TABLE I

METAL (ALKYLPYRIDINE)$_4$-(SCN)$_2$ CLATHRATES

Metal	Alkyl	Foreign molecule	Mole foreign molecule per mole metal complex	Composition of clathrated material
Ni^{++}	3-Methyl	Dichlorobenzenes	No clathrate	
Ni^{++}	3-Methyl	Methylstyrenes	No clathrate	
Ni^{++}	4-*n*-Propyl	Methylstyrenes	No clathrate	
Ni^{++}	4-Methyl	Dichlorobenzenes	0.76	90.5% *p*-, 9.5% *o*-
Ni^{++}	4-Methyl	Methylstyrenes	.60	90.0% *p*-, 10.0% *o*-
Fe^{++}	4-Methyl	Methylstyrenes	.94	82.3% *p*-, 17.7% *o*-
Co^{++}	4-Methyl	Methylstyrenes	.86	82.5% *p*-, 17.5% *o*-

rous complex seems to have the highest capacity for accepting alien molecules into its lattice. The proportion of benzene derivative to Werner complex approaches a one-to-one molar ratio which is observed for the nickel ammonia cyanide clathrate with benzene.

The crystal structure of the clathrate of benzene and dicyanoamminenickel(II) is an extended two-dimensional flat network of alternating nickel and cyanide groups.[4] Attachment of the coördinated ammonia molecules at right angles to this network provides a "box" which captures benzene molecules. Ammoniacal solutions of nickel cyanide will also form clathrates with pyrrole, furan and thiophene but not with the xylenes. Somewhat the same situation may occur with the metal tetra-(4-methylpyridine)-dithiocyanates. Insertion of the longer 4-methylpyridine molecule increases one dimension of the "box" allowing the entrapment of molecules of larger dimensions.

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[4] H. M. Powell, *J. Chem. Soc.*, 319 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XXI. The Resolution of Racemic Substances through Optically Active Complex Inorganic Compounds[1,2]

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RECEIVED APRIL 6, 1957

Apparently only two of the possible isomers of the [Co(pn)$_3$]$^{+++}$ ion (D-[Co(*d*-pn)$_3$]$^{+++}$ and L-[Co(*l*-pn)$_3$]$^{+++}$) are sufficiently stable to be isolated, and it has therefore been suggested that asymmetric complex ions react preferentially with certain favorably oriented stereoisomers of attacking coördinating agents. In addition, ethylenediamine has been reported to displace the ligand of the D-[Co(edta)]$^-$ ion with some retention of configuration to give the D-[Co(en)$_3$]$^{+++}$ cation. Consequently, D-[Co(edta)]$^-$ ion was treated with racemic propylenediamine to determine whether preferential displacement of the coördinated ligand by one stereoisomer of propylenediamine occurs, leaving the other isomer in solution. This is expected to take place if an asymmetric central ion of a complex influences the rate of attack of asymmetric ligands, provided that this complex ion retains its configuration during the displacement. Such preferential displacement is actually found to occur, with *d*-propylenediamine reacting more rapidly than the levo isomer, thereby effecting a partial resolution of *rac*-propylenediamine. Furthermore, treatment of D,L-[Co(edta)]$^-$ with *l*-propylenediamine results in a preferential reaction of the amine with L-[Co(edta)]$^-$, giving a partial resolution of the racemic complex ion. The mechanism by which this displacement occurs has been studied, and the reaction of *l*-propylenediamine with D-[Co(edta)]$^-$ ion, which results in an inversion of configuration of the complex to give L-[Co(*l*-pn)$_3$]$^{+++}$, supports the conclusion that the process is a stepwise displacement of the hexadentate ethylenediaminetetraacetate ligand by three bidentate groups. It is concluded that attack on the asymmetric complex ion by the stereoisomer of preferential configuration of the ligand occurs more rapidly than attack by the opposite isomer, and that attack by this opposite isomer causes an inversion of configuration of the complex resulting in the formation of a stable stereoisomer of the product.

