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The Sterochemistry of Complex Inorganic Compounds. IX. The Diastereoisomers of *dextro*-Tartrato-*bis*-ethylenediamine Cobaltic Ion

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The stereochemistry of the octahedral complex ions offers many problems for which there is no counterpart in the better known stereochemistry of carbon. For example, the union of a metallic ion with three molecules of an optically active bidentate coördinating agent would be expected to lead to a large number of stereoisomeric complex ions.[2] The case of tris-propylenediamine cobaltic ion, [Co pn$_3$]$^{+++}$[3] offers an interesting example. Considering optical activity only, the complex ion would be expected to exist in eight isomeric forms. Taking D and L to represent the signs of rotation of the complex as a whole (at the sodium D line) and *d* and *l* the signs of rotation of propylenediamine, these are D*lll*, D*lld*, D*ldd*, D*ddd*, L*lll*, L*lld*, L*ldd*, L*ddd*. (In addition, there might be several racemoids or partial racemoids.) Experiment has shown, however, that these combinations are not all of equal stability; in fact, only two of the isomeric ions are stable enough to be isolated. They are L*lll* and D*ddd*.[4]

A similar effect is observed if the complex contains only two optically active coördinating groups. It has been shown that such ions as *cis* [Co pn$_2$ Cl$_2$]$^+$ and *cis* [Co cptdin$_2$ Cl$_2$]$^+$ exist[6] in only two of the six possible forms—D*ll*Cl$_2$ and L*dd*Cl$_2$.[4b] If dichloro-bis-*levo*-propylenediamine cobaltic ion, [Cl *l*-pn$_2$ Cl$_2$]$^+$, be treated with *dextro*-propylenediamine, the ion [Co *l*-pn$_2$ *d*-pn]$^{+++}$ apparently forms, but immediately rearranges to a mixture of the more stable L[Co *l*-pn$_3$]$^{+++}$ and D[Co *d*-pn$_3$]$^{+++}$.[4a,5]

These selective effects, while pronounced, are not absolute but only relative. Lifschitz[6] found evidence that cobalt and chromium tris-*dextro*-alanine exist in D*ddd* and L*ddd* forms. Bailar and McReynolds[7] have shown that the ion [Co *l*-pn$_2$ CO$_3$]$^+$ exists in both D*ll* CO$_3$ and L*ll* CO$_3$ forms, but that the latter is unstable, rearranging to the former when warmed gently.

When only one molecule of the optically active base is present in the coördination sphere, there is some tendency toward the formation of preferred orientations, but not enough to completely fix the configurations. Thus, when Jaeger and Blumendal[4b] allowed racemic *trans*-cyclo-pentanediamine to react with [Co en$_2$ Cl$_2$]$^+$, they obtained a true racemic mixture of D[Co en$_2$ *l*-cptdin]$^{+++}$ and L[Co en$_2$ *d*-cptdin]$^{+++}$ without detecting any of the other two possible forms. When, however, they used *levo*-cyclopentanediamine, they observed that the base entered both the D and L forms of the complex, yielding D and L[Co en$_2$ *l*-cptdin]$^{+++}$.[8]

This paper is concerned with another case in which the complex ion contains one optically active bidentate coördinating group—the tartrate ion. It has been found that *dextro* tartaric acid reacts readily with carbonato-*bis*-ethylenediamine cobaltic ion, [Co en$_2$ CO$_3$]$^+$ to give the two diastereoisomers D[Co en$_2$ *d*-tart]$^+$ and L[Co en$_2$ *d*-tart]$^+$, which differ strikingly in stability, reactivity and solubility.

