$ complex was converted to the $(-)^{\mathrm{CD}}_{470}$[Co(CN)(Cl)(NH$_3$)(tacn)]$^+$ complex by the treatment with 6 mol/dm^3 HCl at 40 °C.

The $(-)^{\mathrm{CD}}_{470}$[Co(NCS)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complex could be converted to the $(+)^{\mathrm{CD}}_{470}$[Co(NCS)(NO$_2$)(NH$_3$)(tacn)]$^+$ and $(-)^{\mathrm{CD}}_{470}$[Co(NCS)(N$_3$)(NH$_3$)(tacn)]$^+$ complexes according to the procedures described in 12) and 13), respectively. On the other hand, the oxidation of the $(+)^{\mathrm{CD}}_{470}$[Co(NCS)(NO$_2$)(NH$_3$)(tacn)]$^+$ complex by aqueous H$_2$O$_2$ at *ca.* pH 3 produced the $(+)^{\mathrm{CD}}_{470}$[Co(CN)(NO$_2$)(NH$_3$)(tacn)]$^+$ and $(+)^{\mathrm{CD}}_{470}$[Co(NO$_2$)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complexes, which were separated chromatographically. The similar oxidation of the $(-)^{\mathrm{CD}}_{470}$[Co(NCS)(N$_3$)(NH$_3$)(tacn)]$^+$ complex produced the $(-)^{\mathrm{CD}}_{470}$[Co(CN)(N$_3$)(NH$_3$)(tacn)]$^+$ and $(-)^{\mathrm{CD}}_{470}$[Co(N$_3$)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complexes. The absorption and CD spectra of the optical isomers obtained by the derivations coincided with those of the isomers obtained by the optical resolutions. Through the above derivations from optically active complexes, the absolute configurations of all complexes prepared in this work could be correlated, except for the [Co(Cl)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$ complex.

Measurements. The absorption spectra in aqueous solutions were recorded with a Hitachi 323 recording spectrophotometer. The CD spectra were measured with a JASCO J-40C automatic recording spectropolarimeter equipped with a JASCO Model J-DPZ data processor for CD. The absorption and CD spectra of hydroxo complex species were measured with solutions of the corresponding aqua complexes alkalized with 5 mol/dm^3 NaOH (pH 10). The hydroxo complex species were chromatographically pure, and the absorption and CD spectra of the hydroxo complexes were returned to the original spectra of the parent aqua complexes, when the solutions were again acidified with HClO$_4$. This fact suggests that the base-hydrolysis proceeds with retention of the configuration. To determine the ε values of the complexes which could not be crystallized, a Hitachi 170-150 atomic absorption spectrophotometer was used.



Scheme 1. Pathways of syntheses of $[Co(a)(b)(c)(tacn)]^{n+}$ complexes.



Scheme 2. Derivations of optically active complexes.

Results and Discussion

Preparation and Resolution. Various *fac*(*a*,*b*,*c*)-$[Co(a)(b)(c)(tacn)]^{n+}$-type complexes were prepared by derivations starting from the complexes $[Co(CN)(SO_3)(NH_3)_4]$13) and *cis*-$[Co(NO_2)_2(NH_3)_4](NO_3)$.14) Scheme 1 represents the pathways of the present syntheses. We failed to crystallize the $[Co(CN)(N_3)(NH_3)(tacn)]^+$, $[Co(CN)(CH_3COO)(NH_3)(tacn)]^+$, $[Co(NO_2)(H_2O)(NH_3)(tacn)]^{2+}$, and $[Co(N_3)(H_2O)(NH_3)(tacn)]^{2+}$ complexes, but the formations of these complexes were ascertained by absorption spectra, chromatographic behavior, optical resolutions, and chemical reactivities with other unidentate ligands.

All complexes except for $[Co(CN)(SO_3)(NH_3)(tacn)]$ were partially resolved into optical antipodes by a column chromatography using $K_2[Sb_2(d\text{-tart})_2]$ or $Na_2[Sb_2(d\text{-tart})_2]$ as eluting agent. When the $[Co(Cl)(H_2O)(NH_3)(tacn)]^{2+}$ complex was optically resolved, the counter ion was changed into a perchlorate at the last stage of the elution, since a chloride brought about racemization of the complex and the effluent exhibited no optical activity.