Introduction

Smirnoff[3] and Jaeger[4] reported that only two of the possible stereoisomers of the [Co(pn)$_3$]$^{+++}$ ion[5] are apparently sufficiently stable to be isolated. These are the D-[Co(*d*-pn)$_3$]$^{+++}$ and L-[Co-(*l*-pn)$_3$]$^{+++}$ ions.[6] The other possible combinations of cobalt(III) with propylenediamine (such as [D-(lll)]$^{+++}$, [D(lld)]$^{+++}$, [D(ldd)]$^{+++}$, [L(ddd)]$^{+++}$, [L(ddl)]$^{+++}$, and [L(dll)]$^{+++}$), if formed at all, apparently rearrange to the two stable stereoisomers.

In 1952 Bailar and his co-workers[7,8] partially resolved *rac*-tartaric, α-chloropropionic and lactic acids by treatment with [Co(*l*-pn)$_2$CO$_3$]Cl. In each case one enantiomer of the racemic acid displaced the carbonate preferentially, resulting in a

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[1] Presented in part before the Division of Inorganic Chemistry, 131st Meeting, American Chemical Society, Miami, Florida, April 7-12, 1957.

[2] Taken in part from the Doctoral Dissertation of S. K., University of Illinois, 1954, and the Master of Science thesis of Y. K. W., Wayne State University, 1957.

[3] A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[4] F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 158.

[5] The coördinating agents are designated as follows: en = ethylenediamine, pn = propylenediamine, edta = ethylenediaminetetraacetate anion.

[6] "D" and "L" represent dextrorotatory and levorotatory complex ions, respectively, and "*d*" and "*l*" represent dextrorotatory and levorotatory coördinating agents, respectively.

[7] J. C. Bailar, Jr., H. B. Jonassen and A. D. Gott, THIS JOURNAL, **74**, 3131 (1952).

[8] A. D. Gott and J. C. Bailar, Jr., *ibid.*, **74**, 4820 (1952).

partial resolution of the acid. Hence it appears that an asymmetric complex inorganic compound may exert some influence on the reaction of a racemic attacking ligand by favoring the reaction of one enantiomer over that of the other.

In 1955 Dwyer, Gyarfas and Mellor[9] reported that ethylenediamine displaced the ethylenediaminetetraacetate anion from the D-$[Co(edta)]^-$ anion[6] with some retention of configuration to give the D-$[Co(en)_3]^{+++}$ ion.

Discussion

Since only two isomers of $[Co(pn)_3]^{+++}$ are apparently sufficiently stable to be isolated, and since propylenediamine is expected to displace the ethylenediaminetetraacetate anion from D-$[Co(edta)]^-$ in a manner similar to ethylenediamine, treatment of D-$[Co(edta)]^-$ with *rac*-propylenediamine should result in at least a partial resolution of the amine, since the dextro isomer is expected to react preferentially with the complex anion to form D-$[Co(d\text{-}pn)_3]^{+++}$, leaving *l*-propylenediamine in solution. Furthermore, treatment of *rac*-$[Co(edta)]^-$ with *l*-propylenediamine should result in at least a partial resolution of the complex anion, since the amine is expected to react preferentially with the levo isomer of $[Co(edta)]^-$ to give L-$[Co(l\text{-}pn)_3]^{+++}$, leaving D-$[Co(edta)]^-$ in solution. In addition, the reaction between D-$[Co(edta)]^-$ and *l*-propylenediamine should provide some information concerning the mechanism of these displacement reactions, because D-$[Co(l\text{-}pn)_3]^{+++}$ is apparently not sufficiently stable to be isolated. Therefore, an inversion of configuration of either the complex ion or the ligand is expected, with the formation of a stable stereoisomer of the amine complex.

