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Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. III. The Reaction of Dichlorobis-(ethylenediamine)-cobalt(III) Chloride with *levo*-Propylenediamine

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cis- or *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride reacted with *l*-propylenediamine in water, methanol or dimethylformamide to give tris-(ethylenediamine) and tris-(*l*-propylenediamine)-cobalt(III) chlorides. None of the expected "mixed" tris-(diamine) was detected. The reaction products and the presence of small amounts of Co(II) complexes are consistent with some proportion of a 7- or 8-covalent Co(III) intermediate. These products and the difficulty of separation of the reaction mixture, especially after resolution, suggests the desirability of further confirmation of the alleged *l*-cyclopentanediaminebis-(ethylenediamine)-cobalt(III) bromide.

Asymmetric octahedral complexes containing a single optically active ligand provide the simplest examples of the operation of the stereospecific factor.[1] Two examples have been described: tartratobis-(ethylenediamine)-cobalt (III) chloride[2] and *trans*-1,2-cyclopentanediaminebis-(ethylenediamine)-cobalt (III) bromide.[3] Since the former substance, obtained from carbonatobis-(ethylenediamine)-cobalt(III) chloride and *d*-tartaric acid, behaved inhomogeneously toward a variety of reagents to yield partly active material, it was inferred that the D*d*- and L*d*-isomers exist. Though a partial separation has been effected, the relative amounts of the isomers cannot be assessed. By the resolution of the substance obtained by treating *d,l-trans*-cyclopentanediamine with *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride, two (designated D*l* and L*d*) of the four possible isomers of $[\mathrm{Coen_2cptdin}]\mathrm{Br_3}$ were obtained. By comparison of the rotatory dispersion curves of the D*l*-isomer and the reaction product using *l*-cyclopentanediamine, it was deduced that the L*l* (and hence the D*d*) isomer could be prepared. Though no quantitative evidence was presented, it was concluded that the stereospecific influence of a single asymmetric donor was not great. In this paper are recorded attempts to prepare and resolve *l*-propylenediaminebis-(ethylenediamine)-cobalt(III) salts. The cobalt(III) and rhodium(III) complexes of the optically active sexadentate molecules propylenediaminetetraacetic acid and cyclohexanediaminetetraacetic acid will be described in Part V.

The racemic "mixed" diamine complex has been described[4] as being formed in the reaction between *cis*- or *trans*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ and concentrated aqueous *d,l*-propylenediamine. The reaction using *l*-propylenediamine was found to occur slowly at 20° but rapidly at 80–90° yielding a red solution containing aquo and hydroxo complexes. The yellow tris-(diamine) complex that crystallized after acidification and addition of iodide ion could be separated into a number of fractions of different rotatory power. One fraction was identified by the crystal form, X-ray powder photograph and the absence of optical activity in the recovered base, as the tris-(ethylenediamine) complex. Finely divided *cis*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$, dispersed and partly dissolved in methanol or dimethylformamide, reacted at 20–25° with the separation of the yellow tris-(diamine)-cobalt(III) chloride and very little by-product. In the former solvent the reaction was complete in 2–3 days but in 12 hr. in the latter. The product from methanol after conversion to the iodide was systematically fractionated from aqueous solution in the manner of rare earth separations and the diamine base then recovered from each fraction. The molar ratio

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[1] For previous papers in this series see: F. P. Dwyer, F. L. Garvan and A. Shulman, THIS JOURNAL, **81**, 390 (1959); F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 1943 (1959).

[2] H. B. Jonassen, J. C. Bailar and E. H. Huffman, *ibid.*, **70**, 756 (1948).

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

[4] P. Pfeiffer, I. Grassman and H. Pietsch, *ibid.*, **58**, 301 (1908).

