27. *Complexes between Metal Salts and Long-chain Aliphatic Amines. Part II. The Complexes of Cuprous Halides with Long-chain Aliphatic Amines.*

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Co-ordination compounds of cuprous salts (CuX) with long-chain aliphatic amines have been prepared and their structures investigated (*a*) by molecular-weight determinations and (*b*) by a study of their reactions. Cuprous chloride, bromide, and iodide form tetrameric monoamine complexes, $(CuX,R{\cdot}NH_2)_4$. Cuprous bromide forms also bisamine complexes which have dimeric bridged structures $(CuBr,2R{\cdot}NH_2)_2$ at low temperatures (freezing benzene) but dissociate into the monoamine complex and free amine at higher temperatures, the solid bisamine complex separating again on cooling. The preparation of the chloride and bromide was carried out in an oxygen-free atmosphere. Reaction between the monoamine complexes and pyridine gave, in all cases investigated, the cuprous halide–pyridine complex of empirical formula (CuX,C_5H_5N).

There is no work reported on complexes formed by co-ordination of higher primary aliphatic amines with cuprous salts. The amines chiefly used in the present work were *n*-octadecylamine,

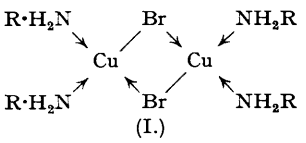
n-dodecylamine, and *n*-octylamine, hexadecylamine being used in a few cases where the fact that the stabilities and solubilities of its complexes are intermediate between those of the octadecyl- and the dodecyl-amine was of particular value. Cuprous chloride, bromide, and iodide were the metallic salts studied.

When cuprous chloride or bromide is added to a solution of about 2 equivs. of an amine in, for example, hot light petroleum, a mixture of blue and green, amine-containing, oxidation products is obtained. If, however, the reaction is carried out in the absence of oxygen, the cuprous salt gradually dissolves to give a green solution, which on cooling deposits a complex as a fine white or very pale green powder. A simple apparatus was devised for filtering off these compounds in the absence of air (see p. 130).

Cuprous iodide complexes are stable in air and are formed when cuprous iodide is dissolved in a hot solution of the amine in light petroleum, benzene, etc. The hexa- and octa-decylamine *complexes* are white crystalline solids. The *compounds* with lower amines are extremely soluble in the presence of the excess of amine necessary for their preparation, and either (*a*) cooling in ice–salt or (*b*) evaporation of the solution *in vacuo* merely gives the complex contaminated with the excess of amine. The pure solids are insoluble in all the usual organic solvents, but in the presence of a trace of free amine, they dissolve readily, giving red solutions, which turn colourless on prolonged heating, but regain their red colour on cooling. Molecular weights were determined by observing the boiling point of the solvent containing a trace of the amine present in the complex and treating this as the " solvent," the elevations due to the amine and complex being additive as long as no interaction occurs. With larger concentrations of amine, the amount present had an effect on the elevation, as is described below.

Cuprous chloride and iodide formed only monoamine *complexes* with the empirical formulæ ($CuCl,R{\cdot}NH_2$) and ($CuI,R{\cdot}NH_2$), although almost 2 mols. of amine per atom of copper were necessary for their preparation. Cuprous bromide formed a monoamine *complex*, ($CuBr,R{\cdot}NH_2$), if one mol. of amine was used, but in the presence of two mols. of amine, a bisamine *complex* ($CuBr,2R{\cdot}NH_2$) was formed.

No question arises as to the co-ordination number of copper for the cupric salt complexes (see Part I), it being 4 for all complexes examined. The empirical formula of the cuprous halide complexes would indicate co-ordination numbers for copper of both 2 (monoamine complex) and 3 (bisamine complex). In all cases examined, however, polymerisation occurs and the usual stable co-ordination number of 4 is attained. The bisamine complexes of cuprous bromide were shown by molecular-weight determinations in freezing benzene to have a dimeric, presumably bridged, structure (I; R = $C_{12}H_{25}$ and C_8H_{17}). The monoamine complexes were shown to have a tetrameric structure, as is described later. It is well established that halogen atoms can act as " bridging " groups between metallic atoms (for summary of work, see Mann, *Ann. Reports*, 1938, **35**, 151).



(I.)

