

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

## Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. VII. The Isolation of the D- and L-Isomers of Bis((-)-propylenediamine)-ethylenediaminecobalt(III) and Bis(ethylenediamine)-((-)-propylenediaminecobalt(III) Ions

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The optical isomers L-[Co(-)pn<sub>3</sub>]Cl<sub>3</sub>, L-[Co(-)pn<sub>2</sub>en]Cl<sub>3</sub>, L-[Co(-)pn(en)<sub>2</sub>]Cl<sub>3</sub>, D-[Co(-)pn<sub>3</sub>]Cl<sub>3</sub>, D-[Co(-)pn<sub>2</sub>en](ClO<sub>4</sub>)<sub>3</sub>, and D-[Co(-)pn(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> have been isolated by a chromatographic separation. The equilibrium constants between the D- and L-isomers were found to be  $K = dl/Ll = 0.47$ ,  $K = Dll/Lll = 0.133$ ,  $K = Dlll/Llll = 0.0685$ , and the stabilities of the isomers have been rationalized with respect to the possible conformations which may be adopted by the en and (-)pn rings (en ≡ ethylenediamine, pn ≡ propylenediamine).

### Introduction

Two principal tenets have been associated with stereospecificity in metal complexes containing three optically active bidentate ligands, namely, that only one configuration of the complex occurred with one antipode of the base<sup>2a</sup> and that complexes containing both ligand antipodes "seem to be unstable from stereometric causes."<sup>2b</sup> Both were disproved by the isolation of L- and D-α-[Co(+)(alanine)<sub>3</sub>]<sup>0,3</sup> of L- and D-[Co(-)pn<sub>3</sub>]I<sub>3</sub>,<sup>4</sup> and L- and D-[Pt(+)-pn<sub>2</sub>(-)-pn]Cl<sub>4</sub><sup>5</sup> (in denoting the optical isomers (-) ≡ / is the sign of rotation of the base in the Na D line). The last two isomers were quite stable even in hot acid or alkali solutions and it has been proposed<sup>6</sup> that the inability of earlier workers<sup>7-9</sup> to isolate tris complexes containing "mixed" d- and l-bidentate amines was not due to the "inherent instability" of the complexes but to the establishment of equilibrium, among all the possible species, during the preparative procedures. Evidence is already available to support this view and more will be presented in a subsequent communication.

In the attempt to clarify the preceding issues the quantitative aspect of stereospecificity has been neglected except for the conformational analysis of the [Co(-)pn<sub>3</sub>]<sup>3+</sup> ion<sup>10</sup> and the measurement of its  $Dlll \rightleftharpoons Llll$  equilibrium constant.<sup>4</sup> The former work had the merit of accounting for the stability of the  $Llll$  isomer over the  $Dlll$  and also gave an equilibrium constant in reasonable agreement with the measured value (revised). Further it gave an explanation for the isolation of roughly equal amounts of both D- and L-α-[Co(+)(alanine)<sub>3</sub>]<sup>0,3</sup> and implied or suggested that appreciable quantities of both D- and L-[Co(-)pn<sub>2</sub>CO<sub>3</sub>]<sup>+,11,12</sup> [Co(en)<sub>2</sub>(+)tartrate]<sup>+,13</sup> [Co(-)pn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>+</sup>], and [Co(-)pn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>-14</sup> ions should occur, a prediction which agreed with the experimental observations.

It is now understood that the degree of stereospecificity in complexes is largely a property of the ligand and

may vary from practically zero as in the [Co(-)pn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>-14</sup> system to the almost total specificity of the [Co(-)PDTA]<sup>-15</sup> ion. The failure of the initial attempts<sup>6</sup> to determine the stereospecific effect of optically active propylenediamine by successively replacing ethylenediamine in [Co(en)<sub>3</sub>]<sup>3+</sup> has now been overcome and the present paper records the equilibrium constants for the D- and L-cobalt(III) complexes containing both en and (-)pn.

