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Circular Dichroism Spectra of Cobalt(III) Complexes Containing One or Two Azido, Isothiocyanato, and Nitro Ligands. I. The Bis(ethylenediamine) Complexes of *cis* Type

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Circular dichroism spectra have been measured for the *cis*-$[Co(X)(NH_3)(en)_2]^{2+}$, *cis*-$[Co(X)_2(en)_2]^+$, and *cis*-$[Co(X)(X')(en)_2]^+$ complexes in the visible and ultraviolet region (X and X'$=N_3^-$, NCS^-, or NO_2^-). The absolute configurations of the complexes have been assigned from the circular dichroism pattern in the first d-d absorption band, region and correlated with that in the near ultraviolet region of the so-called specific absorption band. The origin of the specific absorption band has been discussed.

It is well known that transition metal complexes with some particular ligands, such as azido N_3^-, isothiocyanato NCS^-, nitro NO_2^-, and sulfito SO_3^{2-}, show characteristic intense absorption bands in the near-ultraviolet region. These characteristic absorption bands were named at first "special bands,"[1,2] and later "specific bands."[3] The specific absorption bands, which are specific for the particular ligands, have been investigated by many authors, but alternative characterizations have been assigned to the origin, that is, the one attributed the bands to intraligand transitions,[1,4] and the other to charge transfer transitions.[5-9] Recently Miskowsky and Gray[10] attributed most of the specific bands of $[Co(CN)_5X]^{n-}$ or $[CoX(NH_3)_5]^{n+}$ complexes to ligand-to-metal charge transfer transitions (X$=$ NCS^-, SCN^-, and SO_3^{2-}), but assigned the specific bands of $[Co(CN)_5(NO_2)]^{3-}$ and $[Co(NO_2)(NH_3)_5]^{2+}$ which are located at 35200 and 30700 cm^{-1}, respectively, to a metal-to-ligand charge transfer transition. The latter metal-to-ligand transition has also been assumed for the specific bands of some hexanitro metallates.[11]

The present paper deals with circular dichroism (CD) spectra of *cis*-$[Co(X)(NH_3)(en)_2]^{2+}$, *cis*-$[Co(X)_2(en)_2]^+$, and *cis*-$[Co(X)(X')(en)_2]^+$ complexes (X and X'$=N_3^-$, NCS^-, or NO_2^-), to find the relationship between the CD behavior in the specific band region and the absolute configuration of the complexes, and furthermore to interpret, if possible, the origin of the specific bands on the basis of the CD spectra. A preliminary letter about some of the results has been reported.[12]

Experimental

Preparation and Optical Resolution. *(1) $(-)_{589}$-cis-$[Co(N_3)(NH_3)(en)_2]Cl_2\cdot 0.5H_2O$:* To a solution containing 6.0 g of *cis*-$[CoCl(NH_3)(en)_2]Cl_2$[13] in 30 cm^3 of water were added a few drops of glacial acetic acid and 1.4 g of sodium azide. The solution was heated on a water bath and concentrated until the surface of the solution was covered with a thin crystalline product. After the resulted mixture had been allowed to stand at room temperature for an hour, the crystals were collected by filtration. 4.0 g. Recrystallization was carried out from water (60 °C). The pure crystals deposited were filtered and washed with methanol, and then acetone, and air-dried. Found: C, 15.49; H, 6.14; N, 35.75 %. Calcd for $[Co(N_3)(NH_3)(C_2H_8N_2)_2]Cl_2$: C, 15.54; H, 6.20; N, 36.25%.

The optical resolution of this complex was achieved by a modified procedure of that of Buckingham, Olsen, and Sargeson[14] using NH_4*d*-bcs as a resolving agent (*d*-bcs stands for $(+)_{589}$-(1*R*, 3*S*, 4*S*, 7*R*)-3-bromocamphor-9-sulfonate ion). The less soluble diastereomer was recrystallized from water until it showed a constant rotation. $[\alpha]_{589}=-10°$, $[\alpha]_{546}=+15°$, $[\alpha]_{467}=+371°$. Found: C, 33.34; H, 5.52; N, 12.85%. Calcd for $[Co(N_3)(NH_3)(C_2H_8N_2)_2](C_{10}H_{14}O_4BrS)_2\cdot 0.5H_2O$: C, 33.23; H, 5.58; N, 12.92%. A solution of the diastereomer was passed through a column containing Dowex 1×8 strong-base anion exchange resin (Cl^- form) and the resulted solution was evaporated to dryness below 30 °C. The deposited fine reddish-violet crystals were suspended in methanol to eliminate a contaminant, filtered, washed with methanol and acetone, and dried in a desiccator over $CaCl_2$. $[\alpha]_{589}=-210°$, $[\alpha]_{546}=-116°$. Found: C, 15.06; H, 6.35; N, 34.01%. Calcd for $[Co(N_3)(NH_3)(C_2H_8N_2)_2]Cl_2\cdot 0.5H_2O$: C, 15.10; H, 6.34; N, 35.23%.

(2) $(+)_{589}$-cis-$[Co(N_3)_2(en)_2]ClO_4$: To a solution (50 °C) of 3.0 g of *rac*-$[Co(N_3)_2(en)_2]N_3$[15] in 80 cm^3 of water was added a solution of 1.8 g of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ in 20 cm^3 of water (*d*-tart stands for $(+)_{589}$-tartrate(4−) ion). The mixture was kept in a refrigerator for two days. The resulting dark reddish-violet prismatic crystals were filtered, washed with a little water, methanol, and then acetone, and dried in air. 2.6 g. $[\alpha]_{589}=+140°$, $[\alpha]_{546}=-539°$. The less soluble diastereomer was converted to the perchlorate by adding a large excess of solid $LiClO_4\cdot 3H_2O$ (5 g) to a suspension of the diastereomer in 80 cm^3 of water (40 °C) and stirring sufficiently (1 h). The red violet fine crystals separated were filtered, washed with a little water, methanol, and then acetone, and dried in a vacuum desiccator over $CaCl_2$. 0.5 g. Recrystallization was carried out from a minimum amount of water (40 °C). $[\alpha]_{589}=+237°$, $[\alpha]_{546}=-962°$. Found: C, 13.39; H, 4.46; N, 38.98%. Calcd for $[Co(N_3)_2(C_2H_8N_2)_2]ClO_4$: C, 13.25; H, 4.45; N, 38.62%.

The perchlorate of the $(-)_{589}$ isomer was obtained by the addition of a solution containing 0.7 g of $NaClO_4$ in 10 cm^3 of water to the above filtrate. By recrystallization from hot water this isomer gave the same rotation with the opposite sign as the $(+)_{589}$ perchlorate.