Absolute Configuration and CD Spectra. In order to investigate the relation between CD spectra and absolute configurations of the *fac*(*a*,*b*,*c*)-$[Co(a)(b)(c)(tacn)]^{n+}$-type complexes, we tried to derive optically active complexes directly from optically active parent complexes. The conversions were successful in giving

Table 1. Absorption and CD spectral data

	Absorption $\tilde{\nu}/10^3\ \mathrm{cm^{-1}}$ $(\log \varepsilon)$	CD $\tilde{\nu}/10^3\ \mathrm{cm^{-1}}$ $(\Delta \varepsilon)$
$(+)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(NO_2)(NH_3)(tacn)}]^+$	23.6(2.17)	19.6(−0.01)
		21.5(+0.02)
		24.8(−0.16)
	31.4(3.30)	
$(+)^{\mathrm{CD}}_{450}[\mathrm{Co(CN)(SO_3)(NH_3)(tacn)}]$	24.1(2.21)	19.9(−0.02)
		22.9(+0.26)
		25.9(−0.12)
	35.5(4.27)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(H_2O)(NH_3)(tacn)}]^{2+}$	22.1(1.93)	18.9(+0.04)
		21.6(−0.26)
		24.6(+0.07)
	29.9(1.94)	27.6(−0.01)
		30.1(+0.02)
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(OH)(NH_3)(tacn)}]^+$	*ca.* 20 (*ca.* 1.8 sh)	18.8(+0.13)
	22.0(1.99)	21.8(−0.29)
		25.3(+0.01)
	28.7(2.07)	27.6(−0.01)
		30.1(+0.02)
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(CH_3COO)(NH_3)(tacn)}]^+$	21.5(2.05)	19.3(+0.03)
		21.9(−0.28)
	29.7(2.08)	28.1(+0.03)
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(NCS)(NH_3)(tacn)}]^+$	21.9(2.51)	17.7(+0.01)
		20.7(−0.15)
		24.1(+0.08)
	33.5(3.31)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(N_3)(NH_3)(tacn)}]^+$	21.2(2.50)	21.3(−0.19)
	33.0(3.86)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(Cl)(NH_3)(tacn)}]^+$	19.9(1.81)	18.0(+0.01)
	ca. 22 (*ca.* 1.6 sh)	20.5(−0.13)
		23.7(+0.09)
	29.4(2.00)	28.8(−0.02)
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(Br)(NH_3)(tacn)}]^+$	19.4(1.84)	17.3(+0.01)
	ca. 22 (*ca.* 1.6 sh)	20.0(−0.12)
		23.4(+0.07)
	—	27.4(+0.06)
	ca. 32 (*ca.* 3.1 sh)	
$(+)^{\mathrm{CD}}_{470}[\mathrm{Co(NO_2)(H_2O)(NH_3)(tacn)}]^{2+}$	21.8(2.13)	19.5(+0.08)
		23.4(+0.14)
	30.6(3.24)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(NO_2)(OH)(NH_3)(tacn)}]^+$	21.8(2.32)	19.4(+0.09)
		22.8(−0.04)
	31.3(3.00)	
$(+)^{\mathrm{CD}}_{470}[\mathrm{Co(NCS)(NO_2)(NH_3)(tacn)}]^+$	21.3(2.51)	*ca.* 20 (*ca.* +0.03 sh)
		23.0(+0.06)
	—	27.2(−0.27)
	30.8(3.51)	30.4(+0.49)
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(NCS)(H_2O)(NH_3)(tacn)}]^{2+}$	20.0(2.44)	20.4(−0.20)
	—	25.1(+0.04)
	31.8(3.86)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(NCS)(OH)(NH_3)(tacn)}]^+$	19.8(2.32)	18.7(+0.07)
		20.6(−0.05)
	ca. 27 (*ca.* 2.35 sh)	25.0(+0.07)
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(NCS)(N_3)(NH_3)(tacn)}]^+$	19.7(2.55)	19.3(−0.39)
		23.0(+0.01)
	—	27.9(−0.35)
	31.8(4.00)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(N_3)(H_2O)(NH_3)(tacn)}]^{2+}$	19.5(2.30)	18.3(−0.16)
		19.7(+0.02)
		21.4(−0.08)
	—	24.8(+0.11)
		28.1(+0.10)
	31.1(3.75)	
$(-)^{\mathrm{CD}}_{470}[\mathrm{Co(Cl)(H_2O)(NH_3)(tacn)}]^{2+}$	18.6(1.96)	18.4(+0.011)
		20.7(−0.015)
	26.4(1.89)	24.2(−0.005)
		27.3(+0.018)
$[\mathrm{Co(NO_2)_2(NH_3)(tacn)}]^+$	23.0(2.36)	
	—	
	31.0(3.69)	

the corresponding optically active complexes, except for the $[\mathrm{Co(Cl)(H_2O)(NH_3)(tacn)}]^{2+}$ complex. The derivations are shown in Scheme 2. The $[\mathrm{Co(CN)(SO_3)(NH_3)(tacn)}]$ complex could not be resolved by column chromatography, but its active from $(+)^{\mathrm{CD}}_{450}$-$[\mathrm{Co(CN)(SO_3)(NH_3)(tacn)}]$ was derived from the $(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(H_2O)(NH_3)(tacn)}]^{2+}$ complex.