Partial Resolution of *rac*-Propylenediamine.—D-K$[Co(edta)]$ was treated with *rac*-propylenediamine in an attempt to effect a resolution of the amine according to the equation

$$\text{D-K}[Co(edta)] + 6d,l\text{-pn} = \text{D-}[Co(d\text{-pn})_3]^{+++} + 3l\text{-pn} + K^+ + edta^{-4} \quad (I)$$

Two methods were used to separate the colored complex from the colorless amine. Precipitation of the complex inorganic compound by the addition of a large volume of absolute acetone proved successful in separating the material from the amine, and subsequent treatment of the precipitated D-$[Co(d\text{-}pn)_3]K(edta)$ with hydrobromic acid gave D-$[Co(d\text{-}pn)_3]Br_3$. The second method involved passing the solution over the cation-exchange resin "Dowex 50," through which the *l*-propylenediamine passed without being absorbed. Recovery of the complex from the resin by elution was not complete, so both methods were used on different portions of the solution to obtain samples of *l*-propylenediamine and the complex.

The D-$[Co(d\text{-}pn)_3]K(edta)$ complex was later destroyed by treatment with hydrogen sulfide and the liberated *d*-propylenediamine was distilled under reduced pressure. The specific rotations of the products (see Table I) indicate that a partial resolution of the propylenediamine was actually achieved (approximately 17%).

TABLE I

THE PARTIAL RESOLUTION OF *rac*-PROPYLENEDIAMINE

Compound	Concn. (g./ml., 1 dm. tube)	$\alpha^{25°}_{obsd.}$ (λ = 5890 Å.)	Mean $[\alpha]^{25}_D$
D-$[Co(d\text{-}pn)_3]K(edta)\cdot 2H_2O$	0.00842	+0.040°	
(found)	.00749	+ .036°	+ 4.77°
D-$[Co(d\text{-}pn)_3]Br_3\cdot 2H_2O$	.00710	+ .051°	
(found)	.00545	+ .038°	+ 7.05°
D-$[Co(d\text{-}pn)_3]Br_3\cdot 2H_2O$ (reported)[3,10]			+37°, +40°
l-pn (found)	.00671	− .033°	− 4.92°
	.00671	(− .027°)[13]	(−4.02°) uncorr.[11]
d-pn (found)	.00590	+ .025°	+4.25°
l-pn (reported)[12]			−29.7°

In an effort to determine the reason for partial instead of complete resolution, and to study the mechanism of the displacement, it was decided to attempt the resolution of D,L-K$[Co(edta)]$ with *l*-propylenediamine and to study the reaction between D-K$[Co(edta)]$ and this amine.

Partial Resolution of D,L-K[Co(edta)].—This material was treated with *l*-propylenediamine in an effort to resolve it according to the equation

$$2\text{D,L-K}[Co(edta)] + 3l\text{-pn} = \text{L-}[Co(l\text{-pn})_3]^{+++} + 2K^+ + edta^{-4} + \text{D-}[Co(edta)]^- \quad (II)$$

The resulting solution was passed through the anion-exchange resin "Amberlite IRA-400." The L-$[Co(l\text{-}pn)_3]^{+++}$ cation passed through without being absorbed, and was converted to the bromide with hydrobromic acid. The absorbed D-$[Co(edta)]^-$ was eluted with concentrated potassium chloride solution and recovered as D-K$[Co(edta)]$. The specific rotations of the products (see Table II) indicate that again only a partial resolution was achieved (about 40%).

Reaction between D-K[Co(edta)] and *l*-pn.—Treatment of D-K$[Co(edta)]$ with *l*-propylenediamine at room temperature produced only a slight visible color change during the same period (two hours) for which essentially complete reactions occurred in the previous cases. At 50° noticeable evidence of a reaction was obtained after two hours. The visible absorption spectra and optical rotations of the products indicate that the reaction occurs according to the equation

$$\text{D-K}[Co(edta)] + 3l\text{-pn} = \text{L-}[Co(l\text{-pn})_3]^{+++} + K^+ + edta^{-4} \quad (III)$$

The products were passed over the anion-exchange resin "Amberlite IRA-400" in order to remove any unchanged D-$[Co(edta)]^-$ anion, and the L-$[Co(l\text{-}pn)_3]^{+++}$ cation passed through without being absorbed. It was converted to the bromide by hydrogen bromide, and its rotation was observed (see Table III). Approximately 12% of the cobalt passed from the anionic form (as D-$[Co(edta)]^-$) to the cationic form (as L-$(Co(l\text{-}pn)_3]^{+++}$) during the two-hour period at 50°, but that which did undergo reaction was practically completely "in-

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

[10] M. J. Mathieu, *Ann. phys.*, **19**, 335 (1944).

