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

The Stereochemistry of Complex Inorganic Compounds. VII.[1] The Mechanism of the Walden Inversion in Some Reactions Leading to the Formation of the Carbonato-diethylenediamine Cobaltic Ion

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It has been shown recently[1e] that the carbonato-di-levopropylenediamine cobaltic ion exists in two diastereoisomeric forms. One of these is less stable than the other, and is readily converted into it by warming. Both of them can be prepared from the one known form of the corresponding dichloro salt. The more stable (and, hence, the non-inverted) isomer, evidently is formed through an intermediate aquo complex, for it is obtained only under conditions in which such an intermediate is known to form. The less stable form, on the other hand, is obtained under conditions which would minimize the formation of aquo complexes. This gives a clue to the mechanism of the Walden inversion which takes place in the formation of the carbonato-diethylenediamine cobaltic ion from the corresponding dichloro ion,[1a,b] and has led us to study the mechanism of this and some related reactions.

It is indicated that the change of *L*-dichloro-diethylenediamine cobaltic ion to the *D*-carbonato ion probably proceeds through the formation of the *L*-chloro-aquo ion. Since this takes place under the same conditions which produce the non-inverted carbonato complex in the propylenediamine series,[1e] it is probable that the *L*-dichloro-diethylenediamine salt and the *D*-carbonato salt have the same configuration. Mathieu has come to the same conclusion, but from very different evidence.[3]

That aquation plays an important part in the reaction of dichloro-diethylenediamine cobaltic ion and silver carbonate is shown by the fact that the rotation of the carbonato complex obtained depends upon how long the solution of the dichloro salt is allowed to stand before the silver carbonate is added (Table I).

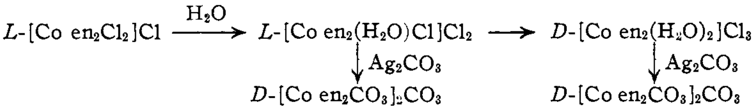
TABLE I

EFFECT OF AGING A 4% SOLUTION OF *L*-$[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl}$ BEFORE TREATING WITH A TEN-FOLD EXCESS OF SILVER CARBONATE

"*t*" represents the time of aging, in minutes, and "$[\alpha]_D$" represents the specific rotation of the resultant carbonato salt, in degrees.

t	$[\alpha]_D$	*t*	$[\alpha]_D$
0	−212	75	+684
1	−183	120	+635
3	− 96	170	+587
6	− 19	186	+539
10	+ 87	235	+520
20	+250	260	+520
40	+501	296	+462
50	+530	360	+433
60	+578	1080	+147

Mathieu[4] has shown that *L*-dichloro-diethylenediamine cobaltic chloride aquates to give both the *L*-chloro-aquo complex and the *D*-diaquo complex. The latter is formed only in small amounts, however, and the equilibrium between the two, when disturbed, is restored very slowly. It thus appears that the chloro-aquo complex is the important intermediate in the reaction under investigation. The diaquo complex may take part to some extent; upon treatment with silver carbonate it also gives the *dextro* carbonato complex. It seems probable that none of the reactions shown in the following scheme involves change of configuration



$$\begin{tikzcd}
L\text{-}[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl} \arrow[r, "\mathrm{H_2O}"] & L\text{-}[\mathrm{Co\,en_2(H_2O)Cl}]\mathrm{Cl_2} \arrow[r] \arrow[d, "\mathrm{Ag_2CO_3}"] & D\text{-}[\mathrm{Co\,en_2(H_2O)_2}]\mathrm{Cl_3} \arrow[d, "\mathrm{Ag_2CO_3}"] \\
& D\text{-}[\mathrm{Co\,en_2CO_3}]_2\mathrm{CO_3} & D\text{-}[\mathrm{Co\,en_2CO_3}]_2\mathrm{CO_3}
\end{tikzcd}$$

Mathieu[3] has come to the same conclusion from studies of circular dichroism. From this and the data of Table I it follows that the conversion of *L*-$[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl}$ to *L*-$[\mathrm{Co\,en_2CO_3}]_2\mathrm{CO_3}$ does not go through an intermediate and involves a change of configuration. These hypotheses completely explain the results of the experiments previously reported.[1a,b,c] The addition of potassium carbonate, or the slow addition of silver carbonate, to solutions of the dichloro salt allows aquation to take place before the carbonate group is introduced into the complex; direct entrance of the

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[1] Previous articles in this series have appeared in THIS JOURNAL: (a) **56**, 774 (1934); (b) **58**, 2224 (1936); (c) **58**, 2226 (1936); (d) **61**, 2402 (1939); (e) **61**, 3199 (1939); (f) **62**, 105 (1940).

