ART. XVIII.—*Researches on the Hexatomic compounds of Cobalt;* by WOLCOTT GIBBS, M.D.

[Continued from vol. vi, p. 116, August, 1873.]

5. THE salts described by Fremy* under the names of chloride, nitrate and sulphate of fuscocobalt contain also eight atoms of ammonia, and may be regarded as belonging to the octamin series. These salts have, according to Fremy, respectively the formulas:

$$Co_2(NH_3)_8.O.Cl_4+3OH_2$$
$$Co_2(NH_3)_8.O.(NO_3)_4+3OH_2$$
$$Co_2(NH_3)_8.O.(SO_4)_2+4OH_2$$

in modern notation. They are brown resinous masses, are difficult to obtain in a state of purity, and have as yet been but little studied. If we admit that the formulas are accurate, we may write them in accordance with the theoretic views which I have adopted, as follows:†

$$Co_2\left\{\begin{matrix}NH_3-Cl\\NH_3-Cl\\NH_3-NH_3\\NH_3-NH_3\\NH_3-Cl\\NH_3-Cl\end{matrix}\right\}>O \quad Co_2\left\{\begin{matrix}NH_3-NO_3\\NH_3-NO_3\\NH_3-NH_3\\NH_3-NH_3\\NH_3-NO_3\\NH_3-NO_3\end{matrix}\right\}>O \quad Co\left\{\begin{matrix}NH_3\\NH_3\\NH_3-NH_3\\NH_3-NH_3\\NH_3\\NH_3\end{matrix}\right\}>\begin{matrix}SO_4\\\\O\\\\SO_4\end{matrix}$$

Jörgensen‡ suggests that these salts may contain hydroxyl in place of oxygen. There is at present no method of deciding the question, and I have adopted the view which seems to me the most probable. Künzel's hyposulphate above mentioned may be regarded as belonging to this series, and as having the structural formula:

$$Co_2\left\{\begin{matrix}NH_3\\NH_3\\NH_3-NH_3\\NH_3-NH_3\\NH_3\\NH_3\end{matrix}\right\}>\begin{matrix}S_2O_6\\\\O\\\\S_2O_6\end{matrix}$$

* Ann. de Chimie et de Physique, [3,] tome xxxv, p. 257.

† Blomstrand has given the same formulas with trifling variations. Chemie der *Jetztzeit*, p. 355.

‡ Gmelin-Krauts' Handbuch, vol. iii, p. 468.

but, according to Geuther, the formula given by Künzel must be tripled, and the salt then belongs to the dodekamin or luteocobalt series. In the absence of direct proof of the existence of luteocobalt in this salt, Künzel's formula appears the more probable of the two. The compounds above mentioned, with those which I have myself described, form the only known members of the octamin group, a further study of which will doubtless yield an ample return.

6. *Action of ammonic nitrite on salts of cobalt.*—To obtain a clear view of the nature and mode of formation of the salts of xanthocobalt, I have carefully studied the relations of ammonic nitrite to salts of cobalt under different conditions. This subject has already been examined by Erdmann, and in my laboratory by Sadtler. Erdmann found that when a neutral solution of cobaltic chloride is mixed with a neutral solution of ammonic nitrite no turbidity ensues, but after spontaneous evaporation in the air a salt crystallizes, with the formula, as Erdmann writes it (old style):

$$Co_2\widehat{O_3.2}NH_3,\ 3NO_3+NH_4O,\ NO_3.$$

This salt is isomorphous with the corresponding potassium salt, the crystals belonging to the rhombic system. Erdmann does not explain the reaction which takes place in the formation of this or the corresponding potassium salt, and regards the compounds in question as double salts. When slightly acid solutions were employed, Erdmann obtained, in addition to the above mentioned salt, an ammonic salt corresponding to Fischer's salt, $Co_2(NO_2)_{12}(NH_4)_6+3OH_2$, as we should now write it. The existence of this salt was first remarked by Genth and myself.* Sadtler studied the action of ammonic nitrite on acid solutions of cobaltic chloride, and obtained two salts having respectively the formulas:

$$Co_2(NO_2)_{10}(NH_4)_4+2OH_2$$
$$Co_2(NO_2)_{12}(NH_4)_6+2OH_2,$$

but did not observe the formation of Erdmann's ammonium salt. In repeating these experiments I always obtained Erdmann's ammonium salt, $Co_2(NH_3)_4(NO_2)_8(NH_4)_2$, in largest quantity. The crystals are uncommonly beautiful and well defined. Of these crystals

0·3390 gr. gave 0·1783 gr. $SO_4Co$=20·02 per cent.

