LX.—*Basic Chlorides and Addition Compounds from Metallic Chlorides and Hexamethylenetetramine. Exceptional Behaviour of Nickel Chloride.*

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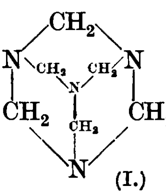
HEXAMETHYLENETETRAMINE is a weak base which can react with hot aqueous solutions of metallic chlorides to yield precipitates of basic chlorides. These precipitates in certain cases remain unchanged on prolonged heating with excess of the base. It seems probable, therefore, that the basic chlorides obtained in this way are definite compounds. The method described below is less likely to lead to the formation of mixtures than methods such as (1) the addition of regulated amounts of alkali in solution to solutions of normal salts, or (2) heating the solution of a normal salt with the corresponding oxide or hydroxide of the metal.

The formation of addition compounds between hexamethylenetetramine and metallic chlorides has also been investigated in order to extend the number of such compounds and to decide between discrepancies in the literature.

The Reactions of Metallic Chlorides with Hexamethylenetetramine in Boiling Aqueous Solution.—There was no evidence of change in the chlorides of magnesium, calcium, strontium, and barium when boiled in aqueous solution with hexamethylenetetramine. Zinc, ferric, chromic, aluminium, antimony, and tin chlorides all yielded the corresponding hydroxide; in the case of stannous chloride the precipitate of stannous hydroxide finally changed to black stannous oxide. From the chlorides of cadmium, lead, and bismuth were obtained the respective basic chlorides Cd(OH)Cl, Pb(OH)Cl, BiOCl.

The five metals which yielded results of most significance in this section were manganese, iron (ferrous), nickel, cobalt, and copper. It is to be noticed that these are placed consecutively in the periodic system. A basic chloride, $3M(OH)_2,MCl_2$ (M = Mn, Fe, Co, Cu), was obtained from the corresponding chloride MCl_2. In the case of nickel, such a basic chloride was not obtained, but the nature of the final product suggests that it had been formed as an intermediate compound. Basic chlorides of the above formulæ for manganese, cobalt, and copper have been obtained by other, but less definite methods. The ferrous *compound*, $3Fe(OH)_2,FeCl_2$, has not been described previously : it is only stable in absence of air.

Nickel chloride behaves in an exceptional way, for (with the possible exception of lead) it afforded the only instance in which the basic chloride underwent further reaction with hexamethylenetetramine. The *compound* so obtained is assigned the formula $N(CH_2{\cdot}OH)_3,3Ni(OH)_2$, but its insoluble nature makes the determination of its constitution difficult. Probably, after some reaction between the basic chloride and the hexamethylenetetramine, the hexagon ring of the latter (I) is removed by hydrolysis as ammonia and formaldehyde, leaving the central part as $N(CH_2{\cdot}OH)_3$, which unites with the nickel hydroxide :



(I.)

$$C_6H_{12}N_4 + 6H_2O + 3Ni(OH)_2 \longrightarrow N(CH_2{\cdot}OH)_3,3Ni(OH)_2 + 3NH_3 + 3CH_2O.$$

Although trihydroxytrimethylamine has not been separated in the free state, several of its derivatives are known, *e.g.*, trimethylolamine sodium sulphite, $N(CH_2{\cdot}O{\cdot}SO_2Na)_3$, and tribenzamidotrimethylamine, $(C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2)_3N$; the latter compound was obtained by Descudé (*Compt. rend.*, 1902, **135**, 694) by heating benzamide with hexamethylenetetramine at 200°, and when boiled with dilute mineral acid yields benzamide, formaldehyde, and ammonia. The nickel compound decomposes in a similar manner, and when dried at 100° loses 3 molecules of water. It has not been found possible to obtain the compound in a state of purity by starting from nickelous hydroxide in place of the chloride, although partial formation was observed.

The behaviour of nickel compounds with amines in the presence of formaldehyde is being investigated.

