

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## STUDIES ON COMPLEX COMPOUNDS. I. REMOVAL OF AMMONIA FROM THE COÖRDINATION SPHERE<sup>1</sup>

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Werner's theory accounts for and predicts clearly the changes which occur when three molecules of ammonia are successively removed from one molecule of a stable hexammine of a trivalent metal; what would happen if more ammonia were removed cannot be definitely foretold. Numerous possibilities present themselves—for example, the coördination number may change or various types of polynuclear compounds may be formed. We are reporting in this paper two such reactions; in one of them a polynuclear compound seems to be the product and in the other a hexacido compound is obtained. In later papers illustrations of change in coördination number will be described.

Cobaltic amines do not lend themselves to investigations of this sort because they undergo complete decomposition when attempts are made to remove ammonia directly. Hexammine chromic salts are known to be readily convertible into pentammines, but what happens on further removal of ammonia has not been thoroughly studied. For this reason chloro pentammine chromic chloride was chosen by us as the starting material. When this substance is heated in air, in hydrogen, in carbon dioxide, or in ammonia, it decomposes into trichloro triammine chromium. This product, however, immediately reacts further to give a black compound unless the temperature is very carefully controlled.<sup>2</sup> If the pentammine is heated in a stream of dry hydrogen chloride, a very rapid reaction occurs at about 270° with considerable evolution of heat and is accompanied by a marked color change of the material from pink to green. If heating is discontinued at this point, the product washed with cold water to which a little hydrochloric acid has been added and then dried with alcohol and ether, a very insoluble green substance, *trichloro triammine chromium* is obtained.<sup>3,4</sup>

<sup>1</sup> The material for this article is taken from a thesis presented in 1925 to the Faculty of the Ogden Graduate School of Sciences of the University of Chicago by Ruby K. Worner in part fulfilment of the requirements for the degree of Doctor of Philosophy. Since the completion of this research considerable further work has been done along these lines, and the report is therefore made very brief. For details not reported herein and aspects of the investigation omitted, reference is made to the thesis.

<sup>2</sup> Ufer, *Ann. Chem.*, **112**, 281 (1859), and Schrötter, *Ann.*, **37**, 148 (1841), report the formation of the black substance, which they describe as a nitride of chromium, and mention the intermediate formation of a green compound, the nature of which they failed to recognize.

<sup>3</sup> It is interesting to note that under no conditions does the pentammine lose but one molecule of ammonia to form tetrammine. Furthermore, the triammine, when

This triammine is markedly different from a substance of the same composition described by Werner.<sup>5</sup> His compound is blue green, dissolves fairly readily in warm water and especially easily in warm dilute hydrochloric acid to give a deep blue solution of trichloro aquo triammine chloride; ours is insoluble in hydrochloric acid or in water, but with the latter it slowly reacts to give a pink solution which has since been shown to contain diaquo tetrammine chromic chloride. Here evidently is a case of isomerism of a type not frequently encountered, but whether it is stereoisomerism, possible according to Werner's theory, or is what is often called "polymerization isomerism" cannot be decided because of the insolubility of the compounds in question.<sup>6</sup>

Attempts to remove some of the three remaining molecules of ammonia from the coordination sphere show the firmness with which chromium retains the coordination number 6. When the triammine is heated to 175° in a stream of hydrogen chloride, ammonia is not withdrawn from the compound, but hydrogen chloride is quantitatively absorbed to give a reddish-purple, very hygroscopic crystalline material which may be considered to be *ammonium chromic hexachloride*.<sup>7</sup> The substance is insoluble in all solvents except water, with which it reacts almost instantly to produce a deep green solution presumably of hydrated chromic chloride.<sup>8</sup>

Those who make a distinction between double and complex salts may prefer to class the substance just described with the former rather than to call it a salt of the complex  $[\text{CrCl}_6]^{---}$  ion.<sup>9</sup> There are, however, several objections to this point of view. Anhydrous chromic chloride, alone or when mixed with ammonium chloride, reacts with liquid ammonia to give a mixture of hexammine and chloro pentammine chromic chlorides without the intermediate formation of a solution. What we have called ammonium chromic hexachloride dissolves readily in liquid ammonia to give treated with liquid ammonia, gives pentammine directly, a reaction which requires weeks for completion. These reactions will be discussed further in later papers.

<sup>4</sup> *Anal.* Found for chromium, 24.81; Cl, 50.39;  $\text{NH}_3$ , 24.29. Calcd. for  $[\text{Cl}_3(\text{NH}_3)_3\text{Cr}]$ : Cr, 24.83, Cl, 50.79;  $\text{NH}_3$ , 24.89. All analyses reported in this paper represent averages of the results with from 3 to 5 samples.

<sup>5</sup> Werner, *Ber.*, **43**, 2286 (1910).

<sup>6</sup> The formation of tetrammines from the triammine here described when they are treated with water or even with acids is a very unusual type of reaction which will be described in more detail in a later paper. It suggests the possibility that these triammines are polynuclear. We are at present attempting to obtain a more soluble example of the type, but have not so far succeeded.

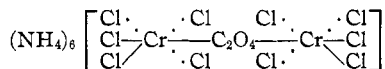
<sup>7</sup> *Anal.* Found: Cr, 16.33; Cl, 66.55;  $\text{NH}_3$ , 15.90. Calcd. for  $(\text{NH}_4)_3[\text{CrCl}_6]$ : Cr, 16.31; Cl, 66.73;  $\text{NH}_3$ , 16.00.

<sup>8</sup> Two stages in the reaction with water may be observed. At first a reddish solution is formed but this changes to green in a fraction of a second.

