133. *Researches on Ammines. Part VIII. Dihydroxotetramminochromic Hydroxide and its Derivatives.*

By Herbert J. S. King.

Cleve (*J. pr. Chem.*, 1862, **86**, 47), by treating chloroaquotetramminochromic chloride with silver oxide, obtained a brownish-violet solution, which soon decomposed with loss of ammonia. When, however, suitable precautions are taken in the preparation of this solution (see p. 521), it is deep red, and does not lose ammonia while kept at 0°. It is strongly alkaline, displacing ammonia from ammonium salts. As it contains no chlorine, possible formulæ for this hydroxide are (1) dihydroxotetramminochromic hydroxide, $[Cr(NH_3)_4(OH)_2]OH$, (2) hydroxoaquotetramminochromic hydroxide, $[Cr(NH_3)_4(H_2O)(OH)](OH)_2$, or (3) diaquotetramminochromic hydroxide,

$$[Cr(NH_3)_4(H_2O)_2](OH)_3.$$

To distinguish between these, the molecular conductivity at 0° was determined; this increased normally until a dilution of 259·2 l. per mol. was reached, giving, on extrapolation to zero concentration, a limiting conductivity of 134·8 mhos. This result eliminated formulæ (2) and (3), for, since the mobility of the hydroxyl ion at 0° is 105·0 mhos, the hydroxide is necessarily that of a univalent kation, of mobility 134·8—105·0 = 29·8 mhos at 0°. Hence the solution contains dihydroxotetramminochromic hydroxide, the cobaltammine analogue of which was described in Part V (J., 1932, 1275). As with the corresponding cobaltammines, it was not possible to isolate any solid salts of the dihydroxotetramminochromic series, but, by treating the hydroxide with one equivalent of hydrochloric acid, a *solution* of dihydroxotetramminochromic chloride, $[Cr(NH_3)_4(OH)_2]Cl$, was obtained. Its molecular conductivity was measured at 0°, and was of the order required for a salt of a univalent base. Extrapolation of the results gave a limiting molecular conductivity of 71·53 mhos, and a mobility for the dihydroxotetramminochromic ion of 30·4 mhos, at 0°, in close agreement with the value 29·8 derived from the conductivity values for the hydroxide. The mobility of the analogous cobaltammine ion at 0° was 23·0 mhos (Part V, *loc. cit.*). These results confirm the conclusion that the hydroxide is of formula (1), for if it had been hydroxoaquo- or diaquo-tetramminochromic hydroxide, with an abnormally low ionisation, the conductivity values obtained, after addition of the hydrochloric acid, would have been much higher than those recorded.

Treatment of the hydroxide with two equivalents of an acid, or its ammonium salt, provided a general method for the preparation of hydroxoaquotetramminochromic salts, the *nitrate, iodide, oxalate,* sulphate, and *picrate* being thus obtained: $[Cr(NH_3)_4(OH)_2]OH + 2HX = [Cr(NH_3)_4(H_2O)(OH)]X_2 + H_2O$. Their identity as hydroxoaquo-salts (rather than hydroxoacido-salts, $[Cr(NH_3)_4(OH)X]X$) was established by determining the electrical conductivity of the nitrate, the values obtained being of the order required for a salt of a bivalent kation. The mobility of the hydroxoaquotetramminochromic ion is 60·5 mhos at 0°; that of the corresponding cobaltammine ion is 60·8 mhos (see Part V, *loc. cit.*). The bromide, sulphate, and dithionate of this series have been obtained previously, by treating diaquo- or chloroaquo-tetramminochromic salts with pyridine (Pfeiffer, *Ber.*, 1907, **40**, 3126; Dubsky, *J. pr. Chem.*, 1914, **90**, 83).

The only chromammine salts hitherto described with a dibasic radical in the complex are the oxalatotetramminochromic series. When the hydroxide was treated with one equivalent of nitric acid and two of oxalic acid, as for the introduction of dibasic radicals into the tetramminocobaltic complex (Part VII, preceding paper), monohydrated oxalatotetramminochromic nitrate, $[Cr(NH_3)_4(C_2O_4)]NO_3,H_2O$, was obtained. The formula was checked by conductivity measurements, and by preparing the corresponding *picrate* by double decomposition. However, replacement of oxalic by sulphuric, malonic, or other dibasic acid yielded syrups which did not solidify on standing.

