268. *The Valency and Covalency of Ruthenium in the Blue Chloride Solution.*

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The blue solution resulting from the reduction of ruthenium trichloride has been reinvestigated. Four well-defined, new co-ordination compounds have been isolated by its interaction with certain amines under suitable conditions.

In these compounds the metal is shown to be bivalent. As expected on theoretical grounds, they possess zero magnetic moment.

In 1804, Vauquelin (*Ann. Chim.*, **49**, 188, 219; **50**, 5) noticed that a blue colour was produced by the action of certain reducing agents on ruthenium solutions, and Claus (*Annalen*, 1846, **56**, 260) and other early workers assumed that such solutions contained bivalent ruthenium. A survey of the literature shows that this assumption has been much discussed, and that as recently as 1927 (Remy and Wagner, *Ber.*, **60**, 493; Zintl and Zaimis, *ibid.*, p. 842), its accuracy was questioned. In 1933, however, Manchot and Schmid (*Z. anorg. Chem.*, **216**, 104) studied the electrolytic reduction of ruthenium trichloride in hydrochloric acid and found that, when reduction was complete, the blue catholyte gave a precipitate of $Ru(OH)_2$ with sodium hydroxide in the absence of air. This affords strong experimental support of the view that the blue solution contains bivalent ruthenium. It appeared to us that the isolation of complex salts of the type $X_2[RuCl_4]$ from the blue solution would settle the question of the valency of the ruthenium and at the same time direct attention to the value of the electrolytic method in investigations dealing with bivalent ruthenium.

Howe (*J. Amer. Chem. Soc.*, 1901, **23**, 782) attempted to isolate such derivatives by the addition of cæsium chloride and of rubidium chloride to the blue solution of the chloride but "failed to obtain results which could be considered trustworthy" (*ibid.*, 1924, **46**, 336); actually, he obtained in two cases a substance which approximated to the formula $3CsCl,2RuCl_2,2H_2O$.

In the present investigation we have isolated a number of well-defined products by the addition of certain amines, under carefully regulated conditions, to the blue solution obtained by the reduction of ruthenium trichloride dissolved in hydrochloric acid. In every case it was necessary to use a high concentration of ruthenium chloride, for the new co-ordination compounds are very soluble. To form the *pyridinium* derivative the reduced blue solution was added to a well-cooled solution of pyridinium chloride in alcoholic hydrogen chloride with exclusion of air. In isolating the *dipyridyl* or the *trimethylammonium* compound this procedure must be modified, as the hydrochlorides of these bases are insoluble in alcoholic hydrogen chloride. Here, the amine was added to alcoholic hydrogen chloride, and the precipitated hydrochloride brought into solution by the careful addition of water. On addition of the blue solution of the chloride, the pure co-ordination compound was readily obtained.

The above new compounds are dark green, but the *ethylenediamine* derivative is bluish-green. When kept in a vacuum desiccator the solids are stable, but their bluish-green aqueous solutions oxidise rapidly in air. The new substances are of two types: $X_2[RuCl_4]$ and $X_3[RuCl_5,H_2O]$. The resolution of $[Ru(dipy)_3]Cl_2$ by Burstall (J., 1936, 173) has proved that bivalent ruthenium may be 6-covalent. The present investigation also shows that, like other metals of Group VIII, such as palladium and platinum, bivalent ruthenium may be 4-covalent.

The stability of the ion $RuCl_4''$ was indicated when a solution of $(C_5H_6N)_2[RuCl_4]$ was mixed with a slight excess of a solution of silver sulphate, lead acetate, or thallium sulphate. In no case was silver, lead, or thallous chloride obtained; instead, dark green precipitates were formed, the nature of which has not yet been studied in detail. The silver salt, however, gave on ignition in hydrogen, a mixture of ruthenium metal and silver chloride, indicating that it must be a silver ruthenium chloride. It was interesting to find that by the double decomposition of trimethylammonium ruthenium chloride,

$(NHMe_3)_2H[RuCl_5,H_2O]$, with pyridinium chloride or with dipyridylium chloride, the precipitated co-ordination compound was of the type $X_2[RuCl_4]$ and the ruthenium had changed its covalency from six to four.

Confirmation of the valency of the ruthenium in these new co-ordination compounds has been obtained by determining their magnetic behaviour. It is well-known that variations in valency can produce related changes in magnetic moment. We find in one of the cases investigated that the co-ordination compound has a negative susceptibility, and in the others a very small positive value, corresponding to zero moment, and hence to a balanced structure. As ruthenium has an atomic number of 44, we deduce an even valency for the metal atom, and as these compounds are formed by the reduction of a tervalent chloride, it is clear that they are derivatives of bivalent ruthenium.

