pound $NH_2Hg_2Cl_3$. Between another pair of solutions, one containing 4.5% of mercuric chloride and 5.1% of ammonium chloride, and another, containing 5.6% of mercuric chloride and 5.1% of ammonium chloride, he found the compound $(NH_3)_2HgCl_2$.

Since, in the determination of nitrogen as ammonia by Nesslerization, the concentration of ammonia is very low, the concentration of HgI_2 as $HgI_2 \cdot 2NaI$ must also be low. This low concentration is obtained due to the high concentration of sodium hydroxide. This favors the formation of the colloidal $NH_2Hg_2I_3$, which gives the color in Nesslerized ammonia solutions.

Summary

1. The compound formed by Nessler's solution and ammonia is represented by the empirical formula $NH_2Hg_2I_3$.

2. The compound is very insoluble and so tends to form in very minute particles, which are negatively charged and form colloidal solutions.

3. When Nessler's solution has an alkalinity of 3 *N*, and it is used to Nesslerize solutions of ammonia, the color can be made more permanent over a wider range of concentration by the addition of stabilized alkaline ash-free gelatin as a protective colloid.

ITHACA, N. Y. RECEIVED JULY 19, 1933

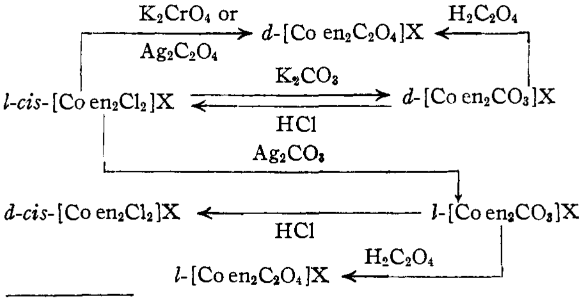
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. I. The Walden Inversion as Exhibited by Diethylenediaminocobaltic Compounds

BY JOHN C. BAILAR, JR., AND ROBERT W. AUTEN

Practically all of the vast amount of work which has been done on the Walden Inversion has been concerned with organic compounds, and no case of the inversion of an optically active compound to its mirror image has ever been discovered outside the realm of carbon compounds. Yet the change in configuration of the groups about the tetrahedral carbon atom represents only a special case of a more general problem. If a group attached to the carbon atom is replaced by another group two compounds may be formed. One has the same configuration as the original compound, the other has that of its mirror image. In the case of any element having a valence greater than four, however, there are more than two possibilities. The current theories of the Walden inversion, all of which are based on the behavior of carbon compounds, cannot be expected to predict the behavior of more complicated compounds. We have therefore undertaken a series of investigations of the Walden inversion as exhibited by inorganic complex compounds. We have been fortunate in that the first series of reactions investigated gave an example of the inversion.

The diethylenediaminocobaltic compounds of the type $[Co\,en_2X_2]X$ (and similar compounds of other metals with a coördination number of six) exist in three isomeric forms—one "trans" form, and two "cis" forms which are mirror images of each other. Many cases are known in which substitution of one of the coördinating groups leads to a change in configuration from "cis" to "trans" or "trans" to "cis." Werner's studies[1] of many reactions of this type led him to suggest a possible mechanism for the Walden inversion. Both Werner[2] and Jaeger[3] have studied the inversion of optical activity in reactions of the type levo-$[Co\,en_2Cl(NCS)]X + NaNO_2 \longrightarrow$ dextro-$[Co\,en_2(NO_2)(NCS)]X + NaCl$ and have suggested that solubilities (Werner) and crystalline forms (Jaeger) may be used to determine whether changes in configuration take place. Neither of these investigators has demonstrated the possibility of the formation of optical antipodes, starting with one optically active form. The study of optical inversion reported in this paper includes the following series of reactions



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(1) Werner, *Ann.*, **386**, 54 (1911).

(2) Werner, *Ber.*, **44**, 3279 (1911).

(3) Jaeger, *Bull. soc. chim.*, **33**, 873 (1923).

The reactions of levo-dichlorodiethylenediaminocobaltic salts with potassium oxalate and potassium carbonate have been studied by Werner;[2,4] the reactions with silver oxalate and silver carbonate have not previously been reported. It will be noticed that potassium and silver oxalate give the same product, the dextro oxalatocobaltic salt. Potassium and silver carbonate, however, yield optical antipodes, the potassium salt giving the dextro carbonato compound, the silver salt giving the levo compound. Clearly a change of configuration has taken place in one of these reactions—probably, though not necessarily, in the reaction with silver carbonate. The analogy of these reactions with the classic examples of the Walden inversion is obvious; the significance of this analogy, however, is not yet apparent.

In the course of this study we have observed that some of the complex compounds show an enormous change in specific rotation with changing concentration of the solution. The exact significance of this cannot yet be stated; we expect to investigate the matter further.

