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Cobalt(III) Complexes Derived from 1,8-Diamino-3,6-dithiaoctane. II.[1] Stereochemistry and Absolute Configurations

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The chemical methods used to resolve *s-cis*-[Co(eee)Cl$_2$]Cl and *s-cis*-[Co(eee)(NO$_2$)$_2$]Cl into both of their optically pure isomers are presented.[2] Optical rotatory dispersion and circular dichroism spectra for the following complex cations are recorded:[3] (+)-*s-cis*-Co(eee)Cl$_2^+$, (+)-*s-cis*-Co(eee)ClH$_2$O^{2+}, (+)-*s-cis*-Co(eee)(H$_2$O)$_2^{3+}$, (+)-*s-cis*-Co(eee)(OH)$_2^+$, (−)-*s-cis*-Co(eee)CO$_3^+$, and (−)-*s-cis*-Co(eee)(NO$_2$)$_2^+$. The relative and absolute configurations of these complex ions are assigned and discussed with a view toward recent advances in the interpretation of circular dichroism curves, in conjunction with interconversion reactions which occur with retention of configuration. Unlike the corresponding compounds of triethylenetetramine, these ions do not isomerize from D-*s-cis* to L-*uns-cis* in the presence of hydroxide ion. The magnitudes of circular dichroism ($\epsilon_l - \epsilon_d$), associated with electronic transitions in the range 740–340 mμ, for cobalt(III) complexes containing pairs of thioether and primary amine groups are two to seven times as intense as those observed for diacidocobalt(III) complexes with nitrogen or nitrogen–oxygen donor atoms.

Introduction

The preparation, characterization, and several general reactions of the diacidocobalt(III) complexes derived from 1,8-diamino-3,6-dithiaoctane have been described in a previous paper.[1] To date only one geometrical isomer has been isolated for the metal chelate compounds prepared from 1,8-diamino-3,6-dithiaoctane. It has the symmetrical *cis* arrangement in which the two terminal primary amine groups are coordinated *trans* to each other. Figure 1 presents the orientation of donor atoms for the D and L optical isomers having both the symmetrical *cis* and the unsymmetrical *cis* geometries. The two *cis* forms are denoted *s-cis* and *uns-cis*. If one eliminates the central backbone ethylene bridges in Figure 2, it becomes apparent that the D-*s-cis* and L-*uns-cis* isomers of Co(eee)L$_2^{n+}$ are related structurally as are D- and L-Co(en)$_2$L$_2^{n+}$ isomers. This is significant because in the course of any reaction such as is illustrated by Figure 2, a change from *s-cis* to *uns-cis* would be detected immediately by examining the optical rotatory dispersion or circular dichroism spectra associated with reactant and product. Such a change, an isomerization which results in a change in the absolute configuration of the complex, would be reflected in a change in shape of the rotatory dispersion curves and a change in sign of the associated circular dichroism band. In this way, any stereochemical change involving the relocation of a terminal –NH$_2$ group in the eee complexes may be followed during substitution reactions.

In this communication we report the results of an extensive stereochemical study designed to provide information related to the relative and absolute configurations for complex ions of the type *s-cis*-Co(eee)L$_2^{n+}$. In addition, this study reaffirms the assignment of the symmetrical *cis* geometry[1] and the absence of isomerization reactions which lead to the production of *uns-cis* isomers, even in the presence of hydroxide ion. This latter aspect is in striking contrast to the stereochemical behavior exhibited by cobalt(III) complexes of triethylenetetramine.[4–7]

Experimental Section

Optical Rotations.—Optical rotations were determined with a Rudolph high-precision photoelectric polarimeter equipped with a mercury arc lamp and a Beckman monochromator. The instrument zero was determined before and after each measurement using the same 10-cm cell and solvent as employed for the sample. All rotations are an average of at least six sets of readings and are accurate to 1% unless otherwise indicated. Rotations are listed as specific rotations and were calculated using the relationship

$$[\alpha]_\lambda = \frac{100\alpha}{\text{grams of solute/100 ml of H}_2\text{O}}$$

where $[\alpha]_\lambda$ is the specific rotation and α is the experimentally observed rotation.

Samples of 4–30 mg were accurately weighed to ±0.001 mg using a Sartorius MPRS Electromicrobalance.

Optical Rotatory Dispersion Curves.—ORD data were obtained using a Bendix Model 460-C Polarmatic recording spectropolarimeter.

Circular Dichroism Spectra.—The CD measurements were made using a Roussel-Jouan Dichrograph equipped with cells 2 and 5 cm in length. A base line was recorded for each spectrum using the same cell and solvent as for the sample. The formula for relating the measured data to circular dichroism is given by

$$\epsilon_l - \epsilon_d = \frac{d \times \text{sensitivity} \times 10^{-4} \times \text{MW}}{c \times l}$$

where d is the distance between the measured curve and the base line in millimeters, MW is the molecular weight of the complex, c is the concentration of solute in grams per liter, and l is the length of the cell in centimeters. Spectra were recorded at a scan speed of 4 sec/mμ.

Analyses.—Nitrogen analyses were obtained in these laboratories using a Coleman nitrogen analyzer. All other microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

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[1] For part I see *Inorg. Chem.*, **8**, 1563 (1969).

[2] eee = NH$_2$CH$_2$CH$_2$SCH$_2$CH$_2$SCH$_2$CH$_2$NH$_2$.

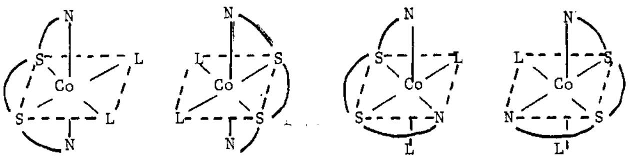
[3] The optical isomers are denoted by the sign of rotation observed at the mercury green line, 546 mμ, or if another wavelength is used, then the wavelength appears as a subscript, *e.g.*, $(+)_{589}$.

[4] G. H. Searle, Ph.D. Thesis, Australian National University, 1963.

[5] E. Kyuno, L. G. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965).

[6] E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1120 (1966).

[7] E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1125 (1966).



D-s-cis L-s-cis L-u-cis D-u-cis

I II III IV

Figure 1.—The optical isomers of *cis*-Co(eee)L_2^{n+}.

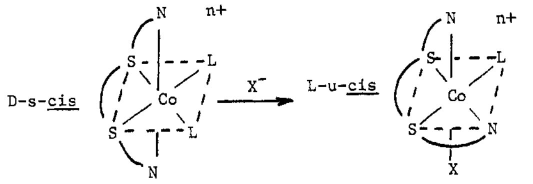


Figure 2.—The isomerization reaction D-*s-cis*-Co(eee)L_2^{n+} → L-*uns-cis*-Co(eee)LX^{n+}.

Resolution of Complexes. **(+)-*s-cis*-Dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Iodide Monohydrate.**—Sodium $(-)_{589}$-bis(oxalato)(ethylenediamine)cobaltate(III) (1.3 g, 3.99 × 10^{-3} mol),[8] with $[\alpha]_{546}$ +1442°, was dissolved in 25 ml of water at 50° and was added to a solution containing (±)-*s-cis*-[Co(eee)$(NO_2)_2$]Cl·H_2O (3.0 g, 7.99 × 10^{-3} mol)[9] also dissolved in 25 ml of water at 50°. Rust-colored needles began to form almost immediately. The solution was allowed to cool slowly for 5 min and was filtered warm, yielding 1.80 g of $(-)_{589}$-[Co(en)$(ox)_2$]-$(+)_{546}$-[Co(eee)$(NO_2)_2$]·$2H_2O$ as the diastereoisomer. A second crop of needles (0.30 g) was obtained by cooling the solution to 0°. The total yield was 2.1 g. The filtrate from above was saved for the recovery of the $(-)_{546}$ isomer.

