

CCLXXXVI.—*Researches on Chromammines. Part II.*
Hydroxopentamminochromic Salts and Electrical
Conductivities of Chromammines.

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A. *Hydroxopentammino-chromic(-cobaltic) Hydroxide.*

It was shown in Part I (King, J., 1924, 125, 1329) that the alkaline solutions obtained by treating chloropentamminochromic or aquopentamminochromic chloride with moist silver oxide, which had until then been regarded as solutions of aquopentamminochromic hydroxide, gave hydroxopentamminochromic picrate with excess of picric acid. (That this is not due to instability of the aquopentamminochromic salt has now been shown by preparing the latter from the nitrate.) Hence the solutions were considered

to contain not aquo- but hydroxo-pentamminochromic hydroxide, a view supported by their intense reddish-violet colour, which is characteristic of "purpureo" rather than "roseo" solutions.

Further investigation showed that the aquopentamminochromic salt was obtained with oxalic acid, which thus behaved similarly to mineral acids (Christensen, *J. pr. Chem.*, 1881, **23**, 26).

$2[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{OH})_2 + 3\text{H}_2\text{C}_2\text{O}_4 = [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{C}_2\text{O}_4)_3 + 4\text{H}_2\text{O}$. 2:4-Dinitrophenol, a much weaker acid than picric acid, gave the aquo-salt with both the chrommamine and the cobaltamine alkaline solutions. Also picric acid gave the aquo-salt with the cobaltamine solution, though 2:4-dinitro- α -naphthol-7-sulphonic acid, a much stronger acid, gave the hydroxo-salt (Part I). In view of these anomalous results, the nature of the alkaline solutions has been investigated from the point of view of electrical conductivity. From measurements of the conductivities of their salts, the conductivities of the aquopentamminochromic and hydroxopentamminochromic ions at zero concentration were found to be 174.3 and 73.3 mhos at 0°, giving 489.3 and 283.3 mhos for the limiting conductivities of the hydroxides. The value obtained by extrapolation of the conductivity data for the chrommamine alkaline solution was 283.9, completely confirming the view that it contained only hydroxopentamminochromic hydroxide. The data of Lamb and Yngve (*J. Amer. Chem. Soc.*, 1921, **43**, 2352) for the conductivity of "aquopentamminocobaltic hydroxide" at 0° (ignoring the figure for $c = 0.0002683$) give on extrapolation ($n = 1.30$) the value 296 at infinite dilution, in fair agreement with the value 287 required for hydroxopentamminocobaltic hydroxide.

Aquopentamminochromic picrate was precipitated, on mixing solutions of aquopentamminochromic nitrate and 200% excess of sodium picrate, as aggregates of golden-yellow needles (Found: Cr, 6.0; NH_3 , 9.9; N, 22.9; H_2O , 3.3).

$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}][\text{C}_6\text{H}_2\text{O}_7\text{N}_3]_{\frac{1}{2}} \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Cr, 6.1; NH_3 , 10.0; N, 23.1; H_2O , 3.2%). The salt lost all its water and also 43% of its ammonia on heating at 100° for 3 hours, so this is not a suitable method for introducing the picrato-group into the complex.

Aquopentamminochromic oxalate was obtained on mixing solutions of hydroxopentamminochromic hydroxide (Christensen, *loc. cit.*) and oxalic acid (3 mols.), precipitation occurring on shaking and cooling. It was washed with a little water, and with alcohol until free from oxalic acid. The air-dried product consisted of irregular, orange plates (Found: Cr, 16.3; NH_3 , 26.4; H_2O of crystallisation, 10.9. $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ requires Cr, 16.1; NH_3 , 26.4; H_2O of crystallisation, 11.2%). After a week in a vacuum over phosphoric

oxide, the water of crystallisation was completely removed, together with 4% of the ammonia. The salt lost 47% of its ammonia on heating at 100° for 3 hours, but still retained more than half of the co-ordinated water. Thus it was not possible to prepare an oxalato-salt from it by heating.