TABLE I

$[\alpha]$	$Coen_3I_3 \cdot H_2O$	L-Co *l*-pn_3] $I_3 \cdot H_2O$	D-[Co *l*-pn_3]$I_3 \cdot H_2O$	Subst. 1		Subst. 2	
				Found	Calcd.	Found	Calcd.
$[\alpha]_{5893}$	± 90	− 24	+214	− 57	− 56	+130	+130
$[\alpha]_{5780}$	±112	− 46	+237	− 79	− 78	+153	+155
$[\alpha]_{5461}$	±253	−184	+404	−219	−218	+307	+301

pn/en, determined from the rotation in benzene solution and the total amount of base, estimated by titration with acid, was found to vary from two to almost zero. The latter material was almost pure tris-(ethylenediamine)-cobalt(III) iodide. The combined fractions, for which the ratio pn/en = 0.5, after resolution through the chloride-*l*-tartrate gave an active iodide, $[\alpha]_D$ −59°. The same substance in 60% yield was obtained after resolution of the reaction product from dimethylformamide and from the more soluble diastereoisomer an iodide, ($[\alpha]_D$ + 130°), was isolated. The molar ratios pn/en for the two active materials were 0.96 and 0.51, respectively. The specific rotations in three wave lengths could be accounted for by an equimolar mixture of L-$[Coen_3]I_3 \cdot H_2O$ and L - [Co *l* - $pn_3]I_3 \cdot H_2O$ for the levorotatory material, and D-$[Coen_3]I_3 \cdot H_2O$ and D-[Co *l*-pn_3]-$I_3 \cdot H_2O$ in the molar ratio 2:1 for the dextrorotatory substance. The compositions are consistent with the pn/en molar ratios. Further, racemic tris-(ethylenediamine)-cobalt(III) iodide could be isolated from the levorotatory substance by fractional crystallization following addition of D-$[Coen_3]I_3$. The comparison of the specific rotations is shown in Table I.

The difficulty of separating optically active mixtures of salts of the $[Coen_3]^{3+}$ and $[Copn_3]^{3+}$ ions and the failure to obtain the "mixed" trisdiamine under a variety of mild preparative conditions suggests the desirability of further confirmation of the substance [$Coen_2$.*l*-cptdin]Br_3. The analytical composition could be explained, as with the dextrorotatory substance above, by a partial racemate containing one molecule of L-[Co *l*-$cptdin_3$]Br_3 and two molecules of D-$[Coen_3]Br_3$. Calculations similar to those in Table I cannot be made, since the former substance has not been isolated and is stated to be excluded on stereospecific grounds. The specific rotations of the isomeric L-[$Coen_2$*l*-cptdin]Br_3 have been derived from rotatory dispersion studies of the isomeric mixture and hence cannot be compared reliably with mixtures of the known D-[Co *l*-$cptdin_3$]Br_3 and L-$[Coen_3]Br_3$.

