more slowly with water, although the reaction is still too rapid to permit studies of constitution.[13]

Summary

1. The new substances $[Cl_3(NH_3)_3Cr]$, $[ClC_2O_4(NH_3)_3Cr]$, $(NH_4)_3[CrCl_6]$, and $(NH_4)_6[Cr_2C_2O_4Cl_{10}]$ 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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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES ON COMPLEX IONS. II. THE PREFERENTIAL REMOVAL OF BROMIDE ION FROM THE COÖRDINATION SPHERE[1]

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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 $[CrR_3X_1X_2X_3]$ in which R represents a non-ionic constituent and X_1, X_2 and 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[2] the three "triammines" $[Br_3(NH_3)_3Cr]_x$, $[ClBr_2(NH_3)_3Cr]_x$, and $[Cl_2Br(NH_3)_3Cr]_x$ were prepared by thermal decomposition of the appropriate pentammine at 175°. The green products thus obtained were thoroughly washed with

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

[1] 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.

[2] Schlesinger and Worner, THIS JOURNAL, 51, 3520 (1929).

water until the washings were colorless. The residues were then dried with alcohol and ether. The properties of the compounds are similar to those of trichloro triammine chromium described by Schlesinger and Worner.[2]

Anal. Calcd. for $[Br_3(NH_3)_3Cr]_x$: Cr, 15.17; NH_3, 14.91; Br, 69.93. Found: Cr, 14.83; NH_3, 15.54; Br, 70.86. Calcd. for $[ClBr_2(NH_3)_3Cr]_x$: Cr, 17.43; NH_3, 17.12; Cl, 11.88; Br, 53.57. Found: Cr, 17.43; NH_3, 17.64; Cl, 12.00; Br, 53.74. Calcd. for $[Cl_2Br(NH_3)_3Cr]_x$: Cr, 20.48; NH_3, 20.12; Cl, 27.93; Br, 31.47. Found: Cr, 19.72; NH_3, 19.36; Cl, 27.81; Br, 31.43.

Compounds of this series containing iodo, nitrato or nitrito groups could not be prepared in this manner nor by removing water from aquo triammines.[3]

Dihalido Tetrammine Chromic Salts, (*Cis* **(?)-Type**).—Ten cc. of hydrobromic acid (sp. gr. 1.20) was added to 1 g. of chloro oxalato triammine chromium,[2] $[Cl{\cdot}C_2O_4{\cdot}(NH_3)_3Cr]$, and the mixture was boiled until the lavender oxalato triammine was completely converted to a dark green material. The green compound was collected on a filter, while the reaction mixture was still warm, washed with dilute hydrobromic acid and dried with alcohol and ether. The compound was purified by reprecipitating it with hydrobromic acid (sp. gr. 1.70) from its saturated aqueous solution; yield, 0.72 g. That the bromine is not coördinated with chromium is shown by the method of recrystallization and by the fact that the bromine can readily be replaced by double decomposition.

Anal. Calcd.: Cr, 19.19; NH_3, 25.15; Cl, 26.17; Br, 29.94. Found: Cr, 19.01; NH_3, 24.85; Cl, 25.66; Br, 28.80.

When carefully heated the tetrammine decomposes into "dichloro bromo triammine chromium" and a purple substance not further investigated; it reacts with ammonium oxalate to give "chloro oxalato triammine chromium"—a reverse of the reaction by which it is prepared—and by double decomposition to give dichloro tetrammine *chloride*, *iodide* and other similar salts. The iodide may also be prepared by treating "chloro oxalato triammine" chromium with boiling hydriodic acid (sp. gr. 1.50) free from iodine.[4] Further reactions need not be described as they have no bearing on this paper.

The corresponding dibromo tetrammine chromic bromide, $[Br_2(NH_3)_4Cr]Br$, the preparation of which is important for reasons which will be-

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[3] In this connection it was noted that when dichloro aquo triammine chromic nitrate was heated in ordinary air at 100°, it took on water, instead of losing it. This extraordinary stability of aquo compounds is unexpected.

