110. *Ionisation Equilibria of Metal Co-ordination Complexes in Benzene Solution. Part II.* The Structures of Some Cuprous Complexes.*

By A. R. Burkin.

Measurements of electrical conductivity in benzene solution show that certain complexes of cuprous halides exist in solution in more than one form. Di-(*o*-phenylenebisdimethylarsine)copper(I) di-iodocuprite(I) in nitrobenzene behaves as a salt, but in benzene the conductance is that of a non-electrolyte. The corresponding bromo-compound behaves as a salt in both solvents. The compound, of empirical formula $[CuBr(C_{12}H_{25}\cdot NH_2)_2]$, in benzene has at first the conductance of a non-electrolyte but the value increases as a salt is slowly formed.

A solution of a pure metal complex compound in an organic solvent cannot always be regarded as a simple system. In some cases the product obtained on crystallisation depends on the composition of the solvent. This is frequently due to solubility relations, but the physical properties of the solvent may also be important. Thus in a solvent of low dielectric constant and co-ordinating power, such as a hydrocarbon, rearrangement of a salt to form a non-ionic complex may occur. The reverse transformation, a non-ionic compound producing a salt in solution, would be expected to occur in such a solvent only under exceptionally favourable conditions (see Part I). The change must have a low activation energy so that in the absence of a catalyst only those metals giving labile complexes would be expected to show such a change. Also, the non-ionic compound would have to be prepared under conditions less favourable for salt formation than those under which dissociation does occur.

Complexes of cuprous halides are labile and are very sensitive to changes of solvent and other experimental conditions. The fact that a compound of empirical formula $CuXA_2$ (A being a monodentate ligand) could exist either as a salt $[CuA_4][CuX_2]$ or as a bridged dimer $[A_2CuX_2CuA_2]$ permits investigation of the possibility that such a compound might

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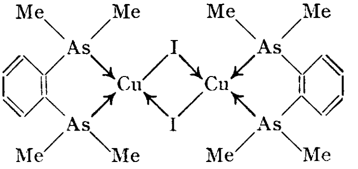
* Part I, *J.*, 1954, 71.

have different structures in different solvents. These points are well shown by the compounds formed between cuprous salts and *o*-phenylenebisdimethylarsine [1] and methyldiphenylarsine.[2] The solvents used for preparing these complexes were of relatively high dielectric constant and both salts and non-ionic compounds were obtained. The molecular constitutions of the substances isolated were investigated in solution by measuring molecular weights under various conditions, and electrical conductivities in nitrobenzene solution. In this paper the electrical conductivities in benzene solution of several such compounds and of some amine complexes are reported. Representative results are shown in the Table; some values reported in Part I are included for comparison. In all cases except one the results confirm the type of formula assigned by Nyholm (non-ionic or ionic). The conductance of tetrakis(methyldiphenylarsine)copper(I) nitrate was lower than that expected by comparison with the other salts. This agrees with the low value obtained in nitrobenzene by Nyholm, although in benzene the discrepancy is smaller. When the compound was dissolved in light petroleum containing a little acetone, and the solvent allowed to evaporate, a crystalline product was obtained with conductance characteristic of a non-electrolyte. This was not investigated further. The conductance of the original nitrate did not change irreversibly when the solution was kept at 45° for several hours.

Compound	Concn. × 10^4 (M)	Temp.	$10^6 \Lambda_M$	$10^{12} \sigma/\sqrt{c}$ at $c = 0$
$[Cu(AsMePh_2)_4]ClO_4$	5·15	35°	5·15	58
$[Cu(diarsine)_2]Br$	10·09	35	8·34	55
$[Cu(diarsine)_2][CuBr_2]$	8·33	33	10·61	63
$[CuI(AsMePh_2)_3]$	20·35	37	0·993	4·7
$[CuI(diarsine)]_2$	12·48	35	1·23	6·5
$[CuI(C_{18}H_{37}\cdot NH_2)]$	41·1	30	1·54	4·6
$[CuBr,2C_{12}H_{25}\cdot NH_2]_2$	10·1	35	5·48	38
	26·6	15	3·83	10
	44	20	1·35	3·8
$[Cu(AsMePh_2)_4]NO_3$	2·73	13	3·19	21
$[Cu(AsMePh_2)_4]NO_3$ (from acetone–light petroleum)	0·935	28	0·190	1·3

