60745-68-8; $Cr(H_2O)_5(SCH_2COOH)^{2+}$, 60745-69-9; $Cr(H_2O)_5(SCH(CH_3)COOH)^{2+}$, 60745-70-2; $(H_2O)_4Cr(HOCH(CH_3)COO)^{2+}$, 60745-71-3; $(H_2O)_4Cr(HOCH_2COO)^{2+}$, 60745-72-4.

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Synthesis and Optical Resolution of *cis,cis*-Dicyanodicarboxylatodiammine and *cis,cis*-Dinitrodicarboxylatodiammine Complexes of Cobalt(III)

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The *cis,cis*-$[Co(CN)_2(O\text{-}O)(NH_3)_2]^-$- and *cis,cis*-$[Co(NO_2)_2(O\text{-}O)(NH_3)_2]^-$-type complexes (O-O represents CO_3^{2-}, ox^{2-}, or mal^{2-}) and the related *cis*-$[Co(CN)_2(O\text{-}O)en]^-$- and *cis*-$[Co(NO_2)_2(O\text{-}O)en]^-$-type complexes have been synthesized essentially based on the successive substitution of CO_3^{2-} ion in the $[Co(CO_3)_3]^{3-}$ complex with desired ligands. The resolution of all the complexes into optically active enantiomers has also been achieved. The complexes have been characterized by their absorption and CD spectra. The absolute configurations of the enantiometric complexes have been discussed on the basis of the CD spectra.

Introduction

Most studies on the optically active metal complexes have been undertaken with those complexes which are dissymmetric because of either the distribution of chelate rings about a central metal ion or the conformations of individual chelate rings.[1] On the other hand, little attention has been paid to complexes that derive their dissymmetry solely from the distribution of unidentate ligands. Russian workers reported some platinum(IV) complexes, *cis,cis,cis*-$[PtCl_2(NO_2)_2(NH_3)_2]$,[2] *cis,cis*-$[PtCl_2(NH_3)_2en]^{2+}$,[3] and *cis,cis*-$[PtCl_2NH_3en(py)]^{2+}$.[4] As far as cobalt(III) is concerned, only one complex, *cis,cis*-$[CoCl_2(NH_3)_2en]^+$, has been reported by Australian workers.[5,6] The paucity of research on such complexes seems mainly due to the lack of preparative methods. Therefore, much work has needed to be done to develop the preparative chemistry of these complexes.

Thus far, we have reported three kinds of complexes: *cis,cis*-$[Co(CN)_2CO_3(NH_3)_2]^-$,[7] *cis,cis*-$[Co(ox)(H_2O)_2(NH_3)_2]^+$,[7] and *cis,cis*-$[Co(NO_2)_2ox(NH_3)_2]^-$.[8] This paper deals with the synthesis and optical resolution of the title complexes, where dicarboxylato ligand stands for oxalate, malonate, or carbonate ion, and analogous complexes with ethylenediamine replacing the two ammonia molecules. With two complexes, $(-)_{589}$-$[Co(NO_2)_2ox(NH_3)_2]^-$ [9] and $(+)_{589}$-$[Co(CN)_2mal(NH_3)_2]^-$,[10] their absolute configurations have already been determined by x-ray analysis in another laboratory, and hence the absolute configurations of the other complexes obtained through this work are discussed on the basis of circular dichroism (CD) spectra.

Experimental Section

(a) Synthesis of ***cis,cis*-Na[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]·2H$_2$O.** The preparation of this complex was described in an earlier paper,[7] but the description will be given here again with a few modifications. To a cold, green solution of tricarbonatocobaltate(III) ($Co(NO_3)_2 \cdot 6H_2O$, 15 g, 0.05 mol in 20 ml of H_2O + 10 ml of 30% H_2O_2),[11] was added potassium cyanide (7.5 g, 0.12 mol) and the mixture was stirred at room temperature for 1 h, whereby a deep red solution of the *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$ [12] was obtained. After this solution had been neutralized with aqueous perchloric acid, ammonium perchlorate (15 g, 0.12 mol) and concentrated aqueous ammonia (50 ml) were added. The mixture was stirred at ~40 °C for 4 h and then filtered and concentrated to a small volume. This concentrate was again filtered, neutralized, and then filtered once more. The filtrate was diluted to 3 l. with water and then charged on an ion-exchange column containing Dowex 1-X8 resin in Cl form (5 × 20 cm). By elution with a 0.3 M NaCl solution, an orange band came out from the column. This effluent was concentrated to a small volume (ca. 10 ml). Upon keeping the solution in a refrigerator after the addition of ethanol, yellow-orange crystals deposited. These were recrystallized from warm water (ca. 40 °C). The yield was about 0.3 g.

Anal. Calcd for $Na[Co(CN)_2CO_3(NH_3)_2] \cdot 2H_2O$: C, 13.64; H, 3.82; N, 21.22. Found: C, 13.89; H, 4.08; N, 20.84.

(b) Synthesis of ***cis,cis*-Na[Co(CN)$_2$ox(NH$_3$)$_2$]·2H$_2$O.** To a solution of *cis,cis*-$Na[Co(CN)_2CO_3(NH_3)_2] \cdot 2H_2O$ (13.2 g, 0.05 mol, in 100 ml of H_2O) was added 30% $HClO_4$ (ca. 25 ml) until the evolution of CO_2 ceased. Excess potassium oxalate dihydrate (18 g, 0.10 mol) was added to the resulting solution and the mixture was stirred at ~40 °C for 4 h. The solution was filtered after neutralization with a 6 M KOH solution, and the filtrate was charged on an ion-exchange column containing Dowex 1-X8 resin in Cl form (100–200 mesh, 4 × 30 cm). After the column had been washed with water, the elution was started with a 0.1 M NaCl solution. Only one band colored yellow descended. This was collected and concentrated to a small volume (ca. 10 ml) and then filtered to remove sodium chloride. Upon keeping the filtrate in a refrigerator, yellow crystals deposited. The crude product thus obtained was recrystallized from a minimum amount of warm water (ca. 50 °C). The yield was about 3 g.

Anal. Calcd for $Na[Co(CN)_2C_2O_4(NH_3)_2] \cdot 2H_2O$: C, 16.45; H, 3.45; N, 19.18. Found: C, 16.61; H, 3.73; N, 19.13.

(c) Synthesis of ***cis,cis*-K[Co(CN)$_2$mal(NH$_3$)$_2$]·H$_2$O.** An aqueous solution of *cis,cis*-$Na[Co(CN)_2CO_3(NH_3)_2] \cdot 2H_2O$ (13.2 g, 0.05 mol) was treated in the same way as described in (b) except for the use of sodium malonate (15 g, 0.10 mol) instead of potassium oxalate. The reacted solution, which had been neutralized and filtered, was diluted to 1 l. and treated in the same way as in (b) except for the use of a 0.1 M KCl solution as the eluent. The crude product was recrystallized from a minimum amount of warm water (ca. 40 °C). The yield was 1 g.

Anal. Calcd for $K[Co(CN)_2(C_3H_2O_4)(NH_3)_2] \cdot H_2O$: C, 19.74; H, 3.31; N, 18.42. Found: C, 19.51; H, 3.39; N, 18.80.

(d) Synthesis of ***cis*-K[Co(CN)$_2$CO$_3$en]·H$_2$O.** To a solution of *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$ (prepared by the same procedure as that in (a)) was added 98% ethylenediamine (4 ml, 0.07 mol). The mixture was stirred overnight at room temperature. The resulting solution was treated as has been described in (a) except for the use of a 0.3 M KCl solution as the eluent. The desired complex was isolated as its potassium salt. The yield was about 0.2 g.

Anal. Calcd for $K[Co(CN)_2CO_3(C_2H_8N_2)] \cdot H_2O$: C, 20.84; H, 3.50; N, 19.44. Found: C, 21.14; H, 3.81; N, 19.77.