In boiling benzene solution the molecular weight found for the bisamine complexes did not correspond to either a monomeric or a dimeric structure. The observed elevation of boiling point did, however, correspond closely to the observed and calculated values caused by an equimolecular mixture of monoamine complex and amine. The same phenomenon was observed in *n*-hexane also. It is concluded therefore that at these slightly higher temperatures, the bisamine complex dissociated into the monoamine complex and free amine, but on cooling the solution the bisamine complex was precipitated again :

$$2(CuBr,2R{\cdot}NH_2)_2 \rightleftharpoons (CuBr,R{\cdot}NH_2)_4 + 4R{\cdot}NH_2$$

$$\downarrow \text{py}$$

$$4(CuBr,py) + 4R{\cdot}NH_2$$

Further evidence supporting this idea of dissociation is that when treated with 1 equiv. of pyridine in hot solvents, the bisamine complexes form monopyridinocuprous bromide, the same compound as is obtained when the monoamine complex is treated with pyridine.

The molecular weights of the monoamine complexes had to be determined ebullioscopically because of their insolubility in cold solvents. Cottrell's apparatus was used and a similar apparatus containing the solvent alone was employed as " reference " thermometer. This method of eliminating the influence of the barometer is more convenient and decidedly more accurate than any method involving barometer reading and the application of a correction. The determinations were carried out in a small, draught-free room, out of the sunlight, and the precautions

mentioned by Washburn and Read (*J. Amer. Chem. Soc.*, 1919, **41**, 729) were observed. The values for the boiling points were extremely steady and reproducible under these conditions, although the method is very sensitive to outside disturbances, so that any rapid movements by the observer appreciably altered the thermometer readings. In order to correct for the amount of solvent refluxing in the apparatus and present as vapour, and to smooth out the irregularities of individual readings, the solutions were progressively diluted and a number of observations made.

It can easily be shown that

$$C = 1000kC_1/\mathrm{d}T \,.\, M + x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is the weight of solvent introduced into the apparatus, C_1 is the weight of solute, and x is the weight of solvent " refluxing "—a constant depending on the size of the apparatus. From (1), the graph of the weight of solvent plotted against the reciprocal of the elevation is a straight line, of slope $1000kC_1/M$. The validity of the argument depends on the fact that the molecular weight is fairly constant over a range of concentrations. The straight lines obtained for a number of complexes when this graph is plotted support this contention.

All the cuprous halide monoamine complexes $(CuX,R{\cdot}NH_2)_x$ examined had values for x between 2·9 and 3·3. Their structures are presumably analogous to those of the complexes formed between cuprous iodide and trialkyl-phosphines or -arsines of empirical formulæ $CuI,P(or\ As)R_3$; X-ray analysis of triethylarsine–cuprous iodide showed that the true molecule was $(CuI,AsEt_3)_4$ (Mann, Wells, and Purdie, *J.*, 1936, 1503). Mann, in addition, carried out a series of molecular-weight determinations on different members of the arsine and phosphine series in various solvents. Values of x in the polymer $(CuI,PR_3)_x$ were found in nearly all cases to lie between 3 and 4. It is possible that the low values of x are due to an inherent error in the molecular-weight determinations such as non-ideality of solution, the use of approximate formulæ, etc. It seems unlikely, however, that such a large and consistent difference is due to those causes and the more probable explanation is that some type of dissociation occurs in the solution.

Mann suggested that it was of the type $(R_3P,CuI)_4 \rightleftharpoons 4(R_3P,CuI)$, leading to a bicovalent cuprous complex. We have obtained, however, a certain amount of evidence for the following type of dissociation, at least with the cuprous iodide–amine complex :

$$(CuI,C_{18}H_{37}{\cdot}NH_2)_4 \rightleftharpoons (CuI,\overline{I-x}C_{18}H_{37}{\cdot}NH_2)_4 + 4xC_{18}H_{37}{\cdot}NH_2 \quad . \quad . \quad . \quad . \quad (2)$$

Thus we suggest that in hot solvents a small amount of amine splits off from the complex tetramer, but leaves the main bridged structure intact, a small proportion of the copper atoms momentarily having no amine attached. On cooling, the amine recombines once more and the original complex separates out. Quite a small degree of dissociation of this type, less than 10% of the amine molecules splitting off, would account for the observed results. The evidence for the type of dissociation postulated is as follows.

