[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Reactions of Nessler's Solution[1]

BY M. L. NICHOLS AND C. O. WILLITS

Introduction

An alkaline solution of mercuric iodide and potassium iodide was first proposed as a reagent for the direct determination of ammonia by Julius Nessler[2] in 1856. Since that time, several modifications of the reagent[3] have been made.

Many studies have been made of the action of ammonia with both mercuric iodide[4] and mercuric chloride[5] in the attempt to establish the composition of the products of Nessler's solution and ammonia. However, a review of the literature fails to indicate that any satisfactory information has been obtained concerning the composition of the products formed when ammonia is added to Nessler's reagent.

Experimental

In studying the reactions occurring upon the addition of Nessler's solution to an ammonium solution it was necessary to make a complete study of the reactions and products formed by the interaction of ammonia and the various components of Nessler's solution. Previous investigation of these reactions had been carried out by adding the Nessler's solution to solutions containing known amounts of ammonia. This method lacked a means of control, so it was decided to make a phase rule study of the action of the components and ammonia in a closed system similar to that used by Bancroft and Barnett.[6]

A weighed amount of the pure powdered component was placed in a vessel of known volume and a known amount of ammonia was run in. From the pressure at equilibrium, the volume of gas remaining in the flask was calculated and the volume removed by the solid was found by difference. Under the circumstances it was quite immaterial whether the substance formed contained the NH_2, NH or the NH_3-metallo group, since it was first most important to know whether the substance formed was a true chemical compound or an adsorption complex. If all the components formed true chemical compounds with ammonia, then upon repeating the experiment with Nessler's solution and ammonia, those compounds formed, as indicated by the flat branches of the curve, should correspond with or closely approach the pressure of a compound formed by one of the components and ammonia. The presence of moisture in the case of Nessler's solution should merely displace the curve without changing its general nature.

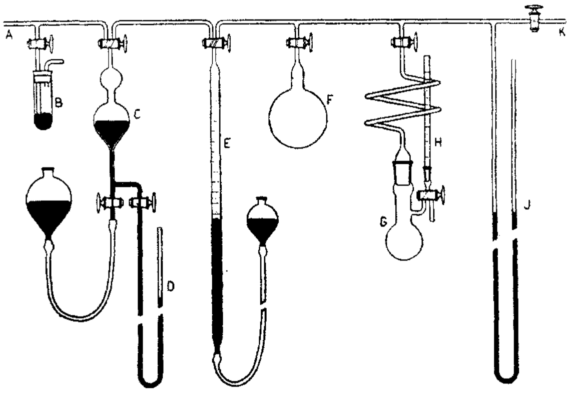

Fig. 1.

The apparatus used is shown in Fig. 1. A weighed sample of the solid or a measured volume of the solution was placed in the reaction vessel G and the entire system was evacuated. A known volume of dry ammonia was run in from the Hempel buret E and the system was allowed to stand at room temperature until the pressure as indicated on the manometer J had become constant. The difference between the total volume of gas added and that left in the system at equilibrium gives the volume taken up by the solid or liquid and from this the volume of ammonia removed by the liquid or by 0.01 mole of the solid can be calculated. The procedure was repeated until the entire curve was obtained. The flask F was of one liter capacity, introduced merely to increase the volume and thus facilitate work at low pressures. The system was calibrated for volume so that for any pressure the volume of gas remaining in the system could be read from the curve.

Table I gives the data for the reaction of mercuric iodide and ammonia. Figure 2 shows the curve obtained by plotting the volume of ammonia at standard conditions taken up by 0.01 mole of solid mercuric iodide, as ordinates, against

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(1) This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by C. O. Willits in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Nessler, *Chem. Centr.*, **27**, neue Folge 1, 529 (1856).

(3) Miller, *J. Chem. Soc.*, **3**, 117 (1856); Nessler, *Z. anal. Chem.*, **7**, 415 (1868); Winkler, *Chem.-Ztg.*, **23**, 454 (1899); French and Mannheim, *Apoth. Ztg.*, **29**, 972 (1914); Folin and Denis, *J. Biol. Chem.*, **26**, 473 (1916); "Standard Methods of Water Analysis," 6th Ed., 1925, p. 13; Willits, unpublished Master's Thesis, 1926.