The *dextro*-tartrato-bis-ethylenediamine cobaltic ion was prepared by the interaction of equivalent quantities of [Co en$_2$ CO$_3$]Cl or [Co en$_2$ CO$_3$] Br and *dextro*-tartaric acid. It makes no difference whether the carbonate salt is racemic or optically active; the final product is the same. Solutions of these substances react rapidly at room temperature with the evolution of carbon dioxide, but the primary product of the reaction is [Co en$_2$ (H$_2$O)$_2$]$^{+++}$. In order to insure complete replacement of the water molecules by tartrate, the solution must be evaporated to dryness and the residue heated on the steam-bath for several hours. The tartrato halides [Co en$_2$ *d*-tart] X are extremely soluble, and form deep red glasses which cannot be crystallized.[9] *Anal.* of [Co en$_2$ *d*-tart]Br·2H$_2$O, calcd.: N, 13.23; Br, 18.04. Found: N, 13.28; Br, 17.56. The rotation of a 0.1% solution at the sodium D line is about −0.19°.

On account of its high solubility, the mixture could not be completely fractionated into the D and L components. Partial fractionation was achieved, however, by dissolving the substance in water and reprecipitating about half of it by the addition of alcohol. The portion remaining in the filtrate was precipitated by addition of a large excess of ether. These fractions were again dissolved and reprecipitated. Repetitions of the process gave specific rotations as high as +2° and as low as −46°.

Reaction of DL[Co en$_2$ *d*-tart]$^+$ with Ethylenediamine.—A mixture of 20 g. of [Co en *d*-tart]Br, 60 ml. of 56% ethylenediamine and 15 ml. of water was shaken at room temperature for definite time intervals. After each time interval, the solution was poured into 75 ml. of ice-cold ethyl alcohol, and the precipitate was removed by filtration. The filtrate was evaporated to 55 ml. in a current of air (to remove the alcohol), 10 ml. of ethylenediamine was added (to compensate for that lost by evaporation and reaction) and the mixture was returned to the shaker for another time interval. The precipitate was thrice dis-

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[1] Most of the work reported in this article was taken from the doctorate theses of Hans B. Jonassen (1946) and E. H. Huffman (1936) at the University of Illinois. The remainder was done by Mr. Jonassen at Tulane University. For the previous paper in this series, see This Journal, **70**, 749 (1948).

[2] Jaeger gives a full discussion of the various possibilities in his book "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., New York, N. Y., 1928.

[3] The following abbreviations are used: pn = propylenediamine, en = ethylenediamine, cptdin = *trans*-cyclopentanediamine, tart = tartrate ion.

[4] For other examples, see (a) Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920), and (b) Jaeger and Blumendal, *Z. anorg. allgem. Chem.*, **175**, 161 (1928).

[5] Bailar, Stiegman, Balthis and Huffman, This Journal, **61**, 2402 (1939); ref. 2, p. 155.

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

[7] Bailar and McReynolds, This Journal, **61**, 3199 (1939).

[8] See also Werner, *Helv. Chim. Acta*, **1**, 5 (1918).

[9] Duff, *J. Chem. Soc.*, **119**, 388 (1921).

solved in 15 ml. of water and reprecipitated by adding 15 ml. of methyl alcohol. This kept the unchanged tartrato salt in solution but precipitated the bright yellow tris-ethylenediamine salt. The filtrates were saved, and the complex in them was finally recovered by evaporation at room temperature to 50 ml. and addition of 150 ml. of a 2:1:1 mixture of methyl and ethyl alcohols and ether. The results are shown in Table I.

TABLE I

Time of shaking	Color of ppt.	Color of filtrate	α(obs.) 1-dm. tube	Yield, g.
10 min.	Pink	Red	+0.13 (0.1% soln.)	0.15
40 min.	Yellow	Red	+0.05 (0.5% soln.)	3.2
100 min.	Yellow	Red	+0.08 (0.5% soln.)	3.5
12 hours	....	Red	....	0.0

From the filtrate, after twelve hours of shaking, it was possible to recover 9 g. of $[\text{Co en}_2\ d\text{-tart}]\text{Br}$; 2 g. was also recovered from the filtrates obtained upon recrystallization of the precipitates. It is evident that the reaction proceeds rapidly for something over an hour, then stops completely.