The formula requires 20·00 per cent. In one experiment, in which a little free acetic acid was present, I obtained large dark sherry-wine colored prismatic crystals, which after solution and recrystallization gave only very thin lozenge-shaped tabular

* This Journal, 2d Series, vol. xxiv, p. 86.

crystals, the form and appearance of which are highly characteristic. These crystals gave no reactions with salts of luteocobalt, purpureocobalt and roseocobalt, and none with potassic chromate and dichromate, ammonic oxalate or argentic nitrate. The absence of the first mentioned reactions shows that they do not contain $Co_2(NH_3)_4(NO_2)_8$ or $Co_2(NO_2)_{12}$, while the fact that they give no reactions with alkaline chromates and oxalates shows that they do not contain any known cobaltamin. Of these crystals

0·1554 gr. gave 0·0974 gr. $SO_4Co$ = 23·86 per cent cobalt.
0·3081 gr. gave 0·0635 gr. $NH_3$ = 20·61 per cent ammonia.

The formula $Co_2(NH_3)_6(NO_2)_6$ requires

| | | |
|---|---|---|
| Cobalt, | 23·79 | 23·86 |
| Ammonia, | 20·56 | 20·61 |

These analyses are sufficient to identify the salt in question with one which Erdmann has described in the paper referred to, as formed by the action of ammonia and potassic nitrite upon cobaltic chloride, unfortunately with but very scanty details. I attribute to this salt the formula

$$Co_2 \begin{cases} NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \end{cases}$$

and consider it to be the nitrous representative of the hexamin $Co_2(NH_3)_6$. I have not succeeded in obtaining from it other members of the same series; but it is, to say the least, probable that the dichrocobalt-chloride of Fr. Rose,* $Co_2(NH_3)_6Cl_6)+2OH_2$, represents the corresponding chloride. Künzel† has described a sulphite to which he attributes the formula

$$Co_2(NH_3)_6(SO_3)_3+OH_2,$$

but according to Geuther† this formula must be doubled, the salt belonging to the dodekamin or luteocobalt series, with the formula

$$Co_2(NH_3)_{12}(SO_3)_6+Co_2(SO_3)_6+2OH_2.$$

Erdmann's hexamin salt is of special interest because, as I shall show, it forms the first term in a remarkable series of metameric bodies; its formation under the circumstances may with great probability be expressed by the equation:

$$2CoCl_2+10NH_4.NO_2+3O=Co_2(NH_3)_6(NO_2)_6+4NH_4Cl+3OH_2,$$

* Untersuchungen über ammoniakalische Kobalt-Verbindungen. Heidelberg. 1871.

† Journal für prakt. Chemie, 72, p. 209. ‡ Ann. de Pharmacie, 128, p. 127.

as the salt is not formed immediately, but only after absorption of oxygen from the air. The formation of Erdmann's ammonium salt may in like manner be represented by the equation:

$$2CoCl_2+8NH_4.NO_2+2O=Co_2(NH_3)_4(NO_2)_8+4NH_4Cl+2OH_2,$$

the presence of oxygen being necessary in this case also.

