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°.

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°.

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.

URBANA, ILL. RECEIVED AUGUST 4, 1936

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

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

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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 chloride[3]

$$\underset{\text{levo } cis}{[\mathrm{Coen_2Cl_2}]\mathrm{Cl}} \longrightarrow \underset{trans,\text{ levo } cis \text{ or dextro } cis}{[\mathrm{Coen_2(NH_3)Cl}]\mathrm{Cl_2}} \longrightarrow \underset{trans,\text{ levo } cis,\text{ or dextro } cis}{[\mathrm{Coen_2(NH_3)_2}]\mathrm{Cl_3}}$$

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.	$[\alpha]^{25°}_{E}$ (av.)
Liquid NH_3	−77	−32
Liquid NH_3	−33	−22
Liquid NH_3	+25	+29
Gaseous NH_3	+80	+43
NH_3 in CH_3OH	+25	+31
NH_3 in C_2H_5OH	+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

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[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.

negative groups. A search for an example of the Walden inversion in such a case is now under way. It seems probable that the two steps of the reaction here reported do not follow the same mechanism, or that the theory of Bergmann, Polanyi and Szabo and of Olson cannot be applied to this case.

A study of the octahedral model will show that if the substitution of the ammonia molecules for the chloride groups follows purely mechanical laws, both *cis* and *trans* isomers will be formed at each step of the reaction. The formation of a *trans* form at any point would, of course, cause racemization. Fortunately, the formation of the *cis* isomer is favored under the conditions of this reaction. In no case did the diammino compound contain more than 10% of the *trans* form, and the rotations, while small, were unmistakable.

Experimental

The dichlorodiethylenediaminocobaltic chloride used was prepared and resolved as previously described.[4] Several different batches were used, but all had about the same specific rotation: +650° for a 0.05% solution for the D line of sodium. The diamino compound rotates yellow light very feebly, so rotations on it were taken at the E line (5270 Å.). The instrument used was a Schmidt and Haensch polarimeter graduated to one-thousandth of a degree, and fitted with a prism to select the desired wave length. The solutions used had a concentration of 0.1%.

The amount of *trans* diamino salt formed in the experiments was determined by precipitating it from the mixture with sodium dithionate in acid solution, according to the directions of Werner.[5] The separation afforded by this method is not entirely quantitative, but was deemed satisfactory for the purposes of this investigation. Since the amount of *trans* salt in every case was very small, it was not removed from those samples which were examined for optical activity, but allowance was made for it in making up the solutions. That the presence of the *trans* salt does not affect the rotation of the *cis* salt was shown by polarimetric examination of various mixtures of the two.

The Reaction of Liquid Ammonia and levo cis $(\mathrm{Coen_2Cl_2})$Cl at −77°.—One-half gram of levo *cis*$(\mathrm{Coen_2Cl_2})$Cl was placed in a small flask in a bath of solid carbon dioxide. Fifty cubic centimeters of liquid ammonia was added and the flask was stoppered and allowed to stand until the reaction was complete—forty-eight to sixty hours. It is easy to follow the progress of the reaction as the original purple color of the solution changes to bright red (the chloro-ammino compound) and then to yellowish-brown (the diammino compound). The ammonia was allowed to evaporate, and the material was examined. Four samples gave specific rotations of −35, −29, −30 and −34°.

The Reaction with Liquid Ammonia at −33°.—The reaction was carried out as before, but the ammonia was allowed to evaporate freely from a well insulated flask, which was fitted with a trap to avoid entrance of moisture. The amount of ammonia used for one-half gram of the sample was varied between 10 and 50 cc. without appreciably affecting the results. Specific rotations of −21, −27, −24, −17, −22, −20 and −25° were obtained.

The Reaction with Liquid Ammonia at +25°.—Two-tenths of a gram of the dichloro salt was placed in one arm of a Y-tube and from 6 to 12 cc. of liquid ammonia in the other. After sealing, the tube was allowed to come to room temperature. The salt is deliquescent toward ammonia and some of the gas distilled over before room temperature was reached. When the temperature reached 25°, the whole of the liquid was poured onto the solid. In other respects the experiment was like the preceding ones. Six samples gave specific rotations of +17, +24, +13, +40, +42 and +37°.

The Reaction with Gaseous Ammonia at +80°.—A half gram of finely powdered dichloro salt was placed in a tube in a bath at 80°. Dry ammonia gas was passed over it until the reaction was complete. Six samples gave specific rotations of +31, +43, +40, +53, +56, +49 and +52°.

Samples of the dichloro salt were placed in an atmosphere of ammonia at room temperature over a year ago. The first step of the reaction was complete in about a month—the second step is now progressing very slowly.

The Reaction with Ammonia Dissolved in Absolute Methyl and in Absolute Ethyl Alcohols at +25°.—One-half gram of the dichloro salt was placed in 35 cc. of the saturated alcoholic ammonia solution. The salt did not dissolve appreciably, so the reaction was slow. After three or four days, the alcohol was evaporated, and the residue examined. Four samples prepared in methyl alcohol gave specific rotations of +29, +27, +34 and +36°. The samples prepared in ethyl alcohol gave rotations of +21, +28, +36 and +33°.

We are indebted to Mr. J. P. McReynolds for some of the polarimeter readings.

Summary

It has been shown that a Walden inversion takes place in the reaction of ammonia with levo-dichlorodiethylenediaminocobaltic chloride, the optical rotatory power of the diamminodiethylenediaminocobaltic chloride formed being conditioned by the temperature at which the reaction is carried out. Prepared at the temperature of boiling ammonia or lower, the product is levorotatory; at 25° and higher, it is dextrorotatory.

It seems probable that the two steps of the reaction do not follow the same mechanism, or that the mechanism of the Walden inversion proposed by Bergmann, Polanyi and Szabo and by Olson is not applicable to this case.

URBANA, ILL. RECEIVED AUGUST 4, 1936

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[4] Bailar and Auten, THIS JOURNAL, 56, 774 (1934).

[5] Werner, *Ann.*, 386, 204 (1912).