[2] From a portion of the doctorate thesis of Donald F. Peppard, 1939.

[3] Mathieu, *Bull. soc. chim.*, [5] **3**, 476–500 (1936).

[4] Mathieu, *ibid.*, [5] **4**, 687–700 (1937).

carbonate group is effected only when an *excess* of silver carbonate is ground with the dichloro salt as soon as it is put in solution, or when a large excess of dry potassium carbonate is ground with the dry complex before solution takes place.[1e]

The dichloro complex reacts rapidly with potassium carbonate; it also aquates rapidly in the presence of potassium carbonate, due to the basicity of the solution. When a fresh solution of the dichloro salt is mixed with a solution of potassium carbonate, a mixture of *D* and *L* carbonato salts is formed, with the *D* in preponderance.[5] If the solution is allowed to age until aquation is essentially complete (about sixty-five minutes for a 4% solution) before the carbonate is added, a nearly pure *D* carbonato salt may be obtained.

The reactions of the chloro-bromo and dibromo-diethylenediamine cobaltic complexes with carbonates also have been studied. These behave just as the dichloro complex does, and their reactions give inversions under the same conditions. They evidently aquate in the same way, and the chloro-bromo, at least, at about the same rate. The data of Table II are strictly comparable to those of Table I.

TABLE II

EFFECT OF AGING A 4% SOLUTION OF *L*-$[\text{Co en}_2\text{ClBr}]\text{Cl}$

t	$[\alpha]_D$
1	−190
10	+ 90
20	+220
65	+510

Experiments with $[\text{Co en}_2\text{ClBr}]\text{Cl}$ showed conclusively that the relative amounts of complex and silver carbonate used are of little significance compared to the time the solution is allowed to stand before the reagent is added. In one series of experiments, the reactants were ground together before the water was added. The amount of silver carbonate used varied from the calculated amount to a ten-fold excess, but the rotation of the resultant carbonato salt varied only slightly, $[\alpha]_D$ −160 to −200°. In another series, the cobalt complex stood in a 4% solution for sixty-five minutes before the reagent was added. The same amounts of silver carbonate were used as before; $[\alpha]_D$ +470 to +500°.

If the hypothesis here suggested is correct, conversion of the chloro-aquo complex to the carbonato complex should proceed under all conditions without inversion. This has been found to be the case: *L*-chloro-aquo-diethylenediamine cobaltic bromide was treated with potassium carbonate and silver carbonate under a wide variety of conditions, and always gave a dextro-rotatory product. The positive rotation was somewhat lower when potassium carbonate was used, but this is evidently due to racemization, rather than to any tendency to form the levo-rotatory product.

These experiments naturally suggest a reinvestigation of the reactions of potassium and silver oxalates with *L*-dichloro-diethylenediamine cobaltic chloride, which have previously been shown[1a] to give a dextro-oxalato complex under all conditions. The formation of the oxalato complex takes place somewhat more slowly than that of the carbonato complex, which suggests that aquation may always take place before the oxalate group enters the complex. A comparison of Table III with Table I shows how differently the silver oxalate and silver carbonate react.

TABLE III

EFFECT OF AGING A 4% SOLUTION OF *L*-$[\text{Co en}_2\text{Cl}_2]\text{Cl}$ BEFORE TREATING WITH A TEN-FOLD EXCESS OF SILVER OXALATE

"t" represents the time of aging, in minutes, and "$[\alpha]_D$" represents the specific rotation of the resultant oxalato salt, in degrees.

t	$[\alpha]_D$
0	+357
1	+357
25	+293
60	+266
100	+238
150	+202
270	+147

It is possible that silver oxalate cannot react directly with the *L*-dichloro complex, but only with the *L*-chloro-aquo complex which is formed by aquation. This ion has been shown to react with silver oxalate to give the dextro-oxalato ion. On the other hand, it is possible that the oxalate and carbonate reactions are entirely different in character.

