26. *Complexes between Metal Salts and Long-chain Aliphatic Amines. Part I. The Complexes of Cupric Salts with Long-chain Amines.*

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Complexes between cupric salts and long-chain amines are described. The chain length affects only the solubility in organic solvents and physical properties of the complexes. The acid radical controls the colour and stability of the compounds, chelation leading to relative instability. The acid radicals are covalently bound to the metal. Cupric carbonate and oxide compounds are basic and decompose chloroform on heating, giving cupric chloride complexes.

The present work was carried out in order to study the relative stabilities, properties, and reactions of complexes of uni- and bi-valent copper salts and primary aliphatic amines with long carbon chains, dealing in particular with the effects of (*a*) the anion used, (*b*) the basicity of the amine, and (*c*) the nature of the solvent.

Water is generally used as the solvent in the study of copper complexes and it may have a considerable effect on the results obtained. In the case of cuprous compounds, this is often shown by a tendency to disproportionate, giving metallic copper and cupric ions. Bivalent copper has a great affinity for oxygen, and the properties of many cupric complexes are probably due to some extent to the partial replacement of the co-ordinating groups by water molecules. The tendency towards such aquation in the case of a salt $(MR_n)^{p+}\ X^-_p$ may be represented by equilibria of the types :

$$(MR_n)^{p+} \rightleftharpoons (MR_{n-1})^{p+} + R$$
$$(MR_{n-1})^{p+} + H_2O \rightleftharpoons (MR_{n-1},H_2O)^{p+}$$

and in addition the anion present may co-ordinate according to the reaction

$$(MR_{n-1})^{p+} + X^- \rightleftharpoons (MR_{n-1}X)^{(p-1)+}$$

n being the normal chemical co-ordination number of the metal M, and R representing the ionically neutral monodentate ligand. The equilibrium position of the first reaction is determined by the normal stability constant of the complex ion and, in addition, more than one R group may be lost by the complex ion, leading to further equilibria involving water and the anion. The extent to which the last two groups enter the co-ordination sphere depends on the relative co-ordinating powers of R, H_2O, and X^-, on the nature of the metal M in the general case, and also on the energies of solvation of the various groups.

King (*J.*, 1930, 2307) studied cuprammonium salts and states that there is no evidence that aquation occurs when the complexes are dissolved in water. There is little evidence that it does not occur, however. He also presents some evidence suggesting that co-ordination of anions may occur to a small extent. Reversible co-ordination of anions is well established, however, since in addition to the obvious evidence presented by the methods of preparation of many complexes of cobalt, platinum, and other metals, containing acid radicals in the complex ion or molecule, King (*J.*, 1938, 1338; 1948, 1912) has shown that in the diammino- and triammino-platinous salts some acid radicals, normally regarded as present in the complex ions or molecules, ionise. This leads to the formation of aquated ammine ions in solution, although on crystallising, the original compounds are obtained. It is noteworthy that nitrate, sulphate, and picrate groups ionise in this way, while chloride remains in the complex molecule, diamminoplatinous chloride being practically a non-electrolyte.

In the present work the question of the influence of water does not arise, since the long-chain aliphatic amines used as ligands give complexes which are soluble in organic solvents such as chloroform, benzene, light petroleum, etc. This study of inorganic chemistry in inert organic solvents enables the properties of the actual complex molecules to be investigated and the effects of different acid radicals can thus be established.

The results obtained show that under these conditions the acid radicals are covalently bound to the copper atom and that the co-ordination number of 4 for copper is maintained. This behaviour is not observed for the copper complexes with lower amines, such as ethylamine, and ammonia, but it is believed that this is not the result of a fundamental change in the nature of the copper–acid radical links caused by changing the ligand from, say, ethylamine to *n*-octylamine, but is due to the solvents used. For example, cupric chloride with ethylamine gives complexes which are insoluble in organic solvents; the solids such as $CuCl_2(C_2H_5{\cdot}NH_2)_4$ are decomposed by water, giving a pale blue precipitate of basic cupric chloride containing a little ethylamine (or cupric hydroxide containing chloride and ethylamine which might be regarded as " adsorbed "). In aqueous ethylamine, however, the substances are soluble, and complex ions such as $[Cu(C_2H_5{\cdot}NH_2)_4]^{2+}$ may be presumed to be present. Octylamine, on the other hand, gives the *complex* $[CuCl_2(C_8H_{17}{\cdot}NH_2)_2]$, which is soluble in organic solvents and behaves as a complex molecule, but it is rapidly decomposed by water giving a pale blue precipitate containing chloride, and liberating octylamine.

