

## On the Stereochemical Configuration of the Aquotriammine and Diammine Cobalt Complex Salts.

By

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### Introduction.

The present investigation was undertaken to determine the stereochemical configuration of the aquo-triammine and diammine cobalt complex salts, by observing the effects on the absorption spectra exercised by water molecules which coördinate in place of ammonia in cobaltamines in their aqueous solutions. The aquocobaltamines are, in general, more soluble in water than other cobalt-ammines and they are of various colours and different solubilities, according to the number of water molecules coördinated in them. The reason why such cobaltamines as  $[\text{Co}(\text{NH}_3)_6\text{NO}_3]\text{X}_2$ ,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{X}$ ,  $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{X}_2$ ,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{X}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{X}_2$  etc., which are not soluble in cold water become readily soluble in warm water, or slightly acidic or alkaline solution, is based upon the facts that the nitrate groups, and halogen atoms are substituted by water; thus the cobaltamines change into  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\frac{\text{NO}_3}{\text{X}_2}$ ,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\frac{(\text{NO}_3)_2}{\text{X}}$ ,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{NO}_3)_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\frac{\text{Cl}}{\text{X}_2}$ ,  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\frac{\text{X}_2}{\text{Cl}}$  and  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\frac{\text{Br}}{\text{X}_2}$  etc. . . . respectively. Therefore the study of the relation of water molecules with cobaltamines appears to be of some importance. Up to the present, the following series of

the aquocobaltamines are known. X denoting a monovalent anion, en is  $\begin{matrix} \text{CH}_2\text{NH}_2 \\ | \\ \text{CH}_2\text{NH}_2 \end{matrix}$ .

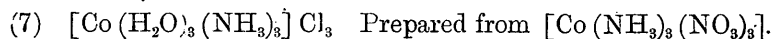
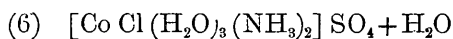
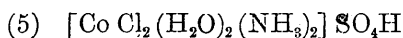
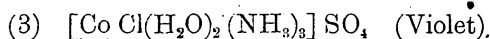
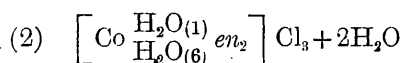
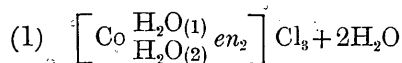
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|-----|--|---|------------------|
| (1) | $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{X}_3$   | Roseo salt.   | Brick red colour |
| (2) | $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{X}_3$   | Diaquotetrammine cobaltic salt.   | Dark red         |
|     | $\left[ \text{Co} \begin{matrix} \text{H}_2\text{O} (1) \\ \text{H}_2\text{O} (2) \end{matrix} \text{en}_2 \right] \text{X}_3$ | a) Cis-diaquodiethylenediamine cobaltic salt.   | Brownish red     |
|     | $\left[ \text{Co} \begin{matrix} \text{H}_2\text{O} (1) \\ \text{H}_2\text{O} (6) \end{matrix} \text{en}_2 \right] \text{X}_3$ | b) Trans. do  | Greyish brown    |
| (3) | $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{X}_3$   | Triaquotriammine cobaltic salt (Prepared from $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$ ).  | Reddish violet   |
| (4) | $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]\text{X}_3$   | Tetraquodiammine cobaltic salt, Aqueous solution only is known.                               |                  |
| ?   | $[\text{Co}(\text{NH}_3)(\text{H}_2\text{O})_5]\text{X}_3$   | Unknown.  |                  |
| (5) | $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2$  | Normal cobaltous salt.  | Rose colour      |
| (6) | $[\text{Co Cl H}_2\text{O}(\text{NH}_3)_4]\text{X}_2$  | Chloraquotetrammine cobaltic salt.  | Reddish violet   |
| (7) | $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3]\text{X}_2$  | Chlorodiaquotriammine cobaltic salt. Two isomers, one is violet and the other greyish indigo. |                  |
| (8) | $[\text{Co Cl}(\text{H}_2\text{O})_3(\text{NH}_3)_2]\text{X}_2$  | Chlorotriaquodiammine cobaltic salt.  | Indigo blue      |
| (9) | $[\text{Co Cl}_2\text{H}_2\text{O}(\text{NH}_3)_3]\text{X}$  | Dichloraquotriammine cobaltic salt (dichro-salt).   |                  |

According to the manner in which the chlorine atoms coördinate to the central cobalt atom, there are two isomers in this salt, one is green and the other grey.

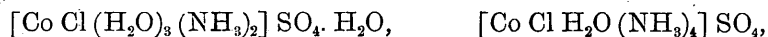
- (10)  $[\text{Co Cl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{X}$  Dichlorodiaquodiammine cobaltic salt.

In the compound (10) three isomers may be theoretically produced, but only one is known, which is green.

Among the above ten series of complex salts, the absorption spectra of (1), (2), (5) and (6) having already been studied in aqueous solution,<sup>(1)</sup> I have now measured the absorption spectra of the following eight salts :



In order to determine whether the coordinated chlorine atoms of these salts dissociate in water or not, I have also measured the conductivities of the following six complex salts :



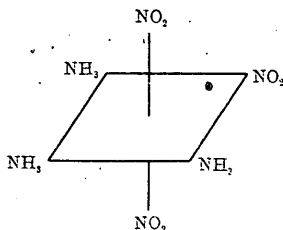
It was found, as the result, that the chlorine atoms (or halogen atoms generally) and the radicals of the strong acids, which coordinate to the central cobalt atom, are apt to dissociate, when they are dissolved in water and are sometimes in equilibrium

(1) Y. Shibata, Journ. College of Science, Imp. Univ. Tokyo Vol. XXXVII, Art. 2, 1915.

as described below. In this investigation I was able to establish the structural formulae of all the cobalt complex salts, mentioned above, by the study of their absorption spectra as well as their conductivities and I have explained clearly the behaviour in aqueous solution of such cobaltamines as have strong acid radicals in their complex nucleus.

### Theoretical Part.

The configuration of the trinitrotriammine cobaltic salt,  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$ , a starting substance of many triammine cobalt complex salts, has already been determined by Y. Shibata,<sup>(1)</sup> as follows:



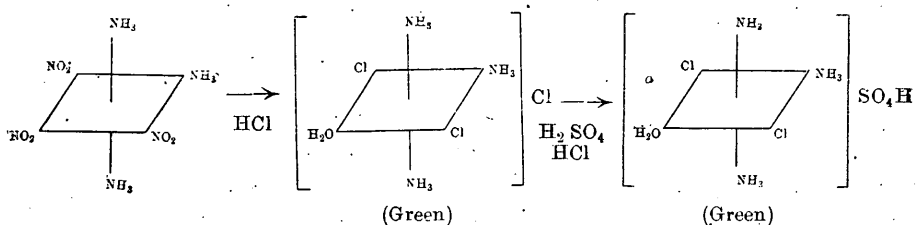
If this salt is treated with conc. hydrochloric acid  $[\text{Co Cl}_2 \cdot \text{H}_2\text{O}(\text{NH}_3)_3] \text{Cl}$  (9), the so-called dichro-salt, which is of a green colour is obtained. On treating the dichro-salt with a cold mixture of 2 Vol. of strong sulphuric acid and 1 Vol. of conc. hydrochloric acid, the greenish grey  $[\text{Co Cl}_2 \cdot \text{H}_2\text{O}(\text{NH}_3)_3] \text{SO}_4 \text{H}$  is produced. On dissolving this last named substance in water and then adding an equal volume of alcohol,  $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4$ , an indigo blue coloured powder, is precipitated. When the indigo-bluish  $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4$  is ground with strong hydrochloric acid, it changes into the grey  $[\text{Co Cl}_2 \cdot \text{H}_2\text{O}(\text{NH}_3)_3] \text{Cl}$ <sup>(2)</sup> which is the isomer of the green  $[\text{Co Cl}_2 \cdot \text{H}_2\text{O}(\text{NH}_3)_3] \text{Cl}$ . If the aqueous solution of  $[\text{Co Cl}_2 \cdot \text{H}_2\text{O}(\text{NH}_3)_3] \text{SO}_4 \text{H}$  is warmed on the water bath for a little while, the colour of the solution is changed into dark violet and, when it is evaporated in vacuo, a violet crystalline precipitate,

(1) Journ. College, Science, Imp. Univ. Tokyo, Vol. XXXVII, Art. 2, 1915.