(4) Böttger, *J. prakt. Chem.*, [1] **8**, 481 (1836); Wittstein, *Repert. Pharm.*, **63**, 322 (1833); Calloit and Corriol, *ibid.*, **9**, 381 (1823); Rose, *Pogg. Ann.*, **20**, 161 (1830); Rammelsberg, *ibid.*, **48**, 170 (1839); *J. prakt. Chem.*, **38**, 558 (1888); François, *Compt. rend.*, **130**, 332, 1022 (1900); Franklin, *Am. Chem. J.*, **47**, 361 (1912); Peters, *Z. anorg. Chem.*, **77**, 183 (1912).

(5) Pesci, *ibid.*, **21**, 361 (1899); Naumann, *Ber.*, **32**, 1000 (1899); Varet, *Compt. rend.*, **109**, 941 (1889); Strömholm, *Z. anorg. Chem.*, **57**, 72 (1909).

(6) Bancroft and Barnett, *J. Phys. Chem.*, **34**, 449 (1930).

Table I

Mercuric Iodide and Ammonia

Weight of HgI_2, 4.5445 g.

NH_3 added, ml.	Gas in gas phase, ml.	Gas taken up by 0.01 mole of solid, ml.	Pressure in system, cm.
45.40	4.17	41.23	0.29
48.40	4.13	88.67	.31
45.70	4.18	135.32	.30
48.60	4.17	183.93	.28
37.00	4.13	220.37	.33
8.00	8.51	224.59	.62
3.40	9.50	227.00	.68
15.10	26.00	225.60	1.88
17.92	37.20	232.32	2.71
36.78	38.20	268.10	2.73
29.00	37.00	298.30	2.70
35.41	56.71	314.00	4.23
50.01	86.72	318.00	6.41

the equilibrium pressures expressed in centimeters of mercury, as abscissas. The curve represents volumes of ammonia combining with 0.01 mole of the solid instead of the arbitrary weight of the solid used and the observed volume of combining ammonia.

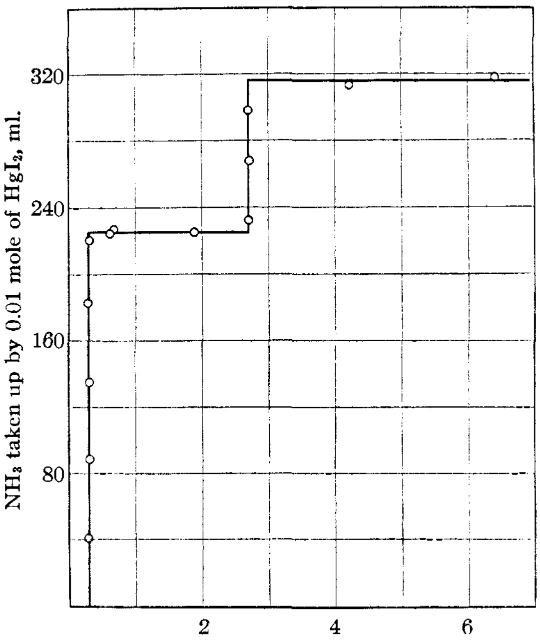

Fig. 2.

The break in the curve occurs at a volume of 224 ml. of ammonia for 0.01 mole of mercuric iodide, which is the volume theoretically required to form the compound $HgI_2 \cdot NH_3$. This combining ratio of mercuric iodide to ammonia is identical with that found by Calloit and Corriol, Naumann and Strömholm. The reaction between mercuric iodide and ammonia was very slow, requiring several days to reach equilibrium after each addition of ammonia.

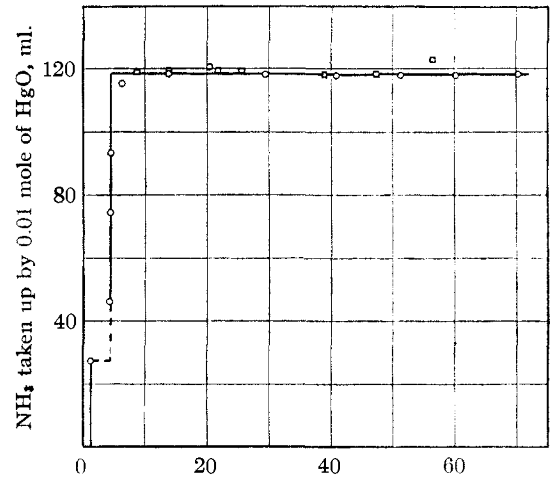

Fig. 3.