Gleu and his co-workers have found that the ruthenium ammines in which the metal is tervalent are paramagnetic (*Z. anorg. Chem.*, 1938, **187**, 197).

We hope to utilise these new compounds for studying the stereochemistry of 4-covalent ruthenium.

EXPERIMENTAL.

Ruthenium trichloride, dissolved in about four times its weight of 6N-hydrochloric acid, was used as the cathode solution in a diaphragm cell, the anode solution being 6N-hydrochloric acid. Smooth platinum electrodes were employed, and a current density of 0·5 amp./sq. cm. The cell was cooled by water at 15°. When reduction was complete (about 6 hours), the liquid in the cathode chamber was deep blue : reduction for a longer period caused deposition of ruthenium. To ensure that no solid material vitiated the following experiments, the blue solution was rapidly filtered in absence of air before being used.

Dipyridinium Ruthenium Tetrachloride.—Pyridine was added to four times its volume of alcoholic hydrogen chloride, and the solution (containing excess of acid) shaken with the blue solution resulting from the reduction. The ratio of pyridine to ruthenium employed was 2·5 : 1. Deposition of the new *compound* began in a few minutes and was complete in an hour. Air was rigidly excluded. The dark green crystalline solid was washed repeatedly with alcohol, and dried in a vacuum desiccator over calcium chloride {Found : Ru, 25·6; Cl, 36·0; N, 7·0. $(C_5H_6N)_2[RuCl_4]$ requires Ru, 25·2; Cl, 35·2; N, 6·9%}.

Dipyridylium Ruthenium Tetrachloride.—Dipyridyl, dissolved in a minimum quantity of alcohol, was added to alcoholic hydrogen chloride, and the precipitated chloride just brought into solution by addition of water. The new *compound* was obtained as described above (Found : Ru, 25·3; Cl, 36·0; N, 6·7. $C_{10}H_8N_2RuCl_4$ requires Ru, 25·4; Cl, 35·4; N, 7·0%).

Bistrimethylammonium Hydrogen Ruthenium Pentachloride.—Trimethylamine was added to four times its volume of alcohol saturated with hydrogen chloride, and the precipitated chloride dissolved as above. This solution was shaken with the blue solution (NMe_3 : Ru = 2·5 : 1), and the precipitated salt removed, washed, and dried in the usual manner {Found : Ru, 24·3; Cl, 41·9; N, 6·5. $(NHMe_3)_2H[RuCl_5,H_2O]$ requires Ru, 24·4; Cl, 42·4; N, 6·7%}. The well-known $(NHMe_3)_2RuCl_5$ is black (*J. pr. Chem.*, 1915, **91**, 103). Another preparation, dried over phosphoric oxide for some days, afforded the *anhydrous* salt {Found : Cl, 44·4; N, 6·7. $(NHMe_3)_2H[RuCl_5]$ requires Cl, 44·3; N, 7·0%}.

Ethylenediammonium Ruthenium Tetrachloride.—This was obtained by double decomposition of an aqueous solution of the trimethylammonium compound and an alcoholic solution of ethylenediamine hydrochloride (Found : N, 9·1; Cl, 46·4. $C_2H_{10}N_2RuCl_4$ requires N, 9·15; Cl, 46·4%).

Analysis.—The ruthenium was determined by ignition of the compound in a stream of hydrogen, and the nitrogen by microchemical methods. Chlorine was determined by decomposition of the substance as in the Carius method, the silver chloride being dissolved in ammonia and reprecipitated with nitric acid after separation of the ruthenium.

Measurements of Magnetic Susceptibility.—The method of Gouy, as modified by Sugden (J., 1932, 161), was used. The tube had an internal diameter of 2 mm., was 12 cm. long, and had a mark etched 8 cm. from the closed end. The carefully dried materials were packed as uniformly as possible up to this mark for the determination.

The calibration of the tube was carried out upon a standard nickel chloride solution of known susceptibility, and before measurements were made, the pull on the empty tube was found, and the appropriate correction made in the observed pull on it when filled. The value of χ was calculated from the formula $\chi \times 10^6 = \alpha/w + \beta F'/w$, where χ is the measured susceptibility per g., α and β are constants for the tube, *w* is the mass of material, and *F′* is the observed pull in mg.

Substance.	*w*, g.	*t*.	*F′*, mg.	$\chi \times 10^6$.	μ.
$(pyH)_2RuCl_4$	0·1633	18°	+0·08	+0·45	0
$(tmH)_2HRuCl_5$	0·1581	17	+0·06	+0·36	0
$dipyH_2RuCl_4$	0·1487	18	−0·02	−0·01	0
enH_2RuCl_4	0·1791	19	0	+0·065	0

The symbols py and dipy have their usual significance, and tm represents trimethylamine.

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