Circular Dichroism of Some Bis(diamine) Complexes of Cobalt(III) and New Procedures for Resolving Oxalatobis(ethylenediamine)cobalt(III) Ion and Ethylenediamine-*N,N,N',N'*-tetraacetatocobaltate(III) Ion[1]

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The preparations and resolutions of the complexes $[Co(l\text{-chxn})_2 L]^+$ where L = carbonate, oxalate, or malonate have been achieved. Complete resolution of $[Co(en)_2 mal]^+$ is also reported. The CD data for these complexes are compared to evaluate the effects of chelate ring size of the dicarboxylato ligand and the vicinal effect due to the *l*-chxn on the rotatory strengths. In addition, convenient new methods are given for the resolutions of two complexes frequently used as resolving agents, $[Co(en)_2 ox]^+$ and $[Co(EDTA)]^-$.

Introduction

Many ionic optically active complexes of cobalt(III) serve as good resolving agents for other ionic dissymmetric metal chelates. A sequence of resolutions which provides several common cationic and anionic resolving agents is shown in Figure 1.[2,3] Previously, two preliminary resolutions, beginning with potassium antimony $(+)_D$-tartrate, were required to resolve $[Co(en)_2 ox]^+$. Now a simple, one-step resolution, using hydrogen $(+)_D$-tartrate anion, has been formulated which provides both optical isomers of $[Co(en)_2 ox]^+$ in high yield (*ca.* 70% each) and in a short period of time. This new resolution, along with the resolution of *cis*-$[Co(en)_2(NO)_2]^+$ by antimony $(+)_D$-tartrate anion, makes any of the resolving agents in Figure 1[4-8] accessible by a maximum of only one preliminary resolution. The resolution of $[Co(EDTA)]^-$ with $[Co(en)_2 ox]^+$, as suggested in the literature[6] and given here in detail, provides a useful anionic resolving agent. Since the success of resolution procedures often depends on exact conditions such as volume, temperature, and time of cooling, the procedures are given in more than the usual detail.

The effect of chelate ring size on the rotatory strengths arising from the d-d transitions of the cobalt(III) ion has been the subject of many experimental[8-10] and theoretical[11] studies. Of particular interest are the variations in the CD intensities under the first (T_{1g}) absorption band for cobalt-(III) complexes involving the dicarboxylato ligands carbonate

$(CO_3{}^{2-})$, oxalate (ox^{2-}), and malonate (mal^{2-}) where the ligands form four-, five-, and six-membered chelate rings, respectively. Circular dichroism data have been reported previously[12,13] for $[Co(en)_2 CO_3]^+$ and $[Co(en)_2 ox]^+$. The CD data for the malonato complex have now been obtained to complete this important series. In addition, the analogous series of bis(*l*-cyclohexanediamine) complexes have been resolved. This permits insight into the vicinal as well as ring-size contributions to the rotatory strengths of dicarboxylato-bis(diamine)cobalt(III) complexes.

Experimental Section

Resolution of Oxalatobis(ethylenediamine)cobalt(III) Chloride Monohydrate, $[Co(en)_2(ox)]Cl \cdot H_2O$. A mixture of 16.0 g (0.0500 mol) of $[Co(en)_2(ox)]Cl \cdot H_2O$,[7] 3.8 g (0.025 mol) of $(+)_D$-tartaric acid, and 9.1 g (0.025 mol) of silver $(+)_D$-tartrate[14] in 150 ml of hot water was stirred at 60–75° for 15 min and then filtered to remove the silver salts which were washed with *ca.* 2 ml of hot water. The combined filtrate and washings were stirred with a glass rod in an ice-water bath to hasten cooling to 10° (no longer than 15 min). The dark red crystals were collected on a Buchner funnel, washed, successively, with 40 ml of 80% aqueous methanol, 40 ml of methanol, and two 40-ml portions of ether, and dried by suction. The CD intensities ($\Delta\epsilon_{520}$ +2.65) were unchanged by further recrystallization. The yield of $(+)_D$-$[Co(en)_2 ox][H$-$(+)_D$-tart$] \cdot H_2O$ was 8.0 g. When the first fraction is incompletely resolved, the diastereomer may be recrystallized by dissolution in water (9 ml/g of diastereomer) at 60–70° and cooling the solution to 4° in an ice-water bath. *Anal.* Calcd for $[Co(C_2H_8N_2)_2(C_2O_4)]H[C_4H_4O_6] \cdot H_2O$: C, 27.65; H, 5.30; N, 12.90. Found: C, 27.90; H, 5.16; N, 12.84.

The $(+)_D$ isomer was converted to the iodide salt by dissolving the diastereomer in hot water (9 ml/g at 70°) and adding an equimolar amount of NaI (0.346 g/g of diastereomer). Precipitation commenced immediately and the mixture was stirred until all of the NaI had dissolved. The mixture was then cooled in ice to 4° and filtered. The fine orange crystals of $(+)_D$-$[Co(en)_2 ox]I$ were washed with methanol and ether and dried on the funnel by suction. The yield from 8.0 g of diastereomer was 7.1 g, 72% of theoretical ($\Delta\epsilon_{520}$ +2.64).

