simple malonate ion in the potassium salt. This band has been assigned to the OCO antisymmetric stretching vibration.

A previous investigation[6] showed that the nature of the metal-to-ligand bond (M–O) may be determined indirectly from the values of the CO stretching frequencies, without determining the low frequencies characteristic of the M–O stretching vibration. The in-phase OCO frequency in malonato metal complexes is lower than the corresponding OCO symmetric frequency of the simple malonate ion, and the out-of-phase frequency is higher than the corresponding antisymmetric frequency. However, these differences are less than those observed for the oxalato metal complexes. Consequently we may conclude that the metal-to-ligand bond of the malonato metal complexes is more ionic than that of the oxalato metal complexes.

Although the OCO bending vibrations are also affected by coördination, the observed frequencies can reasonably be assigned as shown in Table II.

NOTRE DAME, INDIANA

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Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. Part I. Some of the Optical Isomers of Tris-(propylenediamine)-cobalt(III) Ion

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RECEIVED JULY 21, 1958

Oxidation of a mixture of a cobalt(II) salt and *levo*-propylenediamine in the presence of some acid gave two isomeric tris-compounds for which $[\alpha]_D$ −24° and +214°. The optical antipodes were prepared from *dextro*-propylenediamine. The base recovered from each isomer was optically pure, $[\alpha]_D$ (in dry benzene) ±34.4°. The isomers for which $[\alpha]_D$ ±214° are believed to be the D-*lll* and L-*ddd* isomers. For the reaction D-*lll* $\rightleftarrows$ L-*lll* using charcoal as catalyst the equilibrium constant was found to be 5.75 whence $\Delta F^0 = -1.02 \pm 0.05$ kcal./g. mole. The preparation of optically pure *d*- and *l*-propylenediamine is described and also the resolution of DL-$[Co(dl\text{-}pn)_3]^{3+}$ ion.

Introduction

The introduction of asymmetric groups or molecules into metal complexes, that themselves are capable of existence in enantiomeric forms, increases very considerably the number of theoretically possible optical isomers. The bis-(ethylenediamine)-(*d,l*-propylenediamine)-cobalt(III) ion may exist in four possible optical forms designated simply D-*d*, D-*l*, L-*l*, L-*d*,[1] while eight isomers are possible for the tris-(*d,l-trans*-1,2-cyclopentanediamine)-cobalt(III) ion, ($[Co(cptdin)_3]^{3+}$). However, in practice it is believed that the interaction of the ligands with themselves and with the asymmetrical field of the whole complex provide a stereospecific limiting factor that excludes many of the isomers. It is believed that a single asymmetric ligand occasions but partial stereospecificity and certain forms (usually D-*d* and L-*l*), predominate in the mixture of isomers.[2,3] More pronounced stereospecificity appears to be encountered in the synthesis of complexes with two asymmetric donor groups, and isomers containing both optical forms of the donor groups, such as D-*dl* and L-*dl*, have not been detected.[2,4] Very great limitation causing the exclusion of most of the theroretically possible isomers has been claimed to occur in the synthesis of complexes with three asymmetric ligands. Two forms only, designated L-*ddd* and D-*lll*, have been obtained for $[Co(cptdin)_3]^{3+}$, $[Rh(cptdin)_3]^{3+}$ and $[Pt(pn)_3]^{4+}$, when the racemic base was used for the synthesis. Since propylenediamine, (pn), is unsymmetrical as well, each of the optical isomers can exist in *cis* and *trans* forms, making a total of twenty-four theoretical isomers. Frequently, in order to simplify the system in the tris-complexes, one optical form only of the ligand has been used. The number of theoretical isomers is reduced thereby to two (D-*ddd* and L-*ddd*) with symmetrical ligands. With one exception, one isomer only has been isolated. Three forms of the possible four have been obtained of tris-(*d*-alanine)-cobalt(III), of which one presumably is the unusual, thermodynamically unstable form.[5]

Detailed discussions of the principle of stereospecificity will be found in recent reviews and text books.[6-9]

It is unfortunate that the evidence for the principle of stereospecificity is largely negative and that this aspect of the theory has not been sufficiently emphasized. Critical evaluation of the experimental detail of much of the work shows that little quantitative information is available and, as Bailar and Johnson[10] have pointed out in relation to the tris-(propylenediamine)-platinum(IV) complex, that much of the chemical material is un-

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[1] The symbol D or L specifies the theoretical configuration of the whole complex which is not necessarily related to the sign of the rotation in a convenient wave length of light. As the absolute configuration neither of the optical forms of propylenediamine nor of any of its metal complexes is known, the arbitrary designation suggested by Jaeger and used constantly by all authors subsequently has been used in this paper. The capitals refer to the sign of the rotation of the whole complex and the small letters to that of the ligand, usually at the D-line of sodium.

