178. *Rhodium Hydroxopentammines.*

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It has already been shown (J., 1934, 34) that iridium forms a series of hydroxopentammines, $[Ir(NH_3)_5(OH)]X_2$, which resemble the corresponding compounds of cobalt and chromium rather than those of platinum. It is now shown that rhodium forms a similar series of *hydroxopentamminorhodium* salts which bears a strong resemblance to that of iridium. These salts were prepared similarly to the iridium salts by the action of concentrated aqueous ammonia on the aquopentammines, which had been prepared by Jörgensen (*J. pr. Chem.*, 1886, **34**, 394) by heating chloropentamminorhodium hydroxide solution, treating the cooled solution with silver hydroxide, and adding to the filtrate the appropriate acid.

The salts form well-defined, faintly yellow crystals, fairly easily soluble in water. Like the corresponding iridium salts, the rhodium hydroxopentammines are strongly alkaline to litmus, and liberate ammonia in the cold from ammonium salts. They are not basic aquo-salts, since (*a*) the *nitrate* is anhydrous, (*b*) there is no change in properties on heating to 100°, at which temperature an aquo-salt would be decomposed, and (*c*) their behaviour towards specific reagents is quite different from that of aquo-salts. The *bromide* and *sulphate* contain water of crystallisation which is completely expelled at 100°; that of $[Ir(NH_3)_5(OH)]Cl_2,H_2O$ requires a temperature of 135° for expulsion. The normal behaviour of the rhodium ammines in this respect confirms the conclusion previously reached, that the high temperature required for dehydrating $[Ir(NH_3)_5(OH)]Cl_2,H_2O$ was simply a case of the tenacity of water peculiar to some iridium ammines. There appears now no reason to doubt that the water in hydroxopentamminoiridium chloride is water of crystallisation.

* Although the bulk phases contain both components, the interfacial film will consist almost wholly of one component.

The hydroxopentammines resemble the pentammine rather than the hexammine type in their behaviour towards specific ammine reagents.

The general stability of the hydroxopentammines depends, not only on the properties of the hydroxopentammine complex itself, but also on the character of the corresponding aquo-compound, which in many reactions is immediately formed as an intermediate compound. For instance, acetic anhydride leaves chromium hydroxopentammine (King, J., **1925**, **127**, 2100) undecomposed, but acts on the much more stable rhodium hydroxopentammine with the formation of *acetato*-salt. When this factor is taken into consideration, it is seen that the rhodium hydroxopentammines, when they do occasionally differ slightly from their iridium counterparts (*e.g.*, in basicity, solubility, and colour), tend to approach in properties their other vertical neighbour, cobalt.

EXPERIMENTAL.

Titration values are expressed as percentage weight of hydrogen chloride required by the titrated substance.

Hydroxopentamminorhodium Bromide.—10 G. of aquopentamminorhodium bromide were placed in a flask fitted with a soda–lime guard-tube, and 120 ml. of freshly-distilled concentrated aqueous ammonia added from a dropping-funnel. Any substance remaining undissolved was filtered off as rapidly as possible, contact with the air being avoided, and the filtrate was returned to the flask. The flask was cooled, and 500 ml. of alcohol added gradually. The precipitate was filtered off, redissolved in 60 ml. of aqueous ammonia, and reprecipitated with alcohol. The crystals were collected, washed with alcohol and ether, and dried in a desiccator {Found : Rh, 26·8; N, 18·0; Br (total), 42·0; Br (free), 41·8; H_2O (loss at 100°), 4·8; titration, 9·6. $[Rh(NH_3)_5(OH)]Br_2,H_2O$ requires Rh, 26·9; N, 18·3; Br (total), 41·7; Br (free), 41·7; H_2O, 4·7; titration, 9·5%}. The faintly yellow, microcrystalline *salt* does not change in weight on exposure to the air. It is fairly easily soluble in water, forming a solution which is strongly alkaline to litmus and can be sharply titrated with methyl-orange as indicator with one equivalent of acid. The water of crystallisation is expelled at 100°, and no change in colour, titre, or other properties is suffered on heating at 130° for several hours; under these conditions the aquo-salt changes to the brilliant yellow bromopentammine salt. All the bromine is precipitated in the cold by silver nitrate solution. A concentrated hydroxopentammine solution immediately evolves ammonia on the addition of solid ammonium chloride in the cold, and aquo-salt is formed. No precipitate is given when dilute solutions of silver nitrate and hydroxopentammine nitrate are mixed, but a fairly concentrated solution of silver nitrate added to the solid ammine gives a distinct darkening.