The filtrate containing the more soluble diastereomer was stirred at 60° and 5.0 g of NaBr was added whereupon crystallization of $(-)_D$-$[Co(en)_2 ox]Br \cdot H_2O$ commenced. The mixture was cooled in ice to 30° and then filtered. The red crystals were washed and dried as before; yield 8.4 g ($\Delta\epsilon_{520}$ −1.99). The bromide was recrystallized by stirring in 165 ml of water at 75° for *ca.* 5 min, cooled in ice to 15°, and filtered and washed as before; yield 6.5 g or 71% ($\Delta\epsilon_{520}$ −2.61).

Resolution of Potassium Ethylenediaminetetraacetatocobaltate-(III) Dihydrate, $K[Co(EDTA)] \cdot 2H_2O$. Resolution was achieved using $[Co(en)_2 ox]^+$, as suggested[6] in the literature. The resolving agent $(-)_D$-$[Co(en)_2 ox]Br \cdot H_2O$ (10.9 g, 0.030 mol) (or $(+)_D$-$[Co(en)_2 ox]I$ (11.8 g, 0.030 mol)) was stirred in water (50 ml) and silver acetate

(1) This work was supported by Research Grant GM-10829 from the Division of General Medical Studies, U. S. Public Health Service. Presented, in part, at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.

(2) A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 194.

(3) 1970 IUPAC Rules, *Pure Appl. Chem.*, 28, 1 (1971); *Inorg. Chem.*, 9, 1 (1970).

(4) F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, 6, 195 (1960).

(5) F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, 6, 192 (1960).

(6) F. P. Dwyer, I. K. Reed, and F. L. Garvan, *J. Amer. Chem. Soc.*, 83, 1285 (1961).

(7) J. G. Brushmiller, Ph.D. Thesis, University of Pittsburgh, 1962.

(8) See, for example: F. Woldbye, *Proc. Roy. Soc., Ser. A*, 297, 79 (1968); P. G. Beddoe, M. J. Harding, S. F. Mason, and P. J. Peart, *Chem. Commun.*, 1283 (1971); K. R. Butler and M. R. Snow, *ibid.*, 550 (1971); C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, 8, 1145 (1969); W. T. Jordan and B. E. Douglas, *ibid.*, 12, 403 (1973).

(9) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, 2, 1194 (1963).

(10) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, 8, 115 (1969).

(11) See, for example: A. Karipides and T. S. Piper, *J. Chem. Phys.*, 40, 674 (1964); A. D. Liehr, *ibid.*, 68, 665 (1964); C. E. Schaeffer, *Proc. Roy. Soc., Ser. A*, 297, 96 (1968); F. S. Richardson, *Inorg. Chem.*, 11, 2366 (1972), and references found therein; S. F. Mason, *J. Chem. Soc. A*, 667 (1971).
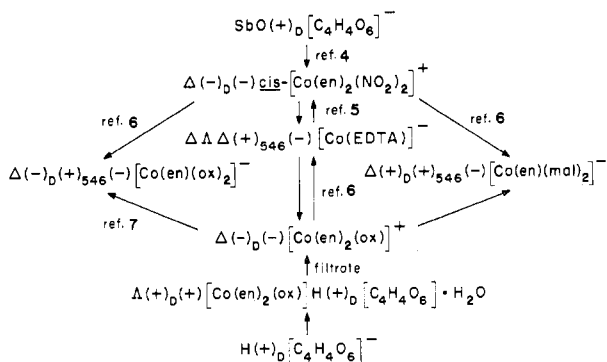
(12) R. A. Haines, Ph.D. Thesis, University of Pittsburgh, 1964.

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

(14) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, 6, 700 (1967).

Figure 1. Flow chart for resolution procedures. The isomers shown at the head of each arrow are those forming the less soluble diastereomer using the resolving agent in the preceding step. (+) or (−) refers to the sign of the dominant CD peak in the visible region; $(+)_\lambda$ or $(−)_\lambda$ refers to the sign of optical rotation at the wavelength λ; and Δ or Λ is the chirality assigned according to IUPAC rules.[3]

(5.0 g, 0.030 mol) was added. The mixture was stirred at *ca.* 50° for *ca.* 15 min and then filtered. The precipitate was washed with hot water (50 ml). The filtrate and washings were added to a solution (*ca.* 50°) of K[Co(EDTA)]·2H₂O[15] (25.4 g, 0.0600 mol) in water (100 ml), to precipitate the diastereomer $(−)_D$-[Co(en)₂ox]-$(−)_{546}$-[Co(EDTA)]·3H₂O. The mixture was homogenized by stirring, cooled in ice with continued stirring, and filtered. The diastereomer was washed with ice-cold water (50 ml), 95% ethanol, ethanol, and ether (50 ml each) and then air-dried on the funnel; yield *ca.* 14 g. The filtrate was evaporated to 50 ml to yield a second fraction of diastereomer (1–2 g); total yield *ca.* 16 g, 80% of theoretical. Precipitation of K[(−)$_{546}$-[Co(EDTA)]]·2H₂O occurred during judicious addition of a large volume (*ca.* 350 ml) of 95% ethanol to the filtrate (50 ml); yield 12.3 g. The (−)$_{546}$ isomer was purified (twice) by dissolving the product in water (50 ml) and precipitating by the addition of 95% ethanol (*ca.* 350 ml); yield 5.4 g ($\Delta\epsilon_{585}$ +1.53). The diastereomer (16 g) was purified by stirring in hot water (100 ml, *ca.* 60°) and filtering while hot (13.9 g obtained) ($\Delta\epsilon_{544}$ −2.11). To the diastereomer (13.9 g, 0.0208 mol) in water (50 ml) was added KI (13.9 g, 0.0840 mol) with stirring to precipitate (−)$_D$-[Co(en)₂(ox)]I after 15–25 min. The mixture was filtered and the resolving agent was washed, successively, with water, 80% methanol, methanol, and ether and then air-dried. Precipitation of K[(+)$_{548}$-[Co(EDTA)]]·2H₂O occurred during judicious addition of a large volume (*ca.* 350 ml) of 95% ethanol to the filtrate. The mixture was filtered and washed as before; yield 8.9 g ($\Delta\epsilon_{585}$ −1.53).

