28. *Complexes between Metal Salts and Long-chain Aliphatic Amines. Part III. The Oxidation of Copper*(I) *Complexes to Copper*(II) *Complexes.*

By R. G. Wilkins and A. R. Burkin.

Cuprous halide complexes with long-chain amines and with pyridine, having empirical formulæ CuX,Z, undergo aerial oxidation and in the presence of amine salts, Z,HX, form the corresponding cupric halide complexes, $CuX_2,2Z$, X representing the halogen atom and Z the ligand. The effect of changing X and Z is studied. The oxidation leads to the formation of hitherto undescribed complexes of cupric iodide with amines, $CuI_2,2R{\cdot}NH_2$. The mechanism of the reactions is not known.

An interesting oxidation reaction, involving the cuprous salt amine complexes (Part II) and the cupric salt amine complexes (Part I) has been discovered and investigated. If tetrakis-[cuprous chloride (or bromide) monoamine], dissolved in a non-hydroxylic solvent such as benzene, chloroform, or *n*-hexane, was heated under reflux with the corresponding amine hydrochloride (or hydrobromide), then aerial oxidation occurred and a cupric chloride (or bromide) amine complex was formed ($R = C_8H_{17}$, $C_{12}H_{25}$, or $C_{18}H_{37}$; $X = Cl$ or Br):

$$(CuX,R{\cdot}NH_2)_4 + 4R{\cdot}NH_3X\ (+\ 2O) \longrightarrow 4CuX_2,2R{\cdot}NH_2\ (+\ 2H_2O) \quad . \quad . \quad . \quad (A)$$

An analogous reaction was observed with the cuprous iodide amine complexes but it was very much slower and less complete, especially with the higher amines, *e.g.*, octadecylamine. These compounds are an interesting example of the stabilisation of an unusual valency state by co-ordination (cf. the formation of cupric iodide complexes with ethylenediamine; Morgan and Burstall, *J.*, 1926, 2018).

This type of oxidation reaction was shown to be fairly general for univalent copper salt complexes with amines. If the complex formed between one molecule of cuprous halide and one molecule of pyridine was treated with the corresponding pyridine salt, then dipyridinocupric halide was formed (X = Cl, Br, or I; py = pyridine):

$$2(\mathrm{CuX,py}) + 2\mathrm{py,HX}\ (+\ \mathrm{O}) \longrightarrow 2\mathrm{CuX_2,2py}\ (+\ \mathrm{H_2O}) \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{B})$$

(1) X = Cl. Dipyridinocupric chloride, $CuCl_2,2C_5H_5N$, is well known. Cox, Sharatt, Wardlaw, and Webster (*J.*, 1936, 129) prepared it in a number of ways in an unsuccessful attempt to obtain the *cis*-form. The product of this oxidation reaction was a blue micro-crystalline solid, which recrystallised from methyl alcohol as fine, pale blue needles, exactly as described by Cox *et al.*, and was, without doubt, the *trans*-compound also.

(2) X = Br. The product of the oxidation reaction, dipyridinocupric bromide, $CuBr_2,2C_5H_5N$, was obtained by Pfeiffer and Pimmer (*Z. anorg. Chem.*, 1905, **48**, 98) as green needles, by direct reaction betweeh the components.

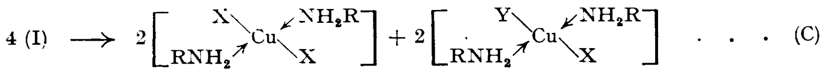
(3) X = I. The reaction was extremely slow, and although it is believed (from colour changes of the solutions) that a small amount of oxidation occurred, no pure dipyridinocupric iodide was obtained, and large amounts of unchanged reactants were recovered.

By the use of this reaction, it was hoped to prepare a compound of the form (I), by an oxidation of the general type:

$$(\mathrm{CuX,R{\cdot}NH_2})_4 + 4\mathrm{R'{\cdot}NH_3Y}\ (+\ 2\mathrm{O}) \longrightarrow 4\left[\mathrm{(RNH_2)(X)Cu(Y)(NH_2R')}\right]\ (+\ 2\mathrm{H_2O})$$

(I.)