The reactions of the rhodium hydroxopentammines with typical ammine reagents are tabulated below; for comparison the reactions of acido- and aquo-salts (Jörgensen, *J. pr. Chem.*, 1883, **27**, 434; 1886, **34**, 394) are also given.

		Pentammines.	Hexammine.
Reagent.	Hydroxo-salt.	Acido-salt.	Aquo-salt.
Potassium ferricyanide, 5% soln.	After 30 mins., very small ppt. (yellowish-red prisms).	No ppt.	Immediate abundant ppt.
Sodium pyrophosphate, 5% soln.	No ppt. After 24 hrs., a few hexagonal plates.	No ppt.	Temporary ppt., dissolving in excess; permanent ppt. forms after 1 min.
Chloroplatinic acid soln.	Ppt. (yellow rhombs).	Ppt.	No ppt.
Sodium phosphate soln. and ammonium hydroxide.	Ppt. (white micro-crystals).	No ppt.	No ppt.
Sodium dithionate, 5% soln.	No ppt.	Ppt.	No ppt.

When carbon dioxide was passed through a cooled solution of the hydroxo-bromide, the resulting solution gave partial precipitates with potassium ferricyanide and sodium pyrophosphate solutions, indicating the presence of some aquo-salt. From the carbonated hydroxo-bromide solution, alcohol precipitated mostly unchanged hydroxo-bromide containing about 10% of carbonate.

Acetic acid reacted with hydroxo-salts to form aquo-salts; owing to its great solubility, aquo-acetate could not be separated from the solution, but, on the addition of potassium bromide, alcohol, and ether, the aquo-bromide was precipitated.

Acetic anhydride (5 ml.) was rubbed with hydroxo-bromide (1 g.) in a mortar for 5 minutes, and the residue filtered off, washed with alcohol, redissolved in water, and reprecipitated with alcohol. The long, easily soluble, slightly yellow needles were *acetatopentamminorhodium bromide* {Found : Rh, 24·3; Br (free), 37·9; H_2O (at 100°), 4·3; titration, nil. $[Rh(NH_3)_5(O{\cdot}CO{\cdot}CH_3)]Br_2,H_2O$ requires Rh, 24·2; Br (free), 37·6; H_2O, 4·2%; titration, nil}, and agreed in composition and properties with the salt formed by heating a solution of aquo-acetate with acetic acid.

From these tests, it is seen that carbonic acid is too weak to convert more than a small portion of the hydroxo-salt solution into aquo-salt, and shows no tendency to enter the complex. Acetic acid behaves as a mineral acid in forming the aquo-salt. With regard to the action of acetic anhydride on the bromide, it seems probable that some of the rather unstable aquo-salt is first formed, which is then decomposed to acetato-salt.

Hydroxopentamminorhodium Sulphate.—4 G. of aquopentamminorhodium sulphate were placed in the flask as before, and 50 ml. of cooled concentrated aqueous ammonia added. To the two immiscible layers so formed, 50 ml. of water were added, and the flask was shaken to dissolve the temporary precipitate. 200 Ml. of alcohol were added, and the slightly yellow crystals were collected and reprecipitated as in the preparation of the bromide {Found : Rh, 30·6; N, 20·6; SO_4 (total), 28·8; SO_4 (free), 28·6; H_2O (loss at 100°), 10·4; titration, 10·7. $[Rh(NH_3)_5(OH)]SO_4,2H_2O$ requires Rh, 30·5; N, 20·8; SO_4 (total), 28·5; SO_4 (free), 28·5; H_2O, 10·7; titration, 10·8%}.

Hydroxopentamminorhodium Nitrate.—This *salt* was prepared from aquopentamminorhodium nitrate in a way similar to that described in the preparation of the bromide {Found : Rh, 31·0; N, 29·5; titration, 11·2. $[Rh(NH_3)_5(OH)](NO_3)_2$ requires Rh, 31·3; N, 29·8; titration, 11·1%}. The nearly colourless crystals were easily soluble in water and did not change in weight or in properties on heating at 100° for 3 hours. The nitrate was decomposed explosively on heating to higher temperatures, being in this respect more unstable than the corresponding iridium nitrate. In order to estimate the rhodium, a few drops of hydrochloric acid were added to the weighed salt in a porcelain crucible, and the contents of the crucible evaporated to dryness. This process was repeated, and the rhodium estimated by ignition in hydrogen as usual.

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