In Figure 3 the curves for the data found in Table II for the experiment on mercuric oxide and ammonia are given. The first break in the ordinate occurs between the points representing 27 ml. and 46 ml. of ammonia per 0.01 mole of mercuric oxide. These two extreme possibilities

Table II

Mercuric Oxide and Ammonia

Weight of HgO, 4.00 g.

NH_3 added, ml.	NH_3 removed, ml.	Gas in gas phase, ml.	Gas taken up by 0.01 mole of solid, ml.	Press. in system, cm.
55.81		5.81	27.08	1.29
48.22		19.18	46.10	4.21
53.67		19.60	74.70	4.45
34.77		19.72	93.40	4.50
47.54		26.77	115.20	6.39
39.95		60.38	118.40	13.87
31.32		89.72	120.50	20.49
38.42		131.10	118.00	29.40
50.20		182.00	117.80	40.88
46.00		229.00	117.50	51.33
41.90		270.50	117.76	60.15
43.81		313.79	117.79	70.20
	62.32	242.12	122.80	56.53
	38.36	211.63	118.30	47.38
	38.71	173.25	118.00	38.99
	31.00			
	28.09	113.14	119.10	25.70
	17.10	95.68	119.20	21.78
	34.19	60.98	119.30	13.86
	21.18	39.15	119.00	8.87

give as the combining ratios of mercuric oxide and ammonia the empirical formulas $10HgO\cdot NH_3$ and $5HgO\cdot NH_3$. The curve shows the second break in the ordinate to be at 118 ml. of ammonia per 0.01 mole of mercuric oxide. This gives the formula $2HgO\cdot NH_3$, which theoretically requires 112 ml. of ammonia per 0.01 mole of mercuric oxide.

Ammonia and 3 *N* sodium hydroxide gave a true solution curve and no true compounds were formed.

The compounds of ammonia and Nessler's solution were determined in three ways: (1) by the phase rule method and comparison of the curve with the curves of various possible components and ammonia; (2) by determining quantitatively the constituents of the Nessler's solution before and after the addition of ammonia; (3) by determining quantitatively the constituents of the solid produced by the action of ammonia with Nessler's solution.

It has long been known that there is a reaction between Nessler's solution and ammonia with a resulting solid. The nature of this solid has never been explained satisfactorily, most workers having given the simple explanation that it is an adsorption compound. For the experiment with Nessler's solution and ammonia, the Nessler's solution was prepared according to directions from previous unpublished work done in this Laboratory;[3] 5.4 g. of mercuric iodide and 3.6 g. of sodium iodide were dissolved in a very small volume of 3 *N* sodium hydroxide and the solution was then made up to 100 ml. with 3 *N* sodium hydroxide.

(1) **Phase Rule Study.**—After the system had been evacuated completely, 10 ml. of the Nessler's solution was placed in the reaction vessel and the system was allowed to come to equilibrium at constant temperature. This equilibrium pressure of the solution was deducted from the observed equilibrium pressure of the system after each addition of the gas so as to obtain the dissociation pressure of the compound of ammonia formed. Ammonia was then added to the system by means of the buret and by the constant volume method using Flask C (Fig. 1), and the system allowed to come to equilibrium after each addition.

