

Citation:

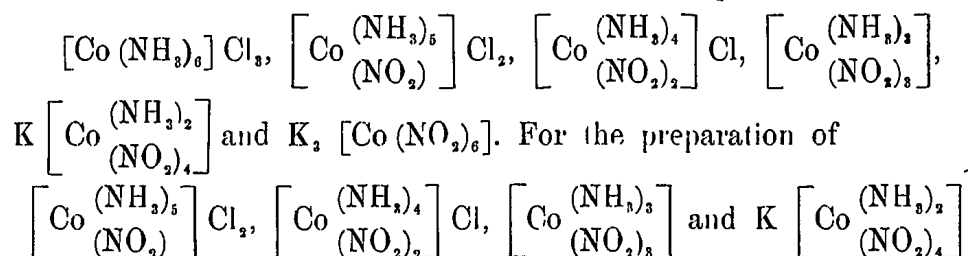
Os, Ch. H. van, Notes on Cobaltammines, in:
KNAW, Proceedings, 22 II, 1920, Amsterdam, 1920, pp. 576-579

Chemistry. — “Notes on Cobaltamines”. By NIL RATAN DHAR.
(Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of November 29 1919).

In two previous investigations (Zeit. Anorg. Chem. 1913, **80**, 43; **84**, 224) I had occasion to study certain properties of the cobaltamines. This note is the result of the continuation of my previous work.

1. Let us consider the following series of compounds



the general method of procedure is to mix a cobalt salt, ammonium chloride, ammonium hydroxide and a nitrite; by this a complex cobaltous compound is formed which is turned into the stable cobaltic compound by oxidation. The amount of a certain compound which will be formed, depends on the concentration of the reacting substances and on the solubility of the resulting complex compound. If the concentration of the nitrite in the solution is large in comparison with the concentrations of ammonium hydroxide and ammonium chloride, we should expect that several (NO_2) groups would enter the complex.

It has been known from a long time that aquopentamine salts can be converted into the corresponding hexamine salts by heating the aquo compound with ammonia in a sealed tube or in a bottle under pressure.

I found that if $\left[\text{Co} \begin{matrix} (\text{NH}_3)_5 \\ (\text{NO}_2)_1 \end{matrix} \right] \text{Cl}_2$ is warmed with a dilute solution of sodium or potassium nitrite, we get mainly $\left[\text{Co} \begin{matrix} (\text{NH}_3)_4 \\ (\text{NO}_2)_2 \end{matrix} \right] \text{Cl}$, which could be purified by recrystallisation.

In a similar way croceo cobalt chloride $\left[\text{Co} \begin{matrix} (\text{NH}_3)_4 \\ (\text{NO}_2)_2 \end{matrix} \right] \text{Cl}$ can be

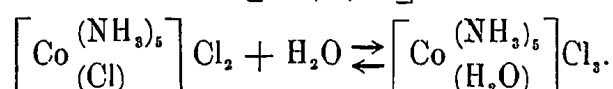
converted into $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{NO}_2)_3 \end{smallmatrix} \right]$ by warming it with a dilute solution of a nitrite, whilst $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{NO}_2)_3 \end{smallmatrix} \right]$ can be converted into $\text{K} \left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_4 \\ (\text{NO}_2)_4 \end{smallmatrix} \right]$ by warming $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{NO}_2)_3 \end{smallmatrix} \right]$ with a concentrated solution of potassium nitrite, ammonia escaping from the solution.

I tried to prepare the compound $\text{K}_2 \left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ (\text{NO}_2) \end{smallmatrix} \right]$, which is still unknown, by warming $\text{K} \left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_2 \\ (\text{NO}_2)_4 \end{smallmatrix} \right]$ with potassium nitrite, but was unsuccessful.

On the other hand, one can convert $\text{K} \left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{NO}_2)_4 \end{smallmatrix} \right]$ into $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{NO}_2)_2 \end{smallmatrix} \right]$ and $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_3 \\ (\text{NO}_2)_3 \end{smallmatrix} \right]$ into $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_4 \\ (\text{NO}_2)_2 \end{smallmatrix} \right] \text{Cl}$ by warming the compound in question with a mixture of ammonium chloride and ammonium hydroxide.

In all these cases, ammonium salts are used along with ammonium hydroxide, and their function is to suppress the ionisation of the base and form undissociated NH_4OH , which is in equilibrium with NH_3 . The NH_3 then enters into the complex molecule.