[11] The solution had a slight yellow color due to a low concentration of D-$[Co(d\text{-}pn)_3]^{+++}$, which was not completely removed by the ion-exchange resin. The concentration of this material was determined spectrophotometrically to be 0.0014 g./ml. The maximum possible correction is therefore (0.0014)(−4.77) = −0.0067°, which is added to the observed rotation of −0.027°.

[12] L. Tschugaeff and W. Sokoloff, *Ber.*, **42**, 55 (1909).

TABLE II

THE PARTIAL RESOLUTION OF *rac*-K[Co(edta)]

Compound	Concn. (g./ml., 1 dm. tube)	$\alpha^{25}_{\text{obsd.}}$	Mean $[\alpha]^{25}$
L-[Co(*l*-pn)$_3$]Br$_3$·2H$_2$O (found)	0.0011	−0.023° (λ = 5890 Å.)	−21.1°
D-[Co(*d*-pn)$_3$]Br$_3$·2H$_2$O (reported)[3,10]		(λ = 5890 Å.)	+37°, +40°
D-K[Co(edta)] (found)	.00015	+0.059° (λ = 5461 Å.)	+401°
	.00012	+0.049° (λ = 5461 Å.)	
D-K[Co(edta)]·2H$_2$O (reported)[13,9]		(λ = 5461 Å.)	+1020°, +1000°

TABLE III

REACTION OF D-[Co(edta)]$^-$ WITH *l*-pn

Compound	Concn. (g./ml., 1 dm. tube)	$\alpha^{25}_{\text{obsd.}}$	$[\alpha]^{25}$
L-[Co(*l*-pn)$_3$]Br$_3$·2H$_2$O (found)	0.0019	−0.062° (λ = 5890 Å.)	−32.6°
D-[Co(*d*-pn)$_3$]Br$_3$·2H$_2$O (reported)[3,10]		(λ = 5890 Å.)	+37°, +40°
D-K[Co(edta)]·2H$_2$O (absorbed in and then removed from resin)	.00010	+0.064° (λ = 5461 Å.)	+640°

verted" in configuration, and L-[Co(*l*-pn)$_3$]$^{+++}$ ion is apparently the sole stereoisomer produced (see the first two lines of Table III). The unchanged D-[Co(edta)]$^-$ ion was removed from the ion-exchange column by elution with concentrated potassium chloride, and this accounted for the remainder of the cobalt. The specific rotation of this anion showed that it was still strongly dextrorotatory (see Table III).

Mechanism of the Displacement Reaction.—Since some resolution of *rac*-propylenediamine can be achieved by the displacement of ethylenediaminetetraacetate anion from D-[Co(edta)]$^-$, it appears that (a) some retention of configuration of the central metal ion is maintained during the reaction, (b) the displacement of ethylenediaminetetraacetate ion by *l*-propylenediamine is a stepwise process, and (c) the configuration of the complex ion influences the rate of reaction of enantiomers of an asymmetric attacking agent.

These experiments indicate that all of the coördinating atoms of the ethylenediaminetetraacetate anion do not dissociate from the metal ion at once, because displacement of this group would then give rise to racemic products, since the attacking groups could enter the coördination sphere in dextro and levo configurations about the metal ion with equal probability. That the products are not racemic implies that a stepwise displacement, such as shown in Fig. 1, takes place, at least in part. If the principle of the "*trans* effect"[14] that negative groups labilize substituents in positions *trans* to themselves is operative in this displacement, it is expected that one of the *trans* carboxylate groups is first displaced by a bidentate chelating agent, and a group *cis* to that is then displaced by the other coördinating group of the attacking agent. The remaining groups are probably displaced in a similar fashion, and the asymmetry of the central atom is not destroyed.

