

paper chromatogram) had no rotation and was identified by chromatographing it with an authentic sample of DL[Co(en)₃]Cl₃.

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(*-*)pn₃]Cl₃ 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-H₂O-HCl (500 ml. of water-saturated BuOH:HCl, 12 ml. of 10 *N*). The first and largest fraction off the column was L(*-*)[Co(*-*)pn₃]Cl₃ and the second was pure D(+)[Co(*-*)pn₃]Cl₃. 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 [CoC₉H₃₀N₆]Cl₃·0.5H₂O: C, 27.25; H, 7.88; N, 21.20. Found: C, 27.44; H, 8.08; N, 21.14.

A sample of D(+)[Co(*-*)pn₃]I₃·H₂O 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:H₂O: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 μ .

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) ₃]Cl ₃	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:H₂O:60% HClO₄ (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 ₃	4.0	4.3

The dispersion ratios α_{5461}/α_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) ₃]Cl ₃	49.2	48.5

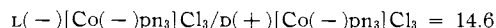
The D-fractions (49% of total) were collected and chromatographed as before.

Fract.

1	DIII	0.5%
2	DII	2.5
3	DI	13.0
4	en ₃	33.0

The dispersion ratios α_{5461}/α_D of the solutions agreed with those of the pure isolated isomers.

Equilibrium Concentrations of Isomers in the Reaction Mixture DL-[Co(*-*)pn₃]Cl₃.—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:H₂O:10 *N* HCl (60:30:10) gave



The dispersion ratios α_{5461}/α_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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[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA]

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 series² 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)₃]Cl₃. 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,^{3a} an anomaly

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

(3) (a) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959); (b) J. C. Bailar, Jr., and E. J. Corey, *ibid.*, **81**, 2620 (1959).

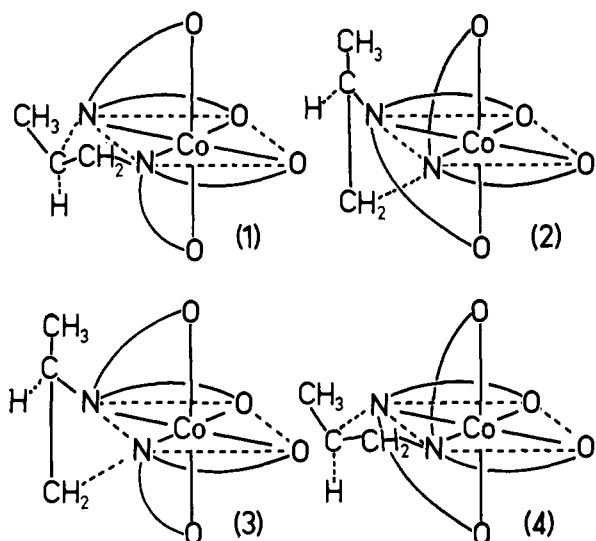
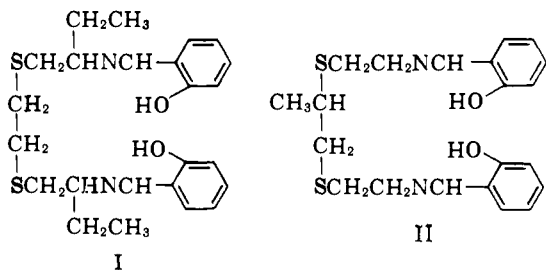


Fig. 1.—(1) L-[Co-*l*-PDTA]⁻ with "equatorial" methyl and strain-free nitrogens. (2) D-[Co-*l*-PDTA]⁻ with "axial" methyl and strain-free nitrogens. (3) L-[Co-*l*-PDTA]⁻ with "axial" methyl and strained nitrogens. (4) D-[Co-*l*-PDTA]⁻ with "equatorial" methyl and strained nitrogens.

