79. *Some Reactions of Tungsten Hexachloride.*

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IN a previous communication (Wardlaw and Webb, J., 1930, 2100) it was shown that molybdenum pentachloride reacted with a wide range of organic substances, and it was considered that much of the conductivity data relating to solutions of this pentachloride in organic solvents was thereby invalidated. It is interesting to find that conductivity data are also recorded (Fischer and Roderburg, *Z. anorg. Chem.*, 1913, **81**, 170) for tungsten hexachloride in a large number of organic solvents. In certain solvents, such as carbon disulphide and carbon tetrachloride, there is evidence that it behaves as a non-electrolyte. There seems little doubt that in these solvents the hexachloride dissolves unchanged in composition, and that we can accept the results as indicating that it is a covalent compound. However, the conductivities for solutions in acetone and ethyl and methyl alcohols must be received with caution, for in these solvents the hexachloride can be shown to be even more reactive than molybdenum pentachloride. The reactivity of the hexachloride is well shown by the reaction with dry ammonia in the cold; Rideal states (J., 1889, **55**, 44) that white fumes of ammonium chloride are produced and a black powder having a semi-metallic lustre is obtained. This substance he considers to be W_2N_3. The formation of this compound is of special interest, for it shows that the reaction is a complex one and not merely a simple decomposition between the ammonia and the hexachloride. In the reaction product the tungsten is no longer sexavalent.

It was thought that by use of a solvent such as carbon tetrachloride and a base like pyridine it ought to be possible to produce a co-ordination compound of the type WCl_6,xC_5H_5N. Instead, we obtained a green insoluble *substance* which on analysis proved to be $(C_5H_6N)_2[WOCl_5,H_2O]$. Here was a clear indication that the initial reaction results in a change of valency from 6 to 5, and that the pentachloride initially formed was decomposed by traces of moisture in the pyridine and the solvent to give the oxychloride, $WOCl_3$, and hydrogen chloride. We attempted to exclude moisture completely from the reaction mixture but always obtained this green substance. Collenberg and Olsson (*Z. anorg. Chem.*, 1918, **102**, 247) had previously tried to prepare the salt but were unable to obtain it pure by the complicated process they used. It is noteworthy that the salts of molybdenum of the type $R_2[MoOCl_5]$ are also green.

When quinoline was used in the above reaction instead of pyridine, an entirely different course was followed: a brown *substance* was deposited of the empirical formula $(C_9H_8N)_8[W_3Cl_{17}]$. Here the tungsten is tervalent, and this salt may be a compound of the well-known series $R_3W_2Cl_9$ associated with the co-ordination compound $(C_9H_8N)_5[WCl_8]$. If so, tungsten exhibits a covalency of eight as in its complex cyanides $R_4[W(CN)_8]$ and $R_3[W(CN)_8]$. We attempted to obtain double chlorides of the type $R_2[WCl_8]$ by the interaction of organic chlorides and tungsten hexachloride in organic solvents but were unsuccessful. Kalischer (*Diss.*, Berlin, 1902) states that he could not prepare double salts of tungsten hexachloride by using alcoholic solutions of organic chlorides. This is not unexpected, as the alcohol itself would react with the tungsten hexachloride and complicate the reaction.

EXPERIMENTAL.

The method used for the preparation of tungsten hexachloride was a modification of that described by Roscoe (*Annalen*, 1872, **162**, 349) and Hill (*J. Amer. Chem. Soc.*, 1916, **38**, 2383). A combustion tube was constricted 9″ from each end. The front portion held the porcelain boat containing finely divided tungsten. Chlorine, from a cylinder and dried by concentrated sulphuric acid, was passed over the tungsten for at least 4 hours. This served to expel air from the apparatus and from the metal. Air must be rigidly excluded during the preparation of the compound, and all joints in the apparatus must be gas-tight. By now lighting the front burners of the furnace, the chlorine was warmed before passing over the tungsten, and this pre-heated chlorine was passed through the apparatus for a further 2 hours. The whole tube was then carefully heated to a temperature which was comfortably hot to the touch and the passage of chlorine continued for another hour. The tungsten was then gradually raised to red heat, whereupon the chloride began to form preceded by an appreciable quantity of the red $WOCl_4$. By heating the upper surface of the tube with a Bunsen burner, the oxychloride could be volatilised and driven beyond the remote constriction in the tube. The hexachloride soon began to form near the front constriction, but from time to time the beautiful steel-blue crystals manifested a reddish tinge due to contamination with $WOCl_4$. This more volatile oxychloride could be separated in the way described previously. By still stronger heating with the Bunsen burner, the hexachloride could be transferred from point to point along the main portion of the tube and thus completely freed from $WOCl_4$. The whole process of forming the hexachloride occupied *ca.* 2½ hours, the tube then being allowed gradually to cool in a current of chlorine. When cold, the tube was cut at the constricted points and the hexachloride removed. We tried Hill's suggestion (*loc. cit.*) of mixing a little spongy platinum with the metallic tungsten but found it of little value in increasing the rapidity of formation of the hexachloride.

Preparation of the Pyridine Compound.—To tungsten hexachloride dissolved in dry carbon tetrachloride, pyridine was added carefully to avoid excess, and the product transferred to a sintered-glass funnel, where it was washed with carbon tetrachloride, all these operations being done in a nitrogen atmosphere. The green product was dried in a vacuum over phosphoric oxide and was then quite stable. It was insoluble in dry alcohol but hydrolysed on treatment with water with partial solution.

Analysis. The green crystalline *substance* was evaporated repeatedly on the water-bath, first with water, then with dilute, and finally with concentrated nitric acid, and the tungsten weighed as trioxide. The chlorine was estimated by digesting the substance with 2*N*-nitric acid for several hours and precipitating the chlorine from the filtrate as silver chloride (this was quite free from tungsten). Nitrogen was estimated by Dumas's method {Found : W, 33·05; Cl, 31·9; N, 5·1. $(C_5H_6N)_2[WOCl_5,H_2O]$ requires W, 33·1; Cl, 32·0; N, 5·04%}.

Preparation of the Quinoline Compound.—Repeated attempts to produce a green compound, by a procedure analogous to the foregoing, invariably yielded a rich brown *compound* {Found : W, 25·3; Cl, 27·6; N, 5·06. $(C_9H_8N)_8W_3Cl_{17}$ requires W, 25·15; Cl, 27·5; N, 5·1%}, which was insoluble in dry alcohol, carbon disulphide, or acetone, but was hydrolysed by water.

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