Aquopentammino-chromic (-cobaltic) 2:4-Dinitrophenoxide.—Finely powdered 2:4-dinitrophenol (2 mols.) was shaken mechanically for an hour with a solution of hydroxopentammino-chromic (-cobaltic) hydroxide, when the pure aquopentammino-salt was obtained, the excess of hydroxide remaining uncombined. The sparingly soluble product was washed with water, then triturated and washed with methyl alcohol, leaving a bright yellow powder. Ammonia was estimated as for picrates (Morgan and King, J., 1922, **121**, 1723). A. (Found: Cr, 7.4; NH₃, 11.7; N, 21.3; H₂O, 5.2.

$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]\{\text{C}_6\text{H}_3\text{O}_5\text{N}_2\}_3\cdot\text{H}_2\text{O}$ requires Cr, 7.2; NH₃, 11.8; N, 21.2; H₂O, 5.0%). 66% of the ammonia was removed in 3 hours at 85°, together with all the water. B. (Found: Co, 7.7; NH₃, 11.0; N, 20.1; H₂O, 9.2. $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\{\text{C}_6\text{H}_3\text{O}_5\text{N}_2\}_3\cdot 3\text{H}_2\text{O}$ requires Co, 7.7; NH₃, 11.1; N, 20.1; H₂O, 9.4%). The compound charred at 100°.

Interaction of Hydroxopentamminocobaltic Hydroxide and Picric Acid Solutions.—Using three mols. of picric acid, the pure aquopentamminocobaltic salt was precipitated (Morgan and King, *loc. cit.*) (Found: Co, 7.1; NH₃, 10.1. Calc., Co, 7.0; NH₃, 10.1%). Two mols. of picric acid gave a mixture of the aquo- and hydroxo-salts.

B. Hydroxopentamminochromic Salts.

The only salts of this series hitherto described are the dithionate (Jørgensen, *J. pr. Chem.*, 1882, **25**, 419; Dubsky, *ibid.*, 1914, **90**, 99), picrate and dipicrylamide (Part I). The sulphate, nitrate, chloride, bromide, iodide, chromate and oxalate have now been obtained. They are rose-red salts, much more soluble in water than the corresponding cobaltammines (Werner, *Ber.*, 1907, **40**, 4098). They give solutions only very slightly alkaline to litmus and do not liberate ammonia from ammonium salts in the cold. Thus the tendency to form aquo-salts is less pronounced than in the case of hydroxopentamminocobaltic salts. The co-ordinated hydroxyl group cannot be acetylated or carbonated. Unlike the hydroxopentamminocobaltic salts, they smell of ammonia and are unstable even in the dark. They can, however, be kept indefinitely in an ammoniacal atmosphere. The salts most readily obtained pure and in quantity are the sulphate and nitrate.

That these are not basic aquo- but hydroxo-salts is demonstrated as follows.

(a) The sulphate and chromate were obtained anhydrous, whilst the nitrate, bromide, and iodide contained less water than is required for an aquo-salt.

(b) Hydroxopentamminochromic picrate was obtained from the sulphate by double decomposition.

(c) The electrical conductivities at 25° and a dilution of 1024 litres were of the order required (234 to 268 mhos) for salts with two univalent ions outside the complex, by Werner's empirical rule (Werner and Miolati, *Z. physikal. Chem.*, 1894, **14**, 506). The values obtained for the sulphate, nitrate, chloride, and oxalate were 234.0, 260.8, 274.6 and 235.5. (The value 266.2 obtained for hydroxopentamminocobaltic nitrate also agrees with the rule.)

Hydroxopentamminochromic sulphate was obtained by adding the hydroxopentamminochromic hydroxide solution (100 c.c.) from 4 g. of chloropentamminochromic chloride to 2.17 g. of ammonium sulphate in 3 c.c. of water and 16 c.c. of concentrated ammonia solution. When 50 c.c. of ice-cold alcohol had been added drop by drop to the cooled solution, rosettes of large, rose-red needles began to form. On addition of 20 c.c. more alcohol most of the sulphate crystallised (3.5 g.). It was collected, washed with ammoniacal alcohol and ether, and kept in a vacuum in presence of soda-lime and ammonium carbonate (Found : Cr, 21.2; NH₃, 33.8; S, 13.0. [Cr(NH₃)₅OH]SO₄ requires Cr, 20.8; NH₃, 34.0; S, 12.8%).

