a 14% exchange of isocyanate ligand was calculated to have taken place at the end of the 3-hr period. Hence a maximum of 14% of the $C_5H_5Fe(CO)_2(N^{14}CO)$ formed in reaction 2 could have resulted from ligand exchange. The conclusion remains that mechanism B is the predominant and perhaps the only mechanism for reaction 2.

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An Improved Procedure for the Resolution of the Bis(oxalato)ethylenediaminecobaltate(III) Ion

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Because the optically active forms of the bis(oxalato)-ethylenediamine cobaltate(III) ion have been and will continue to be excellent resolving agents for many cationic cobalt(III) complexes, it is only proper that a detailed resolution procedure be developed to afford both enantiomorphic forms in useful quantities.

Dwyer, Reid, and Garvan have reported a general method for the resolution of $Co(en)(ox)_2^-$. In their resolution procedure,[1] they failed to indicate such necessary data as volumes, yields, and the details of their fractional crystallization schemes. Although their directions allow one intuitively skilled in the art to obtain an undisclosed quantity of one optically active antipode, the method used to obtain the other optically active form is complicated by the incorrect use of *d* and *l* rotational designations. The preparation of materials used in the resolution as well as the resolution itself is a formidable time-consuming task. This author feels the following experimental details with a view toward clarification will enable future investigators to conserve time and energy in the resolution of the bis(oxalato)ethylenediaminecobaltate(III) ion.

Experimental Section

Reagent Properties.—Racemic sodium and calcium bis(oxalato)-ethylenediaminecobaltate(III) were prepared by the method given by Dwyer, Reid, and Garvan.[1] The yields obtained were consistently 50% less than stated.

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared by the method given by Bailar.[2]

cis-Dinitrobis(ethylenediamine)cobalt(III) nitrite was prepared by dissolving *trans*-$[Co(en)_2Cl_2]Cl$ (20 g) in 50 ml of water which was then warmed to 40–50° with stirring. To this solution was added potassium nitrite (22 g) dissolved in 50 ml of water. The solution was filtered and placed in an ice bath. Yellow *cis*-$[Co(en)_2(NO_2)_2]NO_2$ precipitated as the side of the beaker was scratched with a glass rod. The product (12 g) was collected by filtration, washed with ethanol and ether, and air dried.

An alternate method has been developed by Harbulak and Albinak.[3]

The *cis*-$[Co(en)_2(NO_2)_2]NO_2$ was resolved by the method developed by Dwyer and Garvan[4] using a fourfold increase in reagent quantities.

Optical Rotations.—Optical rotations were determined using a Rudolph high-precision photoelectric polarimeter equipped with a mercury arc lamp and a Beckman monochrometer. 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 within 1% unless otherwise indicated. Samples were weighed using a Sartorius MPRS electromicrobalance.

Analyses.—Microanalyses were obtained from Galbraith Laboratories, Knoxville, Tenn.

Resolution Procedure.—Silver oxalate (3.5 g) was prepared from an aqueous solution of oxalic acid and silver nitrite and collected by filtration. The solid silver oxalate was added to $(+)_{546}$-$[Co(en)_2(NO_2)_2]Br$ (8.25 g, 1.9×10^{-2} mol, $[\alpha]_{546}$ +110 ± 10°) in 300 ml of water at 55°, shaken vigorously for 3 min, and filtered. Racemic $Ca[Co(en)(ox)_2]_2$ (7.05 g, 1.2×10^{-2} mol) was added to the orange-yellow filtrate and the solution was stirred mechanically for 30 min at 50–55°. The calcium oxalate which formed was quickly filtered off and racemic $Na[Co(en)(ox)_2]$ (6.93 g, 2.0×10^{-2} mol) dissolved in 150 ml of water at 50° was added to the red-brown filtrate. The mixture was rapidly stirred and the temperature was maintained at 50–55° for 20 min. The red-brown diastereoisomer of $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(+)_{546}$-$[Co(en)(ox)_2]$ (5.0 g) was collected by rapid filtration at 50°, washed with ethanol, and dried *in vacuo* at 25°. An aqueous solution containing 21.4 mg/100 ml gave α +0.212 whence we have $[\alpha]_{546}$ +991 ± 15°. *Anal.* Calcd for $(+)_{546}$-$[Co(C_4H_{16}N_4)(NO_2)_2]$-$(+)_{546}$-$[Co(C_2H_8N_2)(C_4O_8)]$: C, 21.21; H, 4.24; N, 19.79. Found: C, 21.33; H, 4.31; N, 19.90.

