TABLE V

SALT EFFECTS IN WEAK ACID BUFFERS

	C_{HA}, M	C_A, M	C_{NaClO_4}, M	k'
Trimethylacetate	0.06	0.02	..	0.0328
	.06	.02	0.06	.0369
Acetate	.06	.02	..	.0267
	.06	.02	.06	.0302
Glycolate	.06	.02	..	.0240
	.06	.02	.06	.0269
Chloroacetate	.062	.02	..	.0283
	.062	.02	.06	.0304
Aniline	.04	.11	..	.0702
	.04	.11	.04	.0708
	.04	.11	.08	.0705
	.04	.11	.12	.0718

Discussion

The values of k_3, collected in Table VI, may be compared with the Brönsted relation

$$k_3/q = G_B(K_B p/q)^\beta \qquad (13)$$

The values of k_4 are not sufficiently accurate to apply this equation. Using the factors p and q as suggested by Pedersen,[2] four anions show close agreement with the expression

$$\log k_3/q = -1.61 + 0.273 \log p/(qK_A) \qquad (14)$$

Bases like aniline and glycine usually follow similar equations with somewhat different constants. The value for water, *i.e.* log $k_1/55.5$, is too small by 1.5 units to fit equation (14). Usually water catalysis agrees within less than 1 log unit with the value calculated from anion catalysis (Bell, ref. 2, p. 92), but it is also true that β is usually larger than the value 0.273 found here.

TABLE VI

SUMMARY OF RATE AND STRENGTH CONSTANTS

Base	k_3	K_A
Me_3 acetate	1.02	8.91×10^{-6} [a]
Acetate	0.80	1.754×10^{-5} [b]
Aniline	.52	2.54×10^{-5} [c]
Glycolate	.48	1.475×10^{-4} [b]
Cl acetate	.210	1.396×10^{-3} [d]
Glycine	.229	4.47×10^{-3} [b]
Phosphate	.206	7.52×10^{-3} [b]
Water	2.52×10^{-4}	55.5

[a] J. F. J. Dippy, *J. Chem. Soc.*, 1222 (1938). [b] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 580. [c] K. J. Pedersen, *Det Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, XIV (9) (1937). [d] D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N.Y., 1939, p. 349.

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(2) K. J. Pedersen, "Den Almindelige Syre-og Base-katalyse," Bianco Lunos Bogtrykkeri, Copenhagen, 1932; R. P. Bell "Acid-Base Catalysis," Oxford, Clarendon Press, Chapter V, 1941.

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XIII.[1] A Partial Resolution of Racemic Tartaric Acid by Means of Different Stabilities of Isomers of Complex Ions[2]

BY JOHN C. BAILAR, JR., HANS B. JONASSEN AND ALLAN D. GOTT

RECEIVED DECEMBER 6, 1951

When the cobalt complex made from levo-propylenediamine and racemic tartaric acid, [Co(*l*-pn)$_2$(*rac*-tart)]Cl, is heated in aqueous solution at 70° with an excess of levo-propylenediamine (1,2-diaminopropane), the levo-propylenediamine molecules preferentially displace the levo-tartrate ion. The dextro-tartrate ion appears to be more strongly held in the coördination sphere and is displaced only over a longer period of time at 70°. This paper presents experimental evidence to support this statement as well as other evidence which indicates that the isomers containing the levo-tartrate ion and the dextro-tartrate ion have different stabilities.

Introduction

When unsymmetrical or optically active groups coördinate with a metallic ion, several possibilities for isomerism arise. If, for example, an optically active bidentate coördinating group combines with a metallic ion having a coördination number of six, one might expect the eight stereoisomeric compounds D*ddd*, D*ddl*, D*dll*, D*lll*, L*lll*, L*lld*, L*ldd*, L*ddd*, where *d* and *l* represent the isomeric configurations of the coördinating molecules, and D and L the configurations around the metal nucleus. In the cases which have been studied, however, it has been found that only two of the eight compounds are stable enough to be isolated—D*lll* and L*ddd*. Two factors seem to be important in this. First, efforts to attach molecules of the *same* coördinating agent but of different configuration to the same metallic ion have not been successful; this eliminates the configurations represented by D*ddl*, D*dll*, L*lld* and L*ldd*. Secondly, the configuration of the coördinating agent seems to determine the configuration of the complex as a whole; in the cases studied, this has eliminated the configurations shown by D*ddd* and L*lll*.[3]

Consideration of the first phenomenon suggests that if a complex contains two optically active bidentate groups, a third optically active group might coördinate firmly if it has the same configuration as those already present. The enantiomorph of this third group should coördinate less readily, and the result would be a complex of lower

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(1) For the previous article in the series, see Sister Mary Martinette and Bailar, THIS JOURNAL, **74**, 1054 (1952).