### Results and Discussion

The equilibrium concentrations of the isomers in the reaction mixtures [Co(en)<sub>2</sub>(-)-pn]Cl<sub>3</sub>, [Co(en)(-)-pn<sub>2</sub>]Cl<sub>3</sub>, and [Co(-)pn<sub>3</sub>]Cl<sub>3</sub> are recorded in Table I. The mixtures were prepared by oxidizing solutions of cobalt(II) chloride (1 mole), hydrochloric acid (1 mole), and the appropriate amount of ethylenediamine and/or propylenediamine, with air (3 hr.) in the presence of charcoal at 25°. The concentration of cobalt(II) remaining in these solutions is negligible (<1%). The solutions were chromatographed on paper with 1-butanol-H<sub>2</sub>O-acid eluents and the separation of the L-isomers is depicted in Fig. 1. The spots were identified by authentic samples of the isomers. The L-isomers were separated from the mixed D-isomers and DL-[Co(en)<sub>3</sub>]Cl<sub>3</sub>, using 1-butanol-H<sub>2</sub>O-HCl as eluent and the D-isomers were then separated with 1-butanol-H<sub>2</sub>O-HClO<sub>4</sub>.

TABLE I

	Composition, %			
	en/pn ≈ 1/2		en/pn ≈ 2/1	
	Found	Calcd.	Found	Calcd.
DL-[Co(en) <sub>3</sub> ] <sup>3+</sup>	4	4	33	30
DL-[Co(en) <sub>2</sub> (-)-pn] <sup>3+</sup>	22	22	41	44
DL-[Co(en)(-)-pn <sub>2</sub> ] <sup>3+</sup>	42	44	21	22
DL-[Co(-)pn <sub>3</sub> ] <sup>3+</sup>	32	30	5	4

The method of separation was then applied to a cellulose column and the isomers isolated in gram quantities. They were characterized analytically and by determining their en/pn ratios. Their specific and molecular rotations are recorded in the Experimental section.

Equilibrium between the cobalt(III) complexes and the bases is established rapidly in the presence of a charcoal catalyst since it is known that the rate of electron transfer between [Co(en)<sub>3</sub>]<sup>3+</sup> and [Co(en)<sub>3</sub>]<sup>2+</sup> on charcoal is very fast<sup>16</sup> and the cobalt(II) ion is labile to substitution. Further, both bases have almost identical pK<sub>a</sub> values and therefore the stability constants for [Co(en)<sub>3</sub>]<sup>3+</sup>, [Co(pn)<sub>3</sub>]<sup>3+</sup>, and the "mixed" complexes should be very similar. Assuming this, the statistical

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(2) (a) F. M. Jaeger, "Optical Activity and High Temperature Measurement," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 135; (b) p. 155.

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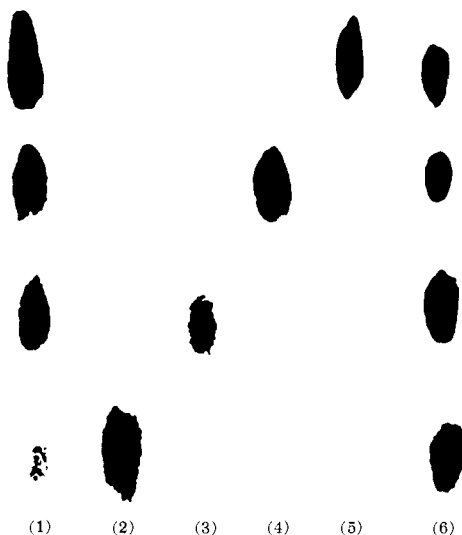


Fig. 1.—(1),  $[\text{Co}(\text{en})_2(-)\text{pn}]^{3+}$  equil. mixture; (2),  $L\text{-}[\text{Co}(-)\text{pn}_3]^{3+}$ ; (3),  $L\text{-}[\text{Co}(-)(\text{pn})_2\text{en}]^{3+}$ ; (4),  $L\text{-}[\text{Co}(-)\text{pn}(\text{en})_2]^{3+}$ ; (5),  $[\text{Co}(\text{en})_3]^{3+}$ ; (6)  $[\text{Co}(-)(\text{pn})_2\text{en}]^{3+}$  equil. mixt.

distribution of bases among the possible compounds is compared with the experimental values in Table I for the en/pn ratios of 2 and 0.5. The agreement between the sets of values is additional evidence for equilibration in these reactions.