When the hydroxide was treated with three equivalents (or the hydroxoaquo-nitrate with one equivalent) of nitric acid, anhydrous *nitratoaquotetramminochromic nitrate*, $[Cr(NH_3)_4(H_2O)(NO_3)](NO_3)_2$, was obtained. No salts of this series have been described previously. The conductivity data obtained for the salt were 24% higher than for hydroxoaquotetramminochromic nitrate, and about 14% lower than for the cobalt analogue (Part VII, *loc. cit.*), at 0° and the same concentrations. Thus the salt was hydrolysed in solution, but less extensively than the corresponding cobaltammine, to the diaquotetramminochromic salt.

When the hydroxide was treated with three equivalents of picric acid, *picratoaquotetramminochromic picrate trihydrate* was obtained. This salt was also precipitated, in place of the expected nitratoaquotetramminochromic picrate, when nitratoaquotetramminochromic nitrate was treated with 2 mols. of ammonium picrate. Its molecular conductivity at 25° and $v = 4096$ was 339·7 mhos, while, for the corresponding cobaltammine, the value 296·2 mhos was obtained (Part VII, *loc. cit.*). Although the chromammine was hydrolysed to a greater extent than the cobaltammine, yet this result clearly indicated that it was the picratoaquo-, not the diaquo-, tetramminochromic salt.

EXPERIMENTAL.

Preparation of Chloroaquotetramminochromic Chloride.—$[Cr(NH_3)_5Cl]Cl_2$, obtained by the action of liq. NH_3 on anhyd. $CrCl_3$, was successively converted into aquopentammino- and oxalatotetrammino-chromic nitrate, and from the latter the required salt was obtained by the method of Benrath and Steinrath (*Z. anorg. Chem.*, 1930, **194**, 351). The aq. solution of $[Cr(NH_3)_4(OH)_2]OH$ was prepared by triturating 4 g. of $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ at 0° exactly as described in the preceding paper (p. 518). The product was filtered by suction, and passed a second time through the residue of Ag_2O and AgCl, which was finally washed with a little ice-cold H_2O. The deep red solution (about 45 c.c.) was now free from Cl, and was kept at about 0° till used. It did not smell of NH_3.

The salts described below were prepared in each case from this amount of hydroxide solution, and were purified for analysis as described for the cobalt salts (p. 518).

Hydroxoaquotetramminochromic Salts.—*Nitrate.* The hydroxide was treated with 2 mols. of $2N$-HNO_3. On gradual addition of 600 c.c. of ice-cold EtOH and 120 c.c. of Et_2O, 3·4 g. of brownish-rose irregular plates were obtained. The *salt* was very sol. in H_2O, to a slightly alk. red solution {Found: Cr, 18·8; NH_3, 24·3; N, 30·0. $[Cr(NH_3)_4(H_2O)(OH)](NO_3)_2$ requires Cr, 18·6; NH_3, 24·4; N, 30·1%}. The aq. solution of this salt was much more stable than that of the corresponding cobaltammine, no noticeable decomp. occurring at room temp. for several hr. After standing over-night, a 15% solution had deposited an amorphous violet solid, containing 3 mols. of NH_3 associated with 2 atoms of Cr.

When the hydroxide was treated with 1 mol. of HNO_3, no ppt. was obtained on adding a large excess of EtOH and Et_2O.

Iodide. The hydroxide was shaken with 2 mols. of NH_4I; NH_3 was liberated, and, on addition of ice-cold EtOH, 2·8 g. of red crystals were obtained (Found: Cr, 12·6; NH_3, 16·7; I, 61·7. $[Cr(NH_3)_4(H_2O)(OH)]I_2$ requires Cr, 12·7; NH_3, 16·7; I, 62·1%).