In another experiment I obtained no hexamin nitrite, but only Erdmann's ammonium salt and the two salts described by Sadtler, and to which he gave respectively the formulas:

$$Co_2(NO_2)_{10}(NH_4)_4+2OH_2$$
$$Co_2(NO_2)_{12}(NH_4)_6+2OH_2.$$

These last salts were found in considerable quantity mixed together as a yellow sparingly soluble crystalline powder, when a strong solution of ammonic nitrite was poured upon finely pulverized cobaltic chloride, and acetic acid was added in small excess. I consider the formation of these two salts to be represented by the equations:

$$2CoCl_2+10NH_4.NO_2+3O=Co_2(NO_2)_{10}(NH_4)_4+6NH_3+3OH_2$$
$$2CoCl_2+12NH_4.NO_2+3O=Co_2(NO_2)_{12}(NH_4)_4+8NH_3+3OH_2.$$

Professor Sadtler has shown that in these cases also an absorption of oxygen from the air takes place. When a solution of ammonic nitrite is added to a strong alcoholic solution of cobaltic chloride, Erdmann's ammonium salt, $Co_2(NH_3)_4(NO_2)_8(NH_4)_2$, is chiefly formed, and only a small quantity of the four and six-atom salts. The compound formed crystallizes from the alcoholic solution in very beautiful and well defined prismatic forms.

From the above it will be seen that at least four distinct compounds are formed by the action of ammonic nitrite upon solutions of cobaltic chloride in presence of a weak acid and of the oxygen of the air. It is at least probable that all four are formed at the same time, though in varying proportions. I have already shown that, in the presence of free ammonia and of ammonic nitrate, cobaltic chloride and ammonic nitrite yield the nitrate of the octamin series. Of the action of ammonic nitrite upon cobaltic salts in the presence of free ammonia, I shall speak in treating of the formation of the salts of xantho-cobalt.

7. I have stated above that Erdmann obtained the hexamin nitrite, $Co_2(NH_3)_6(NO_2)_6$, by the joint action of potassic nitrite and ammonia upon cobaltic chloride. On repeating his experiments, I found that small quantities of this salt were formed, but that the chief products of the action were salts of xantho-cobalt, the formation of which Erdmann does not appear to have noticed. Small quantities of salts of the octamin series are also formed. The filtered solution obtained in this reaction

was precipitated by potassic dichromate, and the orange-red needles obtained recrystallized for analysis; of these crystals

0·6145 gr. gave 0·7393 gr. $CrO_4Ba$=51·40 per cent $Cr_2O_7$.
0·7712 gr. gave 0·9277 gr. $CrO_4Ba$=51·40 per cent $Cr_2O_7$.
0·5615 gr. gave 96·5 c.c. nitrogen (moist) at 15° C. and $763^{mm}·1$= 20·12 per cent nitrogen.
0·5028 gr. gave 86 c.c. nitrogen (moist) at 15° C. and $763^{mm}·1$= 20·05 per cent nitrogen.

The formula $Co_2(NH_3)_{10}(NO_2)_2Cr_2O_7$ requires 53·22 per cent $Cr_2O_7$ and 20·67 per cent nitrogen, while the formula of the octamin salt, $Co_2(NH_3)_8(NO_2)_4Cr_2O_7$, requires 32·91 per cent $Cr_2O_7$ and 19·30 per cent nitrogen, so that the analyses leave no reasonable doubt that the salt was a mixture of a salt of xanthocobalt with a smaller proportion of the corresponding salt of the octamin series.

The above results clearly show that the action of ammonic nitrite upon salts of cobalt in presence of free acid is extremely complex, not less than six classes of salts being formed, of which two belong certainly to basic series, while three may be regarded as salts of ammonium. The sixth, $Co_2(NH_3)_6(NO_2)_6$, is probably also one term in a hexamin series.

8. The ammonia-nitrites discovered by Erdmann are of especial interest. They present the first and at present the only known instance in which cobalt, by uniting with ammonia and nitroxyl, $NO_2$, forms an electro-negative or chlorous radical. The compound $Co_2(NH_3)_4(NO_2)_8$ may be regarded as existing in combination with two atoms of a mon-atomic radical, exactly as the compound $Co_2(NH_3)_8(NO_2)_4$ combines with two atoms of chlorine. The structural formulas may be written respectively:

$$Co_2\begin{cases} NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NO_2 \\ NH_3-NO_2 \end{cases} \qquad Co_2\begin{cases} NH_3-NO_2 \\ NH_3-NO_2 \\ N<\begin{matrix}O\\O\end{matrix}>N-O-OK \\ N<\begin{matrix}O\\O\end{matrix}>N-O-OK \\ NH_3-NO_2 \\ NH_3-NO_2 \end{cases}$$