[2] F. M. Jaeger and H. B. Blumendal, *Z. anorg. Chem.*, **175**, 161, 198, 200, 220 (1928).

[3] J. C. Bailar, H. B. Jonassen and E. H. Huffman, THIS JOURNAL, **70**, 756 (1948).

[4] M. Martinette and J. C. Bailar, *ibid.*, **74**, 1054 (1952).

[5] J. Lifschitz, *Z. physik. Chem.*, **114**, 493 (1925).

[6] F. Basolo, *Chem. Revs.*, **52**, 512 (1953).

[7] A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 307.

[8] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 289.

[9] J. C. Bailar (Ed.), "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 313.

[10] R. D. Johnson, Thesis, University of Illinois, 1948.

accounted for in the total amount of isomer finally isolated. Similarly, it is not certain that some of the complexes from which stereospecific conclusions have been adduced have in fact ever been prepared. As we shall show later the synthetic reaction $[CoA_2Cl_2]^+ + B \rightarrow [CoA_2B]^{3+} + 2Cl^-$, (A and B are diamines), used frequently, does not proceed as a formal displacement and yields with some bases, at least, a difficultly separable mixture of products containing both $[CoA_3]^{3+}$ and $[CoB_3]^{3+}$ ions.

In order to account for the failure to isolate some of the optical isomers of the tris-(diamine) complexes of Co(III) and Rh(III), it has been proposed[3] that while they may be formed initially, they undergo disproportionation

$$3\text{L-}[\text{Rh } lld]^{3+} \longrightarrow 2\text{L-}[\text{Rh } lll]^{3+} + \text{D-}[\text{Rh } ddd]^{3+}$$

This reaction which necessitates dismutation and reformation of the complex from the fragments is at variance with the known robustness of the rhodium(III) complexes which characteristically do not undergo this kind of rearrangement. Cobalt(III) complexes are also robust but the synthetic conditions usually employed to prepare tris-(diamine) complexes can permit equilibrium to be attained between various species by electron transfer with the labile Co(II) intermediates. For the latter reason the suggestion that the isolation of the L-*ddd* and D-*ddd* isomers of tris-(*d*-alanine)-cobalt(III) depended upon greater strength of the chelate rings[11,12] is unlikely. More feasible reasons are that the free energy difference between the D-*ddd* and L-*ddd* isomers is smaller than in the tris-(diamine) complexes or that the solubility relationships are more favorable.

The analogy between the internal diastereoisomeric complexes and organic substances with more than one optical center is obvious. Where purely steric factors are not involved, the free energy difference anticipated from the kind of physicochemical forces likely to exist should be of the same order. From measurements of the equilibrium of organic diastereoisomeric salts in non-ionizing solvents and consideration of the data on sugars and esters with at least two optical centers, Kacser and Ubbelohde[13,14] concluded that the free energy difference between optical isomers was of the order nRT where n is a small number, ($K = \sim 1.5$). From the equilibrium between *d*- and *l*-tris-(1,10-phenanthroline)-nickel(II) ion in the presence of *d*-α-bromocamphor-π-sulfonate ion the free energy difference between diastereoisomeric ion pairs was found[15] to be 70 cal./g.mole. This would suggest that when the interacting groups are held by covalent bonds rather than van der Waals association, free energy differences similar to the organic isomers can be expected, and appreciable amounts of most of the theoretical isomers should be present in the synthetic mixtures.

The synthesis of tris-(propylenediamine)-cobalt-(III) salts was carried out by Pfeiffer and Gassman[16] using the racemic base and later by Tschugaeff and Sokoloff[17] and Smirnoff[18] using the optical forms of the base. The salts isolated[18] were D-$[Co(d\text{-pn})_3]Br_2\cdot 2H_3O$ from the *d*-base and L-$[Co(l\text{-pn})_3]\ Br_3\cdot 2H_2O$ from the *l*-base.[19] No other forms were detected and comparison of the rotatory dispersion curves[18] with the optical forms of tris-(ethylenediamine)-cobalt(III) bromide confirmed the configurational assignment and the absence of other isomers.