(1) Pure cuprous iodide–octadecylamine complex (compound *A*), was heated under reflux for about an hour in *n*-hexane in the presence of a small amount of dodecylamine. If octadecylamine had split off at all there should be competition between it and the dodecylamine when recombination occurred, and the product obtained on cooling and filtering (compound *B*) should contain dodecylamine and so have a higher copper content and lower carbon and hydrogen contents than the original compound *A*. Thus there is no question of any changes in analysis figures being due merely to contamination with excess of amine. The results obtained are given below and clearly indicate that a replacement of this type has occurred :

	$(CuI,C_{18}H_{37}{\cdot}NH_2)_4$ requires :	Compound *A*, found :	Compound *B*, found :
C, %	47·0	46·5	45·5
H, %	8·5	8·35	8·05
Cu, %	13·8	13·85	14·25

(2) When the molecular weight of the complex was determined in the presence of different amounts of octadecylamine, the observed value increased (corresponding to a decrease in the degree of dissociation) as the ratio of the amount of added amine to the amount of complex was increased. This would be expected, as the added amine would force the reaction (2) from right to left.

(3) On boiling a suspension of the pure complex in light petroleum in an open vessel for a few minutes, the solid lost a small amount of amine (which is slightly volatile in the solvent vapour), the copper content of the solid increasing from 13·85 to 14·2%. On recrystallising this from light petroleum containing just enough octadecylamine to make it soluble, the pure monoamine complex was obtained once more.

(4) Dissociation of this type is often encountered with co-ordination compounds of many different types. Thus most ammonia–cupric salt complexes lose ammonia very readily in air, and certain organic arsine complexes with metal salts are highly dissociated even in freezing benzene solution and smell strongly of the arsine, particularly the complexes of $IrCl_2$ with aryldialkylarsines (Dwyer and Nyholm, *J. Roy. Soc. N.S.W.*, 1944, **77**, 116; 1946, **79**, 121). Kharasch *et al.* (*J. Amer. Chem. Soc.*, 1938, **60**, 882) obtained an approximate molecular weight of 409 for the styrene–$PdCl_2$ complex by the depression of the f.p. of benzene. This is intermediate between 282 for the monomeric and 564 for the dimeric form of ($PdCl_2$,C_6H_5·CH:CH_2) which should, by analogy with the $PtCl_2$ complex, be a bridged molecule. Instead of postulating splitting of the bridge, the value can be explained by assuming partial dissociation into free styrene.

We do not suggest that this type of dissociation explains all the observed phenomena of this type, for in the case of the cuprous iodide–trialkylarsine complexes the liberated trialkylarsine might be expected to oxidise easily and so lead to irreversible dissociation and decomposition of the complexes, which does not occur. Also, there is some evidence that dissociation into monomeric units also occurs. In the case of the reversible dissociation of the cuprous bromide bisamine complexes—presumably bridged dimers—into amine and cuprous bromide monoamine complexes—tetramers—it is difficult to see how the reaction can proceed except *via* the bicovalent monomeric units. As is shown in Part III, however, the mechanisms of reactions involving this type of complex in non-aqueous solvents are not clear, and dissociation giving free anions may also occur.

As mentioned above, the amine was readily replaced by a stronger co-ordinating group. Pyridine gave complexes with very low solubilities in organic solvents, thus making the determination of their molecular weights impossible. The compound obtained when cuprous iodide–amine complexes were treated with pyridine had an empirical formula (CuI,C_5H_5N). Varet (*Compt. rend.*, 1891, **112**, 391) obtained the same substance as small yellow crystals by treating cuprous iodide with pyridine; when treated with ether, the substance became white, and when exposed to air, it became green and then brown, as observed by Varet (*loc. cit.*).

The monopyridinocuprous chloride complex, empirical formula (CuCl,C_5H_5N), was obtained as a light yellow solid which rapidly turned green on exposure to air. In contrast to these substances, *monopyridinocuprous bromide* (CuBr,C_5H_5N) was a white microcrystalline solid which showed no tendency to decompose and was extremely stable. This compound is not reported in the literature but CuBr, $2C_5H_5N$ is a well-known golden-green crystalline solid, decomposing rapidly in air (Varet, *Compt. rend.*, 1897, **124**, 1156; Marukhyan, *J. Gen. Chem. Russia*, 1940, **10**, 917).