Preparation of Malonatobis(ethylenediamine)cobalt(III) Iodide Hemihydrate, [Co(en)₂mal]I·0.5H₂O. The procedure formulated by Werner[16] for the synthesis and used by Haines[12] was modified. [Co(en)₂CO₃]Cl[17] (10.0 g, 0.0364 mol) was dissolved in water (40 ml, *ca.* 60°) and a solution of KOH (4.0 g, 0.072 mol) and malonic acid (3.8 g, 0.036 mol) in water (10 ml) was added. The solution was stirred and heated above 60°; then solid malonic acid (3.8 g, 0.036 mol) was added. Effervescence subsided with heating to 80° and stirring during a 0.5-hr period. The solution was cooled in an ice bath, 10 g of KI was added, and the sides of the beaker were scratched with a glass rod. Precipitation of the malonato complex occurred during refrigeration (few days). Additional complex could be obtained by evaporation of the reaction solution. Yield of crude material was 2.6 g,[18] average for four preparations. The complex (11.4 g) was recrystallized from water (160 ml) in two fractions by cooling to give 6.7 g and then by addition of 95% ethanol to yield 1.6 g. *Anal.* Calcd for (±)-[Co(C₂H₈N₂)₂(C₃H₂O₄)]I·0.5H₂O (FW 417): C, 20.14; H, 4.56; N, 13.43. Found:[19] C, 20.20; H, 4.73; N, 13.64.

Resolution. [Co(en)₂mal]I·0.5H₂O (8.3 g, 0.020 mol) was stirred in water (15 ml) and silver acetate (3.3 g, 0.020 mol) was added. After being stirred vigorously for 0.5 hr, the silver salts were filtered and

washed with water (15 ml) which was added to the filtrate. K[(−)-[Co(EDTA)]]·2H₂O (4.2 g, 0.010 mol, $\Delta\epsilon_{585}$ −1.19) was stirred into the solution (apparent volume 37 ml), which was then cooled in an ice bath to precipitate the diastereomer. The diastereomer was filtered, washed with 95% ethanol (*ca.* 30 ml), absolute ethanol (*ca.* 30 ml), and acetone (*ca.* 100 ml), and then air-dried on the funnel; yield 5.1 g (6.3 g theoretical). The filtrate was evaporated in air to an apparent volume of 18 ml and a small amount (*ca.* 4 g) of impure diastereomer was filtered and discarded. The filtrate was stirred with KI (1.7 g, 0.010 mol) and more impure diastereomer (1.7 g) was filtered after cooling the solution for about 0.5 hr. More KI (5.1 g, 0.030 mol) was added to the filtrate and precipitation of the (−) isomer occurred over *ca.* 30 hr of refrigeration. The mixture was filtered, and the complex was washed with cold water (*ca.* 2 ml) and 10-ml portions of 95% ethanol, ethanol, acetone, and ether; yield 1.6 g ($\Delta\epsilon_{531}$ −1.68). The filtrate was discarded. The (−) isomer (1.6 g) was recrystallized from water (15 ml); yield 0.7 g ($\Delta\epsilon_{531}$ −1.81). The circular dichroism was not improved by three subsequent recrystallizations. The diastereomer (5.1 g) was dissolved in hot water (20 ml, 75°), filtered to remove impurities, cooled to *ca.* 20°, filtered, washed, and dried as before; yield 3.0 g ([$\Delta\epsilon$]$_{524}$ +0.266).[20] A second fraction (1.1 g, [$\Delta\epsilon$]$_{524}$ +0.262) was obtained after cooling the filtrate in ice for *ca.* 0.5 hr, and a third fraction (0.2 g, [$\Delta\epsilon$]$_{524}$ +0.275) was obtained by adding 95% ethanol (5 ml) to the filtrate. The three fractions were combined and dissolved in water (15 ml, 60°) and KI (6.8 g, 0.040 mol) was stirred in with subsequent formation of a red precipitate during a 15-min period. The mixture was filtered (67°) and washed; yield 0.8 g ($\Delta\epsilon_{531}$ +1.77). Subsequent fractions from the filtrate gave less pure (+) isomer. The circular dichroism was not improved by two subsequent recrystallizations. *Anal.* Calcd for (+)-[Co(C₂H₈N₂)₂(C₃H₂O₄)]I·0.5H₂O (FW 417): C, 20.14; H, 4.56; N, 13.43. Found: C, 20.05; H, 4.38; N, 13.38.

Preparation of *l*-Cyclohexanediamine *d*-Tartrate. A mixture of *cis*- and *trans*-1,2-diaminocyclohexane, the proportions of the two isomers being unknown, was purchased from Aldrich Chemical Co. The resolution[21] was accomplished by recrystallization of the less soluble diastereomer (*l*-chxn)(*d*-tart) to a constant specific rotation,[22] [α]D +12.0°. A 1:1 mole ratio of the starting material to *d*-tartaric acid was found to be practical.