(e) Synthesis of ***cis*-K[Co(CN)$_2$ox(en)]·H$_2$O.** An aqueous solution of *cis*-$K[Co(CN)_2CO_3en] \cdot H_2O$ (8.6 g, 0.03 mol, in 60 ml of H_2O) was treated in the same way as stated in (b) except for the use of a 0.1 M KCl solution as the eluent. On keeping the final concentrate in a refrigerator, yellow crystals deposited. These were recrystallized from warm water (ca. 50 °C). The yield was about 2 g.

Anal. Calcd for $K[Co(CN)_2C_2O_4(C_2H_8N_2)] \cdot H_2O$: C, 22.79; H, 3.19; N, 17.72. Found: C, 22.79; H, 3.34; N, 17.65.

(f) Synthesis of ***cis,cis*-K[Co(NO$_2$)$_2$CO$_3$(NH$_3$)$_2$]·0.5H$_2$O.** To a mixture of *cis*-$K[Co(CO_3)_2(NH_3)_2] \cdot H_2O$[11] (10.8 g, 0.04 mol) and KNO_2 (8.5 g, 0.10 mol) in water (60 ml) was added 6 M acetic acid (15 ml) dropwise with stirring at room temperature. The solution was further stirred for 0.5 h. Insoluble dark green precipitates were removed by filtration and the filtrate was charged on an ion-exchange column containing 100–200 mesh Dowex 1-X8 resin in Cl form (5 × 20 cm). The column was washed with a large amount of ice-cold water, and then the elution of an adsorbed band was carried out with a 0.1 M KCl solution. Two bands colored orange-yellow and orange descended in this order and were collected in fractions. The second fraction was concentrated to a small volume (ca. 30 ml), and after this concentrate had been filtered, ethanol (ca. 10 ml) was added to it. On keeping the whole in a refrigerator, powdery orange crystals deposited. The material was quickly recrystallized from a minimum amount of warm water (ca. 40 °C). The yield was 2 g.

Anal. Calcd for $K[Co(NO_2)_2CO_3(NH_3)_2] \cdot 0.5H_2O$: C, 4.10; H, 2.41; N, 19.11. Found: C, 4.32; H, 2.34; N, 19.28.

From the first fraction needlelike orange-yellow crystals were obtained with a low yield (0.5 g). The complex was identified as *trans(NH$_3$),cis(NO$_2$)*-$K[Co(NO_2)_2CO_3(NH_3)_2] \cdot H_2O$.

(g) Synthesis of ***cis,cis*-K[Co(NO$_2$)$_2$mal(NH$_3$)$_2$]·H$_2$O.** The complex *cis,cis*-$K[Co(NO_2)_2CO_3(NH_3)_2] \cdot 0.5H_2O$ (12 g, 0.04 mol) was dissolved in water (160 ml), and 30% perchloric acid (18 ml) was added dropwise to the solution under an iced condition. To the resulting solution was added sodium malonate (8 g, 0.056 mol), and the mixture was then stirred at 40 °C for 4 h. After filtering of the solution, the filtrate was chromatographed on an ion-exchange column of 100–200 mesh Dowex 1-X8 resin in Cl form (4 × 20 cm) using a 0.1 M KCl solution. One fraction thus obtained was concentrated to a small volume (40 ml), and this enriched solution was filtered and kept in a refrigerator. The orange crystals deposited were recrystallized from warm water (ca. 40 °C). The yield was 5 g.

Anal. Calcd for $K[Co(NO_2)_2(C_3H_2O_4)(NH_3)_2] \cdot H_2O$: C, 10.47; H, 2.93; N, 16.28. Found: C, 10.85; H, 3.30; N, 16.05.

(h) Synthesis of ***cis*-K[Co(NO$_2$)$_2$CO$_3$en].** To a solution of $K[Co(CO_3)_2en] \cdot H_2O$[11] (12 g, 0.04 mol, in 20 ml of H_2O, 45 °C) were added KNO_2 (6.8 g, 0.08 mol) and then 6 M acetic acid (14 ml) drop by drop with stirring. The mixture was further stirred for 0.5 h more at 45 °C and the resulting orange solution was cooled in an ice bath. After the solution had been filtered, ethanol (ca. 60 ml) was added. On scratching the sides of the vessel in an ice bath, an orange compound crystallized out. The product was recrystallized from water (ca. 40 °C). The yield was about 5 g.

Anal. Calcd for $K[Co(NO_2)_2CO_3(C_2H_8N_2)]$: C, 11.62; H, 2.60; N, 18.06. Found: C, 11.81; H, 2.82; N, 18.04.

(i) Synthesis of ***cis*-K[Co(NO$_2$)$_2$ox(en)].** To a solution of $K[CoCO_3ox(en)] \cdot H_2O$[11] (9.6 g, 0.03 mol, in 90 ml H_2O) was added KNO_2 (6.4 g, 0.075 mol), and then the mixture was acidified with 6 M acetic acid (ca. 8 ml) with stirring. The resulting solution was stirred for 3 h and then filtered; the filtrate was kept in a refrigerator overnight. The crude product obtained was recrystallized from warm water (ca. 40 °C). The yield was about 3.5 g.

Anal. Calcd for $K[Co(NO_2)_2C_2O_4(C_2H_8N_2)]$: C, 14.21; H, 2.38; N, 16.57. Found: C, 13.97; H, 2.58; N, 16.75.

The desired complex could also be obtained by the action of oxalic acid on the *cis*-$[Co(NO_2)_2CO_3en]^-$ complex mentioned in (h).

(j) Resolving Agents. For the optical resolution of the present dicyano and dinitro complexes, two kinds of resolving agents,

$(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ [13] and $(-)_{589}$-[Co(ox)(en)$_2$]$^+$,[14] were used. A half-equimolar amount of the resolving agent, compared to the amount of racemate of the object complex, was prepared in the form of acetate according to the literature method. Crystallization of a less soluble diastereoisomer precipitate was repeated until the $\Delta\epsilon$ value of a dominant CD peak reached a constant value.

(k) Resolution of *cis,cis*-[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]$^-$. The procedure for this complex using $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ was described in an earlier paper.[7] In that case $(+)_{589}$-[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]$^-$ isomer formed the less soluble diastereoisomer.

(l) Resolution of *cis,cis*-[Co(CN)$_2$ox(NH$_3$)$_2$]$^-$. The sodium salt of the complex (4.4 g, 0.015 mol) was dissolved in a hot solution of $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ (30 ml, 50 °C). On scratching the sides of the vessel, the orange diastereoisomer mainly containing the $(-)_{589}$ form of the [Co(CN)$_2$ox(NH$_3$)$_2$]$^-$ complex commenced to separate. The mixture was allowed to stand for 0.5 h in an ice bath. The less soluble diastereoisomer thus separated was recrystallized from warm water (ca. 40 °C). The final yield was about 1 g.

Anal. Calcd for [CoC$_2$O$_4$(C$_2$H$_8$N$_2$)$_2$][Co(CN)$_2$C$_2$O$_4$(NH$_3$)$_2$]·2H$_2$O: C, 22.40; H, 4.89; N, 20.91. Found: C, 22.73; H, 5.25; N, 20.61.

When $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ was used as a resolving agent, the $(+)_{589}$ isomer immediately formed the less soluble yellow diastereoisomer.

(m) Resolution of *cis,cis*-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$. To a solution of this complex (4.5 g, 0.015 mol, in ca. 30 ml of water, ca. 40 °C) was added an aqueous solution of $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ (in 25 ml of H$_2$O). The mixture was cooled in an ice bath and the sides of the vessel were scratched with a glass rod, whereupon a diastereoisomer of the $(+)_{589}$ form of the dicyano complex precipitated as orange crystals. After the solution had been kept for 0.5 h in an ice bath, the crystals were collected and recrystallized from a minimum amount of warm water (ca. 40 °C) to give needlelike crystals. The final yield was about 1 g.

Anal. Calcd for [CoC$_2$O$_4$(C$_2$H$_8$N$_2$)$_2$][Co(CN)$_2$(C$_3$H$_2$O$_4$)(NH$_3$)$_2$]·2.5H$_2$O: C, 23.62; H, 5.23; N, 20.04. Found: C, 23.37; H, 4.83; N, 20.06.