which can be explained by consideration of the conformations of the various possible isomers after the method of Bailar and Corey.^{3b} Figure 1 shows the four possible isomers of [Co-*l*-PDTA]⁻. Isomers 2 and 3 have the methyl group "axial" and this will increase the free-energy of the system by more than 2 kcal./g. mole.^{3b} Isomers 3 and 4 have a strained arrangement of bonds about the two nitrogen atoms. Isomer 1 has the methyl group "equatorial" and a strain-free arrangement of bonds about the nitrogen atoms and so is probably the conformation of the single isomer obtained in the previous study.^{3a}

It is possible to test this explanation of stereospecificity by studying the isomerism of other flexible optically active multidentate ligands. One such ligand, 3,10-bis-(salicylideneamino)-5,8-dithiadodecane (I), has already been described,⁴ but the isomerism of its metal complexes has not been investigated.



The asymmetric sexadentate ligand 4-methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctane — EPE — (II), has now been prepared by the method described by Dwyer, Gill, Gyarfas, and Lions⁵ for similar compounds. The free diamine 4-methyl-1,8-diamino-3,6-dithiaoctane was isolated and purified by distillation and resolved by fractional crystallization of its *d*- and *l*-dibenzoyltartrate⁶ salts. The optical isomers had $[\alpha]_{5893} \pm 50^\circ$. The bis-Schiff bases of the racemic and *d*- and *l*-diamine were formed in the usual way and the cobalt(III) com-

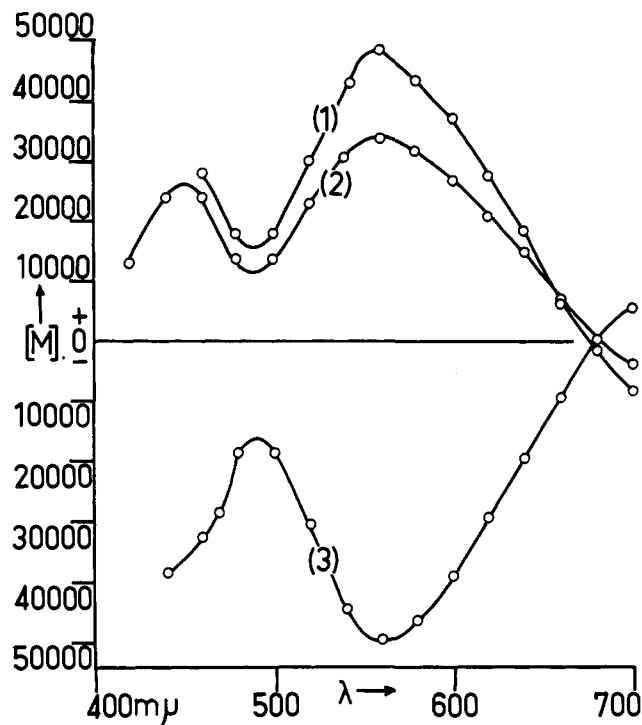


Fig. 2.—Rotatory dispersion curves: (1) D-[Co-*l*-EPE]I; (2) D-[Co-*l*-EPE]I; (3) L-[Co-*d*-EPE]I.

plex of each was prepared by the aerial oxidation of a solution containing cobalt(II) chloride and the sexadentate ligand, either in methanol or in a water-methanol mixture.

A long and careful fractionation of the *d*- and *l*-antimonyltartrate salts of the cobalt(III) complex of the racemic base gave only two isomers designated *dl* and *ld* and having $[\alpha]_{5461} +7500$ and -8100° , and $[M]_{5461} +45300$ and -47500° , respectively. The rotatory dispersion curves for these isomers are shown in Fig. 2, which also includes the curve for the D-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) ion. This comparison indicates that the isomers obtained are enantiomeric with respect to the metal atom.

Quantitative isolation of the cobalt(III) complexes of the optical isomers of the base gave two iodides with $[\alpha]_{5461} +5170^\circ$ and -5930° for the *l*- and *d*- ligand, respectively. Recrystallization as the *l*- and *d*-antimonyltartrate salts, respectively, gave the two isomers described above. So the isomers isolated in the original resolution are D-[Co-*l*-EPE]⁺ and L-[Co-*d*-EPE]⁺.