The diastereoisomer was washed with ethanol and ether, the washings being discarded, and then was air dried. An aqueous solution of the crude diastereoisomer (3.89 × 10^{-2} g/100 ml) gave α +0.486° which corresponds to $[\alpha]_{546}$ +1249 ± 10°. Repeated recrystallizations (five times) from warm water (50°) and ethanol showed that the diastereoisomer reached its maximum specific rotation after two recrystallizations. An aqueous solution of the purified diastereoisomer (3.81 × 10^{-2} g/100 ml) gave α +0.489° which corresponds to $[\alpha]_{546}$ +1883 ± 16°.

Anal. Calcd for [Co$(C_2H_8N_2)(C_4O_8)$][Co$(C_6H_{16}N_2S_2)(NO_2)_2$]·$2H_2O$: C, 21.75; H, 3.93; N, 12.69; S, 9.67. Found: C, 21.81; H, 4.06; N, 12.64; S, 9.69.

The diastereoisomer (1.8 g) was decomposed by grinding it in a mortar with 20 ml of warm (40°), aqueous, saturated sodium iodide solution for a period of 30 min. The mixture was filtered, the purple filtrate being set aside for recovery of the resolving agent. The orange solid was again ground with 10 ml of warm sodium iodide solution and the above process was repeated several times. The product is washed with ethanol and ether and air dried. The yield of $(+)_{546}$-[Co(eee)$(NO_2)_2$]I·H_2O was 0.65 g.

The filtrates were combined, reduced to half the original volume under a stream of air, and placed in the refrigerator overnight. The diastereoisomer which crystallized as rust-colored needles (0.65 g) was recovered by filtration, washed, and dried as before. By repeating the above process, a total of 1.20 g (78%) of $(+)_{546}$-[Co(eee)$(NO_2)_2$]I·H_2O was collected. An aqueous solution (4.87 × 10^{-2} g/100 ml) of this crude product gave α +0.290° which corresponds to $[\alpha]_{546}$ +595 ± 10°. Repeated recrystallizations (three times) from warm water and ethanol increased the specific rotation only 9°. An aqueous solution (3.51 × 10^{-2} g/100 ml) gave α +0.212° which corresponds to $[\alpha]_{546}$ +604 ± 6°.

Anal. Calcd for [Co$(C_6H_{16}N_2S_2)(NO_2)_2$]I·$H_2O$: C, 15.13; H, 3.57; N, 11.77; S, 13.45. Found: C, 15.20; H, 3.57; N, 11.80; S, 13.47.

The $(+)_{546}$-[Co(eee)$(NO_2)_2$]I·H_2O was easily converted to the more insoluble perchlorate salt by adding sodium perchlorate to a warm, aqueous solution of the iodide. Long orange needles formed as the warm solution slowly cooled. The product was collected by filtration, washed with ethanol and acetone, and air dried. An aqueous solution (3.16 × 10^{-2} g/100 ml) gave α +0.196° which corresponds to $[\alpha]_{546}$ +618 ± 10°.

$(-)_{546}$-*s-cis*-Dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Iodide Monohydrate.—Immediately after the diastereoisomer was removed from the solution, the filtrate was warmed to 40° and solid sodium iodide (0.68 g) was added. Crystallization was allowed to proceed for 5 min; then the solution was filtered quickly.[8] The yellow product was washed with ethanol and ether and air dried; yield, 0.60 g. An aqueous solution of the crude product (4.39 × 10^{-2} g/100 ml) gave α −0.260° which corresponds to $[\alpha]_{546}$ −592 ± 10°. Repeated recrystallization (three times) did not improve the specific rotation of the first fraction beyond −604°. An aqueous solution of the recrystallized $(-)_{546}$-*s-cis*-[Co(eee)$(NO_2)_2$]I·H_2O (4.08 × 10^{-2} g/100 ml) gave α −0.245° which corresponds to $[\alpha]_{546}$ −602 ± 10°.

Anal. Calcd for [Co$(C_6H_{16}N_2S_2)(NO_2)_2$]I·$H_2O$: C, 15.13; H, 3.57; N, 11.77; S, 13.45. Found: C, 15.25; H, 3.45; N, 11.83; S, 13.46.

The $(-)_{546}$-[Co(eee)$(NO_2)_2$]I·H_2O was easily converted to the more insoluble perchlorate salt by adding sodium perchlorate to a warm, aqueous solution of the iodide. The product was collected by filtration, washed with ethanol and acetone, and air dried. An aqueous solution (3.36 × 10^{-2} g/100 ml) gave α −0.206° which corresponds to $[\alpha]_{546}$ −612 ± 10°.

$(+)_{546}$-*s-cis*-Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.—Once recrystallized, *s-cis*-dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) chloride (6.00 g, 0.017 mol)[9] was dissolved in 100 ml of water at 40°. To this solution was added potassium antimony *d*-tartrate (2.95 g, 0.0087 mol) dissolved in 40 ml of water at 80°. The beaker containing the resolving agent was rinsed with 10 ml of hot water, the washings being added to the solution. After the mixture was allowed to stand for 10 min at about 35°, it was placed in the refrigerator for 30 min or until the temperature of the mixture was 15–20°. The fine purple-blue needles of diastereoisomer (4.28 g) were collected by filtration and washed with 40 ml of ethanol. An additional 1.14 g of diastereoisomer and complex was obtained by cooling the filtrate to 0° for several hours. The product was collected by filtration and the filtrate was set aside for the recovery of $(-)_{546}$-[Co(eee)Cl_2]Cl.

The diastereoisomer of $(+)_{546}$-[Co(eee)Cl_2][SbO-*d*-tart] (4.28 g, $[\alpha]_{546}$ +934 ± 20°) was recrystallized by dissolution in 300 ml of 7 *M* acetic acid at 70° followed by filtration and rapid cooling to 0° in an ice bath. The most insoluble fraction (2.54 g, $[\alpha]_{546}$ +1188 ± 20°) was collected by filtration, washed with ethanol, acetone, and ether, and air dried. Three recrystallizations from 7 *M* acetic acid will not improve the rotation beyond +1225°. A second crop of fine blue needles (0.76 g, $[\alpha]_{546}$ +1120 ± 20°) was obtained by adding 100 ml of absolute ethanol to the filtrate and cooling the solution for several hours at 0°.

Anal. Calcd for [Co$(C_6H_{16}N_2S_2)Cl_2$][$SbC_4H_4O_7$]·$0.5C_2H_4O_2$: C, 20.95; H, 3.52; N, 4.47. Found: C, 20.94; H, 3.60; N, 4.57.

The pure diastereoisomer (2.54 g, $[\alpha]_{546}$ +1188 ± 20°) was dissolved at room temperature in concentrated hydrochloric acid (20 ml, 12 *N*), and 600 ml of water was added slowly followed by stirring for 30 min. The yellow-green precipitate of antimonyl oxychloride which formed was removed by filtration, washed with several 10-ml portions of water, and discarded. The filtrate was transferred to a 4-l. beaker and 2000 ml of absolute ethanol was added slowly with stirring, followed by 300 ml of absolute ether.

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[8] After this work was completed, elemental analysis of the resolving agent showed it to be a 3.5-water complex. Reagent quantities above were based on the assumption that the resolving agent was an anhydrous salt. The idealized 2:1 ratio of complex to resolving agent was thus not maintained. This additional aspect is consistent with the low yield of $(-)_{546}$ isomer. Also by cooling the filtrate, 0.65 g of very low activity complex was recovered, indicating the presence of racemic material.

[9] For preparation of racemic complexes see ref 1.

