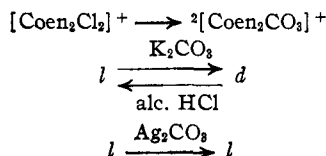


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. II. The Reaction of Carbonates with Dichlorodiethylenediaminocobaltic Chloride

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The factors which commonly determine whether a Walden inversion will occur when a group attached to an asymmetric atom is replaced by another group are the nature of the reagent, its concentration, the temperature and the solvent. That the first of these factors is effective in bringing about a Walden inversion in the reactions of complex inorganic compounds was shown by the discovery that levo-dichlorodiethylenediaminocobaltic chloride reacts with silver carbonate to give a levo carbonato product, while potassium carbonate gives the corresponding dextro salt¹



The present study had for its purpose the determination of the influence of the second two factors mentioned above, *viz.*, the effect of changing concentration of the reagent and the effect of temperature.

Effect of Concentration.—The dichlorodiethylenediaminocobaltic chloride was treated with varying amounts of silver carbonate and the optical rotation of the product was determined. Table I shows that increasing the number of moles of silver carbonate changed the rotation of the product from dextro to levo.

Molar ratio Ag_2CO_3 complex salt	Specific rotation of product
0.75	+362°
1.12	+288°
1.5	-102°
3.0	-160°
4.5	-180°

The data show that changing the concentration of the reagent silver carbonate is certainly an important factor in determining whether a Walden inversion takes place.

On the other hand, potassium carbonate produced the dextro salt at all concentrations (Table II).

Molar ratio K_2CO_3 complex salt	Specific rotation of product
1.0	+240°
1.5	+140°
3.0	+110°
5.0	+ 80°

The marked racemization during the reaction with the higher concentration of potassium carbonate may be due to the formation of the optically inactive *trans* hydroxy-aquo complex $[\text{Coen}_2(\text{H}_2\text{O})(\text{OH})]^{++}$ by the strongly basic solution.

Holmberg³ and Bancroft and Davis⁴ have shown that *l*-bromosuccinic acid and silver oxide react to give *l*-malic acid if the silver oxide is present in limited amount, but *d*-malic acid if it is present in large amount. The rotation of the product is apparently a function of the acidity of the solution. It is evident that neither the acidity nor the carbonate ion concentration is the determining factor in the reaction of carbonates with levo-dichlorodiethylenediaminocobaltic chloride, for the more silver carbonate is present, the more strongly levorotatory the product is, while potassium carbonate, which furnishes an abundance of both hydroxyl and carbonate ions, yields a dextrorotatory product.

Effect of Temperature.—The same reaction was carried out at six different temperatures. The data which are summarized in Table III show that the chief effect of low temperatures is to decrease the rate of reaction, and the effect of higher temperatures is to cause racemization.

Temp., °C.	Specific rotation of product
0	- 10°
15	-100°
25	-106°
50	- 78°
75	- 28°
90	0°

Using a smaller amount of silver carbonate, dextrorotatory products were obtained, the com-

(1) Bailar and Auten, *THIS JOURNAL*, **56**, 774 (1934).

(2) The symbol "en" represents ethylenediamine.

(3) Holmberg, *J. prakt. Chem.*, **87**, 456 (1913).(4) Bancroft and Davis, *J. Phys. Chem.*, **35**, 1253 (1931).

pound prepared at 0° having a smaller rotation than that prepared at 25°.

The reaction of mercurous carbonate with the dichloro salt is of some interest. Mercurous ion and silver ion are both univalent and form insoluble chlorides and carbonates, and they have about the same ionic radii.⁵ They might, therefore, be expected to behave similarly. It was found, however, that *l*-dichlorodiethylenediaminocobaltic chloride reacts with an excess of mercurous carbonate to give the dextrorotatory carbonato salt. The reaction is much slower than that with silver carbonate.

The discovery that the amount of reagent employed affects the rotatory power of the product in this reaction suggested a reëxamination of the reaction between oxalates and dichlorodiethylenediaminocobaltic chloride.¹ Varying the relative amounts of the reactants did not bring about an inversion in this case, however, though the magnitude of the rotatory power was varied somewhat.

Experimental

The materials used were prepared as described in the earlier paper. It has been found that the dextro-ammonium- α -bromo-camphor- α -sulfonate used in resolving the dichloro salt can be recovered in 85–90% yield by adding an excess of ammonium carbonate to the solution and evaporating to crystallization. Attempts to recover the complex inorganic salt have not been successful. The levodichlorodiethylenediaminocobaltic chloride used in this study had a specific rotation of +650°, as measured for a 0.05% solution for the D line of sodium.⁶

All measurements reported in this paper are for the D line of sodium, and, unless otherwise stated, for solutions having a concentration of 0.1%. In most cases, the carbonato salts were not isolated, but the solutions containing them were simply diluted to the proper concentration.