The solubility of all the cuprous halide complexes in organic solvents decreased as the chain length of the amine involved increased. The cuprous chloride and bromide complexes, initially white solids, deepened in colour on storage in air, finally becoming a dark green. Their solutions, on boiling in air, undergo decomposition, and smell strongly of the amine.

Experimental.

General Method of Preparation of Complexes in an Inert Atmosphere.—In the preparation of all cuprous chloride and bromide complexes with amines, the same general method was employed. Variations in the reaction conditions are noted in the separate details of each experiment.

The whole apparatus (Fig. 1) was disconnected at the ground glass joint *A*, and the Buchner flask, funnel, and inlet tube were filled with the solvent to be used in the reaction. This was then displaced by passing a stream of nitrogen through the side-arm of the flask *B*, and allowing the solvent to pass out of the tube *C*. The side-arm and tube were closed and this portion of the apparatus was then placed on one side. The cuprous salt was placed in the reaction vessel *D*, and a stream of nitrogen was passed through the inlet tube *E* for about 15 minutes; this clears out any residual oxygen in the apparatus. The amine, dissolved in the solvent, was then added from the tap-funnel *F*, and the reaction allowed to continue until all the cuprous halide had dissolved (which indicated that the reaction was now complete), the nitrogen stream being continued meanwhile. The solution was cooled, and the complex then separated at a temperature which depended on the cuprous salt and amine used. The resultant solid was then filtered off in an atmosphere of nitrogen. The two separated parts were connected (as shown in Fig. 1), and the side-arm *B* connected to the water-pump. The filter-pump was then turned on, and the ground-glass joint *A* revolved 180°, whereupon the solid and solvent passed, *via* the glass joint and tubing, into the Buchner funnel. The solid was washed with solvent added from the tap-funnel *F*, and the precipitate then sucked dry for about 10 minutes. The Buchner funnel and precipitate were finally transferred quickly to a vacuum desiccator for final drying.

Determination of Molecular Weights.—Since the chloride and bromide complexes decomposed in air, when these complexes were used, the apparatus was filled with nitrogen, which had been washed by alkaline pyrogallol, dried by concentrated sulphuric acid, and saturated with solvent vapour. A slow stream of nitrogen was passed into the Cottrell's apparatus at the top of the condenser throughout the

determination, and the gas led away through about 4 feet of narrow tubing (2 mm.) to minimise back diffusion of air. The values obtained for the molecular weights are recorded below in separate sections, the graph number referring to Fig. 2.

In all the preparative work described below, light petroleum (b. p. 60—80°) was used, although the preparation of the complexes could also be carried out in other organic solvents, *e.g.*, benzene, in which they were much more soluble, the temperature of separation being correspondingly lower.

I. *Preparation of Cuprous Chloride Complexes.—With octadecylamine.* Cuprous chloride (0·9 g., 1 mol.) was heated with 100 ml. of light petroleum containing octadecylamine (5·0 g., 2·05 mols.) for an hour at 70—80°. The complex formed was soluble above about 67°, and the green solution formed was cooled to 55° and filtered. A light green solid *complex* was obtained, which turned dark green when left in air for about 10 days (Found: Cu, 17·34, 17·36, 17·24. $C_{18}H_{39}NClCu$ requires Cu, 17·24%). The analytical figures are for three separate preparations.

With dodecylamine. Cuprous chloride (1·3 g., 1 mol.) was heated with dodecylamine (5·0 g., 2·05 mols.) in 100 ml. of light petroleum for 20 minutes at 60—65°. The cuprous chloride dissolved and gave a dark green solution, which was filtered at about 40°, at which temperature the *complex* separated in large quantities. A white solid, it turned distinctly green within an hour (Found: C, 49·7; H, 9·5; Cu, 22·2; *M*, 2·9% solution in benzene, 590; 5·7% solution in benzene, 640. $C_{48}H_{108}N_4Cl_4Cu_4$ requires C, 50·7; H, 9·6; Cu, 22·4%; *M*, 1137).

FIG. 1.