(n) Resolution of *cis*-[Co(CN)$_2$CO$_3$en]$^-$. The K[Co(CN)$_2$CO$_3$en]·H$_2$O complex (5.8 g, 0.02 mol) was dissolved in a solution of $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ (20 ml) by shaking, followed by addition of ethanol (ca. 5 ml). Then the whole was kept in a refrigerator until a luminous yellow fine diastereoisomer of the $(-)_{589}$ form deposited. Recrystallization was repeated from a minimum amount of warm water (ca. 40 °C). The yield was about 0.1 g.

Anal. Calcd for [Co(NO$_2$)$_2$(en)$_2$][Co(CN)$_2$CO$_3$(C$_2$H$_8$N$_2$)]: C, 21.52; H, 4.82; N, 27.89. Found: C, 21.64; H, 5.02; N, 28.01.

(o) Resolution of *cis*-[Co(CN)$_2$ox(en)]$^-$. Into a solution of the racemate (3.2 g, 0.01 mol, in 5 ml of H$_2$O, ca. 40 °C) was poured a solution of the resolving agent $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ (in 15 ml of H$_2$O). Immediately a less soluble diastereoisomer of the $(+)_{589}$ form deposited as orange crystals and the mixture was allowed to stand for a while. The crystalline solid was collected and recrystallized from warm water (ca. 50 °C). Fine needles were obtained. The yield was about 1.5 g.

Anal. Calcd for [CoC$_2$O$_4$(C$_2$H$_8$N$_2$)$_2$][Co(CN)$_2$C$_2$O$_4$(C$_2$H$_8$N$_2$)]·3H$_2$O: C, 24.84; H, 5.21; N, 19.31. Found: C, 24.82; H, 5.11; N, 19.51.

It was possible to use the $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ complex as the resolving agent. In this case, yellow crystals of the $(-)_{589}$ isomer immediately precipitated.

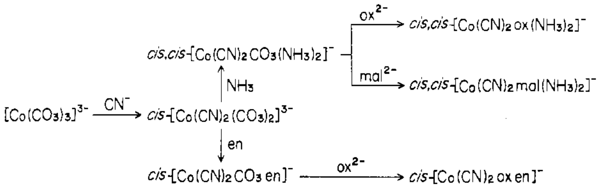
(p) Resolution of *cis,cis*-[Co(NO$_2$)$_2$CO$_3$(NH$_3$)$_2$]$^-$. To a solution of the resolving agent $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ in 20 ml of warm water the ground crystals of the racemate (4.4 g, 0.015 mol) were added little by little with continuous stirring. A red-orange diastereoisomer of the $(-)_{589}$ form crystallized out when the solution was allowed to stand in an ice bath. This was recrystallized from water below 35 °C in order to avoid the decomposition of the carbonato complex. The yield was about 0.5 g.

Anal. Calcd for [CoC$_2$O$_4$(C$_2$H$_8$N$_2$)$_2$][Co(NO$_2$)$_2$CO$_3$(NH$_3$)$_2$]·2H$_2$O: C, 15.34; H, 4.78; N, 20.44. Found: C, 15.45; H, 5.06; N, 20.84.

The use of the $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ complex gave the $(+)_{589}$ isomer as the less soluble diastereoisomer.

(q) Resolution of *cis,cis*-[Co(NO$_2$)$_2$ox(NH$_3$)$_2$]$^-$. This was already published,[8] the $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ complex being used as the resolving agent.

Scheme I. Synthesis of *cis,cis*- and *cis*-Dicyano Complexes



The $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ complex could also be used for the resolution. The less soluble diastereoisomer was of the $(+)_{589}$ form.

(r) Resolution of *cis,cis*-[Co(NO$_2$)$_2$mal(NH$_3$)$_2$]$^-$. The potassium salt of the complex (5.1 g, 0.015 mol) was dissolved in water (120 ml) and converted into the lithium salt by passing the solution through a column (2 × 7 cm) of Dowex 50W-X8 resin in Li form. After the column had been rinsed thoroughly with water, the whole effluent was concentrated to a small volume (ca. 20 ml) under reduced pressure below 35 °C. After filtration of the concentrate, a solution of the $(-)_{589}$-[Co(ox)(en)$_2$]$^+$ complex (in 20 ml of H$_2$O) was added. On scratching the walls of the container in the cold, the diastereoisomer of the $(+)_{589}$ form precipitated. This was recrystallized from warm water, giving red-orange needles. The yield was about 0.5 g.

Anal. Calcd for [CoC$_2$O$_4$(C$_2$H$_8$N$_2$)$_2$][Co(NO$_2$)$_2$(C$_3$H$_2$O$_4$)(NH$_3$)$_2$]·0.5H$_2$O: C, 19.19; H, 4.47; N, 19.90. Found: C, 18.94; H, 4.47; N, 19.94.

(s) Resolution of *cis*-[Co(NO$_2$)$_2$CO$_3$en]$^-$. A solution of the $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ complex in 25 ml of water was poured into a solution of *cis*-K[Co(NO$_2$)$_2$CO$_3$en] (6.2 g, 0.02 mol) dissolved in warm water (40 ml, 40 °C). An orange-yellow fibrous diastereoisomer of the $(+)_{589}$ form began to precipitate when the walls of the container were scratched under cooling. The whole was allowed to stand for 0.5 h more in an ice bath. Recrystallization was repeated from warm water. The yield was about 0.5 g.

Anal. Calcd for [Co(NO$_2$)$_2$(C$_2$H$_8$N$_2$)$_2$][Co(NO$_2$)$_2$CO$_3$(C$_2$H$_8$N$_2$)]·H$_2$O: C, 15.01; H, 4.68; N, 25.00. Found: C, 14.75; H, 4.67; N, 25.05.

(t) Resolution of *cis*-[Co(NO$_2$)$_2$ox(en)]$^-$. To a solution of the racemate (5.1 g, 0.015 mol, in 50 ml of warm water) was added a solution of the $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$ complex (20 ml of water). A yellow diastereoisomer mainly containing the $(+)_{589}$ form of the complex began to separate. The mixture was allowed to stand for a while at room temperature before filtration. The diastereoisomer was recrystallized from warm water (ca. 40 °C) to obtain needles. The yield was about 1 g.

Anal. Calcd for [Co(NO$_2$)$_2$(C$_2$H$_8$N$_2$)$_2$][Co(NO$_2$)$_2$C$_2$O$_4$(C$_2$H$_8$N$_2$)]: C, 16.85; H, 4.24; N, 24.56. Found: C, 17.01; H, 4.24; N, 24.34.

The $(-)_{589}$-[Co(ox)(en)$_2$]$^-$ complex could be used for the resolution of this complex. In this case, too, the $(+)_{589}$-[Co(NO$_2$)$_2$ox(en)]$^-$ isomer formed a less soluble diastereoisomer.

Measurements. The absorption spectra in aqueous solution were recorded with a Hitachi EPU-2A spectrophotometer. The absorption spectrum of a single crystal was measured using a microspectrophotometer constructed by connecting a specially designed microscope with a Hitachi EPU-2A spectrophotometer. The measurements of CD spectra were carried out with a JASCO Model ORD/UV-5 spectrophotometer with CD attachment and the optical rotations were measured with a JASCO Model DIP-SL automatic polarimeter.