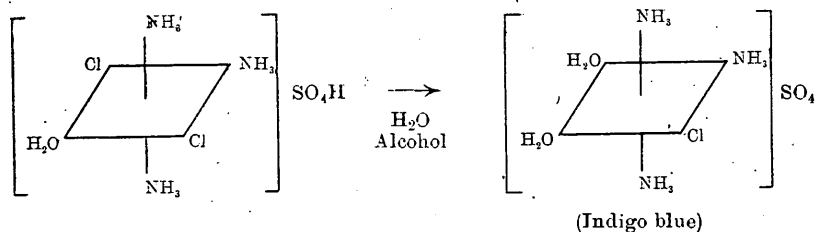
(2) Werner: Zeit. anorg. Chem., 15, 143, 1897.

$[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4 \cdot \text{H}_2\text{O}$  (7)<sup>(1)</sup>, the isomer of the above indigo bluish salt, remains.

Judging from the above reactions, we can build up their stereochemical structures as below. As regards the configuration of the dichloroaquatriammine cobaltic salt, the two chlorine atoms must, as described by Y. Shibata, be coordinated in the trans-position analogous to those of the diethylenediamine praseo cobaltic salt, in which they are in the trans-position and show green colour. The process of formation will be as follows :



Two isomers of  $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4$  (2) can be derived from  $[\text{Co Cl}_2 \text{H}_2\text{O}(\text{NH}_3)_3] \text{SO}_4\text{H}$ . The indigo blue coloured one (which is easily obtained by the action of water upon  $[\text{Co Cl}_2 \text{H}_2\text{O}(\text{NH}_3)_3] \text{SO}_4\text{H}$  and by adding an equal volume of alcohol to it) has the following configuration:

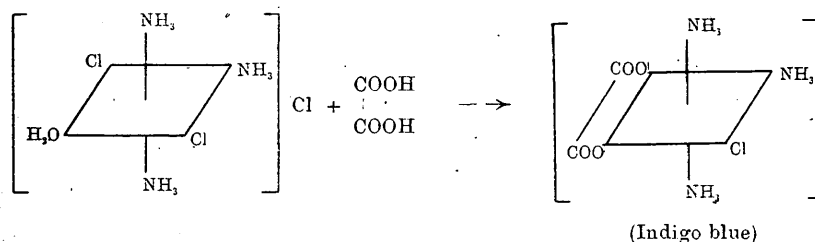


This reaction is analogous to that of the production of the chloroxalatotriammine cobaltic salt,  $[\text{Co Cl C}_2\text{O}_4(\text{NH}_3)_3]$ ,<sup>(3)</sup> from the dichloride. As to the configuration of this salt, only one form can be deduced theoretically, as the following equation shows :

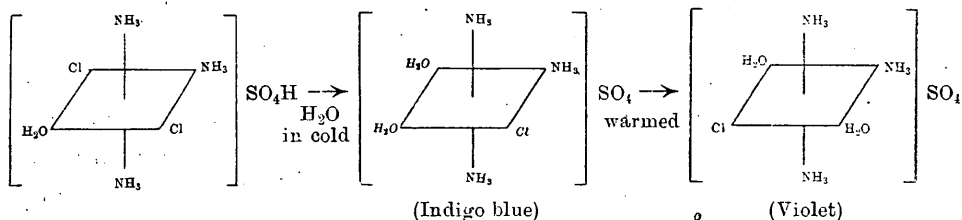
(1) Werner : Ibid.

(2) " "

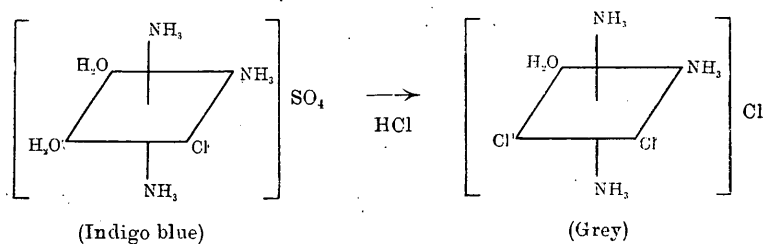
(3) Werner and Miolati : Zeit. physik. Chem., 12, 35 1893.



If we assume that the two water molecules are placed in the cis-position in the indigo blue  $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4$ , they must necessarily be situated in the trans-position in the other isomer, i.e. in the violet  $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4$ . This presumption was clearly verified by the study of the absorption spectra (cf. the part on the absorption spectra). Therefore in the dichro-salt the two chlorine atoms must coordinate in the trans-position. These relations are shown as follows :



If the indigo blue compound  $[\text{Co Cl}(\text{H}_2\text{O})_2(\text{NH}_3)_3] \text{SO}_4$  is ground up with concentrated hydrochloric acid, a grey coloured powder is obtained, analysis of which gives the formula  $[\text{Co Cl}_2\text{H}_2\text{O}(\text{NH}_3)_3]\text{Cl}^{(1)}$ ; this substance must be considered as the isomer of the greenish dichro-salt of the following configuration :

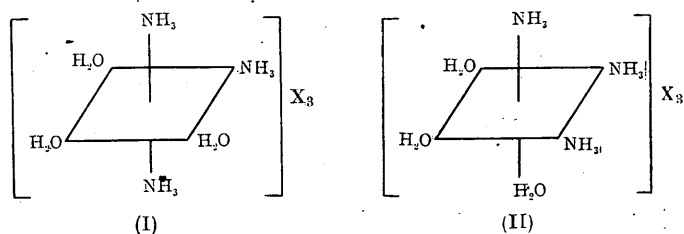


Having come to this conclusion, we have no need for further

(1) Werner: Zeit. anorg. Chem., 15, 144, 1897.

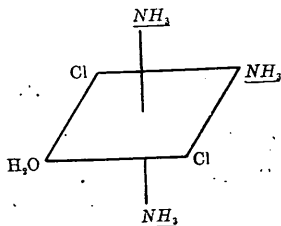
explanations to prove the fact that the two chlorine atoms of the dichro-salt are coordinated in the trans-position.

With regard to the configurations of the triaquotriammine cobaltic salts, we can theoretically establish two isomers: one in which all the three water molecules are coordinated in the cis and consecutive positions and the other in which two of them are in the trans-position as follows:



On addition of hydrochloric acid saturated at  $0^{\circ}\text{C}$  to the acetic acid solution of  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$ , which is kept over night,  $[\text{Co}(\text{H}_2\text{O})_3(\text{NH}_3)_3]\text{Cl}_3$ <sup>(1)</sup> separates in the shape of reddish violet crystals. The stereochemical configuration of this salt, though it cannot be determined by means of ordinary chemical analysis, can be ascertained by the study of its absorption spectra. With the help of this recently well-developed spectrochemical method, I was able to prove that in the above triaquotriammine cobaltic salt, the three water molecules are coordinated in the cis and consecutive positions as indicated by (II). Accordingly, there must exist another isomer of the type (I).

The position of the three ammonia molecules of the dichro salt has already been proved to be as follows:



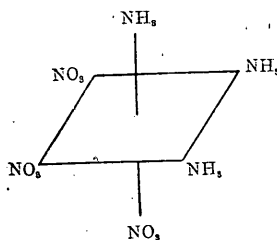
(1) Werner: Ber., **39**, 2678, 1906.

If the two chlorine atoms of this compound are replaced by water, we are able to produce the triaquotriammine cobaltic salt (I). Thus, when the dichro-salt is dissolved in a considerable quantity of water, acidified with hydrochloric acid, and evaporated in vacuo, dark violet crystals separate, analysis of which satisfies the formula  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  not  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2\text{H}_2\text{O}$ . Thus, 0.2032 gr. of the substance gives 0.1138 gr.  $\text{CoSO}_4$ ; 0.1353 gr. of the salt gives 0.2150 gr.  $\text{AgCl}$ .