(2) Most of the work reported in this article was taken from the doctorate thesis of Hans Jonassen (1946), and Allan Gott (1952).

(3) See, however, the paper by Sister Mary Martinette and Bailar, ref. 1, where it is shown that this is not true for the complex ion [Co(levo-pn)$_2$CO$_3$]$^+$, which exists in both D- and L-forms. In this case, however, the complex contains only two molecules of the optically active coördinating agent.

stability than the former. In other words, if a racemic mixture of some organic compound which is bidentate in nature were to react with a complex such as dichloro-bis-levo-propylenediamine cobalt (III) chloride, two isomers would form, one containing the levo form and one the dextro form of the incoming molecule or ion. The resulting isomers would be expected to show different stabilities. Reaction of a mixture of these two isomers with some more powerful coördinating agent (one that would displace the "racemic" organic molecule or ion) would result in resolution if one enantiomorph were displaced in preference to the other. In actual practice, it has been found that molecules of different substances of opposite configuration may enter the same complex ion, though the greatest stability is obtained when the molecules of the coördinating agent are all of the same configuration.

Smirnoff[4] prepared both dichloro-bis-levo-propylenediamine cobalt(III) chloride and dichloro-bis-dextro-propylenediamine cobalt(III) chloride. He treated the complex containing the levo-propylenediamine with dextro-propylenediamine in the hope that displacement of the chloride ions would take place and so form the complex containing two molecules of levo-propylenediamine and one molecule of dextro-propylenediamine. The expected complex apparently formed but was very unstable and decomposed

$$3[\mathrm{Co}(l\text{-pn})_2(d\text{-pn})]\mathrm{Cl}_3 \longrightarrow 2[\mathrm{Co}(l\text{-pn})_3]\mathrm{Cl}_3 + [\mathrm{Co}(d\text{-pn})_3]\mathrm{Cl}_3$$

Similarly, the reaction of the bis-dextro-propylenediamine complex with levo-propylenediamine formed the isomeric mixed complex ion which also "disproportionated." When the coördinated chloride was displaced by a propylenediamine molecule of the same configuration as the one present in the complex, the reaction went very smoothly with the formation of either tris-levo-propylenediamine cobalt(III) chloride or tris-dextro-propylenediamine cobalt(III) chloride.

In the reaction of racemic propylenediamine with dichloro-bis-levo-propylenediamine cobalt(III) chloride, both enantiomorphs of the base seem to enter the complex with equal readiness.[5] The mixed complex ion probably rearranges as Smirnoff has shown.

Jaeger[6] in 1928 showed that a complex ion containing coördinated groups which are optically active due to the structure of the molecule behave in exactly the same manner as one formed by active components whose activity is due to an asymmetric carbon atom. Jaeger prepared tris-(1,2-*trans*-diaminocyclopentane) cobalt(III) chloride, $[\mathrm{Cocpd}_3]\mathrm{Cl}_3$. By using *d*-tartaric acid he was able to separate the isomers and found that only the D*lll* and L*ddd* forms were present. The preparation of the perchlorate salts gave two different kinds of crystals which could be mechanically separated, verifying the former results.

If the complex contains only two optically active coördinating groups, similar considerations hold. For the *trans*-dinitro-bis-propylenediamine cobaltic ion $[\mathrm{Co\ pn}_2(\mathrm{NO}_2)_2]^+$, for example, we might expect isomers containing two molecules of levo-propylenediamine, two of dextro-propylenediamine, or one of each. However, Hürliman[7] was able to isolate only two isomers, one containing two levo-rotatory propylenediamine molecules and the other containing two dextro-rotatory molecules.