The beaker of *clear* blue solution was covered and placed in the refrigerator at about 5° overnight. Deep blue needles of optically pure material were collected by carefully decanting most of the solvent and then carefully scraping the product off the beaker walls. The product was collected by filtration (0.85 g, $[\alpha]_{546}$ $+2290 \pm 20°$), washed with ethanol and acetone, and air dried. A second fraction (0.36 g, $[\alpha]_{546} = 2250 \pm 20°$) was collected by carefully adding more ether to the above filtrate and cooling for several days at 5°. The total quantity of $(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl}$ recovered was 1.21 g or 88% based on diastereoisomer. Both fractions from above were combined and recrystallized from a 1:1 solution of concentrated hydrochloric acid (10 ml/g) and absolute ethanol (10 ml/g) yielding fine blue needles of optically pure complex. A 0.01 *N* HCl solution containing 8.05 mg/50 ml gave α $+0.372°$ whence $[\alpha]_{546}$ is $+2310 \pm 20°$. Three additional recrystallizations did not improve the rotation, $[\alpha]_{546}$, beyond $+2310 \pm 20°$.

Anal. Calcd for $[\mathrm{Co(C_6H_{16}N_2S_2)Cl_2}]\mathrm{Cl}$: C, 20.87; H, 4.64; N, 8.11; Cl, 30.78. Found: C, 20.84; H, 4.7; N, 8.03; Cl, 30.68.

$(-)_{546}$-*s-cis*-Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.—To the filtrate containing the $(-)_{546}$ isomer was added 300 ml of absolute ethanol and the solution was placed in the refrigerator at about 5° for 8 hr. The potassium chloride which first crystallized out on the walls of the flask was separated from the solution containing the $(-)_{546}$ isomer by carefully decanting the blue solution into a clean beaker. Absolute ether (300 ml) was carefully added with stirring to the decanted solution which was then cooled overnight in the refrigerator. The product, composed of fine, deep blue needles, was collected by first decanting the clear solution, then washing the product out onto a filter in a stream of acetone, and air dried. The yield was 1.20 g (40%), with $[\alpha]_{546}$ $-2075 \pm 20°$. Three more fractions were obtained totaling 0.65 g with an average rotation $[\alpha]_{546}$ $-1500 \pm 30°$; however, they required numerous recrystallizations to become optically pure. For the first fraction, five recrystallizations from concentrated hydrochloric acid (10 ml/g) and absolute ethanol (10 ml/g) did not improve the rotation, $[\alpha]_{546}$, beyond $-2313 \pm 20°$. A 0.01 *N* HCl solution containing 8.00 mg/50 ml gave a $-0.370°$ whence $[\alpha]_{546}$ is $-2313 \pm 20°$. The crude first fraction reached its maximum rotation after two recrystallizations giving 1.0 g of optically pure material.

Transformation Reactions.—The following technique was used to obtain both circular dichroism and optical rotatory dispersion spectra for the products obtained in the transformation reactions listed below.

$(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl} \rightarrow (+)_{546}$-*s-cis*-$\mathrm{Co(eee)ClH_2O^{2+}}$.—Optically pure $(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl}$ (20.47 mg/25 ml, 2.37×10^{-3} *M*) was dissolved in 25 ml of 0.01 *N* $\mathrm{HClO_4}$ or 0.01 *N* $\mathrm{HNO_3}$ and allowed to aquate at room temperature for 96 hr. The ORD and CD spectra for samples which had been aquating for 4 days, 1 week, and 2 weeks were found to be the same. The visible absorption spectrum confirmed the presence of the $\mathrm{Co(eee)ClH_2O^{2+}}$ ion.

$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)ClH_2O^{2+}} \rightarrow (-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3^+}$.—Solid sodium bicarbonate (0.05 g) was added directly to the volumetric flask containing the chloroaquo complex, and the solution slowly became pink. The reaction was complete and quantitative in 1 hr as evidenced spectrophotometrically. The pH of the solution was found to be 8 using indicator paper. When the carbonato complex was prepared directly from sodium bicarbonate (0.05 g) and $(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl}$ (20.33 mg/25 ml), the observed ORD and CD were identical with those obtained above.

$(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3^+} \rightarrow (+)_{546}$-*s-cis*$\mathrm{Co(eee)(H_2O)_2^{3+}}$.—Two or three drops of concentrated $\mathrm{HClO_4}$ or $\mathrm{HNO_3}$ was added to the volumetric flask containing the carbonato complex. The reaction, as written above, was quantitative and complete in 30 min as evidenced spectrophotometrically. The observed CD and ORD spectra were the same as those obtained by treating $(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl}$ (20.4 mg/25 ml) with Hg(II) (0.188 *M*) and allowing aquation to become complete (6 hr). Indicator paper showed pH 2 for both solutions.

$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(H_2O)_2^{3+}} \rightarrow (-)_{546}$-*s-cis*$\mathrm{Co(eee)CO_3^+}$.—A portion of the solution containing the diaquo complex from above was treated with solid sodium bicarbonate until the pH was 8 using indicator paper. The ORD and CD spectra were recorded after 1 hr and were found to be identical with those obtained previously.

$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(H_2O)_2^{3+}} \rightarrow (-)_{546}$-*s-cis*-$\mathrm{Co(eee)(NO_2)_2^+}$.—Solid sodium nitrite (0.05 g) was added to the volumetric flask containing the diaquo complex. This reaction was slower than the others and required 4–12 hr for completion. The CD and ORD band positions and signs were the same as for the optically pure $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)(NO_2)_2^+}$ ion; however, the observed intensities were different. Treatment of $(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl}$ with $\mathrm{NaNO_2}$ and $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3^+}$ with $\mathrm{HNO_3}$ and $\mathrm{NaNO_2}$ produced the same ORD and CD spectra as observed above.

$(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)Cl_2}]\mathrm{Cl} \rightarrow (+)_{546}$-*s-cis*-$\mathrm{Co(eee)(OH)_2^+}$.—Three equivalents of sodium hydroxide (0.21 ml of 1.00 *N*) was added (using a 1.0-ml hypodermic syringe) to 20.11 mg of complex dissolved in 20 ml of water. The 25-ml volumetric flask was then diluted to the mark. The reaction was complete within 15 min. Using indicator paper, the pH was 8. At pH 8, the ORD and CD spectra were invariant for several hours. A portion of this solution (10 ml) was made extremely basic, pH 10, and the ORD and CD spectra were recorded over a period of several hours. The intensities slowly decreased but no inversion was observed.

$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(OH)_2^+} \rightarrow (-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3^+}$.—Solid sodium bicarbonate (0.05 g) was added to the volumetric flask containing the dihydroxo complex, the ORD and CD spectra being recorded 0.5 hr later. At pH 8, the carbonato species so produced gave ORD and CD curves identical with those observed previously. At pH 10, the dihydroxo species was converted to the carbonato complex which had the same ORD and CD as observed before; however, with lower intensities.

$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(NO_2)_2^+} \rightarrow (-)_{546}$-*s-cis*-$\mathrm{Co(eee)Cl_2^+}$.—Concentrated hydrochloric acid (20 drops) was added to 12 mg of solid $(+)_{546}$-*s-cis*-$[\mathrm{Co(eee)(NO_2)_2}]\mathrm{ClO_4}$ which had $[\alpha]_{546}$ $+618°$. The mixture was warmed (60°) until the solution became clear blue (about 20 min). Absolute ethanol (5.0 ml) was added and the clear solution was cooled. The fine blue needles were collected by filtration, washed with ethanol and acetone, and air dried. The yield was quantitative. A 0.01 *N* HCl solution containing 4.28 mg/25 ml gave α $-0.338°$ whence $[\alpha]_{546}$ is $-1960 \pm 15°$.

