

Cobalt Hydrotricarbonyl Triphenylphosphine.—This compound can be isolated from the kinetic experiments, but since it is relatively unstable it is more conveniently prepared as follows. To a solution of 0.080 g. of triphenylphosphine in 10 ml. of pentane under nitrogen at 0° was added 1.0 ml. of 0.29 *M* cobalt hydrocarbonyl in pentane. Gas was evolved immediately and on cooling to -80°, the clear solution deposited pale yellow crystals of the triphenylphosphine hydride complex. On warming to 25° or on exposure to air the hydride decomposes into the brown dicobalt hexacarbonyl bistrisphenylphosphine complex and hydrogen. The hydride is the same compound reported by Hieber, judging by its infrared spectrum and reactivity.⁵

Nitrosylcobalt Dicarbonyl Triphenylphosphine.—A solution of nitrosylcobalt tricarbonyl, prepared from 30 ml. of 0.07 *M* sodium cobalt carbonyl in ether solution and nitric oxide at 25°, was treated with 3.0 ml. of 1.0 *M* triphenylphosphine in ether solution. After standing overnight at 25° the solution was evaporated and the red crystalline product obtained was recrystallized twice from methanol. The product decomposed at 134.0–135.5°.

Anal. Calcd. for C₂₀H₁₅O₃PNC_o: C, 59.00; H, 3.73. Found: C, 59.00; H, 3.74.

The complex in carbon tetrachloride had bands in the infrared region at 3.23 (w), 4.88 (s), 5.02 (vs), 6.75 (m), 6.98 (m), 8.50 (w), 9.11 (m), 9.71 (w) and 10.01 (w) μ . In carbon disulfide there were bands at 13.42 (s), 14.19 (m) and 14.42 (s) μ .

Reaction of the Butenolactone-Cobalt Carbonyl Complex with Triphenylphosphine.—To a solution of 0.41 g. (1.04 mmoles) of Co₂(CO)₈(C₄H₂O₂)₂ in 10 ml. of ether at 0° under carbon monoxide, was added 4.0 ml. of 1.0 *M* triphenylphosphine in ether. After about 70 minutes gas evolution stopped. The product had partially crystallized during the reaction. The solvent was removed under vacuum and the residue was dissolved in 5 ml. of methylene chloride. Insoluble material was removed by centrifuging, and

addition of 5 ml. of pentane gave red-brown crystals of the phosphine derivative. Two more crystallizations from methylene chloride gave the pure complex. The product had no melting point but it gradually decomposed on heating.

Anal. Calcd. for C₄₀H₃₂O₇P₂Co₂: C, 62.51; H, 3.73. Found: C, 62.07; H, 4.03.

The infrared spectrum in chloroform had bands at 3.22 (w), 3.30 (w), 4.83 (s), 4.91 (vs), 4.98 (vs), 5.58 (m), 5.81 (s), 6.58 (m), 6.73 (m), 6.97 (m), 7.63 (w), 8.42 (w), 9.13 (m), 9.71 (w), 10.00 (w), 10.40 (w) and 11.28 (w) μ . In carbon bisulfide bands were at 13.49 (w), 13.77 (w) and 14.44 (m) μ .

Acetylene Dicobalt Tetracarbonyl Bis-triphenylphosphine.—To a solution of 0.31 g. of Co₂(CO)₈C₂H₂ (1.0 mmole) in 10 ml. of toluene at 60° was added 1.1 ml. of 1.0 *M* triphenylphosphine in toluene. After the gas evolution stopped (about one hour), the solvent was evaporated at room temperature and the product was extracted from the residue with ether. A small amount of insoluble Co₂(CO)₈[P(C₆H₅)₃]₂ was removed by centrifuging. The ether was evaporated to about 5 ml. and 10 ml. of pentane was added. On cooling to -80° red-brown prisms of the product slowly separated from the solution. Three further recrystallizations from ether-pentane gave a pure sample of the bisphosphine, m.p. 207–208° dec.

Anal. Calcd. for C₄₂H₃₂O₄Co₂P₂: C, 64.46; H, 4.12. Found: C, 64.76, 64.81; H, 4.31, 4.32.

