CXLV.—*The Octammines, with Special Reference to Tin.*

By ARTHUR JAMES COOPER and WILLIAM WARDLAW.

So far, no octammine has been prepared by a reaction between a metallic salt and ammonia in the presence of water, whereas under similar experimental conditions very stable hexammines have been isolated. This supports Sidgwick's view ("The Electronic Theory of Valency," p. 156) that covalencies of eight only arise, even with atoms capable of exhibiting them, in exceptionally favourable circumstances.

Nevertheless, by the action of liquid or gaseous ammonia on metallic salts or their solutions in non-aqueous solvents, a number of compounds containing eight molecules of ammonia have been described, and in many text-books they are formulated and considered as typical co-ordination compounds. This formulation, in the case of unstable substances such as $[Ti,8NH_3]Cl_4$ and $[Ca,8NH_3]Cl_2$, is difficult to justify, for it implies a covalency of eight for the metallic atoms when the weight of chemical evidence is against such an assumption. Even with $BaBr_2,8NH_3$, it is questionable whether the formula $[Ba,8NH_3]Br_2$ is satisfactory, for it is recorded (Joannis, *Compt. rend.*, 1891, **112**, 339) that on exposure to the air the ammonia is completely liberated. It is possible that here, as in the cases cited above, the molecules of ammonia are polymerised or that some form part of the crystal unit but not of the complex molecule.

The zirconium salt $[Zr,8NH_3]Cl_4$, prepared by Stähler and Denk (*Ber.*, 1905, **38**, 2611) by the passage of ammonia into an ethereal suspension of zirconium chloride, is sufficiently stable to yield correct analytical figures, and therefore may be considered a true co-ordination compound; nevertheless, it readily loses ammonia and is affected by moist air. Octammines of cerium, samarium, and neodymium are stated to be formed as intermediate products in the degradation of compounds of higher ammonia content, but here again the evidence in favour of the formation of a true co-ordination compound is very slight. An octammine of thorium is supposed to exist (Ephraim, "Inorganic Chemistry," p. 280), but the experimental evidence (Chauvenet, *Compt. rend.*, 1910, **151**, 387) is not conclusive for such an assumption.

The remaining case of a supposed octammine is the compound $[Sn,8NH_3]I_4$. It was prepared as a white substance by Ephraim and Schmidt (*Ber.*, 1909, **42**, 3856) on passing ammonia into a solution of stannic iodide in carbon disulphide, the solvent then being evaporated by means of warm water. Their product gave Sn, 15·74; NH_3, 16·47 (Calc. for $SnI_4,8NH_3$: Sn, 15·61; NH_3, 17·84%). By direct combination of ammonia and stannic iodide in the absence of a solvent, a compound was obtained giving Sn, 15·71, 15·57, 15·01; NH_3, 16·91, 16·90%. The formation of the co-ordination compound is inferred, therefore, rather than proved by the experimental results.

As stannic iodide is soluble in other organic solvents, it seemed of interest to reinvestigate the reaction in another medium, as well as to repeat the work of Ephraim and Schmidt with carbon disulphide as a solvent. In no case was an octammine formed of sufficient stability for it to be isolated and analysed as such. It appears, therefore, that only in the case of the zirconium salt, $ZrCl_4,8NH_3$, is there any experimental evidence for the existence of a co-ordination compound of the type $[R,8NH_3]X_4$.

We found, however, that in every case the compound could not consist exclusively of tin, halogen, and ammonia: the analytical figures indicated the necessity for a fourth constituent of the molecule. Water was obviously the only possible addendum, and this view was confirmed by the fact that the hydrogen content of the compound was in excess of that required by the nitrogen present. Undoubtedly, therefore, the products were of the type $[Sn,xNH_3,yH_2O]I_4$, and it was found on calculating the value of the different units that $x + y$ was approximately equal to 8. Thus, although the actual octammine was not capable of isolation under the experimental conditions outlined above, yet there is evidence that such an unstable octammine can exist but that the molecules of ammonia are rapidly replaced in the air by water molecules.

A study has also been made of the reaction between stannic iodide in carbon tetrachloride and organic bases such as aniline, pyridine, and quinoline. In no case was there co-ordination of eight molecules of these substances. It appeared that the stable *products* obtained were of the type $SnI_4,2{\cdot}5R$ (R = aniline or pyridine).

Scagliarini (*Atti R. Accad. Lincei*, 1925, **1**, 582) records the isolation of $SnI_4,5C_6H_{12}N_4$ from the reaction of hexamethylenetetramine with stannic iodide in chloroform solution, and also a deep violet substance of the type $SnI_4,4C_6H_{12}N_4,2CHCl_3$, which undergoes little change at 80° or in a vacuum over sulphuric acid but is rapidly decolorised by moist air. Here, if one considers that the non-polar stannic iodide becomes a polar compound after the reaction, a maximum co-ordination number of *six* is attained in the last compound.

EXPERIMENTAL.

The experiment of Ephraim and Schmidt (*loc. cit.*) was repeated, gaseous ammonia being passed through stannic iodide dissolved in carbon disulphide, which at the same time was slowly evaporated. The white product was unstable, continually evolving ammonia, and after a state of stability appeared to have been attained, its *maximum* ammonia content was 13·3%, Sn being 15·3% ($NH_3 : Sn = 6{\cdot}07 : 1$). It was noted that a red intermediate compound was formed during the passage of the ammonia through the solution.

