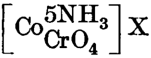
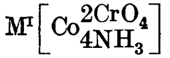
XCVIII.—*Chromatocobaltiammines. Part II. The Dichromatotetramminecobaltiates and the Maximum Co-ordination Number of Cobalt.*

By Samuel Henry Clifford Briggs.

In a former paper (J., 1919, **115**, 67) it was shown that the chromate radical may constitute part of a complex kation, filling either one co-ordination position, as in the chromatopentamminecobaltic salts (I), or two positions, as in the chromatotetramminecobaltic series (II). In the present paper a series of compounds is described in which the chromate radical forms part of a complex anion.


$$\left[\mathrm{Co}{}^{5NH_3}_{CrO_4}\right]X$$
(I.)

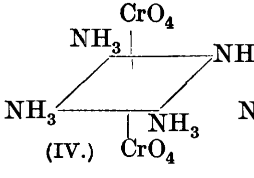

$$\left[\mathrm{Co}{}^{4NH_3}_{CrO_4}\right]X$$
(II.)


$$M^{I}\left[\mathrm{Co}{}^{2CrO_4}_{4NH_3}\right]$$
(III.)

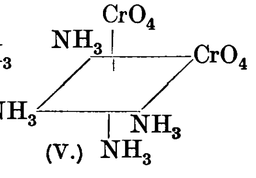
These compounds, the dichromatotetramminecobaltiates (III), are obtained when a solution of a diaquotetramminecobaltic salt is added to a sufficiently large excess of a concentrated solution of an alkali chromate and the solution is kept for several days at the ordinary temperature. Two crystalline forms have been prepared, one being yellowish-green to deep green and the other greenish-yellow to brown. The presence of dichromate in the solution appears to favour the production of the brown form.

The investigation of these substances is complicated by the fact that they are all decomposed by acids, alkalis, or hot water, and are also only slightly soluble in water and therefore cannot be recrystallised. Their solutions in cold water decompose within a few hours.

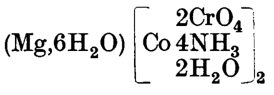
If it be assumed that the cobalt atom has the co-ordination number six, then each chromate radical will occupy one co-ordination position, the two radicals having the *trans*-configuration in the green form (IV) and the *cis*-configuration in the brown form (V) as indicated by the colour of the compounds. *Sodium*, *potassium*, *lithium*, and *magnesium* salts have been investigated. The sodium and magnesium compounds have been prepared in both forms, whereas only the brown lithium salt and the green potassium salt have been obtained.



(IV.)

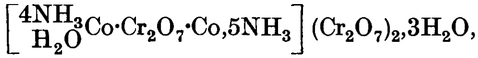


(V.)


$$(\mathrm{Mg},6H_2O)\left[\mathrm{Co}\begin{matrix}2CrO_4\\4NH_3\\2H_2O\end{matrix}\right]_2$$
(VI.)

The green magnesium salt appears to have a different constitution from the others. This salt contains ten molecules of water; six of these, being given off in a few days in a vacuum over sulphuric acid, are presumably the six molecules of water of crystallisation frequently associated with magnesium salts and attached to the magnesium ion, and the other four are evolved very slowly during several weeks, the colour meanwhile changing from green to brown. This colour change shows that the four molecules are associated with the anions. Since the green colour cannot be restored by hydration, the colour change to brown must represent a change in the configuration of the anion itself. Such a change could hardly occur if the water molecules were merely addenda to the anions, and it would therefore appear that they are part of the complex itself, the formula of the compound being (VI), in which the cobalt atom has the co-ordination number eight. From the green colour it may be assumed that the ammonia molecules in (VI) are all in one plane as in (IV), perhaps the diagonal plane of a cube, and on removal of the four water molecules their relative positions are changed, giving the *cis*-form with co-ordination number six (V). On the other hand, if the co-ordination number were eight in all the other compounds of the series, with each chromate radical occupying two co-ordination positions as in (II), and each co-ordination position representing the corner of a cube (compare Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, 1925, **45**, No. 8), then the dichromatotetramminecobaltiates should exist in three forms. It was thought that a third and more soluble form might possibly be present in the very dark solution from which the compounds are prepared, but attempts to isolate it by increasing the proportion of cobalt salt gave only an insoluble *compound* of the formula $Co_2(CrO_4)_3,8NH_3,H_2O$. It should be noted that according to Matsuno (*loc. cit.*) cobalt has the co-ordination number eight in some of the pentammine salts, as shown by the preparation of the compound $[Co(5NH_3)(C_2O_4)Cl]$ in two optically active forms.