Kabesh and Nyholm [1] formulated the compound di-(*o*-phenylenebisdimethylarsine)-copper(I) di-iodicuprite(I) as a salt on account of its conductivity in nitrobenzene, which was too large for a non-electrolyte although smaller than those of the other compounds studied. As they point out, the results indicate only that in the solvent used the solute exists as a salt, but they do not establish with certainty that the compound is not bridged under other conditions. In benzene the conductance of the compound is that of a non-electrolyte and does not change irreversibly when the solution is warmed or stored. This suggests that in this solvent the compound exists as the halogen-bridged dimer as shown :



On the other hand the analogous dibromocuprite(I), $[Cu(diarsine)_2][CuBr_2]$ has a conductance in benzene characteristic of a salt and shows no tendency to form non-electrolytes. Thus the supposition that complexes of this type might exist as salts in nitrobenzene and solvents of high dielectric constant and as non-electrolytes in hydrocarbons, is untrue, although this does occur in the one case described.

The analogous compounds of methyldiphenylarsine formulated by Nyholm [2] as $[Cu(AsMePh_2)_4][CuX_2]$, where X = Cl or Br, gave low conductivities in nitrobenzene solution, and from these and molecular-weight determinations he concludes that this information does not permit a certain decision as to the structure of this class of compound. He considers it probable, however, that in the solid state they are salts but that in solution

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[1] Kabesh and Nyholm, *J.*, 1951, 38.
[2] Nyholm, *J.*, 1952, 1257.

they undergo extensive dissociation, forming non-electrolytes, the most likely reaction being

$$4[Cu(AsMePh_2)_4][CuX_2] \longrightarrow 4[CuX,(AsMePh_2)_3] + [CuX,AsMePh_2]$$

The compound[3] of empirical formula $CuBr(C_{12}H_{25}{\cdot}NH_2)_2$ has a molecular weight in freezing benzene corresponding very closely to that required by the dimeric bridged structure (1028). In boiling hexane and boiling benzene the experimental figures are respectively 650 and 445. In cold benzene, and hence presumably in the solid state, the compound appears, therefore, to exist as a bridged dimer but in the hot solvents dissociation occurs. This was postulated to lead to the formulation of $[CuBr(C_{12}H_{25}{\cdot}NH_2)]_4$ and free amine. Formation of $[CuBr(C_{12}H_{25}{\cdot}NH_2)_3]$ is improbable since no compound of that composition has been prepared. The observed molecular weights in hot solvents would also be explained by dissociation of a bridged complex to form a salt, as mentioned above. These values would then indicate that the salt was completely dissociated for the purpose of boiling-point elevation. This is frequently true for complex salts in a variety of solvents.

To distinguish between the two modes of dissociation the conductance of the compound in benzene solution was measured. The criterion that the complex should be prepared under conditions less favourable for salt formation than those under which dissociation is studied was fulfilled since the complex was prepared in the *n*-hexane fraction, b. p. 68—72°, of light petroleum, free from unsaturated and aromatic hydrocarbons. The measurements were complicated since the complex is rapidly oxidised when dissolved in, or wet with, a solvent. Even traces of oxygen in commercial hydrogen and nitrogen, purified by passing through alkaline pyrogallol or over hot copper, caused decomposition. The most satisfactory atmosphere was hydrogen passed through platinised asbestos at 350° and dried finally by phosphoric oxide. This, however, caused slow reduction of the complex in solution, increasing the conductivity very considerably. A number of results at different concentrations obtained by standardising conditions of dissolution, using both gases, gave a smooth curve on plotting log c against log $\sigma/\sqrt{c}$, parallel with those obtained for other compounds (see Part I) and it is considered that these results are reliable.

The results given in the Experimental section (*b*) show that with an atmosphere of hydrogen the compound had the conductance of a non-electrolyte when prepared and dissolved with rigorous precautions against oxidation and heating above 20° at any stage after the initial preparation of the compound. At 20° the conductance rose slowly, and at 40° rapidly. Oxidation caused it to fall again.

In section (*c*) it is shown that, in an atmosphere of hydrogen or nitrogen, samples which had been prepared or dissolved at higher temperatures gave solutions of higher molar conductance, the values being easily reproducible and much too high for a non-electrolyte, although low for a salt. It is believed that in such solutions partial dissociation to a salt has occurred and the conductance continues to rise slowly.

Results in section (*d*) show that under hydrogen the rate of rise increases with time until after some days the conductance reaches a very high value. (Similar figures are found after keeping many halogen-containing complexes of copper or bivalent palladium and platinum with amines, phosphines, and arsines in sealed glass bulbs in benzene solution under hydrogen at about 40° for some time. In many cases traces of metal are produced after a few days, and the high conductance is obviously associated with reduction.) Under nitrogen the rise proceeds similarly for a few hours and then the rate of increase gets slower and eventually the conductance may begin to fall again. The deceleration of the change and later fall are accompanied by indications that oxidation is occurring. In view of the small quantities of complex present and the relatively large volume of gas contained in the apparatus, a very small oxygen content would permit oxidation of a large proportion of the compound.