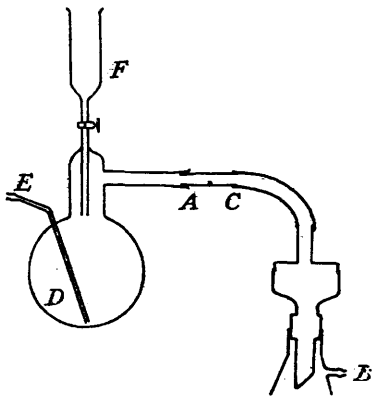
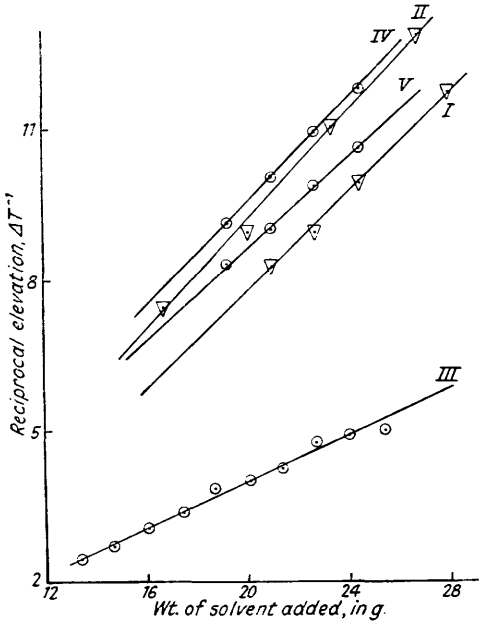


FIG. 2.



With octylamine. Cuprous chloride (1·2 g., 1 mol.) was treated with octylamine (3·2 g., 2·04 mols.) in 60 ml. of light petroleum at 60° for 15 minutes. A green solution was formed and this deposited a white solid on cooling, which must be a complex since octylamine is a liquid at these temperatures. Several attempts were made to filter it, but only a blue-green solid mixture was obtained.

With pyridine The solution of cuprous chloride–octylamine in light petroleum, obtained as above, was treated with an excess of pyridine (1·0 g., 1·04 mols.). A yellow oil formed at the bottom and solidified on cooling to a yellow solid, which was filtered off in air. The yellow crystalline solid, on exposure to air, quickly turned green.

II. *Preparation of Cuprous Bromide Complexes.—With octadecylamine.* (i) Cuprous bromide (1·0 g.) was warmed with octadecylamine (2·0 g., 1·06 mols.) in 100 ml. of light petroleum at 55° for 20 minutes. The *complex* was filtered off at 20°. A white solid, it became dark green fairly quickly (Found: Br, 19·3; Cu, 15·45. $C_{18}H_{39}NBrCu$ requires Br, 19·35; Cu, 15·4%).

(ii) Cuprous bromide (0·77 g.) was treated with octadecylamine (3·0 g., 2·07 mols.) dissolved in 100 ml. of hot light petroleum. All the salt had dissolved in 10 minutes at 58°. The *bisamino*-complex was filtered off at about 50°. A white solid, it changed to a green solid very slowly (Found: Br, 11·8; Cu, 9·4. $C_{36}H_{78}N_2BrCu$ requires Br, 11·7; Cu, 9·3%).

With dodecylamine. (i) Cuprous bromide (1·0 g.) was warmed with dodecylamine (1·35 g., 1·05 mols.) in 100 ml. of light petroleum at 35—40° for 10 minutes; a light green solution was obtained. On cooling to 16°, the *complex* separated and was filtered off. The white solid quickly became green [Found: Br, 24·2; Cu, 19·3; *M*, 2·2% in hexane, 1970; 5·6—8·0% in hexane, 2040; 3·0—4·8% in benzene, 995 (see Fig. 2, I). $C_{78}H_{108}N_4Br_4Cu_4$ requires Br, 24·3; Cu, 19·3%; *M*, 1315]. The graph obtained in *n*-hexane was not a straight line, indicating a change in *M* on dilution. The high value is difficult to interpret.

(ii) Cuprous bromide (1·0 g.) was warmed with dodecylamine (2·7 g., 2·1 mols.) in 150 ml. of light

petroleum at 45°; it dissolved within 5 minutes, and the *complex* began to separate at 38°. It was filtered off at 30°. The white solid slowly became green [Found: Br, 15·5; Cu, 12·4; *M* (cryoscopic), 2·9% in benzene, 1020; 2·8% in benzene, 1121; *M* (ebullioscopic), 3·9—7·5% in hexane, 650 (Fig. 2, III), 6·4% in benzene, 445. $C_{48}H_{108}N_4Br_2Cu_2$ requires Br, 15·5; Cu, 12·4%; *M*, 1040]. The ebullioscopic molecular-weight determinations in hexane and in benzene correspond closely to that required for an equimolecular mixture of the monoamine complex and amine.