One entirely new reaction was studied in the course of this investigation, the change of the chloro-aquo complex to the dichloro complex. This is effected by allowing the complex to stand in a large excess of thionyl chloride for about one hundred hours. The reaction evidently proceeds without inversion.

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[5] Werner and McCutcheon, *Ber.*, **45**, 3284 (1912).

Experimental

L-[Co en$_2$Cl$_2$]Cl was prepared and resolved as previously described.[1a]

L-[Co en$_2$(H$_2$O)Cl]Br$_2$ was prepared according to the directions of Werner and Tschernoff[6] and was resolved following Werner and Schwyzer's[7] description of Fischlin's method.[8] The hydrobromic acid used in the last step of the procedure may be replaced by hydrochloric, thus giving the levo-chloro-aquo chloride.

A more convenient method of preparing the active chloro-aquo salts was devised using racemic *cis* dichloro diethylenediamine cobaltic chloride as the starting material.

Ten grams of *cis* [Co en$_2$Cl$_2$]Cl and 40 cc. of water are shaken with glass beads for twelve hours. The beads and any small amount of residue are removed by filtration and the solution allowed to stand in a stoppered flask for sixty hours. It is then cooled to 20°, 6 g. of ammonium dextro-α-bromocamphor-π-sulfonate added, and the mixture stirred by a mechanical stirrer at 18–20° for ten minutes. The solution is filtered from the green crystalline precipitate, 6 g. more of the resolving agent is added, and the stirring continued. Precipitation of the pink levo-chloro-aquo diethylenediamine cobaltic dextro-α-bromocamphor-π-sulfonate begins after some time. The filtrate from this precipitate (about 35 cc.) is treated with 20 cc. of cold aqueous hydrobromic acid (density, 1.4) and cooled in ice–salt mixture with occasional stirring. In from fifteen to twenty-five minutes precipitation of *D*-[Co en$_2$Cl(H$_2$O)]Br$_2$ begins. After fifteen minutes, this is filtered and washed with absolute alcohol and ether. For purification it is dissolved in water at 33° (5 cc. of water per g. of salt), filtered quickly, treated with one-third its volume of hydrobromic acid (density, 1.4), and cooled in an ice–salt mixture. The salt precipitates almost at once on scraping the sides of the beaker. The yield is 0.7–1.0 g. of purified salt. For a 0.1% solution $[\alpha]_D$ −220°.

The precipitated levo-chloro-aquo diethylenediamine cobaltic dextro-α-bromocamphor-π-sulfonate is washed on the filter with 5 cc. of ice water, followed by alcohol and ether. The dry salt is ground in a cold mortar with 6 cc. of cold hydrobromic acid for one minute. The *L*-[Co en$_2$Cl(H$_2$O)]Br$_2$ is filtered and washed with alcohol and ether. It is purified in the same manner as the dextro isomer. The yield is 0.9 to 1.3 g. of purified salt. For a 0.1% solution, $[\alpha]_D$ is +220°.

Usually one purification is sufficient to give a maximum optical activity for either isomer.

In order to obtain the levo-chloro-aquo chloride the precipitate of levo-chloro-aquo dextro-α-bromocamphor-π-sulfonate obtained from 10 g. of racemic dichloro diethylenediamine cobaltic chloride is ground in a cold mortar with 5 cc. of cold concentrated hydrochloric acid for thirty seconds. Fifteen cubic centimeters of cold alcohol–ether mixture (1:1) is added with grinding. At the end of about two minutes the red crystals are filtered and washed with alcohol and ether. For a 0.1% solution, $[\alpha]_D$ is +200°.

[Co en$_2$ClBr]Br was prepared and resolved according to the directions of Werner and Tschernoff.[6]

trans-[Co en$_2$Br$_2$]Br was prepared by the method of Werner, Gerb, Lorie and Rapiport.[9] A modification of their method was used, however, in converting this to the *cis* form. Fifteen grams of *trans*-[Co en$_2$Br$_2$]Br (heated at 110° for eight hours to remove traces of acid) is heated on the steam-bath in 80 cc. of water for twenty minutes. It is then allowed to stand at room temperature in an acid-free atmosphere for twenty-four hours. Thirty cubic centimeters of water is added, and the mixture is well ground. After standing for a day the gray-violet powder, which is essentially *cis*-[Co en$_2$Br$_2$]Br, is filtered. A further quantity of the salt is obtained by allowing the filtrate to evaporate. It is purified by extracting the admixed *trans*-dibromo- and *cis*-bromo-aquo complexes with water.[9]