The investigation was divided into two stages: (i) changing the anion and using the same amine, and (ii) changing the amine and using the same anion. In reactions of type (i), disproportionation occurred and two products were formed (X = Cl, Y = Br or OAc; X = Br, Y = Cl or OAc; X = I, Y = Cl or OAc):

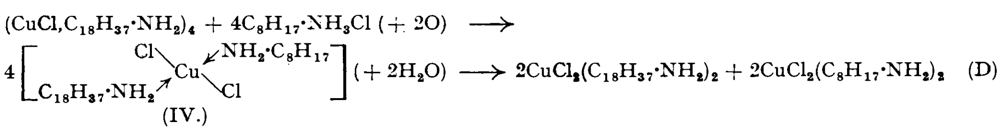


$$4\ (\mathrm{I}) \longrightarrow 2\left[\mathrm{(X)(RNH_2)Cu(NH_2R)(X)}\right] + 2\left[\mathrm{(Y)(RNH_2)Cu(NH_2R)(X)}\right] \quad . \quad . \quad . \quad (\mathrm{C})$$

(II.) (III.)

Possibly the intermediate compound (I) is initially formed but this extremely quickly disproportionates to the products (II) and (III). The mechanism of the reaction is not clear, but must involve the breakage of a metal–halogen (or a metal–acetate) covalent bond. The two ways of effecting this are *via* (*a*) free radicals and (*b*) ions. The former is excluded since no halogenobenzene or phenyl acetate is formed when the reaction is carried out in benzene, unless it is postulated that the free radicals react much more quickly with each other than with benzene. Therefore the reaction involving ions must be explained on the idea that a small equilibrium concentration of ions is present in the non-polar solvents benzene or *n*-hexane. It is hoped to carry out conductivity measurements on the system in an attempt to detect such ions.

Broome, Ralston, and Thornton (*J. Amer. Chem. Soc.*, 1946, **68**, 849) carried out a spectrophotometric study of bisdodecylaminocupric acetate, $Cu(OAc)_2,2C_{12}H_{25}{\cdot}NH_2$, and showed that a 0·04M-solution in chloroform, at room temperature, dissociated into dodecylamine and cupric acetate to the extent of 10%. Further evidence for the comparatively loose attachment of the amine is shown by the fact that an analogous disproportionation reaction to the one described above, but now involving the co-ordinately-bound groups, has been observed; *e.g.*,



$$(\mathrm{CuCl,C_{18}H_{37}{\cdot}NH_2})_4 + 4\mathrm{C_8H_{17}{\cdot}NH_3Cl}\ (+\ 2\mathrm{O}) \longrightarrow$$

$$4\left[\mathrm{(Cl)(C_{18}H_{37}{\cdot}NH_2)Cu(NH_2{\cdot}C_8H_{17})(Cl)}\right]\ (+\ 2\mathrm{H_2O}) \longrightarrow 2\mathrm{CuCl_2(C_{18}H_{37}{\cdot}NH_2)_2} + 2\mathrm{CuCl_2(C_8H_{17}{\cdot}NH_2)_2} \quad (\mathrm{D})$$

(IV.)

Small amounts of the intermediate compounds (I) and (IV) may be formed. These would disproportionate easily, however, and their separation and identification would be extremely difficult.

The ease of oxidation depends on (*a*) the halogen and (*b*) the basicity of the amine. The complexes of cuprous chloride with amines and with pyridine are more rapidly and more completely oxidised than those of the bromide. The effect of the amine is most clearly shown when the cuprous iodide amine complexes are considered. About 40% of cuprous iodide dodecylamine is oxidised in the presence of dodecylamine acetate, when equimolecular proportions of the reactants are heated together in solution for 2 hours (Reaction C; X = I, Y = OAc, R = $C_{12}H_{25}$). The corresponding reaction involving hexadecylamine takes place to the extent of only about 5%, even when the reactants are heated under reflux in solution for 4 or more hours.

The heating together of tetrakis(cuprous iodide octadecylamine) with octadecylamine acetate for several days, in high-boiling solvents, does not result in appreciable reaction.

Cupric iodide bisdodecylamine was obtained, pure, as a dark brown waxy solid. The complexes of cupric iodide with hexadecylamine and octadecylamine were dark brown powders, which could not be obtained free from the reactants, since they were formed in such small amounts.

EXPERIMENTAL.

I. *Oxidation Reactions of Tetrakis(cuprous chloride alkylamines).*—In this section, the reactions of the octadecylamine complex are described as typical for all the other members of the series.

