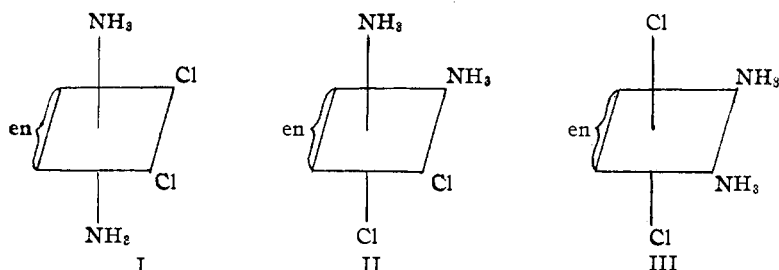


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Stereochemistry of Complex Inorganic Compounds. VI. A Study of the Stereoisomers of the Dichloro-diammino-ethylenediamine Cobaltic Ion

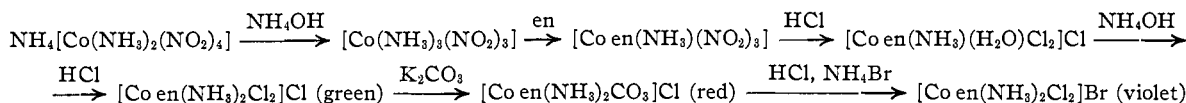
BY JOHN C. BAILAR, JR., AND DONALD F. PEPPARD<sup>1</sup>

The dichloro-diammino-ethylenediamine cobaltic ion can exist in three stereoisomeric forms



stable. The assignment of configurations is based upon the fact that ion II is asymmetric, while ion I is not. Attempts to resolve ion II itself were unsuccessful, but the carbonato salt derived from it was shown to be resolvable.

In attempting to prepare salts of these stereoisomeric ions, we first followed the directions given by Chaussy



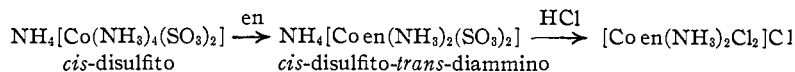
Salts of two of these were prepared by Chaussy,<sup>1a</sup> who designated them as "cis" and "trans" (referring to the relative positions of the chloride groups) or simply as "blue" and "green." Chaussy made no mention of the fact that two *cis* series are possible. This is discussed, however, in a later account of Chaussy's work.<sup>2</sup>

*cis*-Dichloro-*trans*-diammino-ethylenediamine cobaltic ion (I) and *cis*-dichloro-*cis*-diammino-ethylenediamine cobaltic ion (II) would be expected to be violet, like *cis*-dichloro-tetrammino cobaltic ion and *cis*-dichloro-diethylenediamine cobaltic ion. The *trans*-dichloro-*cis*-diammino-ethylenediamine cobaltic ion (III) should be green, like its analogs in the ammino and ethylenediamine series. The colors of these ions determine the relative positions of the chloride groups with certainty but do not distinguish between the two *cis*-dichloro configurations.

This paper reports the preparation and a brief study of the properties of all three of the isomeric ions. It is shown that Chaussy's "blue" compounds are probably salts of the *cis*-dichloro-*cis*-diammino ion (II). This has almost exactly the same color as the *cis*-dichloro-*trans*-diammino ion (I), but its salts are much more soluble and less

The second step was very troublesome, always giving a product containing from 2-5% too much carbon. Trinitrotriammine cobalt prepared according to the directions of Riesenfeld and Klement,<sup>3</sup> however, gave a satisfactory product in good yield. This material, when treated with hydrochloric acid according to Chaussy's directions, did not yield a product exhibiting the properties of the dichloro-aquo-ammino-ethylenediamine cobalt described by him. There is no certainty, of course, that the trinitro-triammine cobalt used in the present study was the same stereoisomer as that used by Chaussy, as it was prepared by a different method. The problem is further complicated by the possibility of four stereoisomers of dichloro-aquo-ammino-ethylenediamine cobaltic chloride.

Chaussy's method finally was abandoned, and an entirely new approach was sought. The desired salts were prepared finally according to the following scheme:



Configurations were first assigned to  $\text{NH}_4[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]$  and  $\text{NH}_4[\text{Co en}(\text{NH}_3)_2(\text{SO}_3)_2]$  by Klement,<sup>4</sup> on the basis of the fact that ethylenediamine replaces two of the ammonia molecules much more readily than the other two. If the

(1) From a portion of the doctorate thesis of Donald F. Peppard, University of Illinois, 1939.