The conformational analysis of the  $[\text{Co}(\text{en})_3]^{3+}$  ion by Corey and Bailar<sup>10</sup> has shown that the most stable conformations of the en-metal ion five-membered rings have their C-C axes parallel to the threefold axis of symmetry of the complex ion. The conformation of the stable en ring (denoted *k*) in the  $D\text{-}[\text{Co}(\text{en})_3]^{3+}$  ion and the projection of the same ion looking down the threefold axis of symmetry are shown in Fig. 2. The stable conformation in the *L*-configuration (*k'*) is the mirror image of *k*. Corey and Bailar calculated that the potential energy difference between the stable  $Dk'k'k'$  and  $Lk'k'k'$  arrangements where the H atoms are completely staggered and the least stable arrangements  $Dk'k'k'$  and  $Lk'k'k'$  was 1.8 kcal./mole, about 0.6 kcal./mole for each conformation. The stability of complexes containing mixed conformations would lie between these two extremes.

*l*-Propylenediamine also coordinates as a five-membered ring and can adopt the *k* and *k'* conformations. Figure 3 shows the absolute configuration of  $D(-)\text{pn}$ <sup>17</sup> (a) and the two conformations possible, (b) and (c), when  $(-)\text{pn}$  is coordinated in the *D*-complex configuration. The methyl group may be either axial (b) or equatorial (c) and Corey and Bailar have assessed the energy difference between these conformations to be greater than 2 kcal./mole in favor of the equatorial form. This is enough to ensure that  $(-)\text{pn}$  adopts the *k'*-conformation in the *D*-configuration, *i.e.*, the unstable conformation. In the *L*-complex  $D(-)\text{pn}$  retains the *k'*-conformation with the methyl group equatorial and hence remains in the stable condition with the C-C axis parallel to the threefold axis of symmetry. In the *D*-configuration the *k*-conformation is favored by 0.6 kcal./mole over the *k'*, but the conformation with the methyl equatorial (*k'*) is much more stable—2 kcal./mole—than that with the group axial (*k*). Since the latter is the far greater effect, the *k'*-conformation predominates even in the *D*-configuration and the *D*- and *L*-complex configurations will not have equal stability.

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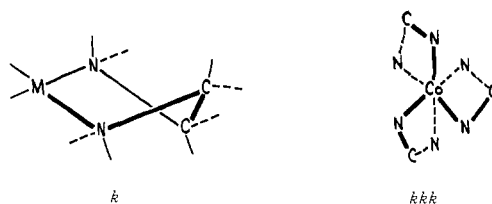


Figure 2.

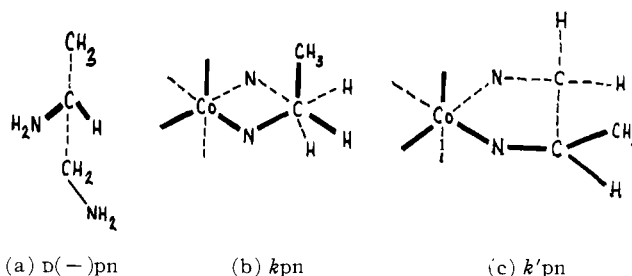


Figure 3.

In the simplest instance,  $[\text{Co}(\text{en})_2(-)\text{pn}]^{3+}$ , the foregoing analysis predicts that the conformations of the individual rings would be  $k_{\text{en}}k_{\text{en}}k_{\text{pn}}$  for the *L*-isomer and  $k_{\text{en}}k_{\text{en}}k_{\text{pn}}$  for the *D*-isomer. The conformations of the en rings change to keep the C-C axes parallel to the threefold symmetry axis of the complex ion while the conformation of  $(-)\text{pn}$  remains unaltered, to maintain the methyl group equatorial. Thus  $L\text{-}[\text{Co}(\text{en})_2(-)\text{pn}]^{3+}$  should be more stable than  $D\text{-}[\text{Co}(\text{en})_2(-)\text{pn}]^{3+}$  by about 0.6 kcal./mole, the difference between the *k*- and *k'*-stabilities for one ring in the complex configuration. The experimental equilibrium concentrations were found to be 2.1/1 (Table II) and this amounts to a free energy difference at 25° of 0.45 kcal./mole, reasonably close to the calculated value. The absolute configurations of these isomers have been established by comparing their rotatory dispersion curves with those of *D*- and *L*- $[\text{Co}(\text{en})_3]^{3+}$ .<sup>18</sup>