Oxalate. The hydroxide was shaken with 1 mol. of powdered $H_2C_2O_4$. This dissolved, and on treatment with a little EtOH the filtered solution deposited brownish-red crystals (Found: Cr, 21·2; NH_3, 27·9. $[Cr(NH_3)_4(H_2O)(OH)]C_2O_4$ requires Cr, 21·4; NH_3, 28·0%).

Sulphate. When the hydroxide was shaken with 1 mol. of solid $(NH_4)_2SO_4$, NH_3 was evolved, and on gradual addition of cooled EtOH, red crystals formed. The compound was also obtained by treating the hydroxide with 1 mol. of H_2SO_4 (Found: Cr, 20·6; NH_3, 27·2; SO_4, 38·0. Calc.: Cr, 20·7; NH_3, 27·1; SO_4, 38·2%).

Picrate. When the hydroxide was treated with a cold solution containing 2 mols. of picric acid, a yellow acicular ppt. was obtained {Found : Cr, 8·1; NH_3, 10·9; N, 23·2. $[Cr(NH_3)_4(H_2O)(OH)](C_6H_2O_7N_3)_2$ requires Cr, 8·5; NH_3, 11·1; N, 22·9%}.

When 1 mol. of picric acid was used, the same *salt* was pptd., leaving a red filtrate which gave a further ppt. with picric acid (Found : Cr, 8·3; NH_3, 11·2%).

Oxalatotetramminochromic Salts.—Nitrate. The hydroxide was treated with 1 mol. of 2*N*-HNO_3, and then shaken with 1 mol. of powdered $H_2C_2O_4$, which readily dissolved. After being heated to 60°, and then rapidly filtered and cooled, the solution deposited reddish-orange crystals (1·8 g.) (Found : Cr, 17·8; NH_3, 23·8; N, 24·2. Calc. for monohydrate : Cr, 18·0; NH_3, 23·6; N, 24·3%). This is the best method of obtaining the pure salt. The product obtained by the action of $H_2C_2O_4$ on aquopentamminochromic nitrate (Werner and Surber, *Annalen*, 1914, **405**, 220) is only purified by two recrystns., involving much loss.

Picrate. A cold aq. solution of ammonium picrate (1 mol.) was added to a solution of the nitrate, yielding a light-brown cryst. ppt. {Found : Cr, 11·9; NH_3, 15·7; N, 22·3. $[Cr(NH_3)_4(C_2O_4)](C_6H_2O_7N_3)$ requires Cr, 11·9; NH_3, 15·6; N, 22·5%}. The filtrate gave no further ppt. with ammonium picrate.

Nitratoaquotetramminochromic nitrate, obtained as a salmon ppt. (1·4 g. of acicular aggregates) when the hydroxide at 0° was treated with 3 mols. of 2*N*-HNO_3 and 2 l. of cooled EtOH and Et_2O, was fairly readily sol., giving a red solution {Found : Cr, 16·0; NH_3, 21·4; N, 30·1. $[Cr(NH_3)_4(H_2O)(NO_3)](NO_3)_2$ requires Cr, 16·0; NH_3, 21·0; N, 30·2%}. A better yield was obtained by shaking $[Cr(NH_3)_4(H_2O)(OH)](NO_3)_2$ (3 g.) with 1 mol. of 2*N*-HNO_3 and 12 c.c. of H_2O. The filtered solution was treated with 250 c.c. of cooled EtOH and Et_2O, giving 2·2 g. of the salmon nitrato-salt (Found : Cr, 16·3; NH_3, 21·0; N, 29·8%). After being kept for a week, the salt had darkened, and smelt of NH_3. It was not possible to prepare from it, by double decomp., other salts of the nitratoaquotetramminochromic series. A conc. aq. solution yielded no ppt. with aq. solutions of NH_4I, $(NH_4)_2CrO_4$, $Na_2S_2O_6$, or sodium naphthalene-β-sulphonate, but with ammonium picrate it yielded a ppt. of *picratoaquotetramminochromic picrate trihydrate*. The solid nitratoaquo-salt was shaken with 2 mols. of ammonium picrate, giving an immediate ppt. of large, bright yellow needles {Found : Cr, 5·6; NH_3, 8·0; N, 20·8. $[Cr(NH_3)_4(H_2O)(C_6H_2O_7N_3)](C_6H_2O_7N_3)_2,3H_2O$ requires Cr, 5·9; NH_3, 7·8; N, 20·8%}. The filtrate yielded a further ppt. with ammonium picrate.