An example of the influence of a complex ion in a particular configuration on the rate of displacement of its ligands by asymmetric attacking agents is seen in reaction (I). During the course of this reaction two reactions, (III) and (IV), occur simultaneously, with reaction (IV) occurring at a faster rate, which accounts in part for only a partial resolution of racemic propylenediamine.

$$\text{D-K[Co(edta)]} + 3d\text{-pn} = \text{D-[Co(}d\text{-pn)}_3]^{+++} + \text{K}^+ + \text{edta}^{-4} \quad \text{(IV)}$$

Likewise, two reactions, (III) and (V), occur during the course of reaction (II), with reaction (V) occurring at a more rapid rate than (III), resulting in only a partial resolution of D,L-[Co(edta)]$^-$. The lower percentage resolution in the first case than in the second probably is due to the relatively large concentration of amine base in reaction (I), which may catalyze the hydrolysis and racemization of the starting material,[9] D-[Co(edta)]$^-$. In addition, the complex ion in reaction (II) is racemic at the start of the reaction and therefore cannot undergo racemization as in the previous case.

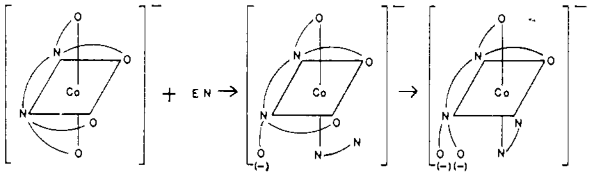

Fig. 1.—The first step of the proposed mechanism of the displacement of ethylenediaminetetraacetate from D-[Co(edta)]$^-$ ion by a bidentate chelating agent.

$$\text{L-K[Co(edta)]} + 3l\text{-pn} = \text{L-[Co(}l\text{-pn)}_3]^{+++} + \text{K}^+ + \text{edta}^{-4} \quad \text{(V)}$$

Experimental

Reagents.—The inorganic salts, acids and bases used were of the standard reagent or C.P. quality. The ethylenediaminetetraacetic acid was purchased from the Antara Division of the General Dyestuff Company.

Compounds. 1. Preparation and Resolution of D,L-[Co(edta)]$^-$. A. D,L-Ba[Co(edta)]$_2$.—Two methods[15,16] were investigated for the preparation of this compound, and the one chosen[16] gave a high yield of the material. Resolution of the compound was attempted by fractional crystallization of the levo strychninium salt.[17,2] However, the specific rotation of the product is only about half that obtained when the compound is resolved by fractional crystallization of the salts formed with D-[Co(en)$_3$]Cl(SO$_4$) according to a modification of the method of Dwyer, Gyarfas and Mellor[9] and the latter method was chosen for this work.

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[13] A rotatory dispersion study of D-K[Co(edta)]·2H$_2$O showed $[\alpha]^{25}_{5461} = +1020°$.

[14] J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50**, 201 (1952).

[15] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

[16] S. Kirschner, "Inorganic Syntheses," Vol. V, T. Moeller, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1957.

[17] D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4574 (1953).

B. D-$[Co(en)_3]Cl(SO_4)$.—*rac*-$[Co(en)_3]Cl_3$ was prepared according to the method of Work[18] and was resolved by the method of Werner[19] using silver *d*-tartrate as the resolving agent. The diastereoisomer, D-$[Co(en)_3]Cl$-*d*-$C_4H_4O_6 \cdot 5H_2O$, ($[\alpha]^{25}D = +101°$), was treated with an equivalent quantity of a saturated solution of copper(II) sulfate according to equation (VI), the solution was allowed to stand at room temperature for 12 hours, and the precipitated copper(II) *d*-tartrate was filtered. The desired enantiomer, D-$[Co(en)_3]Cl(SO_4)$, was crystallized by evaporation, in a stream of air at room temperature.