TABLE III

NESSLER'S SOLUTION AND AMMONIA

10 ml. Nessler's solution

NH_3 added, ml.	Gas in gas phase, ml.	Gas taken up by soln., ml.	Gas taken up per 0.01 mole HgI_2, ml.	Press. in system, cm.
3.47	0.11	3.36	28.28	0.04
4.00	.15	7.32	61.61	.04
5.79	.15	13.11	110.34	.04
3.30	.55	16.01	134.74	.12
16.56	1.38	31.74	267.14	.32
6.51	1.42	38.21	321.58	.37
4.92	1.53	43.02	362.07	.32
8.05	2.11	50.49	424.94	.47
10.37	2.90	60.07	505.57	.62
5.90	3.53	65.34	549.93	.80
18.60	4.45	83.02	698.72	1.02
17.60	5.46	99.61	838.34	1.24
18.67	6.65	117.09	985.46	1.40
19.56	7.71	135.59	1141.2	1.74
16.18	7.59	151.89	1278.4	1.95
15.25	9.27	165.46	1392.6	2.07
19.59	11.80	182.52	1536.1	2.45
20.87	11.35	203.84	1715.6	2.54
14.98	13.40	216.77	1824.4	3.04
23.19	13.21	240.15	2021.1	3.30

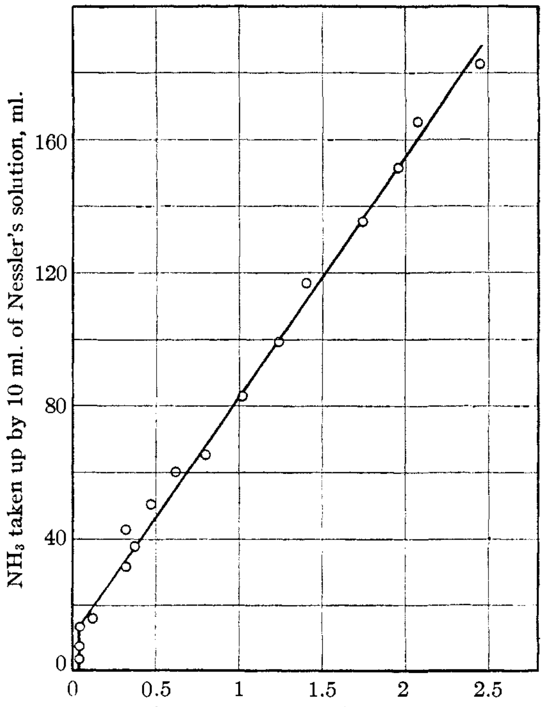

Fig. 4.

From the data (Table III) and the curve (Fig. 4) it is evident that the first formed substance is a true compound and that upon further addition of ammonia a straight line relationship representing the solubility of ammonia in Nessler's solution is obtained. The break in the curve occurs at about 0.04 cm. of mercury, showing the completion of the formation of the true compound. These data were used in the preparation of the precipitate for the quantitative determination.

(2) **Indirect Determination of the Composition of the Precipitate.**—The solid compound was then prepared by placing 90 ml. of Nessler's solution in the evacuated system and adding ammonia until the first equilibrium pressure above 0.04 cm. (about 0.30 cm.) was reached. At this pressure, all of the true compound has been formed. This required 47 ml. of ammonia or 0.0021 mole.

The mercury and the iodine were first determined in 20 ml. of the Nessler's solution before the ammonia had been added and then in 20 ml. of the filtrate obtained by filtering off the precipitate formed by the action of ammonia and Nessler's solution. The molar combining ratios were then calculated. The mercury and iodine were determined gravimetrically according to the methods of Hillebrand and Lundell.[7]

	Orig. soln., g.	Soln. after addn. of NH_3, g.	Combining with NH_3, g.	Moles combining with NH_3	Molar ratio with NH_3
Mercury	2.0988	1.2330	0.8658	0.00431	2
Iodine	5.2782	4.5060	.7722	.00608	3

The indirect analysis shows that the combining ratio of Hg to NH_3 in the product of Nessler's solution and ammonia is 2 to 1. If we assume that the equation of Strömholm for the dissociation of $HgCl_2 \cdot NH_3$ is applicable to $HgI_2 \cdot NH_3$

$$2(HgI_2 \cdot NH_3) \longrightarrow NH_2Hg_2I_3 + NH_4I$$

the ratio of Hg to NH_3 should be 2 to 1. If this equation applies the same ratio should be obtained in the phase rule study since, with the strongly alkaline solution, the ammonia would be liberated from the ammonium iodide. The values in Table III show that in this case at the end of the constant pressure of 0.04 cm., 110.34 ml. of ammonia had combined with 0.01 mole of mercury, which gives a molar ratio of 0.0049 to 0.01. Also if $NH_2Hg_2I_3$ is the product of the reaction between Nessler's solution and ammonia, then the ratio of I to NH_3 should be 3 to 1, as found by this experiment.