Results and Discussion

The assignment of absolute configuration from circular dichroism measurements has been reported by Mason,[10,11] who has developed several criteria for assigning the electronic circular dichroism transitions and absolute configuration for the *cis* $\mathrm{Co(en)_2L_2}^{n+}$ ions of C_2 symmetry. Whether the unidentate ligand L lies above or below the amines in the spectrochemical series, the major of the two circular dichroism bands always lies closer in energy than the minor band to the center of gravity of the ${}^1E_a$ and ${}^1A_2$ circular dichroism bands of D-$\mathrm{Co(en)_3}^{3+}$. In D_3 symmetry, the more intense CD band is assigned as the ${}^1A_1 \rightarrow {}^1E_a$ transition, whereas in complexes of C_2 symmetry, it is considered a composite transition, $A_1 \rightarrow A_2(E_a) + B_2(E_a)$. If the transition with E_a parentage shows a positive Cotton effect, then the complex possesses the D absolute configuration as in the trigonal ion D-$\mathrm{Co(en)_3}^{3+}$. If the dominant E_a

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(10) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(11) S. F. Mason *Quart. Rev.* (London), **17**, 20 (1963).

transition associated with the long-wavelength absorption band has a negative Cotton effect, then the metal complex is of the L absolute configuration.

Using this formalism, the electronic circular dichroism transitions associated with the lowest energy d–d visible absorption band, for the *s-cis*-$Co(eee)L_2^{n+}$ ions, can be assigned using the energy level diagram presented in Figure 3.

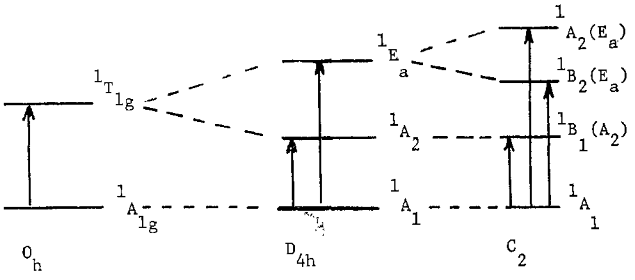

Figure 3.—Energy levels for electronic circular dichroism transitions.

Circular Dichroism Measurements.—The circular dichroism spectra for the $(+)_{546}$-*s-cis*-$Co(eee)Cl_2^+$, $(+)_{546}$-*s-cis*-$Co(eee)ClH_2O^{2+}$, $(+)_{546}$-*s-cis*-$Co(eee)(H_2O)_2^{3+}$, $(+)_{546}$-*s-cis*-$Co(eee)(OH)_2^+$, $(-)_{546}$-*s-cis*-$Co(eee)CO_3^+$, and $(-)_{546}$-*s-cis*-$Co(eee)(NO_2)_2^+$ ions are shown in Figures 4 and 5. All of these ions have C_2 symmetry except the *s-cis*-$Co(eee)H_2OCl^{2+}$ ion and it is assumed to approximate C_2 symmetry.

Figure 4 illustrates the circular dichroism spectra characteristic of the $(+)_{546}$-*s-cis*-$Co(eee)Cl_2^+$, $(+)_{546}$-*s-cis*-$Co(eee)ClH_2O^{2+}$, and $(+)_{546}$-*s-cis*-$Co(eee)(H_2O)_2^{3+}$ ions. Immediately, the most striking difference between the CD spectra of these three ions and the corresponding bis(ethylenediamine) and triethylenetetramine complexes of cobalt(III) is that the intensities of all of the observed electronic transitions between 740 and 340 mμ are generally from two to seven times greater for the *s-cis*-$Co(eee)L_2^{n+}$ ions. The CD data for the $Co(en)_2L_2^{n+}$ and *s-cis*-$Co(trien)L_2^{n+}$ ions are presented in Tables I and II, respectively. Using the formalism suggested by Mason,[10] the low-energy band exhibiting a negative Cotton effect is assigned in each case to the $A_1 \rightarrow B_1(A_2)$ transition and the higher energy component showing a positive Cotton effect is considered as the composite transition $A_1 \rightarrow A_2(E_a) + B_2(E_a)$.

The lowest energy CD component for the $(+)_{546}$-*s-cis*-$Co(eee)(H_2O)_2^{3+}$ ion is of greater intensity than the second band exhibiting a positive Cotton effect. This suggests that this low-energy band may represent a composite transition $^1A_1 \rightarrow {}^1B_1(A_2) + {}^1B_2(E_a)$. Accordingly, the positive Cotton effect observed for this ion may then be due to the $^1A_1 \rightarrow {}^1A_2(E_a)$ transition. Only two electronic CD components are evident in the lowest energy d–d visible absorption band and both components simultaneously shift to higher energy in accordance with the normal spectrochemical series $(+)_{546}$-*s-cis*-$Co(eee)Cl_2^+$, $(+)_{546}$-*s-cis*-$Co(eee)ClH_2O^{2+}$, and $(+)_{546}$-*s-cis*-$Co(eee)(H_2O)_2^{3+}$. The energy difference between these two components decreases in the series 2550, 2400, and 1460 cm^{-1} for the dichloro, aquochloro, and diaquo ions, respectively. In all three cases, the second CD component is positive and lies closest to the reference $^1A_1 \rightarrow {}^1E_a$ transition positioned at 493 mμ for D-$Co(en)_3^{3+}$. In addition, the sign pattern observed for the Cotton effect for these three

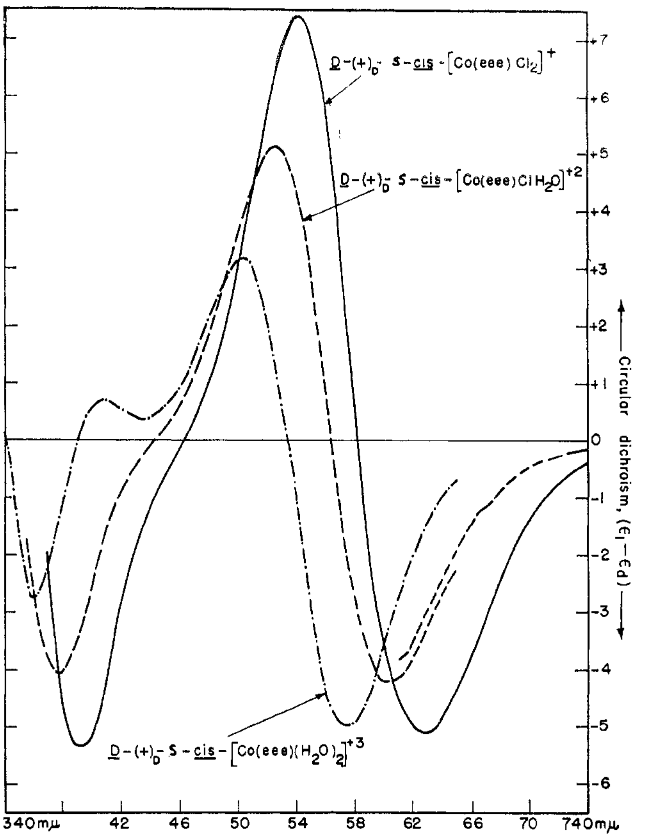

Figure 4.—CD spectra for the dichloro-, aquochloro-, and diaquo-(1,8-diamino-3,6-dithiaoctane)cobalt(III) ions.

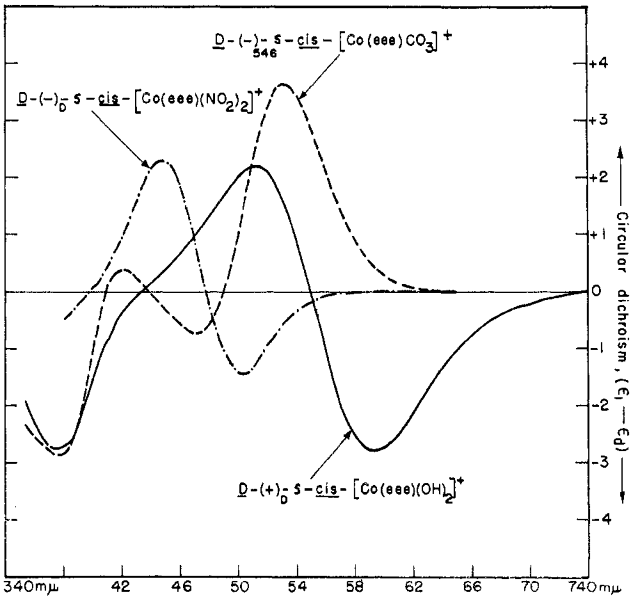

Figure 5.—CD spectra for the dihydroxo-, carbonato-, and dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) ions.