This phenomenon has not been fully studied, and is only incompletely understood. Jaeger has attributed it to the fact that complexes containing coördinating molecules of the same configuration are more symmetrical, and hence more stable, than those containing molecules of different configurations. No experimental support for this hypothesis has been offered, and it is certainly open to question.

An equimolecular mixture of the dextro- and levo-tartrato isomers of $[\mathrm{Co}(l\text{-pn})_2(\mathrm{tart})]\mathrm{Cl}$ was prepared from $[\mathrm{Co}(l\text{-pn})_2\mathrm{Cl}_2]\mathrm{Cl}$ by grinding the latter with silver carbonate to form a solution of the carbonato complex and then adding racemic-tartaric acid and evaporating to dryness. The resulting mixture was treated with levo-propylenediamine in aqueous solution at 70° with the expected result that the tartrate from the less stable isomer was displaced first. This enantiomorph was the levo form of the tartrate ion. The isomer containing the dextro-tartrate ion was the more stable, which would serve to indicate that the dextro-tartrate has the same configuration as the levo-propylenediamine molecule.

Experimental

Resolution of Racemic Propylenediamine.—The method reported by Bailar, *et al.*,[5] was used for the resolution. Three pounds of pure dextrotartaric acid was dissolved in three liters of distilled water with subsequent addition of 430 g. of 70% (commercially available) racemic-propylenediamine. The solution was evaporated on the hot-plate until crystallization began, after which the solution was allowed to cool while being stirred mechanically. The crystals which separated were recrystallized twelve times or until a sufficient purity of levo-propylenediamine dextro-bitartrate was obtained as indicated by preparing the dihydrochloride described below and taking the optical rotation of an aqueous solution. For several experiments $[\alpha]^{20}\mathrm{D}$ varied between 3.99 and 4.10.

One hundred grams of the bitartrate was dissolved in the least possible amount of boiling water to which was slowly added with stirring a hot solution containing 41 g. of potassium chloride in the smallest possible amount of boiling water. After cooling in an ice-bath the precipitated potassium acid tartrate was filtered and the solution was evaporated by a stream of compressed air to less than 25 cc. This solution contained levo-propylenediamine dihydrochloride. Solid potassium hydroxide was added to the latter (with cooling in ice) until the resulting solution was strongly basic to litmus. The levo-propylenediamine was then distilled, the fraction boiling at 116–119° being collected as approximately 80% levo-propylenediamine.

Racemization of Dextro-tartaric Acid.—The naturally occurring dextro-tartaric acid was racemized by the method of Campbell, Slotin and Johnston.[8] Three hundred grams of dextro-tartaric acid was refluxed with two liters of 4 normal sodium hydroxide in a copper flask until the optical rotation of a portion of this mixture was found to be zero. (This takes from a week to ten days.) The resulting solution was made distinctly acid with concentrated hydrochloric

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[4] R. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[5] John C. Bailar, Jr., C. A. Stiegman, J. H. Balthis and E. H. Huffman, This Journal, **61**, 2402 (1939).

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

[7] Hans Hürliman, Thesis, University of Zurich, 1918. Reviewed in Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 167–168.

[8] A. N. Campbell, Louis Slotin and S. A. Johnston, This Journal, **55**, 2604 (1939).

acid and evaporated to 500 ml. on the steam-bath. While still hot, the precipitated sodium chloride was removed by filtration and 250 cc. of concentrated hydrochloric acid was added to the filtrate. More sodium chloride separated and was filtered. A liter of 95% ethanol was added and the precipitated sodium chloride again removed by filtration. Concentration of the filtrate from this mixture gave crystals of racemic-tartaric acid. Several recrystallizations from hot water were necessary to produce a product having a melting point of 206–207° and a specific rotation of zero degrees. The yield was approximately 150 g.

Resolution of Racemic Tartaric Acid.—Marckwald's procedure[9] was used for this resolution, with cinchonine as the resolving agent. Half of the theoretical amount of cinchonine necessary for the formation of the acid salt was used. A solution of 0.06 g. per 10 ml. gives a specific rotation of −15.0° at room temperature. An accepted value at 25° for $[\alpha]_D$ of a 20% aqueous solution is −12.0°.