These results suggest that the rise in conductance is associated with the formation of a compound which is more readily reduced by hydrogen and oxidised by gaseous oxygen than that originally present in the solution. This increased reactivity made it impossible to measure the conductance of the pure product.

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[3] Wilkins and Burkin, *J.*, 1950, 127.

It is concluded that the complex $[CuBr(C_{12}H_{25}{\cdot}NH_2)_2]$ exists in benzene solution as a halogen-bridged dimer but that it changes irreversibly to a compound giving many more ions in the solution, probably $[Cu(C_{12}H_{25}{\cdot}NH_2)_4][CuBr_2]$. No new evidence can be obtained in this way concerning whether or not dissociation to the tetrameric monoamine compound and free amine occurs in hot solutions before salt formation. Evidence as to the changes occurring in the system based on chemical reaction and isolation of solids is obviously unreliable because of the disturbing factors introduced. The compound $[CuBr,C_{12}H_{25}{\cdot}NH_2]_4$ is very difficult to obtain and work with in a reasonably pure state, but a few results indicate that in the presence of a little free amine the conductance is small. The analogous iodide is easier to handle but its conductance varies greatly with the amount of free amine added to aid solution, being small with about 0·3 mol. of amine present and increasing considerably with smaller amounts, decomposition and precipitation being evident after some time.

It is apparent that in the case of the complexes of an element such as univalent copper it is not possible to be certain of the species present in a solution of a pure compound. Change of solvent can cause a change in the structure of the substance, and even in hydrocarbons dissociation can occur. In the latter case the most frequent changes are from salt to non-electrolyte, but the reverse change is possible also.

EXPERIMENTAL

(*a*) Electrical conductivity was measured by the method described in Part I. The molar conductance Λ_M varies greatly with changing concentration and for comparison between different compounds the value $\sigma/\sqrt{c}$ at zero concentration (σ is specific conductance at concentration c) is used.

(*b*) $CuBr(C_{12}H_{25}{\cdot}NH_2)_2$ was prepared by the method described previously [3] except that the suspension was filtered through a sintered-glass disc, the funnel being connected to the flask in which the compound was prepared by means of a ground-glass joint. An atmosphere of hydrogen, which had been passed over platinised asbestos at 350°, through a trap at $-80°$, and over phosphoric oxide, was used and the solid was completely dried in the gas stream before being exposed to air. When prepared by dissolving the cuprous bromide in the solution of dodecylamine in light petroleum at 40° and cooling the solution rapidly to 20° as soom as all traces of solid had disappeared, the compound was white and when dry acquired a green tint in air only after several hours.

A $4{\cdot}4 \times 10^{-3}$M-solution of the white solid (based on M, 1028 for the dimeric structure), prepared by dissolving it at 20° in benzene, gave a practically colourless solution with Λ_M $1{\cdot}35 \times 10^{-6}$ at 20°. After 16 hr. at 20° Λ_M was $2{\cdot}88 \times 10^{-6}$ but after storage at 40° for 20 min. and cooling to 20°, it rose to $4{\cdot}64 \times 10^{-6}$. The solution was now pale green. A little dry air was mixed with the hydrogen stream bubbling through the solution and within a few minutes the conductance began to fall. After an hour the solution was pale brown; it darkened slowly, and Λ_M reached $1{\cdot}27 \times 10^{-6}$ at 15° and $1{\cdot}69 \times 10^{-6}$ at 42° after about 4 hr.

(*c*) Most attempts to prepare the complex resulted in products with a pronounced green tint, giving pale green benzene solutions. Five such solutions with c between 15×10^{-4} and 4×10^{-3}M gave values of Λ_M of between about 3×10^{-6} and 6×10^{-6}. The log $\sigma/\sqrt{c}$ against log c curve was parallel with that for *cis*-$Pt(Et_3P)_2Cl_2$ (see Part I) and gave a value of $\sigma/\sqrt{c}$ at $c = 0$ of $10{\cdot}0 \times 10^{-12}$ at 20°.

(*d*) A dilute solution with $c = 10^{-3}$ was stirred with hydrogen under about 2 atm. pressure at 35°. The conductance increased slowly as shown. Zero time was about 30 min. after dissolution.

Time (hr.)	0	0·17	0·33	1·25	1·75	2·25	3·0	17·5	22
$10^6\Lambda_M$	5·5	5·8	6·3	7·6	7·9	8·6	12·2	90·5	123

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