The resolution of the salt, which has not been previously described, was carried out as follows. Six grams of finely ground racemic [Co en$_2$Br$_2$]Br is added to 500 cc. of water at 20° and stirred rapidly for three minutes. The small amount of residue is removed by filtration and 14 g. of ammonium dextro-α-bromocamphor-π-sulfonate added to the filtrate. The mixture is cooled to about 5° and stirred for fifty minutes. (Precipitation begins in about four minutes.) The precipitate is washed with alcohol and ether. Approximately 1.5 g. of a gray-violet crystal powder is obtained. This is ground in a cold mortar with 8 cc. of ice cold hydrobromic acid (density 1.4). Thirty cubic centimeters of cold alcohol–ether mixture (1:1) is added and the grinding continued. The gray-violet powder is filtered and washed with absolute alcohol and ether. Sometimes it has a pronounced greenish color, probably due to the presence of a small amount of the *trans* dibromo salt. The product always has a slight greenish cast.

For a 0.025% solution at 29°, $[\alpha]_D$ is +520°. The rotation was observed exactly two minutes after adding water to the solid salt.

Werner and McCutcheon's method[5] of preparing the *D*-[Co en$_2$CO$_3$]$^+$ ion gives a product of low activity, so the following modification was developed. Twenty-five grams of *L*-[Co en$_2$Cl$_2$]Cl is dissolved in 500 cc. of water at about 25° and kept at approximately this temperature for eighty-five minutes. Forty-five grams of silver carbonate is then added and the mixture stirred mechanically for two hours. The silver salts are removed and the filtrate is evaporated by blowing a current of air across the surface. For a 0.1% solution at 29°, $[\alpha]_D$ is +740°.

Active [Co en$_2$BrH$_2$O]Br$_2$·$^1/_2$H$_2$O.—Five grams of *D*-[Co en$_2$CO$_3$]$_2$CO$_3$·3H$_2$O is ground with 20 cc. of hydrobromic acid for forty minutes. After cooling to 0°, the red-purple salt is removed by filtration and washed with alcohol and ether. Approximately 4.5 g. of salt is obtained. For purification it is dissolved in water at 30° (5 cc. of water per gram of salt), filtered, and treated with one-third its volume of hydrobromic acid. The solution is cooled rapidly in a salt–ice mixture and the walls of the beaker scraped with a glass rod; yield: about 1 g. For a 0.05% solution at 29°, $[\alpha]_D$ is +260°. For analysis the salt was dried over potassium hydroxide.

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[6] Werner and Tschernoff, *Ber.*, **45**, 3296 (1912).

[7] Werner and Schwyzer, *Helv. Chim. Acta*, **4**, 117 (1921).

[8] Fischlin, Dissertation, Zürich, 1919.

[9] Werner, Gerb, Lorie and Rapiport, *Ann.*, **386**, 111–112 (1912).

Anal. Calcd. for $[\mathrm{Co\,en_2(H_2O)Br}]\mathrm{Br_2\cdot{}^1/_2H_2O}$: Br, 53.81. Found Br, 53.93. Werner[10] reports the air dried racemic product to be the monohydrate.

The reactions of L-$[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl}$, L-$[\mathrm{Co\,en_2ClBr}]\mathrm{Cl}$, and L-$[\mathrm{Co\,en_2Br_2}]\mathrm{Br}$ with silver carbonate were all carried out in essentially the same way. If the complex (say, 0.1 g.) is ground with a large excess of silver carbonate (say 1 g.) in a small amount (5–10 cc.) of water, the *L*-carbonato carbonate is formed. This may be isolated by pouring the solution into a large volume of a 1:1:1 mixture of alcohol, ether and acetone or may be precipitated as the bromide by the addition of solid potassium bromide (about 0.1 g.). In a typical experiment, the bromide showed $[\alpha]_D$ −650° for a 0.1% solution.

Anal. of the carbonate. Calcd. for $[\mathrm{Co\,en_2CO_3}]_2\mathrm{CO_3\cdot 2H_2O}$: C, 22.98; H, 6.27. Found: C, 23.20; H, 6.27. *Anal.* of the bromide. Calcd. for $[\mathrm{Co\,en_2CO_3}]\mathrm{Br}$: Br, 25.05. Found: Br, 25.22, 24.96.