Preparation of *cis*-Dichloro-bis-levo-propylenediamine Cobalt(III) Chloride.—The method of Bailar and co-workers[5] was used for this preparation with a modification developed by Sister Mary Martinette.[10] Fifty grams of cobalt chloride hexahydrate was dissolved in 1200 ml. of water containing 25 g. of 82% levo-propylenediamine. Air was bubbled through the solution for 16 hours or more after which 400 ml. of concentrated hydrochloric acid was added. The solution was concentrated by passing a current of air over it at 60°. The green *trans*-dichloro-bis-levo-propylenediamine cobalt(III) chloride which separated from the solution was filtered and washed with concentrated hydrochloric acid and ether. The yield, in several runs, varied from 20 to 30 g. This *trans* form was kept in an oven at 90–105° until it was converted to the purple *cis* form, less than 24 hours usually being required.

Preparation of Tartrato-bis-levo-propylenediamine Cobalt(III) Chloride.—This complex was prepared by the action of tartaric acid on a solution of carbonato complex, prepared according to the method of Bailar and McReynolds.[11] One-hundredth mole (3.136 g.) of *cis*-dichloro complex was ground for one-half hour with a paste of one-hundredth mole (2.758 g.) of silver carbonate in 0.5 ml. of distilled water. The mixture was filtered and the precipitated silver chloride was washed with ice-cold distilled water until the washings were nearly colorless. To the combined filtrate and washings was added one-hundredth mole of *d*- or *l*- or *dl*-tartaric acid and the solution was evaporated to dryness on the steam-cone. A glassy solid was obtained; this was dried in an oven at 90° for 48 to 96 hours. Long heating is necessary, as the $[\mathrm{Co}(l\text{-pn})_2\ \mathrm{tart}]\ \mathrm{Cl}$ is not formed immediately. When the solid is heated for a sufficiently long period of time, the glass becomes somewhat powdery.

Reactions of the Tartrato Complexes with Propylenediamine.—In the first experiment, the diastereoisomers $[\mathrm{Co}(l\text{-pn})_2(d\text{-tart})]\mathrm{Cl}$ and $[\mathrm{Co}(l\text{-pn})_2(l\text{-tart})]\mathrm{Cl}$ were allowed to react separately in aqueous solution with levo-propylenediamine. Samples of each complex weighing 200 mg. were dissolved in half a milliliter of water. One-half a milliliter of levo-propylenediamine was added to each solution, and the mixtures were heated to 70°. The course of the reaction is easily followed, since the tartrato complexes are red while the tris-propylenediamine complex is yellow-orange. It is evident that the complex containing levo-tartrate reacts much more readily than that containing dextro-tartrate:

Time of heating	Color of *l*-tartrato complex	Color of *d*-tartrato complex
5 min.	Red-orange	Red
40 min.	Orange	Orange-red
1.5 hr.	Orange	Red-orange
2 hr.	Orange	Orange

The solution containing the *d*-tartrato complex did not become orange until it had evaporated to a viscous mass.

In the second experiment, racemic tartaric acid was partially resolved. A gram and a quarter (1.25 g.) of the tartrato complex made from *dl*-tartaric acid was dissolved in 3 ml. of distilled water. After addition of three milliliters of 82% levo-propylenediamine the mixture was heated for definite time intervals at 70°. After each time interval the mixture was poured into 20 ml. of ice-cold methanol to precipitate the tartrate ion in the form of the anion, perhaps as $[\mathrm{Co}(l\text{-pn})_3]\mathrm{Cl}$ tart. This precipitate was recrystallized three times from methanol, the filtrates being combined with the original mother liquor and returned to the steam-cone where the methanol quickly evaporated. The solution was heated for another time interval, and the process was repeated. The samples of bright yellow recrystallized $[\mathrm{Co}\ l\text{-pn}_3]\mathrm{Cl}$ tart were dissolved in the smallest possible amount of water, and the tartrate was precipitated as calcium tartrate. This was dissolved in enough 5 *M* hydrochloric acid to make the resulting solution 1 *M* in tartaric acid.

OPTICAL ROTATIONS TAKEN ON 0.1% SOLUTIONS

Total time of heating	Color of filtrate	Observed rotation of tartaric acid	Yield, g.
0.1 min.	Red	−0.03	0.25
1.5 hr.	Red	− .04	.22
2.5 hr.	Red	....	..
24 hr.	Yellow	+ .03	.15
[a]	Yellow	+ .03	.3

[a] This precipitate was obtained by pouring the filtrate from 24-hour heating into ice-cold acetone.