Geometrical isomerism is not possible with the  $[\text{Co}(\text{en})_2\text{pn}]^{3+}$  system, but the methyl groups on the coordinated pn molecules can be either *cis* or *trans* to each other with the  $[\text{Co}(\text{pn})_2\text{en}]^{3+}$  and  $[\text{Co}(\text{pn})_3]^{3+}$  ions. Whether or not some of these isomers are excluded energetically or whether they have not been separated because their properties are too similar is not yet known. However, both  $[\text{Co}(\text{en})(-)\text{pn}_2]\text{Cl}_3$  and  $[\text{Co}(-)\text{pn}_3]\text{Cl}_3$  were resolved into two forms whose rotatory dispersion curves are related as *D* and *L*.<sup>17</sup> The antipodes may be a mixture of *cis* and *trans* isomers or either may be *cis* or *trans*. If they are mixtures, no separation could be detected by fractional crystallization, resolution, or chromatography and for the purpose of this paper they are described as single optical isomers.

The ratio of the equilibrium concentrations of the pairs of optical isomers, as each en is replaced by  $(-)\text{pn}$ , is given in Table II. The stereospecificity due to each replacement is clearly evident. As each  $(-)\text{pn}$  was introduced the free energy difference between the *L*- and *D*-isomers increased by approximately 0.5 kcal./mole, close to the calculated energy difference for the change of the *k* conformation to the *k'* conformation. The effects observed here are implicit in the conformational analysis by Corey and Bailar and the agreement between the observed and calculated values is most satisfactory.

(18) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

TABLE II

	Ratio	$\Delta G_{\text{obs}}$ , kcal./mole	$\Delta G_{\text{calc}}$ 25°
D-[Co(en)(en)(-pn)] <sup>3+</sup> /L-[Co(en)(en)(-pn)] <sup>3+</sup> <i>k k k' k' k' k'</i>	1/2.1	0.45	0.6
D-[Co(en)(-pn)(-pn)] <sup>3+</sup> /L-Co(en)(-pn)(-pn)] <sup>3+</sup> <i>k k' k' k' k' k'</i>	1/7.5	1.2	1.2
D-[Co(-pn)(-pn)(-pn)] <sup>3+</sup> /L-[Co(-pn)(-pn)(-pn)] <sup>3+</sup> <i>k' k' k' k' k' k'</i>	1/14.6	1.6	1.8

### Experimental

All rotations were measured in a 1-dm. tube unless otherwise stated.

**Reaction Mixture.**—Ethylenediamine (3.2 g., 1 mole), (-)-propylenediamine (7.93 g., 2 moles), and hydrochloric acid (53.6 ml., 1.00 *N*, 1 mole) were added to a solution of cobalt(II) chloride (6H<sub>2</sub>O) (12.75 g., 1 mole) in water (150 ml.). The solution was then aerated in the presence of activated charcoal (5 g.) for 24 hr., filtered, and the charcoal washed thoroughly until the washings were colorless. Hydrochloric acid (10 ml., 3 *N*) was then added and the solution evaporated almost to dryness. The product was precipitated with excess ethanol (300 ml.), washed with ethanol and acetone, and dried at 60°; yield (18.1 g.) 90%.

**Chromatographic Separation of the Components of the Reaction Mixture.**—The cellulose column (3 in. diameter, 12 in. long, approximately 500 g. of Whatman cellulose powder, std. grade) was prepared by suspending the cellulose in water-saturated 1-butanol with vigorous shaking and pouring the slurry into the column with stirring. The column was impacted under a slight vacuum. The reaction product (1.5 g.) was dissolved in a mixture of water-saturated 1-butanol (400 ml.) and dry 1-butanol (250 ml.) with gentle warming and added to the column. The layer of product adsorbed at the top of the column was then eluted with water-saturated 1-butanol-hydrochloric acid mixture (97% BuOH-2% 10 *N* HCl) under a slight vacuum. Four bands separated completely and the complex chlorides were each extracted from the butanol solution by shaking with water (150 ml.) several times until no color remained in the butanol. The aqueous extracts were evaporated almost to dryness on a steam bath and the product precipitated with excess ethanol. The separation was carried out several times to obtain reasonable quantities of the isomers.