Preparation of *trans*-Dichlorobis(*l*-cyclohexanediamine)cobalt(III) Chloride Monohydrate. The initial preparation[23] of this complex has been questioned by several investigators.[22,24] The method adopted for its preparation is a modification of the methods proposed by Asperger and Liu[24] and by Treptow.[22]

An aqueous solution of *l*-chxn was prepared by adding Ba(OH)₂·8H₂O (54.5 g, 0.173 mol) to a stirred suspension of (*l*-chxn)(*d*-tart) (45.3 g, 0.173 mol) in warm water (400 ml; 65°). The mixture was heated with stirring for 90 min and then was cooled in an ice bath for 2 hr and filtered.

To the filtrate was added [Co(NH₃)₄CO₃]NO₃·0.5H₂O[25] (25.8 g, 0.1 mol), followed by stirring for 15 min and then heating on a steam bath for 4.5 hr. After cooling the solution to 10° in an ice bath, it was filtered, and concentrated HCl (100 ml) was slowly added with vigorous stirring. This solution was then evaporated almost to dryness on a steam bath, cooled in ice to 10°, and then filtered. The residue was then triturated with acetone until the filtrate was nearly colorless to give 25 g of crude product, which contained a mixture of *cis*- and *trans*-[Co(*l*-chxn)₂Cl₂]Cl·nH₂O.

The product was converted to *trans*-[Co(*l*-chxn)₂Cl₂]Cl·nH₂O by refluxing the crude material (8 g) in 200 ml of absolute methanol for 90 min. The hot methanolic solution was then filtered and, upon cooling in ice, green *trans*-[Co(*l*-chxn)₂Cl₂]Cl·0.5H₂O precipitated. Depending upon the amount of water present in the solution, one might obtain green needlelike crystals which contain 1 mol of water of crystallization.[22] Assuming that the complex obtained was *trans*-

(20) For diastereomeric salts whose formula weights have not been determined by chemical analysis it is useful to characterize optical purity through the use of the *specific circular dichroism*, [$\Delta\epsilon$]$_\lambda$ in l. g⁻¹ cm⁻¹. Multiplication of the *specific circular dichroism* by the factor (FW/100) gives the *molar circular dichroism*, $\Delta\epsilon_\lambda$. The specific circular dichroism corresponds to specific rotation. It is often an unnecessary expense to analyze each diastereomer and often the extent of hydration is not known.

(15) F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Chem. Phys.*, **59**, 296 (1955).

(16) A. Werner, *Justus Liebigs Ann. Chem.*, **386**, 80 (1912).

(17) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, **85**, 1215 (1963).

(18) If the aqueous solution of KOH and malonic acid is not added to the solution of the carbonato complex, the yield of malonato complex is about half that obtained. Contamination by [Co(en)₃]I₃ also becomes a problem.

(19) The analysis is that reported by Haines.[17]

(21) F. M. Jaeger and L. Bijkerk, *Proc. Kon. Ned. Akad. Wetensch.*, **40**, 12 (1937).

(22) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

(23) F. M. Jaeger and L. Bijkerk, *Proc. Kon. Ned. Akad. Wetensch.*, **40**, 246 (1937).

(24) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1492 (1965).

(25) H. F. Watson, "Inorganic Preparations," Prentice-Hall, Englewood Cliffs, N. J., 1948, p 91.

[Co(l-chxn)$_2$Cl$_2$]Cl·0.5H$_2$O, the optically pure product was found to have $\Delta\epsilon_{610}$ 0.96 (lit.[22] value for [Co(l-chxn)$_2$Cl$_2$]ClO$_4$ $\Delta\epsilon_{610}$ 0.93).

Asymmetric Synthesis of Carbonatobis(l-cyclohexanediamine)-cobalt(III) Chloride Monohydrate. Optically active (–)-[Co(l-chxn)$_2$-CO$_3$]Cl·H$_2$O was prepared from *trans*-[Co(l-chxn)$_2$Cl$_2$]Cl ($\Delta\epsilon_{610}$ 0.96) by using a modification of Werner's[26] method for the preparation of the corresponding racemic ethylenediamine complex.

Solid Na$_2$CO$_3$ (1.1 g, 0.010 mol) was added to a warm solution of *trans*-[Co(l-chxn)$_2$Cl$_2$]Cl (3.95 g, 0.0100 mol) in water (45 ml, 55°) with stirring (the solution changed in color from green to red almost immediately). The solution was reduced in volume on a steam bath to 15 ml and placed in the refrigerator (5°) overnight. The precipitate was filtered from solution, pressed dry, washed with 95% ethanol and then acetone, and air-dried; yield 2.5 g. Recrystallization of the first fraction did not improve the optical purity of the complex ($\Delta\epsilon_{530}$ –4.32). Additional impure complex was obtained by reducing the volume of the filtrate and cooling in ice. It can be purified by recrystallization from warm water. *Anal.* Calcd for [Co(l-chxn)$_2$-CO$_3$]Cl·H$_2$O: C, 38.95; H, 7.50; N, 13.96. Found: C, 38.45; H, 7.39; N, 13.88.