To rule out the possibility that this partial resolution might be caused by a difference in solubility of the diastereoisomers of $[\mathrm{Co}\ l\text{-pn}_3]\mathrm{Cl}\ l\text{-tart}$ and $[\mathrm{Co}\ l\text{-pn}_3]\mathrm{Cl}\ d\text{-tart}$, care was taken in the third experiment to precipitate *all* of the dissolved salt from the solution, and thus eliminate the possibility of solubility differences. Ten grams of *dl*-tartrato bis-levo-propylenediamine cobalt(III) chloride, $[\mathrm{Co}\ l\text{-pn}_2\ rac\text{-tart}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$[12] ($[\alpha]_D$ of *l*-pn = 16.6°) was dissolved in 25 ml. of water. After addition of 18 ml. of 82% levo-propylenediamine, the mixture was heated at 70° for one hour. The solution was then cooled in ice and poured into 150 ml. of a mixture of equal parts of alcohol and ether. This completely precipitated the complex, leaving a colorless supernatant liquid. After washing with acetone and ether, the precipitate was dried for five minutes at 60°. It was then dissolved in 25 ml. of water and treated with an excess of a solution of lead nitrate. The gelatinous precipitate of lead tartrate was filtered immediately and suspended in 2 *N* acetic acid until it became crystalline. It was filtered, washed and decomposed by treatment with hydrogen sulfide. After removal of the lead sulfide, evaporation of the solution yielded 0.7 g. of tartaric acid. In 1% solution, this showed a rotation (sodium D line) of −0.049° $[\alpha]^{20}_D$ −4.9.

The filtrate from the original lead tartrate precipitation was heated on the steam-bath with 5 ml. of propylenediamine for 48 hours. The excess lead nitrate in the solution caused the precipitation of a small amount of lead tartrate during this time. The remaining tartrate was precipitated by the addition of more lead nitrate and the lead tartrate was treated as before. A 1% solution of the tartaric acid recovered from this fraction weighed 1.0 g. and showed a rotation of +0.063°; $[\alpha]^{20}_D$ +6.3°.

Another, similar experiment gave 1.0 g. (75% yield) of levo-tartaric acid showing a specific rotation of −5.50° and 1.1 g. (80% yield) of dextro-tartaric acid having a specific rotation of +6.2°.

As would be expected, the concentration of levo-propylenediamine has a very great effect on the time required for the reaction to take place. Two experiments like the second one described immediately above, but with a propylenediamine concentration of 25% of the total volume of the reaction mixture instead of 41%, gave similar results except that 48 to 50 hours were required for the removal of the levo-tartrate ion and more than 100 hours for the removal of the dextro-tartrate ion. The results are summarized in Table I.

The sign of rotation is perhaps of greater significance than the numerical value. It is evident that at least a partial resolution of tartaric acid was obtained. Further studies

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[9] W. Marckwald, *Ber.*, **29**, 43 (1896).

[10] Sister Mary Martinette, B.V.M., Thesis, University of Illinois, 1949.

[11] John C. Bailar, Jr., and J. P. McReynolds, THIS JOURNAL, **61**, 3201 (1939).

[12] This formula indicates an equimolecular mixture of $[\mathrm{Co}\ l\text{-pn}_2\ d\text{-tart}]\ \mathrm{Cl}\cdot 2\mathrm{H_2O}$ and $[\mathrm{Co}\ l\text{-pn}_2\ l\text{-tart}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$.

TABLE I

Time of heating, hr.	Temp., °C.	Observed rotation	Yield in grams
Experiment IV			
50	70	−0.03	0.14
146	70	+0.04	0.16
Experiment V			
48	73	−0.04	0.23
75[a]	73	+0.02	0.2

[a] In this case excess propylenediamine was added after 75 hours and the resulting solution was boiled to secure a more rapid displacement of the remaining tartrate ion. Excess calcium nitrate was subsequently added and the precipitated calcium *d*-tartrate removed by filtration.

on conditions and concentrations are being undertaken to achieve a more complete resolution.