The absorption and CD spectra of the diaqua complex species were measured with acidified solutions of the carbonato complexes with 10% HClO$_4$; the acid-hydrolyzed species were chromatographically pure and their absorption and CD spectra were re-formed into the original spectra of the parent carbonato complexes when sodium carbonate was added to the acidified solutions. This fact suggests that the acid hydrolyses proceed with retention of configurations. In this connection, it has been confirmed that the acid hydrolysis of $(+)_{589}$-[CoCO$_3$(en)$_2$]$^+$ into $(+)_{589}$-[Co(H$_2$O)$_2$(en)$_2$]$^{3+}$ at 20 °C proceeds with complete retention of configuration.[15]

Results and Discussion

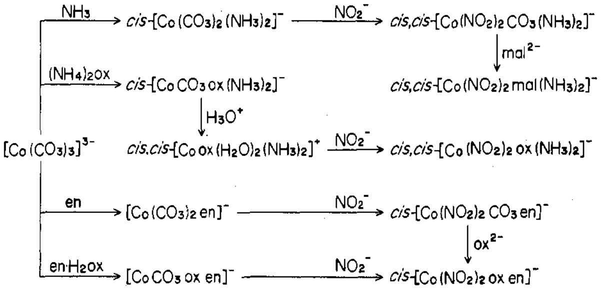
Preparation. Schemes I and II represent the pathways of the present syntheses. The syntheses which we devised depend essentially on the fact that the [Co(CO$_3$)$_3$]$^{3-}$ complex prefers successive cis substitutions by the desired unidentate ligands. From the schemes it can be seen that the successive substi-

Table I. Absorption Spectra of the Dicyano Complexes

Complex	Ia		Ib		II	
	$\tilde{\nu}_{max}$[a]	ϵ	$\tilde{\nu}_{max}$[a]	ϵ	$\tilde{\nu}_{max}$[a]	ϵ
cis,cis-$[Co(CN)_2CO_3(NH_3)_2]^-$	20.7	92.0	23.5	104	{27.8 sh {30.2 sh	
Calcd[b]	19.7, 21.0		23.9			
cis,cis,cis-$[Co(CN)_2(H_2O)_2(NH_3)_2]^+$	21.3	58.1	24.5	79.4	30.5	60.2
cis,cis-$[Co(CN)_2ox(NH_3)_2]^-$	21.3	72.5	24.3	103	31.6	138
Calcd	20.2, 21.5		24.8			
cis,cis-$[Co(CN)_2mal(NH_3)_2]^-$	21.5 sh		24.4	132	30.6	103
Calcd	20.1, 21.4		24.7			
cis-$[Co(CN)_2CO_3en]^-$	20.9	114	23.1	102	{28.0 sh {30.4 sh	
cis,cis-$[Co(CN)_2(H_2O)_2en]^+$	21.6	75.9	24.3	83.1	30.3	70.8
cis-$[Co(CN)_2ox(en)]^-$	21.5	95.5	24.3	104	30.9	156

[a] $\tilde{\nu}_{max}$ values in $cm^{-1} \times 10^3$; sh = shoulder. [b] Calcd = predicted positions.

Scheme II. Synthesis of *cis,cis*- and *cis*-Dinitro Complexes



tutions of ligating carbonate ions in the starting complex by the desired ligands lead to the preparation of the cis,cis- or cis-type complex.

Absorption Spectra. The absorption spectra of the *cis,cis*-$[Co(CN)_2(O\text{-}O)(NH_3)_2]^-$-type complexes and the *cis,cis,cis*-$[Co(CN)_2(H_2O)_2(NH_3)_2]^+$ complex are shown in Figure 1, in which the CD spectra are also contained as a matter of convenience. The absorption spectral data of all the dicyano complexes are summarized in Table I. The absorption spectra resemble one another; they show two peaks, or a peak and a shoulder, in the so-called first absorption band region ($^1T_{1g} \leftarrow {}^1A_{1g}$ region in O_h parentage) and a peak, or two shoulders, in the so-called second absorption band region ($^1T_{2g} \leftarrow {}^1A_{1g}$ region in O_h parentage). Hereafter, the abbreviations Ia and Ib and II (or IIa and IIb) are used for the absorption maxima in both regions.

In order to elucidate the T_{1g} band of the absorption spectra for the present $[Co(CN)_2(O\text{-}O)(NH_3)_2]^-$-type complexes, Yamatera's treatment[16] was carried out. The calculations were performed on the basis of the spectral data for some complexes: *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$, 18 300 and 22 500 cm^{-1}; *cis*-$[Co(CN)_2(ox)_2]^{3-}$, 18 800 and 23 400 cm^{-1}; *cis*-$[Co(CN)_2(mal)_2]^{3-}$, 18 700 and 23 300 cm^{-1};[12] $[Co(NH_3)_6]^{3+}$, 20 970 cm^{-1}; $[Co(CO_3)_3]^{3-}$, 15 500 cm^{-1}. The calculated values are inserted in Table I. The comparison between the calculated values and the observed maxima suggests that the Ia maximum results from the first two components and the Ib maximum mainly from the third component. The absorption spectra of the other dicyano complexes could be understood similarly. By the way, the predicted positions calculated from the spectral data for the $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, and $[Co(O\text{-}O)_3]^{3-}$ complexes were far apart from the observed maxima.

Figure 2 shows crystal spectra, in the T_{1g} region, of *cis,cis*-$Na[Co(CN)_2CO_3(NH_3)_2]\cdot 2H_2O$. The polarized spectra were measured with the light polarized parallel to the crystallographic *c* axis (i.e., ∥ *c*) and also with the light polarized perpendicular to the *c* axis (i.e., ⊥ *c*). The solution spectrum of this complex shows two peaks at 20 700 and 23 500 cm^{-1} in the T_{1g} region. The unpolarized crystal spectrum also reveals apparent splitting in this region. The polarized spectra

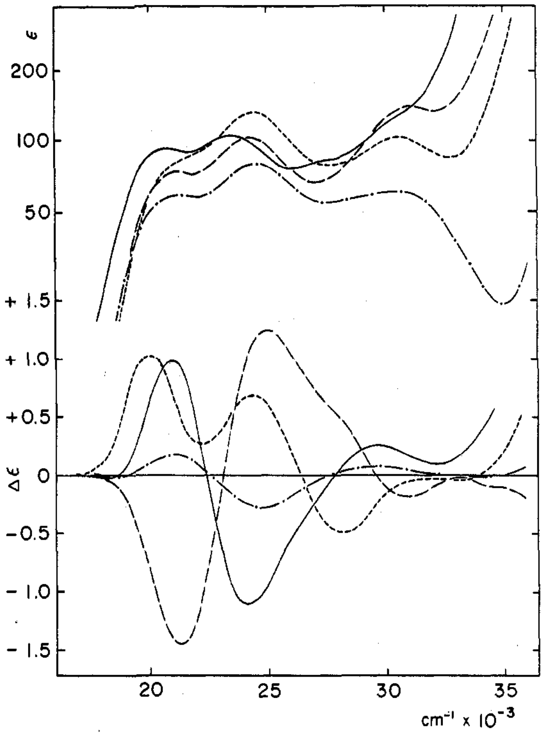


Figure 1. Absorption and CD spectra of *cis,cis*-$[Co(CN)_2CO_3(NH_3)_2]^-$ (—), *cis,cis,cis*-$[Co(CN)_2(H_2O)_2(NH_3)_2]^+$ (- · - · -), *cis,cis*-$[Co(CN)_2ox(NH_3)_2]^-$ (- - -), and *cis,cis*-$[Co(CN)_2mal(NH_3)_2]^-$ (- - - -).

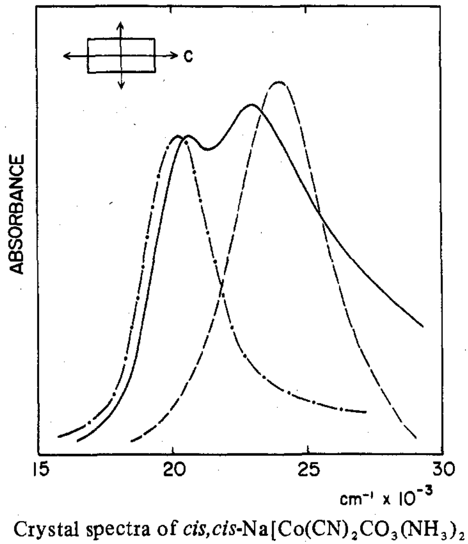


Figure 2. Crystal spectra of *cis,cis*-$Na[Co(CN)_2CO_3(NH_3)_2]\cdot 2H_2O$: ——, unpolarized; - · - · -, ⊥ *c*; - - -, ∥ *c*.