With these formulas we may advantageously compare those of chloride of luteocobalt, of Fischer's salt considered as anhydrous, and of chloride of xanthocobalt:

$$Co_2\begin{cases} NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \end{cases} \qquad Co_2\begin{cases} N<\overset{O}{\underset{O}{>}}N-O-OK \\ N<\overset{O}{\underset{O}{>}}N-O-OK \\ N<\overset{O}{\underset{O}{>}}N-O-OK \\ N<\overset{O}{\underset{O}{>}}N-O-OK \\ N<\overset{O}{\underset{O}{>}}N-O-OK \\ N<\overset{O}{\underset{O}{>}}N-O-OK \end{cases}$$

$$Co_2\begin{cases} NH_3-NO_2 \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NO_2 \end{cases}$$

The manner in which these compounds may be derived from each other by replacement is sufficiently obvious, and is best seen by assuming chloride of luteocobalt and Fischer's salt as the two extreme terms of the series in which the other three are intermediate.

Erdmann's analyses leave no reasonable doubt as to the constitution of the ammonia-nitrites. I have thought it worth while, however, to make a few additional analyses in support of his view. In the potassium salt:

0·4497 gr. gave 0·3397 gr. $SO_4Co$ and $SO_4K_2$=75·54 per cent.
0·7338 gr. gave 0·5615 gr. " " =76·52 per cent.
0·5937 gr. gave 127 c.c. nitrogen at 6°·5 C. and 773$^{mm}$·4=26·45 per cent nitrogen.

The formula $Co_2(NH_3)_4(NO_2)_8K_2$ requires 76·58 per cent $2SO_4Co+SO_4K_2$ and 26·58 per cent nitrogen. In the silver salt:

0·3580 gr. gave 0·2902 gr. $SO_4Co$ and $SO_4Ag_2$.
0·5937 gr. gave 0·1675 gr. silver=28·21 per cent.

The cobalt by difference amounts to 15·33 per cent. The formula $Co_2(NH_3)_4(NO_2)_8Ag_2$ requires 28·05 per cent silver and 15·32 per cent cobalt.

*Thallium salt.*—When a solution of the potassium salt is added to one of thallous nitrate, a beautiful sherry-wine-colored crystalline precipitate is thrown down, which on recrystallization gives very well defined prismatic crystals, having apparently the same form as the corresponding potassium and ammonium salts.

*Mercurous salt.*—A solution of potassic ammonia-cobalt-nitrite gives immediately in solutions of mercurous nitrate a beautiful

orange-colored crystalline precipitate, which may be dissolved in boiling water, but not without partial decomposition. The salt does not crystallize well from the solution. Of this salt:

0·7785 gr. gave 0·1775 gr. $SO_4Co$=8·68 per cent cobalt.

The formula $Co_2(NH_3)_4(No)_2(Hg_2)_2$ requires 8·71 per cent.

A solution of the potassic salt gives no precipitate with salts of cobalt, nickel, barium and copper, and none at first with plumbic acetate. After standing, however, a lead salt separates in fine acicular leafy crystals of a brown-orange color, soluble in hot water, but with partial decomposition. The same is true of the silver salt, but small quantities of this may usually be dissolved and recrystallized without change. The silver salt is extremely well characterized; its moderate degree of solubility and the facility with which it crystallizes in tabular lustrous crystals have made it of great service in my investigations, especially in distinguishing salts containing $Co_2(NH_3)_4(NO_2)_8$ from those which contain $Co_2(NO_2)_{12}$. Compounds of ammonia-cobalt-nitrite with barium, strontium, etc., are easily formed by double decomposition, the metallic chlorides being digested with a solution of the argentic salt. They are pale orange-yellow, soluble salts, which I have not further examined. A solution of the potassic salt gives beautiful crystalline precipitates with salts of various organic alkaloids, especially with those of brucin and strychnin. These are soluble in hot water without sensible decomposition, and may be recrystallized. Salts of anilin give a bright yellow precipitate with potassic ammonia-cobalt-nitrite, which is, however, immediately decomposed, phenol being set free. The potassic salt gives also splendid crystalline precipitates with salts of croceocobalt, xanthocobalt, luteocobalt, etc. I have already noticed the salt of croceocobalt, and will describe the salts of the other bases in due course.

