Ionisation Equilibria of Metal Co-ordination Complexes in Benzene Solution. Part I.

By A. R. Burkin.

[Reprint Order No. 4528.]

A method is described for studying the extent to which an acid radical dissociates from a non-ionic complex of the type MA_2X_2 in benzene solution. The electrical conductivity is measured and interpreted in terms of an equilibrium constant for the dissociation of the ion-pairs and another for the breaking of the metal–acid radical bond. The so-called non-ionic compounds studied show the same sort of variation of equivalent conductance with concentration as do complex salts in benzene solution and tetra-alkylammonium salts in dioxan–nitrobenzene solutions of constant dielectric constant. The concentration of free ions is small and this is largely due to the very slight dissociation of the ion-pairs rather than to very small equilibrium constants for the breaking of the metal–acid radical bond. The stronger the acid from which the acid radical is derived, the greater is the degree of ionisation. Trialkyl-phosphines and -arsines seem to weaken the metal–chlorine bonds in the *cis*-positions when compared with the effect of *n*-octylamine. Results are reported for cupric, palladous, and a few platinous complexes. The crystals of a few complexes of octadecylamine and dodecylamine with cupric salts appear to be electrically anisotropic and positively charged on crystallisation from benzene.

The physicochemical aspects of complex formation, and in particular the equilibrium constants for the successive addition of ligand molecules to the metal ion, have been extensively studied in recent years. Some of the types of equilibria which have been investigated are shown as (I) and (II), where the ion of the metal M has charge $x+$, A is a monodentate non-ionic ligand, X a univalent negatively charged ligand, and N is the maximum co-ordination number of the metal under the experimental conditions employed.

$$\text{(I)} \qquad M^{x+} + A \rightleftharpoons [MA]^{x+}$$
$$[MA]^{x+} + A \rightleftharpoons [MA_2]^{x+}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$[MA_{(N-1)}]^{x+} + A \rightleftharpoons [MA_N]^{x+}$$
$$\text{(II)} \qquad M^{x+} + X^- \rightleftharpoons [MX]^{(x-1)+}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$[MX_{(N-1)}]^{(x-N+1)} + X^- \rightleftharpoons [MX_N]^{(x-N)+}$$

Such data give information about the free-energy changes occurring when groups A or X^- replace water molecules bound to the hydrated metal ion, and are interpreted in terms of a number of factors which are assumed to control the stabilities of the complexes formed (cf. *Quart. Reviews*, 1951, **5**, 1). Some of the experimental conditions required for determining the equilibrium constants are (i) that all reactants in the equilibrium mixture are water-soluble, (ii) that no groups other than water are bound to the metal ion, and on addition of A or X^- water molecules are replaced successively, (iii) that the reversible equilibrium is established rapidly. Other practical requirements are less important for this discussion.

It is difficult or impossible to study by these conventional means metal ions such as Co^{3+}, Pt^{2+}, Pt^{4+}, etc., which form very stable complexes with most ligands and do not give simple hydrated ions, although in a few cases hydrolysis constants can be measured by using a suitable catalyst (Bjerrum and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265). In addition, complexes of the type $[MA_2X_2]$ (when $x = 2$) and the very many interesting classes of compounds which are not water-soluble cannot be investigated. The present work was designed to investigate some of the problems connected with the non-ionic mixed complexes.

Since the reversibility of reactions of class (II) has been proved, it seemed very likely that equilibria of type (III) should exist. In many solvents solvation will occur and may

$$\text{(III)} \qquad [MA_2X_2] \rightleftharpoons [MXA_2]^+ + X^-$$

lead to irreversible decomposition. This seems to be the case in many, if not all, liquids of high dielectric constant. By using a hydrocarbon as solvent it is possible to avoid these difficulties, although others arise, and considerations of solubility led to the choice of benzene. It is very unlikely that in benzene solution the complex ion would lose its remaining X^- group, since this would have to be removed from an oppositely charged ion. Hence for practical purposes the equilibrium may be regarded as the dissociation of a weak uni-univalent electrolyte. There is no evidence to suggest that uncharged acid radical groups can dissociate from any of the complexes considered here.