(3) $(+)_{589}$-cis-$[Co(NCS)(NH_3)(en)_2]Br_2\cdot 0.5H_2O$: $(-)_{589}$-$[CoCl(NCS)(en)_2]Cl$ (0.9 g, see below (10)) was placed in a 250 cm^3 cylinder and purged with ammonia gas in a Dry Ice–methanol bath to condense about 10 cm^3 of ammonia over the complex. The cylinder was tightly covered and allowed to stand at room temperature for about half an hour.

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When the color of the ammonia solution was changed from dark red to deep orange, the ammonia was evaporated by a stream of dry nitrogen. The resulted orange product (0.9 g) was dried in a vacuum desiccator over P_2O_5 to remove the remaining ammonia. A portion (0.45 g) of the dried product was dissolved in 4 cm³ of water, and 0.9 g of NaBr was added to the solution. After it had been kept in a refrigerator overnight, the first precipitate was filtered off (this was optically almost inactive). After the filtrate had been kept in a refrigerator for another day, the second precipitate (partly resolved complex) was filtered. When the filtrate was kept in a refrigerator for further four days, the orange prisms resulted. They were filtered, washed with ethanol and acetone, and dried in a vacuum desiccator over $CaCl_2$. 37 mg. $[\alpha]_{589}=+43°$, $[\alpha]_{546}=+83°$. Found: C, 14.32; H, 4.87; N, 20.12%. Calcd for $[Co(NCS)(NH_3)(C_2H_8N_2)_2]Br_2\cdot 0.5H_2O$: C, 14.47; H, 4.86; N, 20.25%. The $(-)_{589}$ isomer was obtained from $(+)_{589}$-$[CoCl(NCS)(en)_2]Cl$.

(4) $(-)_{589}$-*cis*-$[Co(NCS)_2(en)_2]Cl$: The racemic chloride monohydrate[16] (3.5 g) and the resolving agent $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$ (1.7 g) were dissolved in 300 cm³ of water at 60 °C. After cooling the mixed solution to the room temperature, it was allowed to stand overnight in a refrigerator. The less soluble diastereomer deposited as red orange crystals, and it was recrystallized from hot water (300 cm³, 60 °C). 1.1 g. $[\alpha]_{589}=-61°$, $[\alpha]_{546}=+165°$. To a suspension of 1.0 g of the recrystallized diastereomer in 80 cm³ of water was added 200 cm³ of aqueous solution containing 15 g of lithium chloride. The mixture was stirred for half an hour to transform the diastereomer into the reddish-orange chloride, and this was filtered, washed with 50% ethanol, ethanol and then acetone, and dried in a vacuum desiccator over $CaCl_2$. 0.5 g. $[\alpha]_{589}=-25°$, $[\alpha]_{546}=+134°$. It was confirmed that the optical rotation was not increased by recrystallization. Found: C, 21.77; H, 4.97; N, 25.44%. Calcd for $[Co(NCS)_2(C_2H_8N_2)_2]Cl$: C, 21.79; H, 4.88; N, 25.41%.

(5) $(-)_{589}$-*cis*-$[Co(NO_2)(NH_3)(en)_2]SO_4\cdot H_2O$: The racemic dithionate[13] was converted to the nitrate by an ion-exchange method with Dowex 2×8 resin (NO_3^- form, 50—100 mesh). The racemic nitrate, $[Co(NO_2)(NH_3)(en)_2](NO_3)_2$ (3.2 g), was dissolved in 17 cm³ of water (40 °C), and 1.4 g of NH_4*d*-bcs was added to it.[17] The mixed solution was kept in a refrigerator for about four days. Orange yellow needles separated were filtered, washed with 50% ethanol, ethanol, and then acetone, and air-dried. 0.65 g. $[\alpha]_{589}=+44°$, $[\alpha]_{546}=+33°$, $[\alpha]_{436}=+386°$. The needles were occasionally contaminated with orange yellow prisms. The prisms were the racemic nitrate. The undesired prisms were easily removed by hand picking. The diastereomer was recrystallized from water (50 °C), and filtered, washed with a little ice-cold water, 50% ethanol, and then acetone, and dried in air. 0.5 g. $[\alpha]_{589}=+53°$, $[\alpha]_{546}=+49°$, $[\alpha]_{438}=+440°$. The diastereomer was converted to the sulfate by passing the aqueous solution through a column containing an anion-exchange resin (SO_4^{2-} form) and by evaporating the resulting solution to dryness below 30 °C. After suspending the sulfate in a methanol–water (4:1) mixture and stirring it enough, the sulfate of the $(-)_{589}$ isomer was filtered, washed with methanol and acetone, and dried in a vacuum desiccator over $CaCl_2$. $[\alpha]_{589}=-18°$, $[\alpha]_{546}=-49°$. Found: C, 13.73; H, 5.88; N, 23.21%. Calcd for $[Co(NO_2)(NH_3)(C_2H_8N_2)_2]SO_4\cdot H_2O$: C, 13.49; H, 5.94; N, 23.59%.

(6) $(-)_{589}$-*cis*-$[Co(NO_2)_2(en)_2]Cl$: To the solid complex, $[CoCO_3(en)_2]NO_3\cdot H_2O$[18] (32 g), was poured carefully 225 cm³ of 4% of nitric acid. The complex was dissolved with the evolution of CO_2 gas to give a solution containing *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ complex. After the solution had been stirred for a while to complete the aquation, 20.7 g of $NaNO_2$ was added, and the mixed solution was gradually heated on a water bath and stirred at 70 °C for an hour. The color of solution changed from red to dark orange, and the nitrate of the desired complex separated out. The crystals were filtered and washed with water, and then ethanol. 20 g. The nitrate was recrystallized from water (60 °C) and the fine crystals obtained were filtered, washed with water, and then ethanol, and dried in a vacuum desiccator over $CaCl_2$. Found: C, 14.74; H, 5.10; N, 29.27%. Calcd for $[Co(NO_2)_2(C_2H_8N_2)_2]NO_3$: C, 14.42; H, 4.84; N, 29.42%.

The perchlorate was obtained in a similar way from $[CoCO_3(en)_2]ClO_4$.[19] Found: C, 13.18; H, 4.23; N, 22.66%. Calcd for $[Co(NO_2)_2(C_2H_8N_2)_2]ClO_4$: C, 12.96; H, 4.35; N, 22.68%.

The nitrate was resolved in a usual way using $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$ as resolving agent.[20] The less soluble diastereomer yielded the $(-)_{589}$-$[Co(NO_2)_2(en)_2]Cl$.