All the cupric salts investigated gave bisamine complexes only, with long-chain amines, the acid radicals used being chloride, bromide, acetate, succinate, adipate, carbonate, sulphate, and that of methyl hydrogen succinate. Cupric chloride, acetate, and methyl succinate dissolve readily in a solution of 2 mols. of amine in a solvent, the bisamine complexes being precipitated on cooling to room temperature.

Cupric adipate and succinate give bisamine complexes which are unstable in solution in the absence of excess of amine. Adipic and succinic acids can form strainless rings on chelating with copper and the instability of the complexes is believed to be due to a reduction in the strength of the metal–amine bond caused by the imposition of the *cis*-configuration. The complex carbonates are also unstable and cannot be obtained without a considerable amount of associated amine carbonate.

Cupric sulphate is insoluble in solutions of the amines, but on adding the theoretical quantity of sulphuric acid to a solution of a lilac carbonate complex a pale blue precipitate of $(CuSO_4,2C_{16}H_{33}{\cdot}NH_2)$ is deposited. This *complex* is insoluble in organic solvents, concentrated solutions of amines, and molten amine. A small amount of the same compound was obtained on heating copper sulphate with hexadecylamine at 160° for about 12 hours.

Addition of nitric acid to the carbonate solution caused decomposition to free amine and cupric nitrate, no complex being formed. Thus cupric nitrate complexes do not exist, and the sulphate compounds have exceptional insolubility. This may be due to nitrate and sulphate

radicals being less able to form covalent bonds to copper than the other groups used in this work. These same two anions were found by King (*loc. cit.*) to be less firmly bound to platinum than say Cl^-, tending to give aquated ions from $[Pt(NH_3)_2(NO_3)_2]$, etc.

Experimental.

The method used to prepare the complexes with the higher amines is essentially that of Broome, Ralston, and Thornton (*J. Amer. Chem. Soc.*, 1946, **68**, 67), the anhydrous cupric salt being dissolved in a solution of the amine in chloroform, benzene, light petroleum, etc., by boiling under reflux. On cooling, the complex separates and is purified by recrystallisation. Those authors and Ralston, Broome, Harriman, and Marcous (*J. Amer. Oil Chem. Soc.*, 1947, **24**, 307) prepared the following compounds of cupric chloride, acetate, and oleate : $CuCl_2,2R{\cdot}NH_2$; $Cu(OAc)_2,2R{\cdot}NH_2$, and $Cu(C_{17}H_{35}{\cdot}CO_2)_2,2R{\cdot}NH_2$, where R is *n*-dodecyl or *n*-octadecyl. The former group of authors (*J. Amer. Chem. Soc.*, 1946, **68**, 849) also proved spectrophotometrically that complexes such as $Cu(OAc)_2,4R{\cdot}NH_2$ do not exist in solution.

In agreement with the above authors it was found that oxygen-containing solvents such as alcohols, ethers, and ketones give ill-defined greenish products which contain solvent and are deficient in acid radicals, so that compounds containing oxygen must not be used for either the preparation or the purification of the copper–amine complexes. Apart from this restriction, all the common organic solvents may be used, the choice being controlled, very largely, by solubilities, except in the case of the cupric carbonate complexes which are unstable except in benzene solution.

The amines used were *n*-octyl-, *n*-dodecyl-, *n*-tetradecyl-, *n*-hexadecyl-, and *n*-octadecyl-amine, and there was no difference between any of the cupric complexes as far as their type is concerned. The solubilities of the complexes differed considerably, however. Like many compounds possessing long carbon chains, the cupric bisamine complexes are very slightly soluble in cold solvents, and their solubility increases enormously over a very narrow temperature range, until they seem to be infinitely soluble at a slightly higher temperature (cf. Ralston *et al.*, *J. Org. Chem.*, 1944, **9**, 102). All the complexes prepared show this effect, the critical temperature region and range differing somewhat for different solvents and being higher the longer the carbon chain.