It was shown by Rây and Sarkar (*J. Indian Chem. Soc.*, 1925, **1**, 289) that the dichromate radical also may form part of a cobaltiammine co-ordination complex, and this has been confirmed by the preparation of a *compound* of the formula $Co_2(Cr_2O_7)_3,9NH_3,4H_2O$ by the action of an excess of sodium dichromate on diaquotetramminecobaltic nitrate. One molecule of water appears to be constitutional, and the simplest structure is



$$\left[\begin{matrix}4NH_3\\H_2O\end{matrix}Co\cdot Cr_2O_7\cdot Co,5NH_3\right](Cr_2O_7)_2,3H_2O,$$

but as the compound is almost insoluble in water this cannot be definitely decided.

Attempts to prepare ammonium dichromatotetramminecobaltiate were not successful, a pentammine derivative being obtained. The analysis of this *substance* corresponds to the formula

$$(NH_4)_2CrO_4,\left[Co^{5NH_3}_{CrO_4}\right]_2CrO_4,$$

with co-ordination number six, or $NH_4\left[Co^{5NH_3}_{2CrO_4}\right]$, with co-ordination number eight, but here again the precise determination of the constitution is prevented by the insolubility of the compound.

EXPERIMENTAL.

The general method for preparing the diaquotetramminecobaltic solution was to decompose carbonatotetramminecobaltic nitrate (1 g.) with dilute hydrochloric acid (1 c.c. of concentrated acid to 4 c.c. of water).

Sodium trans-*Dichromatotetramminecobaltiate.*—The solution of the diaquo-compound from 6 g. of carbonatotetramminecobaltic nitrate was added with vigorous stirring in the cold to a solution of 150 g. of sodium chromate tetrahydrate and 5 g. of sodium dichromate dihydrate in 120 c.c. of water, the dichromate being added to reduce the alkalinity of the solution. A green, microcrystalline precipitate began to separate slowly after a few hours, 6·5 g. being deposited during 3 weeks. On adding a solution of diaquotetramminecobaltic salt to the mother-liquor, a further quantity was obtained. The green *compound* was anhydrous (Found : Na, 5·2; Co, 15·4; CrO_3, 52·2; NH_3, 17·8. $Na\left[Co^{2CrO_4}_{4NH_3}\right]$ requires Na, 6·0; Co, 15·4; CrO_3, 52·3; NH_3, 17·8%).

When the salt was shaken with a large amount of cold water it dissolved, leaving a small quantity of a green residue. As it was thought that this might be an impurity with a lower sodium content, 10 g. of the preparation were repeatedly extracted with 750 c.c. of cold water until only 1 g. of solid remained [Found : Na, 4·6; Co, 17·4; CrO_3, 46·7; NH_3, 16·6; H_2O, loss over sulphuric acid, 1·8. $Na_2Co_3(CrO_4)_5OH,10NH_3,2H_2O$ requires Na, 4·5; Co, 17·3; CrO_3, 48·7; NH_3, 16·6; $1H_2O$, 1·8%]. If the material was a homogeneous compound originally present as an impurity, it was evidently a highly complex polynuclear substance. It may, however, have been contaminated by the products of decomposition of the bulk substance by water, and thus it is not possible to draw any definite conclusions as to its constitution.

Sodium *trans*-dichromatotetramminecobaltiate dissolves in about 300 parts of water at 20°. On standing for a few hours in the cold the solution changes in colour from green to yellow and a brown precipitate of impure chromatohydroxotriamminecobalt (J., 1919, **115**, 75) is formed.

