CXXXVIII.—*A New Method of Preparing Chloro- and Bromo-triammino-platinous Haloids (Cleve's Salts).*

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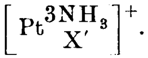
AMONG the salts of ammoniacal platinum bases corresponding with the general formula PtX_2,nNH_3, where the platinum atom is bivalent, the so-called Cleve's salts, in which $n=3$, are of special interest. According to Werner's well-known theory, these salts possess the co-ordination structure $[PtX'3NH_3]X''$, where only one of the two acid radicles (X'') shows the character of an ion, whilst the other radicle (X') is in comparatively stable union with the platinum atom, and enters into the composition of the complex cation  $\left[\mathrm{Pt}\begin{matrix}3NH_3\\X'\end{matrix}\right]^+$.

Unfortunately, hitherto but few investigations have been made on compounds of this type. Nearly all the information we possess on this subject is found in the work of Cleve ("On ammoniacal platinum bases," Stockholm, 1872), who discovered these compounds, a few new data being given by subsequent workers, especially by Cossa (*Atti R. Accad. Lincei*, 1894, ii, 360) and by Klason (*J. pr. Chem.*, 1903, [ii], **67**, 1).

The chloride, $\left[\mathrm{Pt}{}^{3\mathrm{NH}_3}_{\mathrm{Cl}}\right]\mathrm{Cl}$, which has been more fully investigated than the other salts of the series $\left[\mathrm{Pt}{}^{3\mathrm{NH}_3}_{\mathrm{Cl}}\right]\mathrm{X}$, is obtained either by the addition of ammonia to dichlorodiamminoplatinum $\left[{}^{\mathrm{NH}_3}_{\mathrm{NH}_3}\mathrm{Pt}{}^{\mathrm{Cl}}_{\mathrm{Cl}}\right]$, or by the elimination of ammonia from tetra-amminoplatinous chloride (Reiset's Base I), $[\mathrm{Pt4NH_3}]\mathrm{Cl_2}$, by the action of hydrochloric acid:

$$[\mathrm{PtCl_2 2NH_3}] + \mathrm{NH_3} = [\mathrm{PtCl3NH_3}]\mathrm{Cl},$$
$$[\mathrm{Pt4NH_3}]\mathrm{Cl_2} + \mathrm{HCl} = [\mathrm{PtCl3NH_3}]\mathrm{Cl} + \mathrm{NH_4Cl}.$$

Both these methods, however, give only poor, and always varying, yields.

The following convenient method by which the chloride, $[\mathrm{PtCl3NH_3}]\mathrm{Cl}$, can be prepared quickly and easily in any amount will now be described.

The defects of the previous methods consist in the fact that the union and the elimination of ammonia cannot be stopped at the stage required. That is the reason why, in the case of the addition of ammonia, the chloride of Reiset's base I (containing more ammonia than is required) is obtained as a main product of reaction, whilst in the case of the elimination of ammonia Reiset's base II (poorer in ammonia) is formed.

These difficulties were overcome by employing, for the addition of ammonia to the compound, $[\mathrm{PtCl_2 2NH_3}]$, some compound which evolves ammonia gradually when hydrolysed, instead of using free ammonia. The salts of cyanic acid have been found the most convenient for this purpose.

EXPERIMENTAL.

One gram of *cis*dichlorodiamminoplatinum (Peyrone's chloride) is boiled with 0·7 gram of potassium cyanate and 18—20 c.c. of water, the whole being frequently shaken. After the dissolution of the dichlorodiamminoplatinum, the boiling is continued during one minute, the whole reaction requiring about two minutes. (The experiment is most conveniently carried out in a large test-tube).

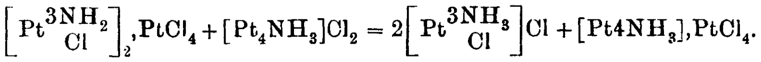
Several portions prepared in this way are poured in a beaker, and an excess of hydrochloric acid (D 1·19) is gradually added, 4 c.c. of the acid being used for each portion. The whole is heated to boiling, and then cooled. A considerable part of the dichloroamminoplatinum, which is left unchanged, crystallises out, and is filtered off; an excess of potassium patinochloride is then added to the filtrate until no more precipitate is formed. The precipitate thus obtained consists of a mixture of tetra-amminoplatinous platinochloride (Magnus's green salt) and of chlorotriamminoplatinous platinochloride (Cleve's salt), $[PtCl3NH_3]_2,PtCl_4$. The latter is flesh-coloured, and crystallises from hot water in characteristic, square-shaped plates, as described by Cleve.

The precipitate is collected and recrystallised from hot water acidified with a few drops of hydrochloric acid, about 40 c.c. of water being used for each gram of dichlorodiamminoplatinum taken.

By this treatment, practically only the chlorotriamminoplatinous platinochloride passes into solution, the tetra-amminoplatinous platinochloride being left behind; the hot filtrate is then left to crystallise overnight.

The yield of chlorotriamminoplatinous platinochloride obtained under these conditions is regularly about 50 per cent. of the theoretical calculated only on the part of the dichlorodiamminoplatinum which actually enters into the reaction. Thus, in one experiment, where 4 grams of dichlorodiamminoplatinum were taken, was obtained: chlorotriamminoplatinous platinochloride, 1·5 grams; dichlorodiamminoplatinum recovered, 1·9 grams; tetra-amminoplatinous platinochloride, 1·0 grams. The amount of dichlorodiamminoplatinum used was therefore 2·1 grams, and in this case the yield is 48 per cent. of the theoretical.