In the present work the ionisation equilibria of complexes of the type $[MA_2X_2]$, where M is Cu^{2+}, Pt^{2+}, Pd^{2+}, and of a few cuprous complexes have been studied by means of their electrical conductivities in benzene solution. The factors influencing the ionisation are considered to be: (i) the properties of the metal ion in the valency state studied, (ii) the properties of the acid radical X^-, in particular the strength of the parent acid HX, (iii) the co-ordinating power of the ligand A, considered in terms of the type of bond formed between it and the metal, and (iv) the geometrical arrangement of the groups around the metal atom. The last of these factors will be considered in Part II.

Interpretation of Conductivity Data.—None of the theoretical methods used for interpreting the conductivity data for weak electrolytes in aqueous solution is applicable to non-aqueous solvents of low dielectric constant. A considerable amount of work has been carried out with strong electrolytes, particularly the tetra-alkylammonium salts, in such solvents, and this has been summarised by Harned and Owen ("Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 2nd edn., 1950). The theoretical treatments used to interpret these data are based on N. Bjerrum's "ion-pair" theory but this is not applicable to solutes for which the incipient ions are bound by covalent bonds rather than electrostatic attraction. No method seemed suitable for interpreting the data to be obtained in the present work, so a technique was evolved which would permit the calculation of relative values of the ionisation constants in terms of the ionisation of a metal complex known to behave as a salt. The method involves a number of assumptions and approximations which are mentioned in this outline. The underlying equation (1) (below) which was obtained has recently been published by Rutgers and De Smet (*Trans. Faraday Soc.*, 1952, **48**, 635), who also give a derivation, and their terminology is used to prevent confusion.

It is found experimentally that all compounds which chemical experience suggests are salts, when dissolved in any solvent of low dielectric constant, behave as though very few ions were present. Theoretical considerations suggest the formation of pairs of oppositely charged ions bound by electrostatic forces, as occurs to some extent in aqueous solutions. Because of its low dielectric constant, however, the solvent has little power to break up such ion-pairs and the compound does not behave as one would expect a completely ionised salt to behave when, for example, an electric field is applied. In dilute solution there will be a certain amount of association of these ion-pairs, giving first $(AB)_n$ and at slightly higher concentrations $(AB)_m$. Let the two association constants be K_{an} and K_{am} where $K_{an} = [(AB)_n]/[(AB)]^n$, and similarly for K_{am}. Each species of associated ions can dissociate to give two ions, any further stages, involving the removal of an ion from an existing ion, being most unlikely in benzene solution. There will then be three ionic dissociation constants, K_{d1}, K_{dn}, and K_{dm} relating to the ionisation of (AB), $(AB)_n$, and $(AB)_m$, respectively. This treatment is equivalent to saying that most of the solute exists as ion-pairs, but the few ions which are present as a result of the dissociation of these pairs do not exist as simple or solvated ions but have associated with them one or more ion pairs leading to " triple ions " such as $(A^+B^-A^+)^+$ and higher aggregates.

Let the equivalent conductance (Λ_1) of the ion pairs be defined as the equivalent conductance at infinite dilution (Λ_∞) and equal to the sum of the mobilities of the resultant ions; also Λ_n is Λ_∞ for $(AB)_n$ and similarly for Λ_m. Let σ be the specific conductance of the solution of concentration c. Then

$$\sigma/\sqrt{c} = \Lambda_1 K_{d1}{}^{\frac{1}{2}} + \Lambda_n (K_{dn}K_{an})^{\frac{1}{2}} c^{(n-1)/2} + \Lambda_m (K_{dm}K_{am})^{\frac{1}{2}} c^{(m-1)/2} \quad . \quad . \quad . \quad . \quad (1)$$

In obtaining this equation all long-range forces are ignored, and it is assumed that the solution has low conductance (dissociation is slight) and that solutions of different concentrations have the same dielectric constant. In the cases of salts and compounds having appreciable dipole moments, therefore, only very dilute solutions and a limited concentration range should be considered unless the dielectric constants of the solutions are adjusted by adding a second solvent as was done by Rutgers and De Smet. This was not practicable in the present work because of the probability of contamination and the difficulty of finding a suitable inert solvent of sufficiently high dielectric constant, and in any case it proved to be unnecessary.