Experimental

The accurate measurement of rotatory power of the compounds used in these studies is difficult. All of them are highly colored, and dichlorodiethylenediaminocobaltic salts, which served as the source of the other salts, undergo racemization and hydrolysis readily. All of the observations recorded were made with a 10-cm. polarimeter tube and an instrument having a vernier scale calibrated to 0.01°. A nearly monochromatic source of light, approaching the D line of sodium in wave length, was used in all measurements. In every reaction in which an optically active compound was transformed into another, partial racemization took place. On this account, some of the rotations recorded are low and can be accepted as approximate only. In every case, however, they represent the average of at least ten polarimeter readings.

The Preparation of Levo-cis-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$.—*cis*-Dichlorodiethylenediaminocobaltic chloride[5] was resolved through the dextro-α-bromocamphor-π-sulfonate. Werner's directions[2] for the preparation of the bromocamphorsulfonate give excellent results if the temperature of the solvent be maintained at 15–17°; his method of regenerating the active chloride from the intermediate compound, however, has proved very troublesome. The following procedure gives nearly quantitative yields. Ten grams of the bromocamphorsulfonate is covered with 25 cc. of cold concentrated hydrochloric acid in a mortar cooled by an ice-bath. Fifty cubic centimeters of a mixture of equal volumes of absolute alcohol and ether is added, and the material is ground to ensure a fine suspension. After several minutes the *l-cis*-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$ is removed by filtration and washed with absolute alcohol and absolute ether. The specific rotation of a 0.4% solution of the material so prepared is −200°. Werner reported the same value.

l-cis-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl} + \mathrm{Ag_2C_2O_4} \longrightarrow$ *d*-$[\mathrm{Co\ en_2C_2O_4}]_2\mathrm{C_2O_4}$.—One gram of the dichloro cobaltic compound was mixed with an excess (2 g.) of silver oxalate. Two cubic centimeters of water was added, and the mixture was heated for a very short time on the steam-bath (until the purple color of the dichloro salt gave way to the light pink of the oxalato salt). The reaction mixture was immediately cooled in an ice-bath, and enough water was added to dissolve the oxalato salt. The insoluble silver salts were removed and the solution was poured into a mixture of 100 cc. of absolute alcohol and 100 cc. of ether. After standing overnight the precipitate was removed by filtration and washed with ether. A 0.4% solution of this material gave a specific rotation of +204°. Werner reported +200° for a 0.25% solution.

l-cis-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl} + \mathrm{K_2CO_3} \longrightarrow$ *d*-$[\mathrm{Co\ en_2CO_3}]\mathrm{Cl}$.—The method of Werner and McCutcheon[2,4] was used in carrying out this reaction. After two extractions with water, the product showed a specific rotation of +235°, as observed for a 0.4% solution. Werner and McCutcheon, by continuing the extractions, obtained a product, a 0.2% solution of which showed a rotation of +350°.

d-$[\mathrm{Co\ en_2CO_3}]\mathrm{Cl} + \mathrm{H_2C_2O_4} \longrightarrow$ *d*-$[\mathrm{Co\ en_2C_2O_4}]\mathrm{Cl}$.—This reaction proceeded readily when an excess (0.2 g.) of oxalic acid was added to 0.2 g. of the carbonato salt described in the preceding paragraph in 2 cc. of water. The excess of undissolved oxalic acid was removed by filtration, and the oxalato salt was precipitated from the filtrate by pouring it into 50 cc. of a mixture of alcohol and ether. A 0.2% solution of the material showed a specific rotation of +51°.

d-$[\mathrm{Co\ en_2CO_3}]\mathrm{Cl} + \mathrm{HCl} \longrightarrow$ *l*-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$.—Thirteen hundredths of a gram (0.13 g.) of the carbonato salt was mixed with a saturated solution of hydrogen chloride in absolute alcohol. After standing for four hours in an ice-bath, 0.08 g. of a purple powder was obtained by filtration. A 0.4% solution of this material showed a specific rotation of −40°.

l-cis-$[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl} + \mathrm{Ag_2CO_3} \longrightarrow$ *l*-$[\mathrm{Co\ en_2CO_3}]_2\mathrm{CO_3}$.—Three grams of the dichloro salt was mixed with a slight excess (4.8 g.) of pure silver carbonate. The mixture was cooled in an ice-bath and 10 cc. of ice water was added with stirring. The temperature of the mixture was allowed to approach that of the room; during this slow warming process the reaction occurred. Fifty cubic centimeters of water was added to dissolve all of the carbonato salt, which was then separated from the silver salts by filtration and partially precipitated by addition of 200 cc. of alcohol and 300 cc. of ether. A 0.4% solution of the material showed a specific rotation of −52°; a 0.2% solution, a rotation of −62°. More of the salt was

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(4) Werner and McCutcheon, *Ber.*, **45**, 3284 (1912).