(1a) Chaussy, Dissertation, Zürich, 1909.

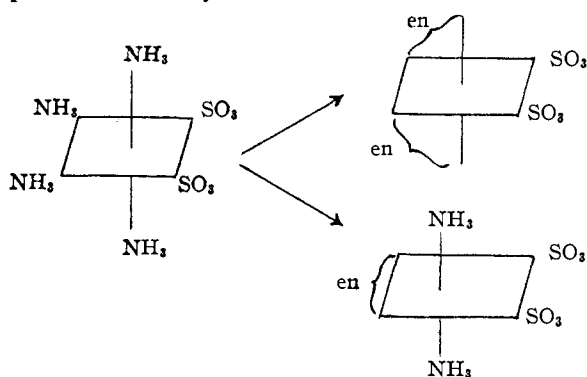
(2) Werner and Chaussy, *Ann.*, **386**, 254-264 (1912).

(3) Riesenfeld and Klement, *Z. anorg. allgem. Chem.*, **124**, 1-21 (1922).

(4) Klement, *Z. anorg. allgem. Chem.*, **150**, 117-125 (1925).

sulfito groups are *trans* to each other, the four ammonia molecules are equivalent, and all of them would

be replaced by ethylenediamine with equal ease. If the sulfito groups are *cis* to each other, however, the introduction of ethylenediamine may follow either of two paths; one of these allows the replacement of only two ammonia molecules:



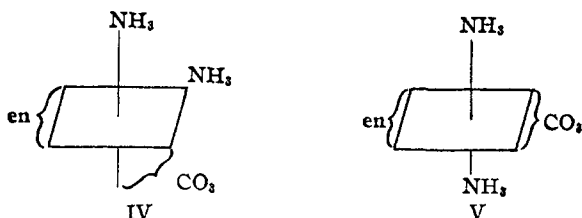
Since only two ammonia molecules are replaced under the conditions used, Klement believed the product to be ammonium *cis*-disulfito-*trans*-diammino-ethylenediamine cobaltate. The evidence to be presented in this paper confirms this view.

Treatment of ammonium *cis*-disulfito-*trans*-diammino-ethylenediamine cobaltate with hydrochloric acid must produce *cis*-dichloro-*trans*-diammino-ethylenediamine cobaltic chloride, unless rearrangement takes place. That the experiment actually yields the green *trans* salt is not at all surprising, however, for the analogous *cis*-dichloro-diethylenediamine cobaltic chloride rapidly rearranges to the *trans* form in aqueous hydrochloric acid. Treatment of the disulfito salt with hydrogen chloride dissolved in absolute alcohol (in which these cobalt compounds are not soluble) yields a nearly pure violet dichloro salt, which can be purified by conversion to the slightly soluble *dextro*- $\alpha$ -bromocamphor- $\pi$ -sulfonate and reversion to the chloride by cold concentrated hydrochloric acid. This *cis* dichloro-salt could not be resolved by means of ammonium *dextro*- $\alpha$ -bromo-camphor- $\pi$ -sulfonate, although it readily forms a nicely crystalline precipitate when treated with this reagent. This ion will later be shown to be the unresolvable *cis*-dichloro-*trans*-diammino form (I).

The *cis*-dichloro-*cis*-diammino isomer is most readily obtained through the following reactions:

The product formed in the second of these reactions is a mixture of the *trans*-dichloro salt (III) and the *cis*-dichloro-*cis*-diammino salt (II). It seems impossible to prevent some rearrangement of this *cis*-dichloro form to the *trans* form.

The configurations of the two *cis*-dichloro forms were assigned through a study of the corresponding carbonate complexes. The carbonate salt prepared by treating *trans*-dichloro-*cis*-diammino-ethylenediamine cobaltic chloride with silver carbonate can be resolved partially by shaking a solution of it with optically active quartz<sup>5</sup> and yields, on treatment with alcoholic hydrogen chloride, a *cis*-dichloro isomer with some admixed *trans*-dichloro isomer. This *cis*-dichloro salt, when treated with silver carbonate, is again transformed into the carbonate complex which can be resolved partially by the use of active quartz. This carbonate complex must have configuration IV, and the related dichloro complex is



almost certainly II. Since Chaussy prepared his "blue" dichloro salt from the carbonate chloride formed from the *trans*-dichloro chloride, it seems probable that his *cis*-isomer has the *cis*-dichloro-*cis*-diammino configuration.