Erdmann has not attempted to explain the formation of this class of salts. He remarks that a yellow insoluble compound is formed at the same time with the potassic salt $Co_2(NH_3)_4(NO_2)_8K_2$, which appears to be a mixture which cannot be obtained pure for analysis. I have also obtained this body, and also regard it as consisting mainly of Fischer's salt, $Co_2(NO_2)_{12}K_6$, though as Erdmann states, it contains a small percentage of ammonia. The formation of the salt $Co_2(NH_3)_4(NO_2)_8K_2$ may be expressed by the equation

$$2CoCl_2+4NH_4Cl+8KNO_2+O=Co_2(NH_3)_4(NO_2)_8K_2+6KCl+2HCl+OH_2,$$

if we suppose oxygen to be absorbed from the air. In consequence, however, of the formation of free chlorhydric acid, $N_2O_3$ is set free, and it is much more probable that this is reduced by the nascent-hydrogen; so that we have

$$N_2O_3+2H=2NO+OH_2.$$

The potassium salt is also formed, as I shall show, in various other cases; the similarity of some of its reactions to those of a solution of $Co_2(NO_2)_{12}Na_6$ in sodic nitrite for a long time misled me; but its relations to salts of silver, mercury and thallium enable us to recognize its presence with absolute certainty. The salt does not enter into combination with iodine.

### XANTHOCOBALT.

9. Genth and I have shown in our memoir that the salts of xanthocobalt may be formed either directly by the action of nitrous acid vapors upon salts of cobalt, or by the action of the same acid upon salts of purpureocobalt and roseocobalt, in each case in the presence of free ammonia. I propose now to give the results of a more detailed study of the subject.

With respect to the constitution of this class of salts, I may remark, in the first place, that Genth and I left it undecided whether the salts in question contain NO or $NO_2$, pointing out the fact that the analyses do not decide in favor of either view, and adopting the former provisionally. Braun first proved conclusively that the salts of xanthocobalt contain $NO_2$, and this view has since been generally adopted. I have already shown (§ 1) that when cobaltic chloride, $CoCl_2$, is mixed with ammonia and ammonic nitrite and nitrate, the solution absorbs oxygen from the air, while the nitrate of the octamin series, $Co_2(NH_3)_8(NO_2)_4(NO_3)_2$, is formed. I have not observed in this reaction the formation of a salt of xanthocobalt. If present at all, such salts must be in very small relative quantity. Genth and I have shown, on the other hand, that when the red gases resulting from the action of nitric acid upon starch, sawdust or arsenous oxide are passed into solutions of cobaltic salts in presence of an excess of ammonia, salts of xanthocobalt are formed in a very short time, and in large quantity.

If we consider the red gas to consist of hyponitric oxide, $N_2O_4$, we may have

$$2Co(NO_3)_2 + 10NH_3 + N_2O_4 = Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4.$$

In preparing sulphate and nitrate of xanthocobalt by this process, I have on several occasions been able to detect only salts of this base among the products of the reaction. In one case, however, in which I employed cobaltic sulphate and added so large a quantity of ammonic sulphate that the solution gave no precipitate with ammonia, I obtained a very large relative quantity of Erdmann's salt $Co_2(NH_3)_6(NO_2)_6$. In other cases in which cobaltic chloride was present I detected crystals of the chloronitrate $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2$. The solutions after the action of the red gases also contain small quantities of the ammonia-cobalt-nitrite of ammonium, $Co_2(NH_3)_4(NO_2)_5(NH_4)_2$, as well as ammonic nitrite and nitrate.