Addition Compounds from Metallic Chlorides and Hexamethylenetetramine.—Rây and Sarkar (J., 1921, **119**, 390) gave a complete series of references to addition compounds of this type. Some of the formulæ recorded differ, principally as regards water of hydration, from those found by us (see Experimental). The formula $MCl_2,2C_6H_{12}N_4,10H_2O$ represents five addition compounds obtained in aqueous solution (M = Co, Ni, Mn, Mg, Ca). New addition *compounds* now described are $FeCl_2,2C_6H_{12}N_4,9H_2O$;

$SrCl_2,2C_6H_{12}N_4,9H_2O$; and $3ZnCl_2,2C_6H_{12}N_4,6H_2O$.

No addition compound of barium chloride could be separated. The cadmium chloride compound, $2CdCl_2,C_6H_{12}N_4,5H_2O$, has recently been described by Scagliarini and Brasi (*Atti R. Accad. Lincei*, 1928, [vi], **7**, 509). We had already prepared it in the course of this work.

Vanino and Schinner (*Arch. Pharm.*, 1914, **252**, 449—459) describe a cupric chloride compound, $2CuCl_2,C_6H_{12}N_4$, in which they did not determine chlorine; actually it is basic, with formula $Cu(OH)Cl,CuCl_2,C_6H_{12}N_4,2H_2O$. We have obtained a new cupric sulphate *compound*, $2CuSO_4,C_6H_{12}N_4,2H_2O$.

Reactions in Alcoholic Solution.—Metallic chlorides not stable in aqueous solution were found capable of yielding crystalline addition compounds with hexamethylenetetramine in alcoholic solution, and the following new *compounds* were thus prepared: $SnCl_2,2C_6H_{12}N_4$; $SnCl_4,4C_6H_{12}N_4$; $SbCl_3,3C_6H_{12}N_4$; $SbCl_5,6C_6H_{12}N_4$. These four have the same crystalline structure and their formulæ agree with those of corresponding addition compounds of the chlorides with ammonia. Bismuth chloride gave a crystalline *compound*, $BiCl_3,C_6H_{12}N_4$.

Where addition compounds can be prepared both in aqueous and in alcoholic solution, the proportions of hexamethylenetetramine in the pairs of compounds usually differ. We have obtained from alcoholic solution a new zinc chloride *compound*, $ZnCl_2,2C_6H_{12}N_4$.

EXPERIMENTAL.

Reactions between Metallic Chloride Solutions and Boiling Aqueous Hexamethylenetetramine Solutions.

Method.—To a 20% aqueous solution of hexamethylenetetramine (3 mols.) boiling under reflux, a 15% (or saturated, if below this strength) solution of the metallic chloride (1 mol.) was gradually added, and boiling was continued for at least an hour. The solution was then cooled and filtered, and the precipitate washed with water. Modifications which were necessary in certain cases are indicated below. Hexamethylenetetramine was usually estimated by hydrolysis to ammonium salt with hydrochloric acid and distillation of the ammonia into standard acid. Wherever possible, the result was checked by hydrolysing the substance with acid under reflux and adding excess of standard iodine, followed by excess of sodium hydroxide; after 30 minutes, the solution was acidified, and the excess of iodine determined by thiosulphate titration. This method determined the formaldehyde, from which the amount of hexamethylenetetramine could be calculated. The two methods together thus checked the possibility of any breaking down of the molecule of the base before uniting with the metallic chloride or its hydroxide. This applies particularly to the case of nickel (see below). The following definite results were obtained in this section.

1. Magnesium chloride gave no basic precipitate. When the solution was cooled, large, colourless, flat needles were obtained and identified as bishexamethylenetetramine magnesium chloride decahydrate, $MgCl_2,2C_6H_{12}N_4,10H_2O$ (Found: Mg, 4·27; Cl, 12·53; $C_6H_{12}N_4$, 49·5; H_2O, 31·4. Calc.: Mg, 4·38; Cl, 12·80; $C_6H_{12}N_4$, 50·4; H_2O, 32·4%). This compound is the same as that formed when cold concentrated solutions of the two components are mixed.