On the other hand, the dichloro salt obtained by treating ammonium *cis*-disulfito-*trans*-diammino-ethylenediamine cobaltate with alcoholic hydrogen chloride, when treated with silver carbonate, gives a carbonate complex which shows no resolution when shaken with active quartz (V). The original *cis*-dichloro salt, with no contamination of *trans*-dichloro-isomer, is obtained when this carbonate salt is treated with alcoholic hydrogen chloride.

It will be noted that the conversion of IV to the *trans*-dichloro salt requires the shift of one nitrogen-cobalt link, but the same conversion, in the case of V, requires the shift of two. The

(5) Tsuchida, Kobayashi and Nakamura, *Bull. Chem. Soc. Japan*, **11**, 38-40 (1936).

fact that only one of the carbonato salts yields any *trans*-dichloro salt thus gives further evidence for the configurations assigned. By the same reasoning, it may be deduced that the *trans*-dichloro salt should form the carbonato complex IV.

Several reactions serving to distinguish the two *cis*-dichloro ions are summarized in Table I. In each case, the solid reagent was added to a nearly saturated solution of the dichloro-chloride and stirred vigorously.

TABLE I

Reagent	<i>cis</i> -Dichloro- <i>trans</i> -diammino (I)	<i>cis</i> -Dichloro- <i>cis</i> -diammino (II)
Ammonium dextro- $\alpha$ -bromocamphor- $\pi$ -sulfonate	Purple crystals	No precipitate
Ammonium iodide	Dark purple crystals	Immediate precipitate of a brown and green gelatinous mixture
Sodium thiocyanate	Purple crystals	Slow deposition of a green powder

An attempt to prepare a *cis*-dibromo-diammino-ethylenediamine cobaltic salt by treating ammonium *cis*-disulfito-*trans*-diammino-ethylenediamine cobaltate with alcoholic hydrogen bromide was unsuccessful. The *trans*-dibromo isomer was obtained under all conditions. This is not surprising, since it is difficult to prepare the *cis*-dibromo salt in the diethylenediamine series<sup>6</sup> and evidently impossible in the tetrammino series.

The *cis*-dichloro-*cis*-diammino-ethylenediamine cobaltic ion is asymmetric. If it were resolved it should afford some interesting studies on the Walden inversion, especially since the only cases of such inversion in inorganic complexes involve the cobalt atom with two ethylenediamine molecules attached.<sup>7</sup>

It may be that two such chelate groups are necessary to prevent complete loss of optical activity during substitution. On the other hand, inversion might occur more readily with only one ethylenediamine molecule in the complex, since the ammonia-cobalt link is probably ruptured more easily than the ethylenediamine-cobalt link.

Thus far, all attempts to resolve the *cis*-dichloro-*cis*-diammino-ethylenediamine cobaltic ion have failed, although the corresponding carbonato ion has been partially resolved by adsorption on active quartz.

Since the racemic dichloro complex could not

(6) Werner, Gerb, Lorie and Rapiport, *Ann.*, **386**, 110-125 (1912).

(7) Bailar and Auten, *THIS JOURNAL*, **56**, 774-776 (1934); Bailar, Haslam and Jones, *ibid.*, **58**, 2224-2226 (1936); Bailar, Jonelis and Huffman, *ibid.*, **58**, 2226-2227 (1936).

be resolved directly, an attempt was made to isolate one of its optical antipodes indirectly. During a study of the active forms of chloro-aquo-diethylenediamine cobaltic ion (not yet published) it was found that if racemic *cis*-dichloro-diethylenediamine cobaltic chloride is allowed to stand in water solution until the requisite aquation has occurred and the solution then treated with a suitable resolving agent, active chloro-aquo-diethylenediamine cobaltic chloride can be obtained. The active salt also can be prepared by heating *trans*-dichloro-diethylenediamine cobaltic chloride in water solution, allowing the solution to stand for a few days, and adding a suitable resolving agent. This active chloro-aquo complex, when suspended in thionyl chloride, is transformed into active dichloro-diethylenediamine cobaltic chloride.

All attempts to isolate an active dichloro-diammino-ethylenediamine cobaltic ion in this way failed.