The infrared spectrum in methylene chloride had bands at 3.25 (w), 4.94 (s), 5.09 (vs), 6.77 (w), 6.98 (m), 7.16 (w), 7.65 (w), 8.43 (w), 9.11 (m), 9.31 (w), 9.70 (w), 9.98 (w) and 11.10 (w) μ . In carbon disulfide there were additional bands at 13.40 (m), 14.16 (m) and 14.40 (s) μ .

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Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. Part VI. Oxalato-*l*-propylenediaminecobalt(III) Complexes

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Sodium bis-(oxalato)-*l*-propylenediaminecobaltate(III) and oxalatobis-(*l*-propylenediamine)-cobalt(III) iodide have been prepared by direct syntheses from cobalt(II) salts, *l*-propylenediamine and oxalate ions using lead(IV) oxide as the oxidizing agent, and the dextro and levo isomers of the complexes separated. The *dl* and *dll* isomers of these two complexes predominated over the *Ll* and *Lll* isomers, respectively, at equilibrium in aqueous solution at 25°. For the former complex $K = dl/Ll = 1.63$, $\Delta F = -270$ cal./g. mole, and for the latter $K = dll/Lll = 1.40$, $\Delta F = -200$ cal./g. mole. Rotatory dispersion measurements showed that *dl* and *dll* forms of the complexes had the same configuration as the dextro forms of the bis-(oxalato)-ethylenediaminecobaltate(III) and oxalatobis-(ethylenediamine)-cobalt(III) ions.

With the exception of the optically active polyamino-carboxylic acids, 1,2-propanediamine- and *trans*-1,2-cyclohexanediaminetetraacetic acids, which appear to be completely stereospecific in their sexadentate and quinquedentate octahedral metal complexes because of atom crowding,² quantitative information is lacking on the free energy differences³ between the optical isomers of complexes containing a single asymmetric ligand. Both isomers appear to have been detected in cobalt complexes containing one molecule of *d*-cyclopentanediamine, or *l*-propylenediamine,^{4a,b} and in the cation bis-(ethylenediamine)-*l*-propylene platinum(IV).⁵ The value found with the latter complex for the ratio $dl/Ll = 1$ was probably due to the similar rates of formation of the isomers rather than to the establishment of equilibrium between them.

In complex ions containing two asymmetric ligands, such as [Co-*l*-pn₂(NO₂)₂]⁺,⁶ [Co-*l*-pn-*d*-pn(NO₂)₂]⁺,⁷ and

[Co-*l*-pn₂CO₃]⁺,^{8,9} evidence has been obtained for the existence of a few of the possible isomers, but equilibrium data on these systems are lacking.

The anion bis-(oxalato)-*l*-propylenediaminecobaltate(III), which can exist only in the optically isomeric forms *dl* and *Ll*, has been prepared in a similar manner to the bis-(oxalato)-ethylenediaminecobaltate(III) ion¹⁰ by the oxidation of a mixture of cobalt(II) acetate, potassium oxalate and *l*-propylenediamine with lead(IV) oxide. The isomeric mixture was isolated as the sparingly soluble salt of the *d,l*-oxalatobis-(ethylenediamine)-cobalt(III) cation, transformed to the very soluble, purplish-violet sodium salts, and then resolved with the optical forms of [Coen₂(C₂O₄)₂]⁺ cation. The optical isomers, designated *dl* and *Ll* by comparison with the rotatory dispersion curves of the corresponding [Coen(C₂O₄)₂]⁻ ions,¹⁰ Fig. 1, were isomerized at 25° on charcoal, and the equilibrium concentrations calculated

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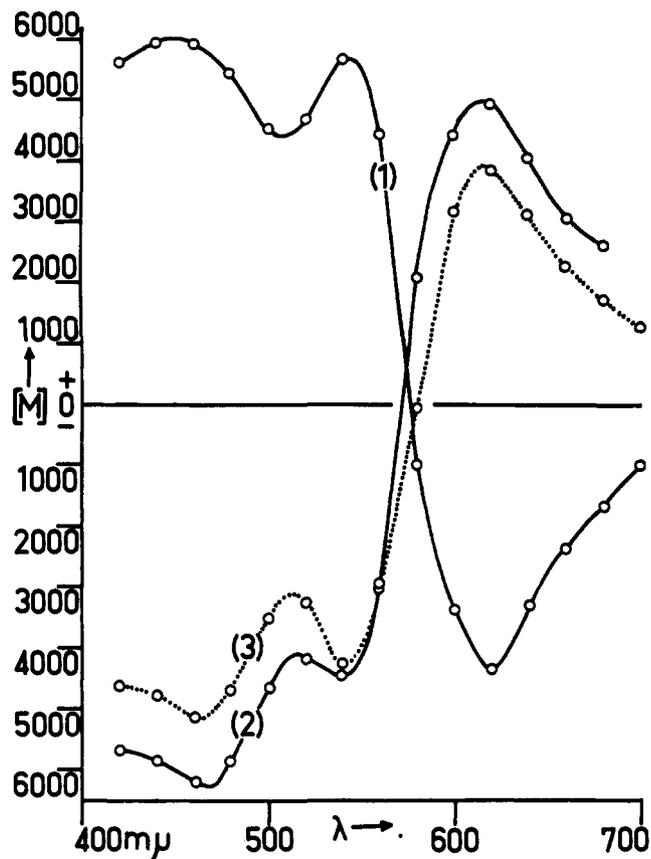