When seeking to prepare ethylenediaminebis-(cyclopentanediamine)-cobalt(III) chloride, ([Co-en.$cptdin_2$]Cl_3), from *cis*- or *trans*-dichlorobis-(cyclopentanediamine)-cobalt(III) chloride, Jaeger[3,5] observed that the result was largely a mixture of $[Coen_3]Cl_3$ and [Co $cptdin_3$]Cl_3 and quoted in retrospect[5] the formation of a little of the former substance during the preparation of the [$Coen_2$·cptdin]$^{3+}$ ion. Similarly, the reaction between *cis*- or *trans*-[Co *l*-$cptdin_2Cl_2$]Cl and *d*-cptdin, yielded only a mixture of D-[Co *l*-$cptdin_3$]Cl_3 and L-[Co *d*-$cptdin_3$]Cl_3. From the failure of the last reaction and the existence of the alleged [$Coen_2$*l*-cptdin]$^{3+}$ ion, it has been suggested, recently,[6] that the presence of unrelated diamines in a complex is a less serious hindrance to the entry of an optically active diamine than is the presence of the same diamine, but of enantiomorphous configuration. Jaeger himself proposed that the lower symmetry of the "mixed" tris-(diamine) complexes (as well as D*ddl*-isomers) caused spontaneous disproportionation: $2[M\ A_2B]^{3+} = 2[M\ A_3]^{3+}$. As pointed out previously, the characteristic inertness of Co(III) complexes is at variance with this kind of dismutation, but the thermodynamically more stable species may arise through the intervention of small amounts of the Co(II) complex. Examination of the methanol and dimethylformamide mother liquors showed the presence of small amounts of Co(II) complexes (0.5–1% calculated as Co^{2+} ion). The latter complexes did not arise under the experimental conditions either by the reduction of dichlorobis-(ethylenediamine)-cobalt-(III) salts by the solvents or by the interaction of propylenediamine on the mixture of tris-(diamine) complexes (*vide infra*). It is felt that, in order to account for the formation of Co(II) complex, some proportion of a more readily reducible 7- or 8-covalent Co(III) complex is indicated as one of the intermediates or by-products in the displacement of the halogen atom(s). Disproportionation may then occur, or the Co(II) complexes which ensue through rapid reduction effect equilibration through electron transfer. It is significant that only a faint optical activity could be detected in the tris-(ethylenediamine)-cobalt(III) chloride prepared in methanol or dimethylformamide from *levo* - *cis* - dichlorobis - (ethylenediamine) - cobalt-(III) chloride and ethylenediamine. It is therefore considered unlikely that the reaction between *cis*- or *trans*-$[Coen_2Cl_2]Cl$ and a strong base will yield other than the (small) equilibrium proportion of the "mixed" tris-(diamine) complex. This preparative difficulty does not occur to the same extent with Pt(IV) complexes, and in Part IV the preparation and resolution of $[Pten_2pn]Cl_4$, $[Ptenpn_2]Cl_4$ and [Pt *d*-pn_2*l*-pn]Cl_4 will be described.

Although ethylenediamine and propylenediamine are without effect on tris-(diamine)-cobalt (III) complexes at 25°, reduction was found to occur at higher temperatures. After heating in aqueous solution at 95° in an atmosphere of nitrogen for 15 minutes, approximately 2% reduction had occurred. When the reaction was performed in the presence of air some re-oxidation occurred with darkening of the color due to the formation of hydroxy-aquo cobalt(III) complexes. In sealed tubes at 110°, using the anhydrous bases, reduction to the pink crystalline, strongly paramagnetic, cobalt(II) complexes was complete in 72 hr. Since

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[5] F. M. Jaeger and H. B. Blumendal, *Proc. Acad. Wetensch. Amsterdam*, **29**, 575 (1926).

[6] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 292.

neither oxygen nor an oxidation product of the halogen could be detected, it seems that the organic base is oxidized during the reaction. Like the reaction, quoted previously, between tris-(propylenediamine)-platinum(IV) chloride and aqueous propylenediamine, reduction probably proceeds through a paramagnetic 7- or 8-covalent Co(III) complex. It is worth recording that *trans*-$[Coen_2Cl_2]Cl$ prepared in the usual manner[7] by heating the hydrogen chloride adduct at 110° has been found to contain up to 8% of Co(II) complexes.

The paramagnetic state of Co(III) appears to be much more accessible than usually is realized, and since it provides a reaction path *via* catalytic amounts of the resulting Co(II) complexes, might need more consideration in reaction kinetics.

Experimental

All rotations were measured in aqueous solution in a 2-dm. tube at 20°.