Asymmetric Synthesis of Malonatobis(l-cyclohexanediamine)-cobalt(III) Iodide Monohydrate. (–)-Malonatobis(l-cyclohexanediamine)cobalt(III) iodide monohydrate was prepared from (–)-[Co-(l-chxn)$_2$CO$_3$]Cl·H$_2$O ($\Delta\epsilon_{530}$ –4.32) and malonic acid. To a stirred solution of (–)-[Co(l-chxn)$_2$CO$_3$]Cl·H$_2$O (3.82 g, 0.0100 mol) dissolved in 35 ml of warm water (60°) was carefully added a solution of malonic acid (3.12 g, 0.0300 mol) and KOH (0.56 g, 0.010 mol) in 10 ml of water (evolution of CO$_2$ is observed). The solution was warmed to 85° and heated and stirred for 2 hr to ensure conversion to the malonato complex (a shift occurs in peak position from 515 to 500 nm in the visible absorption spectrum). The resulting solution which had been reduced in volume to 10 ml was cooled in ice, filtered to remove any impurities which form, and replaced in an ice bath, and excess KI (2.48 g, 0.015 mol) was added to the filtrate with stirring. After 30 min the complex was filtered and air-dried. Recrystallization was effected by dissolution of the compound in a minimum amount of warm water, filtering, and evaporating the filtrate at room temperature ($\Delta\epsilon_{536}$ –1.72). *Anal.* Calcd for [Co-(l-chxn)$_2$mal]I·H$_2$O: C, 33.73; H, 6.05; N, 10.49. Found: C, 33.69; H, 5.99; N, 10.62.

Preparation of Oxalatobis(l-cyclohexanediamine)cobalt(III) Chloride Monohydrate. This complex was prepared in the same manner as the analogous carbonato complex. Six grams of *trans*-[Co-(l-chxn)$_2$Cl$_2$]Cl yielded 3.7 g of pure product in the first fraction. The product had low optical activity so that optical resolution was necessary.

Resolution. A mixture of [Co(l-chxn)$_2$ox]Cl·H$_2$O (4.00 g, 0.00975 mol) and Ag[(–)-[Co(EDTA)]] (2.22 g, 0.00487 mol) in 20 ml of water was stirred for 15 min at 50° and filtered. The combined filtrate and washings (few milliliters of hot water) were evaporated in a rotary evaporator to 20 ml and placed in an ice bath. Approximately 60 ml of absolute ethanol was added to precipitate purple crystals which were filtered and washed with 95% ethanol, ethanol, and ether. A second fraction was removed from the filtrate and the combined yield (2.4 g) was recrystallized from a minimum volume of warm water by cooling in an ice bath. The crystals were filtered and washed as before. The CD intensities ([$\Delta\epsilon$]$_{534}$ –0.336[20]) were unchanged by further recrystallization. The diastereomer (0.9 g) was dissolved in a minimum amount of warm water, excess NH$_4$Br (0.25 g) was added, and the solution was stirred thoroughly. The (–)-[Co-(l-chxn)$_2$ox]Br·H$_2$O was filtered, washed with a little absolute ethanol, and air-dried. It was recrystallized once from a little warm water by cooling slowly at room temperature ($\Delta\epsilon_{524}$ –3.09). *Anal.* Calcd for [Co(C$_{14}$H$_{28}$N$_4$O$_4$)]Br·H$_2$O: C, 35.52; H, 6.34; N, 11.84. Found: C, 34.88; H, 6.50; N, 12.12.

The filtrate from the second fraction of diastereomer was passed through a short (2 × 6 cm) column of Dowex I-X8 anion-exchange resin in the chloride form by eluting with water to remove all [Co-(EDTA)]$^-$ from the solution. Four fractions of orange crystals were obtained by evaporation of the filtrate. In each case the crystals were washed with 95% ethanol and ether and air-dried. Fractions 3 and 4 were combined and recrystallized from water at room temperature by slow evaporation. The crystals obtained were filtered and washed with a little distilled water only and dried by suction on the filter. The CD of the (+)-[Co(l-chxn)$_2$ox]Cl·3H$_2$O ($\Delta\epsilon_{517}$ +3.78) was unchanged by further recrystallization. *Anal.* Calcd for [Co-(C$_{14}$H$_{28}$N$_4$O$_4$)]Cl·3H$_2$O: C, 36.19; H, 7.32; N, 12.05; Cl, 7.62. Found: C, 36.07; H, 6.56; N, 12.08; Cl, 8.03. Samples which were
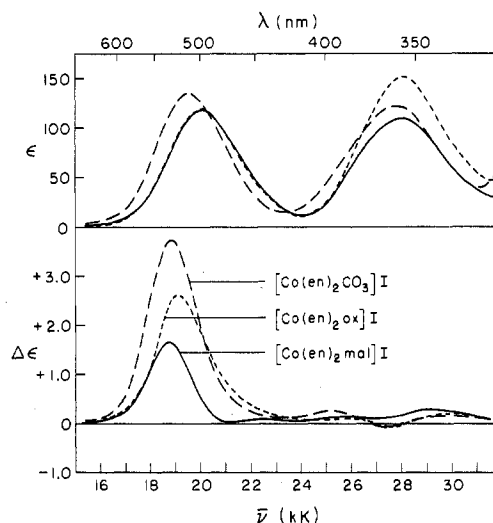
(26) A. Werner, *Ann.*, **386**, 72 (1912).

Figure 2. Absorption and CD spectra for [Co(en)$_2$(O–O)]I complexes.

dried to remove waters of crystallization, even under vacuum at room temperature, failed repeatedly to give consistent or meaningful analytical results.