In experiments with aged solutions, 0.2–0.4 g. of the complex was dissolved in 10 cc. of water and, after a definite length of time, was ground with an excess of silver carbonate. Complete reaction can be obtained only by grinding for half an hour. The solution was evaporated at room temperature, and the salt isolated as before. In one typical experiment, a 4% solution was aged for sixty-five minutes. The product was isolated as the bromide, $[\alpha]_D$ +1040, for a 0.1% solution.

Anal. Calcd. for $[\mathrm{Co\,en_2CO_3}]\mathrm{Br}$: Br, 25.05. Found: Br, 25.11.

The reactions with potassium carbonate were carried out as follows. About 0.1 g. of the complex, 0.04 g. of potassium carbonate, and 0.4 cc. of water were warmed to 80° for a minute. The solution was diluted to 100 cc., and the rotation taken at the sodium D line. The rotations were always positive.

L-$[\mathrm{Co\,en_2(H_2O)Cl}]\mathrm{Br_2}$ and L-$[\mathrm{Co\,en_2(H_2O)Br}]\mathrm{Br_2\cdot{}^1/_2H_2O}$ were treated with silver carbonate in the same ways as the di-halo complexes, and the products were isolated as before. The rotatory power of the product was always positive, and varied between +700 and +850°. The carbonate from a typical run gave the following analysis. Calcd. for $[\mathrm{Co\,en_2CO_3}]_2\mathrm{CO_3\cdot 2H_2O}$: C, 22.98; H, 6.27. Found: C, 23.41; H, 6.10.

Potassium carbonate was allowed to react with the aquo complexes in the same manner as with the di-halo complexes. The solutions obtained all showed strong positive rotations.

The reactions of L-$[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl}$, L-$[\mathrm{Co\,en_2Br_2}]\mathrm{Br}$, L-$[\mathrm{Co\,en_2(H_2O)Cl}]\mathrm{Br_2}$ and L-$[\mathrm{Co\,en_2(H_2O)Br}]\mathrm{Br_2}$ with silver oxalate were carried out under the same conditions as those with silver carbonate, except that the grinding was continued for an hour and a half. The oxalato complexes were not isolated; the solutions were simply diluted to give a 0.1% concentration of the complex. In every case, a positive rotation was obtained.

The conversion of L-$[\mathrm{Co\,en_2(H_2O)Cl}]\mathrm{Cl_2}$ to L-$[\mathrm{Co\,en_2Cl_2}]\mathrm{Cl}$ was carried out by suspending 0.2 g. of the thoroughly dried aquo complex in 8 cc. of thionyl chloride. After one hundred hours, with occasional shaking, the violet salt was removed by filtration and washed with alcohol and ether. That the conversion to dichloro salt was essentially complete was shown by the change in color (purple to violet) and by the fact that the product reacted with silver carbonate to give the levo-rotatory carbonato salt. The chloro-aquo compound, under similar conditions, gives a dextro-rotatory product. In one experiment, a sample of the chloro-aquo salt having $[\alpha]_D$ +160° gave a dichloro salt having $[\alpha]_D$ +260°, both readings being made on a 0.05% solution.

Summary

It has previously been suggested that the conversion of levo-dichloro-diethylenediamine cobaltic chloride to the dextro-carbonato salt proceeds through the formation of an aquated intermediate, while conversion to the levo-carbonato salt proceeds directly. Evidence is now advanced to support this hypothesis.

The conversions of dibromo- and chlorobromo-diethylenediamine cobaltic complexes to the carbonato complex are strictly analogous to the corresponding reaction of the dichloro salt.

Application of these views to the reaction of oxalates with levo-dichloro-diethylenediamine cobaltic chloride has failed to give a product of inverted configuration. Whether this is due to the lower rate of reaction, or to a more fundamental difference, is not known.

Chloro-aquo-diethylenediamine cobaltic carbonate has been changed to the *cis*-dichloro salt by suspending it in thionyl chloride. This reagent, which evidently has not been used before in such reactions, presents several advantages over alcoholic hydrogen chloride.

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(10) Werner, *Ann.*, **386**, 128 (1912).