Plotting $\sigma/\sqrt{c}$ against c and extrapolating to $c = 0$ gives $\Lambda_1 K_{d1}{}^{\frac{1}{2}}$. Fortunately, at sufficiently low concentrations the plot is linear in all cases studied in detail. It is impossible to obtain a value for Λ_1 because of the very low conductivities and the theoretical difficulties due to association, so that K_{d1} cannot be obtained. If, however, it is assumed that Λ_1 is constant for all compounds of similar type, it is possible to obtain relative values of K_{d1} for such compounds. By comparing data with the figures for an analogous substance known to be a salt, the relative degrees of ionisation of other complexes can be estimated. In the case of the salt the value of K_{d1} refers to the dissociation of the ion-pairs bound together by purely electrostatic attraction. The values for the so-called non-ionic complexes are the products of the constant for the ion-pair dissociation and the constant due to the breaking of the metal–acid radical bond. The former appears to be fairly constant for similar compounds (Harned and Owen, *op. cit.*, p. 203), so the estimates will give a fair representation of the relative values of the M–X dissociation constants. It is obvious that great care must be taken in interpreting the figures and, in particular, small differences must be ignored. The results are of considerable interest, however, and a number of conclusions can be drawn with fair certainty.

By using a salt, the method described above may be compared with other methods of interpreting conductivity data in benzene solution. The salt used had to be obtainable in a pure state and stable in 10^{-3}—10^{-4}M-solutions in benzene for several hours over a reasonable temperature range. The substance chosen was tetrakis(methyldiphenylarsine)copper(I) perchlorate $[Cu(AsPh_2Me)_4](ClO_4)$ (Nyholm, *J.*, 1952, 1257), which could also be used as a basis for comparison between other compounds.

A narrow concentration range of 10^{-3}—10^{-4}M minimised dielectric-constant variation of the solution, and plotting $\sigma/\sqrt{c}$ against c at four temperatures gave a set of straight lines (Fig. 1). Thus from (I), $(n - 1)/2 = 1$ and $n = 3$. Extrapolation to zero concentration gave values for $\Lambda_1 K_{d1}^{\frac{1}{2}}$ which showed linear dependence on temperature, as below :

FIG. 1. *Straight-line portion of the* $\sigma/\sqrt{c}$ *against* c *curve for* $[Cu(AsPh_2Me)_4](ClO_4)$ *at several temperatures.*

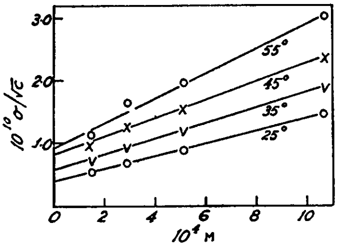


FIG. 3. *Variation of molar conductivity with concentration of cis-*$[Pt(PEt_3)_2Cl_2]$. *Inset shows straight-line portions of the* $\sigma/\sqrt{c}$ *against* c *curves at the same temperatures.*

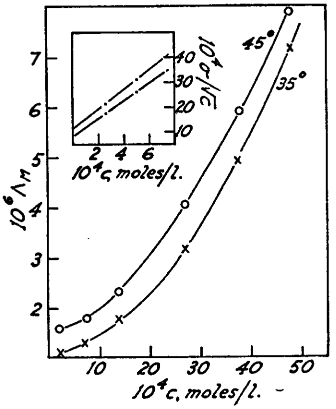


FIG. 2. *Minima in molar conductance–concentration curves at several temperatures, for* $[Cu(AsPh_2Me)_4](ClO_4)$: *plotted logarithmically.*

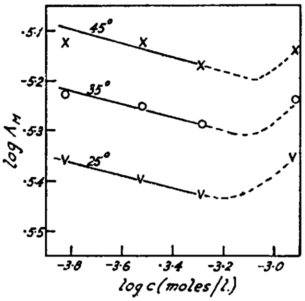
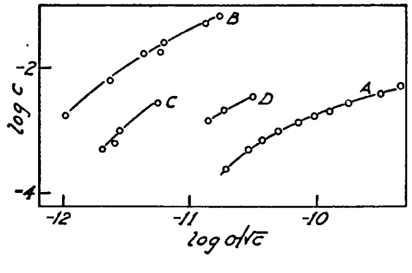


FIG. 4. log $\sigma/\sqrt{c}$ *against* log c *curves showing similarity in slope for :*

(A) *cis*-$[Pt(PEt_3)_2Cl_2]$.
(B) $[Cu(C_{12}H_{25}\cdot NH_2)_2(CH_3\cdot CO_2)_2]$.
(C) $[Cu(C_{12}H_{25}\cdot NH_2)_2(CH_2Cl\cdot CO_2)_2]$.
(D) $[Pd(PBu_3)_2Cl_2]$.