Fig. 1.—The molecular rotatory dispersion curves for the L - $[\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2]^-$ (1), D - $[\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2]^-$ (2) and D - $[\text{Coen}(\text{C}_2\text{O}_4)_2]^-$ (3) ions.

from the rotation of the equilibrium mixture at several wave lengths, the specific rotations of the pure isomers and the concentration of the total complex determined spectrophotometrically. The equilibrium ratio obtained in this way agreed with that determined from the preparative mixture after complete recovery of the isomers.

The cation oxalatobis- $(l$ -propylenediamine)-cobalt(III), prepared by the oxidation of a mixture of cobalt(II) acetate, oxalic acid and l -propylenediamine with lead(IV) oxide, was isolated as the iodide and the isomeric mixture resolved with l -bis-(oxalato)-ethylenediaminecobaltate(III) ion. Only two isomers were isolated which were related as enantiomorphous configurations by a comparison of their rotatory dispersion curves with the optical isomers of the oxalatobis-(ethylenediamine)-cobalt(III) ion, Fig. 2, and were designated Dll and Lll . No evidence of the existence of the possible geometrical isomers was found. The equilibrium mixture was obtained at 25° by shaking aqueous solutions of the isomers with activated charcoal in the presence of a trace of the analogous cobalt(II) complex.¹¹

Experimental

All rotations were measured at 20° in a 1-dm. tube.

D,L -Sodium Bis-(oxalato)- l -propylenediaminecobaltate(III)-0.5-Hydrate.— l -Propylenediamine dihydrochloride¹² (5.9 g., 1.1 moles) was dissolved in a mixture of cobalt(II) acetate-4-hydrate (10 g.) and potassium oxalate (25 g.) in hot water (200 ml.). Lead(IV) oxide (25 g.) was added slowly with stirring, to prevent caking, and the mixture then boiled under reflux for 0.5 hr. The mixture was filtered while hot and oxalic acid-2-hydrate (17 g.) added to the filtrate which was then evaporated

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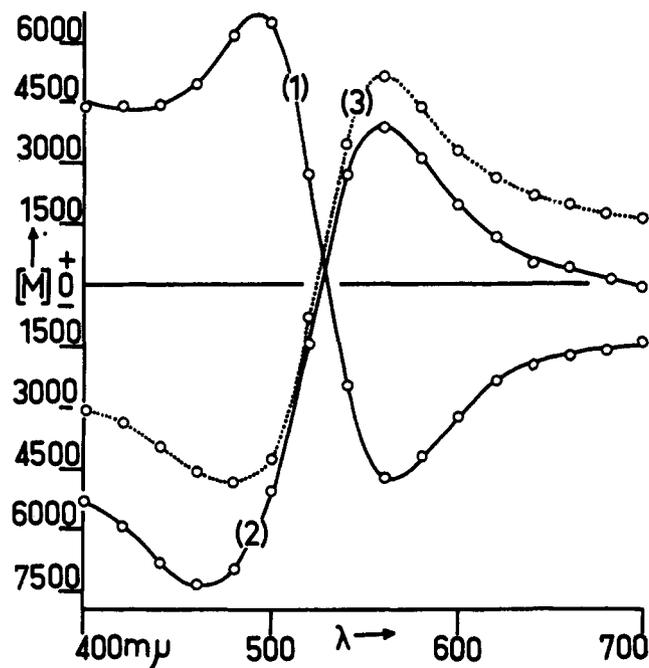