Spectra. The absorption spectra were measured on a Cary 14 spectrophotometer using a tungsten lamp. The CD spectra were recorded with a Roussel-Jouan Dichrograph using a tungsten lamp. The spectra were taken at room temperature at concentrations of *ca.* 10^{-3} *M*.

Results and Discussion

Syntheses and Resolutions. In the resolution of [Co(en)$_2$-ox]$^+$ with hydrogen (+)$_D$-tartrate anion, the optical purity of the less soluble diastereomer is dependent upon the time allowed for crystallization. For example, when the original solution was filtered after cooling in an ice–salt bath to 10° (15 min), 8.7 g of diastereomer with $\Delta\epsilon_{520}$ +2.30 was obtained. In another trial, after 40 min in an ice–salt bath, 10.7 g of diastereomer with $\Delta\epsilon_{520}$ +1.50 was obtained. Both procedures led to *ca.* 6 g of pure (+) isomer after recrystallization and removal of the resolving agent, but the shorter cooling time is more expedient.

Attempts to resolve [Co(en)$_2$(mal)]$^+$ using hydrogen (+)$_D$-tartrate anion were unsuccessful. An exception to the solubility rule[27,28] for relating the absolute configurations of octahedral complexes was noted in this study. Although (+)-[Co(en)$_2$ox]$^+$ and (–)-[Co(en)$_2$mal]$^+$ are assigned opposite absolute configurations (see below), both form the less soluble diastereomer with (–)$_{546}$-[Co(EDTA)]$^-$. It was also noted that there is no correlation of absolute configuration with order of elution from a Cellex P cation-exchange cellulose column. When racemic [Co(en)$_2$ox]Cl·H$_2$O was eluted from the column with 0.05 *M* NaCl, the first fraction was enriched in the (+) isomer (27%) and the last fraction was enriched in (–) isomer (22%). For racemic [Co(en)$_2$mal]I· 0.5H$_2$O the (–) isomer eluted first (24% pure) and the (+) isomer last (19% pure). The results were reproducible for both complexes.

It was found that [Co(en)(mal)$_2$]$^-$ could be resolved with [Co(en)$_2$ox]$^+$ as indicated in Figure 1. However, the yields were poor compared to those obtained using [Co(en)$_2$-(NO$_2$)$_2$]$^+$,[6] and, therefore, no detailed procedure was developed.

The complexes [Co(l-chxn)$_2$CO$_3$]$^+$ and [Co(l-chxn)$_2$ox]$^+$ were both prepared from *trans*-[Co(l-chxn)$_2$Cl$_2$]$^+$ by nearly

(27) A. Werner, *Ber.*, **45**, 1229 (1912).
(28) M. Delepine, *Bull. Soc. Chim. Fr.*, [5] **1**, 1256 (1934).

identical procedures. The reaction was stereospecific in the case of the carbonato complex, however, while the racemic oxalato complex was formed. Another experimental peculiarity occurred in the resolution of $[Co(l\text{-chxn})_2ox]^+$ with $[Co(EDTA)]^-$. Regardless of whether the $(+)$ or $(-)$ isomer of the resolving agent was used, the $(-)$ isomer of the oxalato complex always crystallized first.

Absorption and CD Spectra. The CD and absorption spectra for the complexes $[Co(en)_2L]^+$ where $L^{2-} = CO_3^{2-}$, ox^{2-}, or mal^{2-} are shown in Figure 2. The data for the carbonato and oxalato complexes have been discussed previously[12,13] and are included here for comparison. In the second (T_{2g}) band region (*ca.* 24–32 kK) three peaks are observed in the CD spectra of the carbonato and oxalato complexes while just two occur in the spectrum of the malonato complex. The shape of the CD curve of the malonato complex in this region, however, suggests the same pattern of transitions of T_{2g} (O_h) parentage as in the other two dicarboxylato complexes and the net (T_{2g}) rotatory strengths are small and roughly equal for the three complexes.

In the first (T_{1g}) band region, there is a very pronounced decrease in rotatory strength $CO_3^{2-} > ox^{2-} > mal^{2-}$ with increasing chelate ring size. As the CD intensities diminish through this series there is a progressively larger low energy shift $(\nu_{\epsilon_{max}} - \nu_{\Delta\epsilon_{max}})$ of the CD peak frequencies from the positions of the T_{1g} absorption maxima, CO_3^{2-} (0.7 kK) < ox^{2-} (0.9 kK) < mal^{2-} (1.3 kK). The low energy shift suggests the presence of a component of opposite sign adjacent to the dominant peak. The increasing shift with increasing ring size may mean either that the splitting is changing or that the dominant peak is diminishing to a greater extent than the adjacent peak. In contrast to the CD of the carbonato and oxalato complexes where only one peak occurs in the T_{1g} region, splitting is quite evident in the CD spectrum of $[Co(en)_2mal]^+$. Two peaks of the same sign are observed in this region and the minimum between them suggests the presence of a peak of opposite sign in support of the above argument from the relative frequencies of absorption and CD maxima.

The isomers of the carbonato and oxalato complexes for which the dominant CD peak in the visible region is positive have previously been assigned the Λ configuration.[12,13] Because of the close qualitative similarity of the malonato complex, the absolute configuration of this complex can be assigned in the same way.