Cupric Chloride Complexes.—Cupric chloride (2·5 g.), dried at 110°, and *n*-octylamine (5·7 g., 2 mols.) were heated under reflux with 50 ml. of chloroform until solution was complete (½ hour). On cooling, the *complex* separated as a blue powder and was purified by recrystallising twice from chloroform (Found, in air-dried specimen : Cu, 16·1; Cl, 18·0. $C_{16}H_{36}N_2Cl_2Cu$ requires Cu, 16·2; Cl, 18·0%).

The following compounds were prepared similarly : $CuCl_2,2C_{12}H_{25}{\cdot}NH_2$ (Found : Cu, 12·7; Cl, 14·0. Calc. for $C_{24}H_{54}N_2Cl_2Cu$: Cu, 12·6; Cl, 14·0%). *Tetradecylamine* complex (Found : Cu, 11·15; Cl, 12·6. $C_{28}H_{62}N_2Cl_2Cu$ requires Cu, 11·2; Cl, 12·6%). *Hexadecylamine* complex (Found : Cu, 10·2; C , 11·6. $C_{32}H_{70}N_2Cl_2Cu$ requires Cu, 10·3; Cl, 11·5%). $CuCl_2,2C_{18}H_{37}{\cdot}NH_2$ (Found : Cu, 9·5; Cl, 10·6. Calc. for $C_{36}H_{78}N_2Cl_2Cu$: Cu, 9·4; Cl, 10·5%).

Anhydrous cupric chloride (2·0 g.) was gently warmed under reflux with 50 ml. of benzene containing anhydrous ethylamine (4 g., 6 mols.). The brown solid slowly absorbed ethylamine, turning blue and then purple, no solid dissolving. A further 10 g. of ethylamine were added, and a little purple solid dissolved, giving a deep blue solution. The solid was filtered off under suction and dried in a desiccator containing anhydrous ethylamine and petroleum jelly which absorbed benzene. Exposure to air caused loss of amine, the solid turning greenish-blue but reabsorbing gaseous amine and turning purple (Found : Cu, 19·2. Calc. for $C_8H_{28}N_4Cl_2Cu$: Cu, 20·2%).

Cupric Bromide Complexes.—Cupric bromide will dissolve only in the presence of about 3—4 mols. of amine, light petroleum being the most convenient solvent since the complex does not separate well from other solvents in the presence of the excess of amine. The evidence for the composition of the cupric bromide bisamine complexes is not entirely satisfactory since the copper content cannot be determined accurately by the methods used, the results usually being low and non-reproducible. The same effects are observed with the products obtained by oxidation of cuprous bromide compounds (Part III), so the original cupric bromide is not the cause. Heating the green complexes at 100—200° in high vacuum ($< 10^{-3}$ mm.) with no air leak causes amine to condense in the cold parts of the apparatus, the complex turning brown. This residue is still soluble in organic solvents, and addition of a little amine gives the original green solid, and although this must be free from excess of amine the copper figures are still low. The complex bromides are not volatile. The molecular wieght of the *complex* ($CuBr_2,2C_{18}H_{37}{\cdot}NH_2$) determined ebullioscopically by the graphical method (Part II) in benzene is 990 ($C_{36}H_{78}N_2Br_2Cu$ requires *M*, 762). The high value compares with the value of 603 obtained for $CuCl_2,2C_{12}H_{25}{\cdot}NH_2$ as against the theoretical value of 505 (Ralston, Broome, and Thornton *loc. cit.*).