	Calculated	Obtained
Co	21,3 %	21,8 %
Cl	39,31%	39,32%

When the salt is heated at a temperature of 100-110° C for one hour it does not change in weight, which suggests that there is no water of crystallization. The absorption spectra of this salt were compared with those of the other isomer; the great divergence between them indicates the different configurations.

Thus I was able to obtain one of the isomers of triaquotriammine cobaltic salts, verifying also both of their configurations. As the cis and consecutive triaquotriammine cobaltic salt was prepared by the action of water upon  $[\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3]$ , the constitution of the latter must be as follows :

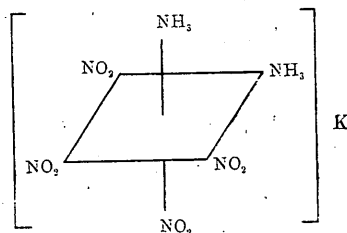


The trans-triaquotriammine cobaltic salt is not stable in water; at first the solution is bluish violet in colour, but afterwards it shows exactly the same colour as the solution of the cis and consecutive, i.e. reddish violet. The same reaction takes place in the case of the diaquodiethylenediamine cobaltic salts. When the trans-salt stands for a long time in water or when it is warmed for



a short time, it produces readily the stable cis-salt. Accordingly, one is much inclined to the conclusion that the cis-aquoocompounds are as a rule more stable than the corresponding trans-compounds in aqueous solution.

Now that I have described the structures of the cobalt complex salts of the triammine series, I shall discuss the configurations of those of the diammine series. As the stereochemical structure of one of these salts, i.e. the tetranitrodiammine cobaltic salt  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]\text{K}$ , a starting substance of these series, has been thoroughly investigated by Y. Shibata<sup>(1)</sup> and the late T. Maruki, no further confirmation as to it is necessary. In this salt the two ammonia molecules are coordinated in the cis-position as follows :



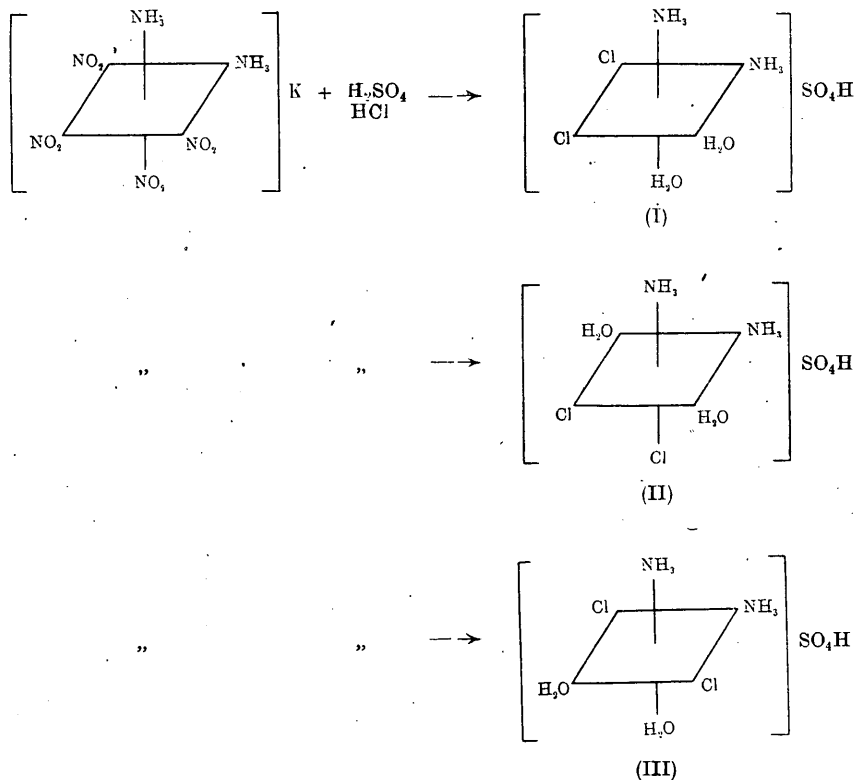
When  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]\text{K}$  <sup>(2)</sup> is treated with a cold mixture of strong hydrochloric acid and sulphuric acid, a malachite green salt  $[\text{CoCl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{SO}_4\text{H}$  is produced, and on this salt being dissolved in water acidified with  $\text{H}_2\text{SO}_4$  and evaporated in the desiccator over sulphuric acid, indigo blue crystals of  $[\text{CoCl}(\text{H}_2\text{O})_3(\text{NH}_3)_2]\text{SO}_4\cdot\text{H}_2\text{O}$  separate out. If the latter is acted upon by strong hydrochloric acid, it changes into a greenish powder which corresponds to the formula  $[\text{CoCl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{Cl}$  <sup>(3)</sup>.

From these reactions, we can now deduce their constitutions as below. With respect to  $[\text{CoCl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{X}$ , we are able theoretically to derive the following three configurations :—

(1) Journ. College of Science, Imp. Univ. Tokyo Vol. XLI., Art. 2, 1917.

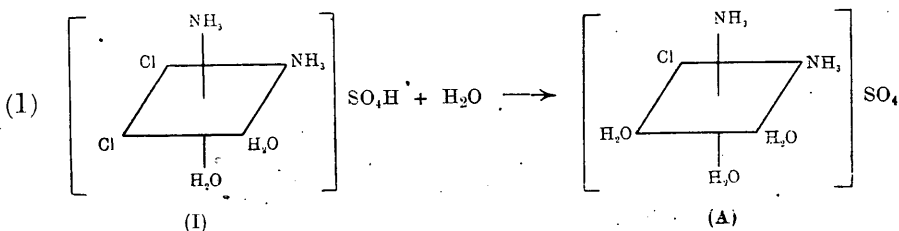
(2) Jørgensen : J. prakt. Chem., [2], 23, 249, 1881.

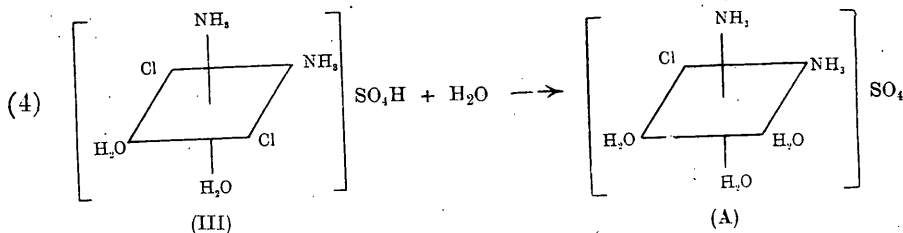
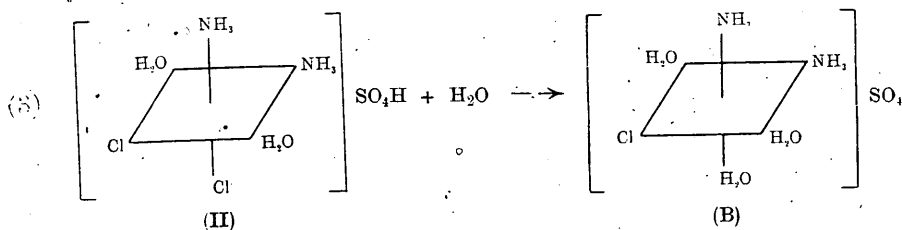
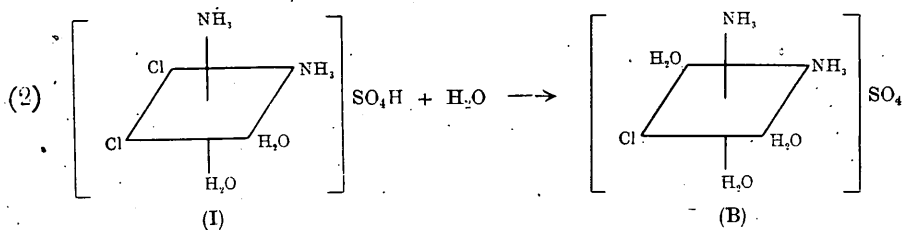
(3) Werner : Zeit. anorg. Chem., 15, 165, 1897.