Table II. Absorption Spectra of the Dinitro Complexes

	I		$\pi^* \leftarrow \pi$		CT	
Complex	$\tilde{\nu}_{max}$[a]	ϵ	$\tilde{\nu}_{max}$[a]	ϵ	$\tilde{\nu}_{max}$[a]	ϵ
cis,cis-$[Co(NO_2)_2CO_3(NH_3)_2]^-$	20.6	208	29.9	3800	39.3	19 500
trans(NH$_3$)-$[Co(NO_2)_2CO_3(NH_3)_2]^-$	20.8	212	29.5	3550	39.7	15 500
cis,cis,cis-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$	21.2	161	29.7	6630	38.2 sh	
					42.3	18 900
trans(NH$_3$)-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$	20.8	147	28.9	4270	37.8	10 500
					43.1	13 700
cis,cis-$[Co(NO_2)_2ox(NH_3)_2]^-$	20.9	161	29.8	4290	39.9	22 500
trans(NO$_2$)-$[Co(NO_2ox(NH_3)_2]^-$	21.0	193	28.4	5010	38.7	20 200
trans(NH$_3$)-$[Co(NO_2)_2ox(NH_3)_2]^-$	20.9	184	29.6	4510	40.3	27 600
cis,cis-$[Co(NO_2)_2mal(NH_3)_2]^-$	20.9	168	29.8	4280	39.9	21 900
trans(NH$_3$)-$[Co(NO_2)_2mal(NH_3)_2]^-$	20.8	154	29.5	4430	40.0	25 200
cis-$[Co(NO_2)_2CO_3en]^-$	20.7	204	30.1	3570	39.7	21 000
cis,cis-$[Co(NO_2)_2(H_2O)_2en]^+$	21.4	170	29.8	5120	38.2 sh	
					41.2	17 000
cis-$[Co(NO_2)_2ox(en)]^-$	21.1	177	30.1	3580	40.2	22 200

[a] In $cm^{-1} \times 10^3$.

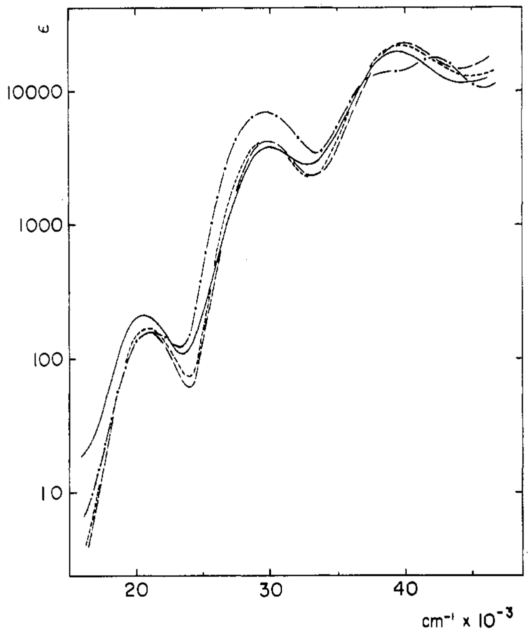


Figure 3. Absorption spectra of *cis,cis*-$[Co(NO_2)_2CO_3(NH_3)_2]^-$ (——), *cis,cis,cis*-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$ (– · – · –), *cis,cis*-$[Co(NO_2)_2ox(NH_3)_2]^-$ (– – –), and *cis,cis*-$[Co(NO_2)_2mal(NH_3)_2]^-$ (- - - -).

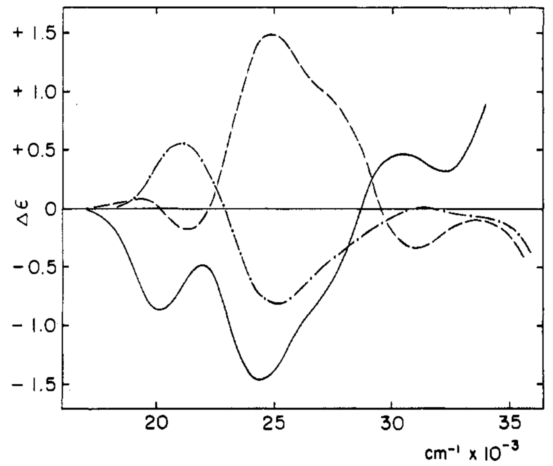


Figure 4. CD spectra of $(-)_{589}$-$[Co(CN)_2CO_3en]^-$ (——), $(-)_{589}$-$[Co(CN)_2(H_2O)_2en]^+$ (– · – · –), and $(+)_{589}$-$[Co(CN)_2ox(en)]^-$ (– – –).

show clear dichroism; the lower frequency band appears at 20 200 cm^{-1} with the ⊥ *c* light and the higher frequency band at 24 000 cm^{-1} with the ∥ *c* axis. Again the observed peaks correspond well with the predicted positions.

In the T_{2g} band region, the spectra of the *cis,cis*-$[Co(CN)_2CO_3(NH_3)_2]^-$ and *cis*-$[Co(CN)_2CO_3en]^-$ complexes exhibit swellings at ca. 28 000 cm^{-1} (IIa) and ca. 30 000 cm^{-1} (IIb). They perhaps originate from the split components of the T_{2g} parentage. By comparing these IIa and IIb maxima with the observed II maxima of the other dicyano complexes, the II maxima should be recognized to be IIb maxima. The corresponding IIa maxima are not observed for complexes other than the carbonato ones. Similar phenomena have been reported for the *fac(N)*-$[CoCN(O\text{-}O)(N)_3]$-[17] and the *trans*-$[Co(O\text{-}O)_2(py)_2]^-$-type[18] complexes.

Absorption spectra of the *cis,cis*-$[Co(NO_2)_2(O\text{-}O)(NH_3)_2]^-$-type complexes and *cis,cis,cis*-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$ complex are given in Figure 3 and the numerical data for all the dinitro complexes are summarized in Table II. In the previous paper,[8] we communicated the characterization of the three isomers of the $[Co(NO_2)_2ox(NH_3)_2]^-$ complex based on the preparative routes and the half-widths of the first absorption bands. In the same way, the *trans(NH$_3$)*-$[Co(NO_2)_2CO_3(NH_3)_2]^-$ and *trans(NH$_3$)*-$[Co(NO_2)_2mal(NH_3)_2]^-$ complexes could be identified. As to the absorption spectra of the isomers of the dinitrodiammine complexes, the maximum of the $\pi^* \leftarrow \pi$ band for the cis,cis (or cis,cis,cis) isomer is at a higher frequency than that for the *trans*-diammine isomer. The relation of the maximum positions of the charge transfer (CT) bands between the cis,cis isomer and the *trans*-diammine isomer is the reverse of that of the $\pi^* \leftarrow \pi$ bands. The spectra of the diaqua complexes, especially of the *trans(NH$_3$)*-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$ species, distinctly reveal two bands of the CT absorption.

CD Spectra. The CD spectra of the $[Co(CN)_2(O\text{-}O)en]^-$-type complexes and the $[Co(CN)_2(H_2O)_2en]^+$ complex are shown in Figure 4.

As one of the representatives of the complexes whose CD spectra reveal two apparent peaks with opposite signs, the $(-)_{589}$-$[Co(CN)_2ox(NH_3)_2]^-$ complex is quoted in order to discuss the CD spectrum in the T_{1g} region. The absorption spectrum of this complex shows two maxima at 21 300 and 24 300 cm^{-1} in the T_{1g} region, while the CD spectrum shows two peaks at 21 200 ($\Delta\epsilon = -1.44$) and 24 900 cm^{-1} ($\Delta\epsilon = +1.24$). The positions predicted by Yamatera's treatment are 20 200, 21 500, and 24 800 cm^{-1}. These facts suggest that the negative peak at 21 200 cm^{-1} is the resultant of two peaks with the same signs, − and −, or the resultant of a + peak with extremely weak intensity and a minus peak with considerably strong intensity, while the positive peak at 24 900 cm^{-1} is predominantly due to the highest component at 24 800 cm^{-1}.