In this investigation, before repeating Smirnoff's work, the preparation of optically pure *d*-and *l*-propylenediamine and its recovery from the cobalt complexes have been studied. The true specific rotation of propylenediamine and a reproducible method of measurement are essential for the valid characterization of the metal complexes, especially those containing more than one optical form of the base.

The resolution was reported originally by Baumann[20] who recrystallized the hydrogen *d*-tartrate ten times to give $[\alpha]_D - 20.96°$. Exactly the same procedure used by Tschugaeff and Sokoloff[21] gave a product for which $[\alpha]_D - 28.04°$. Later[22] these workers carried out fifteen recrystallizations and also used *l*-tartaric acid to obtain the *d*-isomer. The highest specific rotations were +29.70 and −29.78°. Recent workers have not used the specific rotation of the "anhydrous" base as the criterion of optical purity but have quoted the rotation of the dihydrochloride[23] (+3.99° to +4.10°, from *l*-pn) or the melting point of the hydrogen *d*-tartrate[24] (142°). The small rotation of the hydrochloride is a practical objection, and the melting point of the diastereoisomer is unreliable because of decomposition near the melting point, besides giving no indication of the relative amounts of the optical isomers present. It is not clear from the published descriptions how the recrystallizations of the diastereoisomer should be performed, how many are necessary, nor in fact whether the optically pure isomers ever have been obtained, The variation in the specific rotation obviously depends on the hygroscopic nature of the substance and the change in sign that accompanies protonation. Fowles, McGregor and Symons[25] have shown that the preparation of anhydrous ethylenediamine and propylenediamine requires drastic and elaborate procedures involving several distillations over sodium and potassium. The anhydrous bases are reported to be blue.

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

[12] J. C. Bailar, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), **10**, 17 (1949).

[13] H. Kacser and A. R. Ubbelohde, *J. Chem. Soc.*, 2152 (1950).

[14] M. M. Harris, "Progress in Stereochemistry," Butterworth, London, 1958, p. 164.

[15] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 24 (1954).

[16] P. Pfeiffer and T. Gassman, *Liebig's Ann. Chem.*, **346**, 45 (1906).

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

[18] A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177, 194 (1920).

[19] Some confusion has arisen in the literature because Tschugaeff and Sokoloff have stated (presumably in error) that $[Co(pn)_3]I_3\cdot 2H_2O$ derived from the *l*-base had $[\alpha]_D + 23.63°$ (*cf.* $[\alpha]_D - 24°$ reported in this work), suggesting that it was the D-*lll* isomer.

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

[21] L. Tschugaeff and W. Sokoloff, *ibid.*, **40**, 3461 (1907).

[22] L. Tschugaeff and W. Sokoloff, *ibid.*, **42**, 56 (1909).

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

[24] T. D. O'Brien and R. C. Toole, *ibid.*, **75**, 6009 (1954).

[25] G. W. A. Fowles, W. R. McGregor and M. C. R. Symons, *J. Chem. Soc.*, 3329 (1957).

It has been found that the partly dried base can be extracted into benzene and dried therein with caustic potash to give consistent values of the specific rotation. Resolution is best effected by the use of a mixture of tartaric acid and acetic acid. Ten recrystallizations from dilute acetic acid suffice for all practical purposes, $[\alpha]_D$ −34.2° in benzene. The rotation only rises to −34.8° after twenty-three recrystallizations. The preparation of the *d*-isomer from D–$[Co(d\text{-pn})_3]^{3+}$ has been proposed by Johnson and Bailar[10] who obtained indications for the resolution of DL-$[Co(dl\text{-pn})_3]^{3+}$ ion through the chloride *d*-tartrate by extraction of the gummy mixture of the diastereoisomers with methanol, following the failure of Lifschitz and Rosenbohm,[26] who used the tartrate and the α-bromocamphor-π-sulfonate. Resolution can be effected through the chloride *d*-tartrate by the use of ethylene glycol as a solvent, and then recrystallization from aqueous ethanol. The cobalt complex after distillation with caustic potash and potassium metabisulfite gave the pure *d*-isomer in good yield.

