

Ammine Complexes of Ruthenium

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Ammines not previously described, and simple routes to others which have earlier been difficult to prepare, have been discovered as a result of the isolation of the bivalent ruthenium ammine hexammineruthenium(II) chloride and a study of its reactions. Certain of these compounds could have commercial significance, for example in electrodeposition or in the production of supported catalysts.

Only a limited number of ammines of bivalent ruthenium are known and these contain the nitrosyl group or sulphur-containing radicals such as SO_3^{2-} , SO_3H^- or SO_2^0 . In a recently published paper (1) there is described the preparation of the simple ammine complex hexammineruthenium(II) chloride, $[\text{Ru}^{\text{II}}(\text{NH}_3)_6]\text{Cl}_2$ and a number of its analogues by the reaction of zinc dust upon an ammoniacal solution, of a ruthenium compound. The ammine is unstable in moist air and in aqueous solution breaking down to give mixtures of trivalent ruthenium ammines and elemental ruthenium by a mechanism which may be represented as the disproportionation $3\text{Ru}^{\text{II}} \rightarrow 2\text{Ru}^{\text{III}} + \text{Ru}^0$.

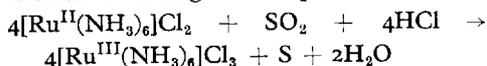
As might be expected, hexammineruthenium(II) chloride is a powerful reducing agent. It reduces silver, gold, mercury and platinum compounds to the metal, and sulphur dioxide to sulphur. Some of these reactions are more complicated than a simple oxidation-reduction and have required quantitative study to elucidate their mechanism. Thus, addition of an excess of sodium chloroaurate to a cold aqueous solution of the hexammine results in the precipitation of gold and a pale yellow compound. On warming, the latter disappears and the amount of gold which has been precipitated is far in excess of that required by simple oxidation of Ru(II) to Ru(III). In fact this is the initial step, hexammineruthenium(III) chloride being formed. This, however, forms a pale yellow chlorochlor-

aurate, $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_2 \cdot \text{AuCl}_4$, which decomposes on warming with water to precipitate all the gold. With an amount of sodium chloroaurate over that required to form this compound, even more gold is deposited and the reaction is extremely complex, resulting in products which have so far not been identified. It seems likely, however, that there are formed polynuclear species, possibly with amido or imido bridges, of ruthenium in a valency state probably higher than three. During the course of the reaction, hydrochloric acid is produced, but if an insoluble base such as zinc oxide or calcium carbonate is incorporated to take up acid as it is formed, the result is remarkable. The ruthenium is oxidised by the chloroaurate to the octavalent state and can be distilled as tetroxide. This reaction is quantitative and provides the basis for an extremely useful method for the determination of ruthenium.

The reaction between the hexammineruthenium(II) chloride and mercuric chloride in stoichiometric amount results in the deposition of mercury and formation of hexammineruthenium(III) chloride, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$. This is a most convenient route to this ammine which has featured, as has the bivalent ammine, in kinetic and other studies carried out by Professor Taube and his collaborators (2) at Stanford University, U.S.A.

In the presence of hydrochloric acid, sulphur dioxide is quantitatively reduced to sulphur

by hexammineruthenium(II) chloride which is itself oxidised to the tervalent ruthenium ammine according to the equation



However, the reaction in the absence of hydrochloric acid is far more complex resulting in an intermediate step, in the formation of a deep red thiosulphate complex, $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{S}_2\text{O}_3)]\text{Cl}_2 \cdot \text{H}_2\text{O}$ in which the S_2O_3 group acts as a unidentate ligand. The final product, and that which results from boiling an aqueous solution of the thiosulphato compound, is a deep purple, extremely stable sulphito complex, the structure of which has not been elucidated but which is probably polynuclear.

Treatment of hexammineruthenium(II) chloride with hydrochloric or sulphuric acid results in the evolution of hydrogen, deposition of a little ruthenium and a deep blue solution from which crystallises the chloride or sulphate, depending upon the acid used, of a cation which may be formulated $[\text{Ru}^{\text{III}}(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cl}_2]^+$. It is difficult to suggest a reason for such a compound having an intensely blue colour and it could be that, rather than being a simple aquodichlorotriammine, the compound has a polynuclear structure. Support for such a view stems from the fact that the ethylenediamine (en) complex $[\text{Ru}^{\text{II}}(\text{en})_3]\text{ZnCl}_4$ prepared by Lever

and Bradford (3) behaves similarly to the ammine compound when boiled with hydrochloric acid; it is, however, not possible to formulate an ethylenediamine compound analogous to a simple triammine.

Boiling hexammineruthenium(II) chloride with nitric acid results in the evolution of nitrous fumes and finally a colourless solution from which crystallises on cooling hexammineruthenium(III) nitrate $[\text{Ru}^{\text{III}}(\text{NH}_3)_6](\text{NO}_3)_3$. This compound is one of but few ruthenium compounds which contain neither alkali metal nor halogen. In the preparation of some supported ruthenium catalysts the presence of these radicals is considered to be undesirable and this ammine may well have application in this field.

Of the many reactions described in the original paper, these which have here been briefly considered have been selected not only because some of the products may be of commercial significance, but also to indicate where further investigations could be most fruitful and lead to the isolation and characterisation of ruthenium complexes so far unknown.

References

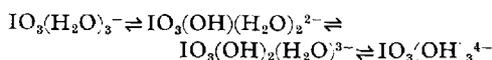
- 1 F. M. Lever and A. R. Powell, *J. Chem. Soc., A*, 1969, 1477
- 2 For instance, J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, 1962, **84**, 4984; *idem*, *Inorg. Chem.*, 1968, **4**, 437
- 3 F. M. Lever and C. W. Bradford, *Platinum Metals Rev.*, 1964, **8**, 106

Iridium Iodate: A New Complex

The iodates of quadrivalent elements such as cerium, zirconium and thorium have, as would be expected, a stoichiometry of $\text{M}(\text{IO}_3)_4$. A short paper by Professor G. Wilkinson and D. Rose of the Inorganic Chemistry Laboratories, Imperial College, and F. M. Lever and A. R. Powell of the Johnson Matthey Research Laboratories (*J. Chem. Soc. (A)*, 1969, 1690) describes the preparation and characterisation of iridium (IV) iodate, produced by the reaction of sodium iodate with a perchloric acid solution of iridium. The reaction yields a quantitative precipitate of an amorphous bluish-black complex. This seems to be a unique compound and entirely different from the iodates

of other quadrivalent elements, having only one iodate radical for each iridium atom.

It is suggested that the compound is a polymeric bridged iodate complex $\text{IrIO}_3(\text{OH})_3$ formed by the following mechanisms:



and