Temp.	25°	35°	45°	55°
$10^{10}\Lambda_1 K_{d1}^{\frac{1}{2}}$	0·39	0·58	0·80	0·94

Plotting log molar conductance against log concentration gave a curve exhibiting a minimum as is usual for salts in solvents of low dielectric constant (Fig. 2). From the values of Λ_m and c at the minimum, a value of $\Lambda_1 K_{d1}^{\frac{1}{2}}$ can be obtained by using the approximate expression $\sqrt{K_{d1}} = (c\Lambda_m)_{\text{min.}}/2\Lambda_1$ (Harned and Owen, *op. cit.*, p. 196). The widest possible variation in the position of the minimum being taken into account, the value of $-\log K_{d1}(\Lambda_1)^2$ obtained is 17·6 ± 0·2 at 35°, which may be compared with the values obtained by Fuoss and Krauss (cf. Harned and Owen, *op. cit.*, p. 203) by this method for some alkylammonium salts in benzene and which gave $-\log K_{d1}(\Lambda_1)^2 = 13{\cdot}05$—16·6. It seems obvious from the similarity that the complex perchlorate is behaving as a salt. The value obtained by extrapolating the $\sigma/\sqrt{c}$ against c curve is 20·6 at 35°. Thus the two methods give considerably different results, which is not surprising in view of the approximations involved in each case, but the discrepancy is not so great as to invalidate the use of the newer method for comparative purposes.

In order to test as fully as possible the applicability of equation (I) it was necessary to use a " non-ionic " complex as well as the salt. The ready reproducibility of results for *cis*-triethylphosphineplatinous chloride $[Pt(PEt_3)_2Cl_2]$, and the great stability of its solutions made this the most suitable compound for this purpose of all those tested. Plotting $\sigma/\sqrt{c}$ against c at several temperatures gave a set of straight lines for values of c up to about 8×10^{-4}M (Fig. 3, inset), so $n = 3$ as for the perchlorate. The difference between the experimental curve and the extension of the straight line to higher values of c (up to 4×10^{-3}M) was measured ($\Delta\{\sigma/\sqrt{c}\}$) at several values of c, and on plotting log $\Delta\{\sigma/\sqrt{c}\}$ against log c a straight line was obtained of slope 2·55, or approximately 5/2. Hence $(m-1)/2 = 5/2$ and $m = 6$, as was found by Rutgers and De Smet for tetra*iso*pentammonium picrate in dioxan–nitrobenzene solution. Use of equation (1) together with the values for n and m for the experimental results at $c = 17{\cdot}5 \times 10^{-4}$M shows that the curve can be represented by $\sigma/\sqrt{c} = (0{\cdot}092 + 392c + 1{,}686{,}000c^{5/2}) \times 10^{-10}$. Values calculated by using this equation are compared below with experimental values.

10^4c	2·50	10·0	27·0	38·4
$10^{10}\sigma/\sqrt{c}$, calc.	0·192	0·537	1·79	3·14
$10^{10}\sigma/\sqrt{c}$, exp.	0·193	0·503	1·79	3·29

The remarkable similarity between the behaviour of the salt and the " non-ionic " complex in benzene and that of the alkylammonium salt in dioxan–nitrobenzene solution indicates that the association and ionisation processes are similar in each case and that over a narrow concentration range the dipole moment of the complex does not seriously affect the conductivity by changing the dielectric constant of the solution.

The value of n gives the composition of the aggregate which, together with the simple ion-pair, is the major species ionising over a particular concentration range. This ionisation may be represented as

$$(AB)_n \rightleftharpoons \{(AB)_wA\}^+ + \{(AB)_yB\}^-$$

where $w + y = (n - 1)$. If $n = 3$, as is found experimentally, we have $w = 2, y = 0$, or $w = 0, y = 2$, or $w = y = 1$. The first two cases would imply that one ion is not associated with solute, and this is much less likely than the state represented by the last case where " triple ions " are formed. The similarity in behaviour between the salts and *cis*-triethylphosphineplatinous chloride suggests that the molecules of the latter complex behave in this respect as ion-pairs, which is not unreasonable in view of the polarity of the Pt–Cl link.