A sample was triturated with acetic anhydride for 20 minutes. The product was dissolved in water and treated with a solution of sodium picrate. Hydroxopentamminochromic picrate (Part I) was precipitated, showing that no acetylation had occurred (Found : Cr, 8.3; NH₃, 12.8; N, 23.3. Calc., Cr, 7.9; NH₃, 13.0; N, 23.5%).

When carbon dioxide was passed into a cooled concentrated solution of the sulphate, 3 to 4 mols. of ammonia were displaced, an insoluble bluish-violet carbonate of variable composition being formed.

Hydroxopentamminochromic nitrate was not readily obtained by adding the hydroxide to ammonium nitrate solution, as a large excess of alcohol and ether was needed for precipitation and the salt then separated as an oil. Five g. of aquopentamminochromic nitrate (Werner and Surber, *Annalen*, 1914, **405**, 220) were dissolved in 30 c.c. of concentrated ammonia, and cooled alcohol (60 c.c.) was added drop by drop to the ice-cold solution until a permanent crystalline precipitate formed (small, irregular, red plates). This was collected immediately and washed with ammoniacal alcohol and ether (Found: Cr, 18.2; NH₃, 29.6; N, 34.3.

[Cr(NH₃)₅OH](NO₃)₂·½H₂O
requires Cr, 18.1; NH₃, 29.7; N, 34.1%). Although the salt had

an ammoniacal odour, it lost only $2\frac{1}{2}\%$ of its ammonia when kept during 10 weeks over phosphoric oxide in a vacuum.

Action of Pyridine on Aquopentamminochromic Nitrate.—A strong solution of the aquo-salt was treated with excess of ice-cold pyridine, the colour changing from orange to dark red. Addition of alcohol gave an orange precipitate, the ammonia content of which (26.1%) indicated that 25% of the aquo- had been hydrolysed to the hydroxo-nitrate.

Aquopentamminochromic halides, prepared by Christensen (*loc. cit.*) from hydroxopentamminochromic hydroxide, were more conveniently obtained in pure condition as follows.

Chloride.—A solution of 7.5 g. of aquopentamminochromic nitrate in 60 c.c. of water was filtered into 160 c.c. of ice-cold strong hydrochloric acid, when partial precipitation of the crystalline salt occurred. Ice-cold alcohol (100 c.c.) was added and the salt was at once collected (3.7 g.) (Found : NH_3 , 32.7. Calc., NH_3 , 32.6%). The chlorine was completely and immediately precipitated in the cold by silver nitrate, showing that no chloropentamminochromic salt was present.

Bromide.—A solution of 5 g. of aquopentamminochromic nitrate was added to 60 c.c. of ice-cold strong hydrobromic acid, an immediate precipitate of 5 g. of the bromide being formed. This was freed from a trace of purpureo-salt by dissolving in water (50 c.c.) and filtering into 50 c.c. of ice-cold hydrobromic acid. The *iodide* was prepared similarly to the bromide.

Hydroxopentamminochromic chloride was obtained as aggregates of small, very soluble, rose needles (2 g.) on dissolving aquopentamminochromic chloride (3 g.) in 15 c.c. of concentrated ammonia and slowly adding ice-cold alcohol (60 c.c.) until precipitation was complete. The salt lost 18.6% of its ammonia in 3 hours at 100° (Found : Cr, 21.4; NH_3 , 35.0; Cl, 28.9. $[\text{Cr}(\text{NH}_3)_5\text{OH}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ requires Cr, 21.4; NH_3 , 35.0; Cl, 29.2%).

Hydroxopentamminochromic bromide separated as a solid mass of pink needles when aquopentamminochromic bromide was dissolved in ammonia, and a little ice-cold alcohol added (Found : Cr, 16.3; NH_3 , 26.1; Br, 49.5; H_2O , 3.0. $[\text{Cr}(\text{NH}_3)_5\text{OH}]\text{Br}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Cr, 16.1; NH_3 , 26.4; Br, 49.5; H_2O , 2.8%).