The cobalt(III) complexes prepared from either optical form of the base can be separated into two isomers of opposite sign but greatly different rotatory power. These have been assigned the configurations D-*ddd*, L-*ddd* and L-*lll*, D-*lll*. The propylenediamine, recovered from each isomer by fusion with sodium sulfide in the presence of sodium hydroxide and extraction with benzene, was optically pure. No evidence was obtained, despite repeated fractionation of the stable isomer, of *cis* and *trans* forms. For all of the fractions of the D-*ddd*–L-*ddd* mixture (Table I) the composition calculated from the observed $[\alpha]_D$ and the specific rotations of the pure components agreed well with the composition calculated from the observed $[\alpha]_{5461}$. It is probable that in the Co(III) complexes the geometrical isomers have similar solubilities or form solid solutions.

The visible absorption curves of the D-*ddd* and D-*lll* isomers appear to be identical with an absorption maximum at 466 mμ. From measurements at 589.3 and 546.1 mμ it is concluded that the rotatory dispersion curves are quite different.

The thermodynamically stable isomer can be isomerized on charcoal at 20° in 0.5 hr. to yield the equilibrium mixture in which the D-*lll* isomer is present to the extent of 14.8 ± 0.7%. The same percentage has been found when the Co(III) complex is synthesized from the base in the presence of charcoal. From the value $K = 5.75$ we calculate $\Delta F^0 = -1.02 \pm 0.05$ kcal./g. mole.

The adjoining table summarizes the optical properties of the substances isolated:

Compound	$[\alpha]_D$	$[\alpha]_{5461}$	$[\alpha]_D$ (in benzene) of recovered propylenediamine
D-$[Co(d\text{-pn})_3]I_3 \cdot H_2O$	+ 24°	+184°	+34.2°
L-$[Co(d\text{-pn})_3]I_3 \cdot H_2O$	−214°	−404°	+34.4°
L-$(Co(l\text{-pn})_3]I_3 \cdot H_2O$	− 24°	−184°	−34.8°
D-$[Co(l\text{-pn})_3]I_3 \cdot H_2O$	+214°	+404°	−34.3°

Recently it has been proposed from a study of the dispersion ratio of various colorless tris-(propylenediamine) metal complexes at 470.5 and 588.0 mμ, that the induced asymmetry inherent in the concept of stereospecificity is spurious and that the optical activity of the complex arises only from the ligand.[24,27] The present work shows that while the ligand may make some contribution to the activity the induced asymmetry is the predominating factor. Substantial support is afforded by the isolation of the corresponding isomers of the colorless tris-(propylenediamine)-platinum(IV) ion to be described in Part (II).

It should be emphasized that we have not obtained completely exclusive evidence that the optical isomers isolated are not simply the *cis* and *trans* isomers. However, the specificity of the resolving agent toward one isomer (*e.g.*, *d*-tartrate and the D-*ddd* isomer), the coprecipitation of the D-*ddd* and D-*lll* isomers as Cl–*d*-tartrate, and the differences in rotatory power of opposite sign suggest strongly that the configurations are as designated.

By using Courtauld models it can be shown that there is no steric interference in isomers such as L-*ddl* or L-*lld* nor in the *cis* and *trans* geometrical isomers. The methyl groups of the asymmetric carbon atoms are directed away from each other and from the metal atom. The separation of isomers containing two optical forms of the base is being pursued by fractionation of the mixture of isomers produced when *dl*-propylenediamine or 80% *d* or *l*-base is used in the synthesis of the complex. The use of partly resolved base might be expected to simplify the separation of some of the isomers. The isolation of an isomer believed to be L-*lld* for which $[\alpha]_D$ −78°, $[\alpha]_{5461}$ −244° and from which the recovered propylenediamine had $[\alpha]_D$ −11.5° (in benzene) will be described later.

Experimental

Rotations were measured at 20° in a one-dm. polarimeter tube unless otherwise stated.