The situation regarding the ionisation of $(AB)_m$ is not so simple. The only value of $(m - 1)/2$ obtained in the present work was 2·55, and Rutgers and De Smet's figures are considerably further from 2·50, which is required to give $m = 6$. Writing

$$(AB)_m \rightleftharpoons \{(AB)_pA\}^+ + \{(AB)_qB\}^-$$

we cannot assume that $p = q$, and although it is tempting to put $p = q = 2$ and identify the ions as those formed with tetrapoles, with a little further association of some sort to raise m from 5 to 6, the evidence is inadequate.

The procedure outlined above could not be used to obtain $\Lambda_1 K_{d1}{}^{\frac{1}{2}}$ for all compounds. In some cases the straight-line portions of the $\sigma/\sqrt{c}$ against c curves could not be studied since sufficiently low concentrations could not be used either because the conductivities were so small or because decomposition was too rapid. It was necessary in such cases to use the lowest practicable concentrations and to correct the conductivity figures for the concentration in order to obtain data for comparison. It was found that the shapes of the curves for all compounds with conductivities of similar magnitude were alike (Fig. 4), so it was possible to obtain approximate values of $\sigma/\sqrt{c}$ at $c = 0$ for these difficult compounds by comparison with curves for others. Although open to many objections, this method of extrapolation seems the only one possible in the circumstances.

If the theoretical basis of the method given above for interpreting the conductivity data were found to be incorrect, the treatment may still be regarded as convenient for correcting the values of Λ_M obtained experimentally for concentration differences in order to get conductivity values suitable for comparison. The variation of Λ_M with concentration for *cis*-triethylphosphineplatinous chloride is shown in Fig. 3, and the inset shows the advantage of using the straight line obtained on plotting $\sigma/\sqrt{c}$ against c.

DISCUSSION OF RESULTS

A number of salts were studied in addition to tetrakis(methyldiphenylarsine)copper(I) perchlorate, but in less detail. The nitrate of the same cation gave unstable solutions, different samples giving widely differing conductivity values, and the results are not reported. Di-(*o*-phenylenebisdimethylarsine)copper(I) bromide, [Cu(diars)$_2$]Br, gave results very similar to those obtained with the complex perchlorate, as did di-(*o*-phenylenebisdimethylarsine)copper(I) cuprobromide [Cu(diars)$_2$][CuBr$_2$] (see following Table). The conductivities of these compounds increased far more rapidly with rising temperature than did that of the perchlorate (Fig. 5). This shows the importance of studying the effect of temperature variation before comparing the conductivities of different compounds. In all other cases studied this effect is small. The low conductivities found for a number of other copper(I)–arsine compounds which do not behave chemically as salts show that the relatively high conductivities for the compounds mentioned above are not to be ascribed to the presence of univalent copper or arsine rather than to the fact that the compounds are salts. These results will be published in a later paper.