**L(-)-Tris((-)-propylenediamine)-cobalt(III) Chloride (L(III)).**—The first fraction off the column was chromatographed again and a 0.5% solution gave  $\alpha_D -0.23^\circ$ ,  $\alpha_{5461} -1.47^\circ$ , whence  $[\alpha]_D -46^\circ$ ,  $[\alpha]_{5461} -316^\circ$ , and  $[M]_D -178^\circ$ ,  $[M]_{5461} -1225^\circ$ . These molecular rotations are slightly different from those recorded by Dwyer, *et al.*,<sup>4</sup> for the iodide (-)[Co(-)pn<sub>3</sub>]I<sub>3</sub>·H<sub>2</sub>O:  $[M]_D -163^\circ$ ,  $[M]_{5461} -1250^\circ$ . A sample of the compound prepared by the method of Dwyer, *et al.*, was chromatographed on Whatman paper No. 1 with the isomer above using the same solvent mixture (*n*-BuOH (60)-H<sub>2</sub>O (30)-10 *N* HCl (10)). The two spots had identical *R<sub>f</sub>* values.

*Anal.* Calcd. for [Co(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>: C, 27.88; H, 7.80; N, 21.68. Found: C, 27.91; H, 7.87; N, 21.38.

A more convenient way of preparing the L-isomer was from the DL-[Co(-)pn<sub>3</sub>]Cl<sub>3</sub> reaction mixture. The procedure is described under the experiment for the D-isomer.

**L(-)-Bis((-)-propylenediamine)-ethylenediaminecobalt(III) Chloride 2-Hydrate (LII).**—The second band off the column was chromatographed again and gave  $[\alpha]_D -74^\circ$  and  $[\alpha]_{5461} -336^\circ$ . This isomer (1.61 g.) and silver (-)-tartrate (1.50 g.) were shaken in warm water (30 ml., 50°) for 10 min. and the AgCl was filtered off. When the filtrate was reduced to 5 ml., the diastereoisomer crystallized out and was filtered off and washed with ice water (1 ml.). It was then dissolved in hydrochloric acid (1 ml., 10 *N*) and the chloride precipitated with ethanol. The product was recrystallized from aqueous acetone and dried under an infrared lamp. A 0.5% aqueous solution of the isomer gave  $\alpha_D -0.38^\circ$ ,  $\alpha_{5461} -1.68^\circ$ , whence  $[\alpha]_D -74^\circ$  and  $[\alpha]_{5461} -336^\circ$ . This resolution procedure left the original isomer unchanged.

The en/pn ratio in this compound was determined as by Dwyer and Sargeson.<sup>6</sup> The compound (0.5 g.) was decomposed by heating with a mixture of sodium sulfide (2 g.), sodium hydroxide (0.4 g.), and the liberated diamines were extracted with benzene (3 lots of 7 ml.) after more sodium hydroxide (5 g.) had been added to the decomposed complex. The benzene solution was dried overnight over solid NaOH and the rotation measured in the Na D line in a 2-dm. tube; found  $\alpha_D -0.48^\circ$ . The benzene solution (5.00 ml.) was then titrated in water with nitric acid (12.9 ml., 0.100 *N*) whence pn/en = 2.17. This procedure repeated gave  $\alpha_D$  (2-dm. tube)  $-0.52^\circ$  and titer with 0.100 *N* HNO<sub>3</sub> = 14.2 ml., whence pn/en = 2.06. The specific

rotation of pure (-)-propylenediamine in dry benzene is  $[\alpha]_D -34.40^\circ$ .<sup>4</sup> *Anal.* Calcd. for [CoC<sub>3</sub>H<sub>28</sub>N<sub>6</sub>]Cl<sub>3</sub>·2H<sub>2</sub>O: C, 23.47; H, 7.82; N, 20.54. Found: C, 23.63; H, 7.52; N, 20.36.