These results indicate that there is partial stereospecificity in this system. The *l*- base gives a mixture containing 85% of the *dl*-isomer and 15% of the *ll*-isomer, while the *d*- base gives 85% of the *ld*-isomer and 15% of the *dd* form. Only very small amounts of the *ll*- and *dd* isomers were actually isolated and these seemed to be largely contaminated with the predominating isomer. Furthermore, all attempts to isolate the ligand from pure *dl*- and *ld*-isomers, and so to confirm these findings, were unsuccessful.

Simply from inspecting scale models it appears possible for either optical isomer of this ligand to form either the D or L form of the octahedral complex. There are in fact three apparently uncrowded and strain-free forms possible for each isomer of the base—one with the opposite absolute configuration to the other two. The larger size of the sulfur atoms makes the metal-ligand ring in which they occur larger than the corresponding ring in [CoPDTA]⁻ or Co-*l*-pn com-

(4) N. S. Gill, Ph.D. Thesis, University of Sydney, 1951, p. 101.

(5) F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Am. Chem. Soc.*, **76**, 383 (1954), and previous papers.

(6) C. L. Butler and L. Cretcher, *ibid.*, **55**, 2605 (1933).

plexes. This may cause the free energy difference between an "axial" and an "equatorial" methyl group to be considerably smaller in this case. One of the three isomers suggested as the most stable has the methyl group "axial." Detailed conformational analyses of such isomers could resolve this point.

Experimental

DL-4-Methyl-1,8-diamino-3,6-dithiaoctane.—The general method described by Dwyer, Gill, Gyrfas, and Lions was adopted using 1 mole (57 g.) of *dl*-propylenedithiol. The yield of the crude diamine was 73 g. (75%). It was distilled under reduced pressure and the fraction boiling at 135–140° at 0.15–0.20 mm. was collected (38 g., 40%). The dihydrochloride derivative was obtained as a white crystalline powder from hot ethanol; m.p. 172° (subl.). *Anal.* Calcd. for $C_7H_{18}S_2N_2 \cdot 2HCl$: C, 31.5; H, 7.5; N, 10.5. Found: C, 31.5; H, 7.4; N, 10.4. The dihydrohydrogen-*d*-tartrate derivative was prepared by mixing hot aqueous solutions of the diamine and *d*-tartaric acid. The white crystalline compound was recrystallized several times from hot water containing a little sodium acetate. This process partly resolved the diamine. *Anal.* Calcd. for $C_7H_{18}S_2N_2 \cdot 2H(C_4H_6O_6)$: C, 36.4; H, 6.1; N, 5.7. Found: C, 36.5; H, 6.1; N, 5.6.

L-4-Methyl-1,8-diamino-3,6-dithiaoctane Dihydro-*d*-dibenzoyltartrate.—The pure racemic diamine obtained above (24 g.) was dissolved in hot water (1100 ml.) together with *d*-dibenzoyltartaric acid (46.5 g.)—made according to the method of Butler and Cretcher⁶—and sodium acetate (24 g.). The solution was filtered while hot and set aside to crystallize. The white crystalline precipitate was collected, washed with ice-water and ethanol, and dried under an infrared lamp (yield 26.3 g.). The mother liquor was evaporated to 650 ml. and deposited a further 10 g. of diastereoisomer. The filtrate was reserved for the recovery of the *d*-isomer. This diastereoisomer was fractionally crystallized several times from hot water containing a little sodium acetate. The fractions containing diamine with a rotation greater than -45° were combined and refractionated and the process was repeated until each fraction gave the diamine with a rotation of $[\alpha]_D -50^\circ$ (total yield 12.5 g.). The rotation of the diamine present in each fraction of the diastereoisomer was ascertained by heating a small sample (0.35 g.) of the fraction with water (1 ml.) and sodium hydroxide pellets (4 g.). The melt was extracted by refluxing with benzene (3 lots, 10 ml. each) which was decanted, dried overnight over KOH pellets, and filtered through a dry filter paper. The rotation of the diamine was measured in a 2-dm. tube and its concentration obtained by titration against standard hydrochloric acid (about 0.01 *N*). *Anal.* Calcd. for $(C_7H_{20}N_2S_2)(C_{18}H_{12}O_8)$: C, 54.4; H, 5.8; N, 5.1. Found: C, 54.0; H, 5.8; N, 4.7.