Anhydrous cupric bromide (3·0 g.) was boiled under reflux for 2 hours with octadecylamine (10·0 g., 2·8 mols.) and 50 ml. of light petroleum (b. p. 100—120°). The solid dissolved, giving a brownish solution (more amine gave green solutions) which turned green on cooling, depositing a green solid. This was recrystallised 3 times from light petroleum, the solution being filtered at 64°, and the green solid washed with several portions of fresh solvent. The product is apparently $CuBr_2,2C_{18}H_{37}{\cdot}NH_2$ (m. p. 116—117°) (Found : Cu, 6·8, 6·9; Br, 21·4, 21·4; C, 57·7; H, 10·8. $C_{36}H_{78}N_2Br_2Cu$ requires Cu, 8·3; Br, 20·95; C, 56·7; H, 10·3%). The analysis figures are the best obtained from many preparations, other amines giving such varied results that they are not quoted. After several recrystallisations a more soluble brown compound, apparently a cupric bromide complex containing less amine, could be obtained.

Cupric Acetate Complexes.—Cupric acetate was prepared by dissolving the commercial " neutral " salt in dilute acetic acid, filtering hot, cooling, and washing the crystals well with water and drying the air-dried solid *in vacuo* over phosphoric oxide until fresh desiccant extracted no more water. The anhydrous solid (1·1 g.) was boiled with octadecylamine (3·4 g.; 2·1 mols.) in 40 ml. of benzene for 30 minutes. The clear blue liquid on cooling gave a lilac solid which on recrystallising from benzene gave transparent lilac plates of $Cu(OAc)_2,2C_{18}H_{37}{\cdot}NH_2$, m. p. 89° (Found : Cu, 8·7; C, 64·6; H, 11·9. Calc. for $C_{40}H_{84}O_4N_2Cu$: Cu, 8·8; C, 66·6; H, 11·8%).

Cupric Methyl Succinate Complexes.—*Cupric methyl succinate* was prepared by boiling 50 g. of methyl hydrogen succinate with 30 g. (0·5 mol.) of cupric oxide and 50 ml. of water for 15 minutes. The considerable residue of cupric oxide was filtered off from the hot solution, which was cooled in ice, giving a mass of green crystals contaminated with excess of ester. The solid was dissolved in water with the minimum of heating, and the small amount of pale blue decomposition product filtered off from the hot solution. This was cooled rapidly in ice, and the green crystals were filtered off and dried in air and finally *in vacuo* over phosphoric oxide (Found : Cu, 19·50. $C_{10}H_{14}O_8Cu$ requires Cu, 19·50%).

Cupric methyl succinate (2·3 g.), octadecylamine (3·8 g.; 2·1 mols.) and 40 ml. of benzene were heated under reflux for 10 minutes. No solid separated from the clear blue liquid on cooling to room temperature, but on cooling in ice a blue solid separated. It was filtered off and recrystallised twice from benzene with rejection of the first third of the solid which separated in each case (this contained the excess amine). Pure *cupric methyl succinate bisoctadecylamine* was finally obtained (Found : Cu, 7·3. $C_{46}H_{92}O_8N_2Cu$ requires Cu, 7·35%).

Cupric methyl succinate bisdodecylamine was obtained similarly but was recrystallised from light petroleum (b. p. 60—80°) (Found : Cu, 9·05. $C_{34}H_{68}O_8N_2Cu$ requires Cu, 9·1%).

Cupric Succinate Complexes.—Cupric succinate was prepared by boiling cupric oxide in an aqueous solution of excess of succinic acid, filtering off the blue solid, and boiling it with more succinic acid solution. The crystals were dehydrated *in vacuo* over phosphoric oxide (Found : Cu, 35·7. Calc. for $C_4H_4O_4Cu$: Cu, 35·4%).

Cupric succinate (1·06 g.), octadecylamine (6·4 g., 4·2 mols.) and 80 ml. of benzene were heated under reflux for one hour. The boiling liquid was filtered, the filtrate cooled slowly, and the solid *complex* filtered off under suction at about 40°. It decomposed to cupric succinate on attempted recrystallisation, and amine impurity was removed by warming the lilac solid with benzene at about 45°, and filtering at that temperature. It was air-dried (Found : Cu, 8·75. $C_{40}H_{82}O_4N_2Cu$ requires Cu, 8·85%).