2. Zinc, ferric, aluminium, and chromic chlorides gave the corresponding hydroxides. Stannous chloride gave first stannous hydroxide, which later changed on continued boiling to black glistening plates of stannous oxide.

3. Bismuth chloride, dissolved in the minimum amount of hydrochloric acid, yielded a white precipitate of the oxychloride, BiOCl (Found: Cl, 13·42. Calc.: Cl, 13·68%). There was no change on prolonged boiling except above the surface of the liquid, where any white precipitate on the glass became black through the reducing action of formaldehyde vapour and ammonia arising from decomposition of hexamethylenetetramine.

4. Mercuric chloride gave mercury as a final product. A basic yellow precipitate of varying composition was first formed; it was unchanged in the dark but turned grey on exposure to sunlight.

5. Cadmium chloride yielded a white precipitate of the basic salt $Cd(OH)Cl$ (Found: Cd, 68·1, 68·2; Cl, 21·3, 21·4. Calc.: Cd, 68·2; Cl, 21·5%).

6. Lead chloride yielded a white precipitate of basic lead chloride, $Pb(OH)Cl$ (Found: Pb, 79·4; Cl, 13·6. Calc.: Pb, 79·6; Cl, 13·7%). On prolonged boiling, the precipitate turned brown, losing its chlorine and becoming an amorphous product containing complex organic matter. The solution also turned dark brown, and when evaporated became a thick treacle-like syrup.

7. Cupric chloride yielded a pale blue precipitate of basic cupric chloride, $3Cu(OH)_2,CuCl_2$ (Found: Cu, 59·1; Cl, 16·9. Calc.: Cu, 59·5; Cl, 16·6%).

8. Cobaltous chloride yielded a pink precipitate of basic cobaltous chloride, $3Co(OH)_2,CoCl_2$ (Found: Co, 57·4; Cl, 17·2. Calc.: Co, 57·7; Cl, 17·4%).

9. Manganese chloride gave a definite result when air was excluded and more concentrated solutions were used. The white precipitate obtained was identified as the basic chloride, $3Mn(OH)_2,MnCl_2$ (Found: Mn, 55·5; Cl, 17·8. Calc.: Mn, 55·9; Cl, 18·1%); it became brown in air. From the hot filtrate there were obtained pale pink crystals of the addition compound, $MnCl_2,2C_6H_{12}N_4,10H_2O$ (Found: Mn, 9·4; Cl, 12·1. Calc.: Mn, 9·4; Cl, 12·1%).

10. Ferrous chloride yielded a white precipitate of *basic ferrous chloride*. The preparation was made in a hydrogen atmosphere, and the precipitate protected by hydrogen during filtration and washing [Found: Fe, 56·7; Cl, 16·9. $3Fe(OH)_2,FeCl_2$ requires Fe, 58·9; Cl, 17·9%]. The compound readily became brown in air. For a more accurate check on the proportions of iron and chlorine, freshly precipitated samples were washed and at once dissolved in dilute sulphuric acid; two determinations with different samples then gave Cl : Fe = 1 : 2·020 and 1 : 2·024.

11. The precipitate formed on adding nickel chloride solution to a boiling aqueous solution of hexamethylenetetramine always contained some portion of the base. Even after 30 minutes' boiling, the precipitate had a chlorine content of about 5%, and ammonia and formaldehyde could be obtained from it on decomposition. A definite compound was finally obtained by boiling the precipitate for about 8 hours, the solution being changed for fresh solution of hexamethylenetetramine three times, until the precipitate was free from chloride. A pale green sandy powder was obtained and identified as an addition *compound* of nickel hydroxide and trihydroxytrimethylamine [Found: Ni, 45·7, 45·7; N, 3·4, 3·6; CH_2O, 23·3, 23·4. $N(CH_2{\cdot}OH)_3,3Ni(OH)_2$ requires Ni, 45·7; N, 3·6; CH_2O, 23·4%]. The nitrogen was estimated as ammonia and