### Experimental

Ammonium *cis*-disulfito-tetrammino cobaltate is readily prepared by a modification of the method of Werner and Gruger.<sup>8</sup> Solutions of 160 g. of cobalt chloride hexahydrate in 240 cc. of water and 400 g. of ammonium carbonate in 2000 cc. of water are mixed with 1000 cc. of 28% ammonium hydroxide. Air which is first drawn through 14% ammonium hydroxide in three flasks connected in series is rapidly drawn through the solution for eight hours. Three hundred and ten grams of solid sodium bisulfite is added to the solution in the flask, and air is drawn through the solution for three or four minutes. The solution is poured into a large evaporating dish and allowed to stand open to the air for fifteen hours. It is then cooled in ice and salt for four hours, leaving the beakers open to the air and stirring occasionally. The brown salt forms in small crystals. These are filtered with suction, washed with a little cold water, absolute alcohol, and ether, and dried in air. The yield is 150 to 160 g. (62-66%). The salt is sufficiently pure without recrystallization.

*Anal.* Calcd. for  $\text{NH}_4[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ : S, 17.83; N, 19.50; H, 6.13. Found: S, 17.74; N, 19.25; H, 6.14.

Ammonium - *cis* - disulfito - *trans* - diammino - ethylenediamine Cobaltate.—The following method was found to give a much better yield than that of Klement.<sup>4</sup> Fifty grams of ammonium-*cis*-disulfito-tetramminocobaltate and 50 or 60 glass beads are covered, in a round-bottomed flask, with a solution of 12 cc. of 60% ethylenediamine in 200 cc. of absolute ethanol. The flask is stoppered with a cork carrying a calcium oxide drying tube bent downward. The mixture is shaken continuously for one hundred and sixty hours. The suspension is drawn through a Büchner funnel without filter paper to free it from the glass beads; the powder is filtered from the liquid,

(8) Werner and Gruger, *Z. anorg. allgem. Chem.*, **16**, 398-423 (1898).

and washed with ethanol. The material from four such runs is combined and recrystallized by extracting at about 90° for eight or ten minutes with 400 cc. of water. After filtering, the residue is similarly extracted with 300 cc. of water. The filtrates from these extractions are cooled in ice. The precipitates are combined, washed with a little water, ethanol and ether, and dried in air. The yield of pure product is about 120 g. (56%). For analysis, the salt was dried over potassium hydroxide.

*Anal.* Calcd. for  $\text{NH}_4[\text{Co en}(\text{NH}_3)_2(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ : C, 6.54; H, 5.99; S, 17.44. Found: C, 6.48; H, 6.10; S, 17.26, 17.31.

Klement reported that the air-dried material contains three molecules of water.

*trans*-Dichloro-*cis*-diammino-ethylenediamine Cobaltic Chloride.—Twenty-two grams of ammonium *cis*-disulfito-*trans*-diammino-ethylenediamine cobaltate is covered with 27 cc. of concentrated hydrochloric acid. The mixture is kept at 70° until the solid dissolves and the solution becomes purple. Sixteen cubic centimeters of water is added and the solution warmed at 70° for one minute. After three days the green crystals are removed by filtration and purified by suspension in a little water. They are finally washed with 50% ethanol, absolute ethanol, and then ether. The yield is about 5 g. (32%) at best. The compound can be purified by recrystallization from concentrated hydrochloric acid, but the solution must not be heated to a temperature higher than 70°.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ : C, 8.96; H, 5.60; N, 20.90; Cl, 39.40. Found: C, 8.95; H, 5.88; N, 20.87; Cl, 39.01, 39.12.

*trans*-Dichloro-*cis*-diammino-ethylenediamine cobaltic bromide, iodide, and thiocyanate were prepared according to Chaussy's directions and conform to his descriptions.

*cis*-Dichloro-*trans*-diammino-ethylenediamine Cobaltic Chloride.—Six grams of finely powdered ammonium *cis*-disulfito-*trans*-diamminoethylenediamine cobaltate is covered with 90 cc. of absolute alcoholic hydrogen chloride (saturated at room temperature) and allowed to stand for twenty-four hours with occasional shaking. A blue salt contaminated with ammonium chloride is obtained. None of the *trans*-isomer is formed. The filtered salt is washed with absolute ethanol and ether to remove all of the hydrogen chloride. After being dried in air to remove most of the ether it is suspended three times in 3 cc. of water at room temperature, and filtered. The salt is washed with alcohol and ether.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ : C, 8.66; H, 5.78; N, 20.22; Cl, 38.27. Found: C, 8.76; H, 5.96; N, 19.98; Cl, 38.47, 38.59.