(*a*) *In the presence of octadecylamine hydrochloride* (*Reaction* A; X = Cl, R = $C_{18}H_{37}$). Freshly prepared cuprous complex (0·75 g., 1 mol.) was dissolved in 30 ml. of hot chloroform and added to octadecylamine hydrochloride (0·63 g., 1·05 mols.) dissolved in 20 ml. of hot chloroform. The hot green solution changed to blue almost immediately, and was heated under reflux for ½ hour. The solution was cooled and filtered at 45°. The solid deposited was recrystallised three times from chloroform. A blue powder, m. p. 125°, was obtained (Found : Cl, 10·6; Cu, 9·4. Calc. for $C_{36}H_{78}N_2Cl_2Cu$: Cl, 10·6; Cu, 9·4%). The reaction involving dodecylamine was carried out in a similar manner, and a blue solid was isolated, m. p. 124° (Found : Cl, 14·1; Cu, 12·6. Calc. for $C_{24}H_{54}N_2Cl_2Cu$: Cl, 14·05; Cu, 12·6%).

(*b*) *In the presence of octadecylamine acetate* (*Reaction* C; X = Cl, Y = OAc, R = $C_{18}H_{37}$). Cuprous chloride mono-octadecylamine (1·5 g., 1 mol.) was treated with octadecylamine acetate (1·08 g., 0·9 mol.) in 100 ml. of benzene. The green solution quickly changed to a deep blue colour, and was heated under reflux for 45 minutes and then cooled. A solid separated and was filtered off at about 35°; this was dark lilac-blue [fraction (i)]. The filtrate was dark blue and, when left overnight, deposited a lilac solid [fraction (ii)]. Fraction (i) was dissolved in 100 ml. of boiling benzene and cooled to 45°, at which temperature the solid was filtered off. It was recrystallised from 80 ml. of hot chloroform, giving a pale blue solid, m. p. 125° (Found : C, 64·8; H, 11·7; N, 4·3; Cl 10·6; Cu, 9·4. Calc. for $C_{36}H_{78}N_2Cl_2Cu$: C, 64·2; H, 11·7; N, 4·2; Cl, 10·6; Cu, 9·4%). Fraction (ii) was dissolved in 30 ml. of hot benzene and cooled. At about 45°, a solid separated which was filtered off at about 40°. Recrystallisation was repeated from 30 ml. of benzene. A lilac solid was obtained, m. p. 95° (Found : Cu, 8·8. Calc. for $C_{40}H_{34}N_2O_4Cu$: Cu, 8·8%). The reaction involving dodecylamine was carried out in a similar manner and two solids were obtained : blue, m. p. 124° (Found : Cl, 14·0; Cu, 12·5%), and lilac, transparent rectangular plates, m. p. 78° (Found : Cu, 11·1. Calc. for $C_{28}H_{60}O_4N_2Cu$: Cu, 11·5%). The reactions were also carried out in chloroform and in *n*-hexane with similar results.

(*c*) *In the presence of octylamine hydrochloride* (*Reaction* D). The cuprous complex (1·2 g., 1·0 mol.) was dissolved in 60 ml. of hot benzene and added to octylamine hydrochloride (0·43 g., 0·9 mol.) dissolved in 30 ml. of hot benzene. The hot green solution formed was heated under reflux for 45 minutes. It was then cooled; a solid separated at room temperature. This was filtered off and a light blue solid was obtained [fraction (i)] together with a green filtrate, which when left overnight deposited more blue solid [fraction (ii)]. Fraction (i) was recrystallised twice from 70 ml. of chloroform, the solid separating at about 45° being filtered off at 35° (Found : Cu, 9·1. Calc. for $C_{36}H_{78}N_2Cl_2Cu$: Cu, 9·4%). Fraction (ii) was not further treated (Found : Cu, 12·6. Calc. for $C_{16}H_{38}N_2Cl_2Cu$: Cu, 16·2%). Fraction (ii) appears to be a mixture of the two complexes of cupric chloride with octylamine and with octadecylamine; there is no doubt, however, that disproportionation occurs.

(*d*) *Oxidation of monopyridinocuprous chloride in the presence of pyridine hydrochloride* (*Reaction* B; X = Cl). Pyridinocuprous chloride (as prepared in Part II) was separated from the supernatant green liquid by decantation and dissolved in benzene (green solution). An excess (1·2 mols.) of pyridine hydrochloride dissolved in hot chloroform was added. The resulting dark solution quickly deposited a blue solid in large amounts. This was heated under reflux for a few minutes (the blue solid remaining insoluble) and then cooled. A light-blue micro-crystalline powder was filtered off. This was recrystallised from methyl alcohol, and fine pale blue needles were obtained (Found : Cl, 24·2; Cu, 21·9. Calc. for $C_{10}H_{10}N_2Cl_2Cu$: Cl, 24·2; Cu, 21·7%).