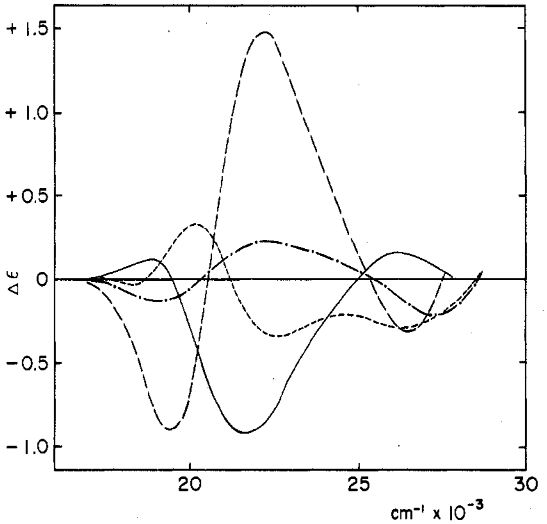


Figure 5. CD spectra of $(-)_{589}$-$[Co(NO_2)_2CO_3(NH_3)_2]^-$ (——), $(+)_{589}$-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$ (– · – · –), $(-)_{589}$-$[Co(NO_2)_2ox(NH_3)_2]^-$ (– – –), and $(+)_{589}$-$[Co(NO_2)_2mal(NH_3)_2]^-$ (- - - -).

As a result of mutual cancelation, the positive peak would shift to the higher frequency side compared with the absorption maximum. The CD spectra of the $(+)_{589}$-$[Co(CN)_2CO_3(NH_3)_2]^-$, $(+)_{589}$-$[Co(CN)_2(H_2O)_2(NH_3)_2]^+$, and $(-)_{589}$-$[Co(CN)_2(H_2O)_2en]^+$ complexes could be understood similarly.

The CD spectrum of the $(+)_{589}$-$[Co(CN)_2mal(NH_3)_2]^-$ complex shows two positive peaks at 20 000 ($\Delta\epsilon = +1.02$) and 24 400 cm^{-1} ($\Delta\epsilon = +0.68$). The absorption spectrum of this complex exhibits a shoulder at ca. 21 500 cm^{-1} and a peak at 24 400 cm^{-1}. The predicted positions of the components are 20 100, 21 400, and 24 700 cm^{-1}. By comparison of these values it is anticipated that the CD pattern in the T_{1g} region results from the three components with the +, −, and + signs from the lower frequency side. In this case, the lower frequency CD peak (20 000 cm^{-1}) differs more from the Ia maximum (ca. 21 500 cm^{-1}). This fact is probably due to a larger cancelation between the two closed components with opposite signs. Similar discussion seems to be applicable to the $(-)_{589}$-$[Co(CN)_2CO_3en]^-$ complex exhibiting − and − peaks as well as the $(+)_{589}$-$[Co(CN)_2ox(en)]^-$ complex exhibiting +, −, and + peaks; for the former complex three components each with −, +, and − signs are assumed, and for the latter complex three components each with +, −, and + signs are assumed.

As for the CD spectrum in the T_{2g} region, each of the $(-)_{589}$-$[Co(CN)_2ox(NH_3)_2]^-$, $(-)_{589}$-$[Co(CN)_2CO_3en]^-$, and $(+)_{589}$-$[Co(CN)_2ox(en)]^-$ complexes reveals a swelling due to the lowest frequency component in the T_{2g} region; when the peak arising from the component has the same sign as the highest frequency component in the T_{1g} region, the resultant should have such a swelling. The more gentle slope in the 28 000–30 000-cm^{-1} region in the CD spectrum of $(-)_{589}$-$[Co(CN)_2(H_2O)_2en]^+$ may arise from the same source. The CD spectrum of the $(+)_{589}$-$[Co(CN)_2mal(NH_3)_2]^-$ shows a relatively intense peak at 28 200 cm^{-1} ($\Delta\epsilon = -0.48$).

When the $(+)_{589}$-$[Co(CN)_2CO_3(NH_3)_2]^-$ complex is acid hydrolyzed, the CD spectrum of the produced diaqua complex species, $(+)_{589}$-$[Co(CN)_2(H_2O)_2(NH_3)_2]^+$, shows the same pattern as that for the parent carbonato complex, though the $\Delta\epsilon$ values are decreased considerably and each peak is shifted slightly to the higher frequency side. However, the acid hydrolysis of the $(-)_{589}$-$[Co(CN)_2CO_3en]^-$ complex to give the $(-)_{589}$-$[Co(CN)_2(H_2O)_2en]^+$ species makes the sign of the CD peak of the lowest frequency component in the T_{1g} region reverse. In addition, the $\Delta\epsilon$ value decreases and the peak shifts hypsochromically. Similar changes in the CD spectrum have been reported with the $(+)_{589}$-$[CoCO_3ox(NH_3)_2]^-$ and $(+)_{589}$-$[Co(ox)(H_2O)_2(NH_3)_2]^+$ complexes.[7]

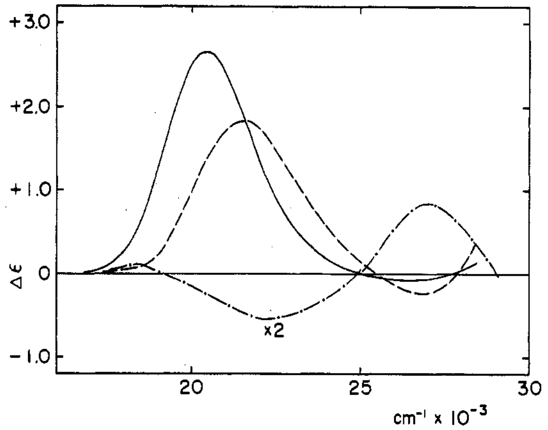


Figure 6. CD spectra of $(+)_{589}$-$[Co(NO_2)_2CO_3en]^-$ (——), $(+)_{589}$-$[Co(NO_2)_2(H_2O)_2en]^+$ (– · – · –), and $(+)_{589}$-$[Co(NO_2)_2ox(en)]^-$ (– – –).

The CD spectra of the dinitro complexes are presented in Figures 5 and 6. In these cases, too, the CD spectra are discussed in connection with split components predicted by Yamatera's treatment; the $\bar{\nu}_{NO_2}$ value in the T_{1g} region was estimated to be 24 900 cm^{-1} by applying the "rule of average environment"[19] to the spectral data for the *mer*-$[Co(NO_2)_3(NH_3)_3]$ complex.[20] In the case of the dinitro complexes, the signs of the split components cannot be precisely defined because of narrower separations of components compared with the separations of the dicyano complexes. For the $(-)_{589}$-$[Co(NO_2)_2ox(NH_3)_2]^-$ complex whose CD spectrum exhibits a − peak at 19 500 cm^{-1} ($\Delta\epsilon = -0.89$) and a + peak at 22 300 cm^{-1} ($\Delta\epsilon = +1.47$), the lowest component calculated to be at 19 800 cm^{-1} corresponds to the − peak at 19 500 cm^{-1} and the highest one at 21 900 cm^{-1} corresponds to the + peak at 22 300 cm^{-1}. The middle component at 21 000 cm^{-1} probably has a positive sign. The CD spectrum of the $(-)_{589}$-$[Co(NO_2)_2CO_3(NH_3)_2]^-$ complex can be interpreted similarly. The CD spectrum of the $(+)_{589}$-$[Co(NO_2)_2mal(NH_3)_2]^-$ complex results from three components with −, +, and − signs. The spectra of $(+)_{589}$-$[Co(NO_2)_2CO_3en]^-$ and $(+)_{589}$-$[Co(NO_2)_2ox(en)]^-$, each of which shows only one positive peak in the T_{1g} region, cannot be interpreted precisely.