The salt can be purified more easily by conversion to the much less soluble *dextro*- $\alpha$ -bromocamphor- $\pi$ -sulfonate. Two grams of the salt is stirred with 60 cc. of water at about 15° for two minutes. Five grams of ammonium *dextro*- $\alpha$ -bromocamphor- $\pi$ -sulfonate is added to the filtered solution and the mixture stirred for thirty minutes at about 15°. The blue-purple salt is washed with absolute ethanol and ether and dried in air. It is then covered with 7 cc. of concentrated hydrochloric acid in an ice-cooled mortar and ground for a few seconds. Fourteen cubic centimeters of a mixture of equal volumes of absolute

ethanol and ether are added and the grinding continued for several minutes. The blue salt is washed with absolute ethanol and ether.

The product is not optically active at the D line of sodium.

Several derivatives of the *cis*-dichloro-*trans*-diammino-ethylenediamine cobaltic ion were prepared to further characterize it. The bromide,  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Br}$ , was obtained as follows. Slightly more than an equivalent amount of solid ammonium bromide is added with stirring to a filtered concentrated solution of *cis*-dichloro-*trans*-diamminoethylenediamine cobaltic chloride. After stirring and scraping the walls of the beaker, the blue-purple salt precipitates. It is purified by two or three suspensions in water and finally washed with alcohol and ether.

A product more easily purified is obtained by using slightly less than the calculated amount of ammonium bromide, but the yield is poorer.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Br} \cdot 2\text{H}_2\text{O}$ : C, 7.06; H, 5.29; N, 16.47. Found: C, 6.98; H, 5.59; N, 16.95.

The iodide, prepared in similar manner, precipitates in good yield as beautiful purple crystals. In contrast to the iodide of the *cis*-dichloro-*cis*-diammino isomer, this salt is stable.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{I}$ : C, 6.84; H, 3.99; N, 15.95. Found: C, 7.17; H, 4.15; N, 16.11.

The purple thiocyanate, prepared in a similar way by the use of sodium thiocyanate, precipitates readily in good yield.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{SCN} \cdot \text{NaSCN}$ : C, 13.19; N, 23.14; S, 17.63. Found: C, 13.23; N, 23.13; S, 17.39, 17.51.

The formation of this double compound is reminiscent of the crystallization of *trans*  $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl}$  from hydrochloric acid.

*cis*-Dichloro-*cis*-diammino-ethylenediamine Cobaltic Chloride.—Two grams of carbonato-*cis*-diammino-ethylenediamine cobaltic carbonate prepared from *trans*-dibromo-*cis*-diammino-ethylenediamine cobaltic bromide is covered with 40 cc. of alcoholic hydrogen chloride and a few glass beads added. The flask is fitted with a mercury seal allowing gases to escape but maintaining a pressure exceeding atmospheric. The apparatus is shaken for twenty-four hours, at the end of which time the light blue precipitate is filtered. It is suspended in a little water, filtered quickly from the green contamination, and 15 or 20 volumes of ethanol are added to the filtrate. A purple oil precipitates. The alcohol is decanted and the oil kept *in vacuo* over potassium hydroxide for twenty-four hours. The salt is then powdered and the drying continued.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$ : C, 9.27; H, 5.45; N, 21.62; Cl, 40.93. Found: C, 9.47; H, 5.49; N, 21.36; Cl, 40.60, 40.71.

The bromide of the *cis*-dichloro-*cis*-diammino series is prepared by treatment of a concentrated solution of the chloride with the equivalent amount of solid ammonium bromide.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Br}$ : C, 7.90; H, 4.64; N, 18.47. Found: C, 7.97; H, 4.71; N, 18.32.

*trans*-Dibromo-*cis*-diammino-ethylenediamine cobaltic bromide was used in some of the preparations of the

carbonato-*cis*-diammino carbonate, as it is easier to purify than the dichloro salt. It is prepared as follows. Thirty-five cubic centimeters of 40% aqueous hydrobromic acid is heated to approximately 80° in a small beaker, and 5 g. of ammonium-*cis*-disulfito-*trans*-diammino-ethylenediamine cobaltate is added with stirring. The heating and stirring are continued at approximately 80° until a dark green solution is formed. If the heating is continued longer than three minutes some decomposition takes place. The solution is allowed to stand at room temperature for three hours, then cooled in ice. The green crystals are filtered and purified once or twice by suspension in a little water. They are washed with absolute ethanol and ether. The yield from five such runs is 8 g. of pure product.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Br}_2]\text{Br}$ : C, 6.11; H, 3.56; N, 14.25; Br, 61.07. Found: C, 6.29; H, 3.64; N, 14.01; Br, 60.73, 60.89.