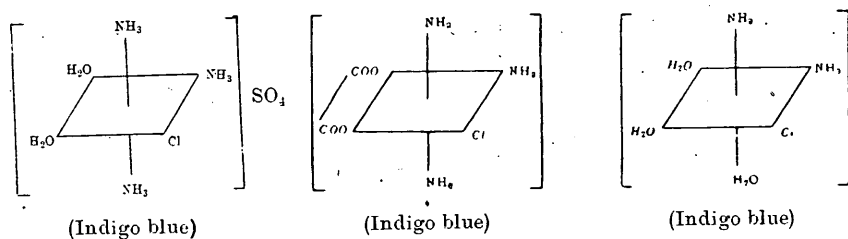
On the action of water upon  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2] \text{SO}_4\text{H}$ , we obtain the indigo blue salt  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}] \text{SO}_4 \cdot \text{H}_2\text{O}$  (6), the configuration of which must be, as the following equations illustrate, either of (A) or (B) (below).

Whichever of the formulae (I), (II) and (III) one may assume for the configuration of  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2] \text{SO}_4\text{H}$ , that of  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}] \text{SO}_4$  will be as shown by either of the following two formulae (A) or (B), thus :



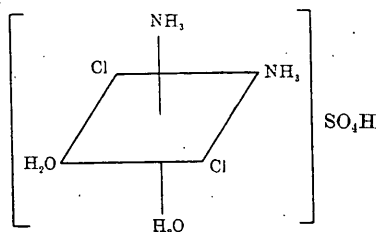


By the study of the absorption spectra, it is confirmed that the above triaquochlorodiammine cobaltic salt,  $[\text{Co}(\text{NH}_3)_2 \text{Cl}(\text{H}_2\text{O})_3] \text{SO}_4$  has the configuration shown under (A). (For full explanations see under the section on absorption). It is naturally to be expected that some relations exist between the configuration and the colour of these chemical compounds; examples in which the salts have analogous configurations and the same colour are shown below :

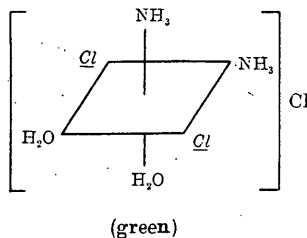
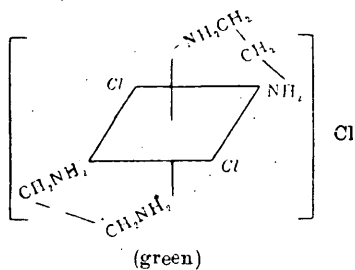
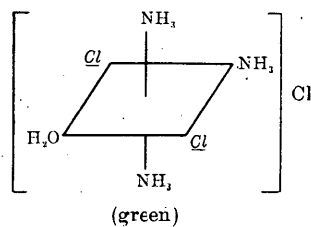
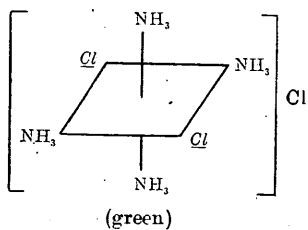


As we easily obtain from  $[\text{Co} \text{Cl}_2 (\text{H}_2\text{O})_2 (\text{NH}_3)_2] \text{SO}_4 \text{H}$ ,  $[\text{Co} \text{Cl} (\text{H}_2\text{O})_3 (\text{NH}_3)_2] \text{SO}_4$  as above mentioned, which has the structure shown by (A), the configuration of the former is not as

in (II); if it were so,  $[\text{CoCl}(\text{H}_2\text{O})_3(\text{NH}_3)_2]\text{SO}_4$  should have the configuration of the type (B) as indicated by the above equation (3). However this is not in keeping with experimental results, therefore it must be either as shown in (I) or (III). If it were like (I), then since the possibility of producing the chlorotriaquodiammine cobaltic salts shown by (A) and (B) should be exactly equal, the product obtained from it would be a mixture of these two isomers. But the compound thus obtained, i.e.  $[\text{CoCl}(\text{H}_2\text{O})_3(\text{NH}_3)_2]\text{SO}_4$  crystallizes homogeneously and the absorption curve thereof suggests to us that the three water molecules are in the cis and consecutive position as shown by (A). Accordingly the above dichlorodiaquodiammine cobaltic salt has the constitution of the type (III), thus:—

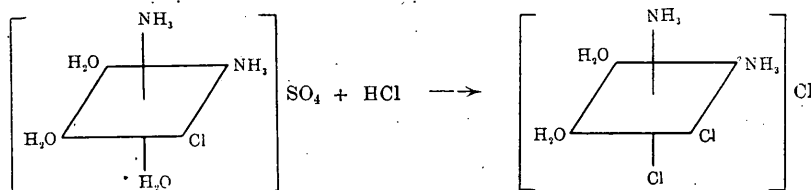


And also from the consideration of the colour, we can confirm this configuration, comparing it with the compounds which have analogous configurations and the same colour, thus:—

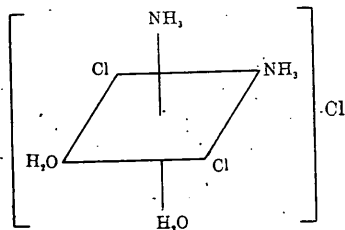


From this, it seems to be a rule that the cobaltamine in which the two chlorine atoms are coordinated in the trans-position is green in colour:

When one of the water molecules is replaced by a chlorine atom by the direct action of concentrated hydrochloric acid upon  $[\text{Co Cl}(\text{H}_2\text{O})_3(\text{NH}_3)_2] \text{SO}_4$ , a green salt is produced which corresponds to the formula  $[\text{Co Cl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2] \text{Cl}$ . This salt is soluble in water, thereby changing its colour to violet. Werner<sup>(1)</sup> supposed this salt to be the isomer of the above  $[\text{Co Cl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2] \text{X}$  (III). If that be correct, we are inclined to the view that the two chlorine atoms of the salt coordinate in the cis-position as shown:



In supporting this statement, this salt should be regarded as one of the exceptions to the general rule that the cobaltamines in which the two chlorine atoms coordinate in the trans, are, as already described, green coloured. But is it not more probable that this salt is identical with  $[\text{Co Cl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2] \text{X}$  shown by (III) and that the two chlorine atoms are situated in the trans-position? So I suggest that the formula of the salt may be :



Up to this point, I have determined the configurations of the isomers of  $[\text{Co}(\text{NH}_3)_3\text{H}_2\text{O Cl}_2] \text{X}$ ,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2 \text{Cl}] \text{X}_2$  and  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3] \text{X}_3$  respectively and  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2 \text{Cl}_2] \text{X}$ ,  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3 \text{Cl}] \text{X}_2$  and  $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$ , but this is not sufficient without an explanation of the study of the absorption spectra.

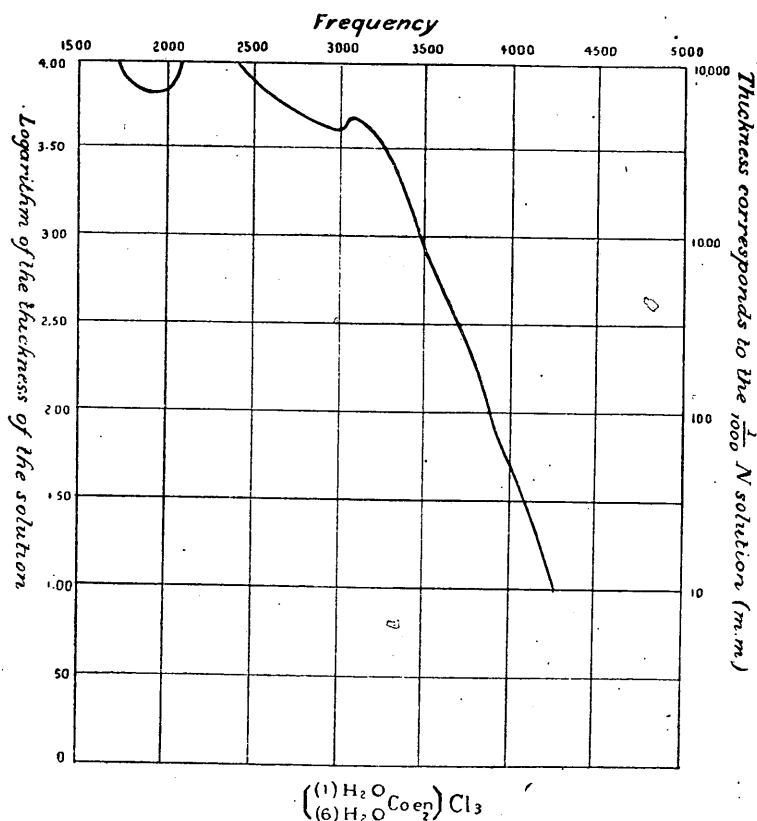
(1) Zeit. anorg. Chem., 15, 172, 1897.