When the $(-)_{589}$-$[Co(NO_2)_2CO_3(NH_3)_2]^-$ species was aquated, the CD spectrum of the resulting $(+)_{589}$-$[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+$ species showed the inverse pattern to the parent carbonato complex and the peaks had extremely decreased $\Delta\epsilon$ values and were shifted slightly to the higher frequency sides. The CD spectrum of the $(+)_{589}$-$[Co(NO_2)_2(H_2O)_2en]^+$ species derived from the $(+)_{589}$-$[Co(NO_2)_2CO_3en]^-$ complex, whose CD spectrum shows only one peak with a large intensity ($\Delta\epsilon = +2.66$), gives two peaks with opposite signs and small $\Delta\epsilon$ values (+0.05 and −0.27 from lower frequencies). Each of these diaqua complex species should have the same distribution of ligands as that of the parent carbonato complex.

As is seen in the above description, alternation of a bidentate ligand (e.g., en or CO_3^{2-}) by two unidentates (e.g., NH_3 or H_2O) considerably changes their CD spectra. Thus the optically active complexes deriving their dissymmetry from only the distribution of unidentates show characteristic differences from those containing two bidentates, both in the shapes of the CD spectra and in the $\Delta\epsilon$ values.

Through the present work, two series of the complexes involving carbonate, oxalate, or malonate ion have been prepared and resolved into optically active complexes. Up to

Table III. CD Spectra and Tentative Absolute Configurations

Complex	$\tilde{\nu}_{max}{}^{a}$ ($\Delta\epsilon$)	Confign
$(+)_{589}$-[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]$^-$	18.2 (−0.02) 20.9 (+0.98) 24.1 (−1.11) 29.7 (+0.25)	*R*
$(+)_{589}$-[Co(CN)$_2$(H$_2$O)$_2$(NH$_3$)$_2$]$^+$	18.6 (−0.01) 21.1 (+0.17) 24.6 (−0.27) 29.6 (+0.08) 33.9 (−0.01)	*R*
$(-)_{589}$-[Co(CN)$_2$ox(NH$_3$)$_2$]$^-$	21.2 (−1.44) 24.9 (+1.24) 27.8 sh 30.9 (−0.18) 34.5 sh	*S*
$(+)_{589}$-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$	20.0 (+1.02) 24.4 (+0.68) 28.2 (−0.48) 32.9 (−0.05)	*S*^{b}
$(-)_{589}$-[Co(CN)$_2$CO$_3$en]$^-$	20.7 (−0.86) 24.4 (−1.46) 27.0 sh 30.4 (+0.48)	*R*
$(-)_{589}$-[Co(CN)$_2$(H$_2$O)$_2$en]$^+$	21.1 (+0.56) 25.3 (−0.80) 31.8 (+0.01)	*R*
$(+)_{589}$-[Co(CN)$_2$ox(en)]$^-$	19.3 (+0.08) 21.3 (−0.18) 24.8 (+1.49) 27.0 sh 31.0 (−0.33)	*S*
$(-)_{589}$-[Co(NO$_2$)$_2$CO$_3$(NH$_3$)$_2$]$^-$	18.8 (+0.12) 21.7 (−0.91) 26.0 (+0.16)	*S*
$(+)_{589}$-[Co(NO$_2$)$_2$(H$_2$O)$_2$(NH$_3$)$_2$]$^+$	19.2 (−0.12) 22.2 (+0.23) 27.3 (−0.21)	*S*
$(-)_{589}$-[Co(NO$_2$)$_2$ox(NH$_3$)$_2$]$^-$	19.5 (−0.89) 22.3 (+1.47) 26.5 (−0.31)	*R*^{b}
$(+)_{589}$-[Co(NO$_2$)$_2$mal(NH$_3$)$_2$]$^-$	18.3 (−0.03) 20.2 (+0.33) 22.6 (−0.34) 26.2 (−0.28)	*S*
$(+)_{589}$-[Co(NO$_2$)$_2$CO$_3$en]$^-$	20.4 (+2.66) 26.3 (−0.08)	*R*
$(+)_{589}$-[Co(NO$_2$)$_2$(H$_2$O)$_2$en]$^+$	18.4 (+0.05) 22.2 (−0.27) 26.9 (+0.84)	*R*
$(+)_{589}$-[Co(NO$_2$)$_2$ox(en)]$^-$	21.6 (+1.83) 26.9 (−0.24)	*R*

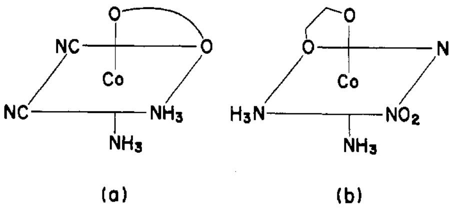
^{a} In cm^{-1} × 10^3. ^{b} X-ray analysis.

now, several series of cobalt(III) complexes containing these three dicarboxylato ligands have been resolved into optically active complexes.[21-23] Every complex of the present two series is characteristic of a rhombic chromophore. Changes in the CD spectra caused by the alternation of such dicarboxylato ligands are known to be more marked in the *u-cis*-[Co(O-O)(edda)]$^-$-type complexes than in the *s-cis*-[Co(O-O)(edda)]$^-$-type complexes.[22] It is anticipated from these facts that the lowering in symmetry of the complex causes apparent changes in the CD spectra.

Absolute Configurations. The absolute configuration of a complex can usually be assigned by comparing the sign of a CD peak with that of the standard complex whose absolute configuration is known.[24,25] Such determinations of absolute configurations have been widely applied to the complexes not only with the same chromophore as that of the standard complex but also with chromophores of lower symmetry.[26,27] The complexes resolved through the present work contain three kinds of ligand which are considerably separated in the spectrochemical series. In such complexes, determination of the absolute configuration presents some difficulty because of the lack of standard complex to be compared.

Of the present dicyano and dinitro complexes, the absolute configurations of the $(-)_{589}$-[Co(NO$_2$)$_2$ox(NH$_3$)$_2$]$^-$ [9] complex and $(+)_{589}$-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$ [10] complex were determined by x-ray analysis. The absolute configurations are presented in Figure 7, in which the *S* configuration is assigned to the $(+)_{589}$-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$ complex and the *R* configuration to the $(-)_{589}$-[Co(NO$_2$)$_2$ox(NH$_3$)$_2$]$^-$ complex. The nomenclature of the absolute configurations *R* and *S* follows the rule proposed by Cahn et al.[28]

We now presume the absolute configurations of the present complexes by comparing their CD spectra in the T$_{1g}$ region with those of these two standards. Hereafter we use the symbols *R* and *S* for not only cis,cis complexes but also cis complexes.



(a) (b)

Figure 7. Absolute configurations of (a) $S(+)_{589}$-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$ and (b) $R(-)_{589}$-[Co(NO$_2$)$_2$ox(NH$_3$)$_2$]$^-$.

By comparison of the features of the CD spectra and the signs of the split components between the $(-)_{589}$-[Co(CN)$_2$CO$_3$en]$^-$ complex and the $S(+)_{589}$-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$ complex, it can be said that the carbonato complex is in the *R* configuration. The $(-)_{589}$-[Co(CN)$_2$(H$_2$O)$_2$en]$^+$ species derived from this carbonato complex by acid hydrolysis must have the same configuration as the parent complex, namely, *R*. Since the CD spectrum of the $(+)_{589}$-[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]$^-$ complex resembles that of the $R(-)_{589}$-[Co(CN)$_2$(H$_2$O)$_2$en]$^+$ complex and has the signs −, +, and −, which are inverted with respect to those for $S(-)_{589}$-[Co(CN)$_2$mal(NH$_3$)$_2$]$^-$, its absolute configuration is assumed to be *R*. The $(+)_{589}$-[Co(CN)$_2$(H$_2$O)$_2$(NH$_3$)$_2$]$^+$ species derived from $R(+)_{589}$-[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]$^-$ will be in the same distribution of unidentates, namely, in *R*. The $(-)_{589}$-[Co(CN)$_2$ox(NH$_3$)$_2$]$^-$ complex will have the *S* configuration, because of its almost reversed CD pattern with respect to those of $R(-)_{589}$-[Co(CN)$_2$(H$_2$O)$_2$en]$^+$ and R-$(+)_{589}$-[Co(CN)$_2$CO$_3$(NH$_3$)$_2$]$^-$. As to the $(+)_{589}$-[Co-

$\mathrm{(CN)_2ox(en)]^-}$ complex, the anticipated CD signs are identical with those of the $S(+)_{589}\text{-}\mathrm{[Co(CN)_2mal(NH_3)_2]^-}$ complex and opposite to those of the $R(-)_{589}\text{-}\mathrm{[Co(CN)_2CO_3en]^-}$ complex, and the feature of CD is reversed with respect to that for the $R(-)_{589}\text{-}\mathrm{[Co(CN)_2CO_3en]^-}$ complex; consequently, the complex is regarded as being in the *S* configuration.