With octylamine. (i) Cuprous bromide (1·0 g.) was treated with octylamine (1·0 g., 1·1 mols.) in 50 ml. of light petroleum at 25°. After about 5 minutes the copper salt had dissolved and the green solution was cooled in ice–salt. A white solid separated at −10°. It was filtered off and washed with ice-cold light petroleum. Little solid was obtained, it having apparently redissolved; it was very dark green.

(ii) Cuprous bromide (1·0 g.) was warmed with octylamine (2·0 g., 2·2 mols.) in 100 ml. of light petroleum. On warming above 40° for about 10 minutes, the salt dissolved to form a complex which gave a green solution. On cooling, the *complex* began to separate at 34° as a silvery-white solid [Found: Br, 19·65; Cu, 15·95; *M* (cryoscopic), 3·1% in benzene, 891. $C_{32}H_{76}N_4Br_2Cu_2$ requires: Br, 19·9; Cu, 15·8%; *M*, 804].

With pyridine. Pyridine (0·35 g., 1·1 mols.), dissolved in warm light petroleum, was added to a solution of cuprous bromide bisdodecylamine (2·0 g.) dissolved in 40 ml. of light petroleum at 40°. A feathery crystalline solid was deposited and filtered off while warm. It was washed with warm light petroleum and recrystallised from 20—30 ml. of light petroleum containing a little pyridine. A fluffy solid, the *complex* darkened rapidly at 130° without melting (Found: C, 26·9; H, 2·2; N, 6·8; Cu, 28·9. C_5H_5NBrCu requires C, 27·0; H, 2·3; N, 6·3; Cu, 28·6%).

III. *Preparation of Cuprous Iodide Complexes.—With octadecylamine.* Octadecylamine (0·95 g., 1·34 mols.), dissolved in 15 ml. of hot light petroleum, was added to a suspension of cuprous iodide (0·5 g., 1 mol.) in 10 ml. of hot light petroleum. Within about 15 minutes at 65°, in the air, the cuprous iodide had dissolved, giving a deep-red solution, which on continued heating under reflux changed to an almost colourless solution. This was then cooled to about 30°; a very light-coloured solid separated, which was filtered off, washed with warm light petroleum, and recrystallised twice from light petroleum. A white feathery crystalline *complex*, m. p. 98°, was obtained [Found: C, 46·5; H, 8·35; Cu, 13·8; *M*, 3·8—6·1% in hexane, 1492 (Fig. 2, II); 3·8—5·3% in benzene, 1332 (Fig. 2, IV). $C_{72}H_{156}N_4I_4Cu_4$ requires C, 47·0; H, 8·5; Cu, 13·8%; *M*, 1840].

With hexadecylamine. Hexadecylamine (2·8 g., 1·46 mols.) was heated under reflux with cuprous iodide (1·5 g., 1 mol.) in 60 ml. of light petroleum. The resulting colourless solution was cooled in a refrigerator and a light straw-coloured *complex* separated, which was filtered off and washed with cold light petroleum. Recrystallisation from 30 ml. of light petroleum yielded a pale yellow, microcrystalline solid [Found: C, 44·0; H, 8·3; Cu, 14·8; *M*, 4·0—6·1% in benzene, 1335 (Fig. 2, V). $C_{64}H_{140}N_4I_4Cu_4$ requires C, 44·5; H, 8·2; Cu, 14·7%; *M*, 1728].

With pyridine. Tetrakis(cuprous iodide octadecylamine) (1 g., 1 mol.) was dissolved in 50 ml. of light petroleum containing a small amount of octadecylamine. To the hot solution, pyridine (0·18 g., 1·05 mols.) was added. A precipitate of light feathery crystals was slowly formed, and was filtered off while warm. On exposure to air, these commenced to turn light green, but when they were washed with ether, a white solid was obtained (Found: Cu, 23·6. Calc. for C_5H_5NBrCu: Cu, 23·6%). The reaction was repeated with a solution of cuprous iodide dodecylamine in the presence of excess of dodecylamine; a similar result was obtained. The final solid was washed with ether as before (Found: Cu, 23·7%). Several other reactions have been carried out on a solution of the complex between cuprous iodide and dodecylamine in solution (see Paper III) without the isolation of the solid complex.

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