Compound *	Concn. × 10^4, M	Temp.	$10^6\Lambda_M$	$10^{12}\sigma/\sqrt{c}$ at $c = 0$
$[Cu(Ph_2AsMe)_4]ClO_4$	1·50	35°	5·91	58
	5·15	35	5·15	—
$[Cu(diars)_2]Br$	10·09	35	8·34	55
$[Cu(diars)_2][CuBr_2]$	8·33	33	10·61	63
$[(C_{12}H_{25}\cdot NH_2)_2CuCl_2]$	8·67	40	0·52	4·0
$[(C_{18}H_{37}\cdot NH_2)_2CuCl_2]$	40·5	60	1·20	4·2
$[(C_{12}H_{25}\cdot NH_2)_2Cu(OAc)_2]$	166·0	34	0·033	0·26
$[(C_{18}H_{37}\cdot NH_2)_2Cu(OAc)_2]$	150·0	41	0·026	0·22
$[(C_{12}H_{25}\cdot NH_2)_2Cu(\text{Me succ.})_2]$	85·4	35	0·051	0·48
$[(C_{18}H_{37}\cdot NH_2)_2Cu(\text{Me succ.})_2]$	113·0	35	0·089	0·48
$[(C_{12}H_{25}\cdot NH_2)_2Cu(CH_2Cl\cdot CO_2)_2]$	29·0	35	0·102	0·83
$[(C_{18}H_{37}\cdot NH_2)_2Cu(CH_2Cl\cdot CO_2)_2]$	33·2	35	0·112	0·85
$[(C_{12}H_{25}\cdot NH_2)_2Cu(CHCl_2\cdot CO_2)_2]$	15·7	35	0·48	3·2
$[(C_{18}H_{37}\cdot NH_2)_2Cu(CHCl_2\cdot CO_2)_2]$	12·4	35	0·98	6·2
$[(C_{12}H_{25}\cdot NH_2)_2Cu(CCl_3\cdot CO_2)_2]$	22·4	59	1·97	7·6
$[(C_{18}H_{37}\cdot NH_2)_2Cu(CCl_3\cdot CO_2)_2]$	35·9	57	1·56	4·9
$[(PBu_3)_2PdCl_2]$	33·3	36	0·64	2·6
$[(PBu_3)_2PdBr_2]$	4·23	26	0·33	2·8
$[(PBu_3)_2PdI_2]$	16·4	35	0·18	1·4
$[(PBu_3)_2Pd(NO_2)_2]$	6·05	35	0·20	1·5
$[(PBu_3)_2Pd(SCN)_2]$	4·40	35	0·22	1·7
$[(PBu_3)PdCl_2]_2$	44·0	28	0·096	0·58
$[(C_8H_{17}\cdot NH_2)_2PdCl_2]$	22·5	34	0·019	0·17

* Me succ. = $CO_2Me\cdot CH_2\cdot CH_2\cdot CO_2$ (see p. 77).

Acid Strength.—For complexes which are not salts, the dissociation constants for ionisation equilibria of type (III) will obviously depend on the properties of the acid radicals. The strength of an acid is a measure of the tendency of the acid radical to attach itself to a hydrogen ion in aqueous solution. The conductivity of a complex containing that acid radical, in benzene solution, is a measure of the tendency of the acid radical to attach itself to the metal ion in a particular electronic state. The complexes of a series of acids which have different K_a values being considered, it will be expected that the conductivity will increase with increasing strength of the acid. The situation is similar to that found in the study of the relation between the stability constants (in aqueous solution) of complexes of bases with metals and K_b for the bases (Bjerrum, *Chem. Reviews*, 1950, **46**, 381), and in studying the constants for complexes of diketones and hydroxy-aldehydes in terms of the K_{H^+} values (Calvin and Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003). A general relationship will not exist for all acids since if the radicals bound to the metal have very different electronic structures the bond type may be different in each case. This factor will, in most cases, far outweigh the effect of acid strength.

The complexes of long-chain primary *n*-aliphatic amines with cupric salts of aliphatic acids are soluble in benzene and in most cases give stable solutions. The strengths of the acids may be changed by substitution in the α-position, while the acid radical is in every case attached to the metal by the $CO{\cdot}O^-$ group. Results were obtained by using acetic, and mono-, di-, and tri-chloroacetic acid and methyl hydrogen succinate. The last was studied because the conductivities of the acetate complexes seemed extremely low. The acid dissociation constant for the acid was not determined but will presumably be similar to that for acetic acid.

The K_a values ($\times 10^5$) for acetic and mono-, di-, and tri-chloroacetic acid are 1·75, 140, 5000, and 20,000 respectively, and the conductivity values for the complexes involving these acids rise in the same order. In practice, great difficulty was experienced in obtaining the copper salts of di- and tri-chloroacetic acid without causing hydrolysis and, apparently, partial removal of chlorine. Complexes prepared from different samples of both salts gave different conductivities, and the results quoted are based on six samples of each compound. Although little reliance can be put on these figures, the qualitative relation between conductivity and acid strength seems established.

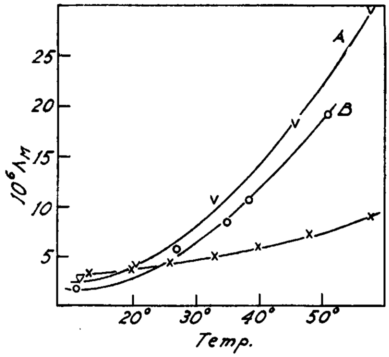


FIG. 5. *Variation of molar conductance with temperature for:*

(A) $[Cu(diars)_2][CuBr_2]$.
(B) $[Cu(diars)_2]Br$.
(C) $[Cu(AsPh_2Me)_4](ClO_4)$.