L-4-Methyl-1,8-diamino-3,6-dithiaoctane.—The diastereoisomer obtained above (12.5 g.) was suspended in water (200 ml.) and boiled for 15 min. with excess hydrochloric acid (7 ml., 10 *N*). The oily *d*-dibenzoyltartaric acid which separated was induced to crystallize by cooling, seeding, and scratching the sides of the beaker with a glass rod. It was allowed to stand overnight, collected at the pump, and ground up with water (50 ml.) containing hydrochloric acid (1 ml., 10 *N*) and again filtered off. The filtrate and washings were reduced to 20 ml. and filtered. The residue was washed with water (5 ml.) and the filtrate and washings were treated with solid sodium hydroxide (15 g.) and the diamine which separated was extracted with ether in the usual way. The ether extract was dried over anhydrous sodium sulfate and filtered through a dry paper. The ether was removed by distillation leaving the almost colorless oily diamine (yield 4.5 g., ~100%, $[\alpha]_D -50^\circ$). The dihydrochloride derivative was prepared and recrystallized several times from hot ethanol. It had $[\alpha]_D -5.8^\circ$ and $[\alpha]_{5461} -6.5^\circ$, m.p. 193°. *Anal.* Found: C, 31.3; H, 7.6; N, 10.4. The bis-5-bromo-salicylidene derivative formed yellow crystals from hot ethanol; m.p. 63°. *Anal.* Calcd. for $C_{21}H_{24}N_2S_2O_2Br_2$: C, 45.0; H, 4.3; N, 5.0. Found: C, 44.9; H, 4.1; N, 4.9.

D-4-Methyl-1,8-diamino-3,6-dithiaoctane Dihydro-*l*-dibenzoyltartrate.—The filtrate left after the separation of the above diastereoisomer was treated with hydrochloric acid, evaporated to a small volume, treated with solid sodium hydroxide, and the crude oily *d*-4-methyl-3,6-dithiaoctane was extracted into ether. This product (12.1 g.) was dissolved in boiling water (600 ml.) containing *l*-dibenzoyltartaric acid (23.4 g.) and sodium acetate (12 g.). The solution was filtered and evaporated at 70° under a stream of air to 300 ml. and cooled in the refrigerator overnight. The white crystalline product was collected, washed with ice water and then ethanol, and dried under the lamp (yield 20 g.). On reducing the volume to 100 ml. and cooling, an additional 6.2 g. was obtained. The two fractions were combined and fractionally crystallized. The fractions containing diamine with a rotation greater than $+45^\circ$ were combined and refractionated

until all fractions yielded a diamine having a rotation $[\alpha]_D +50^\circ$. The method of determining this rotation is described above (total yield 9.0 g.). *Anal.* Found: C, 54.4; H, 5.8; N, 5.1.

d-4-Methyl-1,8-diamino-3,6-dithiaoctane.—The diastereoisomer obtained above was decomposed by the method described above for the opposite isomer. The yield was 2.8 g. (90%). The dihydrochloride derivative was recrystallized several times from hot ethanol. *Anal.* Found: C, 31.0; H, 7.3; N, 10.3.