(7) $(+)_{589}$-*cis*-$[Co(N_3)(NCS)(en)_2]Cl\cdot 0.5H_2O$: To a 60 °C solution of 6.0 g of *cis*-$[CoCl(NCS)(en)_2]ClO_4$[13] in 45 cm³ of water was added 1.2 g of NaN_3, and the resulting solution was stirred at 60 °C for about 80 min. After the solution had been diluted with an appropriate amount of water, it was poured on a column (27×800 mm) containing Dowex 50 W×8 cation-exchange resin (200—400 mesh, H^+ form). The adsorbed band was eluted first with 0.2 M LiCl solution at a rate of 1.5—2.0 cm³/min for a week. The eluates were discarded, because it was confirmed from the absorption measurement that the eluates contained some *trans* complexes. After these operations, the remaining colored band which was placed on the upper half of the column was eluted with 0.5 M LiCl (about 13 dm³ in total) during the next week. The broad bands eluted were fractionated by 200 cm³ portions. The eluted ten fractions which have the first absorption band at 510—509 nm were combined and concentrated to a volume as little as possible (about 50 cm³) in a vacuum evaporator at 35 °C. After the mixture had stood in a refrigerator overnight, the resulting precipitates, *cis*-$[Co(N_3)(NCS)(en)_2]Cl\cdot 1.5H_2O$ and LiCl, were filtered. To remove the LiCl, the mixture was suspended in 200 cm³ of ethanol and the suspension was stirred enough. The dark reddish-violet precipitate was filtered, washed with five 20 cm³ portions of ethanol, and then ether, and dried in a vacuum desiccator. 0.41 g. This was recrystallized from water (50 °C), and the product was washed with ethanol and ether, and dried in a vacuum desiccator over $CaCl_2$. Found: C, 17.63; H, 5.67; N, 32.28%. Calcd for $[Co(N_3)(NCS)(C_2H_8N_2)_2]Cl\cdot 1.5H_2O$: C, 17.58; H, 5.60; N, 32.79%.

The resolving agent $K_2[Sb_2(d\text{-}tart)_2]\cdot 3H_2O$ (120 mg) was dissolved in 40 cm³ of water at 60 °C, and 220 mg of *cis*-$[Co(N_3)(NCS)(en)_2]CH_3CO_2$, which was obtained from the chloride by the usual ion-exchange method, was added to it with stirring. After cooling the mixed solution to room temperature, it was kept in a refrigerator overnight. The fine dark reddish-violet crystals separated were filtered, washed with ethanol and ether, and air-dried. 115 mg. $[\alpha]_{589}=+135°$, $[\alpha]_{546}=+60°$. The less soluble diastereomer (110 mg) was dissolved in 3 cm³ of water at 45 °C. After the solution had stood for two weeks in a refrigerator, the resulted crystals were filtered, washed with a little water, ethanol and ether, and air-dried. 18 mg. $[\alpha]_{589}=+178°$, $[\alpha]_{546}=+50°$. The recrystallized diastereomer (18 mg) was dissolved in 10 cm³ of water, and the solution was passed through an anion-exchange resin column (Cl^- form). The chloride solution obtained was evaporated to dryness in a vacuum desiccator over P_2O_5.

$[\alpha]_{589}=+125^\circ$, $[\alpha]_{546}=-138^\circ$. Found: C, 18.70; H, 5.29; N, 34.52%. Calcd for $[Co(N_3)(NCS)(C_2H_8N_2)_2]Cl\cdot0.5H_2O$: C, 18.55; H, 5.29; N, 34.62%.

(8) $(+)_{589}$-*cis*-$[Co(N_3)(NO_2)(en)_2]ClO_4$: To a solution of 5.7 g of *cis*-$[CoCl(NO_2)(en)_2]Cl$ in 90 cm^3 of water at 70 °C was added 1.3 g of NaN_3. The mixture was heated on a steam bath in a draft chamber. When the solution was concentrated to 10—15 cm^3, a solution containing 2.4 g of $Na_2S_2O_6\cdot2H_2O$ in 10 cm^3 of water was added to it with stirring. After cooling the mixture to room temperature and then keeping it in an ice bath for an hour, the reddish-orange fine crystals precipitated were filtered, washed with a little water, and dried in air. 2.8 g. This was recrystallized twice from water (60 °C) and washed with a little water, ethanol, and then ether, and air-dried. Found: C, 13.70; H, 4.63; N, 31.87%. Calcd for $[Co(N_3)(NO_2)(C_2H_8N_2)_2]_2S_2O_6$: C, 13.84; H, 4.65; N, 32.27%.

The racemate, *cis*-$[Co(N_3)(NO_2)(en)_2]_2S_2O_6$ (6.0 g), was dissolved in 600 cm^3 of water at 60 °C, and transformed into the chloride solution by an ion-exchange method. The resulted chloride solution was evaporated at 40 °C to 75 cm^3 in a vacuum evaporator, and a solution of 2.6 g of NH_4*d*-bcs in 20 cm^3 of water was added to it. After the mixed solution had been cooled in a refrigerator for two days, the red orange needles separated were filtered, washed with a little water, methanol and ether, and air-dried. 2.7 g. $[\alpha]_{589}=+77^\circ$, $[\alpha]_{546}=+80^\circ$, $[\alpha]_{472}=-542^\circ$. The diastereomer was recrystallized from water (45 °C, 160 cm^3). 0.9 g. $[\alpha]_{589}=+68^\circ$, $[\alpha]_{546}=+72^\circ$, $[\alpha]_{472}=-598^\circ$. Found: C, 29.11; H, 5.26; N, 18.68%. Calcd for $[Co(N_3)(NO_2)(C_2H_8N_2)_2](C_{10}H_{14}O_4BrS)$: C, 29.13; H, 5.24; N, 19.41%. The recrystallized diastereomer (0.5 g) was dissolved in a minimum amount of water (35 cm^3) at 40 °C, and 10g of $NaClO_4$ was added to it with stirring. After the mixture had stood for two hours, the resulted fine red orange lustrous prisms were filtered, washed with ethanol and ether, and air-dried. 144 mg. $[\alpha]_{589}=+32^\circ$. $[\alpha]_{546}=+43^\circ$. The perchlorate was recrystallized from water (40 °C, 6 cm^3). 66 mg. It was confirmed that the optical rotation of this isomer was not increased by the recrystallization. Found: C, 13.27; H, 4.30; N, 30.61%. Calcd for $[Co(N_3)(NO_2)(C_2H_8N_2)_2]ClO_4$: C, 13.10; H, 4.40; N, 30.56%.