Since cupric iodide complexes with long-chain amines do not exist, and the cupric bromide compounds are ill defined (Burkin, *J.*, 1950, 122), it was not possible to study the halide complexes by using these copper compounds. By using the tri-(*n*-butylphosphine) complexes of palladous salts, however, the halides could be investigated and the results compared with those for compounds containing other acid radicals often used in complexes such as the thiocyanato- and the nitro-group. All of these well-known compounds are stable in benzene solution. The $\sigma/\sqrt{c}$ value at zero concentration for $[Pd(PBu_3)_2I_2]$ is appreciably smaller than the values for the chloride and bromide, which are similar. The nitro- and thiocyanato-complexes also have small conductivities, as expected in view of the covalent character of the bonds which these groups form with metals such as platinum and palladium.

The importance of the structure of the molecule as a whole rather than the nature of a particular pair of atoms is shown by the small conductivity of the bridged compound $[Pd(PBu_3)Cl_2]_2$. This value is calculated on the binuclear formula weight, so that two chlorine atoms are available for ionisation in addition to the two assumed to be bridging the metal atoms and which, presumably, will not be readily lost by ionisation.

Nature of the Ligand.—The evidence concerning the effects of different ligands on the ionisation of the acid radicals is inconclusive. Of the amines, dodecylamine and octadecylamine were used mainly, and the change in size seems to make little difference. This is borne out by a few preliminary, unreported measurements with *n*-octylamine complexes. The basic strengths of the amines are similar and no indication of the influence of this factor can be expected.

In the palladous series the bridged compound $[Pd(PBu_3)Cl_2]_2$ has a much lower conductivity than $[Pd(PBu_3)_2Cl_2]$, and the *n*-octylamine complex $[Pd(C_8H_{17}\cdot NH_2)_2Cl_2]$ has a much smaller conductivity still. All of these compounds have, presumably, a *trans*-configuration, and comparison with the results for *trans*-platinous complexes with trialkylphosphines and -arsines to be reported in Part II suggests that the phosphines and arsines behave similarly in weakening the metal–chlorine bonds in the *cis*-positions to some extent, compared with the effect of octylamine. Further evidence is, however, needed on this point.

Effect of the Metal.—On comparing chloride complexes of the three metals investigated, *viz.*, bivalent copper, platinum, and palladium, it appears that the copper–chlorine link is more ionic than the palladium–chlorine bond and that this is more ionic than that present in the *trans*-platinous complexes but is similar in this respect to that in the *cis*-platinous compounds (see Part II). In general, however, it is apparent that the other factors discussed above can very greatly modify the properties of the bonds formed by a metal in its complex compounds, and hence the properties of all the compounds of the metal involving largely covalent bonds.

General Conclusions.—The close correlation between the results given above and the general chemical characteristics of the compounds suggests that in many types of reaction the ionic character of the metal–acid radical link is of primary importance, although this is not always so. With a bridged complex in the presence of a suitable ligand, for instance, the instability of the complex is due to the splitting of the bridge and subsequent formation of two stable molecules.