Sodium cis-*Dichromatotetramminecobaltiate.*—The solution of diaquotetramminecobaltic salt from 6 g. of the carbonatotetramminecobaltic nitrate was added in the cold to a solution of 110 g. of sodium chromate and 60 g. of hydrated dichromate in 160 c.c. of water. At the winter temperature a mixture of compounds first separated and two fractions were discarded, but the third was homogeneous, consisting of greenish-brown crystals (Found : H_2O, 5·0. A *monohydrate* requires H_2O, 4·5%. Found in anhydrous *compound* : Na, 5·2; Co, 15·4; CrO_3, 52·6; NH_3, 18·0%). The salt was very slightly soluble in water, giving a yellow solution.

Lithium cis-*Dichromatotetramminecobaltiate.*—Lithium chromate was prepared by heating an excess of lithium carbonate with chromic acid on the water-bath and evaporating it to crystallisation, but analysis showed the salt to contain some dichromate. To a solution of this preparation containing 47 g. of the chromate and 9 g. of the dichromate in 100 c.c. of water, a solution of the diaquotetramminecobaltic salt from 4 g. of carbonatotetramminecobaltic nitrate was added; after twelve days, 1·5 g. of greenish-brown crystals had separated (Found: Li, 1·4; Co, 15·1; CrO_3, 50·2; H_2O, 6·6; NH_3, 17·7. $2Li\left[Co^{2CrO_4}_{4NH_3}\right],3H_2O$ requires Li, 1·8; Co, 15·0; CrO_3, 50·9; H_2O, 6·9; NH_3, 17·3%).

Lithium chromate free from dichromate was then prepared by adding to a solution of the mixed chromate and dichromate the calculated amount of a solution of lithium carbonate. The salt obtained by crystallising this solution was used in an attempt to prepare the green lithium compound, but the product was identical with the greenish-brown salt just described.

Potassium trans-*dichromatotetramminecobaltiate* was prepared in a very impure condition as a dark green powder when a solution of the diaquotetrammine nitrate was added to a large excess of a concentrated solution of potassium chromate. When a little dichromate was also present, what appeared to be a mixture of the green and brown forms was produced, but, owing to the slight solubility of potassium dichromate in a solution of chromate, the suitable conditions for preparing the brown compound could not be attained. The green form was obtained in a purer state accidentally when the mother-liquor from the preparation of trichromato-octamminedicobalt (J., 1919, **115**, 73) was kept for some days in the neighbourhood of 0°. The compound was analysed after being kept for some months in a desiccator over calcium chloride (Found : K, 8·7; Co, 14·6; CrO_3, 50·5. $K\left[Co^{2CrO_4}_{4NH_3}\right]$ requires K, 9·8; Co, 14·8; CrO_3, 50·2%). Its green solution gave a greenish-brown precipitate with copper sulphate, no precipitate with zinc sulphate, and with silver nitrate a brown precipitate which rapidly became dark red, the colour of silver chromate.

Magnesium Salts.—The green compound was prepared by adding the diaquotetramminecobaltic solution from 10 g. of carbonatotetramminecobaltic nitrate to a solution of 150 g. of magnesium chromate and 5 g. of chromic anhydride in 400 c.c. of water. After six days, 2·9 g. of the compound were obtained in brilliant, dark green, doubly refracting crystals [Found: Co, 12·9; CrO_3, 43·6; NH_3, 14·8. Loss at 95° in 2 hours, 11·2; in 98 hours, 18·2. Loss in a vacuum over sulphuric acid in 2 weeks, 11·4; in 12 weeks, 19·3. (VI) requires Co, 12·8; CrO_3, 43·4; NH_3, 14·8; $6H_2O$, 11·7; $9\frac{1}{2}H_2O$, 18·3; $10H_2O$, 19·5%].