Cupric Adipate Complexes.—Cupric adipate was prepared as for the succinate (Found : Cu, 30·4. Calc. for $C_6H_8O_4$ Cu : Cu, 30·6%). Its *bisoctadecylamine* complex was obtained as a lilac powder by the same method as the foregoing. It is insoluble in benzene and light petroleum in the absence of excess of amine, and is decomposed by boiling or long storage with these and all other solvents. Some of the product was very carefully recrystallised from chloroform. (Found : Cu, 8·8. $C_{42}H_{86}O_4N_2Cu$ requires Cu, 8·52%). The *bisdodecylamine* complex was obtained similarly but was purified only by washing with warm benzene (Found : Cu, 11·2. $C_{30}H_{62}O_4N_2Cu$ requires Cu, 11·0%).

Cupric Carbonate Complexes.—Copper oxide and hydroxide are completely unaffected by amine solutions in the absence of carbon dioxide, but in its presence they dissolve if about 4 mols. of amine are used, lilac cupric carbonate complexes separating on cooling. Benzene is the only suitable solvent of those tried, light petroleum giving only small quantities of a green complex oxide and chloroform being decomposed, the cupric chloride bisamine complex separating. The lilac complexes, including the insoluble ethylamine complex, are of the type $(CuCO_3,2R{\cdot}NH_2)[(R{\cdot}NH_2)_2CO_3]_x$, where x is variable between 0·7 and 2. Recrystallisation alters the value of x and must be done in the presence of gaseous carbon dioxide. If the solution is too hot or not enough carbon dioxide is present, a greyish-blue solid is obtained containing more copper and less carbon dioxide but of indeterminate composition, which absorbs carbon dioxide, turning lilac. The same blue products are obtained when lilac compounds are kept over soda–lime, etc., to remove carbon dioxide. Further loss of carbon dioxide from solutions of complex carbonates causes precipitation of green solids, very difficult to filter, the solution often setting to a gel on cooling. The green substances have the composition $(CuO,2R{\cdot}NH_2)$ but are contaminated with a slight excess of amine which could not be removed by solvents. They absorb carbon dioxide, turning lilac; there is no intermediate formation of a blue solid; the dodecylamine complex absorbs carbon dioxide much more readily than does the octadecylamine compound. The composition of the lilac complexes was proved by titration of a solution of $(CuCO_3,2C_{18}H_{33}{\cdot}NH_2)[(C_{18}H_{33}{\cdot}NH_2)_2CO_3]_2$ with alcoholic hydrogen chloride, a glass electrode and saturated calomel reference half-cell being used with a Marconi battery-operated pH meter. The pH titration technique was checked by titrating $(C_{14}H_{29}{\cdot}NH_2)_2CuCl_4$ with alcoholic sodium hydroxide.

Cupric hydroxide was prepared from cupric sulphate by Bullnheimer and Seitz's method (*Ber.*, 1900, **33**, 817) but was repeatedly washed and drained by filtration under suction instead of by decantation. It was free from chloride, sulphate, and soluble hydroxy-radicals, and was dried at 70° for 2 hours.

This hydroxide (1·36 g.) and dodecylamine (10·0 g., 4 mols.) in 75 ml. of benzene were heated under reflux for 12 hours with a soda–lime tube in the top of the condenser. There was no reaction. The soda–lime tube was removed, and the solution quickly turned blue, cupric hydroxide slowly dissolving. The reaction was more rapid when the solution was kept at 65—70° instead of being boiled, and dissolution was much faster when a current of carbon dixoide washed by saturated sodium hydrogen carbonate solution was bubbled through the suspension. Traces of solids were removed by filtering the liquid hot, and on cooling a lilac solid separated. The general method of preparation was to warm the benzene suspension in an open flask on a water-bath, carbon dioxide being passed in continuously until solution was almost complete. The lilac products were recrystallised from benzene. Too low a concentration of complex, too high a temperature, and too high a vacuum in the Buchner flask caused loss of carbon dioxide, blue and finally green solids being obtained. Carbon dioxide was passed through when the lilac compounds were being redissolved.

Dodecylamine gave a lilac *complex* {Found : Cu, 7·95; C, 66·2; H, 11·8%.

$(CuCO_3,2C_{12}H_{25}{\cdot}NH_2)[(C_{12}H_{25}{\cdot}NH_2)_2CO_3]_x$ containing Cu, 7·95, requires C, 64·0; H, 11·8%}. Recrystallisation from benzene gave another compound (Found : Cu, 8·20; C, 64·0; H, 11·4%).