The filtrate was transferred to a graduated 500-ml beaker and treated as indicated in the flow sheet. By cooling the filtrate to 35°, a second fraction of red-brown solid (0.55 g, $[\alpha]_{546}$ −292 ± 10°) was collected. The filtrate was stirred and heated to 45°, and the solvent was evaporated under a stream of air until the volume was 200 ml. The volume was measured with the stirring apparatus turned off. The solution was filtered giving 0.35 g of solid with $[\alpha]_{546}$ −875 ± 12°. Again the volume was reduced at 45° under an air stream to 125 ml. The mixture was filtered yielding 3.75 g of red-brown solid with $[\alpha]_{546}$ −880 ± 16°. The third and fourth fractions contained $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(-)_{546}$-$[Co(en)(ox)_2]$. A portion of the diastereoisomer was recrystallized from hot ethanol–water solution, collected by filtration, washed with ethanol and ether, and dried *in vacuo* at 25°. An aqueous solution containing 26.86 mg/100 ml gave α −0.237 whence we have $[\alpha]_{546}$ −890 ± 15°.

Nine additional fractions of diastereoisomer and starting material were obtained as the volume was slowly reduced to 35 ml; however, the rotations were not sufficient to warrant recovery of optically pure $Co(en)(ox)_2^-$. The resolving agent present in these latter fractions was recovered as the iodide by grinding the solid with sodium iodide in a water slurry followed by filtration. Ethanol was added to the purple-red filtrate and $Na[Co(en)(ox)_2]$ precipitated. It could be purified by recrystallization from water–ethanol. *Anal.* Calcd for $(+)_{546}$-$[Co(C_4H_{16}N_4)(NO_2)_2]$-$(-)_{546}$-$[Co(C_2H_8N_2)(C_4O_8)]$: C, 21.21; H, 4.24; N, 19.79. Found: C, 21.15; H, 4.14; N, 19.99.

The diastereoisomers were broken up and the resolved complex was recovered as the sodium salt as indicated below. The first fraction (5.0 g) of $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(+)_{546}$-$[Co(en)(ox)_2]$ was ground with 30 ml of warm (35–40°) water containing 6.0 g of sodium iodide. The solution was cooled and the insoluble yellow $(+)_{546}$-$[Co(en)(NO_2)_2]I$ was collected by filtration. Absolute ethanol (15 ml) was added to the purple-red filtrate and the solution was cooled in the refrigerator for 6 hr. The first

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(1) F. P. Dwyer, I. Reid, and F. Garvan, *J. Amer. Chem. Soc.*, **83**, 1285 (1961).

(2) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

(3) F. P. Harbulak and M. J. Albinak, *J. Inorg. Nucl. Chem.*, **25**, 232 (1963).

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

crop of red-violet crystals (2.0 g) was collected by filtration, washed with acetone, and air dried. More absolute ethanol was added to the filtrate and cooling was continued for 4 hr. Three additional fractions were collected in this way totaling 0.85 g of complex. An aqueous solution of the first fraction containing 32.7 mg/100 ml gave α +0.471 whence we have $[\alpha]_{546}$ +1440 ± 10°. The rotation of the monohydrate given by Dwyer, *et al.*, is $[\alpha]_{546}$ +1400°.[1] The $(+)_{546}$-$Na[Co(en)(ox)_2]$ obtained above was not recrystallized prior to analysis. *Anal.* Calcd for $(+)_{546}$-$Na[Co(C_2H_8N_2)(C_4O_8)]\cdot 3.5H_2O$: C, 18.90; H, 4.05; N, 7.35. Found: C, 19.10; H, 4.17; N, 7.18.

The other antipode, $(-)_{546}$-$Na[Co(en)(ox)_2]$, was isolated as follows. Fractions three and four were combined giving 4.0 g of $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(-)_{546}$-$[Co(en)(ox)_2]$ which was ground up with 5.0 g of sodium iodide dissolved in 30 ml of water at 40°. The mixture was filtered to remove yellow $(+)_{546}$-$[Co(en)_2(NO_2)_2]I$ (2.9 g) and the filtrate was treated as before with absolute ethanol to cause $(-)_{546}$-$Na[Co(en)(ox)_2]$ to crystallize. The ethanol was added slowly with stirring until the very first signs of crystallization (clouding) occurred; then the solution was cooled for 4 hr. If crystallization was not evident, more ethanol was carefully added and the cooling was continued. Two fractions of red-violet crystals were obtained, totaling 2.60 g. These were washed with acetone and air dried. An aqueous solution containing 26.7 mg/100 ml gave α −0.385 whence we have $[\alpha]_{546}$ −1442 ± 16°. The rotation reported by Dwyer, *et al.*, for $(-)_{546}$-$Na[Co(en)(ox)_2]\cdot H_2O$ is −1400°.[1] This sample was not recrystallized prior to analyses. *Anal.* Calcd for $(-)_{546}$-$Na[Co(C_2H_8N_2)(C_4O_8)]\cdot 3.5H_2O$: C, 18.90; H, 4.05; N, 7.35. Found: C, 19.16; H, 3.86; N, 7.30.