The thiocyanate of the dibromo series was prepared as a pale green salt, in the same manner as the thiocyanate of the *cis*-dichloro-*trans*-diammino series.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{Br}_2]\text{SCN}$ : C, 9.70; N, 18.87; S, 8.63. Found: C, 9.63; N, 19.12; S, 8.76, 8.83.

**Carbonato-*cis*-diammino-ethylenediamine Cobaltic Carbonate.**—Eight grams of *trans*-dibromo-*cis*-diammino-ethylenediamine cobaltic bromide or 5.3 g. of the dichloro chloride, is ground with 8.4 g. of dry silver carbonate. The mortar is cooled in ice, 5 cc. of water is added and the grinding continued for half an hour. The solid is filtered and washed with a small amount of water. The combined filtrate and washings are evaporated *in vacuo*.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{CO}_3]_2\text{CO}_3$ : C, 17.26; H, 5.76; N, 23.05; C/N, 1.333. Found: C, 17.20; H, 6.15; N, 22.68; C/N, 1.319.

This salt was partially resolved by shaking it, in dilute solution, with optically active quartz, ground to 100-mesh. In each case, 80 cc. of the solution was shaken with 4 g. of quartz. At intervals, portions of the solutions were withdrawn, diluted, and the rotation at the sodium D line observed. The partially resolved salt is completely racemized in three minutes at 90°, or in three days at room temperature.

TABLE II

Concn. of soln., %	Time of shaking, minutes	Dilution H <sub>2</sub> O:soln.	Rotation ( <i>D</i> quartz)	Rotation ( <i>L</i> quartz)
0.5	25	6/1	-0.03	+0.02
.5	120	6/1	- .03	+ .02
.5	980	6/1	- .03	+ .02
.2	60	1/1	- .04	+ .03
.2	120	1/1	- .04	+ .03
.2	300	1/1	- .04	+ .03

Aqueous hydrochloric acid converts the carbonato carbonate to *trans*-dichloro-*cis*-diammino-ethylenediamine cobaltic chloride.

**Carbonato-*trans*-diammino-ethylenediamine cobaltic carbonate** is prepared in the same way, using 4 g. of *cis*-dichloro-*trans*-diammino-ethylenediamine cobaltic chloride and 6.2 g. of silver carbonate. It is difficult to dry this salt completely.

*Anal.* Calcd. for  $[\text{Co en}(\text{NH}_3)_2\text{CO}_3]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ : C, 15.56; N, 20.75; H, 6.30. Found: C, 15.67; N, 19.32; H, 6.02.

Its solutions, on being shaken with active quartz, show no sign of activity. Treatment of this salt with alcoholic hydrogen chloride converts it to the original *cis*-dichloro salt, while aqueous hydrogen chloride gives the green *trans*-dichloro salt.

**Attempts to Prepare Chloro-aquo-diammino-ethylenediamine Cobaltic Chloride.**—Two grams of *trans*-dichloro-*cis*-diammino-ethylenediamine cobaltic chloride, heated at 80–90° for sixteen hours to remove any traces of acid, was heated with 12 cc. of water in a test-tube at 85° for forty-five minutes. The solution became red a few minutes after the heating was begun. After twenty-four hours 3 g. of ammonium *dextro*- $\alpha$ -bromocamphor- $\pi$ -sulfonate was added and the solution cooled to -5° for twelve hours. There was no precipitate. The use of ammonium *dextro*-camphor- $\pi$ -sulfonate also gave only negative results.

One-half gram of *cis*-dichloro-*trans*-diammino-ethylenediamine cobaltic chloride was dissolved in 2 cc. of water at room temperature. At the end of forty-eight hours 0.6 g. of ammonium *dextro*- $\alpha$ -bromocamphor- $\pi$ -sulfonate was added. After twenty minutes in an ice-bath the dark pink salt was filtered. It was ground with 0.5 cc. of cold concentrated hydrochloric acid, and 5 cc. of cold alcohol-ether mixture (1:1) was added. The pink-purple salt was filtered, keeping liquid on the solid at all times while washing with absolute ethanol and ether. As soon as the last of the ether was removed, the salt became sticky and assumed a deeper color. A solution of this substance exhibited no optical activity at the D line of sodium.

### Summary

The three isomeric forms of the dichloro-diammino-ethylenediamine cobaltic ion have been prepared and some of their properties are described.

Improved methods of preparing several other compounds, which were obtained as intermediates, have been worked out.

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