TABLE I

CD DATA FOR *cis*-$\mathrm{Co(en)_2L_2}^{n+}$ IONS

Complex	$\lambda_{\max}$, Å	$(\epsilon_l - \epsilon_d)_{\max}$	Transition
(+)D-$\mathrm{Co(en)_3}^{3+}$	4930	+1.89	$\mathrm{E_a}$
(D_3 symmetry)	4280	−0.16	$\mathrm{A_2}$
	3510	+0.25	$\mathrm{E_b}$
(+)D-$\mathrm{Co(en)_2(NH_3)_2}^{3+}$	4920	+0.42	$\mathrm{E_a}$
(C_2 symmetry)	4300	−0.04	$\mathrm{A_2}$
	3560	+0.05	$\mathrm{E_b}$
(+)D$\mathrm{Co(en)_2Cl_2}^{+}$	6150	−0.60	$\mathrm{B_1}$
	5380	+0.70	$\mathrm{(A_2 + B_2)}$
	4200	+0.20	
	3000	−1.10	
(+)D-$\mathrm{Co(en)_2CO_3}^{+}$	5300	+3.70	$\mathrm{(A_2 + B_1 + B_2)}$
	3900	+0.27	
	3630	−0.10	
	3440	+0.15	
(+)D-$\mathrm{Co(en)_2(H_2O)_2}^{3+}$	5600	−0.30	$\mathrm{B_1}$
	4850	+1.05	$\mathrm{(A_2 + B_2)}$
	3780	+0.20	
	3400	+0.15	
(+)D-$\mathrm{Co(en)_2(NO_2)_2}^{+}$	4600	+1.40	$\mathrm{(A_2 + B_2)}$
	4000	−0.65	$\mathrm{B_1}$
	3360	+0.15	

TABLE II

CD DATA FOR *s-cis*-$\mathrm{Co(trien)L_2}^{n+}$ COMPLEXES

s-cis complex	$\lambda_{\max}$, Å	$(\epsilon_l - \epsilon_d)_{\max}$	Transition
(+)D-$\mathrm{Co(trien)Cl_2}^{+}$	5950	−1.6	$\mathrm{B_1}$
	5250	+2.9	$\mathrm{(A_2 + B_2)}$
	4200	+0.4	
	3800	−9.0	
	3200	−1.6	
(+)D-$\mathrm{Co(trien)ClH_2O}^{2+}$	5900	−1.1	$\mathrm{B_1}$
	5100	+2.2	$\mathrm{(A_2 + B_2)}$
	4000	+0.4	
	3700	−0.3	
(+)D-$\mathrm{Co(trien)CO_3}^{+}$	5200	−4.5	$\mathrm{(A_2 + B_1 + B_2)}$
	3900	+0.8	
	3600	−0.1	
	3300	+0.2	
$(+)_{546}$-$\mathrm{Co(trien)(H_2O)_2}^{3+}$	5600	−1.1	$\mathrm{B_1}$
	4900	+1.9	$\mathrm{(A_2 + B_2)}$
	3800	+0.7	
	3500	−0.05	
	3250	+0.05	
$(+)_{546}$-$\mathrm{Co(trien)(NO_2)_2}^{+}$	4600	+1.2	$\mathrm{(A_2 + B_2)}$
	3950	−0.2	$\mathrm{B_1}$
	3400	−3.2	

$(+)_{546}$ ions is −, + and is in agreement with the sign patterns exhibited by the corresponding cobalt(III) complexes of ethylenediamine and triethylenetetramine which are of the D absolute configuration. The $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)Cl_2}^{+}$, $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)ClH_2O}^{2+}$, and $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(H_2O)_2}^{3+}$ ions are thus assigned the D absolute configuration.

The circular dichroism spectra characteristic of the $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(OH)_2}^{+}$, $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3}^{+}$, and $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)(NO_2)_2}^{+}$ ions are presented in Figure 5. The $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(OH)_2}^{+}$ ion exhibits a spectrum consisting of three components with a sign sequence −, +, −. It should be noted that the lowest energy transition showing a negative Cotton effect, in both this ion and the $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(H_2O)_2}^{3+}$ ion, is more intense than the second band. This suggests that the two lowest energy B states are mixed, thus resulting in the composite transition $\mathrm{A_1 \rightarrow B_1(A_2) + B_2(E_a)}$. The second component showing a positive Cotton effect is assigned the $\mathrm{A_1 \rightarrow A_2(E_a)}$ transition and is used to deduce the absolute configuration. Since this latter band is positive, the $(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(OH)_2}^{+}$ ion is assigned the D absolute configuration. Addition of acid to a solution containing this ion converts it quantitatively to the D-$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(H_2O)_2}^{3+}$ ion.

The $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3}^{+}$ ion exhibits a CD curve characteristic of complexes containing a bidentate conjugated ligand.[10] One and three circular dichroism bands are associated, respectively, with the longer and shorter wavelength d–d absorption spectral bands. That the $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3}^{+}$ ion exhibits an intense low-energy circular dichroism band showing a positive Cotton effect, as do the D-$\mathrm{Co(en)_2CO_3}^{+}$, D-$\mathrm{Co(trien)CO_3}^{+}$, D-$\mathrm{Co(en)_2ox}^{+}$, D-$\mathrm{Co(trien)ox}^{+}$, and D-$\mathrm{Co(pn_2)CO_3}^{+}$ ions,[4,10,12] strongly suggests that the $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3}^{+}$ ion also possesses the D absolute configuration. In accord with Mason's formalism,[10] the composite transition assigned to this positive Cotton effect is $\mathrm{^1A_1 \rightarrow B_1(A_2) + B_2(E_a)}$. This structural assignment is especially important since one might have expected a D-*s-cis* to L-*uns-cis* isomerization. Such a process occurs in the case of D-*s-cis*-$\mathrm{Co(trien)CO_3}^{+}$.[4,13,14]

Whereas this ion exhibited an optical rotatory dispersion which could not be used to assign configuration confidently, the CD spectrum is explicit. In addition, this ion could be converted quantitatively and *reversibly* to the D-$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(H_2O)_2}^{3+}$ ion. Treatment of D-$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)Cl_2}^{+}$ with sodium hydroxide to give the D-$(+)_{546}$-*s-cis*-$\mathrm{Co(eee)(OH)_2}^{+}$ ion, followed by addition of lithium carbonate, resulted in the quantitative production of $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3}^{+}$. The CD spectrum of the solution obtained by treating D-$(+)_{546}$-*s-cis*-$\mathrm{[Co(eee)Cl_2]Cl}$ directly with lithium carbonate also is the same as that obtained for the $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)CO_3}^{+}$ ion prepared by these other methods.

The $(-)_{546}$-*s-cis*-$\mathrm{Co(eee)(NO_2)_2}^{+}$ ion exhibits a CD spectrum quite different from those of the dinitrobis(ethylenediamine)cobalt(III) and dinitro(triethylenetetramine)cobalt(III) ions. In these latter two complexes, substitution of nitrite ion into the coordination sphere causes the in-plane electrostatic field to become considerably greater than the axial field. As a result, the electronic levels derived from the $\mathrm{T_{1g}}$ manifold are inverted, the lowest enegy transition being $\mathrm{A_1 \rightarrow A_2(E_a) + B_2(E_a)}$ and the second CD band being $\mathrm{A_1 \rightarrow B_1(A_2)}$. The electric field caused by the in-plane thioether groups is so weak that, even with the substitution of two nitrite groups into the in-plane positions, the axial field remains greater than the in-plane field. Thus the energy levels are *not* inverted. The negative low-energy CD component is therefore assigned the $\mathrm{A_1 \rightarrow B_1(A_2)}$ transition and the positive higher energy component is

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(12) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

(13) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(14) E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965); L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *ibid.*, **86**, 3656 (1964).