Hydroxopentamminochromic iodide was obtained as bunches of minute, pink needles by dissolving 5 g. of aquopentamminochromic iodide in 30 c.c. of concentrated ammonia and adding slowly 100 c.c. of ice-cold alcohol. It was somewhat less soluble than the other salts (Found : Cr, 12.7; NH_3 , 20.6; I, 60.9. $[\text{Cr}(\text{NH}_3)_5\text{OH}]\text{I}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Cr, 12.5; NH_3 , 20.4; I, 60.9%). When solid potassium iodide was added to a solution of aquopentamminochromic nitrate

in concentrated ammonia, an addition compound of the hydroxide with potassium iodide was obtained (pink needles).

Hydroxopentamminochromic chromate was obtained by adding the hydroxide solution (55 c.c.) from 4 g. of chloropentamminochromic chloride to 2.5 g. of ammonium chromate dissolved in ammonia. The intense reddish-brown solution was treated with alcohol until a permanent crystalline precipitate just formed (aggregates of thin, brown plates). This was collected and washed with ammoniacal alcohol and ether (Found : Cr, 38.7; NH_3 , 31.3. $[\text{Cr}(\text{NH}_3)_5\text{OH}]\text{CrO}_4$ requires Cr, 38.5; NH_3 , 31.5%).

No reduction in weight occurred when the salt was kept for a fortnight over phosphoric oxide.

Hydroxopentamminochromic Oxalate.—The hydroxide solution from 5 g. of chloropentamminochromic chloride (100 c.c.) was added to 2.92 g. of ammonium oxalate in 100 c.c. of water, when ammonia was immediately evolved. Ammonia solution (10 c.c.) was added, and a considerable excess of alcohol and ether; the precipitate of large, pink needles was readily soluble in water (Found : Cr, 18.6; NH_3 , 30.4. $[\text{Cr}(\text{NH}_3)_5\text{OH}]\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ requires Cr, 18.7; NH_3 , 30.6%).

Hydroxopentamminocobaltic Nitrate.—The following is a more convenient method than that given by Werner (*loc. cit.*) for preparing the pure monohydrated salt. To a filtered solution of 20 g. of aquopentamminocobaltic nitrate in 100 c.c. of concentrated ammonia, 240 c.c. of boiling alcohol are added and the mixture is cooled quickly to prevent separation of an oil. The precipitate is dissolved in ammonia, and to the ice-cold filtered solution cooled alcohol is added drop by drop until crystallisation begins (yield 7 g.) (Found : Co, 19.4; NH_3 , 28.1. Calc., Co, 19.5; NH_3 , 28.1%).

C. Electrical Conductivities of Chromammines and Cobaltammines.

The $\lambda\text{-C}^{1/3}$ Graph (see Porter, *Trans. Faraday Soc.*, 1919, **15**, 122).

—The electrical conductivities of a large number of salts of bivalent chromamine and cobaltamine cations give, for the concentration range $v = 32$ to $v = 1024$, a rectilinear $\lambda\text{-C}^{1/3}$ graph. This has been found to be the case for hydroxopentamminochromic nitrate, chloride and hydroxide, hydroxopentamminocobaltic nitrate, chloropentamminochromic chloride and bromide, chloropentamminocobaltic sulphate, bromide, chloride and nitrate, nitropentamminochromic chloride (xantho), nitropentamminocobaltic nitrite and chloride (xantho), dinitrotetramminocobaltic nitrate (flavo) and chloride (croceo). It has therefore been concluded that in normal cases the $\lambda\text{-C}^{1/3}$ graph for such salts over this range should be rectilinear and that deviations are due to such

phenomena as polymerisation in concentrated solution, hydration and hydrolysis. This view was supported by the fact that in several cases where deviation was found at 25° the graph was rectilinear at 0° (*e.g.*, chloropentamminochromic bromide, Table III). Further, in cases where this graph is rectilinear, extrapolation to zero concentration by means of the $1/\lambda - (C\lambda)^{n-1}$ graph gives concordant values for the mobility of the complex ion, whilst extrapolation of data for the same ion which give a curved $\lambda - C^{1/3}$ graph leads to a quite different mobility value. Thus for the bivalent hydroxopentamminochromic ion, extrapolation of the conductivity data for the nitrate and chloride gives mobility values 131.6 and 131.9 at 25°, whilst the oxalate and sulphate data, which deviate from the straight-line rule (probably owing to polymerisation in concentrated solution), lead to mobility values 380.9 and 195.0.

