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10. *Iridium Hydroxopentammines.*

By Bertram E. Dixon.

Iridium forms a series of ammines derived from its trichloride which are extremely stable and are similar in many respects to the platinic ammines. Attempts now made to form amino-compounds, as in the case of platinum, by the action of alkalis, *e.g.*, silver oxide (Dixon, J., 1932, 2948), ammonia (Tschugaev, *Z. anorg. Chem.*, 1924, **137**, 401), or sodium hydroxide, on iridium chloropentammines have, however, failed.

By the action of silver oxide on chloropentamminoiridium chloride, Palmaer (*ibid.*, 1895, **10**, 320) obtained a yellow, strongly alkaline solution, which absorbed carbon dioxide from the atmosphere. From this solution has now been isolated the *compound* $[Ir(NH_3)_5Cl](OH)_2,H_2O$, which appears to be more stable than any other simple ammine hydroxide yet described. The light buff crystals do not deliquesce on exposure to the atmosphere, but absorb carbon dioxide slowly. The molecule of water of crystallisation is expelled with extreme difficulty at 140° under reduced pressure without altering the chemical properties of the compound, and further dehydration is effected only at much higher temperatures with disruption of the molecule. This extraordinary stability of the hydroxide groups shows that there is no tendency towards amino-formation by scission in the chloropentammine molecule.

From the solution obtained by dissolving acidopentamminoiridium salts in hot caustic potash, Palmaer (*loc. cit.*) separated aquopentammine salts by treatment with cold acids. By the action of concentrated ammonia on the aquopentammine salts, a new series of *hydroxopentamminoiridium salts*, $[Ir(NH_3)_5(OH)]X_2$, has now been prepared; these form well-defined, colourless crystals, easily soluble in water. In the dry state they approach in stability the corresponding platinum compounds (Tschugaev, *Z. anorg. Chem.*, 1924, **137**, 1), but differ from them by their readiness to combine in solution with one equivalent of acid to form aquo-compounds. The chloride contains a molecule of water of crystallisation, expelled only by heating to 135° for several hours; this tenacity of water is not uncommon amongst iridium ammines (cf. Palmaer, *ibid.*, 1897, **13**, 211; Werner and de Vries, *Annalen*, 1909, **364**, 117; Delépine, *Z. physikal. Chem.*, 1927, **130**, 227; and the chloropentammine hydroxide just described). The hydroxopentammines of iridium are rather stronger bases than those of cobalt (Werner, *Ber.*, 1907, **40**, 4098), and much stronger than those of chromium (King, J., 1925, **127**, 2100). They are strongly alkaline to litmus, liberate ammonia in the cold from ammonium salts, and partially precipitate silver hydroxide from silver nitrate. In their behaviour towards Palmaer's specific reagents for the iridium chloropentammine, aquopentammine, and hexammine series, the hydroxopentammines are distinctive, but resemble the pentammine rather than the hexammine type.

The alternative formulæ $[Ir(NH_3)_5H_2O](OH)X_2$ and $[Ir(NH_3)_4(NH_2)H_2O]X_2$ would also satisfy the titration values and the analysis (of the chloride). The substances obtained are not basic aquo-salts, since (*a*) the nitrate is anhydrous, (*b*) no change in properties is observed on heating to 100°, at which temperature an aquo-salt would be decomposed, and (*c*) their behaviour towards sodium pyrophosphate, potassium ferricyanide, etc., is quite different from that of aquo-salts. The last two reasons also furnish evidence against the formation of an aminoaquo-compound. Further, the evidence advanced earlier (see above) against the likelihood of amino-formation by scission also holds here, and the stability of the substance obtained does not accord with the presence of an amino-group and an aquo-group within the same complex.

By the isolation of the hydroxopentamminoiridium salts, iridium is shown to fall into line with those elements, *e.g.*, cobalt and chromium, which form the two well-defined and readily interconvertible series hydroxo $\rightleftarrows$ aquo, and to differ in this respect from platinum, whose amino $\rightleftarrows$ ammino series show a parallel behaviour towards acids and alkalis.

EXPERIMENTAL.

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

Chloropentamminoiridium Hydroxide.—The chloride was rubbed in a mortar with an excess of freshly precipitated silver oxide and a little water, contact with carbon dioxide being avoided as much as possible. The filtrate was evaporated over phosphoric oxide in a vacuum desiccator. The yellowish liquid yielded a light buff residue, mostly amorphous, but with some irregular prisms {Found: Ir, 53·0; N, 19·4; Cl, 9·95; CO_2, trace; titration, 19·95. $[Ir(NH_3)_5Cl](OH)_2,H_2O$ requires Ir, 52·8; N, 19·2; Cl, 9·7; titration, 19·9%}. Heated under reduced pressure in an Abderhalden drier at 140° for 8 hours, the *substance* lost 3·8% ($1H_2O$ requires 4·9%); it thereby suffered no appreciable change in titre or other properties, although a trace of brown flocculent insoluble matter was formed. The water expelled on heating in a tube at much higher temperatures was determined directly by collection and weighing (J., 1931, 2312) (Found: H_2O, 13·8. Required for $3H_2O$: 14·8%). The formation of the two extra water molecules is evidence that the scission of the hydroxide groups and of the hydrogen atoms in the complex takes place only at high temperatures and with disruption of the ammine molecule. A solution of the hydroxide is strongly alkaline, expels ammonia from ammonium salts, and precipitates silver hydroxide from silver nitrate solution.