A lilac compound was prepared from tetradecylamine but the solution was divided into two equal parts before cooling. The two crops of lilac powder were recrystallised from benzene under conditions as nearly as possible exactly similar [Found (i) : Cu, 6·40; CO_3^{--}, 12·3%; Cu : CO_3 = 1 : 2·03. Found (ii) : Cu, 5·85; CO_3^{--}, 12·7%; Cu : CO_3 = 1 : 2·30. $C_{58}H_{126}O_6N_4Cu$ requires Cu, 6·13; CO_3^{--}, 11·55%].

A lilac hexadecylamine complex was prepared as usual and recrystallised once from benzene. In one case the complex was *cupric carbonate bishexadecylamine–hexadecylamine carbonate* (Found : Cu, 5·54,

5·56; CO_3^{--}, 10·3. $C_{66}H_{140}O_6N_4Cu$ requires Cu, 5·53; CO_3^{--}, 10·4%). Attempts to repeat this preparation gave compounds with varying copper contents. Heating at 75° with carbon dioxide under pressure gave a complex (Found : Cu, 5·88%).

Octadecylamine gave similar *complexes* {Found, in one case : Cu, 5·70; C, 70·5; H, 12·3. $(CuCO_3,2C_{18}H_{37}\cdot NH_2)[(C_{18}H_{37}\cdot NH_3)_2CO_3]_x$ containing Cu = 5·70 requires C, 69·9; H, 12·5%}.

Cupric hydroxide (3 g.) was warmed gently with ethylamine (large excess) in 50 ml. of benzene with a soda–lime tube in the top of reflux condenser; there was no reaction. On removal of this tube the cupric hydroxide slowly turned dark blue. When homogeneous in appearance it was filtered off under gravity, warmed gently with more ethylamine in benzene, under continuous passage of carbon dioxide, filtered off as before, washed with warm benzene, and dried in a desiccator containing anhydrous ethylamine carbonate and petroleum jelly in an atmosphere of carbon dioxide {Found : Cu, 24·3; CO_3^{--}, 31·2; Cu : CO_3 = 1 : 1·36. $(CuCO_3,2C_2H_5\cdot NH_2)[(C_2H_5\cdot NH_3)_2CO_3]_x$ containing Cu 24·3% requires CO_3^{--}, 30·3%}. The *complex* lost ethylamine and carbon dioxide readily in air, turning green.

Blue cupric carbonate complexes are described by one typical example. A lilac cupric carbonate dodecylamine complex was recrystallised from benzene after being warmed to a higher temperature than usual, with no carbon dioxide passing. A blue solid was deposited (Found : Cu, 8·60; CO_3^{--}, 7·40%) : after a further recrystallisation (Found : Cu, 8·91; CO_3^{--}, 7·60%). Analysis of a different preparation gave : Cu, 9·30; CO_3^{--}, 9·05 ($C_{25}H_{54}O_3N_2Cu$ requires Cu, 12·86; CO_3^{--}, 12·14%. $C_{49}H_{108}O_3N_4Cu$ requires Cu, 7·35; CO_3^{--}, 6·94%).

Cupric oxide bisoctadecylamine (impure) was obtained by boiling a lilac carbonate complex in benzene until it completely decomposed, giving a green suspension which set to a gel on cooling. The hot suspension was centrifuged; the green solid was washed three times with hot benzene, being centrifuged each time, and was dried in a vacuum desiccator containing soda–lime, under continuous pumping (Found : Cu, 8·95; CO_3^{--}, nil. $C_{36}H_{78}ON_2Cu$ requires Cu, 10·28%).

Cupric hydroxide (1·4 g.) and dodecylamine (10 g., 4 mols.) in 40 ml. of chloroform were heated under reflux for 2 hours. The blue solution gave a dark blue solid on cooling; this was recrystallised twice from benzene–light petroleum and once from benzene, and was found to be cupric chloride bisdodecylamine (Found : Cu, 12·1; Cl, 13·6. Calc. for $C_{24}H_{54}N_2Cl_2Cu$: Cu, 12·58; Cl, 14·04%).