Fig. 2.—The molecular rotatory dispersion curves for the L - $[\text{Co-}l\text{-pn}_2(\text{C}_2\text{O}_4)]^+$ (1), D - $[\text{Co-}l\text{-pn}_2(\text{C}_2\text{O}_4)]^+$ (2) and D - $[\text{Coen}_2(\text{C}_2\text{O}_4)]^+$ (3) ions.

at 70° in a stream of air to a volume of 50 ml. The potassium hydrogen oxalate, (18 g.) that separated on freezing was filtered off and washed with a little ice-water. The purple filtrate was heated to 80° and solid finely divided d,l -oxalatobis-(ethylenediamine)-cobalt(III) chloride-1-hydrate¹⁰ (14 g.) added with stirring. The salt $[\text{Coen}_2(\text{C}_2\text{O}_4)][\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2]$ separated immediately and, after cooling the mixture, the solid was collected and washed with a little ice-water and then ethanol. The cation was eliminated as the insoluble $[(\text{Coen}_2(\text{C}_2\text{O}_4)]\text{ClO}_4$ salt by heating at 60° with a 40% solution of sodium perchlorate (50 ml.) and filtering after double decomposition was complete. The red-violet sodium salt $\text{Na}[\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2] \cdot 0.5\text{H}_2\text{O}$ that separated on the addition of acetone to the filtrate was collected, washed with ethanol, and recrystallized from water by adding acetone (yield 8.2 g., 65%).

Anal. Calcd. for $\text{Na}[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)(\text{C}_2\text{O}_4)_2] \cdot 0.5\text{H}_2\text{O}$: C, 24.63; H, 3.22; N, 8.21. Found: C, 24.82; H, 3.16; N, 8.09.

L -Sodium Bis(oxalato)- l -propylenediaminecobaltate(III)-0.5-Hydrate.—The D,L -sodium salt above (34 g.) was dissolved in a solution of d - $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{Cl} \cdot \text{H}_2\text{O}$ (14.5 g.) in water (300 ml.) at 80° . The diastereoisomer d - $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{-}L$ - $[\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2]$ separated at once, and the mixture was allowed to crystallize at 20° for 10 hours. After filtration, the solid was stirred with cold water (100 ml.), the mixture filtered, the diastereoisomer washed with ethanol and acetone and air-dried (yield 21.2 g.). A further amount of d - $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{Cl} \cdot \text{H}_2\text{O}$ (2.5 g.) was dissolved in the filtrate and washings from the initial separation, when more diastereoisomer (3 g.) separated (total yield 24.2 g., 92%). The substance was too insoluble to purify by recrystallization. It was ground up in a mortar with sodium iodide (13 g.) and water (50 ml.), and after filtration the process was repeated with the solid residue. The combined filtrate was cooled to 5° to remove traces of $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{I}$ and, after filtration, was concentrated to 50% in a stream of air to 50 ml., and the sodium salt of the complex precipitated by the addition of a 50% mixture of ethanol and acetone. It was reconverted to the diastereoisomer as before, the resolving agent eliminated as the iodide, and the pure L -sodium salt (8.2 g.) was isolated by the addition of ethanol. A 0.04% solution gave $[\alpha]_D -315^\circ$; $[\alpha]_{546} +1850^\circ$, $[\alpha]_{5780} -150^\circ$.

Anal. Calcd. for $\text{Na}[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)(\text{C}_2\text{O}_4)_2] \cdot 0.5\text{H}_2\text{O}$: C, 24.63; H, 3.22; N, 8.21. Found: C, 24.91; H, 3.09; N, 8.33.

D -Sodium Bis(oxalato)- l -propylenediaminecobaltate(III)-0.5-Hydrate.—The filtrate remaining from the initial separation of the diastereoisomer above was concentrated at 50° to a volume of 50 ml., sodium perchlorate (5 g.) was added and the mixture was cooled to 5° for 2 hours. After filtration to remove the small amounts of d - $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{ClO}_4$, ethanol was added to precipitate the crude D - $\text{Na}[\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2] \cdot 0.5\text{H}_2\text{O}$. After cooling at 5° , the salt was collected, washed with ethanol and air-dried. The diastereoisomer l - $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{-}D$ - $[\text{Co-}l\text{-pn}(\text{C}_2\text{O}_4)_2]$ was obtained by dissolving the crude D -isomer (18 g.) in a solution of l - $[\text{Coen}_2(\text{C}_2\text{O}_4)]\text{Cl} \cdot \text{H}_2\text{O}$, (16.4 g.) in water (350 ml.) at 60° and