At the present time the mechanism of this reaction is not fully understood. It was originally felt that the sole reaction was the one involved in the formation of the tris-levo-propylenediamine cobalt(III) chloride tartrate by the action of excess levo-propylenediamine on the tartrate complex according to the equation

$$[\mathrm{Co}(l\text{-pn})_2(\mathrm{tart})]\mathrm{Cl} + l\text{-pn} \longrightarrow [\mathrm{C\text{-}po}(ln)_3]\mathrm{Cl\ tart}$$

but it is now believed that additional reactions may occur also.

Experiment VI.—Further evidence that the two tartrato complexes have different stabilities was obtained by measuring the *p*H of aqueous solutions of the individual tartrato isomers containing excess levo-propylenediamine. The formation of the tris-propylenediamine complex is indicated by a gradual drop in the *p*H as propylenediamine molecules are removed from solution by coördination. A sample of each complex weighing 3.75 g. was dissolved in 9 ml. of water with subsequent addition of 9 ml. of 70% levo-propylenediamine. The solutions were then heated to 70°.

Time interval, hr.	*p*H of levo-tartrate solution	*p*H of dextro-tartrate solution
Zero	10.29	10.00
1	10.19	10.00
2	10.19	9.98
5	10.18	9.98
6	10.17	9.98
18	10.12	9.90
24	10.12	9.88
30	10.11	9.84
42	10.11	9.76
54	10.11	9.76
66	10.11	9.76
78	10.11	9.76
90	10.11	9.76

Here again it is seen that the complex containing the levo-tartrate ion appears to be less stable and undergoes a more rapid reaction than does the isomer containing the dextro-tartrate ion. Further efforts are being made to establish more precisely the differences in stabilities and reaction rates of these two isomers.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. IV

BY JAMES COLLINS, FRANCIS P. DWYER AND FRANCIS LIONS

RECEIVED OCTOBER 23, 1951

The base 1,8-diamino-3,6-dithiaoctane has been condensed with several different ortho-hydroxylated aromatic aldehydes to give Schiff bases which function as sexadentate chelate compounds. The coördination complexes derived from their combination with cobalt(III) ions show absorption minima between 540 and 580 mu. The cobalt(III) complex derived from *o*-vanillin has been resolved and appears to be suitable for rotatory dispersion studies.

It was pointed out in Part I[1] that the bis-salicylidene derivative of 1,8-diamino-3,6-dithiaoctane (EEE base) gave complex cobalt(III) salts when reacting with cobalt(II) salts in presence of oxidizing agents which showed maximum light transmission in 0.2% solution in 15% methanol of 65% at wave length 560 mμ. The relatively high molecular rotation of these optically active complex cobalt(III) salts suggests that despite their opacity they might prove of value in studies of rotatory dispersion. The present incomplete studies (which have had to be halted temporarily because of the transference of one of us (J. C.) to other work) were designed to prepare substances with greater optical transparency and more suitability for rotatory dispersion studies.

1,8-Diamino-3,6-dithiaoctane was condensed in hot ethanol with 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, 2-hydroxy-4-methylbenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde and 2-hydroxy-5-bromobenzaldehyde. Passage of air through a hot methanolic solution of any of the resulting Schiff bases containing cobalt(II) acetate led to formation of a cobalt(III) complex, the method being quite similar to that described for the bis-salicylidene complex described in Part I.[1]

All of these cobalt(III) salts had similar absorption curves (Figs. 1 and 2) showing in 0.2% solution a very steep rise in the transmission curve from about 20% at 400 mμ to about 85% at the maximum which lay between 540 and 580 mμ. Each of the substances showed an absorption maximum in the range 650–690 mμ and there was evidence that a weak absorption maximum existed at about 400 mμ, just outside the range of the recording spectrophotometer employed except for the complex derived from 5-bromosalicylaldehyde.

It was shown that the complex cobalt(III) ion derived from the Schiff base from *o*-vanillin exists in enantiomorphic forms by resolution through the *d*-antimonyl tartrates. The molecular rotations of the optically active iodides were found to be ±36,700°, for the sodium D line at 20°.

Experimental

1,8-Bis-(salicylideneamino)-3,6-dithiaoctanes.—These Schiff bases were readily prepared by admixture of hot methanolic solutions of 1,8-diamino-3,6-dithiaoctane (1 mole) and the substituted salicylaldehyde (2 moles) the yields be-

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(1) F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950).