**L(-)-Bis(ethylenediamine)-(-)-propylenediaminecobalt(III) Chloride 1-Hydrate (LI).**—The third fraction run off the column was chromatographed again and a 0.5% solution gave  $\alpha_D -0.55^\circ$  and  $\alpha_{5461} -1.85^\circ$ , whence  $[\alpha]_D -110^\circ$  and  $[\alpha]_{5461} -370^\circ$ . The compound (1.23 g.) and silver (-)-tartrate (1.18 g.) were shaken in warm water (20 ml., 40°) for 10 min. and the silver chloride filtered off. On evaporation of the filtrate to 5 ml. and cooling, the diastereoisomer separated out and was filtered off. It was then dissolved in hydrochloric acid (3 ml., 10 *N*) and the chloride precipitated with ethanol. The chloride was recrystallized from aqueous acetone, washed with acetone, and dried under an infrared lamp. A 0.5% solution gave  $[\alpha]_D -110^\circ$  and  $[\alpha]_{5461} -384^\circ$ . The rotation is unchanged by the resolution procedure. The pn/en ratio was determined as before. For the benzene solution  $\alpha_D -0.30^\circ$  in a 2-dm. tube and the titration for 5 ml. of the benzene solution was 14.85 ml. of 0.100 *N* HNO<sub>3</sub>, whence pn/en = 0.52.

*Anal.* Calcd. for [CoC<sub>7</sub>H<sub>26</sub>N<sub>6</sub>]Cl<sub>3</sub>·H<sub>2</sub>O: C, 22.25; H, 7.47; N, 22.25. Found: C, 22.50, 22.28; H, 7.29, 7.33; N, 22.26, 22.55.

**Separation of the Components of Fraction 4.**—The fourth fraction off the column was dextrorotatory and contained all the D-isomers and racemic [Co(en)<sub>3</sub>]Cl<sub>3</sub>. It was reabsorbed on the column and eluted with 1-butanol-H<sub>2</sub>O-HClO<sub>4</sub> mixture (*n*-BuOH, water-saturated, 800 ml.; *n*-BuOH, dry, 200 ml.; concd. HClO<sub>4</sub>, 13 ml.). Twelve fractions (about 100 ml.) were collected and the initial and final fractions were discarded (D(+)) [Co(-)pn<sub>3</sub>]Cl<sub>3</sub> and [Co(en)<sub>3</sub>]Cl<sub>3</sub>, respectively). The middle fractions, combined, were extracted into water and the complexes recovered as the insoluble triiodides. The triiodide was then converted to the iodide in absolute alcohol using SO<sub>2</sub> gas and finally to the chloride with AgCl. The chloride mixture was then chromatographed as a strip on large Whatman Grade 3 papers (23 in. × 27 in.) overnight, using *n*-BuOH-H<sub>2</sub>O-HClO<sub>4</sub> 60% (70:20:10) as the eluent. The first (fastest running D(+)) [Co(-)pn<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> and last ([Co(en)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>) bands were discarded.

**D(+)-Bis((-)-propylenediamine)-ethylenediamine)-cobalt(III) Perchlorate 1-Hydrate (DII).**—The second band was cut out and eluted from the paper with water and then chromatographed again on paper. The fractions from several of these runs were collected, evaporated to dryness, and recrystallized from water and alcohol. The complex is soluble in acetone. The sample was then dried in a pistol at 79° and 0.1 mm. for 2 hr. A 0.5% solution in water gave  $\alpha_D +0.98^\circ$ ,  $\alpha_{5461} +1.97^\circ$ , whence  $[\alpha]_D +196^\circ$ ,  $[\alpha]_{5461} +394^\circ$ , and  $[M]_D +1152^\circ$ ,  $[M]_{5461} +2317^\circ$ . These values may be compared with those obtained by eluting a single band from the paper chromatogram which gave  $[M]_D +1160^\circ$  and  $[M]_{5461} +2400^\circ$ . The isomer concentration was estimated spectrophotometrically.

*Anal.* Calcd. for [CoC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O: C, 16.46; H, 5.18; N, 14.40. Found: C, 16.56; H, 5.25; N, 14.16.

**D(+)-Bis(ethylenediamine)-(-)-propylenediamine)-cobalt(III) Perchlorate 1-Hydrate (DI).**—The third band from a series of paper chromatograms was collected and chromatographed again under the same conditions. The band containing the pure isomer was then cut out and the complex eluted from the paper with water and evaporated to near dryness. Several fractions obtained in this manner were recrystallized from water by adding sodium perchlorate, washed with alcohol, and dried in a vacuum desiccator overnight. A 0.5% solution in water gave  $\alpha_D +0.70^\circ$ ,  $\alpha_{5461} +1.58^\circ$ , whence  $[\alpha]_D +140^\circ$ ,  $[\alpha]_{5461} +316^\circ$ , and  $[M]_D +797^\circ$ ,  $[M]_{5461} +1800^\circ$ . These values may be compared with those obtained by eluting a single band from the paper and estimating the complex spectrophotometrically when  $[M]_D +686^\circ$ ,  $[M]_{5461} +1500^\circ$ .