When the $(+)^{\mathrm{CD}}_{470}[\mathrm{Co(NCS)(NO_2)(NH_3)(tacn)}]^+$ complex was treated with H_2O_2, the $(+)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(NO_2)(NH_3)(tacn)}]^+$ and $(-)^{\mathrm{CD}}_{470}[\mathrm{Co(NO_2)(H_2O)(NH_3)(tacn)}]^+$ complexes were obtained with an optically inactive $[\mathrm{Co(CN)(NH_3)_2(tacn)}]^{2+}$ complex. The $(-)^{\mathrm{CD}}_{470}[\mathrm{Co(NCS)(N_3)(NH_3)(tacn)}]^+$ complex was also converted to the $(-)^{\mathrm{CD}}_{470}[\mathrm{Co(CN)(N_3)(NH_3)(tacn)}]^+$, $(-)^{\mathrm{CD}}_{470}[\mathrm{Co(N_3)(H_2O)(NH_3)(tacn)}]^{2+}$, and $[\mathrm{Co(N_3)(NH_3)_2(tacn)}]^{2+}$ complexes. Similar degradation reaction has been reported for $(-)_{589}[\mathrm{Co(NCS)(gly)(tacn)}]^+$; it is considered to proceed with retention of the configuration of the complex.[8] Since optically active isomers are obtained in the substitution or degradation reactions, it is concluded that two complexes which are connected with an arrow in Scheme 2 have the same absolute configuration with respect to the common ligands. Numerical data of absorption and CD spectra of the complexes drawn in Scheme 2 are summarized in Table 1.

For the present chiral complexes, two sources of d-electron optical activity can be considered: 1) A chiral conformation of three chelate rings of tacn and 2) a chiral arrangement of four kinds of donor atoms. However, it is considered that the tacn chelate rings are not fixed to a preferential conformation (λ or δ) and have little effect on the solution CD spectra, since CD spectra of three diastereoisomers of a $[\mathrm{Co(gly)(NH_3)(Metacn)}]^{2+}$ complex are known to be appreciably different from that of an enantiomeric $[\mathrm{Co(gly)(NH_3)(tacn)}]^{2+}$ isomer (Metacn represents (2*R*)-2-methyl-1,4,7-triazacyclononane, the chelate rings of Metacn in the former complex being fixed to λ conformation).[8,9] Therefore, it is considered that the op-

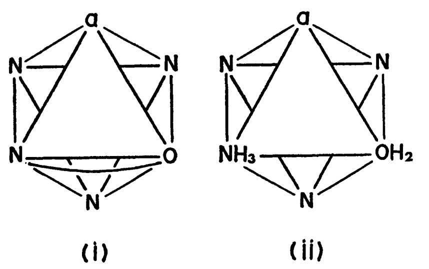


Fig. 1. Absolute configurations of (i) $[Co(a)(gly)(tacn)]^{n+}$ and (ii) $[Co(a)(H_2O)(NH_3)(tacn)]^{n+}$.