$$\text{D-}[Co(en)_3]Cl(d\text{-}C_4H_4O_6) + CuSO_4 = \text{D-}[Co(en)_3]Cl(SO_4) + Cu(d\text{-}C_4H_4O_6) \quad \text{(VI)}$$

C. Formation and Resolution of Diastereoisomers.—This was accomplished according to the reaction

$$2\text{D-}[Co(en)_3]Cl(SO_4) + 2\text{D,L-}Ba[Co(edta)]_2 = 2BaSO_4\downarrow + [\text{D-}Co(en)_3][\text{D-}Co(edta)]_2Cl + [\text{D-}Co(en)_3][\text{L-}Co(edta)]_2Cl \quad \text{(VII)}$$

D,L-$Ba[Co(edta)]_2 \cdot 4H_2O$ (9.03 g., 0.01 mole) dissolved in 10 ml. of water was treated with 3.70 g. of D-$[Co(en)_3]Cl(SO_4)$ (0.01 mole), the precipitated barium sulfate was filtered after being digested for two hours at room temperature (in order to avoid racemization), and the diastereoisomers were fractionally crystallized by cooling the filtrate to 8° and adding absolute ethanol dropwise. The first crop of crystals was recrystallized from water by the addition of ethanol. For D-$[Co(en)_3][Co(edta)]_2Cl \cdot 4H_2O$[11]: a 0.013% solution in a 1 dm. polarimeter tube showed $\alpha D = +0.060°$; $[\alpha]^{25}D = +460°$. The diastereoisomer was converted to D-$K[Co(edta)] \cdot 2H_2O$ by the method of Dwyer, Gyarfas and Mellor.[9]

The less soluble of the diastereoisomers from reaction (VII) was treated with potassium iodide and hydrogen peroxide[9] to replace the asymmetric cation with potassium ion

$$[\text{D-}Co(en)_3][\text{D-}Co(edta)]_2Cl + 9KI + 3H_2O_2 = \text{D-}[Co(en)_3]I_9\downarrow + 2\text{D-}K[Co(edta)] + KCl + 6KOH \quad \text{(VIII)}$$

The desired material was crystallized from solution (after filtration of the precipitated ethylenediamine complex) by the addition of ethanol, and was then recrystallized from water. For D-K-$[Co(edta)] \cdot 2H_2O$: a 0.0185% solution in a 1 dm. polarimeter tube showed $\alpha_{5461} = +0.189°$; $[\alpha]^{25}{}_{5461} = +1020°$.

2. Partial Resolution of *rac*-Propylenediamine, *d,l*-$C_3H_{10}N_2$.—To a solution of 2.11 g. of D-$K[Co(edta)] \cdot 2H_2O$ (0.005 mole) in 5 ml. of water there was added (at 25°) 2.22 g. of *rac*-propylenediamine (0.03 mole). After two hours the solution was diluted to 30 ml. and was passed successively through three sintered glass Buchner funnels, each packed with 15 g. of "Dowex 50" cation exchange resin, in order to separate any unchanged propylenediamine from the mixture. Since the solution containing the propylenediamine had a slight yellow color due to the incomplete removal of D-$[Co(d\text{-}pn)_3]^{+++}$, the concentration of this complex was determined spectrophotometrically (0.0013 g./ml.) and the calculated correction[11] of $-0.0067°$ was added to the observed rotation of the *l*-propylenediamine (see Table I). Since the D-$[Co(d\text{-}pn)_3]^{+++}$ could not be completely recovered by elution, the original experiment was repeated, omitting the resin procedure, and the complex was recovered by pouring the 30 ml. of solution slowly and with vigorous stirring into two liters of absolute acetone. The precipitate of D-$[Co(d\text{-}pn)_3]K(edta)$ was filtered, dried under vacuum over anhydrous calcium chloride, and converted to the bromide by addition of an equivalent quantity of aqueous hydrobromic acid (see Table I). To a solution of 1.29 g. of D-$[Co(d\text{-}pn)_3]K(edta) \cdot 2H_2O$ (0.002 mole) in 10 ml. of water there was added 1 g. of potassium hydroxide, and hydrogen sulfide was passed through the solution for 30 minutes. The precipitated cobalt(II) sulfide was allowed to digest at room temperature for 12 hours, and was filtered and washed with 2 ml. of water which was then added to the filtrate. The filtrate was distilled under reduced pressure and the aqueous propylenediamine was collected and its rotation observed (see Table I).