Reaction of *cis*-$[Coen_2Cl_2]Cl$ with *l*-Propylenediamine in Methanol.—Finely divided $[Coen_2Cl_2]Cl$ (25 g.) in methanol (120 ml.) was treated with *l*-propylenediamine[1] (12 ml., 70%; $[\alpha]_D$ in benzene −34.6°) and shaken mechanically at 20–25° for 2 days. The resulting yellow precipitate was dissolved in the minimum volume of ice-water, filtered from traces of unchanged $[Coen_2Cl_2]Cl$ and the iodide precipitated by the gradual addition of solid sodium iodide (40 g.). The small amount of tris-(diamine) complex remaining in solution was separated as the black crystalline salt of the I_3^- anion by the addition of glacial acetic acid (1 ml.) and hydrogen peroxide (30%, 5 ml.). After washing with ice-water and air-drying, it was suspended in absolute ethanol (50 ml.) and reduced to the simple iodide with sulfur dioxide gas. The whole of the tris-(diamine) iodide was dissolved in water and recovered in the form of eight fractions by evaporation, the last fraction being obtained by evaporation to dryness. The material was then refractionated, commencing with the most soluble fraction, in such a way as to concentrate the least soluble material in the head fractions. This was repeated five times.

The diamine base was recovered from each fraction by a modification of the procedure described previously.[1] The cobalt complex (0.8 g.) was added to a fused mixture of sodium sulfide 9-hydrate (2 g.) and sodium hydroxide (0.2 g.) in a test-tube with a ground-glass neck. A small condenser was fitted and the mixture heated cautiously until it became uniformly black and vapor commenced to enter the condenser. Benzene (7 ml.) was added, and sodium hydroxide pellets (5 g.) (through the condenser) and the mixture refluxed for 0.3 hr. After cooling, the benzene was filtered rapidly through a dry filter on to a few pellets of sodium hydroxide. A fresh portion of benzene (7 ml.) was added to the black residue. This procedure was repeated twice. The combined extracts were dried for 12 hr. After determination of the rotation of the benzene solution, portion (10 ml.) was added to water and titrated to the methyl orange end-point with approximately 0.1 N acid. The molar ratio pn/en $= 3.17\alpha/(NV - 3.91\alpha)$ where α is the rotation in dry benzene in 2 dm. tube and V is the volume of acid of normality N required to titrate 10 ml. of the benzene solution. Because of the different partition coefficients of the two bases and the slightly greater salt forming ability of ethylenediamine toward sodium hydroxide, the ratio usually tended to be a little high. For an equimolar mixture of $[Coen_3]I_3 \cdot H_2O$ and $[Co\ l\text{-}pn_3]I_3 \cdot H_2O$ values of 1.05 and 1.10 were found.

The fraction numbers commencing with the least soluble and respective pn/en molar ratios were: (1) 2.0; (2) 2.0; (3) nil; (4) 0.36; (5) 0.47; (6) 0.47; (7) 0.50; (8) 0.61; (9) 0.93; (10) 1.17; (11) 1.37. The X-ray powder photograph of fraction 3 showed it to be $[Coen_3]I_3 \cdot H_2O$.

Fractions 5, 6, 7 were combined (4.3 g.), transformed with silver chloride to the chloride and then with silver *l*-tartrate to the chloride *l*-tartrate in the usual way and the solution concentrated to a small volume. The diastereoisomer that separated on cooling in ice was recrystallized four times from water by the addition of 20% by volume of methanol. After removal of the *l*-tartrate radical as described previously,[1] the substance was precipitated as the iodide and recrystallized from a little hot water. A 0.5% solution gave $[\alpha]_D$ −59°, $[\alpha]_{5780}$ −79°, $[\alpha]_{5461}$ −200°. The elementary analysis was inconsistent with the constitution $[Coen_2pn]I_3 \cdot H_2O$. Calcd.: C, 12.90; H, 4.33; N, 12.89. *Found*: C, 14.48; H, 4.18; N, 12.45.