[4] If the hydriodic acid contains free iodine, the reaction yields, instead of the green tetrammine, a well crystallized brown substance from which iodine is freely evolved when heat is applied. It dissolves in water to give a brown solution which slowly turns green and contains free iodine. Organic solvents such as chloroform and ether extract no iodine from it. It also is a tetrammine but has not yet been further characterized.

come obvious later, was obtained by treatment of bromo oxalato triammine chromium with hydrobromic acid. Details of purification and the properties correspond exactly to those for the analogous chlorine derivatives except in one respect.[5] Unlike the chlorotetrammines, the green bromo tetrammines give a red solution in water, but this change is not a transformation into the isomer to be described below. From the red solution the green tetrammine may be reprecipitated either by the addition of alcohol–ether mixtures or of hydrobromic acid, provided the solution is freshly prepared. After the solution has stood for several days both of these reagents precipitate from it red diaquo tetrammine chromic bromide. Obviously the hydration begins as soon as the solution is prepared, but is a slow reaction. Further evidence that the green bromo tetrammine is of the same type as the chloro tetrammine is found in the fact that both react with oxalic acid to give halido oxalato chromium compounds.

Trans (?) **Dibromo Tetrammine Chromic Bromide.**—When "tribromo triammine chromium" is heated with hydrobromic acid (sp. gr. 1.20), a reddish-brown mixture of a tetrammine and a pentammine is obtained.[6] The two components may be separated by treating the mixture with a small amount of ice water, and filtering the solution rapidly. The pink pentammine remains undissolved, and the tetrammine may be reprecipitated by the addition of hydrobromic acid (sp. gr. 1.70) to the solution. Re-solution and reprecipitation effect purification. Analysis leads to the formula $[Br_2(NH_3)_4Cr]Br$.

Anal. Calcd.: Cr, 14.45; NH_3, 18.93; Br, 66.62. Found: Cr, 14.46; NH_3, 19.21; Br, 67.22.

This tetrammine, in contrast to the others described, is dark red instead of green. It dissolves in water to give a red solution, as does the green dibromo tetrammine chromic bromide, but from the solution of the red tetrammine the original substance, not an aquo compound, is precipitated by addition of hydrobromic acid or by alcohol–ether mixtures. The red tetrammine is neither formed from nor does it give "bromo oxalato triammine chromium." It may be noted that the transformation of one type of the tetrammine into the other, a very common reaction in other *cis* and *trans* series, does not seem to occur with the compounds here described under any conditions we have observed. We have provisionally assigned the *cis* structure to the green tetrammines because they are formed from and can readily be converted to oxalato compounds. Inasmuch

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[5] Bromo oxalato triammine was prepared by heating tribromo triammine chromium with ammonium oxalate. Analyses of the various compounds mentioned in this paragraph as well as other details are described in the thesis of Dr. Rickles (University of Chicago, 1928).

[6] The pentammine is formed directly from the triammine, for the pure tetrammine does not yield pentammine under analogous conditions. Obviously the reaction of triammines with acids is very complex.

as the reaction involves a transformation of a triammine to a tetrammine or *vice versa,* in other words a very deep-seated change in the complex ion, the basis for this conclusion is not as secure as might be desired. In fact, there is some evidence which might be considered to favor the opposite interpretation. Oxalato tetrammine chromium[7] compounds are orange-red. Oxalato compounds are always assumed to be the *cis* type; hence, the red bromo tetrammine might also be considered to be of this structure; but we have preferred to lay more weight on the evidence obtained from its reactions than on that based on color similarities, because it is well known that substitution of different groups in complex ions is very often responsible for color changes.

Possible Structure of the "Triammines."—The reactions of the "triammines" with acids to give tetrammines, as described above, suggests the possibility that they are polymerization complexes which contain a tetrammine ion. Thus what we have called trichloro triammine chromium $[Cl_3(NH_3)_3Cr]$, may be a compound such as $[Cl_2(NH_3)_4Cr]$ $[Cr(NH_3)_2Cl_4]$. There are, on the other hand, rather serious objections to formulas of this type. In the first place, it would be difficult to explain on this basis why in a single reaction the compound, $[Br_3(NH_3)_3Cr]$, should yield both a triammine and a pentammine. In the second place, the formulation suggested would not explain why the tetrammines yield triammines on heating, for a reaction such as

$$2[Cl_2(NH_3)_4Cr]Cl \longrightarrow [Cl_2(NH_3)_4Cr][Cr(NH_3)_2Cl_4] + 2NH_3$$

seems highly improbable. The question is being further investigated.[8]

Reaction of Oxalates with Mixed Halide Complexes.—One gram of $[Cl_2Br(NH_3)_3Cr]_x$ was heated with 5 cc. of a saturated aqueous solution of ammonium oxalate and a solid was obtained which was apparently $[ClC_2O_4(NH_3)_3Cr]_x$.