## Experimental Part:

### The Measurement of the Absorption Spectra.

The absorption spectra of these salts were measured by means of the quartz spectrograph of Adam Hilger & Co, London. The concentrations of the solutions were varied from 1/100 N to 1/1000. The salts used were specially purified by recrystallization, the formulae of some of which were ascertained by analysis. We might go into discussions from the standpoint of the absorption curves, which were drawn by the method suggested by Hartley & Baly. As the result, the eight compounds can be grouped into two classes: to the first class belong

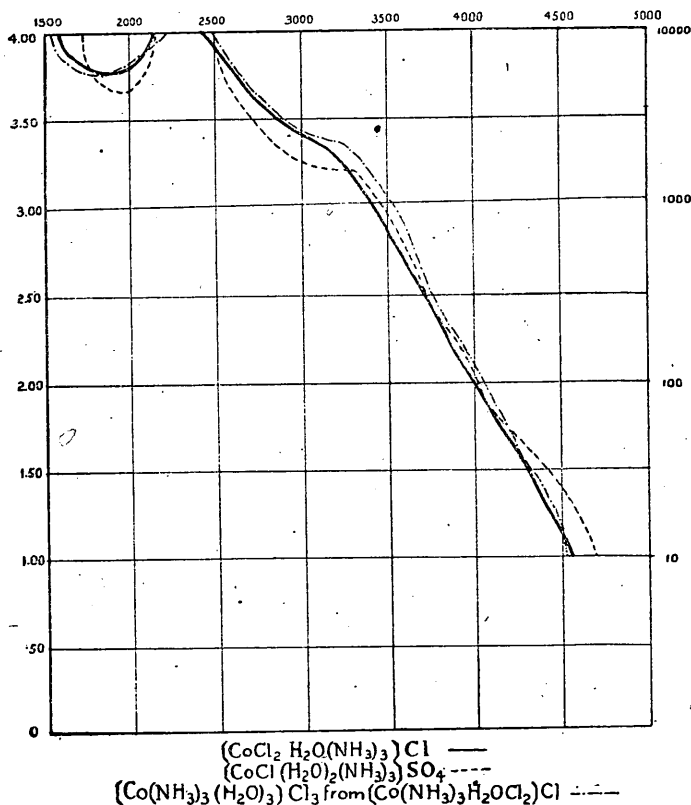
Fig. 1.



$\left[ \text{Co} \begin{matrix} \text{H}_2\text{O}(1) \\ \text{H}_2\text{O}(6) \end{matrix} \text{en}_2 \right] \text{Cl}_3$  (fig. I), green  $[\text{CoCl}_2\text{H}_2\text{O}(\text{NH}_3)_3] \text{Cl}$  (fig. II), violet  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2] \text{Cl} \text{SO}_4$  (fig. II) and  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3] \text{Cl}_3$  (fig. II) which are prepared from the green  $[\text{Co}(\text{NH}_3)_3\text{Cl}_2\text{H}_2\text{O}] \text{Cl}$  and the second class includes the following four salts :

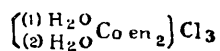
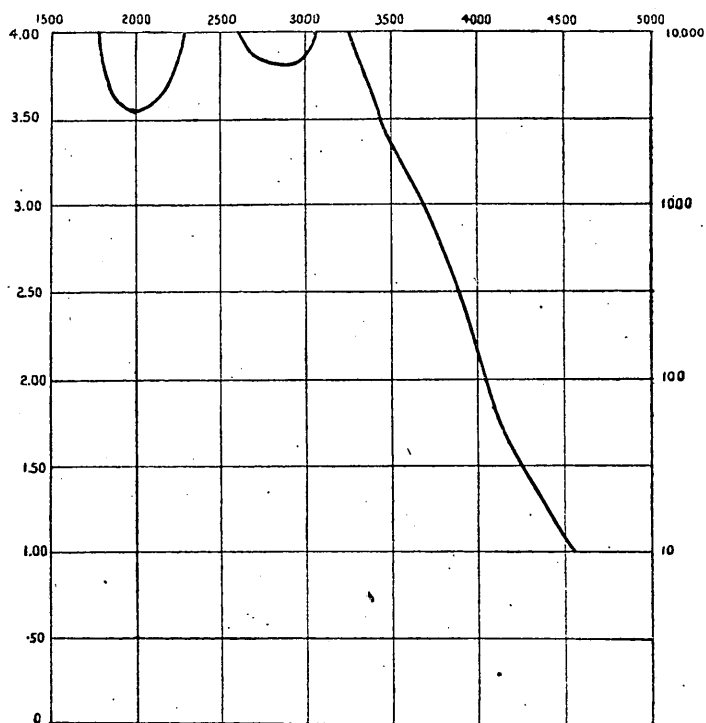
$\left[ \text{Co} \begin{matrix} \text{H}_2\text{O}(1) \\ \text{H}_2\text{O}(2) \end{matrix} \text{en}_2 \right] \text{Cl}_3$  (fig. III),  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2] \text{SO}_4 \cdot \text{H}_2\text{O}$  (fig. IV)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3] \text{Cl}_3$  (fig. IV) which are prepared from  $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$  and  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}] \text{SO}_4$  (fig. IV).

Fig. 2.

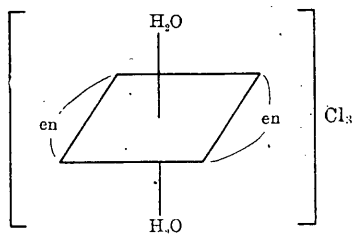


In the first class as well as in the second, all the absorption curves in their own groups are remarkably similar to each other, although they differ much from those in the other class, which

Fig. 3.



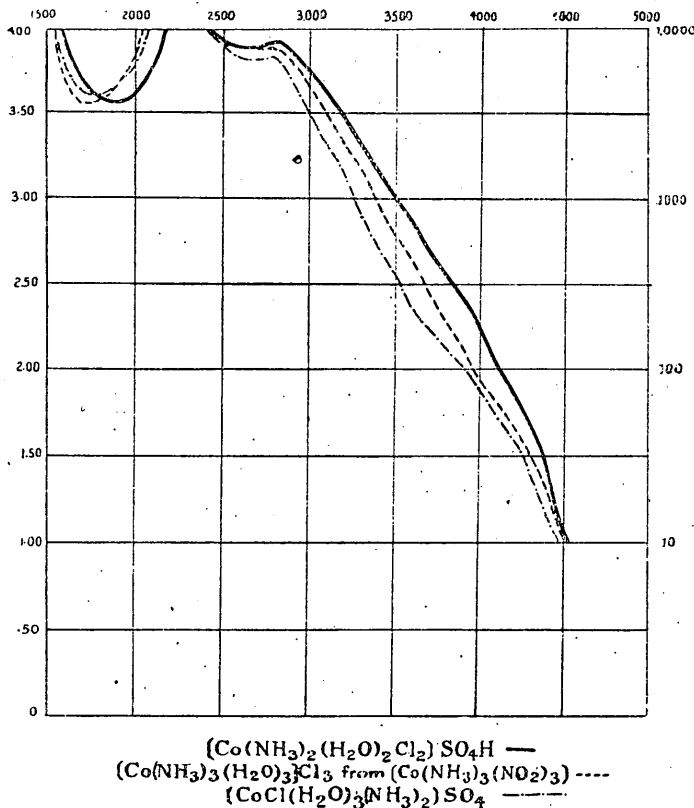
proves that their constitutions are also identical in their groups. The structural formula of  $\left[ \text{Co} \begin{array}{c} \text{H}_2\text{O} (1) \\ \text{H}_2\text{O} (2) \end{array} \text{en}_2 \right] \text{Cl}_3$  was previously determined by Werner<sup>(1)</sup> as below, the two water molecules of which are in the trans-position thus :