(9) $(+)_{589}$-*cis*-$[Co(NCS)(NO_2)(en)_2]Cl$: To a solution of 1.6 g of barium acetate in 200 cm^3 of water (60 °C) was added 3.9 g of *cis*-$[Co(NCS)(NO_2)(en)_2]_2SO_4$.[13] After the mixture had been stirred for half an hour at 60 °C, the barium sulfate deposited was removed by filtration. The filtrate was evaporated to dryness with a vacuum evaporator, and the resulted fine yellow orange crystals were collected and washed with 70% ethanol, ethanol and then ether, and air-dried. 3.5 g. Found: C, 24.54; H, 5.62; N, 24.48%. Calcd for $[Co(NCS)(NO_2)(C_2H_8N_2)_2]CH_3CO_2$: C, 24.57; H, 5.60; N, 24.55%. The racemic acetate, *cis*-$[Co(NCS)(NO_2)(en)_2]CH_3CO_2$ (2.0 g), was dissolved in 10 cm^3 of water at 40 °C, and a solution of 1.0 g of $K_2[Sb_2(d\text{-tart})_2]\cdot3H_2O$ in 10 cm^3 of water at 40 °C was added to it. A large amount of yellow orange precipitate separated soon, and was filtered after an hour (the filtrate was used for separating the $(-)_{589}$-isomer), washed with ethanol and ether, and air-dried. 1.5 g. $[\alpha]_{589}=+110^\circ$, $[\alpha]_{546}=+160^\circ$. This was recrystallized from water (45 °C, 500 cm^3). Yellow orange needles. 0.9 g. $[\alpha]_{589}=+125^\circ$, $[\alpha]_{546}=+191^\circ$.

The recrystallized diastereomer (0.3 g) was dissolved in 150 cm^3 of water at 40 °C, and was converted into the chloride solution by an ion-exchange method. The resulted chloride solution was evaporated to dryness below 30 °C in a vacuum evaporator. After being suspended in ethanol with stirring, the fine yellow orange prisms were filtered, washed with ethanol and ether, and dried in air. 0.13 g. $[\alpha]_{589}=+87^\circ$, $[\alpha]_{546}=+197^\circ$. Recrystallization of the chloride caused no increase in the optical rotation. Found: C, 18.89; H, 5.05; N, 26.29%. Calcd for $[Co(NCS)(NO_2)(C_2H_8N_2)_2]Cl$: C, 18.85; H, 5.06; N, 26.37%.

The $(-)_{589}$ optical isomer appeared soon after a solution of 1.0 g of LiCl in 2 cm^3 of water was added to the above mentioned filtrate freed from the diastereomer. The crystals were filtered after about 5 min, washed with ethanol and ether, and air-dried. 0.41 g. $[\alpha]_{589}=-82^\circ$, $[\alpha]_{546}=-186^\circ$. This was recrystallized from water (45 °C, 16 cm^3). 0.22 g.

(10) $(-)_{589}$-*cis*-$[CoCl(NCS)(en)_2]ClO_4$: The racemic perchlorate was prepared from *trans*-$[CoCl_2(en)_2]Cl$ by the Werner's method.[13] The perchlorate obtained was contaminated with the diisothiocyanato complex, and then purified as follows. The crude perchlorate salt was fractionally extracted with water, and to each extract was added one-fourth volume of 70% $HClO_4$ and the resulted solution was cooled in an ice bath for several hours. The fine orange crystals of the contaminant, $[Co(NCS)_2(en)_2]ClO_4$, precipitated from the earlier extracts, whereas the dark red crystals of *cis*-$[CoCl(NCS)(en)_2]ClO_4$ precipitated from the later extracts. No crystallization occurred from the middle extracts. The crystals of the desired complex were recrystallized from water by the addition of perchloric acid as described above, and filtered, washed with ethanol and ether, and sucked dry. Found: C, 16.00; H, 4.18; N, 18.74%. Calcd for $[CoCl(NCS)(C_2H_8N_2)_2]ClO_4$: C, 16.14; H, 4.33; N, 18.82%.

A solution of 12 g of racemic *cis*-$[CoCl(NCS)(en)_2]ClO_4$ in 160 cm^3 of water (50 °C) and a solution of 5.3 g of NH_4*d*-bcs in 30 cm^3 of water (50 °C) were mixed. The mixture was allowed to stand at room temperature for an hour, and then cooled gradually to 10 °C. The dark reddish violet crystalline precipitate was filtered, washed with ethanol and ether, and dried in air. 8.6 g. The filtrate was used for obtaining the $(+)_{589}$-isomer. $[\alpha]_{589}=+11^\circ$, $[\alpha]_{546}=+226^\circ$. This was recrystallized from water (45 °C). $[\alpha]_{589}=+27^\circ$, $[\alpha]_{546}=+317^\circ$. Found: C, 30.37; H, 5.43; N, 11.57%. Calcd for $[CoCl(NCS)(C_2H_8N_2)_2](C_{10}H_{14}O_4BrS)\cdot H_2O$: C, 29.98; H, 5.37; N, 11.66%. The recrystallized diastereomer (3.5 g) was stirred with 6 cm^3 of 70% $HClO_4$ for an hour. After the mixture had been stirred in an ice bath for another hour, the separated fine crystals of the perchlorate were filtered, washed with ethanol and ether. 1.2 g. $[\alpha]_{589}=-31^\circ$, $[\alpha]_{546}=+389^\circ$. The perchlorate was dissolved in a minimum amount of water (20 cm^3), and 4 cm^3 of 70% $HClO_4$ was added to it. After the mixture had stood overnight, the reddish violet crystals separated were filtered, washed with ethanol and ether, and dried in a vacuum desiccator over $CaCl_2$. 0.7 g. $[\alpha]_{589}=-39^\circ$, $[\alpha]_{546}=+440^\circ$. Found: C, 16.34; H, 4.31; N, 18.45%. Calcd for $[CoCl(NCS)(C_2H_8N_2)_2]ClO_4$: C, 16.14; H, 4.33; N, 18.82%.

The filtrate freed from the less soluble diastereomer was evaporated at 25 °C to 170 cm^3, and after cooling the solution in an ice bath, the second crop of the diastereomer was removed. The filtrate was evaporated further to 55 cm^3, and 18 cm^3 of 70% $HClO_4$ was added to it. After cooling the mixture by ice, the precipitated perchlorate was filtered. This was found to be an optically impure perchlorate of the $(+)_{589}$-isomer. The filtrate was kept in a refrigerator for three days, and then the dark reddish violet needles separated. The crystals were filtered, washed with ethanol and ether, and air-dried. 0.4 g. These showed the same optical rotation with the opposite sign in comparison with the $(-)_{589}$ perchlorate.