Like en, l-chxn forms a five-membered chelate ring, but it is forced into a fixed conformation (λ) by the puckered cyclohexane ring. A second difference is the presence of two asymmetric atoms in the l-chxn chelate ring. It has been suggested,[29] however, that the vicinal contribution to the rotatory strengths from the two asymmetric centers is quite small compared to the conformational effect since l-pn (only one asymmetric center) and l-chxn give rise to CD curves of nearly equal intensity in analogous complexes.[30,31]

Not surprisingly, the trends among the absorption and CD spectra (Figure 3) of the complexes $(-)$-$[Co(l\text{-chxn})_2L]^+$ where $L^{2-} = CO_3^{2-}$, ox^{2-}, or mal^{2-} parallel those for the analogous en complexes (Figure 2). The dominant peak intensities decrease in the order $CO_3^{2-} > ox^{2-} > mal^{2-}$ and the frequency displacements of the CD peaks from the absorption maxima are almost identical with those of the en series.

(29) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, pp 202–203.

(30) B. J. Brennan, Ph.D. Thesis, University of Pittsburgh, 1971.

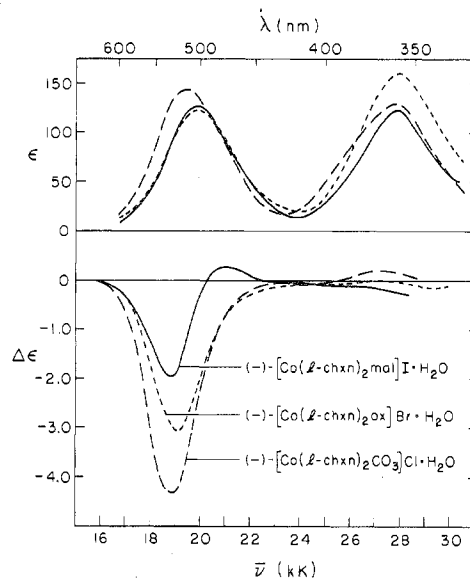(31) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, 19, 1915 (1965).

Figure 3. Absorption and CD spectra for $[Co(l\text{-chxn})_2(O\text{-}O)]X$ complexes.

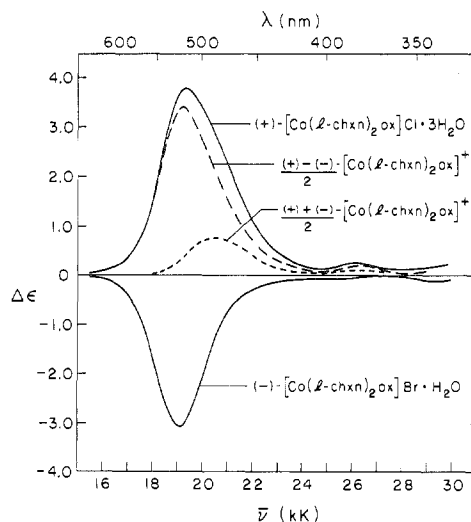**Figure 4.** Differential CD curves for $[Co(l\text{-chxn})_2ox]^+$.

A major difference is that the dominant CD peak intensities for the $(-)$-l-chxn complexes are all greater than for the en analogs.

While only the $(-)$ diastereomers of the carbonato- and malonatobis(l-cyclohexanediamine) complexes were obtained, both the $(+)$ and $(-)$ diastereomers of $[Co(l\text{-chxn})_2ox]^+$ were isolated and the CD spectra are shown in Figure 4. The vicinal-conformational contribution, also shown in Figure 4, was calculated by the usual method[32] of adding the CD curves of the diastereomers and dividing by two. Likewise, the configurational effect (Figure 4) was obtained by subtracting one curve from the other and halving the result.

The vicinal-conformational curve for $[Co(l\text{-chxn})_2ox]^+$ is similar to the curves calculated for other Co^{III}-l-chxn complexes.[22,30,31] The dominant peak is almost twice as intense as in the case of complexes involving only one l-chxn ligand. The contribution should be comparable for the carbonato and malonato complexes.

The configurational effect, calculated by subtracting the vicinal-conformational contribution, for $[Co(l\text{-chxn})_2ox]^+$ is very similar to the CD curve obtained for the related $(en)_2$

(32) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, 3, 1356 (1964).

complex (Figure 2). The T_{1g} rotatory strength, however, is substantially greater for the *l*-chxn complex. Since the effects of the ligand conformation and asymmetric atoms have been removed, the difference must be due to some other property of the *l*-chxn chelate rings such as the displacement of ligating atoms from octahedral positions.

For both sets of bis(diamine)(dicarboxylato)cobalt(III) complexes, the T_{1g} rotatory strength decreases sharply, $CO_3{}^{2-} > ox^{2-} > mal^{2-}$, with increasing size of the dicarboxylato chelate ring. This trend may be analyzed in terms of the distortion of ligand–metal–ligand bond angles observed in other complexes from the octahedral value (90°): *ca.* 70° for carbonate ion,[33] *ca.* 84° for oxalate ion,[34] and *ca.* 96° for malonate ion.[35] By emphasizing distortions from octahedral geometry rather than the number of atoms in each chelate ring, we see that the net T_{1g} rotatory strength decreases with increasing O–Co–O bond angle in the complexes [Co(diamine)₂(dicarboxylate)]⁺ where diamine = en or *l*-chxn.