The same salt (3·5 g.) was obtained by treating the hydroxide with a cold solution of 3 mols. of picric acid (Found : Cr, 5·8; NH_3, 7·9; N, 20·4%). It decomposed at 100°, and at 85° it lost, in 8 hr., 3 mols. of H_2O and ¾ mol. of NH_3.

Electrical Conductivities.

Details of the procedure were given in Part V (*loc. cit.*); and all other details are as given on p. 519 of the preceding paper. Data in parentheses were considered to be affected by hydrolysis, and were ignored in calculating λ_∞.

Dihydroxotetramminochromic hydroxide, $[Cr(NH_3)_4(OH)_2]OH$.

v	31·67	63·34	128·0	259·2	512·0	1024	∞	
λ_{0°	124·2	127·0	128·8	130·2	127·2	123·3		
λ_{0° corr....	124·3	127·2	129·2	131·0	(128·7)	(126·3)	134·8	($n = 1·50$)

A fresh solution of the hydroxide (approx. *M*/32) was prepared for each measurement, conductivity water being used. After determination of the concn. in one portion by estimation of NH_3, the rest was diluted to the required concn. with conductivity H_2O. A positive water correction was applied (Lamb and Yngve, *J. Amer. Chem. Soc.*, 1921, **43**, 2354).

Dihydroxotetramminochromic chloride, $[Cr(NH_3)_4(OH)_2]Cl$.

v	32·13	63·80	128·5	252·6	521·2	∞	
λ_{0°	54·98	58·51	61·80	64·14	(67·56)	71·53	($n = 1·50$)

An approx. *M*/32-solution of the hydroxide, prepared and checked as above, was treated with the calc. amount of *N*/10-HCl, and diluted to the required concn.

Hydroxoaquotetramminochromic nitrate, $[Cr(NH_3)_4(H_2O)(OH)](NO_3)_2$.

v	32	64	128	256	512	1024	∞	
λ_{0°	101·4	110·3	117·2	123·4	127·5	131·2	141·3	($n = 1·50$)

Oxalatotetramminochromic nitrate, $[Cr(NH_3)_4(C_2O_4)]NO_3$.

v	64	128	256	512	1024	∞	
$\lambda_{0°}$	55·89	59·36	62·22	64·17	66·54	71·03	(n = 1·50)
$\lambda_{25°}$	107·2	112·9	117·4	122·5	133·3		

There was no increase of conductivity on standing. At 0° and v = 1024, the conductivity remained unchanged for 20 min., with the solution in contact with the electrodes.

Nitratoaquotetramminochromic nitrate, $[Cr(NH_3)_4(H_2O)(NO_3)](NO_3)_2$.

v	32	64	128	256	512	1024
$\lambda_{0°}$	124·1	136·0	144·8	152·7	161·7	173·0

Even at v = 32, λ increased slowly on standing, while at v = 1024, an increase of 14% was found after the solution had stood for 1 hr. at room temp.

Picratoaquotetramminochromic picrate, $[Cr(NH_3)_4(H_2O)(C_6H_2O_7N_3)](C_6H_2O_7N_3)_2$. $v = 4096$; $\lambda_{25°} = 339·7$; even at this low concn., the salt dissolved very slowly, 20 mins.' shaking at 40° being required.

Ionic Mobilities.—Dihydroxotetramminochromic ion. The data for the hydroxide and chloride gave mobility 29·8 and 30·4 mhos at 0°. The latter value is adopted.

Oxalatotetramminochromic and hydroxoaquotetramminochromic ions. At 0° the data give mobilities 30·6 and 60·5 mhos.

The values employed for the mobilities of the anions are: NO_3', 40·4; Cl′, 41·1; OH′, 105·0 mhos.

NORTHERN POLYTECHNIC, LONDON, N. 7.

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