Measurements. The absorption spectra were measured by a Shimadzu UV-200 or a Beckman DU spectrometer. The CD spectra were recorded with a Jasco Model ORD/UV-5, J-10, or J-20 spectropolarimeter, and the optical rotation by a Yanagimoto Model 185 or a Jasco Model ORD/UV-5 spectropolarimeter. The measurements were made at room temperature in aqueous solutions. The concentration of the solution ranged from 0.005 to 0.0001 M. The cell length was 1, 2 cm, or 1 mm.

Results and Discussion

Absorption and CD Spectra. The absorption and CD data are listed in Tables 1 and 2. In Fig. 1 the CD spectra of $(-)_{589}$-$[Co(N_3)(NH_3)(en)_2]^{2+}$ and $(+)_{589}$-$[Co(N_3)_2(en)_2]^+$ complexes are shown together with their absorption spectra. In the "azido-specific band" region around 33000 cm^{-1}, the ammineazido complex shows a single CD band with its peak in almost the same position as that of the absorption peak, while the diazido complex shows two CD bands of opposite signs. This observation supports that the broadening of the specific absorption band in the diazido complex is due to the overlapping of two split components of the band. The weak negative CD band at 26100 cm^{-1} of the ammineazido complex and the positive CD band at 25800 cm^{-1} of the diazido complex correspond to the second d-d absorption band ($^1A_{1g} \rightarrow {}^1T_{2g}$ in O_h symmetry). The positive CD band of the diazido complex has the intensity comparable to the CD band in the first d-d absorption band ($^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h symmetry) region. This is unusual, but this behavior should be considered to be only the result of the contiguity of the intense

TABLE 1. ABSORPTION AND CD DATA OF *cis*-$[Co(X)(NH_3)(en)_2]^{2+}$ AND *cis*-$[Co(X)_2(en)_2]^+$ COMPLEXES

Complex ion	$\sigma_{\max}$[a] (log ε)	σ_{ext}[a] ($\Delta\varepsilon$)
$(-)_{589}$-$[Co(N_3)(NH_3)(en)_2]^{2+}$	19.8(2.52)	19.4(−0.60)
	≈27 sh[b]	26.1(−0.15)
	33.3(3.90)	33.5(+1.9)
		≈43 sh(+)
	48.1(4.28)	
$(+)_{589}$-$[Co(N_3)_2(en)_2]^+$	19.3(2.52)	17.6(+0.80) 20.0(−1.17)
	≈26 sh	25.8(+1.92)
	33.1(4.06)	30.8(+5.8) 36.9(−6.0)
		≈42 sh(−)
	46.5(4.30)	46.3(+12)
$(-)_{589}$-$[Co(NCS)(NH_3)(en)_2]^{2+}$	20.5(2.32)	20.0(−0.28)
	≈28 sh	27.7(−0.05)
	33.2(3.23)	34.9(+0.18)
		41.8 (+1.2)
$(-)_{589}$-$[Co(NCS)_2(en)_2]^+$	20.4(2.54)	17.9(−0.12) 20.5(+0.32)
	≈28 sh	25.3(−0.04) 27.3(+0.10)
	32.5(3.46)	30.8(−0.45) 35.2(+0.12)
		40.7(−1.2) 43.7(+1.0)
$(-)_{589}$-$[Co(NO_2)(NH_3)(en)_2]^{2+}$	22.3(2.08)	21.1(−0.67) 23.9(+0.16)
	31.1(3.23)	31.0(−0.19) 36 sh(+)
	42.1(4.23)	40.8(+2.5)
$(-)_{589}$-$[Co(NO_2)_2(en)_2]^+$	22.8(2.23)	21.7(−1.66) 24.6(+0.62)
	31.1(3.56)	29.6(+2.48) 35 sh(−)
	41.7(4.32)	37.8(−3.7) 43.2(+16)

a) Wave numbers are given in 10^3 cm^{-1}. b) "sh" means a shoulder band.

TABLE 2. ABSORPTION AND CD DATA OF *cis*-$[Co(X)(X')(en)_2]^+$ COMPLEXES

Complex ion	$\sigma_{\max}$[a] (log ε)	σ_{ext}[a] ($\Delta\varepsilon$)
$(+)_{589}$-$[Co(N_3)(NCS)(en)_2]^+$	19.6(2.51)	18.4(+0.39) 20.9(−0.20)
		27.0(+0.26)
	32.4(3.91)	32.8(−1.3)
		41.7(−0.5)
$(+)_{589}$-$[Co(N_3)(NO_2)(en)_2]^+$	20.4(2.65)	19.8(+0.74) 22.5(−1.07)
		28.4(+1.05)
		31.0(−0.7)
	33.1(3.92)	33.9(+3.0)
	≈41 (4.05)	38.6(−5.1)
		45.8(−11)
$(+)_{589}$-$[Co(NCS)(NO_2)(en)_2]^+$	21.2(2.48)	20.3(+0.58) 23.0(−0.20)
		26.8(−0.31)
	31.0(3.52)	30.2(+2.44)
	≈41 (4.1)	37.8(−3.7)
		43.3(−1.4)
		46.0(+1.4)
$(-)_{589}$-$[CoCl(NCS)(en)_2]^+$	≈18 (2.1sh)[b] 19.9(2.24)	17.4(−0.36) 20.3(+0.59)
		27.9(+0.18)
	≈32 (3.2)	32.6(−0.6)
		37.1(+0.3)
	44.4(4.25)	45.0(−5.0)

a) Wave numbers are given in 10^3 cm^{-1}. b) "sh" means a shoulder band.

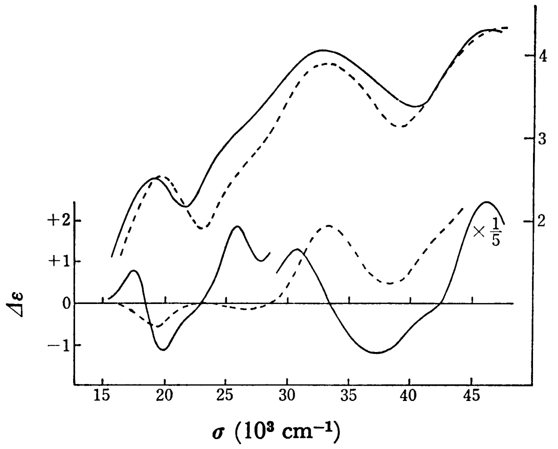

Fig. 1. Absorption and CD spectra of $(+)_{589}$-*cis*-$[Co(N_3)_2(en)_2]ClO_4$ (——) and $(-)_{589}$-*cis*-$[Co(N_3)(NH_3)(en)_2]Cl_2 \cdot H_2O$ (------).

positive CD band of the specific band. In Fig. 2 the CD spectra of isothiocyanato complexes are shown with their absorption spectra. Concerning their specific bands the CD behavior similar to the azido complexes are observed; A single weal CD band is observed at 34900 cm^{-1} for the ammineisothiocyanato complex, while two CD bands of opposite signs are observed for the diisothiocyanato complex. This fact suggests the band splitting of the diisothiocyanato complex. The nagative CD band of the ammineisothiocyanato complex at 27700 cm^{-1} and the two CD bands of the diisothiocyanato complex at 25300 and 27300 cm^{-1} are assigned to the second d-d transitions.