allowing the mixture to cool. After washing with ice-water, the diastereoisomer was decomposed as described above, with sodium iodide, and, after filtration, the pure *D*-sodium salt was crystallized from the filtrate by the addition of ethanol (yield 11 g.). A 0.04% solution gave $[\alpha]_D +730^\circ$, $[\alpha]_{5461} -1200^\circ$, $[\alpha]_{5780} +450^\circ$. The molecular rotatory dispersion curves, Fig. 1, were obtained with the polarimetric attachment to the Shimadzu spectrophotometer, using 0.04% solutions of the optical isomers, and a solution of the analogous *d*-Na[Coen(C₂O₄)₂]H₂O for comparison.

Anal. Found: C, 24.71; H, 3.34; N, 8.29.

The Equilibrium between *D*- and *L*-Isomers.—The preparation of the mixture of isomers from cobalt(II) acetate and *l*-propylenediamine was repeated as above, the potassium hydrogen oxalate was recovered as a by-product, recrystallized to free it completely from traces of the intensely colored [Co-*l*-pn(C₂O₄)₂]⁻ ion, and the salt [Coen₂(C₂O₄)][Co-*l*-pn(C₂O₄)₂] precipitated as completely as possible.

Quantitative recovery of the anion was effected by successive treatments with cold 30% sodium perchlorate solution leaving a pink residue of [Coen₂(C₂O₄)]ClO₄. The deep red-violet solution was diluted to a suitable concentration, which was estimated spectrophotometrically. From the mean values, $\alpha_D -0.045^\circ$, $\alpha_{5780} +0.033^\circ$ and $\alpha_{5461} 0.00^\circ$, and the specific rotations of the pure isomers quoted above, the synthetic mixture was found to contain approximately 40% of the *L*-isomer.

Equilibration of the pure *D*- and *L*-isomers was also effected by shaking 0.2% solutions (20 ml.) with activated charcoal (0.3 g.) at 25° for 0.75 hour. After filtering, the charcoal was washed with water, the volume of filtrate and washings made up to 100 ml., and the concentration of [Co-*l*-pn(C₂O₄)₂]⁻ ion estimated spectrophotometrically. The rotatory dispersion curves were prepared and compared with the specific rotations of the pure isomers at nine wave lengths. The mean concentration of the *L*-isomer at equilibrium obtained from six equilibrations, at 25° was $38 \pm 2\%$, whence $K = 1.63$ and $\Delta F = -290$ cal./g. mole.

***D, L*-Oxalatobis-(*l*-propylenediamine)-cobalt(III) Iodide-0.5-Hydrate.**—Lead(IV) oxide (10 g.) was added slowly to a rapidly stirred solution (300 ml.) at 80° containing cobalt(II) sulfate-7-hydrate (22.5 g.), oxalic acid-2-hydrate (15 g.) and optically pure *l*-propylenediamine¹² (13.0 g.). After 1 hour at 80°, further lead(IV) oxide (5 g.) was added, the heating and stirring continued for a further hour, and the mixture filtered. Excess oxalic acid was neutralized by stirring with lithium carbonate (5 g.). After filtration, barium iodide-2-hydrate (34 g.) in hot water (80 ml.) was added to the hot filtrate. The mixed precipitate of barium sulfate and oxalate was digested at 80–90° for 1 hour, and then filtered off. The deep red solution deposited some of the solid substance on cooling in ice, and further fractions were obtained by evaporation. When the volume had reached 50 ml. the solution was cooled to 5° and glacial acetic acid (5 ml.), potassium iodide (5 g.) and 3% hydrogen peroxide (10 ml.) were added. The dark brown crystalline salt of the triiodide anion was washed with ice-water, dried, suspended in ethanol and converted to the iodide by passing sulfur dioxide gas. The yield of crude product was 34.5 g. (100%). The substance was purified by dissolving it in hot water and then cooling it at 5° for some hours, but a partial separation of the isomers occurred.

Anal. Calcd. for [Co(C₃H₁₀N₂)₂(C₂O₄)₂]I·0.5H₂O: C, 22.30; H, 4.87; N, 12.99. Found: C, 22.45; H, 4.77; N, 12.97.