If, instead, the reaction between Nessler's solution and ammonia were one comparable to that of mercuric oxide and ammonia, the reacting ratio of Hg to NH_3 would be 10 to 1 and not 2 to 1, as shown by the data of the indirect analysis. Furthermore, should such a reaction have taken place, it would be impossible to account for the removal of iodine from the solution in the ratio of 3 parts of iodine to 1 part of ammonia.

(3) **Direct Analysis of the Precipitate.**—The red precipitate formed was removed from the mother liquor by filtering through a sintered glass filter and dried over solid potassium hydroxide. The amount of solid was so small that in order to make a complete analysis microchemical methods were used.

The determination of nitrogen was made by the micro Dumas method according to Pregl.[8] A micro method,[9] which separated the iodine from the mercury, was used for the determination of mercury. The iodine was determined by fusing the sample in a small sealed tube with twenty times its weight of sodium hydroxide (by alcohol). After fusion the soluble contents were dissolved and the iodine in the filtrate was determined by Mohr's method, using 0.01 *N* silver nitrate. This method was tried with pure mercuric iodide and results agreeing within 0.4% of the theoretical were obtained. Pregl's micro organic combustion method[10] was used for the determination of hydrogen. The combustion tube was modified by placing a small coil of gold wire in the exit end, so that any mercury, volatilized during the combustion, would amalgamate with the gold and not pass into the calcium chloride tube.

	Calcd. for $NH_2Hg_2I_3$, %	Found, %	Atomic ratio
Nitrogen	1.76	2.04	0.1450
Hydrogen	0.25	0.99	.9820
Mercury	50.22	46.32	.2308
Iodine	47.77	51.37	.4044

The combining ratio of nitrogen to mercury is 1 to 2 and of nitrogen to iodine is 1 to 3. The ratio of hydrogen to nitrogen is about 7 to 1. This is probably due to some of the mercury not being retained by the gold wire and being weighed as water. If the difference between 100 and the summation of the analysis is deducted from the hydrogen, the combining ratio is 2 to 1. These results are in agreement with those found by the indirect method and with the data for the phase rule studies, which gave the combining moles as $2(HgI_2 \cdot NH_3)$, which yields $NH_2Hg_2I_3$ and

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[7] "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, pp. 174, 591.

[8] "Quantitative Organic Microanalysis," P. Blakiston's Son and Co., Philadelphia, Pa., 1930, p. 81.

[9] Rutgers, *Compt. rend.*, **190**, 746 (1930).

[10] Ref. 8, p. 19.

NH_4I. The original precipitate obtained from Nessler's solution and ammonia was examined spectroscopically and found to be free of sodium.

The compound $NH_2Hg_2I_3$ resulting from the reaction of Nessler's solution and ammonia is very insoluble and forms instantaneously. The particles are very small and colloidal in nature. They can, however, be separated from the mother liquor by means of an ultrafilter, using 0.06 gage Cellophane as the filtering medium, under a pressure of 133 kg. (290 pounds) of nitrogen. The filter retained a yellow deposit and the filtrate was clear and colorless. The cataphoresis of these colloidal particles was examined by subjecting the yellow solution to a potential difference of 2 volts between the electrodes. The particles migrated to the anode, showing that they are negatively charged. The color of Nesslerized ammonia solutions is due to these finely-divided negatively-charged particles.

The effect of various protective colloids[11] in preventing the formation of a precipitate was examined to determine whether Nessler's solution could be used with solutions of higher ammonia content than is ordinarily feasible for Nessler's solution of this alkalinity. When ammonia solutions are Nesslerized without the presence of a protective agent, the color changes from yellow to red with increasing concentration of nitrogen as ammonia, due to the agglomeration of the particles. The best results were obtained by adding to 50 ml. of Nessler's solution, 1 ml. of a 0.5% alkaline, ash-free gelatin solution containing 1% of perhydrol. The color produced by the Nesslerization of dilute solutions of ammonia with Nessler's solution containing the stabilized alkaline gelatin is of as great or a greater intensity than that produced when they are Nesslerized by the standard method. The Nessler's solution containing stabilized alkaline gelatin is also better over a wider range of concentrations of nitrogen and gives a more stable solution.