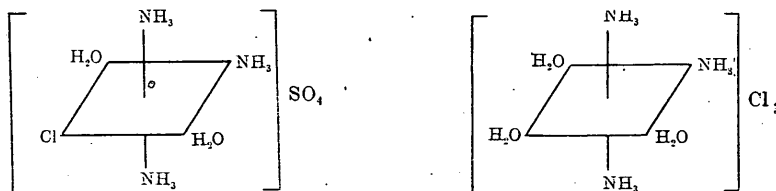
(1) Ber., 40, 285, 1907



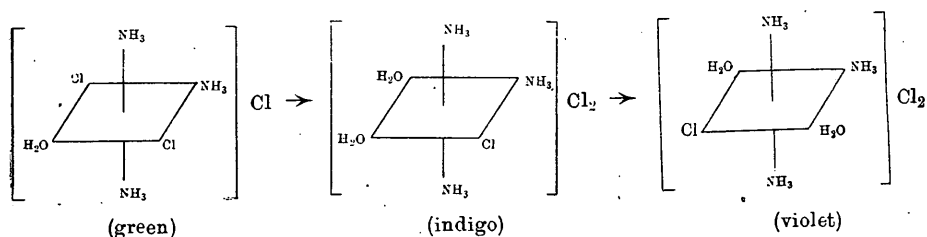
Fig. 4.



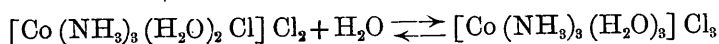
As the absorption curve of  $\left[ \text{Co} \begin{matrix} \text{H}_2\text{O}^{(1)} \\ \text{H}_2\text{O}^{(6)} \end{matrix} \text{en}_2 \right] \text{Cl}_3$  is the fundamental one of the first class, the configuration of the other three compounds must be analogous to that of this salt; in other words, the two water molecules in them coordinate in the trans-position. So  $\text{[Co(NH}_3)_3(\text{H}_2\text{O})_2\text{Cl]SO}_4$  and  $\text{[Co(NH}_3)_3(\text{H}_2\text{O})_3\text{]Cl}_3$  (8) have the following configurations respectively:



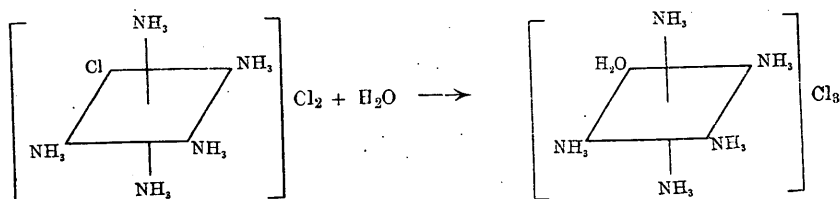
That the dichro-salt gives the same curve (fig. II) as those of the rest of the first class is to be explained by the fact that although at first while the colour of its solution is yet green, it has the configuration already mentioned, with the gradual transformation of the colour to indigo and at last to violet, the conversion of the structure must take place as follows :



And  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2$  will be also in equilibrium with  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  in the water solution thus :

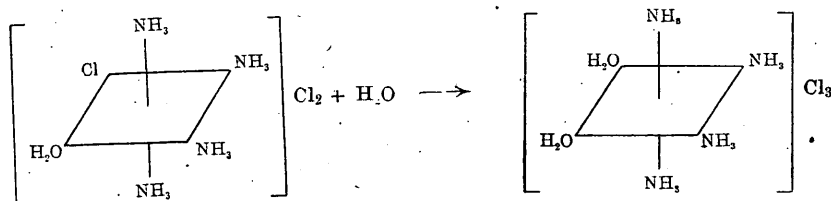


As regards this point, it will be fully discussed later. There are many examples where, when the chlorocobaltamines are dissolved in water their chlorine atoms are easily replaced by water molecules. The absorption spectra<sup>(1)</sup> of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$  in aqueous solution are identical, which proves that the following substitution occurs to a certain extent:—

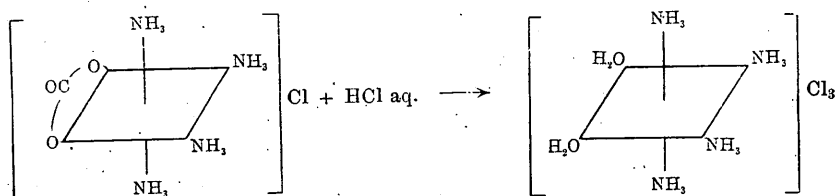


$[\text{CoClH}_2\text{O}(\text{NH}_3)_4]\text{Cl}_2$  and  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_3$  have also the same absorption curves, which are confirmed as follows:

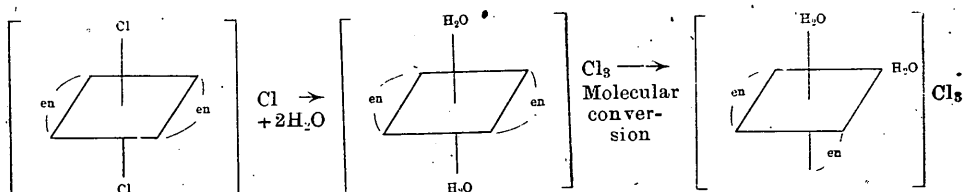
(1) Y. Shibata, Journ. College of Science, Imp. Univ., Tokyo, Vol. XXXVII, Art. 2, 1915.



The fact that the two water molecules of  $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_3$  coördinate in the cis-position can easily be recognized from the absorption curve, which is very similar to that of the second class, and also by the process of formation as follows :

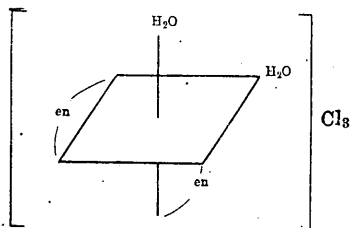


When  $[\text{Co} \begin{smallmatrix} \text{Cl}^{(1)} \\ \text{Cl}^{(6)} \end{smallmatrix} \text{Co en}_2] \text{Cl}$  is kept overnight in aqueous solution, its colour changes to carmine red and then it shows the same absorption curve as that of the cis-diaquodiammine cobalt chloride,  $[\text{Co} \begin{smallmatrix} \text{H}_2\text{O}^{(1)} \\ \text{H}_2\text{O}^{(6)} \end{smallmatrix} \text{en}_2] \text{Cl}_3$ . This will be verified below. At first its two chlorine atoms are replaced by water, producing the trans-diaquodiammine cobalt chloride,  $[\text{Co} \begin{smallmatrix} \text{H}_2\text{O}^{(1)} \\ \text{H}_2\text{O}^{(6)} \end{smallmatrix} \text{en}_2] \text{Cl}_3$  and then it is converted into the more stable cis-salt, i.e.  $[\text{Co} \begin{smallmatrix} \text{H}_2\text{O}^{(1)} \\ \text{H}_2\text{O}^{(2)} \end{smallmatrix} \text{en}_2] \text{Cl}_3$  thus :