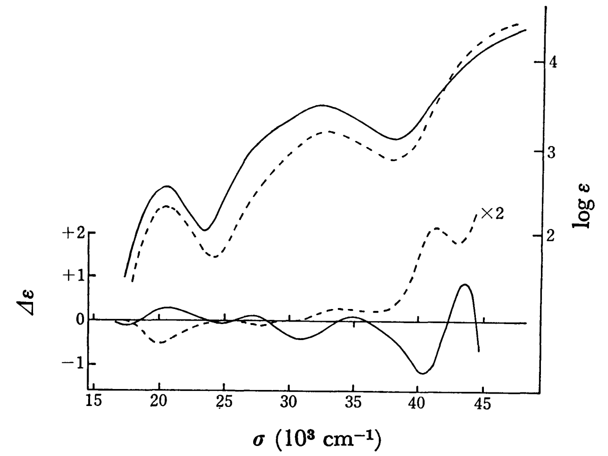

Fig. 2. Absorption and CD spectra of $(-)_{589}$-*cis*-[Co(NCS)$_2$(en)$_2$]Cl (——) and $(-)_{589}$-*cis*-[Co(NCS)(NH$_3$)(en)$_2$]Br$_2$·0.5H$_2$O (------).

The azido and isothiocyanato complexes show very similar absorption curves to each other (Figs. 1 and 2). The specific absorption band at 33000 cm^{-1} of *cis*-[Co(N$_3$)$_2$(en)$_2$]$^+$ is 1.23 times as broad (and 1.45 times as intense) as that of *cis*-[Co(N$_3$)(NH$_3$)(en)$_2$]$^{2+}$. The same situation is also found for the isothiocyanato complexes, that is, the specific band at 32700 cm^{-1} of *cis*-[Co(NCS)$_2$(en)$_2$]$^+$ is 1.23 times as broad (and 1.70 times as intense) as that of *cis*-[Co(NCS)(NH$_3$)(en)$_2$]$^{2+}$. This absorption behavior concerning the band width of the azido and isothiocyanato complexes is quite a contrast to that of the corresponding nitro complexes, where the *cis* dinitro complex shows the specific band similar in width to the amminenitro one (Fig. 3). The absorption band broadening in the diazido and diisothiocyanato complexes suggests a band splitting, and this is confirmed from the CD spectra as above. It has been pointed out in earlier days for isothiocyanato complexes of chromium(III),$^{1)}$ and isothiocyanato$^{3)}$ and nitro$^{2)}$ complexes of cobalt(III) that the specific band intensity is proportional to the number of the coordinated particular ligand, and this has been taken as an evidence for the theory that the specific band is due to the intraligand transition. As for the present complexes the (dianiono/ammineaniono) ratio of integrated intensities of the specific bands is approximately 2 for all of the azido, isothiocyanato, and nitro ligands. It is significant, however, in the case of the diazido and diisothiocyanato complexes, that the specific bands are shifted to the lower energy side than the corresponding ammineaniono complexes, and that the shift direction is the same as that of the first d-d absorption bands. The parallel shift of the specific and the first d-d bands may be taken as an evidence of the theory that the specific absorption band is due to the ligand-to-metal charge transfer transition, because the wider is the separation between the occupied d$_\pi$ and the empty d$_\sigma$ orbitals, the higher should be the energy of the charge transfer transition from the almost unaffected ligand orbital to the empty d$_\sigma$ orbital.

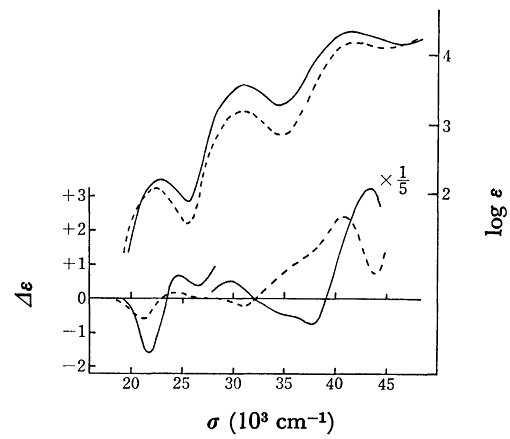

Fig. 3. Absorption and CD spectra of $(-)_{589}$-*cis*-[Co(NO$_2$)$_2$(en)$_2$]Cl (——) and $(-)_{589}$-*cis*-[Co(NO$_2$)(NH$_3$)(en)$_2$]SO$_4$·H$_2$O (------).

Miskowsky and Gray$^{10)}$ assigned the isothiocyanato specific band to the π(ligand)→d$_{z^2}$(metal) transition as in the case of the longer wavelength charge transfer bands of amminehalogeno cobalt(III) complexes. As for the latter halogeno charge transfer bands, Yamatera$^{21)}$ established the assignments that the longer and the shorter wavelength charge transfer bands are due to the p$_\pi$(ligand)→d$_{z^2}$(metal) and p$_\sigma$(ligand)→d$_{z^2}$(metal) transitions, respectively. The p$_\pi$(ligand)→d$_{z^2}$(metal) transition of a C_{4v} complex such as [CoX(NH$_3$)$_5$]$^{2+}$ is expected to split into two transitions for a C_{2v} complex such as *cis*-[CoX$_2$(NH$_3$)$_4$]$^+$.$^{22)}$ If it is presumed that the chelate ring effect of ethylenediamine is negligible, and the ligand fields of the diamine and the ammine are quite the same, the symmetry of *cis*-[CoX(NH$_3$)(en)$_2$]$^{2+}$ is approximated to C_{4v} and that of *cis*-[CoX$_2$(en)$_2$]$^+$ to C_{2v}. Then, the splitting of the specific absorption band in the diisothiocyanato complex can reasonably be explained by the theory that the isothiocyanato specific bands are due to the charge transfer transitions from π orbitals of the pseudohalogeno ligand to the lower empty d$_\sigma$ orbital (d$_{z^2}$) of the central cobalt(III) ion. The similarity of the azido and isothiocyanato complexes in the CD and absorption spectra may be related to the fact that both the ligands are linear triatomic pseudohalide ions having sixteen valence electrons.$^{23)}$ Therefore the azido specific band is also considered to be the ligand-to-metal charge transfer band.