II. *Oxidation Reactions of Tetrakis(cuprous bromide alkylamines).*—The reactions of the octadecylamine complex are described as typical of those of all the cuprous bromide–amine complexes.

(*a*) *In the presence of octadecylamine hydrobromide* (*Reaction* A; X = Br, R = $C_{18}H_{37}$). Freshly prepared tetrakis(cuprous bromide octadecylamine) (1·0 g., 1 mol.) was dissolved in 25 ml. of warm benzene, and to it was added octadecylamine hydrobromide (0·85 g., 1 mol.) dissolved in 35 ml. of hot benzene. The resulting dark green solution was heated under reflux for about ½ hour, and then cooled to room temperature. A green solid was deposited, and the dark greenish-brown filtrate when left overnight deposited a further amount of green solid. This was separated and recrystallised from 60 ml. of benzene. A solid separated on cooling, and was filtered off, washed with cold benzene, and dried. A light green solid, m. p. 114°, was obtained (Found : C, 57·2; H, 10·2; N, 4·0; Br, 21·1. Calc. for $C_{36}H_{78}N_2Br_2Cu$: C, 56·6; H, 10·3; N, 3·7; Br, 21·0%).

(*b*) *In the presence of octadecylamine hydrochloride* (*Reaction* C; X = Br, Y = Cl, R = $C_{18}H_{37}$). Tetrakis(cuprous bromide octadecylamine) (1·0 g., 1 mol.) was dissolved in 25 ml. of hot benzene, and octadecylamine hydrochloride (0·74 g., 1 mol.), dissolved in 35 ml. of benzene, was added. The dark green solution was heated under reflux for about 45 minutes, and then cooled. An apple-green solid separated and was filtered off. The dark green filtrate deposited more green solid when kept. The apple-green solid dissolved in 80 ml. of chloroform to give a dark green solution, which on cooling re-deposited solid, which was filtered off. This had a different shade of green colour, and if it was recrystallised a further three times from 50 ml., 30 ml., and 20 ml. of chloroform, respectively, a blue solid was obtained, m. p. 125° (Found : Cu, 9·4%). The filtrate deposited a green solid on each occasion, m. p. 113° (Found : Br, 21·3%).

(*c*) *In the presence of octadecylamine acetate* (*Reaction* C; X = Br, Y = OAc, R = $C_{18}H_{37}$). Tetrakis(cuprous bromide octadecylamine) (1·0 g., 1 mol.) and octadecylamine acetate (0·82 g., 1·02 mols.), dissolved in 25 ml. and 30 ml. of hot benzene, respectively, were heated together under reflux for about 2 hours. The hot green-blue solution on cooling deposited first a green solid and then a small amount of lilac solid. The blue-green filtrate, on further storage, deposited more lilac solid. The green solid, recrystallised from benzene, had m. p. 113° (Found : Br, 21·0. Calc. for $C_{36}H_{78}N_2Br_2Cu$: Br, 21·0%). The lilac solid, recrystallised twice from small quantities of benzene (20 ml.), had m. p. 95° (Found : Cu, 8·8%).

(*d*) *Oxidation of monopyridinocuprous bromide in the presence of pyridine hydrobromide* (*Reaction* B; X = Br). Pure pyridinocuprous bromide (0·1 g., 1 mol.), suspended in benzene, was treated with a solution of pyridine hydrobromide (0·07 g., 1 mol.) in 15 ml. of benzene–alcohol. Most of the complex dissolved and on being heated under reflux for a short time, a deep-brown solution was formed, together with an insoluble green solid. The brown solution, on cooling, deposited more green solid, m. p. 142°. This solid gave, with excess of pyridine, hexapyridinocupric bromide, $CuBr_2,6C_5H_5N$, and with hydrobromic acid, reddish-black pyridinium cupribromide $(C_5H_6N)_2CuBr_4$ (Pfeiffer and Pimmer, *loc. cit.*).

III. *Oxidation Reactions of Tetrakis*(*cuprous iodide alkylamines*).—(*a*) *Attempted reaction between tetrakis*(*cuprous iodide octadecylamine*) *and octadecylamine acetate* (*Reaction* C; X = I, Y = OAc, R = $C_{18}H_{37}$). A suspension of the cuprous iodide complex (0·5 g., 1 mol.) in 40 ml. of light petroleum (b. p. 80—100°) dissolved when octadecylamine acetate (0·36 g., 1 mol.) was added. The light-green solution was heated under reflux for several days (*a*) alone and (*b*) in the presence of excess of octadecylamine (to make the reaction conditions similar to those used in the dodecylamine work). The red solution finally obtained, on cooling, deposited first a white solid, m. p. 80—81° (m. p. of octadecylamine acetate 84°), and then unchanged cuprous complex.