Resolution of *dl*-Propylenediamine, (1,2-Propanediamine) *levo*-Isomer.—Technical propylenediamine (260 g., 325 ml.) was added *slowly* with stirring to a solution of *d*-tartaric acid (700 g.) in cold water (750 ml.). The mixture, which had almost boiled, was allowed to cool slowly to 40° and then cooled rapidly in ice to 5° and kept at that temperature for 0.75 hr. The crystalline diastereoisomer was filtered through a large buchner funnel, sucked very dry and washed with ice-water (250 ml.). The yield of air-dried material (fraction 1) was 420 g. A further crop of crystals (200 g. Fraction 1A) was obtained by the addition of glacial acetic acid (150 ml.) to the hot filtrate and washings and allowing to cool overnight. Recrystallization was effected by dissolution in boiling water (850 ml.) followed by glacial acetic acid (50 ml.) and cooling to 10°. For each additional crystallization the volume of water was reduced by 50 ml. and the acetic acid by 3 ml. Ice-water (100 ml.) was used for washing the crystals. At the end of each recrystallization a sample was reserved for recovery of the base. After 10 recrystallizations a portion of the product (100 g.) was recrystallized a further 13 times from 20% acetic acid. The base from each sample (8 g.) in water (40 ml.) containing sodium hydroxide (22 g.) was extracted by boiling benzene (50 ml.) for 0.75 hr. in an extraction tube. The extract was dried over solid potassium hydroxide (5 g.) for three days. The rotation was measured in a well dried polarimeter tube (2 dm.) and the concentration of the base determined, after extraction into water, by titration with 0.1 *N* acid to the methyl orange end-point. (α_D average = −0.8°, titer average, 10 ml. benzene = 30 ml.). The specific rotation $[\alpha]_D$ in dry benzene was −25.2

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(26) J. Lifschitz and E. Rosenbohm, *Z. wissenschaftliche Photographie*, **19**, 198 (1919).

(27) T. D. O'Brien and R. C. Toole, This Journal, **77**, 1368 (1955).

and −26.5° for fractions 1 and 1A, rising to −34.2° after ten recrystallizations and −34.8 ± 0.4° after twenty-three. The specific rotation was independent of the concentration in dry benzene in the range 0.53 to 2.84%. The separation of propylenediamine from benzene is impracticable because of codistillation in the boiling range 82 to 119°.

In all subsequent work ten recrystallizations were considered sufficient and yielded 430 g. of the diastereoisomer, which was converted to the hydrochloride by the method of Bailar, Jonassen and Gott.[23] The best yield of the base was obtained by cautious distillation from the hydrochloride (dried for 15 hr. at 90°), mixed intimately with sodium hydroxide flakes (200 g.). This gave 110 g. of aqueous *l*-propylenediamine, equivalent to 74 g. of the pure base.

dextro-**Isomer.**—The filtrate after the separation of the second crop of crystals (Fraction 1A) was evaporated in a large dish on a steam-bath in a strong current of air. In this way much of the acetic acid evaporated leaving a thick sirup which was transferred to a 2-l. flask. Sodium hydroxide flakes were added until alkaline and then 200 g. more. The mixture was distilled using a current of air for agitation, until the base was removed and frothing commenced. The distillate contained 130 g. of the base in aqueous solution, ($[\alpha]_D$ in dry benzene +25°). This was partly neutralized with 10 *N* hydrochloric acid (58.3 ml.) and added to a solution of cobalt(II) sulfate 7-hydrate (163 g.) in water (1000 ml.). After the addition of charcoal (50 g.), a brisk current of air was passed for 24 hr. through the solution. The charcoal was filtered from the resulting tris-(propylenediamine)-cobalt(III) chloride sulfate and washed with hot water (300 ml.). Barium *d*-tartrate 1-hydrate (178 g.) was stirred in and the mixture kept at 90° for 2 hr. with mechanical stirring. After removal of the barium sulfate, the filtrate was evaporated to about a liter on the steam-bath and then cooled and an equal volume of ethanol added. The red oil that separated, crystallized on standing overnight at 4°. The solid was recrystallized by dissolution in 500 ml. of water (45°) and addition of ethanol (400 ml.) with cooling in ice. The yield of yellow D-[Co(*d*-pn)$_3$]Cl-*d*-$C_4H_4O_6\cdot 3H_2O$ was 163 g. (*d*-pn recovered gave $[\alpha]_D$ +31.3°, in benzene). It was recrystallized twice from water (400 ml.) by the addition of methanol (250 ml.) and cooling in ice for 0.5 hr. (yield 132 g.).