In Fig. 3 the CD curves of the remaining pair of the mono- and dianiono type complexes, $(-)_{589}$-[Co(NO$_2$)(NH$_3$)(en)$_2$]$^{2+}$ and $(-)_{589}$-[Co(NO$_2$)$_2$(en)$_2$]$^+$, are shown with their absorption curves. In these complexes the second d-d absorption band is completely overlapped with the nitro specific band. Both the dinitro and amminenitro complexes show two CD bands of opposite signs in the region. However, if the weak CD band of the amminenitro complex in the lower energy side is assumed to correspond to a component of the second d-d absorption band, the more intense CD band in the higher energy side corresponds to the specific band. It may be unreasonable to consider the nitro specific band in the same way as the pseudohalogeno specific band, because the NO_2^- ligand is much different from the N_3^- and NCS^- ligands, that is, the latter two ions are linear pseudohalides which have no absorption band in the near ultraviolet region,[23] while the former nonlinear ion has two weak absorption bands in this region, which have been assigned to $n \rightarrow \pi^*$ transitions.[24] Nevertheless, it is found experimentally that the CD behavior in the nitro specific band region rather resembles that in the pseudohalogeno specific band region.

For the second intense absorption band in the higher energy region (38000—45000 cm^{-1}) of the $(-)_{589}$ nitro complexes, a positive CD band is observed for the amminenitro complex and two CD bands of opposite signs, negative and positive from lower energy side, are observed for the dinitro one (Fig. 3). A similar splitting of the shorter wavelength CD band is also observed for the diisothiocyanato complex. That is, the complex has two CD bands of opposite signs in the region of 37000—44000 cm^{-1}, while the corresponding ammineisothiocyanato complex has only one CD band in this region (Fig. 2 and Table 1).

In Figs. 4—6 the absorption and CD curves of the three mixed complexes of the *cis*-$[Co(X)(X')(en)_2]^+$ type containing different two of N_3^-, NCS^-, and NO_2^- are shown together with the absorption curves of the "parent complexes," *cis*-$[Co(X)_2(en)_2]^+$ and *cis*-$[Co(X')_2(en)_2]^+$. The d-d absorption band positions of the mixed complexes are nearly intermediate between those of the parent ones, but the d-d band intensities are not necessarily intermediate. In the region of specific absorption bands, the absorption curves of the mixed complexes are nearly intermediate between those of the parent ones, but not exactly so, especially for the azidoisothiocyanato complexes. The deviation seems to suggest an interaction between two aniono ligands in the *cis* positions through the central cobalt(III) ion.

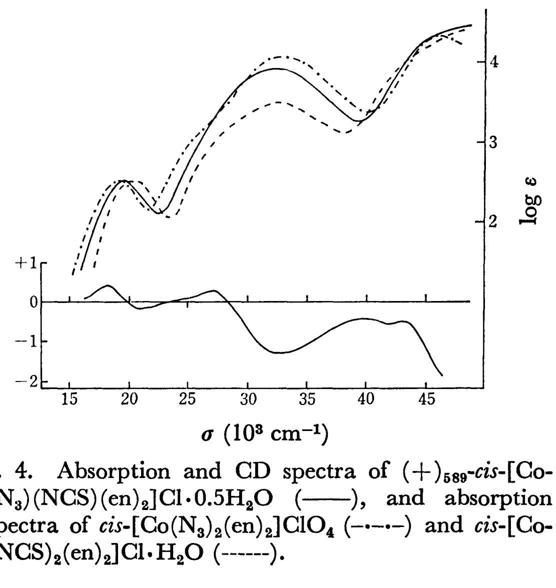

Fig. 4. Absorption and CD spectra of $(+)_{589}$-*cis*-$[Co(N_3)(NCS)(en)_2]Cl\cdot 0.5H_2O$ (——), and absorption spectra of *cis*-$[Co(N_3)_2(en)_2]ClO_4$ (-·-·-) and *cis*-$[Co(NCS)_2(en)_2]Cl\cdot H_2O$ (------).

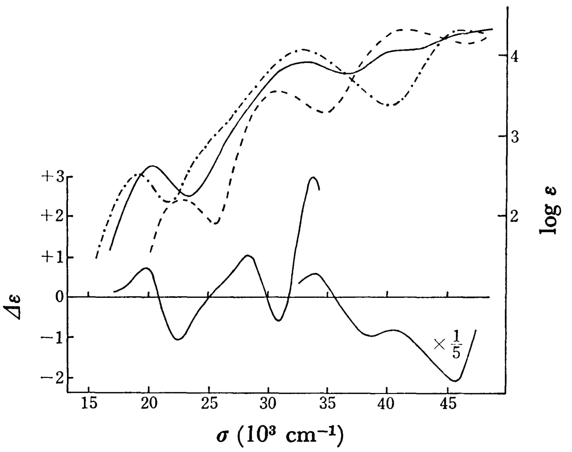

Fig. 5. Absorption and CD spectra of $(+)_{589}$-*cis*-$[Co(N_3)(NO_2)(en)_2]ClO_4$ (——), and absorption spectra of *cis*-$[Co(N_3)_2(en)_2]ClO_4$ (-·-·-) and *cis*-$[Co(NO_2)_2(en)_2]ClO_4$ (------).

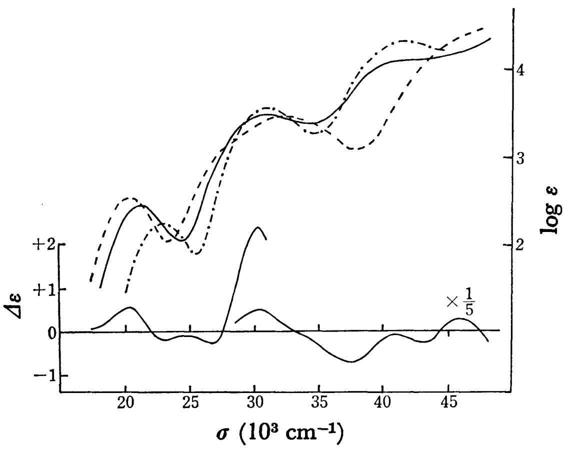

Fig. 6. Absorption and CD spectra of $(+)_{589}$-*cis*-$[Co(NCS)(NO_2)(en)_2]Cl$ (——), and absorption spectra of *cis*-$[Co(NCS)_2(en)_2]Cl\cdot H_2O$ (------) and *cis*-$[Co(NO_2)_2(en)_2]ClO_4$ (-·-·-).