It is of interest to compare these results with those obtained for other systems of C_2 symmetry involving dicarboxylato chelate rings of different sizes. For the complexes [Co(ox)₂en]⁻ and [Co(mal)₂en]⁻ it was found[12] that while the T_{1g} component peaks for the malonato complex were more intense than for the oxalato complex, the net T_{1g} rota-

tory strength was clearly greater in the latter case. The relative intensities of the individual component peaks depend greatly on the peak separation and the resulting mutual cancelation of peaks of alternating signs. For the complexes [Co(ox)₂gly]²⁻ and [Co(mal)₂gly]²⁻ it was again found[36] that the complex with the larger chelate rings (mal²⁻) gave a smaller net T_{1g} rotatory strength. Likewise, *s-cis*-[Co(trien)-CO₃]⁺ [37] gives a greater T_{1g} rotatory strength than its analog with a larger chelate ring, *s-cis*-[Co(trien)ox]⁺.[38] In all of these systems, the changes in CD intensities on changing ring size are substantial. A notable exception is the series[10] *s-cis*-[Co(EDDA)L]⁻ where $L^{2-} = CO_3{}^{2-}, ox^{2-}, mal^{2-}$. The CD curves for these three complexes are quite similar in both shape and intensity.

Registry No. [Co(en)₂(ox)]Cl, 17439-00-8; (+)ᴅ-[Co-(en)₂ox][H-(+)ᴅ-tart], 40031-95-6; (+)ᴅ-[Co(en)₂ox]I, 40028-98-6; (−)ᴅ-[Co(en)₂ox]Br, 31126-57-5; K[Co(EDTA)], 14240-00-7; K[(+)-Co(EDTA)], 40029-01-4; K[(−)-Co(EDTA)], 23594-44-7; [Co(en)₂mal]I, 40029-03-6; (−)-[Co(en)₂mal]I, 40029-04-7; (+)-[Co(en)₂mal]I, 40029-05-8; *trans*-[Co(*l*-chxn)₂Cl₂]Cl, 15693-93-3; (−)-[Co(*l*-chxn)₂CO₃]Cl, 40029-07-0; (−)-[Co(*l*-chxn)₂mal]I, 40029-08-1; (−)-[Co(*l*-chxn)₂ox]-Br, 40029-09-2; [Co(*l*-chxn)₂ox]Cl, 40029-10-5; (+)-[Co(*l*-chxn)₂ox]Cl, 40029-11-6; [Co(en)₂CO₃]Cl, 15842-50-9; [Co-(NH₃)₄CO₃]NO₃, 15040-52-5.

(33) G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 586 (1962); G. J. Gene and M. R. Snow, *J. Chem. Soc. A*, 2981 (1971); M. R. Snow, *Aust. J. Chem.*, 25, 1307 (1972).
(34) K. R. Butler and M. R. Snow, *J. Chem. Soc. A*, 565 (1971).
(35) K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jap.*, 45, 1755 (1972).

(36) K. Yamasaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, 42, 119 (1969).
(37) G. P. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971).
(38) G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 10, 968 (1971).

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Photoaquation of Some Complexes of Rhodium(III)[1]

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Photoaquation reactions of complexes of the type Rh(AA)₂X₂⁺ and RhA₄X₂⁺, where X is Cl, Br, or I, AA is en, bipy, or phen, and A is py or NH₃, have been studied. Photoaquation of halide was observed for all the complexes while photoaquation of amine could be observed only for complexes with pyridine. The yield of halide increased in the order Cl < Br < I no matter what the amine or the geometry of the complex. The quantum yields were independent of wavelength in the region of d–d transitions and decreased somewhat in the uv region.

Introduction

Photochemical reactions of several complexes of Rh(III) have been reported, although few quantitative studies have been done.[3-10] Attention has been directed to the possibil-

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(2) Abstracted from the thesis presented by W.-L. H. to the University of Puerto Rico in partial fulfillment of the requirements for the M.Sc. degree, 1971.
(3) R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, 90, 2437 (1968).
(4) J. A. Broomhead and W. Grumley, *Chem. Commun.*, 1211 (1968).
(5) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 310.
(6) M. Delepine, *C. R. Acad. Sci.*, 236, 1713 (1953).
(7) P. Poulenc, *Ann. Chim. (Paris)*, 4, 567 (1935).
(8) F. Lareze, *C. R. Acad. Sci.*, 259, 2438 (1964).
(9) T. L. Kelly and J. F. Endicott, *Chem. Commun.*, 1061 (1971).
(10) L. Moggi, *Gazz. Chim. Ital.*, 97, 1089 (1967).

ities for improved synthetic procedures for Rh(III) complexes such as Rh(AA)₂XY⁺ *via* the photoaquation of Rh-(AA)₂X₂⁺, where AA is en,[3,11] bipy,[4] or phen,[4] and X and Y are halide or pseudohalide.

Complexes of Rh(III) which contain three or four pyridine molecules have been reported to undergo photoaquation of the pyridine.[5-8] The photochemistry of Rh(NH₃)₅X²⁺ depends on the nature of X. When X is I, photoaquation of the NH₃ trans to the I is observed,[9] whereas when X is Cl, the photoaquation of Cl⁻ is observed,[10] and when X is Br, photoaquation of both Br⁻ and NH₃ is observed.[9]

The low-temperature luminescent behavior of some Rh(III) complexes has been studied, and the luminescence of glassy

(11) Abbreviations used in this work: ethylenediamine, en; pyridine, py; 2,2-bipyridyl, bipy; 1,10-phenanthroline, phen; AA, a diamine; A, an amine.