LIII.—*The Reaction between Cupric Chloride and Hydrazine Sulphate.*

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DOUBLE compounds of the salts of hydrazine and copper, both cuprous and cupric, have been described (Curtius and Jay, *J. pr. Chem.*, 1894, **50**, 311; Hofmann and Marburg, *Annalen*, 1899, **305**, 191, 222; Ranfaldi, *Atti R. Accad. Lincei*, 1906, **15**, ii, 95; Franzen and Lucking, *Z. anorg. Chem.*, 1911, **70**, 152; Ferratini, *Gazzetta*, 1912, **42**, i, 138), and copper salts have been used for the gasometric estimation of hydrazine (Purgotti, *ibid.*, 1896, **26**, 559; de Girard and de Saporta, *Bull. Soc. chim.*, 1904, **31**, 905; Rimini, *Atti R. Accad. Lincei*, 1905, **14**, i, 386; Ebler, *Z. anorg. Chem.*, 1905, **47**, 371). The cupric double compounds are usually formed without any chemical action other than perhaps a double decomposition. This is possible as a rule only in neutral or somewhat acid solutions; in alkaline solutions reduction to a cuprous salt, finally giving cuprous oxide, takes place, with evolution of nitrogen: $8Cu^{\cdot\cdot} + 2N_2H_5^{\cdot} + 10OH' = 8Cu^{\cdot} + 10H_2O + 2N_2$. According to Gutbier (*Z. anorg. Chem.*, 1902, **32**, 355), colloidal cuprous oxide may sometimes be formed in this way under certain conditions; with high concentrations of hydrazine, however, copper itself may be the final reduction product (Rimini, *loc. cit.*; Curtius and Jay, *Ber.*, 1887, **20**, 1632). Brown, amorphous solids of uncertain composition are sometimes precipitated which deposit copper on standing. On exposure to air they form basic copper carbonates.

By working under certain conditions, we have prepared from hydrazine sulphate and cupric chloride a new *compound* which is more complex than any hitherto described, and has some unusual properties.

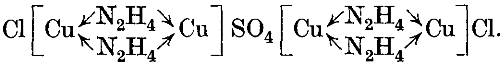
EXPERIMENTAL.

N-Cupric chloride solution is run drop by drop into a mixture of 40 g. of hydrazine sulphate in 250 c.c. of water with 25 g. of potassium hydroxide (or the equivalent sodium hydroxide) in 250 c.c. of water. The solution turns blue at first, and then becomes brown, with evolution of nitrogen. A brown precipitate begins to form, and if the cupric chloride is run in slowly, a stage is reached where glistening brown plates separate. Further quantities of the chloride should be added cautiously in order to avoid formation of a blue solution due to excess of copper salt. The crystals are allowed to settle, filtered off as rapidly as possible on a Buchner funnel, washed with 95% alcohol and finally with absolute alcohol, kept over sulphuric acid in a vacuum desiccator, and analysed without further purification.

Analysis. (i) From the solution in hydrochloric acid, hydrogen sulphide precipitated copper sulphide; this was dissolved in nitric acid, and the metal estimated by the iodide method. (ii) The filtrate from the sulphide was freed from excess of hydrogen sulphide by a current of carbon dioxide, and the hydrazine was estimated in the solution by the iodine–bicarbonate method. (iii) Chlorine was estimated either by direct weighing as silver chloride, or by the Volhard method after an ammoniacal solution of the compound had been acidified with nitric acid. (iv) Sulphate was estimated as barium salt in the original hydrochloric acid solution (Found: Cu, 46·4; Cl, 12·1; N_2H_4, 21·1; SO_4, 18·0. $2CuCl,Cu_2SO_4,4N_2H_4$ requires Cu, 46·3; Cl, 12·9; N_2H_4, 23·3; SO_4, 17·5%).

Properties. The *substance* is readily decomposed by cold water, but can be preserved for some time under anhydrous conditions. Hot water precipitates cuprous oxide, leaving a nearly neutral (methyl-orange) solution of hydrazine sulphate and chloride. The complex is insoluble in alcohol and in most organic solvents, but dissolves in formamide and pyridine to give straw-coloured solutions which rapidly become blue owing to oxidation; it also gives a similar solution in concentrated aqueous ammonia in an inert atmosphere, but access of oxygen rapidly produces the blue solution characteristic of cupric complexes. This rapid oxidation makes satisfactory recrystallisation from formamide difficult. Dilute sulphuric or nitric acid causes precipitation of copper, but hydrochloric acid at first yields a white precipitate which dissolves to a colourless solution when the concentration of acid is increased, doubtless owing to the solubility of cuprous chloride in the concentrated acid.

The compound might simply be a double salt, but there appear to be at least three reasons for regarding it as fully co-ordinated : (1) the small number of acid radicals compared with hydrazine molecules and copper atoms ; (2) the dark colour of the compound, probably indicating a large ion—the simpler double salts of cuprous copper are usually colourless, but the ammino-cuprous chlorides are brown (Lloyd, *J. Physical Chem.*, 1908, **12**, 398) ; (3) the ease with which it reacts with water to give cuprous oxide, suggesting the structure



$$\mathrm{Cl}\left[\mathrm{Cu}\begin{matrix}\swarrow \mathrm{N_2H_4} \searrow\\ \nwarrow \mathrm{N_2H_4} \nearrow\end{matrix}\mathrm{Cu}\right]\mathrm{SO_4}\left[\mathrm{Cu}\begin{matrix}\swarrow \mathrm{N_2H_4} \searrow\\ \nwarrow \mathrm{N_2H_4} \nearrow\end{matrix}\mathrm{Cu}\right]\mathrm{Cl}.$$

Estimations of the molecular weight in pyridine and formamide were not satisfactory, owing to rapid oxidation and to the formation of other complexes.

Attempts to prepare related compounds have not been successful. When cupric sulphate is substituted for the chloride in the preparation, metallic copper separates.

We are indebted to Mr. W. J. Lawrence for checking some of the analyses.

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