2. If a fairly concentrated solution of aquopentammine cobaltic chloride $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ (\text{H}_2\text{O}) \end{smallmatrix} \right] \text{Cl}_2$ is left, it slowly gives a precipitate of the corresponding purpureo salt $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ (\text{Cl}) \end{smallmatrix} \right] \text{Cl}_2$



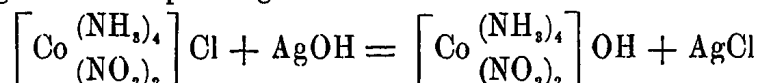
This is a case of equilibrium in solution and the purpureo salt being much less soluble comes out as a precipitate.

If we start with a solution of purpureo cobalt chloride $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ (\text{Cl}) \end{smallmatrix} \right] \text{Cl}_2$ and add ammonium hydroxide and warm the mixture, we get the aquopentammine salt $\left[\text{Co} \begin{smallmatrix} (\text{NH}_3)_5 \\ (\text{H}_2\text{O}) \end{smallmatrix} \right] \text{Cl}_2$ in solution, and this is the usual method of preparation of the aquo salt.

I find that the ammonium hydroxide has only a catalytic effect on the hydrolysis of the purpureo salt into the aquopentammine salt. A solution of the purpureo chloride takes up a molecule of water

and passes into the aquo salt very slowly even at the ordinary temperature. This hydrolysis is markedly accelerated by the presence of hydroxyl (OH') ions. The greater the concentration of the hydroxide ions, the greater is the acceleration. The study of the reaction velocity of this hydrolysis may serve as a means of determining the concentration of hydroxide ions in a dilute solution of a base. Thus if we make a solution of the purpureo salt and add a few drops of a dilute solution of potassium hydroxide, the purple colour changes and becomes rose in a few minutes; but with a weak base like ammonium hydroxide the colour change takes a long time. This explanation may be true in the case of hydrolysis with the corresponding compounds of chromium and platinum. There is evidence to show that in some other cases of hydrolysis by alkali, the action of the hydroxide ions is catalytic. The decomposition of sodium chloracetate by alkali is a case in point (SEETER, *Trans Chem. Soc.* 1907, **91**, 473).

One can get the hydroxides of the cobaltamines in solution by treating the corresponding halide with moist silveroxide :



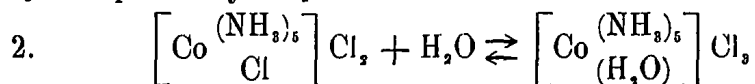
The solution slowly decomposes even at the ordinary temperatures. The hydroxides of the other members of this series can also be prepared by this double decomposition. These hydroxides turn phenolphthalein pink and electric conductivity measurements show that they are strong bases of the type of sodium hydroxide.

But one cannot prepare the hydroxide from purpureo cobalt chloride $\left[\text{Co} \begin{array}{c} (\text{NH}_3)_5 \\ \text{Cl} \end{array} \right] \text{Cl}_2$ by double decomposition with silver oxide. The explanation becomes simple on the light of the catalytic effect of hydroxide ions on the hydrolysis of purpureo salts into the aquo compounds. The hydroxide ions set free by the double decomposition act catalytically on the purpureo salt and actually one gets the aquopentammine hydroxide $\left[\text{Co} \begin{array}{c} (\text{NH}_3)_5 \\ (\text{H}_2\text{O}) \end{array} \right] (\text{OH})_2$, which is stable in alkaline solution, (compare URBAIN et SÉNÉCHAL, *Chimie des complexes*, p. 280, "Les sels purpureo ne donnent pas une réaction de ce genre").

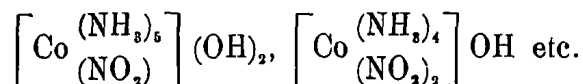
Summary and Conclusion.

1. The principle of the preparation of the cobaltamines is guided by the law of mass action and thus depends on the concentration

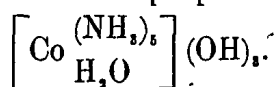
of the reacting substances. One can substitute a nitro (NO_2) group in a compound by the group (NH_3) on warming it with a mixture of ammonium hydroxide and a ammonium salt and on the other hand, NH_3 is replaced by NO_2 when the salt is warmed with a nitrite solution.



This hydrolysis reaction is catalytically accelerated by the presence of OH' ions and the velocity is proportional to the concentration of hydroxide ions.



are strong bases and can be prepared in solution. The base obtained from the purpleo cobalt chloride is the aquopentammine hydroxide



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