the CH_2O group as formaldehyde. The compound loses 15·0% of water at 95° (Calc. for $3H_2O$: 14·02%) without marked change in colour or in chemical nature. It is odourless and insoluble in water. It differs from nickel hydroxide in being insoluble in boiling formaldehyde solution. There is no reaction with boiling sodium hydroxide solution, and attempts to reduce the compound with sodium and alcohol and with sodium hydrosulphite failed. When left over-night in cold *N*-hydrochloric acid solution, very little dissolves, but the residue on drying contains chloride and smells of formaldehyde. The compound is decomposed on boiling with dilute mineral acid, yielding ammonia, formaldehyde, and a nickel salt. A suspension of the compound in water is decomposed by hydrogen sulphide, yielding an aqueous solution of ammonium sulphide and an insoluble grey product having the unpleasant odour of polymerised thioformaldehyde and containing nickel sulphide. The probable reaction is $N(CH_2{\cdot}OH)_3,3Ni(OH)_2 + 7H_2S = NH_4HS + 3NiS + 3CH_2S + 9H_2O$. Freshly precipitated nickel hydroxide was boiled with excess of 20% aqueous hexamethylenetetramine solution for 6 hours. Analysis of the resulting insoluble green product (Found : N, 1·28; CH_2O, 8·35%; N : CH_2O = 1 : 3·03) showed that partial formation of the above addition compound had resulted. Complete conversion was not expected because of the insoluble gelatinous nature of nickel hydroxide. This supports the view that the addition compound described above is derived from a basic nickel chloride, probably $3Ni(OH)_2,NiCl_2$, formed as an intermediate product from nickel chloride.

Addition Compounds in Alcoholic Solution.

Method.—Cold solutions of the chlorides in absolute alcohol were added gradually with constant stirring to excess of hexamethylenetetramine dissolved in absolute alcohol. The crystalline compounds separated immediately and were at once collected and washed with absolute alcohol. The four tin and antimony compounds all formed colourless, microscopic, oblong plates. The following compounds were thus obtained.

1. *Bishexamethylenetetramine stannous chloride* (Found : Sn, 25·04; Cl, 15·17; $C_6H_{12}N_4$, 58·53. $SnCl_2,2C_6H_{12}N_4$ requires Sn, 25·27; Cl, 15·12; $C_6H_{12}N_4$, 59·60%). When heated, this compound chars extensively, giving ammonia and formaldehyde, and leaving a residue of tin; it is decomposed by cold water, with formation of stannous hydroxide.

2. *Tetrakishexamethylenetetramine stannic chloride* (Found : Sn, 14·4; Cl, 17·2; $C_6H_{12}N_4$, 67·3. $SnCl_4,4C_6H_{12}N_4$ requires Sn, 14·5; Cl, 17·3; $C_6H_{12}N_4$, 68·2%). When heated, this compound behaves

like the stannous chloride compound; with water it is hydrolysed to α-stannic acid.

3. *Trishexamethylenetetramine antimony trichloride* (Found: Sb, 18·6; Cl, 16·5; $C_6H_{12}N_4$, 63·9. $SbCl_3,3C_6H_{12}N_4$ requires Sb, 18·6; Cl, 16·5; $C_6H_{12}N_4$, 5·0%) decomposes in water to give antimony hydroxide, $Sb(OH)_3$ (Found: Sb, 71·0. Calc.: Sb, 70·2%).

4. *Hexakishexamethylenetetramine antimony pentachloride* (Found: Sb, 10·15; Cl, 15·2; $C_6H_{12}N_4$, 72·9. $SbCl_5,6C_6H_{12}N_4$ requires Sb, 10·55; Cl, 15·6; $C_6H_{12}N_4$, 73·8%) decomposes in water but not completely until the mixture is heated, whereupon antimonic acid, $HSbO_3$, is obtained (Found: Sb, 71·1. Calc.: Sb, 71·0%). Although much formaldehyde is produced on boiling antimony pentachloride with aqueous hexamethylenetetramine solution, there is no noticeable reduction to antimonous compound.