Effect of Varying the Proportions of $[\text{Co}^{\text{en}_2}_{\text{Cl}_2}] \text{Cl}$ and Silver Carbonate.—Three grams of levo-*cis*-dichlorodiethylenediaminocobaltic chloride was ground in a mortar with 2.14 g. of silver carbonate (molar ratio 1:0.75). The mixture was shaken in 10 cc. of water until the color change indicated that reaction was complete. The solution was allowed to stand for a day to ensure racemization of the unreacted dichloro salt, and the silver chloride was removed by filtration. One hundred cubic centimeters of absolute alcohol was added to precipitate the carbonato-diethylenediaminocobaltic chloride, which was filtered off at once. On standing, the filtrate yielded a second crop of

(5) Pauling, *THIS JOURNAL*, **49**, 765 (1927).

(6) Mathieu, who confirmed the results of our earlier investigation [*Bull. soc. chim.*, [5] **3**, 495 (1936)], commented on the great discrepancy between the rotation of the dichloro salt as given by us ($M_D - 600^\circ$) and as found by him ($M_D + 2500^\circ$). This is no doubt due to differences in the concentrations of the solutions, which affect the specific rotatory power enormously, causing a change in sign at about 0.17%. This will be discussed in detail in a subsequent paper.

the material. The first precipitate had very little optical activity; the second had a specific rotation of +362°. The experiments using larger amounts of silver carbonate were carried out in the same way. The negative ion of the complex compound is chloride in some cases, and carbonate in others, but this does not affect the specific rotations.

A sample of the dextro carbonato compound was prepared for analysis by adding 3.8 g. of silver carbonate in small portions to 2.4 g. of levo $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ while the mixture was ground with water in a mortar. The complex compound was present in excess until the very end of the reaction. The product had a specific rotation of +370° and showed C, 22.34; H, 6.30, and N, 19.22. Calcd. for $[\text{Coen}_2\text{CO}_3][\text{CO}_3 \cdot 3\text{H}_2\text{O}]$: C, 22.29; H, 6.47; N, 18.92. A sample of this material was reconverted to the dichloro salt by alcoholic hydrogen chloride. This salt had a specific rotation (0.05% soln.) of +240°. Chlorine, 37.08. Calcd., 37.37.

A sample of the levorotatory carbonato salt (C, 22.12; H, 6.43; N, 19.08) with a specific rotation of -180° was converted to the dichloro compound (Cl, 37.60) having a specific rotation (0.05%) of -132° .

The Effect of Varying the Concentration of Potassium Carbonate.—Samples of 0.3 g. of *l*- $(\text{Coen}_2\text{Cl}_2)\text{Cl}$ were mixed with varying amounts (0.145, 0.218, 0.436 and 0.725 g.) of potassium carbonate and dissolved in 10 cc. of water at room temperature. At the completion of the reaction, 1 cc. of each solution was diluted to 33 cc. to give a 0.1% solution and the rotation was taken. The excess carbonate remaining in solution does not affect the rotation, as was shown by adding potassium carbonate to the solutions and taking the rotations again.

The Effect of Changing Temperature.—Intimate mixtures of 0.3 g. *l*- $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ and 0.5 g. of silver carbonate were shaken in 10 cc. of water at 0, 15, 25, 50, 75 and 90° until the color of the reaction mixture indicated complete reaction. This required eight hours at 0°, but only a few seconds at 90°. At the three higher temperatures, the solution was cooled as quickly as possible after the reaction was ended. The silver salts were filtered out and 1 cc. of each filtrate was diluted to 33 cc. to give a 0.1% solution.

In the same manner 0.3 g. of *l*- $(\text{Coen}_2\text{Cl}_2)_2\text{Cl}$ was allowed to react with 0.3 g. of silver carbonate at 0 and 25°. In this case the solutions were allowed to stand until the unreacted dichloro salt had racemized. The observed rotations were +0.13 and +0.24°.

The Reaction with Mercurous Carbonate.—An intimate mixture of 0.4 g. of $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ and 4 g. of mercurous carbonate was moistened with enough water to make a paste and ground intermittently until the color indicated completion of the reaction. This required about eight hours. Enough water was added to dissolve the complex, the solution was filtered, and the carbonato salt precipitated by adding alcohol and ether. It has a specific rotation of +120°.

The Reaction with Oxalates.—Samples of $[\text{Coen}_2\text{Cl}_2]\text{Cl}$, each weighing 0.30 g., were allowed to react with 0.245, 0.49 and 0.735 g. of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in 10 cc. of water at room temperature. After dilution of 1 cc. of each solution to 33 cc., they showed specific rotations of +160, +200 and +220°. The soluble potassium salts remaining in the solutions do not affect the rotatory power, as was shown by

