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

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

By John C. Bailar, Jr., Frank G. Jonelis and E. H. Huffman

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

$$[\operatorname{Coen}_{2}\operatorname{Cl}_{2}]^{+} \longrightarrow {}^{2}[\operatorname{Coen}_{2}\operatorname{CO}_{3}]^{+}$$

$$l \xrightarrow{K_{2}\operatorname{CO}_{3}} d$$

$$l \xrightarrow{d} d$$

$$l \xrightarrow{Ag_{2}\operatorname{CO}_{3}} l$$

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.

TABLE I		
Molar ratio Ag2CO3 complex salt	Specific rotation of product	
0.75	$+362^{\circ}$	
1.12	$+288^{\circ}$	
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).

TABLE II		
Molar ratio K2CO3 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 $[Coen_2(H_2O)(OH)]^{++}$ 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.

TABLE III		
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-

(4) Bancroft and Davis, J. Phys. Chem., 35, 1253 (1931),

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

⁽²⁾ The symbol "en" represents ethylenediamine.

⁽³⁾ Holmberg, J. prakt. Chem., 87, 456 (1913).

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*-dichlorodiethylenediamino-cobaltic 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- π -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 $+650^{\circ}$, 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 $\begin{bmatrix} Co_{Cl_2}^{en_2} \end{bmatrix}$ 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 carbonatodiethylenediaminocobaltic chloride, which was filtered off at once. On standing, the filtrate yielded a second crop of

(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 $+362^{\circ}$. 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 $[Coen_2Cl_2]Cl$ 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 $+370^{\circ}$ and showed C, 22.34; H, 6.30, and N, 19.22. Calcd. for $[Coen_2CO_3]CO_3 \cdot 3H_2O$: 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 $+240^{\circ}$. 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 (C1, 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-(Coen₂Cl₃)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-[Coen₂Cl₂]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 dijuted to 33 cc. to give a 0.1% solution.

In the same manner 0.3 g, of l-[Coen₂Cl₂]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 $[Coen_2Cl_2]Cl$ 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 $+120^\circ$.

The Reaction with Oxalates.—Samples of $[Coen_2Cl_2]Cl_2$ each weighing 0.30 g., were allowed to react with 0.245, 0.49 and 0.735 g. of K₂C₂O₄·H₂O 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

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

adding a large amount of potassium oxalate to each of them and taking the rotations again.

Likewise, three samples were ground with 0.31, 0.62 and 0.93 g. of silver oxalate and allowed to react in 10 cc. of water. After filtration and dilution (1 to 33 cc.) the solutions showed specific rotations of +170, +390 and $+430^{\circ}$.

Another sample, weighing 0.6 g., was dissolved in 20 cc. of water. Eight-tenths of a gram of silver oxalate was added in small portions while the mixture was ground continuously, so that the complex was present in great excess until the end of the reaction. The solution was diluted as before and showed a rotation of $+240^{\circ}$.

Summary

It has been shown that levo-dichlorodiethylenediaminocobaltic chloride reacts with a limited amount of silver carbonate to give the dextro carbonato salt, whereas a larger amount of silver carbonate causes inversion in the direction of rotation to give the levo salt.

The reaction with potassium carbonate gives the dextro salt, no matter what the concentration of the reagent.

It appears that temperature is not an important factor in determining whether a Walden inversion occurs in this reaction.

Mercurous carbonate, present in large excess, reacts with levo-dichlorodiethylenediaminocobaltic chloride to give the dextro-rotatory carbonato salt. In this respect it is like potassium carbonate, and unlike silver carbonate.

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URBANA, ILL.

The Stereochemistry of Complex Inorganic Molecules. III. The Reaction of Ammonia with Levo-Dichlorodiethylenediaminocobaltic Chloride

By John C. Bailar, Jr., J. H. Haslam and Eldon M. Jones

One of the mechanisms suggested for the Walden inversion postulates that every reaction which involves a single step in the substitution of one group by another on a tetrahedral atom should lead to inversion.^{1,2} Accordingly, if the over-all reaction takes place in an odd number of steps the product should be the enantiomorph of the original material, but if it takes place in an even number of steps, the starting material and the product should have the same configuration.

The object of the present study was to see whether this theory might be applied to reactions of the octahedral complex inorganic compounds. The reaction studied was that between ammonia and levo-dichlorodiethylenediaminocobaltic chloride³

 $[Coen_2Cl_2]Cl \longrightarrow [Coen_2(NH_3)Cl]Cl_2 \longrightarrow$ $levo \ cis \qquad trans, levo \ cis \\ or \ dextro \ cis \\ [Coen_2(NH_3)_2]Cl_3$

trans, levo cis, or dextro cis

The two chloride groups of the complex ion are attached to the cobalt in exactly the same way and occupy like positions in the molecule. It seems logical to assume, therefore, that the same mechanism functions in their displacement from the complex. If this is correct, the conversion of the dichloro salt to the diammino salt must take place in an even number of steps, and the theory mentioned would allow no inversion. However, as the data in Table I show, the reaction does lead to a Walden inversion, the product prepared at low temperatures being levorotatory while that prepared at higher temperatures is dextrorotatory. It is of some interest to note that this is the first case of a Walden inversion of complex inorganic compounds brought about by a change in temperature.

TABLE I		
Reagent	Temp., °C.	[α] ^{25°} Ε (av.)
Liquid NH ₈	-77	-32
Liquid NH3	-33	-22
Liquid NH ₈	+25	+29
Gaseous NH ₂	+80	+43
NH ₃ in CH ₃ OH	+25	+31
NH ₃ in C ₂ H ₅ OH	+25	+29

It is possible, of course, that the displacement of a negative chloride group by a neutral ammonia molecule produces such a profound change in the complex ion that the second step of the reaction does not follow the same mechanism as the first. The theory of Bergmann, Polanyi and Szabo and of Olson might be more applicable if the chloride groups were displaced by other univalent

⁽¹⁾ Bergmann, Polanyi and Szabo, Z. physik. Chem., **B20**, 161 (1933).

⁽²⁾ Olson, J. Chem. Phys., 1, 418 (1933).

⁽³⁾ The symbol "en" represents ethylenediamine.