5. *Hexamethylenetetramine bismuth trichloride* was obtained as white microscopic crystals (Found: Bi, 45·4; Cl, 22·9; $C_6H_{12}N_4$, 31·4. $BiCl_3,C_6H_{12}N_4$ requires Bi, 45·8; Cl, 23·4; $C_6H_{12}N_4$, 30·8%). This compound was decomposed by water to bismuth oxychloride, BiOCl (Found: Cl, 13·52. Calc.: Cl, 13·68%).

6. *Bishexamethylenetetramine zinc chloride* separated as a very voluminous, white, microcrystalline powder (Found: Zn, 15·9; Cl, 17·3; $C_6H_{12}N_4$, 66·5. $ZnCl_2,2C_6H_{12}N_4$ requires Zn, 15·7; Cl, 17·05; $C_6H_{12}N_4$, 67·2%); unlike the compound prepared from aqueous solutions (p. 418), this dissolves readily in water, but on standing, slowly deposits zinc hydroxide.

Addition Compounds prepared in Aqueous Solution.

Method.—A concentrated aqueous solution of the chloride was stirred into excess of a concentrated aqueous solution of hexamethylenetetramine. This yielded crystalline precipitates immediately for the cadmium, zinc, and calcium compounds, but evaporation was necessary to obtain the strontium compound. Air was excluded by hydrogen in the preparation of the ferrous compound. All the precipitates were washed finally with alcohol. The estimation of the hexamethylenetetramine portion of the compounds was made by the methods indicated on p. 414. Water of crystallisation was determined where possible at 95°.

1. Hexamethylenetetramine di-cadmium chloride pentahydrate, $2CdCl_2,C_6H_{12}N_4,5H_2O$, was obtained as a white microcrystalline powder (Found: Cd, 37·2, 37·1; Cl, 23·7, 24·0; $C_6H_{12}N_4$, 23·7, 23·5; H_2O, 14·0, 14·1. Calc.: Cd, 37·7; Cl, 23·8; $C_6H_{12}N_4$, 23·5; H_2O, 15·1%). When stirred in *N*-hydrochloric acid it dissolved, and the colourless needles which separated were identified as $CdCl_2,C_6H_{12}N_4,HCl,H_2O$ (Found: Cd, 29·4; Cl, 28·1; $C_6H_{12}N_4$,

37·7. Calc.: Cd, 29·7; Cl, 28·2; $C_6H_{12}N_4$, 37·0%), which had previously been obtained from hydrochloric acid solutions of the chloride and the base.

2. *Bishexamethylenetetramine tri-zinc chloride hexahydrate* was obtained as a white microcrystalline powder (Found: Zn, 24·8; Cl,25·9; $C_6H_{12}N_4$, 35·0. $3ZnCl_2,2C_6H_{12}N_4,6H_2O$ requires Zn, 24·7; Cl, 26·7; $C_6H_{12}N_4$, 35·1%). When stirred with water it is hydrolysed to basic zinc chloride of indefinite composition.

3. *Bishexamethylenetetramine calcium chloride decahydrate* was obtained in minute colourless crystals (Found: Ca, 7·1; Cl, 12·5, 12·4; $C_6H_{12}N_4$, 49·15, 48·5; H_2O, 30·9. $CaCl_2,2C_6H_{12}N_4,10H_2O$ requires Ca, 7·0; Cl, 12·4; $C_6H_{12}N_4$, 49·0; H_2O, 31·5%). The compound is not deliquescent. It can be boiled in solution and recovered unchanged. We have prepared it both from cold solutions and by mixing boiling solutions of the components, but it has always separated as a decahydrate: we have been unable to prepare the hexahydrate which Vanino and Schinner (*loc. cit.*) describe.