On the other hand, however, I have already shown (§ 3) that salts of this radical are formed in large quantity, together with a smaller proportion of the octamin nitrate, by the action of a mixture of potassic nitrite and ammonia upon cobaltic nitrate in presence of air; but that xanthocobalt is exclusively formed by the action of the same mixture upon a solution of ammonic and cobaltic sulphates. I am unable to offer any plausible explanation for the difference of the products in the two cases.

When cobaltic nitrate, ammonic nitrite and ammonia are mixed and placed in a tightly-corked bottle, no action whatever appears to take place, even after the mixture has stood some days. But if plumbic hyperoxide, $PbO_2$, is added, the mixture soon becomes yellow, and after a few hours large crystals of nitrate of xanthocobalt are formed with distinct reduction of the plumbic hyperoxide. The reaction in this case may be represented by the equation:

$$2Co(NO_3)_2+10NH_3+2NO_2.NH_4+PbO_2=Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4+PbO+(NH_4)_2O.$$

Potassic hypermanganate may also be employed as an oxidizing agent, but is less convenient. The experiment just detailed appears to me to render it most probable that in the action of the red gases upon salts of cobalt in presence of ammonia, the resulting salts of xanthocobalt are not formed by the direct union of the cobaltic salt with ammonia and nitroxyl, but that ammonic nitrite is first formed, and that the oxygen necessary for the completion of the reaction is derived from the decomposition of some element of the complex mixture of NO, $NO_2$, $N_2O_3$ and $NO_3H$, which make up the red vapors.

The formation of salts of xanthocobalt by the action of the red gas upon salts of purpureocobalt and roseocobalt in the presence of free ammonia is easily explained. We have here simple cases of double decomposition, a particular instance of which, covering in substance the whole ground, may be expressed by the equation:

$$Co_2(NH_3)_{10}(NO_3)_6+2NH_4.NO_2=Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4+2NO_3.NH_4.$$

Salts of xanthocobalt are always formed when salts of purpureocobalt and roseocobalt are heated or even digested in the cold with alkaline nitrites. I have made a special study of the action of potassic and sodic nitrites upon chloride of purpureocobalt, the details of which are as follows:

10. *Action of sodic and potassic nitrites upon chloride of purpureocobalt.*—A quantity of chloride of purpureocobalt was dissolved in boiling water, with a little free acetic acid to prevent decomposition, and added to a hot solution of potassic nitrite in excess. The dark brown-red solution was evaporated at a

gentle heat to half its volume. On cooling, a small quantity of Fischer's salt $Co_2(NO_2)_{12}K_6+2OH_2$ separated; afterward sherry-wine colored prismatic crystals were formed in abundance. After recrystallization these were analyzed.

0·2824 gr. gave 0·1519 gr. $CoSO_4$=20·47 per cent cobalt.
0·5557 gr. gave 0·2092 gr. silver=12·37 per cent chlorine.

The same experiment was made with sodic nitrite, and with similar results. After two recrystallizations the salt formed was analyzed.

0·4163 gr. gave 0·2235 gr. $CoSO_4$=20·43 per cent cobalt.
0·2332 gr. gave 0·0876 gr. silver=12·38 per cent chlorine.
0·6625 gr. gave 192·12 c.c. nitrogen (moist) at 14° C. and 764$^{mm}$·1 =34·29 per cent.
1·2310 gr. gave 0·5825 gr. water=5·24 per cent hydrogen.
1·6542 gr. gave 0·7996 gr. water=5·37 per cent hydrogen.