The ultraviolet CD of the mixed complexes is too complicated to interpret systematically, and this may be also the reflection of the symmetry lowering and the interaction between the ligands. A comparison of the CD curves of the mixed complexes with those of the parent complexes having the same absolute configuration and further with their average CD curves was attempted on trial, but any simple regularity was not found.

Absolute Configurations of the Complexes. McCaffery *et al.*[25] have correlated the CD pattern in the first d-d absorption band of a bis(ethylenediamine) cobalt(III) complex with its absolute configuration by employing a model, in which a *cis*-$[Co(X)_2(en)_2]^+$ complex with C_2 symmetry is regarded as an intermediate between $[Co(en)_3]^{3+}$ with D_3 symmetry and *cis*-$[Co(X)_2(NH_3)_4]^+$ with C_{2v} symmetry. When the ligand X lies far above or below the ethylenediamine ligand in the spectrochemical series, the complex is near the C_{2v} limit, and the major one of the two CD components is observed closer in energy to the first d-d absorption band of $[Co(en)_3]^{3+}$ than the minor CD component. Then the positive major CD component is correlated to the positive E_a component of Λ-$(+)_{589}$-$[Co(en)_3]^{3+}$.[26] From this criterion and the CD data in Table 1, the absolute configuration Δ was assigned to the two present dianiono complexes, $(+)_{589}$-diazido and $(-)_{589}$-dinitro complexes, and Λ to the remaining $(-)_{589}$-diisothiocyanato complex. The absolute configuration of $(-)_{589}$-dinitro complex has been determined as Δ by an X-ray analysis.[27]

The same treatment can be applied to the mixed complexes of the *cis*-$[Co(X)(X')(en)_2]^+$ type by regarding them as the *cis*-$[Co(Z)_2(en)_2]^+$ complexes, where Z is an imaginary unidentate ligand having the average ligand strength of X and X', if X and X' are not so different in the ligand strength from each other. Thus the $(-)_{589}$ isomer of *cis*-$[CoCl(NCS)(en)_2]^+$, which has the major positive CD component at the higher energy side in the first absorption band region, was assigned to Λ. The $(+)_{589}$ isomer of *cis*-$[Co(N_3)(NCS)(en)_2]^+$ complex was assigned to Δ, because the higher energy CD component of the this isomer has a negative sign ($\Delta\varepsilon = -0.20$), though this negative component is not the major one.

As for the ammineaniono complexes, the isomers having a negative CD band in the first d-d absorption band region, that is, $(-)_{589}$-ammineazido and $(-)_{589}$-ammineisothiocyanato, were assigned to the Δ configuration according to Norman's proposal.[28] The Λ configuration of $(+)_{589}$-ammineisothiocyanato complex is consistent with the fact that this isomer was derived from the Λ-$(-)_{589}$-chloroisothiocyanato complex.

Garbett and Gillard[29] derived the $(+)_{589}$ isomer of amminenitro complex from the Λ-$(-)_{589}$-$[CoCl(NCS)(en)_2]^+$ through $(+)_{589}$-$[Co(NCS)(NO_2)(en)_2]^+$. This means that the configuration of $(-)_{589}$-amminenitro isomer in Table 1 is Δ, which has a major negative CD component at the lower energy side in the first absorption band region. It is consistent with the results for the other Δ nitro mixed complexes such as $(-)_{589}$-dinitro,[27] $(-)_{589}$-chloronitro,[29] and $(-)_{546}$-cyanonitro[30] complexes. In this relation, the present two mixed complexes, $(+)_{589}$-$[Co(N_3)(NO_2)(en)_2]^+$ and $(+)_{589}$-$[Co(NCS)(NO_2)(en)_2]^+$, were assigned to the Λ absolute configuration, because both the two complexes have a positive CD component at the lower energy side in the first absorption band region (Table 2).

TABLE 3. ABSOLUTE CONFIGURATIONS OF THE OPTICAL ISOMERS FORMING THE LESS SOLUBLE DIASTEREOMERS

Complex ion	Resolving agent	Optical rotation	Absolute configuration
(1) *cis*-$[Co(N_3)(NH_3)(en)_2]^{2+}$	a)	$(-)_{589}(-)_{546}$	Δ
(2) *cis*-$[Co(N_3)_2(en)_2]^+$	b)	$(+)_{589}(-)_{546}$	Δ
(3) *cis*-$[Co(NCS)(NH_3)(en)_2]^{2+}$	c)	$(+)_{589}(+)_{546}$	Λ
(4) *cis*-$[Co(NCS)_2(en)_2]^+$	b)	$(-)_{589}(+)_{546}$	Λ
(5) *cis*-$[Co(NO_2)(NH_3)(en)_2]^{2+}$	a)	$(-)_{589}(-)_{546}$	Δ
(6) *cis*-$[Co(NO_2)_2(en)_2]^+$	b)	$(-)_{589}(-)_{546}$	Δ
(7) *cis*-$[Co(N_3)(NCS)(en)_2]^+$	a)	$(+)_{589}(-)_{546}$	Δ
(8) *cis*-$[Co(N_3)(NO_2)(en)_2]^+$	a)	$(+)_{589}(+)_{546}$	Λ
(9) *cis*-$[Co(NCS)(NO_2)(en)_2]^+$	b)	$(+)_{589}(+)_{546}$	Λ
(10) *cis*-$[CoCl(NCS)(en)_2]^+$	a)	$(-)_{589}(+)_{546}$	Λ

a) NH_4(*d*-bcs). b) $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$. c) Derived from Λ- $(-)_{589}$ -$[CoCl(NCS)(en)_2]^+$.

The assignments of absolute configurations for the present ten complexes are collected in Table 3. From this table and the CD signs of the "specific band" (Tables 1 and 2), the following relationship is obtained. In the ammineaniono complexes, all the Λ isomers show a negative CD band in the regions of the specific absorption bands, if a weak CD band of the amminenitro complex at 31000 cm^{-1} is neglected. As mentioned already, this longer-wavelength weak CD band may be due to the second d-d absorption band, which is completely overlapped with the nitro specific band. In the dianiono complexes, Λ isomers show regularly a CD pattern of negative and then positive signs in the order of increasing energy (Figs. 1—3). In the mixed type complexes, *cis*-$[Co(X)(X')(en)_2]^+$ (X and X'$=N_3^-$, NCS^-, or NO_2^-), the CD patterns are complicated, but the following regularity is found out for the specific band region; that is, the dominant CD band in this region is positive for all of their Λ isomers (Figs. 4—6).

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