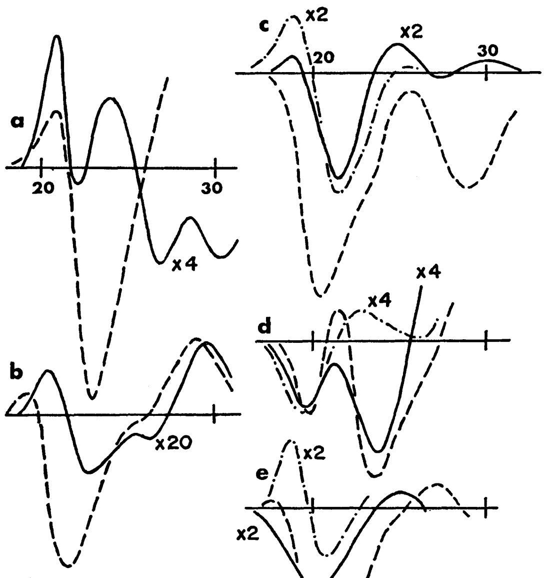


Fig. 2. CD spectra of a) $(+)^{CD}_{470}[Co(N_3)(H_2O)(NH_3)(tacn)]^{2+}$ (——), $(+)_{589}[Co(N_3)(gly)(tacn)]^{+}$ (----), b) $(-)^{CD}_{470}[Co(Cl)(H_2O)(NH_3)(tacn)]^{2+}$ (——), $(-)_{589}$-$[Co(Cl)(gly)(tacn)]^{+}$ (----), c) $(-)^{CD}_{470}[Co(CN)(H_2O)(NH_3)(tacn)]^{2+}$ (——), $(-)_{589}[Co(CN)(gly)(tacn)]^{+}$ (----), $(-)^{CD}_{470}[Co(CN)(OH)(NH_3)(tacn)]^{+}$ (—·—), d) $(-)^{CD}_{470}[Co(NO_2)(H_2O)(NH_3)(tacn)]^{2+}$ (——), $(-)_{539}$-$[Co(NO_2)(gly)(tacn)]^{+}$ (----), $(+)^{CD}_{470}[Co(NO_2)(OH)(NH_3)(tacn)]^{+}$ (—·—), and e) $(-)^{CD}_{470}[Co(NCS)(H_2O)(NH_3)(tacn)]^{2+}$ (——), $(-)_{589}[Co(NCS)(gly)(tacn)]^{+}$ (----), $(-)^{CD}_{470}[Co(NCS)(OH)(NH_3)(tacn)]^{+}$ (—·—).

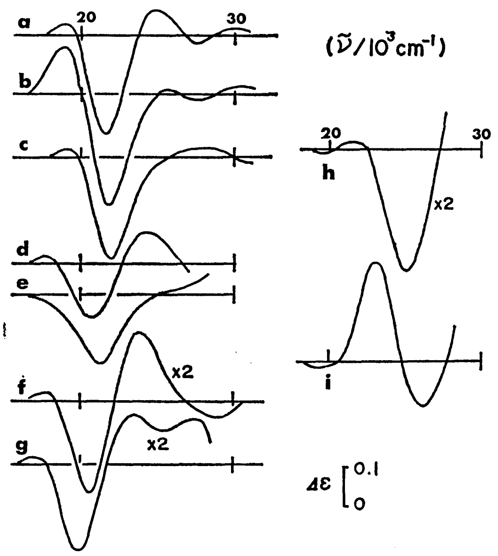


Fig. 3. CD spectra of a) $(-)^{CD}_{470}[Co(CN)(H_2O)(NH_3)(tacn)]^{2+}$, b) $(-)^{CD}_{470}[Co(CN)(OH)(NH_3)(tacn)]^{+}$, c) $(-)^{CD}_{470}[Co(CN)(CH_3COO)(NH_3)(tacn)]^{+}$, d) $(-)^{CD}_{470}$-$[Co(CN)(NCS)(NH_3)(tacn)]^{+}$, e) $(-)^{CD}_{470}[Co(CN)(N_3)(NH_3)(tacn)]^{+}$, f) $(-)^{CD}_{470}[Co(CN)(Cl)(NH_3)(tacn)]^{+}$, g) $(-)^{CD}_{470}[Co(CN)(Br)(NH_3)(tacn)]^{+}$, h) $(+)^{CD}_{470}[Co(CN)(NO_2)(NH_3)(tacn)]^{+}$, and i) $(+)^{CD}_{450}[Co(CN)(SO_3)(NH_3)(tacn)]$.

tical source 1) causes little optical activity in the *fac*-(*a*,*b*,*c*)-$[Co(a)(b)(c)(tacn)]^{n+}$ complexes.

A series of $[Co(a)(gly)(tacn)]^{n+}$ complexes (a$=CN^-$, NO_2^-, NH_3, NCS^-, N_3^-, H_2O, OH^-, or Cl^-) possess the same source of dissymmetry as the present complexes, and the absolute configurations of the glycinato complexes have been determined on the basis of X-ray analysis and chemical derivations.[8,15] The CD spectra of the $[Co(a)(gly)(tacn)]^{n+}$ complexes which have the absolute configuration shown in Fig. 1 (i) are illustrated in Fig. 2 with broken lines. The CD spectra of the $[Co(a)(H_2O)(NH_3)(tacn)]^{2+}$ complexes (a$=CN^-$, NO_2^-, NCS^-, N_3^-, or Cl^-) are also drawn in Fig. 2 with solid lines. As to the cyano, nitro, isothiocyanato and azido complexes, the enantiomers which exhibit the CD spectra shown in Fig. 2 are considered to have the same absolute configuration, judging by the chemical derivations drawn in Scheme 2.

When the unidentate, a, is CN^-, NO_2^- or NCS^-, each CD spectrum of the $[Co(a)(H_2O)(NH_3)(tacn)]^{2+}$ complex resembles that of the corresponding $[Co(a)(gly)(tacn)]^{+}$ complex, although the CD spectra of the azido complexes are somewhat different from each other. Thus, it is concluded that the$(-)^{CD}_{470}[Co(CN)(H_2O)(NH_3)(tacn)]^{2+}$, $(-)^{CD}_{470}[Co(NO_2)(H_2O)(NH_3)(tacn)]^{2+}$, $(-)^{CD}_{470}[Co(NCS)(H_2O)(NH_3)(tacn)]^{2+}$, and $(+)^{CD}_{470}[Co(N_3)(H_2O)(NH_3)(tacn)]^{2+}$ complexes have the absolute configuration as shown in Fig. 1 (ii).