The salt being found anhydrous, the analyses agree with the formula:

$$Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2,$$

which requires

| | | Found. | |
|---|---|---|---|
| Cobalt | 20·52 | 20·47 | 20·43 |
| Chlorine | 12·34 | 12·37 | 12·38 |
| Hydrogen | 5·26 | 5·24 | 5·37 |
| Nitrogen | 34·09 | 34·29 | |

and which is fully sustained by other considerations, as I shall show. As the solutions of the alkaline nitrites employed also contained nitrates, the formation of the new salt may be represented by the equation:

$$Co_2(NH_3)_{10}Cl_6+2KNO_2+2KNO_3=4KCl+Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2.$$

The salt itself is then a nitroso-chloro-nitrate, and belongs probably to the $\alpha$-dekamin or purpureocobalt series; but it may be more conveniently regarded as the chloro-nitrate of xantho-cobalt. It has the wine color of the salts of the so-called xantho-cobalt series, but crystallizes usually in prismatic forms, which are moderately soluble in hot water, and separate readily from the solution. With neutral potassic chromate the salt gives the beautiful yellow crystalline chromate of xanthocobalt:

$$Co_2(NH_3)_{10}(NO_2)_2(CrO_4)_2+2OH_2.$$

With potassic ferrocyanide it gives the characteristic red prismatic crystals of

$$Co_2(NH_3)_{10}(NO_2)_2FeCy_6+6OH_2,$$

and with ammonic oxalate, oxalate of xanthocobalt,

$$Co_2(NH_3)_{10}(NO_2)_2(C_2O_4)_2,$$

the reactions being too obvious to require explanation by equations.

As it is difficult to prevent the action of the alkaline nitrites upon chloride of purpureocobalt from going too far and decomposing the new salt first formed, I had recourse to a different mode of preparation, by which the salt can be prepared in any quantity and with the greatest facility. A hot solution containing one molecule of chloride of xanthocobalt was mixed with a solution containing one molecule of nitrate of xanthocobalt. On cooling, the nitroso-nitro-chloride crystallized in beautiful prismatic forms. In this case we have

$$Co_2(NH_3)_{10}(NO_2)_2Cl_4+Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4=2Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2.$$

Of the crystals so formed

0·6203 gr. gave 0·3310 gr. $CoSO_4$=20·31 per cent cobalt.
0·9268 gr. gave 0·3450 gr. silver=12·24 per cent chlorine.

The formula requires 20·51 per cent cobalt and 12·34 per cent chlorine. A portion of the crystallized salt was dissolved and precipitated by argentic nitrate. The filtrate from AgCl gave on evaporation crystals of nitrate of xanthocobalt, in which

0·2972 gr. gave 0·1469 gr. $CoSO_4$=18·81 per cent cobalt.

The formula of the nitrate requires 18·73 per cent. These results leave no doubt as to the constitution and true relations of the chloro-nitrate.

*Gold salt.*—When the chloro-nitrate is dissolved and a solution of aurochloride of sodium, $AuCl_4Na$, is added in excess, long prismatic wine-yellow crystals are formed. Of these crystals

0·8564 gr. decomposed by zinc and sulphuric acid gave 0·6300 gr. silver=24·16 per cent chlorine and 0·2858 gr. gold=33·36 per cent.
0·4084 gr. gave 0·1770 gr. Au+Co=43·34 per cent and by difference 9·98 per cent cobalt.

This formula, $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2+2AuCl_3$, requires

| | | Found. |
|---|---|---|
| Cobalt | 9·98 | 9·98 |
| Gold | 33·33 | 33.36 |
| Chlorine | 24·03 | 24·16 |

The salt is readily decomposed by boiling with reduction of metallic gold.

*Platinum salt.*—Platinic chloride in solution precipitates the chloro-nitrate almost immediately in the form of wine-yellow needles. After recrystallization this salt was analyzed with the following results:

0·6405 gr. fused with potassio-sodic carbonate gave 0·5564 gr. silver=28·55 per cent chlorine, 0·1986 gr. platinum=31·00 per cent, and 0·0597 gr. cobalt=9·33 per cent.

The platinum and cobalt were weighed together as metals after reduction by hydrogen, and the cobalt was then dissolved by long boiling with nitric acid.

This formula, $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2 + 2PtCl_4$, requires

| | | Found. |
|---|---|---|
| Cobalt | 9·40 | 9·33 |
| Platinum | 31·55 | 31·00 |
| Chlorine | 28·28 | 28·55 |

The salt had no water on heating to 140° C.

(To be continued.)