Reaction of *cis*-$[Coen_2Cl_2]Cl$ with *l*-Propylenediamine in Dimethylformamide. (1) Levorotatory Substance.—Finely divided $(Coen_2Cl_2)Cl$ (28.5 g.), suspended in dimethylformamide (200 ml.) and *l*-propylenediamine (12.5 ml., 80%), were stirred mechanically for 12 hr. The yellow tris-(diamine)-cobalt(III) chloride that separated was removed and a further small amount was obtained by adding ether to the filtrate. The whole of this material (34.5 g., 95%), $[\alpha]_D$ −5°), was transformed to the chloride *l*-tartrate as before, the solution evaporated to 60 ml. and allowed to crystallize for 2 days at 4°. A second crop of crystals was obtained by concentration of the mother liquors to 30 ml. The diastereoisomer (24.5 g.) after three recrystallizations from water, was converted to the iodide which was recrystallized. A 0.5% solution gave $[\alpha]_D$ −57°, $[\alpha]_{5780}$ −79° $[\alpha]_{5461}$ −219°. Found: C, 13.95; H, 4.65; N, 12.70; molar ratio, pn/en, 0.96. Calcd. for equimolar mixture $(Coen_3]I_3 \cdot H_2O$ and $[Co\ l\text{-}pn_3]I_3 \cdot H_2O$: C, 12.65; H, 4.45; N, 12.75, molar ratio pn/en, 1.00. The composition of this material changed very slowly with repeated crystallization. After 4 recrystallizations as the iodide, followed by two as the chloride *l*-tartrate, which was then reconverted to the iodide, the latter gave molar ratio pn/en = 0.75, $[\alpha]_D$ −59°, $[\alpha]_{5780}$ −80°, $[\alpha]_{5461}$ −220°. These values are consistent with a mixture of $[Coen_3]I_3 \cdot H_2O$ and $(Co\ l\text{-}pn_3]I_3 \cdot H_2O$ in the molar ratio $^3/_4$. A mixture of D-$[Coen_3]I_3 \cdot H_2O$ (3 g.) and D$[Co\ d\text{-}pn_3]I_3 \cdot H_2O$ (2 g.) recrystallized four times as the iodide, then twice as the chloride *d*-tartrate which was then reconverted to the iodide gave a molar ratio pn/en = 0.54.

(2) **Dextrorotatory Substance.**—Potassium acetate (10 g.) and glacial acetic acid (5 ml.) were added to the mother liquor above containing the more soluble diastereoisomer and the potassium hydrogen *l*-tartrate allowed to crystallize at 4° for 10 hr. After filtration, sodium iodide (10 g.) was added and the yellow complex iodide collected and fractionally recrystallized from water. The optically active material collected in the most soluble fractions. A 0.5% solution gave $[\alpha]_D$ + 130°, $[\alpha]_{5780}$ + 153°, $[\alpha]_{5461}$ + 307°. *Anal.* Calcd. for $[Co(C_2H_8N_2)_2 \cdot C_3H_{10}N_2]I_3 \cdot H_2O$ *or* a mixture $[Co(C_2H_8N_2)_3]I_3 \cdot H_2O$ (2 mole) and $[Co(C_3H_{10}N_2)_3]I_3 \cdot H_2O$, (1 mole): Co, 9.04; I, 58.38; N, 12.89: molar ratio pn/en, 0.50. Found: Co, 9.1; I, 58.6; N, 13.08; molar ratio pn/en, 0.52.

Estimation of Co(II) Complexes Formed in Preparative Reaction.—Finely divided *cis*- and *trans*-$[Coen_2Cl_2]Cl$ (1.75 g.) free from Co(II) complexes were each suspended and partly dissolved, in an atmosphere of nitrogen, in oxygen-free methanol (or dimethylformamide) (30 ml.) and oxygen-free anhydrous ethylenediamine (or propylenediamine) (0.4 g.) added. The vessels were sealed and shaken for 12 hr. At the end of this time the mixture whilst under nitrogen was made acid with hydrochloric acid, (5 N, 3 ml.) to decompose Co(II) complexes and then filtered. The filtrate was diluted to 250 ml. and the Co^{2+} ion estimated colorimetrically[8] as triphenylmethyl tetrathiocyanatocobaltate. The concentrations of Co^{2+} ion derived from *cis*- and *trans*-$[Coen_2Cl_2]Cl$ were, respectively, 3.4×10^{-5} M, 4.7×10^{-5} M (methanol) and 5.4×10^{-5} M, 6.8×10^{-5} M (dimethylformamide). These represent approximately 0.5 to 1.0% of Co(II). Similar values were obtained when propylenediamine was used.