Though the absolute configuration of $(-)^{CD}_{470}[Co(Cl)(H_2O)(NH_3)(tacn)]^{2+}$ could not be correlated with those of others, it is considered that the $(-)^{CD}_{470}$-isomer has the same absolute configuration as shown in Fig. 1 (ii), since $(-)_{589}[Co(Cl)(gly)(tacn)]^{+}$ exhibits a CD spectrum similar to that of the $(-)^{CD}_{470}$-isomer.

The $[Co(a)(H_2O)(NH_3)(tacn)]^{2+}$ complexes are bivalent cations, while the $[Co(a)(gly)(tacn)]^{+}$ complexes are univalent cations. The $[Co(CN)(CH_3COO)(NH_3)(tacn)]^{+}$ complex is the same univalent cation as $[Co(CN)(gly)(tacn)]^{+}$, and the $(-)^{CD}_{470}$-isomer of the acetato complex exhibits a CD spectrum similar to that of $(-)_{589}$-isomer of the glycinato complex. On this basis, it is predicted that both have the absolute configurations shown in Fig. 1. The absolute configurations of the others can be determined by tracing a pathway in Scheme 2.

a) *[Co(a)(CN)(NH₃)(tacn)]ⁿ⁺ Complexes.* In this series, the unidentate, a, stands for NO_2^-, SO_3^{2-}, NCS^-, H_2O, OH^-, CH_3COO^-, N_3^-, Cl^-, or Br^-. Each of the complexes has a rhombic ligand field, in which there are three electronic transition com-

TABLE 2. ASSIGNMENT OF COTTON PEAKS IN $[Co(a)(CN)(NH_3)(tacn)]^{n+}$

	Transition component		
$[Co(a)(CN)(NH_3)(tacn)]^{n+}$	$(xy \rightarrow x^2-y^2)$	$(yz \rightarrow y^2-z^2)$	$(zx \rightarrow z^2-x^2)$
$a=H_2O$	(+)	$(-)_d$	(+)
$a=OH^-$	(+)	$(-)_d$	(+)
$a=CH_3COO^-$	(+)	$(-)_d$	
$a=NCS^-$	(+)	$(-)_d$	(+)
$a=N_3^-$		$(-)_d$	
$a=Cl^-$	(+)	$(-)_d$	(+)
$a=Br^-$	(+)	$(-)_d$	(+)

$[Co(a)(CN)(NH_3)(tacn)]^{n+}$	$(xy \rightarrow x^2-y^2)$	$(zx \rightarrow z^2-x^2)$	$(yz \rightarrow y^2-z^2)$
$a=NO_2^-$	(−)	(+)	$(-)_d$
$a=SO_3^{2-}$	(−)	$(+)_d$	(−)

The subscript d shows the peak is dominant.

ponents for the first absorption band. The absorption spectra of the chloro, bromo, and hydroxo complexes exhibit clear splittings of the first absorption bands, while the aqua and acetato complexes show the broad absorption bands.

The CD spectra of $[Co(a)(CN)(NH_3)(tacn)]^{n+}$ with the same absolute configuration are shown in Fig. 3. Our interest is focused on the spectra in the first absorption band region, and the Cotton peaks in the region are described unless otherwise noted. The $(-)^{CD}_{470}$-azido and $(-)^{CD}_{470}$-acetato complexes exhibit one and two Cotton peaks, respectively. The remaining ones exhibit three Cotton peaks with alternating signs; however, the CD spectral pattern on the $(+)^{CD}_{470}$-nitro and $(+)^{CD}_{460}$-sulfito complexes is opposite to that on the $(-)^{CD}_{470}$-aqua, $(-)^{CD}_{470}$-hydroxo, $(-)^{CD}_{470}$-isothiocyanato, $(-)^{CD}_{470}$-chloro, and $(-)^{CD}_{470}$-bromo complexes, the former group exhibits (−), (+), and (−) signs from a lower-frequency side, and the latter group exhibits (+), (−), and (+) signs.