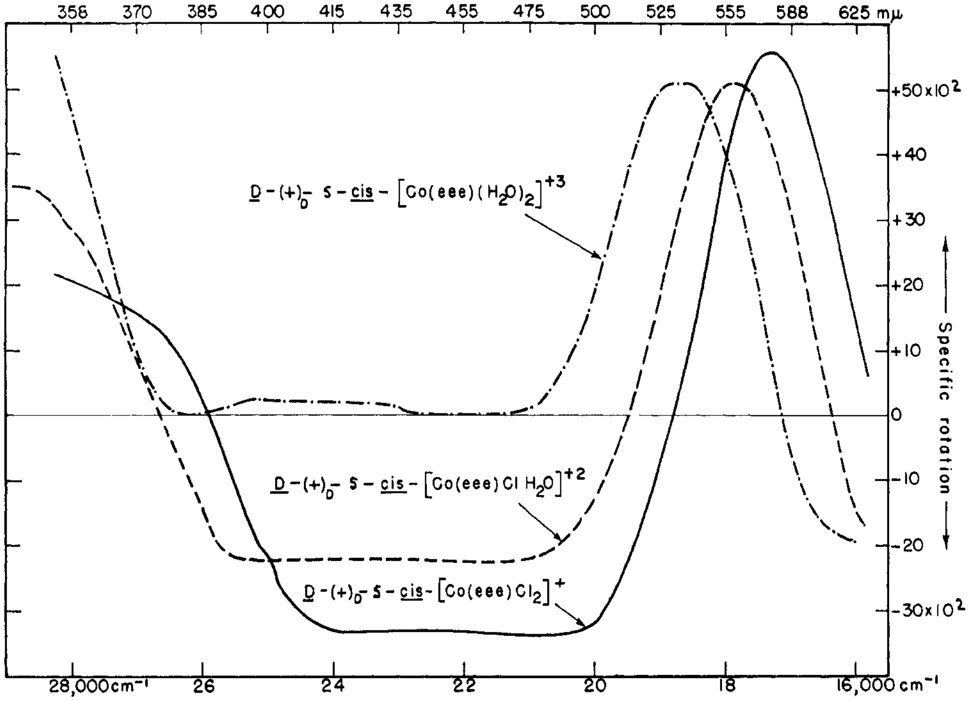

Figure 6.—ORD curves for the dichloro-, aquochloro-, and diaquo(1,8-diamino-3,6-dithiaoctane) cobalt(III) ions.

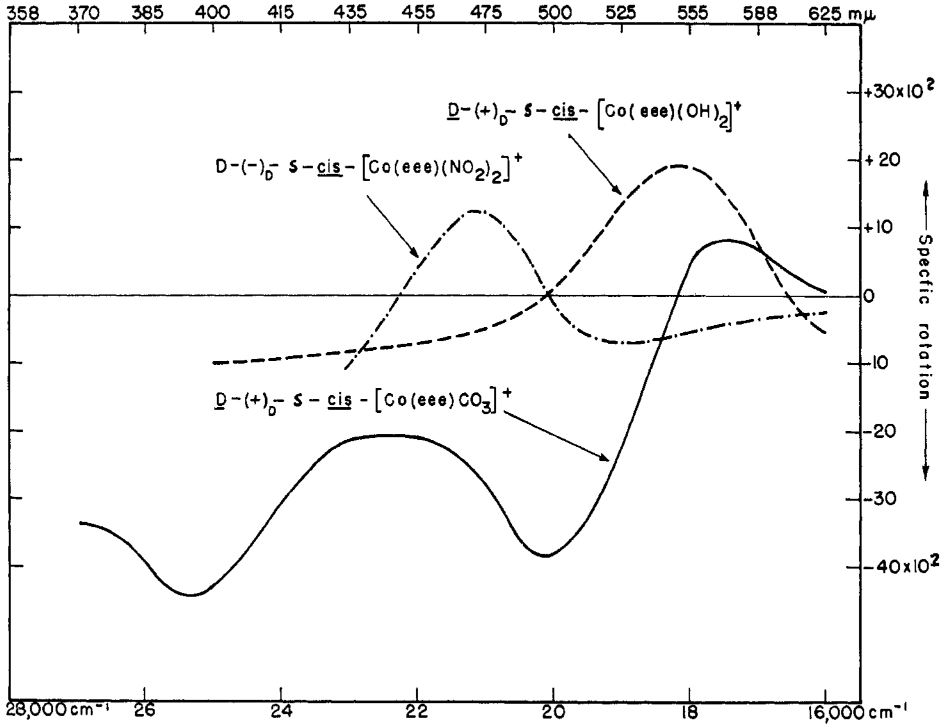

Figure 7.—ORD curves for the dihydroxo-, carbonato-, and dinitro(1,8-diamino-3,6-dithiaoctane) cobalt (III) ions.

assigned the composite transition $A_1 \rightarrow A_2(E_a) + B_2(E_a)$. This latter transition is diagnostic of absolute configuration as related to the $A_1 \rightarrow E_a$ component for the trigonal ion D-Co(en)$_3^{3+}$. It is positive for the $(-)_{546}$ isomer of *s-cis*-Co(eee)$(NO_2)_2^+$ and therefore this ion must also be of the D absolute configuration. Table III tabulates the wavelength of the CD maximum, the value of $\epsilon_l - \epsilon_d$, and the corresponding electronic assignment for the particular CD components observed for the cobalt(III) complexes of eee.

Optical Rotatory Dispersion Measurements.—The optical rotatory dispersion curves for the ions $(+)_{546}$-*s*-*cis*-Co(eee)Cl_2^+, $(+)_{546}$-*s*-*cis*-Co(eee)ClH_2O^{2+}, $(+)_{546}$-*s*-*cis*-Co(eee)$(H_2O)_2^{3+}$, $(+)_{546}$-*s*-*cis*-Co(eee)$(OH)_2^+$, $(-)_{546}$-*s*-*cis*-Co(eee)CO_3^+, and $(-)_{546}$-*s*-*cis*-Co(eee)$(NO_2)_2^+$ are given in Figures 6 and 7.

From the ORD curves given in Figure 6, it is evident that the $(+)_{546}$-*s*-*cis* isomers of the dichloro-, aquochloro-, and diaquo(1,8-diamino-3,6-dithiaoctane)cobalt(III) ions all have the same relative configuration.

Table III

Circular Dichroism Data for $Co(eee)L_2^{n+}$ Complexes

D-*s-cis* compounds	λ_{max}, Å	$(\epsilon_l - \epsilon_d)_{max}$	Transition
$(+)_{546}$-$Co(eee)Cl_2^+$	6230	−4.85	B_1
	5390	+7.30	$A_2 + B_2$
	3920	−5.20	B_2
$(+)_{546}$-$Co(eee)ClH_2O^{2+}$	6020	−4.20	B_1
	5260	+5.15	$A_2 + B_2$
	3780	−4.05	B_2
$(+)_{546}$-$Co(eee)(H_2O)_2^{3+}$	5750	−4.95	$B_1 + B_2$
	5040	+3.15	A_2
	4710	+0.70	
	3600	−2.75	
$(+)_{546}$-$Co(eee)(OH)_2^+$	5940	−2.80	$B_1 + B_2$
	5140	+2.20	A_2
	3760	−2.75	
$(-)_{546}$-$Co(eee)CO_3^+$	5320	+3.65	$(B_1 + A_2 + B_2)$
	4710	−0.75	
	4210	+0.40	
	3800	−2.90	
$(-)_{546}$-$Co(eee)(NO_2)_2^+$	5040	−1.99	B_1
	4480	+2.30	$A_2 + B_2$

Table IV

Wavelength of Maximum Positive, Zero, and Negative Rotation for the *s-cis*-$Co(eee)L_2^{n+}$ Complexes

D-*s-cis* compounds	λ, mμ	ν, cm^{-1}	[α],[a] deg
$Co(eee)Cl_2^+$	576	17,350	+5600
	530	18,850	0
	488	20,500	−3400
$Co(eee)ClH_2O^{2+}$	611	16,350	0
	559	17,900	+5100
	514	19,450	0
	466	21,250	−2250
$Co(eee)(H_2O)_2^{3+}$	564	17,150	0
	534	18,750	+5100
	470	21,250	0
$Co(eee)(OH)_2^+$	606	16,500	0
	550	18,200	+1950
	498	20,100	0
	409	24,500	−1050
$Co(eee)CO_3^+$	564	17,450	+850
	550	18,200	0
	496	20,150	−3900
$Co(eee)(NO_2)_2^+$	526	19,000	−725
	500	20,050	0
	474	21,150	+1250
	449	22,250	0

[a] Specific rotation.