3. Partial Resolution of Racemic Potassium Ethylenediaminetetraacetatocobaltate(III)-2-hydrate, D,L - $K[Co(C_{10}H_{12}N_2O_8)] \cdot 2H_2O$.—*l*-Propylenediamine[7,12,20-22] (2.22 g., 0.03 mole) was added to a solution of 4.22 g. of D,L-$K[Co(edta)] \cdot 2H_2O$ (0.01 mole, prepared from the barium salt and aqueous potassium sulfate) dissolved in 5 ml. of water at 25°. The solution was allowed to stand for two hours, after which it was passed through a sintered glass Buchner funnel packed with 20 g. of "Amberlite IRA-400" anion-exchange resin. The $[Co(pn)_3]^{+++}$ passing through the column was converted to the bromide by the addition of hydrobromic acid, its concentration was determined spectrophotometrically, and its rotation observed (see Table II). The resin was washed with water, and the absorbed $[Co(edta)]^-$ was eluted with saturated potassium chloride. Its concentration was determined spectrophotometrically, and its rotation was measured (see Table II).

4. The Action of *l*-Propylenediamine on Dextro Potassium Ethylenediaminetetraacetatocobaltate(III) - 2 - hydrate.—To 0.8 g. of D-$K[Co(edta)] \cdot 2H_2O$ (0.002 mole) dissolved in 5 ml. of water there was added 0.444 g. of *l*-propylenediamine (0.006 mole). The solution was kept at 50° for two hours, and its color changed from violet to red-violet. It was then passed through an ion-exchange resin similar to the one described above. The L-$[Co(l\text{-}pn)_3]^{+++}$ which passed through the resin without being absorbed was converted to the bromide with hydrobromic acid, was crystallized from solution and its rotation was measured (see Table III). The D-$[Co(edta)]^-$ absorbed on the resin was removed by elution with saturated potassium chloride, its concentration was determined spectrophotometrically, and its rotation was measured (see Table III). The yield of L-$[Co(l\text{-}pn)_3]Br_3 \cdot 2H_2O$ was 0.133 g. (2.39×10^{-4} mole) or about 12% of the quantity calculated for complete reaction.

Instruments.—Determinations of optical rotations at single wave lengths (NaD or Hg_{5461}) were carried out on a Rudolph High Precision Visual Polarimeter, Model 80. The observed rotations had an average deviation of ±0.003°. Rotatory dispersion measurements were made on a Rudolph Spectrophotometric Photoelectric High Precision Polarimeter, which contains quartz optics and which utilizes a Model DU Beckman spectrophotometer as a monochromator. Spectrophotometric determinations of the concentrations of the complex ions were made with a Bausch and Lomb Spectronic "20" spectrophotometer and a Warren "Spectracord" attachment used in conjunction with a Model DU Beckman spectrophotometer.

Acknowledgment.—The authors wish to express their sincere appreciation to the Research Corporation for a fellowship grant to one of us (Y.K.W.) and for funds which helped purchase the high precision visual polarimeter used in this work.

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[18] J. B. Work, "Inorganic Syntheses," Vol. II, W. C. Fernelius, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 221.

[19] A. Werner, *Ber.*, **45**, 121 (1912).

[20] M. Delepine and R. Cheritat, *Bull. soc. chim. France*, **11**, 320 (1944).

[21] G. Baumann, *Ber.*, **28**, 1176 (1895).

[22] T. D. O'Brien and R. C. Toole, THIS JOURNAL, **76**, 6009 (1954).