It is predicted by an angular overlap model[16] that three electronic transition components of the first absorption band are well separated with one another in the $[Co(a)(CN)(NH_3)(tacn)]^{n+}$ complexes. The predicted values well coincide with the extrema of the Cotton peaks. When a coordinate system is defined for the $[Co(a)(CN)(NH_3)(tacn)]^{n+}$ complexes as shown in Fig. 4 (i), the transition energy order becomes $E(xy \rightarrow x^2-y^2) < E(yz \rightarrow y^2-z^2) < E(zx \rightarrow z^2-x^2)$ for the aqua, hydroxo, acetato, isothiocyanato, azido, chloro and bromo complexes, and $E(xy \rightarrow x^2-y^2) < E(zx \rightarrow z^2-x^2) < E(yz \rightarrow y^2-z^2)$ for the nitro and sulfito complexes, where the symbols, $E(xy \rightarrow x^2-y^2)$, $E(yz \rightarrow y^2-z^2)$ and $E(zx \rightarrow z^2-x^2)$, designate the transition energies of the electronic transitions in XY, YZ, and ZX plane, respectively. The assignments of the Cotton peaks are listed in Table 2. As to the acetato complex, the two observed Cotton peaks are assigned to the lower-lying two transition components, *i.e.* $(xy \rightarrow x^2-y^2)$ and $(yz \rightarrow y^2-z^2)$, by comparing with the CD spectra of the aqua and hydroxo complexes. As to the azido complex, the observed Cotton peak is assigned to the $(yz \rightarrow y^2-z^2)$ transition, on the basis of the prediction by the angular overlap model.

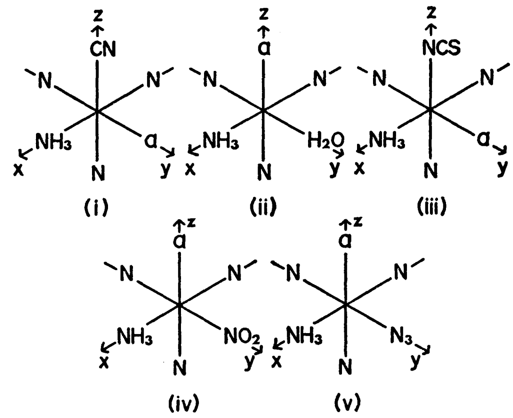


Fig. 4. Absolute configurations and coordinate systems for (i)$[Co(a)(CN)(NH_3)(tacn)]^{n+}$, (ii) $[Co(a)(H_2O)(NH_3)(tacn)]^{n+}$, (iii) $[Co(a)(NCS)(NH_3)(tacn)]^{n+}$, (iv)$[Co(a)(NO_2)(NH_3)(tacn)]^{n+}$, and (v) $[Co(a)(N_3)(NH_3)(tacn)]^{n+}$.

As is seen in Table 2, there are obvious relations between the Cotton signs and the corresponding transition components. The Cotton peaks corresponding to $(zx \rightarrow z^2-x^2)$ exhibit positive signs in every complex. As to the peaks corresponding to $(yz \rightarrow y^2-z^2)$, negative signs are observed in every complex. On the other hand, the signs of the peaks corresponding to $(xy \rightarrow x^2-y^2)$ are variable depending upon the unidentate a. When the unidentate is nitro or sulfito, the sign becomes negative. When the unidentate is aqua, hydroxo, acetato, isothiocyanato, azido, chloro or bromo, the peak has a positive sign. The inversion of the Cotton sign corresponding to the $(xy \rightarrow x^2-y^2)$ transition component is considered to relate to the ligand field strengths of the unidentate ligands lying in the XY plane. Nitro and sulfito ligands afford stronger ligand fields than an ammine ligand, and the Cotton peaks corresponding to $(xy \rightarrow x^2-y^2)$ exhibit negative signs. On the other hand, the ligand field strengths of H_2O, OH^-, CH_3COO^-, NCS^-, N_3^-, Cl^-, or Br^- are weaker than that of NH_3, and the peaks corresponding to $(xy \rightarrow x^2-y^2)$ exhibit positive signs.

As to the YZ plane, the ligand field strength of the unidentate a on the Y axis is weaker than that of the cyano ligand on the Z axis in every complex, and the concerned Cotton peaks exhibit negative signs. The common sign of the peaks corresponding to (zx→z^2—x^2) associates with the fact that the cyano ligand on the Z axis affords stronger ligand field than the ammine ligand on the X axis. Since the Cotton signs associated with the (zx→z^2—x^2) transition are independent with the variation of the unidentate a on the Y axis, the sign of the peak corresponding to a given electronic transition is considered to be determined by the ligands ligating in the plane where the electronic transition occurs. It is notable that all negative dominant peaks are assignable to the (yz→y^2—z^2) transition component, except for the sulfito complex. This electronic transition component is associated with the YZ plane, which contains no ammine ligand.