The diastereoisomer, first air-dried and then heated at 90° for 1 hr. was ground with a finely powdered mixture of potassium metabisulfite (20 g.) and sodium hydroxide flakes (200 g.) and distilled cautiously with a large free flame. The yellowish distillate was redistilled from solid potassium hydroxide (10 g.); yield 53 g. of 73% (w./w.) aqueous *d*-propylenediamine, $[\alpha]_D$ in benzene +32–33°.

Purer *d*-propylenediamine, but in lower yield, could be obtained by evaporation of the original solution of the chloride *d*-tartrate to a thick sirup, stirring in ethylene glycol (360 ml.) and then adding cold methanol (360 ml.) The solid that separated was recrystallized by dissolution in water (600 ml.) adding an equal volume of methanol and cooling in ice (yield 104 g.). This gave 42 g. of 73% (w./w.) *d*-propylenediamne, $[\alpha]_D$ +34.0°. A small portion (20 g.) of this purer diastereoisomer was recrystallized another five times. The pn. was extracted into benzene giving $[\alpha]_D$ +34.8 ± 0.6.

Recovery of Propylenediamine from Small Samples of the Co(III) Complexes.—Sodium sulfide 9-hydrate (2 g.) and potassium hydroxide (0.4 g.) were just fused in a test-tube with a ground glass joint. The cobalt compound (0.5 to 0.8 g.) was poured onto the fused mass, which immediately became black. Sodium hydroxide pellets (5 g.) were added, a reflux condenser attached and the mixture heated for a few minutes to complete the decomposition. Benzene (10 ml.) was added through the condenser and the mixture refluxed for 20 min. After cooling, the benzene was filtered on to solid potassium hydroxide (4 g.) and the extraction repeated with a fresh portion (10 ml.) of benzene. After drying for 24 hr. the rotation of the benzene solution was measured in a 2 dm. tube and the concentration of the base determined as before by titration with acid. For pure isomers containing only one optical form of the base the average rotation measured was 0.6 to 0.7°.

Resolution of D,L-[Co(*d*,*l*-pn)$_3$]$I_3\cdot H_2O$ to Yield the Isomers D-[Co(*d*-pn)$_3$]$I_3\cdot H_2O$ and L-[Co(*l*-pn)$_3$]$I_3\cdot H_2O$.—A solution (1 l.) of D,L-[Co(*d*,*l*-pn)$_3$]$_2$(SO_4)$_3$ was prepared by the aerial oxidation of cobalt(II) sulfate 7-hydrate (45 g.), technical propylenediamine (48 ml.), sulfuric acid (16.4 ml. 10 *N*) and charcoal (10 g.). The charcoal was removed after 10 hr., the solution heated to 90° and barium iodide 2-hydrate (100 g.) added. After digestion, the barium sulfate was removed and the filtrate evaporated to 500 ml. on the steam-bath. The orange-yellow iodide separated on cooling and was recrystallized three times from the minimum volume of water at 90° followed by cooling to 20°. This substance was substantially the racemic form of the D-*ddd* and L-*lll* isomers. The other isomers remained in solution.

dextro-**Isomer.**—The racemate (22.5 g.) in water (200 ml.) was transformed to the chloride by shaking with silver chloride. After filtration and washing of the silver halide precipitate, silver *d*-tartrate (12.1 g.) was added to the filtrate and vigorously shaken at 80°. The silver halide was removed, washed with hot water and the filtrate and wash liquid evaporated to a thick sirup. Acetone (500 ml.) was added whereupon the mixed chloride *d*-tartrates crystallized. The solid was washed with acetone and dried in the oven at 70°. It then was dissolved in ethylene glycol (100 ml.) by warming and stirring. On cooling and scratching the sides of the vessel the D-diastereoisomer crystallized in very fine yellow needles. The crystals were washed with 50% methanol–ethylene glycol, then with methanol and acetone. After separation of most of the D-diastereoisomer in this way, the substance could be crystallized easily from water by the addition of half the volume of methanol.

Anal. Calcd. for $[Co(C_3H_{10}N_2)_3]Cl\cdot C_4H_4O_6\cdot 3H_2O$: C, 30.08; H, 7.77. Found: C, 30.22; H, 7.67.