Reaction of Tris-(ethylenediamine)-cobalt(III) Chloride with Ethylenediamine.—A solution of $[Coen_3]Cl_3 \cdot 3H_2O$ (5 g.) in oxygen-free water (250 ml.) was treated with anhydrous ethylenediamine (1 ml.) and heated at 98° for 0.25 hr. No detectable color change occurred and after cooling in nitrogen, the mixture was made acid with hydrochloric acid (5 N, 3 ml.). The concentration of Co^{2+} ion, estimated as above, was 10^{-3} M (approximately 2%). In a sealed glass tube at 110°, a mixture of $[Coen_3]Cl_3 \cdot 3H_2O$ (0.5496 g.) and anhydrous ethylenediamine (0.5 g.) gave a pink crystalline material. At this stage the tube and contents had become strongly paramagnetic (μ = 3.4 B.M. assuming that $[Coen_3]$-

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[7] J. C. Bailar, *Inorg. Syntheses*, **2**, 222 (1946).

[8] K. W. Ellis and N. A. Gibson, *Anal. Chim. Acta*, **9**, 275 (1953).

Cl_2 had formed). The substance was washed successively with oxygen-free anhydrous ethylenediamine, absolute alcohol and ether and dried under an infrared lamp. It was completely decomposed by dilute acids to give the usual pink solutions characteristic of Co^{2+} ion; C. 20.81; H, 8.09; N, 24.28. Calcd. for $[Coen_3]Cl_2 \cdot 2H_2O$: Found: C, 20.93; H, 7.88; N, 24.29.

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[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY]

Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. Part IV. The Preparation and Resolution of "Mixed" Tris-(diamine)-platinum(IV) Complexes

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Bis-(ethylenediamine)-*l*-propylenediamine-platinum(IV), bis-(*l*-propylenediamine)-ethylenediamine-platinum(IV) and bis-(*d*-propylenediamine)-*l*-propylenediamine-platinum(IV) chlorides have been prepared in dimethylformamide solution by the reactions between tetrachloro-(*l*-propylenediamine)-platinum(IV) or tetrachloro-(ethylenediamine)-platinum(IV) and either ethylenediamine or *d*-propylenediamine. The optical isomers of each compound, separated through the *d* and *l*-tartrates, showed no evidence of disproportionation or racemization in boiling aqueous solution.

In previous papers in this series[1] it has been proposed that the failure of workers to isolate "mixed" tris-(diamine) complexes such as *d*-propylenediaminebis-(*l*-propylenediamine)-platinum(IV) and -cobalt(III) chlorides is not due to the inherent instability of the complexes[2-4] but to the establishment of equilibrium among all the possible species during the preparative reactions. As a result, the thermodynamically more favored complexes such as $[Pt\ l\text{-}pn_3]Cl_3$ and $[Pt\ d\text{-}pn_3]Cl_4$ which predominate in the equilibrium mixture have been isolated and the small amount of the "mixed" tris-(diamine) complex has been overlooked. In general it appears that equilibrium is attained either through a 7- or 8- covalent transition state or through small catalytic amounts of the Co(II) and Pt(II) complexes.