***D*-Oxalatobis-(*l*-propylenediamine)-cobalt(III) Iodide-1.5-Hydrate.**—A suspension of lead *d*-bis-(oxalato)-ethylenediamine-

cobaltate(III)-3-hydrate¹⁰ (35 g.) in water (300 ml.) at 70° was added to a solution of *D, L*-[Co-(*l*-pn)₂(C₂O₄)₂]I·0.5H₂O (40 g.) in water (300 ml.) at 70°, and the mixture shaken until double decomposition was complete. After cooling rapidly to room temperature, the lead iodide was removed, and the filtrate concentrated at 60° in a stream of air. At intervals, the solution was cooled, and fractions of the diastereoisomer were collected. The specific rotations of fractions varied from -400° to $+360^\circ$ at 578 m μ . Further fractionation gave fractions with maximum specific rotations of -490° and $+720^\circ$. The levorotatory fractions were reserved, the dextrorotatory fractions ($[\alpha]_{5780} +200^\circ$) were dissolved in warm water (50 ml.), and the lead salt of the resolving agent precipitated by the cautious addition of warm 10% lead nitrate solution. After filtration, the excess lead ion was precipitated with dilute sulfuric acid. The partly resolved cation was recovered as the iodide by the addition of excess sodium iodide and, after filtering, the more soluble portion in the filtrate was recovered as the triiodide as before. The latter salt, after reduction with sulfur dioxide, was added to the first portion of iodide, and the whole amount fractionally crystallized from a little hot water. The most active fraction gave $[\alpha]_{5780} +1010^\circ$, and this value was not improved by fractional crystallization. Purification through the very insoluble diastereoisomer *D*-[Co(*l*-pn)₂(C₂O₄)₂]-*l*-[Coen(C₂O₄)₂], which separated on mixing warm solutions of the *D*-iodide and sodium *l*-bis-(oxalato)-ethylenediaminecobaltate(III), was impractical because of the drastic conditions (warm 50% HI and I₂) needed to remove the resolving agent.

Anal. Calcd. for [Co(C₃H₁₀N₂)₂(C₂O₄)₂]I·1.5H₂O: C, 21.38; H, 5.12; N, 12.47. Found: C, 21.44; H, 4.99; N, 12.39.

***L*-Oxalatobis-(*l*-propylenediamine)-cobalt(III) Iodide.**—The levorotatory fractions of the diastereoisomer *L*-[Co-*l*-pn₂(C₂O₄)₂]-*d*-[Coen(C₂O₄)₂] reserved above (9.5 g.) were ground up with a slight excess of a 40% solution of sodium iodide and the *L*-[Co-*l*-pn₂(C₂O₄)₂]I filtered off. Repeated recrystallization of the iodide gave the pure isomer $[\alpha]_{5780} -750^\circ$.

The molecular rotatory dispersion curves, Fig. 2, show that the isomers are antipodal as far as the arrangement about the metal is concerned. For comparison the curve for *d*[Coen₂(C₂O₄)₂]I was also prepared.

Anal. Calcd. for [Co(C₃H₁₀N₂)₂(C₂O₄)₂]I: C, 22.75; H, 4.74; N, 13.27. Found: C, 22.71; H, 4.81; N, 13.04.

Equilibrium between *D/L*- and *L/L*-Isomers.—Solutions (100 ml.) of the isomers (0.1%), were heated, in the presence of activated charcoal, for 1 hour while a stream of oxygen-free nitrogen was passed through. To each solution was then added cobalt(II) chloride hexahydrate (1 ml., 0.28% solution) and potassium oxalate (1 ml., 0.22% solution) and the passage of nitrogen continued for a further 0.3 hour. After cooling to 25°, *l*-propylenediamine (1 ml., 0.171% solution) was added and the passage of nitrogen continued for a further 12 hours. The equivalent cobalt(II) and cobalt(III) complexes were thereby equilibrated catalytically by the charcoal.¹¹ The charcoal was then removed and the rotations and concentrations of the solutions measured. The specific rotations were, respectively, $[\alpha]_{5780} +256^\circ (\pm 15^\circ)$, $+266^\circ (\pm 15^\circ)$, whence $43 \pm 2\%$ and $42 \pm 2\%$ of the *L*-form is present in the equilibrium mixture ($K = 1.40$ and $\Delta F = -200$ cal./g. mole).

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