DL-*dl*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide 1-Hydrate.—The racemic diamine prepared above (8.0 g.) was heated with salicylaldehyde (8.0 g.) in ethanol for 10 min. The appearance of a bright yellow color indicated the formation of the bis-Schiff base 1,8-bis-(salicylideneamino)-3,6-dithiaoctane. Removal of the solvent gave a yellow oil which could not be induced to crystallize. This product was dissolved in ethanol and added to an aqueous solution of cobalt(II) acetate 4-hydrate (10 g.). Hydrogen peroxide solution (3 ml., 100 vol.) and charcoal (7 g.) were added and a stream of air was blown through the mixture for 2 days. The charcoal was filtered off and the product precipitated as the iodide by the addition of excess sodium iodide (yield 21 g., 54%). A small sample was recrystallized from methanol by the addition of ether. *Anal.* Calcd. for $[CoC_{21}H_{24}N_2O_2S_2] \cdot H_2O$: C, 41.7; H, 4.3; N, 4.6. Found: C, 41.8; H, 4.4; N, 4.6.

The method described below for the small scale preparation of the cobalt(III) complex of each optical isomer of the ligand could probably be adapted to give a better large-scale preparation of the above complex.

L-*d*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) *d*-Antimonyltartrate 4-Hydrate and D-*l*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) *l*-Antimonyltartrate 4-Hydrate.—The racemic iodide (18 g.) was shaken with freshly precipitated silver chloride (10 g.) in water (350 ml.) at 60° for 10 min. The silver halides were filtered off and shaken with several lots (20 ml.) of hot water. (The complex salt adheres strongly to the precipitated silver halide and repeated extraction is necessary to remove all but a small trace.) The volume of the filtrate and washings was reduced to 300 ml. at 70° in a steam of air. Sodium *d*-antimonyltartrate (3.9 g.) was stirred into the hot solution which was allowed to cool to room temperature. The lustrous dark green (almost black) crystals which separated were filtered off, washed with a little ice water and then ethanol, and dried under the lamp (yield 8.9 g.). This diastereoisomer was fractionally crystallized by dissolving in hot water (800 ml., 80°), cooling, collecting the precipitate, reducing the volume, and repeating the procedure until more than 95% of the material had been recovered. The dextrorotatory fractions (most soluble) were heated in solution on the steam bath with excess sodium acetate. The solutions were filtered and treated with excess sodium iodide to precipitate the complex as the iodide. This solid material was added to the iodide obtained from treating the original filtrate with excess sodium iodide. This material (10 g.) was converted to the chloride and treated with sodium *l*-antimonyltartrate (5.6 g.). The crystalline diastereoisomer which resulted was subjected to fractional crystallization.

In the fractionation of these two diastereoisomers, fractions with the same anion and similar rotations were combined and refractionated. The more soluble fractions, containing L-[Co-*d*-EPE]-*l*-SbO₄ and D-[Co-*l*-EPE]-*d*-SbO₄, were reconverted to iodides, thence to chlorides, and so to the *d*- and *l*-antimonyltartrate salts, respectively, and returned to the main fractionations.

Only two pure diastereoisomers were obtained after a long fractionation. These were (1) L-[Co-*d*-EPE]-*d*-SbO₄·4H₂O, $[\alpha]_{5461} -6400^\circ$. *Anal.* Calcd. for $[CoC_{21}H_{24}N_2S_2O_2](C_4H_4O_6 \cdot SbO) \cdot 4H_2O$: C, 37.6; H, 4.8; N, 3.5. Found: C, 37.4; H, 4.4; N, 3.4. (2) D-[Co-*l*-EPE]-*l*-SbO₄·4H₂O, $[\alpha]_{5461} +6400^\circ$. *Anal.* Found: C, 37.2; H, 4.4; N, 3.5.

L-*d*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide.—Some of the pure fractions of L-[Co-*d*-EPE]-*d*-SbO₄ (5.1 g.) were combined and dissolved in a minimum of hot water. Sodium acetate (3 g.) was added and the solution heated on a water bath for 30 min. and filtered. Sodium iodide (3 g.) was added and the mixture cooled. The resulting L-[Co-*d*-EPE]I was fractionally crystallized, the best fraction having $[\alpha]_{5461} -8100^\circ$. *Anal.* Calcd. for $[CoC_{21}H_{24}N_2S_2O_2]I$: C, 42.9; H, 4.1; N, 4.8. Found: C, 42.7; H, 4.2; N, 4.7.