All exhibit a long-wavelength negative component followed by a very intense positive band in the visible region. As one progresses toward the ultraviolet region, the curves again become negative. The usual spectrochemical shift for the wavelength of maximum positive rotation is also observed, changing from 578 to 560 to 534 mμ for the sequence of dichloro, aquochloro, and diaquo ions, respectively. On the basis of their similarity to the curves for the corresponding D-$Co(en)_2L_2^{n+}$ ions,[13] as well as for the D-*s-cis*-$Co(trien)L_2^{n+}$ complexes,[4,12] it can be stated that these three ions—$(+)_{546}$-*s-cis*-$Co(eee)Cl_2^+$, $(+)_{546}$-*s-cis*-$Co(eee)ClH_2O^{2+}$, and $(+)_{546}$-*s-cis*-$Co(eee)(H_2O)_2^{3+}$—are also of the D absolute configuration represented by structure I. As in these cases the ORD spectra of the remaining compounds generally agree with the CD spectra discussed earlier. Table IV lists the wavelength of maximum positive, zero, and maximum negative rotation for this series of *s-cis*-$Co(eee)L_2^{n+}$ ions.

Transformation Reactions.—The configurations for the D- and L-*s-cis*-$Co(eee)L_2^{n+}$ ions were also independently correlated by a series of transformation reactions which occur with retention of configuration. Figure 8 illustrates the reactions which were followed to completion using both ORD and CD techniques when the initial compound was optically pure $(+)_{546}$-*s-cis*-$Co(eee)Cl_2^+$.

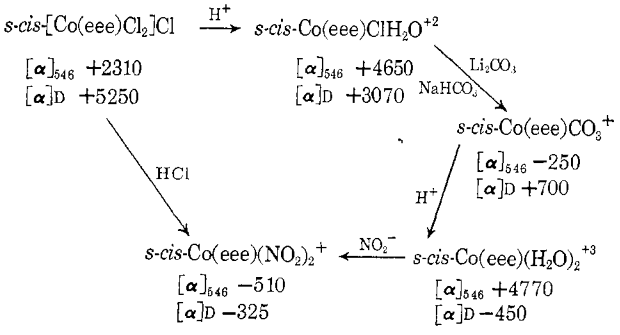

Figure 8.—Transformation reactions for the $(+)_{546}$-*s-cis*-Co(eee)-L^{2n+} ions.

Optically pure $(+)_{546}$-*s-cis*-$Co(eee)Cl_2^+$ ion with $[\alpha]_{546}$ of +2313 ± 20° was allowed to aquate for 96 hr in dilute solution, at which time the predominant species in solution was the $(+)_{546}$-*s-cis*-$Co(eee)ClH_2O^+$ ion which has a specific rotation $[\alpha]_{546}$ of +4650 ± 50° as determined from its optical rotatory dispersion curve. Both the ORD and CD data are in accord with the complete retention of configuration for aquation. The Hg(II)-catalyzed aquation produces the chloroaquo species in 2 min at pH 2 and 25°. The diaquo complex is obtained in 4 hr under the same conditions. Again, retention of configuration prevails.

The $(+)_{546}$-*s-cis*-$Co(eee)ClH_2O^{2+}$ ion was converted quantitatively, as evidenced spectrophotometrically, into the $(-)_{546}$-*s-cis*-$Co(eee)CO_3^+$ ion by treating the solution with either lithium carbonate or sodium bicarbonate. The *s-cis*-$Co(eee)CO_3^+$ ion has specific rotations $[\alpha]_{546}$ and $[\alpha]_{589}$ of −250 ± 25 and +700 ± 25°, respectively.

The mechanism proposed for the fission of the carbonato group in $Co(NH_3)_4CO_3^+$ is consistent with the observed retention of configuration in the $Co(eee)CO_3^+$ complexes.[15]

Acidification of the carbonato compound gave the $(+)_{546}$-*s-cis*-$Co(eee)(H_2O)_2^{3+}$ ion also with full retention of configuration. It could be reversibly converted to the $(-)_{546}$-*s-cis*-$Co(eee)CO_3^+$ ion by adding lithium carbonate to the solution without any loss of optical activity as evidenced by both ORD and CD spectra. The specific rotation $[\alpha]_{546}$ for the *s-cis*-$Co(eee)(H_2O)_2^{3+}$ ion is +4775 ± 50°.

The mechanism by which nitrite ion replaces coordinated water has been investigated[16] and tracer

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(15) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953).

(16) R. K. Murman and H. Taube, *ibid.*, **78**, 4886 (1956).

studies indicate retention of the original Co–O bond for the first step. Nitrite ion or, more probably, N_2O_3 adds to the coordinated water molecule to form the nitrito complex, which subsequently rearranges intramolecularly to the nitro compound with retention of configuration. Presumably in a diaquo complex, nitrite ion will replace the second water molecule in a similar manner.

The *s-cis*-Co(eee)$(NO_2)_2^+$ ion was completely resolved into its optical enantiomorphs which exhibit a specific rotation of ±604° at 546 mμ. The addition of nitrite ion to a solution of the diaquo complex resulted in a rotation at 546 mμ which is 10–15% less than that observed for the optically pure *s-cis*-dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) complex. The observed rotation was found to be a function of the acidity of the diaquo solution and the concentration of nitrite ion added.

As a result of numerous experiments it was found that the $(+)_{546}$-*s-cis*-Co(eee)$(H_2O)_2^{3+}$ ion could be converted into the optically active $(-)_{546}$-*s-cis*-Co(eee)$(NO_2)_2^+$ ion with an average specific rotation $[\alpha]_{546}$ of $-510 \pm 50°$. Formation of the yellow dinitro complex from the diaquo requires 4–12 hr and proceeds *via* a distinct red to red-orange intermediate, presumably the nitrito complex. The above rotation demonstrates that the entire transformation sequence occurs with 85–90% retention of configuration and supports previous mechanistic investigations. It is believed that the observed loss in optical activity is due entirely to an equilibrium situation in which the *s-cis*-Co(eee)$(NO_2)_2^+$ ion is not produced in 100% yield and is not indicative of a change in the configuration of the dinitro compound from *s-cis* to *uns-cis* or *trans*. Searle observed the same phenomenon with the corresponding transformation for the *s-cis*-Co(trien)$(NO_2)_2^+$ ion.[4,12]

The *s-cis*-Co(eee)$(NO_2)_2^+$ ion produced from this transformation scheme was isolated as the nitrate salt and its high-resolution infrared spectrum was identical with that of the corresponding *s-cis*-[Co(eee)$(NO_2)_2$]NO_3 produced directly from the ligand eee, sodium nitrite, and a cobalt salt.[1] The transformation sequence independently establishes that the relative configuration is the same for all ions in the series from the dichloro- to the dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) species. This is further supported by the absolute configurational assignments made using ORD and CD techniques.