The rectilinear $\lambda - C^{1/3}$ graph does not appear to be suitable for extrapolation of conductivity data to infinite dilution, since accurate data for concentrations less than $\frac{1}{1000}$ (*e.g.*, for potassium chloride) are lower than those required by the graph. For amines of chromium and cobalt it leads usually to results 6% higher at 25° than those obtained by the $1/\lambda - (C\lambda)^{n-1}$ graph.

In many cases at $v = 2000$, and sometimes at higher concentrations, the conductivities of amines are *higher* than those required by the rectilinear $\lambda - C^{1/3}$ graph. Such data have been considered to be influenced by decomposition of the complex ion, and have been ignored in calculating λ_∞ . They are bracketed in the tables.

The rule does not appear to apply to salts of tervalent complex kations. The $\lambda - C^{1/3}$ graphs for hexammino-chromic (-cobaltic) and aquopentammino-chromic (-cobaltic) salts are curved. Nevertheless, extrapolation leads to concordant results from different salts of the same ion.

Conductivity Data.—The usual Kohlrausch method was employed, resistances being measured by a standardised Post Office box. An open cylindrical cell of constant 0.1197 was used for the salts. The conductivity water was obtained by a single distillation of distilled water with a little potassium bisulphate, and its specific conductivity varied between 0.66×10^{-6} and 1.1×10^{-6} mho, at 0°. Except in the case of hexammino-salts, the method of successive dilutions was not employed. A fresh solution was prepared for each measurement, and its conductivity was determined forthwith. This was particularly necessary in the case of hydroxo-salts, since their conductivity increased rapidly when they were kept in contact with the electrodes.

TABLE I.

Hydroxopentammino-chromic and -cobaltic Salts.

v is the reciprocal of the concentration in mols. per litre, and λ the molecular conductivity in mhos.

Bracketed data have been ignored in calculating λ_{∞} .

| | [Cr(NH ₃) ₅ OH]Cl ₂ . | | [Cr(NH ₃) ₅ OH](NO ₃) ₂ . | | [Cr(NH ₃) ₅ OH]SO ₄ . | |
|-------|---|------------------------|---|------------------------|---|------------------------|
| v . | λ_0° . | λ_{25}° . | λ_0° . | λ_{25}° . | λ_0° . | λ_{25}° . |
| 32 | 108.8 | 206.2 | 106.4 | 201.5 | (59.4) | (117.6) |
| 64 | 119.0 | 225.7 | 115.7 | 219.4 | (69.5) | (132.9) |
| 128 | 127.5 | 239.0 | 124.7 | 233.6 | (82.0) | (158.3) |
| 256 | 134.9 | 253.0 | 132.0 | 244.3 | (94.1) | (181.2) |
| 512 | 138.8 | 261.9 | 138.9 | 254.2 | (108.3) | (208.2) |
| 1024 | 147.2 | 274.6 | 141.4 | 260.8 | (118.9) | (234.0) |
| 2048 | — | — | (152.7) | (279.9) | (132.3) | (254.2) |

| | [Cr(NH ₃) ₅ OH]C ₂ O ₄ . | | [Co(NH ₃) ₅ OH](NO ₃) ₂ . | |
|-------|---|------------------------|---|------------------------|
| v . | λ_0° . | λ_{25}° . | λ_0° . | λ_{25}° . |
| 32 | — | (132.8) | — | 196.5 |
| 64 | — | (150.4) | — | 215.2 |
| 128 | — | (169.6) | 124.2 | 229.5 |
| 256 | — | (190.0) | 132.2 | 241.5 |
| 512 | — | (213.4) | 138.4 | (253.4) |
| 1024 | — | (235.5) | 143.4 | (266.2) |

TABLE II.

Hydroxopentamminochromic Hydroxide, [Cr(NH₃)₅OH](OH)₂.