Preparation and Resolution of *d*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide.—*d*-4-Methyl-1,8-diamino-3,6-dithiaoctane (0.30 g.) was dissolved in methanol (50 ml.) and added to a solution of salicylaldehyde (0.38 g.) in methanol (50 ml.). The mixture was heated on the steam bath for 10 min. A bright yellow color indicated the formation of the bis-Schiff base. Cobalt(II) acetate 4-hydrate (0.39 g.) was stirred in and air was bubbled through the deep green solution overnight, at such a rate that all the solvent had evaporated by

morning. The residue was dissolved in water (30 ml.) and filtered. Sodium iodide (0.5 g.) in water (3 ml.) was added to the filtrate and the precipitate was allowed to stand overnight, filtered, washed with sodium iodide solution, a little ice water and then ether, and air dried (yield 0.67 g.); $[\alpha]_{3461} - 5900^\circ$. Further fractions, 0.19 g., $[\alpha]_{3461} - 6500^\circ$; 0.06 g., $[\alpha]_{3461} - 4500^\circ$, were obtained by evaporating the filtrate stepwise. Total yield was 0.92 g. (98.5%), average $[\alpha]_{3461} - 5920^\circ$.

The product of the above preparation (0.89 g.) was transposed to the chloride and treated with sodium *d*-antimonytartrate (0.36 g.). The diastereoisomer which resulted (0.78 g.) had $[\alpha]_{3461} - 5400^\circ$. It was recrystallized from hot water twice giving a final product with $[\alpha]_{3461} - 6700^\circ$. This diastereoisomer gave an iodide on decomposition which had $[\alpha]_{3461} - 7500^\circ$. The filtrate from the resolution yielded an iodide which had zero rotation. The original complex formed was therefore a mixture containing 88% L-[Co-*d*-EPE]I and 12% D-[Co-*d*-EPE]I.

D-*l*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide 1-Hydrate.—The diastereoisomer D-[Co-*l*-EPE]-*l*-SbOtart·4H₂O (1.8 g.) was converted to the iodide and fractionally crystallized. The best fraction had $[\alpha]_{3461} + 7500^\circ$. *Anal.* Calcd. for [CoC₂₁H₂₄N₂S₂O₂]I·H₂O: C, 41.7; H, 4.3; N, 4.6. Found: C, 41.7; H, 4.4; N, 4.5.

Preparation and Resolution of *l*-4-Methyl-1,8-bis-(salicylideneamino)-3,6-dithiaoctanecobalt(III) Iodide.—The preparation was identical with that described above save that *l*-4-methyl-1,8-diamino-3,6-dithiaoctane was used. The yield was 0.86 g. (95%) having an average rotation $[\alpha]_{3461} + 5170^\circ$.

This product was resolved using sodium *l*-antimonytartrate. The diastereoisomer was collected immediately on forming. The filtrate was treated with excess sodium iodide (0.6 g.) and the precipitated iodide collected quickly and washed with a little water and then ether (yield 0.02 g.). It had $[\alpha]_{3461} - 2500^\circ$, while the diastereoisomer had $[\alpha]_{3461} + 5000^\circ$ which improved to +6500° on recrystallization.

These results indicate that the original compound formed was a mixture of D-[Co-*l*-EPE]I (84%) and L-[Co-*l*-EPE]I (16%).

The rotatory dispersion curves for the isomers L-[Co-*d*-EPE]I and D-[Co-*l*-EPE]I were prepared for 0.01% solutions in a 1-dm. tube using a Shimadzu manual spectrophotometer with a photoelectric polarimeter attachment. They are shown in Fig. 2 together with the curve for D-[Co-EEE]I.