Several other reactions whose mechanisms do not require retention of configuration were investigated. When treated directly with sodium nitrite or lithium carbonate, optically pure $(+)_{546}$-*s-cis*-[Co(eee)Cl_2]Cl is converted into the optically active $(-)_{546}$-*s-cis*-Co(eee)$(NO_2)_2^+$ and $(-)_{546}$-*s-cis*-Co(eee)CO_3^+ ions, respectively, both exhibiting specific rotations within 10% of the values stated for the reactions shown in Figure 8.

One of the most remarkable transformations found is the conversion of optically pure $(-)_{546}$-*s-cis*-[Co(eee)$(NO_2)_2$]ClO_4 into the corresponding $(+)_{546}$-*s-cis*-[Co(eee)Cl_2]ClO_4. Solid optically pure $(-)_{546}$-*s-cis*-[Co(eee)$(NO_2)_2$]ClO_4 was treated with hot (60°) concentrated hydrochloric acid for 20 min. The deep blue solution was then filtered and a small volume of absolute ethanol was added. Upon cooling, fine, deep blue needles were isolated. The molar rotation $[M]_{546}$ of +8018° for this compound compares well with the molar rotation of the optically pure D chloride salt having $[M]_{546}$ +7982°. This strongly supports retention of configuration, even under conditions usually conducive to reduction and racemization.

Stereochemical Changes.—Any stereochemical change in the ion D-*s-cis*-Co(eee)Cl_2^+, or related ions, that requires the movement of two chelate rings is assumed to be much less likely than a change that requires the movement of only one chelate ring. The conversion of a complex with the absolute configuration D-*s-cis* to the configuration L-*s-cis*, D-*uns-cis*, or *trans* requires the movement of at least two chelate rings. This, in turn necessitates the simultaneous cleavage of two S–Co bonds or a Co–N and a Co–S bond followed by subsequent rearrangement. On this basis alone, the conversion of D-*s-cis* to L-*s-cis* or *trans* is quite unlikely. The conversion of D-*s-cis* to L-*uns-cis* requires the simple movement of only one chelate ring and as such would be the favored stereochemical change.

From this and the relationships developed earlier concerning configurational assignments based on ORD and CD measurements, it is immediately obvious that an isomerization of the type *s-cis* to *uns-cis*, or vice versa, for any reaction with an optically pure quadridentate cobalt(III) complex, can best be detected by ORD and CD measurements. Two pronounced changes in the ORD and CD spectra are expected for the isomerization of *s-cis* to *uns-cis*. The intensities of the circular dichroism bands characteristic of an *uns-cis* complex are expected to be markedly less than for the corresponding *s-cis* compounds.[12] This results from the lower molecular symmetry introduced by the chelate rings and is clearly evident if one compares the CD band intensities for the *s-cis* and *uns-cis*-Co(trien)L_2^{n+} ions.[12] In addition, a complete reversal in the signs of the Cotton effects observed in both the ORD and CD spectra should also occur, demonstrating the change in absolute configuration from D in the *s-cis* complex to L for the *uns-cis* arrangement. In order to make a reliable judgment as to whether or not isomerization did occur, it is absolutely necessary that the shape of the ORD and/or CD spectra characteristic of both the D-*s-cis* reactant and the corresponding D-*s-cis* product be known over the range 650–400 mμ.

Kyuno, Boucher, and Bailar[14,17] have studied the base hydrolysis of optically active *s-cis*- and *uns-cis*-[Co(trien)Cl_2]Cl complexes. It was found that the D-*s-cis*-Co(trien)Cl_2^+ ion rapidly isomerizes through the dihydroxo species to the L-*uns-cis* isomer, which then rapidly loses optical activity. To circumvent this problem, the dihydroxo complex was immediately converted to the stable Co(trien)CO_3^+ ion which invariably

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[17] E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 1120 (1966); L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., **86**, 3656 (1964).

had the L-*uns-cis* geometry as evidenced by ORD spectra. It is interesting to note that the L-*uns-cis*-Co(trien)Cl_2^+ does *not* hydrolyze or rearrange under any conditions to give the D-*s-cis* isomer.[5]

In an attempt to effect and observe a similar phenomenon with the cobalt(III) complexes of eee, the base hydrolysis of D- and L-*s-cis*-[Co(eee)Cl_2]Cl was studied using both ORD and CD techniques. From these studies, several contrasting features were obvious. Addition of excess sodium hydroxide to a solution containing optically pure D- or L-*s-cis*-[Co(eee)Cl_2]Cl immediately produces the dihydroxo species with the characteristic ORD and CD spectra as illustrated in Figures 6 and 8, respectively. The dihydroxo complex loses optical activity only very slowly, a 5% decrease in optical activity being observed over a period of several hours at pH 8 as evidenced by both ORD and CD curves. At pH 10, a slow loss of optical activity is detectable and is accompanied by the development of a brown coloration and rank odor characteristic of decomposition. This reaction was followed by ORD and CD spectra for approximately 5 hr without any indication of change in the absolute configuration. In addition, samples of the dihydroxo complex were periodically converted to the corresponding carbonato complex and the ORD and CD spectra were compared with the spectrum of the optically pure D-*s-cis*-Co(eee)CO_3^+ ion. Again at pH 8, no significant changes were observed in the signs, intensities, or energies of the ORD and CD Cotton effects, thus substantiating retention of configuration, and the absence of any isomerization of D-*s-cis* to L-*uns-cis*. Numerous other attempts to produce chemically such an isomerization have been unsuccessful with the *s-cis*-Co(eee)L_2^{n+} ions.[1]

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The Preparation and Spectral Properties of Bis(halogenoacetato)(β,β',β''-triaminotriethylamine)cobalt(III) Complexes

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Bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes, [Co(halac)$_2$(tren)]ClO_4 (halac = $CF_3CO_2^-$, $CH_2ClCO_2^-$, $CHCl_2CO_2^-$, $CCl_3CO_2^-$, $CH_2BrCO_2^-$, $CHBr_2CO_2^-$, and $CBr_3CO_2^-$), have been prepared from carbonato(triaminotriethyl-, amine)cobalt(III) perchlorate, and their infrared and electronic absorption spectra have been examined. Assignments of the bands arising from the amino groups have been made by a comparison of the spectra with those of the deuterated complexes, [Co(tren-d_6)Cl_2]Cl·0.5H_2O and [Co(tren-d_6)Br_2]Br. Comparison of the visible spectra of these tren complexes with the spectra of the corresponding tetraammine, bis(ethylenediamine), and triethylenetetramine (trien) complexes suggests that the ligand field strength of tren ligand is between that of ethylenediamine and ammonia.

Introduction

Kuroda and Gentile[2] have described the preparation and the physical and chemical properties of a large series of halogenoacetatopentaamminecobalt(III) complexes. Both *cis*- and *trans*-bis(halogenoacetato) complexes of tetraamminecobalt(III), bis(ethylenediamine)-cobalt(III), and triethylenetetraminecobalt(III) were also reported. From the visible spectra of these complexes it was found that, regardless of the amine ligand, those halogenoacetato anions with the lowest basicity were highest in the spectrochemical series. However, for any given halogenoacetato ligand in the *cis* complexes, the frequencies of the visible and ultraviolet absorption maxima were not identical, but always increased in the order

$$\nu_{(NH_3)_4} > \nu_{(en)_2} > \nu_{trien}$$

It was also found that the absorption intensities increased in the same order.

Previous work has shown that the triaminotriethylaminecobalt(III) complexes which had been reported were found to be the *cis* isomers.[3,4] Since the bis(halogenoacetato)(triaminotriethylamine)cobalt(III) complexes have not been reported in the literature, we have now synthesized these new complexes and have investigated their spectral properties in order to see how they compare with those of the other amine analogs.

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