α = degree of dissociation.

| | | | | | | |
|-------------------------|-------|-------|-------|-------|-------|-------------------------|
| v | 22.53 | 32.85 | 42.92 | 65.70 | 365.8 | ∞ (extrapolated) |
| λ_0° | 237.8 | 245.5 | 250.0 | 254.1 | 273.7 | 283.9 |
| α | 83.8 | 86.5 | 88.1 | 89.5 | 96.4 | — |

The hydroxide solution was prepared by triturating chloropentamminochromic chloride with moist silver oxide (Christensen, *loc. cit.*), filtering, and washing the oxide with a little ice-cold conductivity water. Air was excluded as much as possible during the preparation, and the conductivity was measured in a stoppered flask-shaped cell. The concentration was determined by an ammonia estimation. The hydroxide prepared from aquopentamminochromic chloride gave similar results. A positive water correction was applied (Lamb and Yngve, *loc. cit.*). The water used was practically "equilibrium water," its specific conductivity being 0.66×10^{-6} mho at 0° .

TABLE III.

Chloropentamminochromic Salts.

| | [Cr(NH ₃) ₅ Cl]Cl ₂ . | | [Cr(NH ₃) ₅ Cl]Br ₂ . | |
|-------|---|------------------------|---|------------------------|
| v . | λ_0° . | λ_{25}° . | λ_0° . | λ_{25}° . |
| 64 | 123.1 | 230.3 | — | (232.3) |
| 128 | 131.1 | 244.5 | 134.8 | (247.7) |
| 256 | 137.2 | 255.0 | 142.1 | (261.5) |
| 512 | 142.3 | 264.4 | 146.8 | (272.9) |
| 1024 | (147.6) | (276.8) | 151.2 | (280.6) |

The conductivity increased rapidly on standing, particularly in the case of the bromide.

TABLE IV.
Aquopentammino-salts.

| | | | | | | |
|---|-------|-------|-------|-------|-------|---------|
| ν | 32 | 64 | 128 | 256 | 512 | 1024 |
| λ_0 for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ | 169.5 | 186.3 | 203.4 | 218.4 | 232.9 | (247.8) |
| λ_0 for $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$... | 163.0 | 179.0 | 197.6 | 212.2 | 225.9 | 238.0 |

TABLE V.
Hexamminochromic Salts.

| $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ | | | $\text{Cr}(\text{NH}_3)_6\text{Br}_3$ | $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ | | | $\text{Cr}(\text{NH}_3)_6\text{Br}_3$ |
|---|---------------------|------------------------|---------------------------------------|---|---------------------|------------------------|---------------------------------------|
| ν . | λ_0° . | λ_{25}° . | λ_{25}° . | ν . | λ_0° . | λ_{25}° . | λ_{25}° . |
| 32 | — | 307.5 | — | 512 | 236.3 | 439.9 | 453.5 |
| 64 | 182.6 | 340.2 | 355.5 | 1024 | 250.0 | 465.9 | 480.5 |
| 128 | 201.6 | 375.3 | 391.1 | 2048 | 260.5 | 489.8 | — |
| 256 | 219.7 | 408.0 | 423.3 | 4096 | 269.9 | 512.3 | — |

The conductivities for hexamminochromic nitrate at 25° are considerably higher than those recorded by Werner and Miolati (*loc. cit.*).

Ionic Mobilities.—The conductivity at infinite dilution has been obtained in every case from the $1/\lambda - (C\lambda)^{n-1}$ graph (Noyes and Coolidge, *Carnegie Inst. Pub.*, **63**, 50).

Hydroxopentamminochromic ion. The data for the chloride and nitrate (Table I) give mobility 73.0 and 73.5 ($n = 1.56$ and 1.52) at 0° and 131.9 and 131.6 ($n = 1.60$) at 25° . The means of these closely concordant values are adopted in Table VI. The data for hydroxopentamminochromic hydroxide give mobility 73.9 at 0° , in excellent agreement with the figure derived from the salts.

Hydroxopentamminocobaltic ion. The data for the nitrate (Table I) give mobility 76.6 at 0° ($n = 1.50$) and 131.0 at 25° ($n = 1.60$).