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Copper Complexes of *o*-Hydroxy Schiff Bases and the Hydrolysis of the Schiff Bases¹

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Copper complexes (2:1) of *N*-salicylideneaniline (III), *N*-salicylidene-*p*-anisidine (IV), *N*-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (V), and *N*-(2-hydroxy-3-methoxybenzylidene)-aniline (VI) have been prepared in water-ethanol solution. Similar methods did not yield the chelates of the Schiff bases derived from *o*-aminophenol (*N*-benzylidene-*o*-hydroxyaniline (I) and *N*-(4-methoxybenzylidene)-*o*-hydroxyaniline (II)) because of hydrolytic cleavage of the Schiff bases. The Cu chelate (2:1) of II was prepared in absolute ethanol. The hydrolytic cleavage of the Schiff bases was followed spectrophotometrically. All of the Schiff bases were found to hydrolyze in a matter of minutes in 50% v./v. water-dioxane and almost instantaneously in acidified water-dioxane. The spectra of the conjugate acids of the Schiff bases could be obtained in absolute ethanol in which gaseous HCl is dissolved. In this medium the decomposition was slow enough for the spectra to be recorded in most cases.

During the course of the investigation of the spectra of some Schiff bases and their metal complexes, several new copper complexes were isolated. The Schiff bases derived from *o*-aminophenol did not give the corresponding copper chelates by the usual preparative methods because of hydrolysis of the ligand in the presence of water. An investigation of the changes in the spectra of the Schiff bases in water-dioxane and in acid solution as a function of time was carried out in order to determine the importance of hydrolysis in the present work and in other studies in the literature.

Lane and Kandathil² reported a series of *o*-hydroxy Schiff bases of three types: Type A, derived from *o*-aminophenol and benzaldehyde or *p*-substituted benzaldehydes; type B, derived from salicylaldehyde and aniline or *p*-substituted anilines; and type C, derived from 2-hydroxy-3-methoxybenzaldehyde and aniline or *p*-substituted anilines. The acid dissociation constants of these compounds and the formation constants of some of their metal chelates were determined by potentiometric titrations. No hydrolysis of the Schiff bases was noted, even though Charles and Freiser³ reported that they were unable to carry out potentiometric titrations of Schiff bases of *o*-aminophenol (type A) because of hydrolysis of the ligand. Eichhorn and Bailar⁴ observed that hydrolysis of the ligand prevented the preparation of metal complexes of the Schiff bases obtained from 2-thiophenylaldehyde and *o*-aminophenol. Eichhorn and Marchand⁵ found that Schiff bases of

this type were made more susceptible to hydrolytic cleavage by coordination to copper(II) (and presumably by protonation).

Experimental

The following Schiff bases were prepared by condensing the appropriate aldehyde and amine²: *N*-benzylidene-*o*-hydroxyaniline (I), *N*-(4-methoxybenzylidene)-*o*-hydroxyaniline (II), *N*-salicylideneaniline (III), *N*-salicylidene-*p*-anisidine (IV), *N*-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (V), and *N*-(2-hydroxy-3-methoxybenzylidene)-aniline (VI). The melting points agreed closely with those reported and elemental analyses were available for all of the Schiff bases and for the copper chelates of all except I. Commercial *o*-aminophenol used in these preparations and for the spectra was recrystallized several times from 50% water-ethanol in an atmosphere of nitrogen.

Dioxane was purified⁶ within a couple of weeks of the time used.

The spectra were recorded on a Cary Model 14 recording spectrophotometer. The pH titrations were carried out as described in the reference cited by Lane.⁷

Preparation of Copper Chelates.—The copper chelates of III, IV, V, and VI were prepared by the following general method.

An aqueous ethanolic solution of copper acetate was mixed with a warm ethanolic solution of the Schiff base in a molar ratio of 2:1 (ligand-metal), followed by addition of a 5% solution of sodium acetate in water with constant and rapid stirring. The precipitated copper compounds were allowed to settle for about 1 hr., filtered with suction, redissolved in the minimum quantity of warm ethanol, and recrystallized by the addition of water to the ethanolic solution. The products were filtered and washed several times with 50% ethanol and finally dried *in vacuo* at room temperature for several days.

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