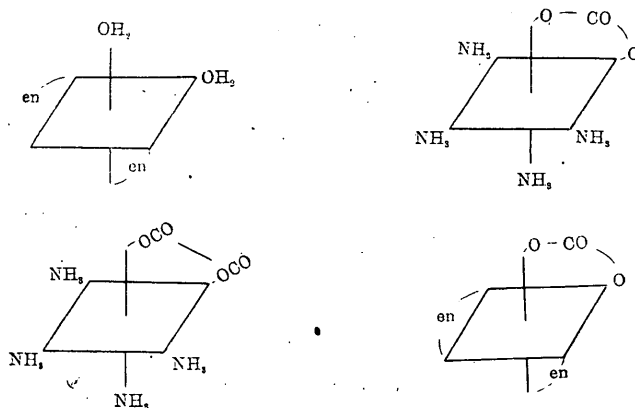


As to the complex salts of the second class, discussions follow quite in the same way as in the case of the first class. Werner

has already studied the constitution of  $\left[ \text{Co} \begin{array}{l} \text{H}_2\text{O}^{(1)} \\ \text{H}_2\text{O}^{(2)} \text{en}_2 \end{array} \right] \text{Cl}_3^{(1)}$ , two water molecules of which are coordinated in the cis-position, thus :



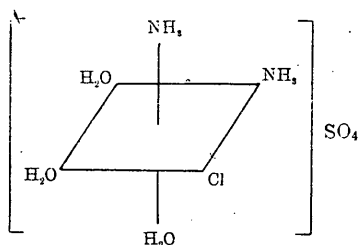
The compounds belonging to this series are generally more stable than those of the first class, while the latter seems to have a great tendency to be converted into the former. From the fact that the absorption curve of the cis-diaquodiamminecobaltic chloride (fig. III) is analogous to the curves of  $[\text{Co CO}_3(\text{NH}_3)_4] \text{Cl}$ ,  $[\text{Co C}_2\text{O}_4(\text{NH}_3)_4] \text{Cl}$  and  $[\text{Co CO}_3 \text{en}_2] \text{Cl}$ , we can affirm that, when the water molecules coordinate to a cobalt atom to form a complex salt, then unite with the central atom by the residual affinity of the oxygen of water as illustrated below :



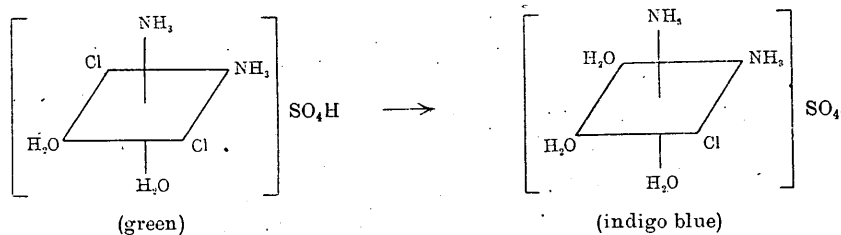
The chlorotriaquodiammine cobaltic sulphate must have the following configuration. For its absorption curve (fig. IV) is very similar to that of the cis-diaquodiamminecobaltic chloride,

(1) Ber., 40, 285, 1907.

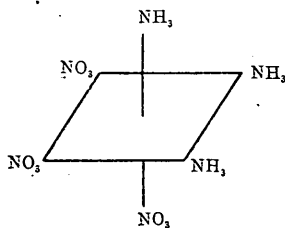
which suggests that its three water molecules coordinate in the cis and consecutive position, thus:—



As a consequence, the structure of  $[\text{CoCl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{SO}_4\text{H}$  could also be determined, as has been already mentioned. The compound  $[\text{CoCl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{SO}_4\text{H}$  has at first a green colour in aqueous solution, but this changes gradually until its colour becomes indigo blue. This change of colour is a proof that the following substitution takes place :



The curve of  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  (7) is very different from that of  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  (8), which is the best verification that the two salts are isomeric; and the former is very stable in water. It is prepared from  $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$  the configuration of the latter will be as follows :



### General Consideration of the Absorption Spectra.

The aquocobaltamines in which the water molecules coördinate in the cis-position tend remarkably with an increase in the number of water molecules, to produce the bathochromic phenomenon and their absorption spectra differ greatly from those of the trans-salts. All the aquocobaltamines, according to the number of the coördinated water molecules, are apt to diminish the second absorption band, which affords an additional proof that the second absorption band of these salts is, as Prof. Y. Shibata has suggested, due to the coördinated ammonia.

### Measurements of Electrolytic Conductivity.

Although I have in the previous chapter demonstrated by means of the absorption spectra that in some of the chlorocobaltamines the chlorine atoms are replaced by water molecules in aqueous solution, the confirmation will not be satisfactory without another verification. Therefore I have measured the conductivities of solutions of these salts in order to confirm the above opinion. The method used was that devised by Ostwald. The data are as follows:

Table I.

$[\text{CoCl}(\text{NH}_3)_5]\text{SO}_4$		$[\text{CoClH}_2\text{O}(\text{NH}_3)_4]\text{SO}_4$		$[\text{CoCl}(\text{H}_2\text{O})_2(\text{NH}_3)_3]\text{SO}_4$	
$\varnothing$	U	$\varnothing$	U	$\varnothing$	U
100	200,3	.....	.....	.....	.....
200	231,4	.....	.....	.....	.....
400	263,4	400	190,1	.....	.....
800	300,4	800	218,7	800	259,2
1600	343,9	1600	259,2	1600	462,9
$[\text{CoCl}(\text{H}_2\text{O})_3(\text{NH}_3)_2]\text{SO}_4$		$[\text{CoCO}_3(\text{NH}_3)_4]_2\text{SO}_4$		$[\text{CoH}_2\text{O}(\text{NH}_3)_5]_2(\text{SO}_4)_3$	
100	184,2	100	78,83	100	117,0
200	222,8	200	87,18	200	151,8
400	267,6	400	92,13	400	182,2
800	332,7	800	99,13	800	217,9
1600	412,3	1600	106,2	1600	265,1

Where  $\emptyset$  is the dilution, U the molecular conductivity. Measurements were made at the temperature of 25°C. The following table shows the variation of the conductivity with time.

Table 2.

$\emptyset$	[Co.H <sub>2</sub> O(NH <sub>3</sub> ) <sub>5</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	
	Time (Min.)	U
100	0	117,0
"	5	122,3
"	10	124,3
"	20	129,3
"	30	133,6
"	40	137,9
"	50	141,3
"	60	143,5

Summary of the data at the dilutions of 800 & 1600 :—

Table 3.

$\emptyset$	[Co $\begin{matrix} \text{CO}_3 \\ (\text{NH}_3)_4 \end{matrix}$ ] <sub>2</sub> SO <sub>4</sub>	[Co $\begin{matrix} \text{H}_2\text{O} \\ (\text{NH}_3)_5 \end{matrix}$ ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	[Co $\begin{matrix} \text{Cl} \\ (\text{NH}_3)_5 \end{matrix}$ ] <sub>2</sub> SO <sub>4</sub>
800	99,13	217,9	300,4
1600	106,2	265,1	343,9

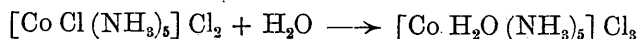
$\emptyset$	[Co $\begin{matrix} \text{Cl H}_2\text{O} \\ (\text{NH}_3)_4 \end{matrix}$ ] <sub>2</sub> SO <sub>4</sub>	[Co $\begin{matrix} \text{Cl}(\text{H}_2\text{O})_2 \\ (\text{NH}_3)_3 \end{matrix}$ ] <sub>2</sub> SO <sub>4</sub>	[Co $\begin{matrix} \text{Cl}(\text{H}_2\text{O})_3 \\ (\text{NH}_3)_2 \end{matrix}$ ] <sub>2</sub> SO <sub>4</sub>
800	218,7	259,2	332,7
1600	259,2	462,9	412,3

As seen in the above tables the carbonatotetrammine cobaltic sulphate is stable in water and shows little variation of conductivity with the dilution. The molecular conductivity at the dilution of 800-1600 is about 100. The conductivity of the aquopentamine cobaltic sulphate varies more with its dilution than that of the carbonatotetrammine cobaltic salt. The dilution from 800 to

that of 1600 causes an increase of about 20%, giving a mean value of about 250. The effect of time will be seen in table 2. It increases 11,5% during one hour. Werner and his co-workers<sup>(1)</sup> had previously expressed both the chemical and electrochemical behaviour of the cobaltammine chlorides by the graphic representation of their molecular conductivities and gave the following data:

Number of ions	Molecular conductivity at the dilution of 1000
2	Approx. 100
3	„ 250
4	„ 480

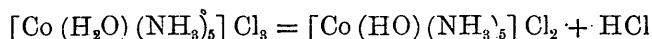
It shows that the number of ions of the cobaltamines is proportional to the conductivity of the salts. While  $[\text{Co CO}_3(\text{NH}_3)_4]_2 \text{SO}_4$  and  $[\text{Co H}_2\text{O}(\text{NH}_3)_5]_2 (\text{SO}_4)_3$  have three and five ions, as well as the molecular conductivities of about 100 and 250 respectively, the chlorocobaltamines mentioned above should have molecular conductivities of less than 100, if there occurs no transformation in water because they have two ions, judging from the molecular formula only. The results of the experiments are contrary to this supposition and show two or three times the required value for the molecular conductivities. They vary very much with the dilution, especially in the triammine and diammine complex salts, which have values approximating to the maximum conductivity of hydrochloric acid, i.e. 403, at a dilution of 1600. The fact that strong acid radicals such as Cl or  $\text{NO}_3$  when coordinated in the cobalt complex nucleus to form a complex salt sometimes show ionic reactions, in other words, dissociate in aqueous solution, was demonstrated by Werner. For example, the purple cobaltammine chloride, if dissolved in water, undergoes to a certain extent the following substitution:



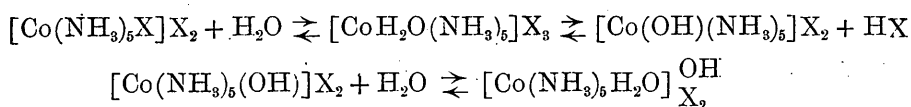
The above system reacts sometimes acidic when the conversion takes place, thus:

(1) Werner: *New Ideas of Inorganic Chemistry*, P 157 & 184.





According to Urbain's<sup>(1)</sup> opinion, such reactions are not so simple and it is more probable that they are in equilibrium under definite surrounding conditions. No doubt the equilibrium can be affected by the atoms, atom groups and molecules coordinated around the central metallic atom, as well as by the atoms and atom groups outside the complex nucleus. One of such complicated examples will be shown below :



The above assumption is exactly in keeping with my experiments. In the case of the diammine and triammine cobalt complex salts the substitutions are apt to take place when the dilution is large. It seems that the absorption spectra of  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}]\text{SO}_4$  confirm the reverse of the conclusion that the chlorine atom is not separated from the complex nucleus, but it can be soon restored, re-establishing the equilibrium.

Thus, I have given a clear explanation, by means of absorption spectra and conductivity measurements, of the substitution phenomena in aqueous solutions of the cobaltamines; in which the strong acid radicals coordinate.

In conclusion, I will describe the complex salt which is obtained by the action of silver nitrate upon  $[\text{CoClC}_2\text{O}_4(\text{NH}_3)_3]$ .

Werner<sup>(2)</sup> gave to it the molecular formula of  $\left[ \begin{matrix} (\text{H}_2\text{O})_2 \\ \text{Co} \\ \text{C}_2\text{O}_4 \\ (\text{NH}_3)_3 \end{matrix} \right] \text{NO}_3$ ,

but I also prepared this salt in the same way and after analysis found it must be amended to  $[\text{CoNO}_3\text{C}_2\text{O}_4(\text{NH}_3)_3]\cdot\text{H}_2\text{O}$ . The following data will confirm this :

0,1023 gr. and 0,1090 gr. of the salt gave 0,0620 gr. and 0,0642 gr.  $\text{CoSO}_4$ . After heating for one hour and a half at the temperature of  $100^\circ\text{--}115^\circ\text{C}$ , it loses the weight of one molecule of water.

(1) Introduction à la Chimie des Complexes (P, 178)

(2) Zeit. anorg. Chem., 15, 162, 1897.

	Theoretical	Observed		
H <sub>2</sub> O	6,92 %	7,20 %	6,15 %	6,42 %
Co	22,68 %	22,65 %	22,41 %	

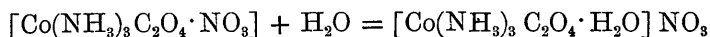
The molecular conductivity of this salt was also measured,

∅	U
500	99,8
1000	105,8

which corresponds to the data given for the salts which have two ions, as the following examples indicate :

∅	[Co(NO <sub>2</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ]Cl	[Co(NO <sub>2</sub> ) <sub>4</sub> (NH <sub>3</sub> ) <sub>2</sub> ]K	[PtCl <sub>3</sub> (NH <sub>3</sub> ) <sub>3</sub> ]Cl	[PtCl <sub>5</sub> NH <sub>3</sub> ]Cl
1000	98,35	99,29	96,75	108,5

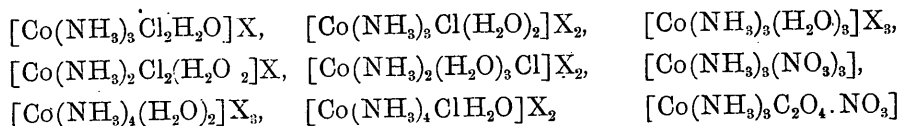
If the compound [Co(NH<sub>3</sub>)<sub>3</sub>C<sub>2</sub>O<sub>4</sub>NO<sub>3</sub>]·H<sub>2</sub>O does not change its constitution in aqueous solution, the conductivity should be zero. Therefore, there is no doubt that the following substitution occurs and gives two ions thus :



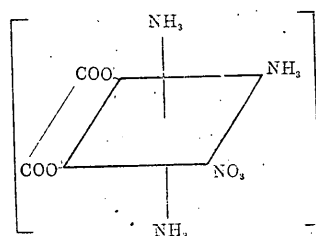
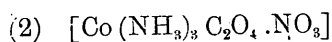
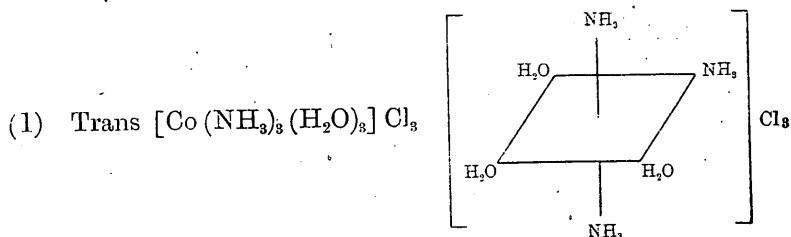
The aqueous solution of the salt shows the reactions of NO<sub>3</sub>, which confirms the above assumption. The fact that the oxalate radical is firmly fixed to the central atom is the parallel phenomenon of the carbonatotetrammine cobaltic salt, which in water is stable. Consequently, it can be generalised that in the cobaltamines the radicals of the strong acids have the less coördinating power, whilst, on the contrary, the radicals of the weak acids, molecules, such as NH<sub>3</sub> and its derivatives and water have the greater coördinating power.

### Summary.

- 1.—I have measured the absorption spectra of the aquocobaltamines and thereby demonstrated the influence of the coördinated water molecules.
- 2.—The stereochemical configurations of the following cobaltamines were thoroughly determined.



3.—The following two new cobalt complex salts were produced.



4.—The formula  $[\text{Co}(\text{NH}_3)_3\text{C}_2\text{O}_4(\text{H}_2\text{O})_2]\text{NO}_3$ , which was given by Werner, must be amended to  $[\text{Co}(\text{NH}_3)_3\text{C}_2\text{O}_4\cdot\text{NO}_3]\cdot\text{H}_2\text{O}$ .

5.—With regard to the substitution reactions of the cobaltamines which have radicals of the strong acids in the complex nucleus, a clear explanation has been given by the study of absorption of light and electrolytic conductivity.

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