Potentiometric Titration.—Cupric carbonate bishexadecylamine–hexadecylamine carbonate (p. 125) (0·2100 g.) was dissolved in 15 ml. of warm benzene and a mixture of 60 ml. of benzene and 15 ml. of redistilled commercial absolute alcohol added slowly at 40°, carbon dioxide being passed through the whole time. One drop of water was added. By this method, decomposition of the complex was avoided. The solution was titrated with 0·101N-hydrogen chloride in absolute alcohol, the course of the reaction being followed by a glass electrode and a saturated calomel half-cell with a ground-glass joint flowing junction. The e.m.f. was measured by means of a Marconi battery-operated pH meter (pH scale), previously standardised by using the same electrodes in an aqueous buffer at pH 6·46. The curve obtained is shown in Fig. 1 (I). The two sharp falls at 7·5 and 11·0 ml. of acid correspond to the addition of 4 and 6 equivs. of HCl per g.-mol. of complex. There is a significant flattening of the curve when 4 ml. (2 equivs.) of acid are present. The reaction proceeds in 3 stages, identified by the experiments described below :

(1) $CuCO_3,2C_{16}H_{33}\cdot NH_2 + 2HCl = CuCl_2,2C_{16}H_{33}\cdot NH_2 + H_2O + CO_2$
(2) $(C_{16}H_{33}\cdot NH_3)_2CO_3 + 2HCl = 2C_{16}H_{33}\cdot NH_3Cl + H_2O + CO_2$
(3) $CuCl_2,2C_{16}H_{33}\cdot NH_2 + 2HCl = (C_{16}H_{33}NH_3)_2CuCl_4$

Stage 1. 0·194 g. of lilac complex used in the titration was dissolved in 30 ml. of benzene, and alcoholic 0·101N-hydrogen chloride (3·5 ml., 2·0 equivs.) added slowly. The blue solid separating on cooling slightly was filtered off and recrystallised from benzene (Found : Cu, 10·1; Cl, 11·4. Calc. for $C_{32}H_{70}N_2Cl_2Cu$: Cu, 10·3; Cl, 11·5%).

Stages 1 + 2. 0·193 g. of lilac complex in 30 ml. of benzene was treated with 0·101N-hydrogen chloride (7·1 ml., 4 equivs.). The blue solid obtain on filtration was recrystallised from benzene and chloroform (Found : Cu, 10·2%).

Cupric Sulphate Complex.—0·1925 g. of a hexadecylamine cupric carbonate complex containing 4·42% of Cu was titrated with 0·101N-alcoholic sulphuric acid, with vigorous stirring, the reaction being followed as before. The 0·00851 g. of Cu ≡ 2·64 ml. of the acid, and the 0·1113 g. of amine carbonate present ≡ 4·03 ml. of acid. The experimental curve (Fig. 1, II) shows a slight break between 2·6 and 2·8 ml. and a distinct break at 6·7 ml. of acid added, corresponding to the formation of cupric sulphate bishexadecylamine and amine sulphate, respectively. There is no formation of a cuprisulphate (9·3 ml.).

Anhydrous copper sulphate is insoluble in solutions of amines. The lilac hexadecylamine complex used above (1·75 g.) was dissolved in 50 ml. of benzene, and 75 ml. of alcohol added, with passage of carbon dioxide. 0·101N-Alcoholic sulphuric acid (24·1 ml., Cu : SO_4 = 1 : 1) was run in slowly with stirring, and after standing overnight the pale blue *cupric sulphate bishexadecylamine* was filtered off. It was insoluble in organic solvents and molten amine, and was purified by extracting it several times with hot benzene (Found : Cu, 9·80. $C_{32}H_{70}O_4N_2SCu$ requires Cu, 9·90%).

Anhydrous copper sulphate (0·8 g.) was heated in a tube with excess of dodecylamine at 160° (oil-bath) for 40 minutes; the white solid then turned uniformly pale blue. The excess of amine was removed by extracting 4 times with hot benzene, giving *cupric sulphate bisdodecylamine* (Found : Cu, 11·9. $C_{24}H_{54}O_4N_2SCu$ requires Cu, 12·0%).