(5) Jörgensen, *J. prakt. Chem.*, **39**, 16 (1889); **41**, 448 (1890).

obtained by evaporating the solution at room temperature under reduced pressure. The specific rotations of 0.4 and 0.2% solutions of the product so obtained were −84 and −91°, respectively. Partial racemization had taken place during the reaction.

A micro-analysis of this active product showed the formula to be $[Co\ en_2CO_3]_2CO_3 \cdot 3H_2O$. Calcd.: C, 22.29; H, 6.47; N, 18.92. Found: C, 21.96; H, 6.46; N, 18.94.

The two following reactions further confirm the fact that this is the levorotatory carbonato salt.

$l\text{-}[Co\ en_2CO_3]_2CO_3 + HCl \longrightarrow d\text{-}cis\text{-}[Co\ en_2Cl_2]Cl$.—A sample of material obtained in the experiment outlined above was treated with alcoholic hydrogen chloride as described in a preceding paragraph. The purple powder so obtained had a specific rotation of +16° in 0.4% solution and of −33° in 0.1% solution within eleven minutes after the preparation of the solution. It racemized almost completely in two and a half hours; this is characteristic of aqueous solutions of the dichloro salt. Another sample of the product obtained from the same reaction showed a specific rotation of +14° in 0.4% solution.

$l\text{-}[Co\ en_2CO_3]_2CO_3 + H_2C_2O_4 \longrightarrow l\text{-}[Co\ en_2C_2O_4]_2C_2O_4$.—Only a small amount of material was available for this reaction; consequently, quantitative measurements were not attempted. The product of the reaction had the characteristic color of the oxalato salt and showed a small but distinct levo-rotation.

Summary

It has been observed that levo-dichlorodiethylenediaminocobaltic chloride reacts with potassium carbonate to give the dextro carbonato salt, but with silver carbonate to give the levo carbonato salt. This is the first indisputable example of the Walden inversion to be discovered among inorganic compounds.

Potassium oxalate and silver oxalate, reacting with levo-dichlorodiethylenediaminocobaltic chloride, yield the same product—the dextro oxalato salt.

Several other reactions of these compounds have been carried out.

These studies are being continued.

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

The Magnetic Susceptibilities of the Ions of Uranium in Aqueous Solution

BY ROBERT W. LAWRENCE

The magnetic susceptibilities of uranyl, quadrivalent, and trivalent uranium ions in aqueous solution have been determined by means of a modified Gouy method.

Magnetic measurements have been made on solid uranous oxalate and uranyl nitrate at room temperature by Bose and Bhar;[1] and on the solid oxides of uranium, also at room temperature, by Wedekind and Horst.[2] The magnetic susceptibilities of solid UCl_4, UO_2 and $U(SO_4)_2$ from 90°K. to somewhat above room temperature have been determined by Sucksmith.[3] The only measurements in solution were by Pascal[4] who obtained, apparently as the result of a single experiment, a molal susceptibility of 3375×10^{-6} for uranous ion in 10% sulfuric acid.

Experimental Part

Method.—A modified Gouy method, described in detail by Freed,[5] was used for determining the magnetic susceptibilities of quadrivalent and trivalent uranium solutions. A glass cylinder filled with nickel chloride solution is suspended from the knife edge in a bath of the solution being examined as illustrated in Fig. 1. The end of the tube near K′ is at the center of the pole gap of an electromagnet of the Weiss type, which was described by Shaffer and Taylor.[6] The tubes used were standardized by balancing them magnetically against solutions of nickel chloride which were then analyzed to determine their nickel chloride concentration. From these data and the known susceptibilities of nickel chloride and water, the magnetic susceptibility of the solution and hence, also, the equivalent susceptibility of the tube was calculated. The equivalent susceptibilities of the tubes used are given in Table I. The calibrated tubes were then used to determine the susceptibilities of uranium salt solutions.

For calculating magnetic susceptibilities in solutions, Wiedemann's law, that the magnetic susceptibility of a solution is an additive function of the susceptibilities of the constituents of the solution, has been employed.

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[1] Bose and Bhar, *Z. Physik*, **48**, 716 (1928).

[2] Wedekind and Horst, *Ber.*, **48**, 105 (1915).

[3] Sucksmith, *Phil. Mag.*, [7] **14**, 1115 (1932).

[4] Pascal, *Ann. chim. phys.*, [8] **16**, 520 (1909).

[5] Freed, THIS JOURNAL, **49**, 2456 (1927).

[6] Shaffer and Taylor, *ibid.*, **48**, 843 (1926).