A similar experiment was carried out at a higher temperature, the procedure differing only in that after each removal of tris-ethylenediamine salt the unchanged tartrato salt was completely precipitated by adding 100 ml. of a 2:1:1 mixture of methyl and ethyl alcohols and ether. This precipitate was then dissolved in twice its weight of water, and twice this volume of ethylenediamine was added. A small portion of the resulting solution was used each time for a determination of the rotation. The results are shown in Table II.

TABLE II

Time of shaking, hr.	Temp., °C.	Yield of $[\text{Co en}_3]^{+++}$ salt, g.	α observed ppt. (0.5%) 1-dm. tube	% purity of D$[\text{Co en}_3]^{+++}$	Filtr. (0.1%) 1-dm. tube
0	20				−0.07
0.25	20	2.2	+0.43	90	− .08
0.75	20	2.3	+ .38	85	− .13
2	20	4.7	+ .35	80	− .17
12	20	0.6	+ .40	85	− .20
28	50	2.3	+ .45	90	− .26
48	50	2.0	+ .30	75	− .33
68	50	0.5	+ .25	70	− .40
82[a]	50	1.1	+ .01		− .45
106[a]	50	0.2	+ .02		− .06

[a] Two grams of activated charcoal was added in each of the last two time intervals. This greatly catalyzes the reaction, but the product is racemic. The filtrate from each of the last two filtrations was orange or brown (the color of $[\text{Co en}_3]^{+++}$), while the filtrates from the earlier shakings were a brilliant cherry red (as is $[\text{Co en}_2\ \text{tart}]^+$).

The fact that the $[\text{Co en}_3]^{+++}$ fractions all show positive rotations, while the material which has not reacted shows an increasing negative rotation, indicates that the original material is a mixture of two isomers rather than a single individual, D or L $[\text{Co en}_2\ d\text{-tart}]^+$.

The filtrate from the precipitate obtained after one-hundred six hours of shaking could not be precipitated by addition of 100 ml. of 2:1:1 mixture of methyl and ethyl alcohols and ether. The excess of ethylenediamine was therefore removed by bubbling gaseous hydrogen chloride through the ice cold solution until most of the ethylenediamine was precipitated as the hydrochloride and before the solution began to change to a purple color (indicative of the formation of $[\text{Co en}_2\ \text{Cl}_2]^+$). The ethylenediamine hydrochloride was filtered off, and the filtrate was evaporated in a stream of air. The residue was dried for four hours at 65°; yield about 3.5 g. The rotation was −0.06 for a 0.5% solution.

Similar results were obtained in several other runs although no exact duplications of the rotations were obtained. The tris-ethylenediamine salt obtained in the sixty-eight hours represents a little more than 12 g. of optically pure tris-ethylenediamine cobaltic bromide. Since 1.3 g. of almost inactive $[\text{Co en}_3]\text{Br}_3$ was recovered, as well as 3.5 g. of unchanged starting material, it is evident that an asymmetric synthesis has taken place.

In the best run, a 70% yield of *dextro*-$[\text{Co en}_3]^{+++}$ was obtained (out of a possible 100% for *dextro*- and *levo*-combined). Either the two isomers of $[\text{Co en}_2\ d\text{-tart}]^+$ are not present in equal amount or the less reactive is converted to the more reactive as the latter is used up by the reaction with ethylenediamine. The fact that the DL-$[\text{Co en}_2\ d\text{-tart}]^+$ mixture has a high negative rotation would suggest that the L isomer is somewhat more abundant and therefore more stable than the D. This leads to the conclusion that the D form is the more reactive and so is the one which reacts with ethylenediamine the more readily. Whether the difference in rate of reaction takes place in the formation of the tartrato complex or in its conversion to the *tris*-ethylenediamine salt, we have here a partially asymmetric synthesis of $[\text{Co en}_3]^{+++}$.