The complete resolution was repeated using identical reagent quantities and $(-)_{546}$-$Co(en)_2(NO_2)_2^+$ having $[\alpha]_{546}$ −115 ± 10° as the resolving agent. The results are indicated in Scheme I for the isolation of the two diastereoisomers. As in the first procedure, at least 2.2 g of each optically pure enantiomorph was obtained.

Results and Discussion

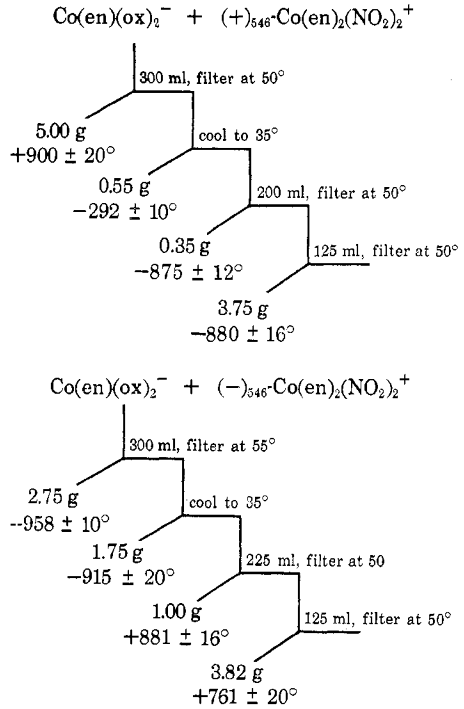
A resolution procedure for obtaining both optically active isomers of $Co(en)(ox)_2^-$ in pure form is presented. Scheme I presents a partial fractional crystallization procedure corresponding to the isolation of diastereoisomers when $(+)_{546}$-$Co(en)_2(NO_2)_2^+$ and $(-)_{546}$-$Co(en)_2(NO_2)_2^+$ are utilized as resolving agents, respectively. By carefully controlling the temperature and volume of the mixture, one can obtain a clean separation of $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(+)_{546}$-$[Co(en)(ox)_2]$ from the more soluble diastereoisomer $(+)_{546}$-$[Co(en)_2(NO_2)_2]$-$(-)_{546}$-$[Co(en)(ox)_2]$. A similar situation exists when $(-)_{546}$-$Co(en)_2(NO_2)_2^+$ is employed as the resolving agent.

The diastereoisomers are easily decomposed by treatment with aqueous sodium iodide, causing the resolving agent to precipitate as the very insoluble iodide salt. Optically pure $Na[Co(en)(ox)_2]$ is recovered from the filtrate as shown in Scheme II. Both optically pure isomers were found to be 3.5-hydrates having equal and opposite specific rotations at 546 mμ of + and −1440 ± 16°, respectively.

The optical isomers are stable indefinitely in the solid state. Photoracemization, especially in direct sunlight, occurs both in the solid state and in aqueous solution. Slow racemization accompanied by some decomposition occurs in boiling aqueous solution in the dark and in cold 0.1 *N* sodium hydroxide solution.[1]

SCHEME I[a]

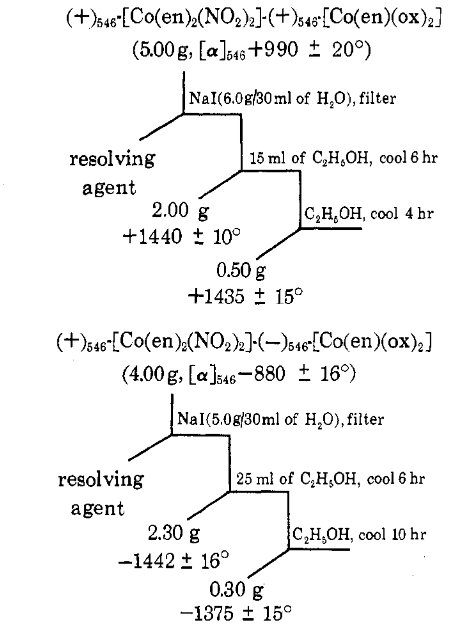
CRYSTALLIZATION PROCEDURE FOR DIASTEREOISOMER ISOLATION



[a] All rotations are at the mercury green line, 546 mμ.

SCHEME II[a]

RECOVERY OF OPTICALLY PURE $Na[Co(en)(ox)_2]$



[a] All rotations are at the mercury green line, 546 mμ.

Optical rotatory dispersion and circular dichroism spectra have been reported.[5] The electronic absorption spectrum of $Na[Co(en)(C_2O_4)_2]\cdot H_2O$ exhibits two bands in the visible region at 541 and 384 nm with molar extinction coefficients of 112 and 177, respectively.

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