Anal. Calcd. for $[ClC_2O_4(NH_3)_3Cr]$: Cr, 22.92; NH_3, 22.45; Br, 0.00; Cl, 15.64. Composition of solid: Cr, 22.04; NH_3, 21.90; Br, 0.06; Cl, 16.09.

The low results for chromium and ammonia, the high value for chlorine and the presence of a slight trace of bromine in the reaction product, all point to a slight amount of unchanged starting product rather than to admixture with $[BrC_2O_4(NH_3)_3Cr]_x$. This result suggests that bromo groups are more readily removed from the coördination sphere than chloro groups, but until the exact character of the hypothetical triammines has been established, this conclusion cannot be considered as definitely proved.

The treatment of the compound $[ClBr_2(NH_3)_3Cr]_x$ with ammonium oxalate in the same manner leads to the formation of mixtures.

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[7] P. Peiffer, *Ber.*, 38, 3598 (1905).

[8] Recently we have discovered a new type of "triammine" which is pink instead of green and which yields hexammines on treatment with acids.

Anal. Calcd. for $[ClC_2O_4(NH_3)_3Cr]$: Cr, 22.92; NH_3, 22.45; Cl, 15.64; Br, 0.00. Calcd. for $[BrC_2O_4(NH_3)_3]Cr$: Cr, 19.17; NH_3, 18.80; Cl, 0.00; Br, 29.42. Analysis of reaction product: Cr, 21.10; NH_3, 21.20; Cl, 10.96; Br, 10.42.

The indications are that a larger percentage of the chloro compound was obtained, but exact calculations are impossible because of the presence of unknown amounts of the starting product. In general the results corroborate the tentative conclusion reached above.

Reaction of Mixed Triammines with Ammonia.—Dry ammonia at atmospheric pressure and 200° passed over the triammines $[ClBr_2(NH_3)_3Cr]_x$ and $[Cl_2Br(NH_3)_3Cr]_x$ produces mixtures of pentammines. The analytical results need not be given here since they do not permit calculation of the relative amounts of the various pentammines, but when air was mixed with the ammonia in such proportion as to reduce the partial pressure of ammonia to 182 millimeters (as determined by measuring the proportion of the two components by two flowmeters) only $[Br_2Cl(NH_3)_3Cr]_x$ reacted to give appreciable quantities of pentammine in from fifty to seventy hours. The reaction product was washed with water and the aqueous filtrate was treated with ammonium oxalate to precipitate the oxalate of the pentammine. In this way ionized halogen is removed from the compound, thus making the identification of the halogen group in the coördination sphere more exact. Only chloride was present; the quantitative analysis yielded 13.73% of chlorine, in good agreement with 13.62% required for the chloro pentammine chromic oxalate. Again these results suggest that the bromo group is more readily displaced from the complex, but in this case this conclusion is warranted only if the starting products are simple triammines. The interpretation of the results will be given in a later paper.

Summary

1. Several new "triacido triammine chromic" salts, $[Br_3(NH_3)_3Cr]_x$, $[Br_2Cl(NH_3)_3Cr]_x$, $[BrCl_2(NH_3)_3Cr]_x$ and $[Br\cdot C_2O_4\cdot(NH_3)_3Cr]_x$ have been prepared.

2. A method of obtaining chloro and bromo tetrammine chromic salts, hitherto unknown, has been devised. Both *cis* and *trans* salts have been obtained.

3. The action of mixed "triammines" such as $[ClBr_2(NH_3)_3Cr]$ with ammonia and with oxalates has been studied. In all cases the bearing of the results on the question of the factors which determine the stability of complex ions will be taken up in later papers.

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