The "mixed" tris-(diamines) $[Pten_2pn]Cl_4$, $[Pten\ pn_2]Cl_4$ and $[Pt\ d\text{-}pn_2.l\text{-}pn)Cl_4$ have now been prepared by the reaction between tetrachloroethylenediamine or tetrachloropropylenediamine-platinum(IV) and the appropriate diamine base in dimethylformamide at 20–25°. The "mixed" tris-(diamine) complexes were sparingly soluble in dimethylformamide and separated immediately on formation.

$$[\text{Pt } l\text{-pn Cl}_4] + 2\text{en} = \text{DL-}[\text{Pten}_2\ l\text{-pn}]\text{Cl}_4 \qquad (1)$$

$$[\text{Pten Cl}_4] + 2l\text{-pn} = \text{DL-}[\text{Pten } L\text{-pn}_2]\text{Cl}_4 \qquad (2)$$

$$[\text{Pt } l\text{-pn Cl}_4] + 2d\text{-pn} = \text{DL-}[\text{Pt } d\text{-pn}_2\text{-}l\text{-pn}]\text{Cl}_4 \qquad (3)$$

Although it might be supposed that the addition of the two molecules of base would be stepwise, no evidence was found for the formation of the *trans*-dichlorobis-(diamine) complex, nor could the *cis*-dichlorobis-(diamine) complex be prepared when only one additional molecule of base was allowed to react in very dilute solution. From studies of the reaction between ethylenediamine and ethylenediaminetetrachloroplatinum(IV) in aqueous solution, other workers concluded that the first molecule of the base attached rather slowly as a monodentate ligand, replacing one of the two chlorine atoms *trans* to each other. Rapid replacement of a second chlorine atom, necessarily in the *cis* position, gave the *cis*-dichlorobis-(ethylenediamine) complex which immediately formed the tris-(ethylenediamine) complex.[5] Bis-(ethylenediamine)-*l*-propylenediamineplatinum(IV) ion can exist in only two isomeric forms, (D*l* and L*l*). Because propylenediamine also is unsymmetrical the ions $(Pt\ D\text{-}pn_2\text{-}l\text{-}pn]^{4+}$ and $[Pt\ l\text{-}pn_2en]^{4+}$ can exist in eight and six isomeric forms,[6] respectively.

Resolution of all three substances was effected through the *d*- and *l*-tartrates. The specific rotations of the chlorides are shown in Table I and for comparison the values for $[Pten_3]Cl_4$ and $[Pt\ pn_3]Cl_4$. The values show an obvious regularity when it is remembered that the contribution of the coordinated propylenediamine is opposite in sign to the free base.[7] The approximate composition of the mixture of isomers as prepared has been calculated from the rotation of the mixture and the specific rotations of the pure isomers (Table I). The accuracy of the estimate is limited by the difficulty of isolating the whole of the material, especially the more soluble isomer, from the dimethylformamide solution. It is evident that the relative amounts of the isomers formed in each reaction are necessarily not the equilibrium amounts. If it is assumed that the reaction proceeds through the *cis*-dichlorobis-(diamine) complex and the tris-(diamine) complex is formed therefrom, with retention of con-

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(1) F. P. Dwyer, F. L. Garvan and A. Shulman, THIS JOURNAL, **81**, 290 (1959); F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 1043 (1959); F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5269 (1959).

(2) F. M. Jaeger and H. B. Blumendal, *Proc. Acad. Wentensch. Amsterdam*, **29**, 575 (1926).

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

(4) L. Tschugaeff and W. Sokolov, *Ber.*, **40**, 3461 (1907); **42**, 56 (1909).

(5) F. Basolo, J. C. Bailar and B. R. Tarr, THIS JOURNAL, **72**, 2433 (1950).

(6) The isomeric forms could be designated by the assignment of the usual octahedral position number to the methyl group in proximity. The four isomeric forms of the *levo series* of $\text{DL}[\text{Pt-}d\text{-pn}_2\text{-}l\text{-pn}]^{4+}$ ion can then be written L-(2,3,5)-*ddl*, L-(1,3,6)-*ddl*, L-(1,3,5)-*ddl* and L-(2,3,6)-*ddl*.

(7) T. D. O'Brien and R. C. Toole, *ibid.*, **77**, 1368 (1955).