The diastereoisomer (5 g.) in warm water (20 ml.) was treated with concentrated ammonia solution (0.2 ml.) and 25% sodium iodide solution added. On scratching the sides of the vessel and cooling in ice the *dextro*-iodide crystallized. The fine orange powder was washed with cold 25% sodium iodide and recrystallized three times by dissolution in hot water, followed by the addition of a little solid sodium iodide. The crystals were washed with acetone and air-dried. A 1.00% aqueous solution gave α_D + 0.24°, whence $[\alpha]_D$ +24°; and a 0.50% solution gave α_{5461} +0.92°, whence $[\alpha]_{5461}$ +184° (dispersion ratio, 7.66). The recovered *d*-propylenediamine gave $[\alpha]_D$ +34.2 ± 0.7°.

Anal. Calcd. for $[Co(C_3H_{10}N_2)_3]I_3\cdot H_2O$: C, 15.9; H, 4.74; N, 12.40. Found: C, 16.12; H, 4.75; N, 12.47.

levo-**Isomer.**—The same procedure as above, using silver *l*-tartrate, was employed. The iodide had $[\alpha]_D$ −24°, $[\alpha]_{5461}$ −184°, and the recovered *l*-propylenediamine gave $[\alpha]_D$ −34.8 ± 0.7°.

Anal. for $[Co(C_3H_{10}N_2)_3]Cl\cdot C_4H_4O_6\cdot 3H_2O$. Found: C, 30.30; H, 7.34.

Anal. for $[Co(C_3H_{10}N_2)_3]I_3\cdot H_2O$. Found: C, 16.16; H, 4.50; N, 12.54.

L-Tris-(*d*-propylenediamine)-cobalt(III) Iodide 1-Hydrate, L-*ddd*.—*dextro*-Propylenediamine (28.4 g., $[\alpha]_D$ +33°) was used to prepare the sulfate of the Co(III) complex as described previously. This was transformed to the iodide with the required weight of barium iodide 2-hydrate in aqueous solution, and crystallization effected fractionally by evaporation on a steam-bath in a current of air (theoretical yield 87.0 g.). The results are shown in Table I. The most soluble fraction A_6 was separated as the sparingly soluble salt of the anion I_3^- by addition of hydrogen peroxide, sodium iodide and acetic acid. After air-drying it was suspended in absolute ethanol and converted to the iodide by passage of sulfur dioxide.

TABLE I

Fraction	Vol. of soln., ml.	Wt. of fraction, g.	$[\alpha]_D$	$[\alpha]_{5461}$
A_1	700	36.0	+ 21°	+176°
A_2	400	23.3	+ 22°	+182°
A_3	150	12.6	+ 15°	+160°
A_4	80	2.3	− 3°	+110°
A_5	30	2.7	−122°	−188°
A_6	..	0.4	−136°	−216°
Total		77.3		

Fractions A_1, A_2, A_3, A_4 were combined, dissolved in water (500 ml.), activated charcoal (10 g.) added and the mixture refluxed for 1 hr. The solution then was cooled and the small amount of Co(II) complex formed during the isomerization reaction re-oxidized by the passage of air for 2 hr.

The slightly alkaline solution was neutralized with a few drops of dilute sulfuric acid, the charcoal removed and washed with a little hot water. The solution was evaporated on a steam-bath in a current of air until the solid which separated was still wet. After cooling in ice, the solid was separated and the isomerization repeated as before. The filtrate (average volume 10 ml.) rich in the L-*ddd* isomer was added to fractions A_5 and A_6 and retained. The isomerization with charcoal was repeated ten times. The combined solutions containing the L-*ddd* isomer were evaporated to dryness (yield 22.6 g., [α]D −110°). This was converted to the chloride by shaking the aqueous solution (80°) with freshly precipitated silver chloride (20 g.) and then to the chloride *d*-tartrate with silver *d*-tartrate (12.1 g.). This was evaporated to dryness and the semi-solid residue treated with acetone (100 ml.). Crystallization ensued overnight, and the solid was collected and dried at 110° for 20 minutes. It was then dissolved in ethylene glycol (60 ml. at 50°), the solution seeded with the chloride *d*-tartrate of the D-*ddd* isomer and allowed to crystallize in a desiccator for three days. The crystalline diastereoisomer was collected and the filtrate reserved. The diastereoisomer *after washing with 30% ethylene glycol/ethanol and then* ethanol was recrystallized from water by the addition of ethanol. The iodide obtained as described previously was the optically pure D-*ddd* isomer, [α]D +24°.