The brown form was only obtained mixed with the green form, from which it could not be separated. The above experiment was repeated with 3 g., 60 g., and 10 g. of the respective compounds in 140 c.c. of water; the deposit which separated after two days was removed, and after 16 days at the summer temperature 1·1 g. of a mixture of brown and green salts were produced, a further quantity being obtained after addition of more of the diaquotetramminecobaltic solution. Under the microscope, the preparation appeared to consist of approximately equal amounts of the two compounds. The total loss of water on dehydration was 12·3% (equivalent to $5{\cdot}8H_2O$), of which 3·6% was evolved very slowly during three months as against 7·7% required for the pure green compound. As the two salts appeared to be present in approximately equal proportions, it may be taken for granted that the whole of the "constitutional" water came from the green component, from which it follows that the brown anion is anhydrous and the formula of the brown salt in the mixture is $(Mg,2H_2O)\left[Co\begin{matrix}2CrO_4\\4NH_3\end{matrix}\right]_2$. The analysis of the dehydrated mixture gave MgO, 5·3; Co, 15·8; CrO_3, 53·8; NH_3, 18·8. $Mg\left[Co\begin{matrix}2CrO_4\\4NH_3\end{matrix}\right]_2$ requires MgO, 5·4; Co, 15·9; CrO_3, 53·9; NH_3, 18·4%.

When the green magnesium salt was completely dehydrated and then treated with water at the winter temperature, a brown *hexahydrate* was obtained {Found: total loss at 95°, 13·9. $(Mg,6H_2O)\left[Co\begin{matrix}2CrO_4\\4NH_3\end{matrix}\right]_2$ requires $6H_2O$, 12·8%}.

The *compound* $Co_2(CrO_4)_3,8NH_3,2\frac{1}{2}H_2O$ separated after four hours as a dark chocolate-coloured powder when the diaquotetramminecobaltic solution from 4 g. of the carbonato-nitrate was added to a solution of 21 g. of sodium chromate in 27 c.c. of water. In a vacuum over sulphuric acid it lost $1\frac{1}{2}H_2O$ (Found : loss, 4·1, 4·2. Calc. : 4·2%) to give the *monohydrate* [Found : Co, 18·7; CrO_3, 48·2; NH_3, 23·0. $Co_2(CrO_4)_3,8NH_3,H_2O$ requires Co, 19·0; CrO_3, 48·4; NH_3, 22·0%]. A similar preparation from magnesium chromate contained Co, 19·0; CrO_3, 48·5; NH_3, 23·7%.

The Action of Sodium Dichromate on Diaquotetramminecobaltic Salts.—The diaquotetramminecobaltic solution from 5 g. of carbonatotetramminecobaltic nitrate was added to a solution of 150 g. of sodium dichromate dihydrate in 150 c.c. of water and the solution was kept at the summer temperature (below 10° a mixture of compounds is produced). After three days, 3·9 g. of brownish-black crystals were obtained [Found : Co, 11·8; CrO_3, 60·8; H_2O, after 56 days in a vacuum over sulphuric acid, 5·5; NH_3, 15·6. $Co_2(Cr_2O_7)_3,9NH_3,4H_2O$ requires Co, 11·9; CrO_3, 60·5; $3H_2O$, 5·45; NH_3, 15·5%]. When the *compound* was heated to a sufficiently high temperature to expel the fourth molecule of water, general decomposition occurred with evolution of ammonia.

The Action of Ammonium Chromate on Diaquotetramminecobaltic Salts.—The diaquotetramminecobaltic solution from 5 g. of the carbonato-nitrate was added to a solution of 100 g. of ammonium chromate and 5 g. of chromic anhydride in 270 c.c. of water. A slight precipitate was removed by filtration and the solution kept in a warm room. A dark reddish-brown crystalline deposit slowly separated which was only very slightly soluble in water {Found : Co, 15·1; CrO_3, 50·6; NH_3, 25·0. $(NH_4)_2CrO_4,\left[Co{}^{5NH_3}_{CrO_4}\right]_2CrO_4$ requires Co, 15·0; CrO_3, 50·7; NH_3, 25·9%}.

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