Double Cupribromides.—Cupric bromide bisoctadecylamine (1·0 g.) was dissolved in benzene, and excess of hydrobromic acid in aqueous alcohol added. Alcohol was added to the violet solution until the water which settled out redissolved. Dark violet *bisoctadecylamine cupribromide* which separated on cooling was filtered off and recrystallised from alcohol–benzene (Found : Cu, 6·85; Br, 34·3. $C_{36}H_{80}N_2Br_4Cu$ requires Cu, 6·90; Br, 34·7%).

Bistetradecylamine cupribromide (Found : Cu, 7·90. $C_{28}H_{56}N_2Br_4Cu$ requires Cu, 7·85%) and *bis-*

octylamine cupribromide (Found: Cu, 9·80. $C_{16}H_{40}N_2Br_4Cu$ requires Cu, 9·91%) were prepared similarly.

Double Cuprichlorobromides.—Alcoholic hydrogen chloride was added to a solution of cupric bromide bisoctadecylamine (1·0 g.) in benzene until the colour was orange. On standing, orange yellow *bisoctadecylamine cuprichlorobromide* separated and was recrystallised from benzene–alcohol (Found: Cu, 7·55. $C_{36}H_{80}N_2Cl_2Br_2Cu$ requires Cu, 7·60%). *Bisoctylamine cuprichlorobromide* was prepared similarly (Found: Cu, 11·30. $C_{16}H_{40}N_2Cl_2Br_2Cu$ requires Cu, 11·45%). The same orange yellow solids were obtained by treating the cupric chloride bisamine complexes with alcoholic hydrogen bromide. Excess of hydrogen bromide gave the violet cupribromides; and excess of hydrogen chloride with the cuprichlorobromides gave the yellow cuprichlorides.

FIG. 1.

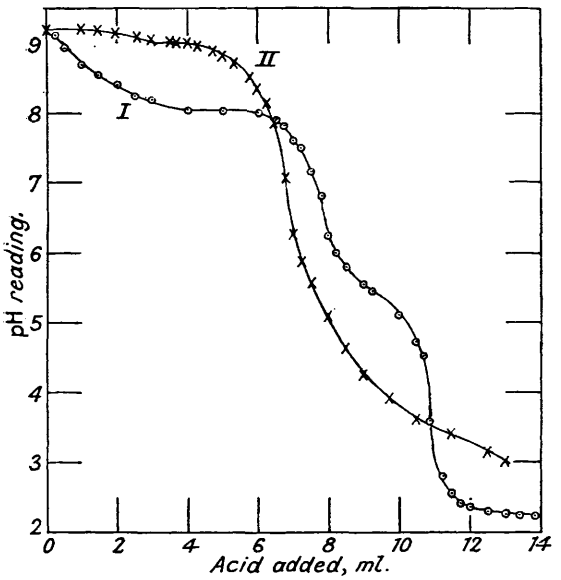
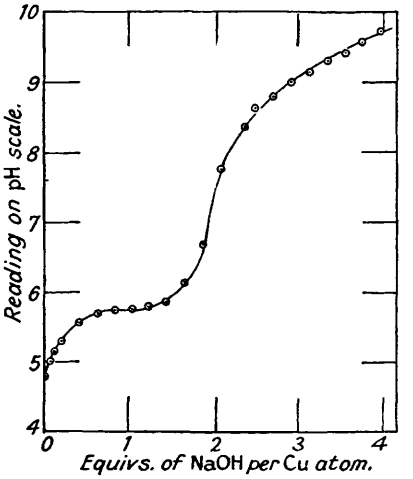


FIG. 2.



Double Cuprichlorides.—These were obtained by the methods of Ralston *et al.* (*loc. cit.*). Bistetradecylamine cuprichloride (0·1944 g.) in pure methanol (150 ml.) was titrated with 0·118N-aqueous sodium hydroxide, the glass electrode assembly described under cupric carbonate complexes being used. The curve (Fig. 2) shows a sharp break when 2 equivs. of alkali are added, confirming the formulation as a double salt and the applicability of the glass electrode under such conditions.

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