A new series of experiments was instituted in which carbon tetrachloride was used as the solvent instead of carbon disulphide. The stannic iodide was dried in a vacuum over phosphoric oxide, and the tetrachloride kept for several days over phosphoric oxide and then distilled from fresh phosphoric oxide. The ammonia was carefully dried by passage over lime and solid caustic potash. The same red intermediate product referred to above resulted and gradually turned white. The tetrachloride could not conveniently be removed by simultaneous evaporation, as in the case of carbon disulphide, so the product was obtained by filtration. An immediate analysis gave Sn, 15·74; NH_3, 12·7%. In other experiments, similarly conducted, the figure for ammonia was never exceeded. After the substance had been kept for several days in a desiccator over calcium chloride, the ammonia content fell to 9·38% and the tin to 15·4%.

The red intermediate compound when dried yielded a dull brown substance which was quite stable in air and gave Sn, 16·23; NH_3, 6·63. Since $SnI_4,3NH_3$ requires Sn, 17·53; NH_3, 7·53, it was evident that the red compound had absorbed moisture from the air in place of liberated ammonia. This view was confirmed by microanalysis of a sample of a white compound which yielded Sn, 15·52; N, 6·8; H, 2·8. Such a substance corresponds to the composition Sn, 15·52; I, 66·4; NH_3, 8·25; H_2O, 10·05% ($Sn : I : NH_3 : H_2O = 1 : 4{\cdot}00 : 3{\cdot}71 : 4{\cdot}27$; *i.e.*, $Sn : NH_3 + H_2O = 1 : 7{\cdot}98$). Hence the compound can be considered as $Sn[xNH_3 + (8 - x)H_2O]I_4$, with a co-ordination number of eight. Moreover, a similar expression can be deduced for the composition of each of the white compounds described above.

The white compounds are generally unstable, and dissolve easily in the cold in dilute hydrochloric or nitric acid to a colourless solution. With more concentrated nitric acid they give a copious yield of iodine.

Stannic Iodide and Pyridine.—The attempt to prepare a pyridine compound by acting on stannic iodide in carbon tetrachloride proved abortive; the dark red product proved to be stannic iodide. Other solvents were tried, and finally benzene dried by two distillations over phosphoric oxide was chosen. The pyridine was dried by standing for a week over solid caustic potash, followed by two distillations from barium oxide. When the pyridine was added to a benzene solution of stannic iodide, a brown stable precipitate resulted which was insoluble in dry alcohol. It was washed with benzene and with dry alcohol and dried in a desiccator over calcium chloride. The *substance* was crystalline, and soluble in dilute hydrochloric and sulphuric acids. It was partly soluble in water and underwent hydrolysis on standing. With dilute nitric acid, iodine was liberated.

Analysis. The tin was estimated by repeated evaporation with dilute nitric acid and twice with concentrated acid. The residue was ignited slowly at first and afterwards over the blowpipe till of constant weight (Found: Sn, 14·4; I, 61·4; N, 4·37. $SnI_4,2{\cdot}5C_5H_5N$ requires Sn, 14·3; I, 61·7; N, 4·25%).

Stannic Iodide and Aniline.—Considerable difficulty was found in preparing this compound. A red crystalline substance formed on addition of dry aniline to a solution of the iodide in dry carbon tetrachloride, but immediately on exposure to the air the colour changed to a light fawn. This could not be due to loss of aniline and was attributed to hydrolysis. To obviate exposure to the air, the preparation flask was attached by means of a wide V-shaped tube, in which the apex was replaced by a ground joint, to a sintered-glass funnel fitted with a rubber stopper. On rotating the flask about the joint, the mixture it contained was transferred to the sintered-glass funnel without exposure to air. Carbon tetrachloride was introduced into the flask through a second side-tube in the cork, and the product washed repeatedly on the funnel. It was then quickly dried on filter paper and transferred to a vacuum desiccator. A rich-brown *substance* resulted which was quite stable. It dissolved in dilute nitric acid on warming, but on boiling, iodine was copiously evolved. It readily dissolved in dilute hydrochloric or sulphuric acid to a yellow solution. It was rapidly hydrolysed by dilute acetic acid.

Analysis. Treatment with dilute nitric acid and evaporation was unsatisfactory, for the presence of the aniline produced a somewhat violent reaction on concentration, and the base could not be quantitatively expelled. Finally, the compound was decomposed by treating it with ammonia (*d* 0·880), and evaporating the mixture first to dryness on the water-bath, and then several times with water to expel the aniline which had been set free. The residue was treated with concentrated nitric acid, evaporated to dryness on the water-bath, gently heated for some time in an air-bath, and finally heated till of constant weight over the blowpipe (Found : Sn, 13·0; N, 3·76; Sn : N = 1 : 2·45. $SnI_4,2{\cdot}5C_6H_5{\cdot}NH_2$ requires Sn, 13·7; N, 4·0. $SnI_4,2C_6H_5{\cdot}NH_2$ requires Sn, 14·6; N, 4·35%).

Stannic Iodide and Quinoline.—On addition of quinoline to a solution of stannic iodide in carbon tetrachloride, a black solid resulted which, on removal from the solvent, rapidly turned stone-coloured, owing probably to hydrolysis. A stable product was obtained, however, by refluxing the mixture for 2 hours. The product was washed with carbon tetrachloride and dried in a vacuum desiccator for 2 days. It remained unaltered in colour, was sparingly soluble in water, and soluble in dilute hydrochloric or sulphuric acid, whilst dilute nitric acid liberated iodine. Nevertheless, analysis (Found: Sn, 12·8; I, 51·9. $SnI_4,2{\cdot}5C_9H_7N$ requires Sn, 12·45; I, 53·5%) indicates that the substance was not pure.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, February 20th,* 1930.]