Delépine (*loc. cit.*) prepared the compound $[Ir(C_5H_5N)_2(NH_3)_4](OH)Cl_2,5H_2O$ or
$[Ir(C_5H_5N)_2(NH_3)_3(NH_2)]Cl_2,6H_2O$
and regarded the amino-formula as the more probable since a solution of this substance does not precipitate potassium ferricyanide until the solution is acidified (with the formation of $[Ir(C_5H_5N)_2(NH_3)_4]Cl_3$). Perhaps the entry of pyridine into the complex has rendered possible the formation of an amino-group, but, on the other hand, (*a*) a salt of the hexammine type might not be precipitated by potassium ferricyanide in the presence of hydroxyl ions (*e.g.*, aquopentamminoiridium salts form no precipitate with ferricyanide in the presence of a little ammonia), and (*b*) Delépine finds that the sixth molecule of water cannot be completely expelled.

Hydroxopentamminoiridium Chloride.—4 G. of aquopentamminoiridium chloride were placed in a flask provided with a soda–lime guard-tube and dissolved in 30 ml. of ice-cold, freshly distilled, concentrated ammonia added from a dropping-funnel. The flask containing the clear solution was immersed in a freezing mixture, and 100 ml. of cooled alcohol added drop by drop. The precipitate was filtered off rapidly, redissolved in 20 ml. of ammonia, and reprecipitated as before with alcohol. The crystals were collected, washed with cooled alcohol and ether, and dried in a desiccator {Found : Ir, 50·1; N, 18·6; Cl (total), 18·7; Cl (free), 18·6; titration, 9·3. $[Ir(NH_3)_5(OH)]Cl_2,H_2O$ requires Ir, 50·3; N, 18·2; Cl (total), 18·5; Cl (free), 18·5; titration, 9·5%}. The colourless crystals appear as minute grains, forming aggregates; no change in weight occurred on exposure to the air for 48 hours. They are soluble in about 3 parts of cold water. The solution is strongly alkaline to litmus, and can be titrated with methyl-orange as indicator to a sharp end-point with one equivalent of acid. The *substance* lost 2·1% in weight on being heated at 110° for 3 hours, and 4·1% at 135° for 6 hours ($1H_2O$ requires 4·7%); no change in titre or other properties had then occurred. The two chlorine atoms can be completely precipitated in the cold by silver nitrate.

The hydroxo-salts can be distinguished from the corresponding aquo-salts by the following tests. On the addition of sodium pyrophosphate solution (5%) to the hydroxo-salt, no temporary precipitate is obtained, and only after 24 hours is a small permanent precipitate of hexagonal plates formed. Potassium ferricyanide solution (5%), which yields a copious precipitate with the aquo-salt, gives no immediate precipitate with the hydroxo-salt. After 30 minutes there commences to form a small quantity of extremely slender yellowish-brown acicular crystals, which does not increase in bulk on standing; if the solution is now neutralised with acetic acid, the abundant aquo-salt precipitate is obtained. If the test solutions are boiled before the addition of the ferricyanide, the difference in behaviour is still more striking, since the aquo-salt precipitate is now much reduced in bulk and is not increased by the addition of acetic acid, whereas the behaviour of the hydroxo-salt is unaltered. The hydroxo-salt differs from the chloro-salt in forming no precipitate with sodium dithionate.

A concentrated solution of the hydroxopentammine nitrate partially precipitates silver oxide from a solution of silver nitrate. Ammonia is immediately evolved in the cold on the addition of solid ammonium chloride to the concentrated hydroxopentammine solution; the solution can then be shown to contain aquo-salt by the addition of pyrophosphate. The formation of the aquo-salt is also indicated by the pyrophosphate test after the passage of carbon dioxide through a hydroxo-salt solution. Hydroxo-salts give a white precipitate with potassium ferrocyanide, but none with potassium iodide solution.

Hydroxopentamminoiridium Nitrate.—Chloropentamminoiridium chloride was converted into aquopentamminoiridium nitrate by Palmaer's method (*loc. cit.*). 3 G. of the aquo-nitrate were dissolved in 30 ml. of cooled concentrated ammonia, precipitated with alcohol, and a second precipitation carried out as described in the preparation of the chloride {Found : Ir, 46·0; N, 23·4; titration, 8·9. $[Ir(NH_3)_5(OH)](NO_3)_2$ requires Ir, 46·1; N, 23·4; titration, 8·7%}. The colourless microcrystalline needles forming large clusters did not lose in weight on being heated for 4 hours at 125°. They were easily soluble in water, and had properties similar to the chloride.

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