Since the CD spectrum of the $(-)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3(NH_3)_2]^-}$ complex gives a + and a − peak from the lower frequency side, the comparison of this CD spectrum with that of $R(-)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$ gives the *S* configuration for this complex. The absolute configuration of the $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+}$ species derived from $S(-)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3(NH_3)_2]^-}$ can be assigned to *S* because of the retention of configuration through the ligand substitution. It will be seen from the above discussions that, for the dinitro complexes such as $R(-)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$ and $S(-)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3(NH_3)_2]^-}$, treatment on the CD spectra is inverted with respect to that for the dicyano complexes. Since the $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2mal(NH_3)_2]^-}$ complex shows a reversed CD pattern with respect to that of $R(-)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$, the absolute configuration is presumed to be *S*. Each of the $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3en]^-}$ and the $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(en)]^-}$ complexes has a large positive peak in the T_{1g} region. From the fact that the dominant peaks for the $S(-)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3(NH_3)_2]^-}$ and $R(-)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$ complexes have − and + signs, respectively, and also from the comparison of the CD patterns of these ethylenediamine complexes with those of the $R(-)_{589}\text{-}\mathrm{[Co(CN)_2CO_3en]^-}$ and $S(+)_{589}\text{-}\mathrm{[Co(CN)_2ox(en)]^-}$ complexes, the absolute configurations of the dinitro complexes can be determined to be *R*. The $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2(H_2O)_2en]^+}$ species derived from $R(+)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3en]^-}$ should have the same distribution of ligands as that of the original carbonato complex, namely, *R*. All of the CD spectral data and presumed absolute configurations are summarized in Table III.

In each series of dinitro and dicyano complexes, with $(-)_{589}\text{-}\mathrm{[Co(NO_2)_2(en)_2]^+}$ used as the resolving agent, the solubility rule[29] seems to hold, although it does not always hold when $(-)_{589}\text{-}\mathrm{[Co(ox)(en)_2]^+}$ is used.

In the present work, we obtained the cobalt(III) complexes which derive dissymmetries solely from the distribution of unidentates (unidentate system) and also those complexes which derive dissymmetries from the distribution of bidentates (bidentate system). It was found that, even if a unidentate system with a certain chromophore and a bidentate system with the same chromophores are in the same absolute configurations, the two systems do not always have the same signs in the CD peaks due to the comparable transitions. The observed CD spectra showed different patterns according to the chelate rings of dicarboxylate ions ($\mathrm{CO_3^{2-}}$, $\mathrm{ox^{2-}}$, and $\mathrm{mal^{2-}}$). The situation was the same between a chelate system and the corresponding unidentate system. However, when a bidentate ligand is replaced by the corresponding two unidentates or a dicarboxylate ion is alternated with another one, the sign of the peak on the higher frequency side in the T_{1g} region never changes for a certain absolute configuration.

Registry No. *cis,cis*-$\mathrm{Na[Co(CN)_2CO_3(NH_3)_2]}$, 60745-73-5; *cis,cis*-$\mathrm{Na[Co(CN)_2ox(NH_3)_2]}$, 60745-74-6; *cis,cis*-$\mathrm{K[Co(CN)_2mal(NH_3)_2]}$, 60745-75-7; *cis*-$\mathrm{K[Co(CN)_2CO_3en]}$, 60745-76-8; *cis*-$\mathrm{K[Co(CN)_2ox(en)]}$, 60745-77-9; *cis,cis*-$\mathrm{K[Co(NO_2)_2CO_3(NH_3)_2]}$, 60801-74-3; *trans*($NH_3$),*cis*($NO_2$)-$\mathrm{K[Co(NO_2)_2CO_3(NH_3)_2]}$, 60801-75-4; *cis,cis*-$\mathrm{K[Co(NO_2)_2mal(NH_3)_2]}$, 60801-76-5; *cis*-$\mathrm{K[Co(NO_2)_2CO_3en]}$, 60745-78-0; *cis*-$\mathrm{K[Co(NO_2)_2ox(en)]}$, 60745-79-1; *cis,cis,cis*-$\mathrm{[Co(CN)_2(H_2O)_2(NH_3)_2]^+}$, 60801-77-6; *cis,cis*-$\mathrm{[Co(CN)_2(H_2O)_2en]^+}$, 60745-80-4; *cis,cis,cis*-$\mathrm{[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+}$, 60801-78-7; *trans*($NH_3$)-$\mathrm{[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+}$, 33865-42-8; *cis,cis*-$\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$, 60762-11-0; *trans*($NO_2$)-$\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$, 60745-81-5; *trans*($NH_3$)-$\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$, 60745-82-6; *trans*($NH_3$)-$\mathrm{[Co(NO_2)_2mal(NH_3)_2]^-}$, 60801-79-8; *cis,cis*-$\mathrm{[Co(NO_2)_2(H_2O)_2en]^+}$, 60745-83-7; *cis*-$\mathrm{[Co(CN)_2(CO_3)_2]^{3-}}$, 51120-38-8; *cis*-$\mathrm{K[Co(CO_3)_2(NH_3)_2]}$, 26176-51-2; $\mathrm{K[Co(CO_3)_2en]}$, 60745-84-8; $\mathrm{K[CoCO_3ox(en)]}$, 60745-85-9; $(-)_{589}\text{-}\mathrm{[Co(ox)(en)_2]}(-)_{589}\text{-}\mathrm{[Co(CN)_2ox(NH_3)_2]}$, 60827-58-9; $(-)_{589}\text{-}\mathrm{[Co(ox)(en)_2]}(+)_{589}\text{-}\mathrm{[Co(CN)_2mal(NH_3)_2]}$, 60801-81-2; $(-)_{589}\text{-}\mathrm{[Co(NO_2)_2(en)_2]}(-)_{589}\text{-}\mathrm{[Co(CN)_2CO_3en]}$, 60801-83-4; $(-)_{589}\text{-}\mathrm{[Co(ox)(en)_2]}(+)_{589}\text{-}\mathrm{[Co(CN)_2ox(en)]}$, 60801-85-6; $(-)_{589}\text{-}\mathrm{[Co(ox)(en)_2]}(-)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3(NH_3)_2]}$, 60827-60-3; $(-)_{589}\text{-}\mathrm{[Co(ox)(en)_2]}(+)_{589}\text{-}\mathrm{[Co(NO_2)_2mal(NH_3)_2]}$, 60827-62-5; $(-)_{589}\text{-}\mathrm{[Co(NO_2)_2(en)_2]}(+)_{589}\text{-}\mathrm{[Co(NO_2)_2CO_3en]}$, 60801-87-8; $(-)_{589}\text{-}\mathrm{[Co(NO_2)_2(en)_2]}(+)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(en)]}$, 60801-89-0; $(+)_{589}\text{-}\mathrm{[Co(CN)_2CO_3(NH_3)_2]^-}$, 60801-90-3; $(+)_{589}\text{-}\mathrm{[Co(CN)_2(H_2O)_2(NH_3)_2]^+}$, 60801-91-4; $(-)_{589}\text{-}\mathrm{[Co(CN)_2(H_2O)_2en]^+}$, 60801-92-5; $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2(H_2O)_2(NH_3)_2]^+}$, 60801-93-6; $(-)_{589}\text{-}\mathrm{[Co(NO_2)_2ox(NH_3)_2]^-}$, 59433-51-1; $(+)_{589}\text{-}\mathrm{[Co(NO_2)_2(H_2O)_2en]^+}$, 60801-94-7.

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