(*b*) *Reaction between tetrakis*(*cuprous iodide hexadecylamine*) *and hexadecylamine acetate* (*Reaction* C; X = I, Y = OAc, R = $C_{16}H_{33}$). A solution of cuprous iodide monohexadecylamine (0·6 g., 1 mol.) in 30 ml. of light petroleum, containing a small amount of hexadecylamine, was heated under reflux with a solution of hexadecylamine acetate (0·4 g., 1·05 mols.) in 20 ml. of light petroleum. The initial green solution slowly became brown; after about 3 hours the solution was cooled, and a small amount of solid separated. This was filtered off, and a lilac solid was obtained; the brown filtrate on cooling continued to deposit a light-brown solid (a mixture of unchanged reactants and small amounts of the cupric iodide complex). When about 5—10 ml. of solution were left, no further solid separated and the brown solution on complete evaporation left a dark brown viscous solid, which on cooling in the refrigerator solidified and could be crushed to a brown powder, which however was not obtained pure.

(*c*) *Reaction between cuprous iodide dodecylamine and dodecylamine acetate* (*Reaction* C; X = I, Y = OAc, R = $C_{12}H_{25}$). Cuprous iodide (0·5 g., 1 mol.) was treated with dodecylamine (0·75 g., 1·4 mols.) in 40 ml. of light petroleum. After about 15 minutes, all the cuprous iodide had dissolved and a red solution was formed. To this hot solution, dodecylamine acetate (0·66 g., 1 mol.), dissolved in 30 ml. of light petroleum, was added, and the pale green solution formed was heated under reflux for 20 minutes. On cooling, this solution became dark green, but no solid was deposited. However, when it was left in an open dish for about 20 minutes, some solid was deposited. This was filtered off and a brown-lilac solid [fraction (i)] was obtained together with a green filtrate. This filtrate, on further storage, deposited more solid (lilac-brown, smelling strongly of free iodine) together with a dark brown filtrate which deposited no more solid, but left a dark brown, almost black, waxy solid [fraction (ii)] on complete evaporation. Passage of carbon dioxide through the dark brown light-petroleum solution precipitated, as the carbonate any excess of amine remaining in solution at this stage. The limited solubility of the cupric acetate amine complex and the extreme solubility of the cupric iodide amine complex thus makes a very effective separation possible. Fraction (i) was dissolved in 30 ml. of hot benzene, and the blue solution kept for an hour in an open beaker, whereupon a crystalline solid was deposited. This was filtered off, washed, and dried, transparent, lilac, rectangular plates being obtained (Found : Cu, 11·1%). Fraction (ii), *cupric iodide bisdodecylamine*, was extremely soluble in organic solvents (Found : Cu, 9·3. $C_{24}H_{54}N_2I_2Cu$ requires Cu, 9·25%).

(*d*) *Reaction between cuprous iodide dodecylamine and dodecylamine hydriodide* (*Reaction* A; X = I, R = $C_{12}H_{25}$). Cuprous iodide–dodecylamine, in benzene solution (1·0 g., 1 mol.) (see preceding paragraph), was treated with dodecylamine hydriodide (0·8 g., 0·97 mol.) in 20 ml. of benzene, and the solution heated under reflux for 5 hours. The light-brown solution obtained, on cooling, became dark red, and finally brown-red. The solution was transferred to an evaporating dish and kept overnight; a dark brown, waxy solid, very similar to that obtained as described in paragraph (*c*), remained. The solution of the solid, in light petroleum, was cooled in a freezing mixture; some solid separated (dodecylamine hydriodide ?) and was filtered off. Carbon dioxide was passed through the filtrate, and once more the solid was filtered off. The filtrate was evaporated to dryness. Analysis of the waxy residue indicated that it was the cupric iodide complex contaminated with unchanged dodecylamine hydriodide and probably some iodine (Found: I, 43·5; Cu, 7·25. Calc. for $C_{24}H_{54}N_2I_2Cu$: I, 36·9; Cu, 9·25%).

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UNIVERSITY COLLEGE, SOUTHAMPTON.

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