<sup>9</sup> No success attended attempts to prepare less soluble salts of this ion by double decompositions.

a green solution which is transformed to the pentammine only after complete evaporation of the liquid. Anhydrous chromic chloride reacts exceedingly slowly with dry gaseous ammonia; the new compound reacts rapidly at ordinary temperatures to give the pentammine. Double salts should possess a color which is the summation of the colors of the constituent salts; the compound here prepared is decidedly different in color from any known form of chromic chloride, the only colored constituent.<sup>10</sup>

In this instance, then, chromium, rather than changing its coordination number as the result of removal of ammonia, takes up hydrogen chloride, and the ammonia, although removed from the coordination sphere, remains in the molecule. A slightly different course is taken by the reaction when the compound *chloro oxalato triammine chromium* is treated as was the simple triammine. The oxalato compound is prepared quite simply by warming our trichloro triammine chromium with solutions of oxalic acid or of oxalates. It is a brick red, microcrystalline powder very insoluble in water or in acids, but when warmed with concentrated hydrochloric acid is reconverted into the triammine from which it was prepared.<sup>11</sup> At 190° it reacts slowly with gaseous hydrogen chloride. When the material attains constant weight, its composition always corresponds to the empirical formula  $2CrCl_3 \cdot (NH_4)_2C_2O_4 \cdot 4NH_4Cl$ .<sup>12</sup> According to Werner's theory this might be formulated as



in other words, a compound of polynuclear type. Its properties are similar to those of ammonium chromic chloride except that it reacts somewhat

<sup>10</sup> If trichloro triammine chromium is heated at 270°, instead of 175°, in a stream of hydrogen chloride, a rapid reaction occurs and continues until the composition of the material corresponds to the formula  $2CrCl_3 \cdot 3NH_4Cl$ . (*Anal.* Found: Cr, 21.76; Cl, 66.54;  $NH_3$ , 10.85. Calcd.: Cr, 21.79; Cl, 66.87;  $NH_3$ , 10.70.) Thereafter reaction is very slow and leads to anhydrous chromic chloride. On account of the difference in the rate of reaction before and after the attainment of the composition mentioned, the material can be isolated in fairly pure condition. It is purple in color, but also reacts with water to give hydrated chromic chloride. The fact that this substance has a markedly different color from that of the ammonium chromic chloride shows that we are not dealing with double salts of an unknown form of chromic chloride, for, if that were the case, both double salts should possess the same color. It might be mentioned that in the preparation of trichloro triammine chromium by the method described, some of the purple compound is always obtained. It is removed completely by washing the mixture with cold water.

<sup>11</sup> Further details of this reaction, which leads to rather unusual results when slightly varied, will be described in a later paper. Analytical data are as follows: calcd. for  $ClC_2O_4(NH_3)_3Cr$ : Cr, 22.96; Cl, 15.65;  $NH_3$ , 22.54;  $C_2O_4$ , 38.83. Found: Cr, 22.89; Cl, 16.02;  $NH_3$ , 22.24;  $C_2O_4$ , 38.74.

<sup>12</sup> *Anal.* Calcd.: Cr, 15.89; Cl, 54.16;  $NH_3$ , 15.60;  $C_2O_4$ , 13.44. Found: Cr, 16.37; Cl, 54.40;  $NH_3$ , 15.45;  $C_2O_4$ , 13.38.

more slowly with water, although the reaction is still too rapid to permit studies of constitution.<sup>13</sup>

### Summary

1. The new substances  $[\text{Cl}_3(\text{NH}_3)_3\text{Cr}]$ ,  $[\text{ClC}_2\text{O}_4(\text{NH}_3)_3\text{Cr}]$ ,  $(\text{NH}_4)_3\text{[CrCl}_6]$ , and  $(\text{NH}_4)_6[\text{Cr}_2\text{C}_2\text{O}_4\text{Cl}_{10}]$  are prepared and described. The first is an isomer of the trichloro triammine chromium prepared by Worner.

2. The removal of ammonia from the coördination sphere of chromium is briefly discussed.

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## STUDIES ON COMPLEX IONS. II. THE PREFERENTIAL REMOVAL OF BROMIDE ION FROM THE COÖRDINATION SPHERE<sup>1</sup>

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In order to study the relative tendency of various simple negative ions to become a part of complex positive ions, attempts have been made in this Laboratory to prepare compounds of the type  $[\text{CrR}_3\text{X}_1\text{X}_2\text{X}_3]$  in which R represents a non-ionic constituent and  $\text{X}_1$ ,  $\text{X}_2$  and  $\text{X}_3$  are univalent negative ion constituents. The determination of which one of the ionic constituents is driven out in preference to the others by the addition of one or two moles of R per mole of the compound would give evidence of the relative ability of each simple negative ion to form complex positive ions with chromium. A number of compounds having empirical formulas of the character mentioned have been prepared, but some additional data recently obtained have raised the question whether these substances, all of which are insoluble in all solvents, are not perhaps compounds of more complex type. For these reasons, the experimental results only are described in this paper and their interpretation is deferred to a later time.

Following the procedure of Schlesinger and Worner<sup>2</sup> the three "triammines"  $[\text{Br}_3(\text{NH}_3)_3\text{Cr}]_x$ ,  $[\text{ClBr}_2(\text{NH}_3)_3\text{Cr}]_x$ , and  $[\text{Cl}_2\text{Br}(\text{NH}_3)_3\text{Cr}]_x$  were prepared by thermal decomposition of the appropriate pentammine at  $175^\circ$ . The green products thus obtained were thoroughly washed with

<sup>13</sup> The formation of this compound again suggests that the triammines here described may really have a more complex structure than the name employed implies.

<sup>1</sup> This article is a résumé of a thesis presented by D. N. Rickles to the Graduate Faculty of the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Schlesinger and Worner, *THIS JOURNAL*, **51**, 3520 (1929).