4. *Bishexamethylenetetramine strontium chloride nonahydrate*, obtained in colourless minute crystals like those of the calcium compound (Found: Sr, 14·75; Cl, 11·9, 11·8; $C_6H_{12}N_4$, 46·6, 46·9; H_2O, 26·5. $SrCl_2,2C_6H_{12}N_4,9H_2O$ requires Sr, 14·6; Cl, 11·8; $C_6H_{12}N_4$, 46·6; H_2O, 27·0%), is stable in boiling water.

5. *Bishexamethylenetetramine ferrous chloride nonahydrate*, $FeCl_2,2C_6H_{12}N_4,9H_2O$, was obtained as very pale green microscopic plates when a fresh solution of ferrous chloride (made from iron and concentrated hydrochloric acid) was run into cold concentrated aqueous hexamethylenetetramine solution in an atmosphere of hydrogen. The crystals were washed with alcohol and then ether, pressed between filter paper, and at once analysed (Found: Fe, 10·1; Cl, 12·7; $C_6H_{12}N_4$, 48·4; H_2O, 28·9. $FeCl_2,2C_6H_{12}N_4,9H_2O$ requires Fe, 9·8; Cl, 12·5; $C_6H_{12}N_4$, 49·2; H_2O, 28·5%). The compound is not stable in air, becoming brown through oxidation; even in a closed tube it becomes brown and wet from its own water content.

6. *Basic hexamethylenetetramine cupric chloride dihydrate*, $Cu(OH)Cl,CuCl_2,C_6H_{12}N_4,2H_2O$. We have not been able to obtain the compound $2CuCl_2,C_6H_{12}N_4$ described by Vanino and Schinner (*loc. cit.*). In attempts to avoid formation of a basic compound, the following method was tried: Saturated aqueous cupric chloride solution was added drop by drop and with vigorous shaking to excess of hexamethylenetetramine in alcoholic solution. The brown precipitate obtained was not apparently crystalline [Found, for two preparations: Cu, 29·3, 30·2; Cl, 24·4, 24·3; $C_6H_{12}N_4$, 31·1, 31·3. $Cu(OH)Cl,CuCl_2,C_6H_{12}N_4,2H_2O$ requires Cu, 29·8; Cl, 24·95; $C_6H_{12}N_4$, 32·8%]. Vanino and Schinner gave no figures for chlorine

in their compound. When the brown compound was stirred in water it gave immediately the pale blue basic cupric chloride $3Cu(OH)_2,CuCl_2$ (Found: Cu, 58·87; Cl, 16·37. Calc.: Cu, 59·54; Cl, 16·61%).

7. *Hexamethylenetetramine di-cupric sulphate dihydrate* was obtained in grass-green microscopic crystals when concentrated aqueous cupric sulphate solution was added in drops to alcoholic hexamethylenetetramine solution (Found: Cu, 25·7; SO_4, 38·8; $C_6H_{12}N_4$, 27·2; H_2O, 7·0. $2CuSO_4,C_6H_{12}N_4,2H_2O$ requires Cu, 25·7; SO_4, 38·8; $C_6H_{12}N_4$, 28·3; H_2O, 7·3%); it decomposed in water, yielding pale blue basic cupric sulphate, $3Cu(OH)_2,CuSO_4$ (Found: Cu, 56·50; SO_4, 21·47. Calc.: Cu, 56·23; SO_4, 21·22%).

8. Hexamethylenetetramine di-cupric acetate was obtained as dark green microscopic needles on mixing concentrated aqueous cupric acetate solution with excess of alcoholic hexamethylenetetramine solution [Found: Cu, 25·2; OAc, 46·1; $C_6H_{12}N_4$, 28·0. Calc. for $2(CH_3{\cdot}CO_2)_2Cu,C_6H_{12}N_4$: Cu, 25·3; OAc, 46·9; $C_6H_{12}N_4$, 27·8%]. Vanino and Schinner (*loc. cit.*) prepared this compound, but used cupric chloride solution, acetic acid, and hexamethylenetetramine in aqueous solution.

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[*Received, December 8th, 1928.*]