The diastereoisomer remaining in the ethylene glycol solution above was precipitated by a large volume of acetone and transformed in aqueous solution to the iodide (yield 8.1 g., [α]D −162°). It was again resolved through the chloride *d*-tartrate as before and sufficient acetone added to the ethylene glycol solution to cause separation of about 25% of the diastereoisomer. The latter, which crystallized slowly, was rejected and the more soluble diastereoisomer transformed to the iodide. Separation of the iodide into two fractions gave [α]D −194° and −210°. The less soluble (bigger) fraction was recrystallized from water by the addition of sodium iodide and the fraction that remained in solution separated as the salt of the I_3^- anion. After drying and passsage of sulfur dioxide in absolute ethanol, the latter gave a yellow powder having [α]D −214° and $[\alpha]_{5461}$ −404° (dispersion ratio, 1.89). The rotation of the substance was unchanged after recrystallization from 20% aqueous methanol by the addition of ether. The recovered propylenediamine had [α]D in benzene +34.4 ± 0.7°. No change in rotation occurred when a 0.4% aqueous solution was allowed to stand for six months. On refluxing this solution for 6 hr. the specific rotation fell to −200°.

Anal. Calcd. for $[Co(C_3H_{10}N_2)_3]I_3 \cdot H_2O$: C, 15.90; H, 4.74; N, 12.40. Found: C, 16.12; H, 4.97; N, 12.24.

D-Tris-(*l*-propylenediamine)-cobalt(III) Iodide 1-Hydrate, D-*lll* Isomer.—This was prepared from *l*-propylenediamine ([α]D −33°, 25.6 g.) in the same manner as the *levo*-isomer above. Fractionation of the initial iodide gave a series of fractions for which [α]D varied from −21° for the least soluble to +196° for the most soluble. After repeated isomerization of the combined fractions as before with charcoal, the product was resolved through the chloride *l*-tartrate in ethylene glycol solution. The iodide from the least soluble diastereoisomer had [α]D −24° and was pure L-*lll* isomer. The *dextro*-isomer was obtained after a second resolution, as before, as the iodide, which after rigid purification gave [α]D +214°, $[\alpha]_{5461}$ +404°, and the recovered propylenediamine had [α]D −34.3 ± 0.7°.

Anal. Found: C, 15.94; H, 5.06; N, 12.11.

The Equilibrium between D-*ddd* and L-*ddd* Isomers and between L-*lll* and D-*lll* Isomers.—The mixture was prepared by synthesis from 0.695 g. of cobalt(II) sulfate 7-hydrate, 0.761 g. of 73.5% (w./w.) *d*-pn. ([α]D in benzene +34°), 2.6 ml. of 1 *N* hydrochloric acid. The volume of the solution was adjusted to about 100 ml., 3 g. of charcoal was added and the mixture oxidized for 3 hr. with an air stream. It was then shaken for 7 days. The amount of L-*ddd* isomer was calculated using the values of $[\alpha]_{5461}$ +184° and −404°.

Alternatively, the pure L-*lll* isomer (1.283 g., [α]D −24°, $[\alpha]_{5461}$ −184°) in water (100 ml.) was shaken with 3 g. of charcoal for various periods of time. The volume was adjusted to 500 ml. and the *p*H to 2 in either method and the rotation measured in a 2 dm. tube (Table II).

Table II

Manner of obtaining equilibrium	Time shaken	$[\alpha]_{5461}$	% L-*ddd*
Synthesis using *d*-pn	7 days	+ 94.5°	15.2%
Synthesis using *d*-pn	7 days	+ 95.2°	15.1%
Synthesis using *d*-pn	7 days	+100.7°	14.1%
			% D-*lll*
Pure L-*lll* shaken with charcoal	22.5 hr.	− 97.4°	14.7%
Pure L-*lll* shaken with charcoal	45 hr.	− 93.7°	15.3%
Pure L-*lll* shaken with charcoal	0.5 hr.	− 98.0°	14.6%
		Mean	14.8%

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