*Anal.* Calcd. for [CoC<sub>7</sub>H<sub>26</sub>N<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O: C, 14.76; H, 4.95; N, 14.76. Found: C, 14.82; H, 4.80; N, 14.58.

**DL-Tris(ethylenediamine)-cobalt(III) Chloride (en<sub>3</sub>).**—The fourth band (the slowest moving, on both the column and the

paper chromatogram) had no rotation and was identified by chromatographing it with an authentic sample of DL[Co(en)<sub>3</sub>]Cl<sub>3</sub>.

**D(+)-Tris-(*-*)-propylenediamine-cobalt(III) Chloride 0.5 Hydrate (DIII).**—This isomer was the fastest running band on the paper. It was cut out and eluted from the paper with water. The concentration of the aqueous solution (6.0 ml.,  $\alpha_D + 0.18^\circ$ ,  $\alpha_{5461} + 0.32^\circ$ ) was estimated spectrophotometrically ( $1.14 \times 10^{-3} M$ ). This gave  $[M]_D + 1580^\circ$  and  $[M]_{5461} + 2810^\circ$ . The isomer was prepared in better yield from the DL[Co(*-*)pn<sub>3</sub>]Cl<sub>3</sub> reaction mixture. Cobalt(II) chloride 6-hydrate (23.8 g.) was dissolved in HCl (100 ml., 1 *N*) and (*-*)-propylenediamine (22.2 g.) added with activated charcoal (10 g.). The mixture was aerated for 12 hr., the charcoal was filtered off, and the filtrate evaporated to dryness. Samples of the product (1.5 g.) were adsorbed on the cellulose column and eluted with 1-butanol-H<sub>2</sub>O-HCl (500 ml. of water-saturated BuOH:HCl, 12 ml. of 10 *N*). The first and largest fraction off the column was L(*-*)[Co(*-*)pn<sub>3</sub>]Cl<sub>3</sub> and the second was pure D(+)[Co(*-*)pn<sub>3</sub>]Cl<sub>3</sub>. The latter was extracted from the butanol with water, the aqueous solution evaporated to dryness, and the isomer recrystallized from aqueous acetone and dried in a vacuum desiccator 12 hr. A 0.5% aqueous solution gave  $\alpha_D + 1.97^\circ$ ,  $\alpha_{5461} + 3.70^\circ$ , whence  $[\alpha]_D + 394^\circ$ ,  $[\alpha]_{5461} + 740^\circ$ , and  $[M]_D + 1580^\circ$ ,  $[M]_{5461} + 2960^\circ$ .

*Anal.* Calcd. for [CoC<sub>9</sub>H<sub>30</sub>N<sub>6</sub>]Cl<sub>3</sub>·0.5H<sub>2</sub>O: C, 27.25; H, 7.88; N, 21.20. Found: C, 27.44; H, 8.08; N, 21.14.

A sample of D(+)[Co(*-*)pn<sub>3</sub>]I<sub>3</sub>·H<sub>2</sub>O prepared by Dwyer, *et al.*, gave  $[M]_D + 1455^\circ$  and  $[M]_{5461} + 2745^\circ$ , somewhat less than the values recorded here. This sample contained a trace of the L-isomer which was removed by chromatographing the chloride on the column under the conditions described previously. The rotations obtained for the purified sample then agreed with the values reported above.

**Equilibrium Concentrations for the Isomers in the Reaction Mixture en/pn = 1/2.**—Cobalt(II) chloride 6-hydrate (2.38 g.) dissolved in HCl solution (10 ml., 1 *N*) was treated with (*-*)-propylenediamine (1.48 g.), ethylenediamine (0.6 g.), and activated charcoal (2 g.) and aerated for 3 hr. The reaction mixture then showed only a trace of cobalt(II) and was evaporated to approximately 3 ml. This solution was applied in strips to Whatman 3 MM sheets (23 in. × 27 in.) and eluted with *sec*-butyl alcohol:H<sub>2</sub>O:10 *N* HCl (70:20:10) overnight. Four fractions separated which were cut out and eluted with water and their concentrations estimated spectrophotometrically at 465 m $\mu$ .