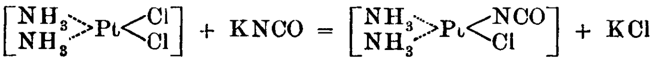
For the preparation of the chloride, $[PtCl3NH_3]Cl$, the method described by Cleve and by Clason is used. The platinochloride, $[PtCl3NH_3]_2,PtCl_4$, is dissolved in hot water slightly acidified with hydrochloric acid, and is precipitated with tetra-amminoplatinous chloride:



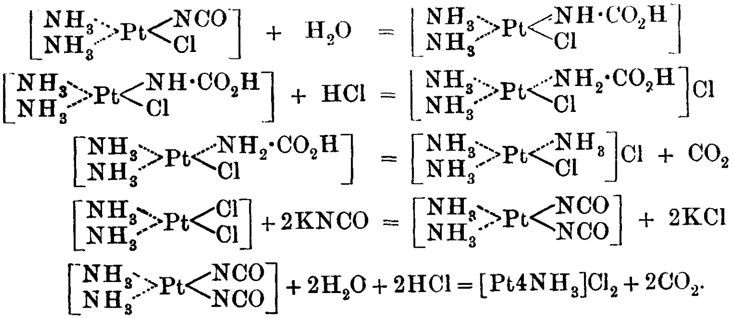
$$\left[Pt\begin{matrix}3NH_2\\Cl\end{matrix}\right]_2,PtCl_4+[Pt_4NH_3]Cl_2=2\left[Pt\begin{matrix}3NH_3\\Cl\end{matrix}\right]Cl+[Pt4NH_3],PtCl_4.$$

The cooled solution is then filtered from the tetra-amminoplatinous platinochloride formed, and evaporated in a vacuum.

The reactions resulting from the action of potassium cyanate on dichlorodiamminoplatinum, and the subsequent action of the hydrochloric acid, may be probably represented by the following equations:



$$\left[\begin{matrix}NH_3\\NH_3\end{matrix}{>}Pt{<}\begin{matrix}Cl\\Cl\end{matrix}\right]+KNCO=\left[\begin{matrix}NH_3\\NH_3\end{matrix}{>}Pt{<}\begin{matrix}NCO\\Cl\end{matrix}\right]+KCl$$



$$\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NCO}\\\mathrm{Cl}\end{matrix}\right]+\mathrm{H_2O}=\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NH\cdot CO_2H}\\\mathrm{Cl}\end{matrix}\right]$$

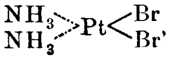
$$\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NH\cdot CO_2H}\\\mathrm{Cl}\end{matrix}\right]+\mathrm{HCl}=\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NH_2\cdot CO_2H}\\\mathrm{Cl}\end{matrix}\right]\mathrm{Cl}$$

$$\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NH_2\cdot CO_2H}\\\mathrm{Cl}\end{matrix}\right]=\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NH_3}\\\mathrm{Cl}\end{matrix}\right]\mathrm{Cl}+\mathrm{CO_2}$$

$$\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right]+2\mathrm{KNCO}=\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NCO}\\\mathrm{NCO}\end{matrix}\right]+2\mathrm{KCl}$$

$$\left[\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{NCO}\\\mathrm{NCO}\end{matrix}\right]+2\mathrm{H_2O}+2\mathrm{HCl}=[\mathrm{Pt4NH_3}]\mathrm{Cl_2}+2\mathrm{CO_2}.$$

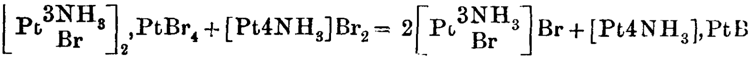
If in the reaction described above, instead of dichlorodiamminoplatinum, the corresponding bromine compound,



$$\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{Br}\\\mathrm{Br}\end{matrix},$$

is used, and the hydrochloric acid in the subsequent operations replaced by hydrobromic acid, a solution containing the salt, $[\mathrm{PtBr3NH_3}]\mathrm{Br}$, together with tetra-amminoplatinous bromide, $[\mathrm{Pt4NH_3}]\mathrm{Br_2}$, is obtained. From this solution, a copious precipitate is produced by the addition of potassium platinobromide. This precipitate consists of a mixture of two different compounds, which can be easily separated from one another by crystallisation from hot water acidified with a few drops of hydrobromic acid. The green platinobromide, $[\mathrm{Pt4NH_3}],\mathrm{PtBr_4}$, already prepared by Biilmann and Andersen (*Ber.*, 1903, **36**, 1565), is left on the filter, whilst a new compound, which has not yet been described, is contained in the filtrate, and separates on cooling in violet plates; these are sometimes of a curiously waved shape, and are comparatively readily soluble in hot water.

From the analytical data and its chemical behaviour, this compound consists of bromotriamminoplatinous platinobromide, $[\mathrm{PtBr3NH_3}]_2,\mathrm{PtBr_4}$, being an analogue of the platinochloride, $[\mathrm{PtCl3NH_3}]_2,\mathrm{PtCl_4}$. It crystallises with 1 mol. of water, which it readily loses at 100°. From solutions of this compound tetra-amminoplatinous salts precipitate Biilmann and Andersen's green platinobromide, a fact indicating the presence of the ion $[\mathrm{PtBr_4}]$:



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{3NH_3}\\\mathrm{Br}\end{matrix}\right]_2,\mathrm{PtBr_4}+[\mathrm{Pt4NH_3}]\mathrm{Br_2}=2\left[\mathrm{Pt}\begin{matrix}\mathrm{3NH_3}\\\mathrm{Br}\end{matrix}\right]\mathrm{Br}+[\mathrm{Pt4NH_3}],\mathrm{PtBr_4}.$$

The study of the reactions described in this paper is being continued in this laboratory.

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