Chloropentamminochromic ion. The data in Table III give the ionic mobility as 75.2 and 76.8 (chloride and bromide) at 0° ($n = 1.50$) and as 139.7 (chloride) at 25° ($n = 1.50$). The data of Werner and Miolati (*loc. cit.*) for the chloride at 25° give a slightly lower value (138.4). The lower figure 75.2 at 0° has been adopted, since the bromide results are probably affected by hydration.

Chloropentamminocobaltic ion. The data of Werner and Miolati (*loc. cit.*; *Z. physikal. Chem.*, 1896, **21**, 235) for chloropentamminocobaltic salts at 25° give an ionic mobility 3.5% higher than that of the corresponding chromamine ion, but extrapolation of the more recent results obtained by Harkins, Hall, and Roberts (*J. Amer. Chem. Soc.*, 1916, **38**, 2643) for the chloride gives values 74.8 at 0° and 140.8 at 25° ($n = 1.60$ and 1.82). These are the values adopted in Table VI.

Aquopentammino-chromic and *-cobaltic* ions at 0°. The data of Table IV give mobilities 174.3 ($n = 1.40$) and 161.7 ($n = 1.44$). The latter agrees well with the estimated value of 160 given by Lamb and Yngve (*loc. cit.*).

Hexamminochromic ion. The data of Table V give mobility 180.0 at 0° ($n = 1.46$) and 369.6 and 370.8 (nitrate and bromide) at 25° ($n = 1.42$ and 1.40).

The diminution in mobility of the complex ion at 0° on replacing one ammonia molecule of the hexammine by water is 5.7 in the chromammine, 5.3 in the cobaltammine series (see Table VI).

The values employed for the mobilities of the anions at 0° and 25° were Cl', 41.1 and 75.5; Br', 43.1 and 77.8; NO₃', 40.4 and 70.6; OH', 105.0 (0°); $\frac{1}{2}$ SO₄'', 78.0 (25°); $\frac{1}{2}$ C₂O₄'', 72.7 (25°).

The ionic mobilities of the complex kations are collected in Table VI. Those indicated by an asterisk are taken from the table given by Lamb and Yngve (*loc. cit.*). Q = valency of kation.

TABLE VI.

| Kation. | Λ_0 . | Λ_0/Q^2 . | Λ_{25} . | Λ_{25}/Q^2 . |
|--|---------------|-------------------|------------------|----------------------|
| 1 : 2-[Co(NH ₃) ₄ (NO ₂) ₂] | 18.1* | 18.1 | 36.3* | 36.3 |
| 1 : 6-[Co(NH ₃) ₄ (NO ₂) ₂] | 17.9* | 17.9 | 36.1* | 36.1 |
| [Cr(NH ₃) ₅ OH]'' | 73.3 | 18.3 | 131.8 | 33.0 |
| [Co(NH ₃) ₅ OH]'' | 76.6 | 19.2 | 131.0 | 32.8 |
| [Cr(NH ₃) ₅ Cl]'' | 75.2 | 18.8 | 139.7 | 34.9 |
| [Co(NH ₃) ₅ Cl]'' | 74.8 | 18.7 | 140.8 | 35.2 |
| [Cr(NH ₃) ₆]''' | 180.0 | 20.0 | 370.2 | 41.1 |
| [Co(NH ₃) ₆]''' | 167.0* | 18.6 | 327.0* | 36.3 |
| [Cr(NH ₃) ₅ H ₂ O]''' | 174.3 | 19.4 | — | — |
| [Co(NH ₃) ₅ H ₂ O]''' | 161.7 | 18.0 | 314.0* | 34.9 |

The mobilities of corresponding chromammine and cobaltammine bivalent ions are practically identical.

The marked increase in mobility of the complex ions with increase of valency has no parallel among ordinary metallic kations. If the mobility is divided by the square of the valency, an approximate constant is obtained throughout the table, showing that the mobility is proportional to the square of the ionic charge. The mean values of Λ/Q^2 for univalent, bivalent and trivalent ions are 18.0, 18.8 and 19.0 at 0° and 36.2, 34.0 and 37.4 at 25°. For metallic kations, Λ/Q is approximately constant.

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