b) [Co(a)(H_2O)(NH_3)(tacn)]$^{2+}$ Complexes. In these complexes, the unidentate a stands for CN^-, NO_2^-, NCS^-, N_3^-, or Cl^-. The CD spectra of [Co(a)(H_2O)(NH_3)(tacn)]$^{2+}$ are shown in Fig. 2, along with those of the corresponding hydroxo complexes, and the absolute configurations of these enantiomers are illustrated in Fig. 4 (ii). Since the [Co(CN)(H_2O)(NH_3)(tacn)]$^{2+}$ and [Co(N_3)(H_2O)(NH_3)(tacn)]$^{2+}$ complexes exhibit three Cotton peaks, the peaks can be assigned to the electronic transition components in the same manner as in the [Co(a)(CN)(NH_3)(tacn)]$^{n+}$ complexes. In both the complexes, (+), (−), and (+) peaks are observed from a lower frequency side. These peaks are assigned to (xy→x^2—y^2), (yz→y^2—z^2), and (zx→z^2—x^2), respectively, for the cyano complex, and to (yz→y^2—z^2), (zx→z^2—x^2), and (xy→x^2—y^2) for the azido complex. The Cotton peaks corresponding to the (xy→x^2—y^2) component have (+) signs in these complexes. However, the signs associated with (yz→y^2—x^2) and (zx→z^2—x^2) in the cyano complex are opposite to those in the azido complex. These phenomena are also explained in the same manner as in the [Co(a)(CN)(NH_3)(tacn)]$^{n+}$ complexes. The inversions of the Cotton signs are related to the fact that a cyano ligand affords a stronger ligand field than an ammine or aqua ligand, but an azido ligand affords a weaker one than an ammine or aqua ligand. The common Cotton sign associated with (xy→x^2—y^2) is related to the common ligands in the XY plane. It is also found that the variation of the unidentate on the Z axis does not influence the sign of the peak corresponding to the electronic transition in the XY plane. In both the cyano and azido complexes, the dominant Cotton peaks correspond to the transition component in the plane which contains no ammine ligand (*i.e.*, the YZ plane).

The [Co(NO_2)(H_2O)(NH_3)(tacn)]$^{2+}$ and [Co(Cl)(H_2O)(NH_3)(tacn)]$^{2+}$ complexes exhibit two extrema, and the [Co(NCS)(H_2O)(NH_3)(tacn)]$^{2+}$ complex exhibits one extremum. It is difficult to assign the peaks to the transition components in these complexes. However, if the dominant Cotton peaks can be related to the (yz→y^2—z^2) component, the negative dominant peaks in the nitro and isothiocyanato complexes support the result in the cyano and azido complexes. A dominant peak with a (−) sign in [Co(Cl)(H_2O)(NH_3)(tacn)]$^{2+}$ may be explained by an overlapping of a peak at 24200 cm^{-1} in the second absorption band region. The chloro complex exhibits a positive Cotton peak at the lowest frequency side like the azido complex.

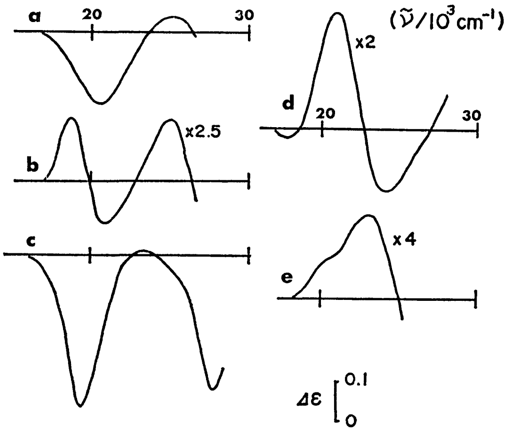


Fig. 5. CD spectra of a) $(-)^{CD}_{470}$[Co(NCS)(H_2O)(NH_3)(tacn)]$^{2+}$, b) $(-)^{CD}_{470}$[Co(NCS)(OH)(NH_3)(tacn)]$^+$, c) $(-)^{CD}_{470}$[Co(NCS)(N_3)(NH_3)(tacn)]$^+$, d) $(+)^{CD}_{470}$[Co(CN)(NCS)(NH_3)(tacn)]$^+$, and e) $(+)^{CD}_{470}$[Co(NO_2)(NCS)(NH_3)(tacn)]$^+$.