Discussion

It was found that dry ammonia gas reacts with mercuric iodide to form a monomercuriammonium compound, $NH_3 + HgI_2 \longrightarrow NH_3{\cdot}HgI_2$, two moles of which react to give a stable product, $NH_2Hg_2I_3$.

$$2(NH_3{\cdot}HgI_2) \longrightarrow NH_2Hg_2I_3 + NH_4I$$

This agrees with the compound, $NH_2Hg_2Cl_3$, of Strömholm. According to Franklin's theory, $NH_2Hg_2I_3$ is a basic amino mercury compound, in which the $HO-$ group of the hypothetical mercury acid has been replaced by an NH_2- group.

In the system mercuric iodide, sodium iodide and water, mercuric iodide is dissolved by the sodium iodide and the dissolved mercuric iodide can be represented as being in solution as $HgI_2{\cdot}2NaI$. This is in accordance with the work of Dawson[12] on the three-component system of mercuric iodide, potassium iodide and water. Bugarsky,[13] however, represents the solution of mercuric bromide in aqueous potassium bromide as K_2HgBr_4.

When sodium hydroxide is added to the system mercuric iodide, sodium iodide and water, mercuric oxide is probably formed in the same manner as Bugarsky found with the system sodium hydroxide, mercuric bromide, sodium bromide and water.

$$HgI_2{\cdot}2NaI + 2NaOH + nH_2O \longrightarrow HgO + 4NaI + (2 + n)H_2O$$

Since the reaction follows the law of mass action, the concentration of the added variable constituent, sodium hydroxide, controls the concentration of the $HgI_2{\cdot}2NaI$ in solution.

Nessler's solution gives a system identical with that described above. When this solution is added to an aqueous solution containing nitrogen as ammonia, the ammonia reacts with the dissolved $HgI_2{\cdot}2NaI$ as follows

$$\begin{array}{r} 2(HgI_2{\cdot}2NaI) + 2NH_3 \longrightarrow 2(NH_3{\cdot}HgI_2) + 2NaI \\ 2(NH_3{\cdot}HgI_2) \longrightarrow NH_2Hg_2I_3 + NH_4I \\ \hline 2(HgI_2{\cdot}2NaI) + 2NH_3 \longrightarrow NH_2Hg_2I_3 + 2NaI + NH_4I \end{array}$$

The ratio of the concentration of NH_3 to the concentration of $HgI_2{\cdot}2NaI$ must be low or the compound $NH_2Hg_2I_3$ will not be formed. This low ratio agrees with that given by Strömholm, as a result of his work with mercuric chloride and ammonia. He found that the compound $NH_2Hg_2Cl_3$ does not exist in the presence of high concentrations of ammonia. With high concentrations of ammonia as ammonium chloride, he always obtained $(NH_3)_2HgCl_2$ and never a mercuric chloride addition product. Between two solutions, one containing 2.0% of mercuric chloride and 2.1% of ammonium chloride, and the other, containing 4.3% of mercuric chloride and 2.0% of ammonium chloride, he found the com-

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(11) Chiles, THIS JOURNAL, **50**, 217 (1928).

(12) Dawson, *J. Chem. Soc.*, **95**, 870 (1909).

(13) Bugarsky, *Z. physik. Chem.*, **12**, 223 (1893).

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]

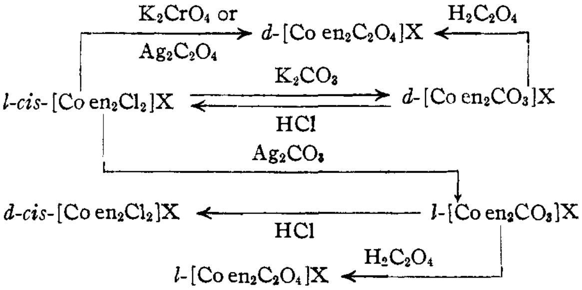
The Stereochemistry of Complex Inorganic Compounds.

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-$[Co\,en_2Cl(NCS)]X$ + $NaNO_2$ ⟶ 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).