Reaction of DL-$[\text{Co en}_2\ d\text{-tart}]^+$ with Hydrochloric Acid.—A solution of ten grams of the tartrato salt in ten milliliters of water was treated with 10 ml. of concentrated hydrochloric acid. At given time intervals the mixture was poured into 50 ml. of ice cold methanol, which caused precipitation of the unchanged tartrato salt, but kept the violet colored *cis*-dichloro salt in solution. After filtration, the red precipitate was again treated with hydrochloric acid. The violet filtrate was treated with 75 ml. of concentrated nitric acid to precipitate the dichloro salt. This precipitate was filtered as quickly as possible, washed with ether and dried in a vacuum desiccator over potassium hydroxide for two weeks. This long drying is essential to remove the last traces of acid. Without it, the crystals turn green (*trans*-dichloro salt) when exposed to moist air. Table III shows the results of two runs. It will be observed that samples of the *cis*-dichloro salt obtained in the second run showed no optical activity. This is probably due to the fact that the acid was not entirely removed, and caused very rapid racemization. This *cis*-dichloro salt racemizes rapidly even under the best conditions, and the measurements of optical rotation must be made immediately. While the rotations of the *cis*-$[\text{Co en}_2\ \text{Cl}_2]\text{Cl}$ could never be duplicated, the increasing negative rotation of the unchanged tartrato salt was demonstrated repeatedly. Here again, the results show that $[\text{Co en}_2\ d\text{-tart}]^+$ is not a single individual, but is a mixture of two forms which differ greatly in reactivity.

Optical rotations were taken on 0.1% solutions at the sodium D line in a 1-dm. tube. *Anal.* Calcd. for $[\text{Co en}_2\ \text{Cl}_2]\text{Cl}$: Cl, 37.3. Found for sample B: first run, Cl, 37.21; second run, Cl, 37.45.

Reaction of DL-$[\text{Co en}_2\ d\text{-tart}]\text{Br}$ with Calcium Nitrite.—Four grams of the DL tartrato salt, in about 10 ml. of water, was mixed with 2.4 g. (100% excess) of calcium nitrite. Reaction was very slow, but over a period of several weeks calcium tartrate and a brown powder of $[\text{Co en}_2\ (\text{NO}_2)_2]\text{Br}$ gradually precipitated. This was recrystallized from water containing a little ammonium bromide. It was dextrorotatory; analysis showed 23.06% bromine; calcd., 22.77%. The reaction can be greatly accelerated by heating the mixture near the boiling point for five minutes and cooling immediately, or by heating to 50–60° for three hours. For the best sample prepared by the first of these techniques $[\alpha]_D$ was found to be +50°. Werner[10] reports $[\alpha]_D$ for $[\text{Co en}_2\ (\text{NO}_2)_2]\text{Br}$ to be +44°. For a typical sample prepared by the second technique, $[\alpha]_D$ was found to be +42°, and the percentage of bromine, 22.84.

In every case the filtrate still had the brilliant red color of the tartrato salt, and it was evident that much of this remained. When the reaction mixture was heated long enough to bring about complete reaction, the product was always racemic, probably because of the easy racemization

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(10) Werner, *Ber.*, **44**, 2450 (1911).

TABLE III

Sample	Total time of reaction, hours	First run			Second run		
		cis-Dichloro, g.	[α] of *cis*-dichloro	[α] of filtrate	*cis*-Dichloro, g.	[α] of *cis*-dichloro	[α] of filt.
Original				(−0.09)			(−0.09)
A	1	1.92	+0.06	− .13	1.13	+0.01	−0.12
B	5	3.64	+ .05	− .18	4.30	.00	− .19
C	12	0.96	+ .05	− .26	0.75	.00	− .24
D	24	0.88	+ .02	− .34	0.80	.01	− .33
E	48	0.24	+ .04	− .40	0.34	.00	− .40

of [Co en_2 $(NO_2)_2$]$^+$. The best yield of optically active dinitro product that was ever obtained was 40%. It is apparently possible to convert one form of the [Co en_2 *d*-tart]Br to the dinitro salt without affecting the other form. When the reaction is allowed to proceed at room temperature, the precipitation of calcium tartrate goes on slowly but steadily until about half is precipitated; the reaction then stops unless the temperature is raised.