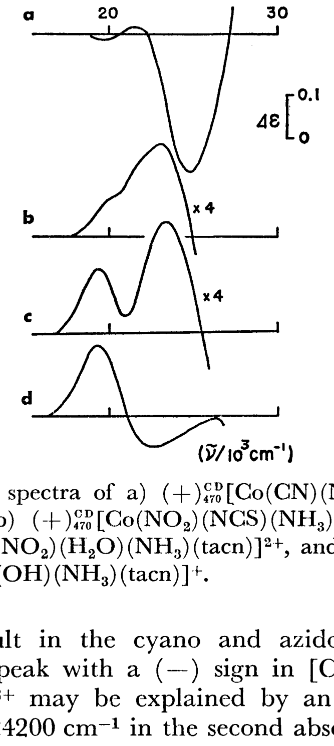


Fig. 6. CD spectra of a) $(+)^{CD}_{470}$[Co(CN)(NO_2)(NH_3)(tacn)]$^+$, b) $(+)^{CD}_{470}$[Co(NO_2)(NCS)(NH_3)(tacn)]$^+$, c) $(+)^{CD}_{470}$[Co(NO_2)(H_2O)(NH_3)(tacn)]$^{2+}$, and d) $(-)^{CD}_{470}$[Co(NO_2)(OH)(NH_3)(tacn)]$^+$.

The [Co(CN)(OH)(NH_3)(tacn)]$^+$ complex exhibits a similar CD spectrum to that of the parent aqua complex, but the spectra of [Co(NO_2)(OH)(NH_3)(tacn)]$^+$ and [Co(NCS)(OH)(NH_3)(tacn)]$^+$ are different from those of the parent aqua complexes. However, the [Co(NO_2)(OH)(NH_3)(tacn)]$^+$ complex also exhibits a (−) dominant peak like the parent aqua complex. It is characteristic that the [Co(NCS)(OH)(NH_3)(tacn)]$^+$ complex exhibits an intense peak with positive sign at 25000 cm^{-1} in the second absorption band region.

c) [Co(a)(NCS)(NH_3)(tacn)]$^{n+}$ Complexes. In this series, the unidentate a stands for CN^-, NO_2^-, H_2O, OH^-, or N_3^-. The complexes which have a

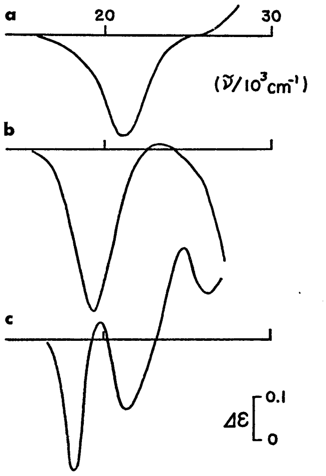


Fig. 7. CD spectra of a) $(-)^{\mathrm{CD}}_{470}$[Co(CN)(N$_3$)(NH$_3$)(tacn)]$^+$, b) $(-)^{\mathrm{CD}}_{470}$[Co(NCS)(N$_3$)(NH$_3$)(tacn)]$^+$, and c) $(-)^{\mathrm{CD}}_{470}$[Co(N$_3$)(H$_2$O)(NH$_3$)(tacn)]$^{2+}$.

common absolute configuration drawn in Fig. 4 (iii) exhibit the CD spectra as shown in Fig. 5. Except for the cyano complex, these complexes exhibit one or two Cotton peaks. Positive dominant peaks are observed at the cyano and nitro complexes, and negative ones, at the aqua and azido complexes. This phenomenon is also explained in terms of the ligand field strengths of the unidentates in YZ plane.

d) [Co(a)(NO$_2$)(NH$_3$)(tacn)]$^{n+}$ Complexes. In these complexes, the unidentate, a, stands for CN$^-$, NCS$^-$, H$_2$O, or OH$^-$. The isothiocyanato, aqua and hydroxo complexes exhibit two extrema. As to the complexes with the absolute configuration as shown in Fig. 4 (iv), only the cyano complex exhibits a (−) dominant peak (Fig. 6). This sign is related to the ligand field strength of CN$^-$, which is stronger than that of NO$_2$$^-$.

e) [Co(a)(N$_3$)(NH$_3$)(tacn)]$^{n+}$ Complexes. In this series, the unidentate a stands for CN$^-$, NCS$^-$, or H$_2$O. The CD spectra of the enantiomers illustrated in Fig. 4 (v) exhibit (−) dominant peaks (Fig. 7). This observation is also related to the fact that CN$^-$, NCS$^-$, and H$_2$O ligands have stronger ligand field strengths than N$_3$$^-$.

As described above, the sign of the Cotton peak of a given electronic transition in the [Co(a)(b)(c)(tacn)]$^{n+}$ complex is associated with the ligand field strengths of two unidentate ligands contained in the plane where the electronic transition occurs. However, we can not find the obvious participation of two N donors of tacn contained in the same plane. The fact that the Cotton signs are related only with the characters of the unidentates may be concerned with the symmetrical nature of the terdentate ligand. It is notable to point out the followings. The complex, in which the ligand field strengths of three kinds of unidentates decrease clockwise on the octahedral face, exhibits negative, positive, and negative Cotton peaks from the lower frequency side in the first absorption band region, and the complex in which those decrease counterclockwise exhibits positive, negative, and positive Cotton peaks.

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