Fract.					
1	LIII	29.6	30.3	31.2	31.0
2	LII	37.1	36.9	34.0	34.8
3	LI	15.0	15.2	14.3	14.2
4	D-Isomers + ( $\pm$ )[Co(en) <sub>3</sub> ]Cl <sub>3</sub>	18.3	17.6	20.5	20.0

The D-fractions (19% of total) from the L-isomer separations were collected and adsorbed on the paper in strips. Elution with 1-butanol:H<sub>2</sub>O:60% HClO<sub>4</sub> (70:20:10) gave

Fract.			
1	DIII	1.9	2.1
2	DII	5.4	6.0
3	DI	7.7	6.6
4	en <sub>3</sub>	4.0	4.3

The dispersion ratios  $\alpha_{5461}/\alpha_D$  of the solutions agreed with those of the pure isolated isomers.

**Equilibrium Concentrations of the Isomers in the Reaction Mixture en/pn = 2/1.**—The reaction mixture was prepared in exactly the same manner as before except that the concentration ratios of en:pn were reversed. The solution was chromatographed on paper as before and gave

Fract.			
1	LIII	4.6%	5.1%
2	LII	18.7	18.7
3	LI	27.5	27.7
4	D-Isomers + [Co(en) <sub>3</sub> ]Cl <sub>3</sub>	49.2	48.5

The D-fractions (49% of total) were collected and chromatographed as before.

Fract.		
1	DIII	0.5%
2	DII	2.5
3	DI	13.0
4	en <sub>3</sub>	33.0

The dispersion ratios  $\alpha_{5461}/\alpha_D$  of the solutions agreed with those of the pure isolated isomers.

**Equilibrium Concentrations of Isomers in the Reaction Mixture DL-[Co(*-*)pn<sub>3</sub>]Cl<sub>3</sub>.**—Cobalt(II) chloride (0.01 mole), (*-*)-propylenediamine (0.03 mole), and hydrochloric acid (0.01 mole) were mixed with activated charcoal in 20 ml. of water and the solution was aerated for 3 hr. The charcoal was filtered off and the solution made slightly acid with HCl and concentrated to a small volume. The solution chromatographed on paper with 1-butanol:H<sub>2</sub>O:10 *N* HCl (60:30:10) gave

$$L(-)[Co(-)pn_3]Cl_3/D(+)[Co(-)pn_3]Cl_3 = 14.6$$

The dispersion ratios  $\alpha_{5461}/\alpha_D$  of the eluted solutions agreed with those of the pure isomers and the ratio L(*-*)(*-*)(*-*)/D(*-*)(*-*)(*-*) = 15 calculated from the rotations was also in agreement with the spectrophotometric value (14.6).

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## Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. VIII. Isomerism of the Cobalt(III) Complex of the Sexadentate *d,l*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctane

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*d,l*-4-Methyl-1,8-diamino-3,6-dithiaoctane was prepared and resolved into *d*- and *l*-forms by means of its *d*- and *l*-dibenzoyltartrate salts. The cobalt(III) complexes of the Schiff bases, formed from salicylaldehyde and the racemic and each optical form of the diamine, were prepared and resolved by means of their *d*- and *l*-anti-monyltartrate salts. The dextro isomer of the ligand gave chiefly the levo form of the complex (85%) while the levo base gave a similar excess of the dextro complex. Resolution of the cobalt(III) complex of the racemic ligand gave these same isomers.

In previous papers in this series<sup>2</sup> it has been shown that the asymmetric bidentate ligand *l*-propylenediamine is only partially stereospecific in the formation of its metal complexes even when there are several such

ligands present as in [Co(*l*-pn)<sub>3</sub>]Cl<sub>3</sub>. However *l*-propylenediaminetetraacetic acid exhibits absolute stereospecificity in the formation of metal complexes, even though it contains only one asymmetric center which is similar to that in *l*-propylenediamine,<sup>3a</sup> an anomaly

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(2) F. P. Dwyer, *et al.*, *J. Am. Chem. Soc.*, **81**, 290, 1043 (1959).

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