Summary

The presence of two or three optically active chelate groups in an octahedral complex tends to fix a definite configuration upon the complex ion as a whole, and in some cases the number of stereoisomers which can be isolated is limited to a small fraction of those theoretically possible. No such effect has been observed in complex ions containing only one asymmetric chelate group. It is now shown that while both the D and L forms of *dextro*-tartrato-*bis*-ethylenediamine cobaltic ion, [Co en_2 *d*-tart]$^+$, form when *dextro*-tartaric acid reacts with [Co en_2 CO_3]$^+$, they differ greatly in reactivity. When the mixture of the two is shaken with ethylenediamine at room temperature, part of the material reacts within two hours, giving *dextro*-[Co en_3]$^{+++}$. The remainder does not react even in twelve hours and can be recovered. At 50°, a 70% yield of *dextro*-[Co en_3]$^{+++}$ is obtained, and very little of the original material can be recovered. Evidently the less reactive form changes to the more reactive as the latter is used up. The reaction with hydrochloric acid seems to follow a similar course, and gives a large yield of *dextro*-rotatory *cis*-[Co en_2 Cl_2] Cl.

Reaction with calcium nitrite gives similar results; at room temperatures or slightly above, about half of the tartrato salt reacts, yielding *dextro*-[Co en_2 $(NO_2)_2$]$^+$. The remainder will not react at room temperatures. At higher temperatures the product is racemized.

These are evidently the first examples of asymmetric synthesis in the field of inorganic complex ions.

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Hydrofluorination in the Presence of Boron Fluoride

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The addition of hydrogen fluoride to an olefinic hydrocarbon occurs with great ease[1]; addition also takes place easily with asymmetrically halogenated olefins such as $CH_2{=}CHX$, $RCH{=}CX_2$ or $RCX{=}CH_2$,[2] while the presence of the vinylic halogens on both sides of the double bond impedes or prevents it.[2] We have now observed that when the addition is carried out in the presence of small quantities of boron fluoride the reaction is greatly hastened, and even occurs where it had failed in the absence of boron fluoride.

Besides plain hydrofluorination, an alternation of HF additions and HX removals is observed, so that $RCH{=}CX_2$ gives not only RCH_2CX_2F, but also $RCH{=}CFX$, RCH_2CXF_2, $RCH{=}CF_2$ and RCH_2CF_3 in sequence. The presence of the boron fluoride increases the number of these steps and the extent to which they occur; the net effect is to increase the fluorine content of the final product.

The use of boron fluoride is particularly advantageous with heavily halogenated olefins, or with olefins bearing a CF_3 group which slows down the reactivity of their double bond. For more reactive olefins, boron fluoride may not be so desirable because it hastens resinification as well as addition; the economy of each case should be individually considered. The literature statement[1] that BF_3 is of no help should be restricted to non-halogenated olefins, where addition is so easy that it does not need any help.

Eleven different olefins were treated with hydrogen fluoride in the molar ratio of 1/2; when BF_3 was added, it was in the concentration shown in grams per mole of olefin in the table of experimental results.

The observed improvements can be explained by the formation of a coördinated complex $HF \rightarrow BF_3$, which enhances the percentage of ionic character of the H–F bond; this facilitates the separation of hydrogen as a proton, and makes it more available for addition to the more negative of the

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(1) Grosse and Lind, *J. Org. Chem.*, **3**, 26 (1938).

(2) Henne and Plueddeman, THIS JOURNAL, **65**, 1271 (1943), also Renoll, *ibid.*, **64**, 1115 (1942).