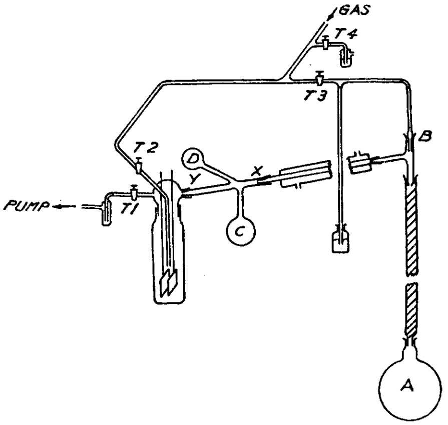
The absolute values of $\Lambda_1 K_{d1}^{\frac{1}{2}}$ demonstrate an important point in connection with the general chemical properties of complexes of the type discussed here. For the salts studied, $\Lambda_1 K_{d1}^{\frac{1}{2}}$ was found to be about 60×10^{-12}. Although it is not possible to measure Λ_1, its value may be taken as about 100, so that K_{d1} is of the order of $3{\cdot}6 \times 10^{-25}$. This is the equilibrium constant for the ionisation of an ion-pair bound together only by electrostatic forces. For the compounds which are not salts, $\Lambda_1 K_{d1}^{\frac{1}{2}}$ ranges from about 4×10^{-12} to $0{\cdot}1 \times 10^{-12}$ and taking Λ_1 as 100 again gives K_{d1} as $1{\cdot}6 \times 10^{-27}$ to 1×10^{-30}. The latter values are assumed to be products of the equilibrium constants for the ionisation of the acid radical caused by the breaking of the metal–acid radical link, and the constant for the ionisation of the ion-pair, which will have about the same value as in the case of the salts. The constant for the dissociation of the complex molecle is therefore of the order of 10^{-2} to 10^{-5} and it is obvious that the very great apparent stability shown by complexes in solvents of low dielectric constant is due to the stability of the ion-pairs. If, for example, ligand A is added to a solution of the complex $[MA_2X_2]$ it would be expected that in many cases the compounds $[MA_3X]X$ and $[MA_4]X_2$ would be produced. This is the case in aqueous solution, and often in solvents such as the lower alcohols. In a solvent such as benzene, however, the effective activity of the acid radical is enormously increased because of the very small value of K for the splitting of the ion-pair, whereas neutral ligand molecules produced by the reversible dissociation of the ions $[MA_3X]^+$ and $[MA_4]^{++}$ can readily escape from the vicinity of the resulting ion. For this reason ionic complexes can very rarely be produced by reaction in solvents of low dielectric constant.

Formation of Charged Crystals.—During measurements on complexes of the long-chain amines with cupric acetate and cupric methyl succinate a noteworthy phenomenon was observed. With suitable concentrations the complexes crystallise as long needles on cooling, and with a potential of about 100 v across the electrodes of the conductivity cell the crystals were held between the plates and did not fall until the electrical circuit was broken. The needles were attracted to the cathode and oriented themselves along the lines of force, but even when the space between the electrodes contained a considerable amount of solid there was a clear space around the anode. Thus the crystals appear to be positively charged and electrically anisotropic. This phenomenon may be connected with the fact that on very slow cooling, the conductivity of the solution was found to increase just before crystals appeared and did not fall to its former value until a considerable amount of solid had separated. This was observed only with the compounds mentioned which all have long carbon chains and are unique among the long-chain amine complexes of cupric salts in forming well-defined crystals instead of the more usual powders. It appears almost as though ionic micelles were produced.

EXPERIMENTAL

Measurement of Conductivity.—In order to avoid contamination of the benzene by traces of water the apparatus shown in Fig. 6 was devised. Benzene, previously purified by careful fractionation of the commercial " AnalaR " product, was kept over metallic sodium in flask *A* and was distilled slowly up a Dufton column with a 12-inch spiral, condensed, and run into the measuring assembly. This consisted of two flasks *C* and *D* of about 50 and 25 c.c. capacity sealed at right angles to one another by tubes about 7 cm. long to another tube perpendicular to both of these. The neck of each flask was marked at the bottom and either one was filled to above the mark with benzene which was at the temperature of the condenser water. The height of the benzene level above the mark was measured, and the assembly rotated about the joints *X* and *Y* so that the liquid ran into the conductivity cell. The flasks were calibrated for delivery. The ground-glass joints were all re-ground to ensure perfect fit after the components were blown. No grease was used since benzene readily dissolved this, but strips of plasticine were sealed around the outside of each joint, and when the apparatus was evacuated leakage was negligible.

FIG. 6.



The approximately 3-cm. square electrodes of the conductivity cell were of heavy platinum sheet to prevent buckling in use and were separated top and bottom by glass spacers sealed to glass protecting rods extending around the faces. These rods were sealed to two thick-walled tubes which carried the electrode leads and suspended the assembly from a B40 glass cone which carried the gas outlet tube and tap, gas inlet tube which extended to the bottom of the electrodes, and the joint fitting to the measuring assembly. The cell tube fitted on to the cone and the electrodes reached almost to the bottom. About 56 c.c. of liquid were required to cover the electrodes. These had been coated with platinum black by electrolysis of pure chloroplatinic acid solution in hydrochloric acid, washed well, and flamed in an oxy-hydrogen flame to give a dull coating of " white platinum."

The experimental procedure was as follows. The distillation unit, electrodes, and cell tube were dismantled and baked at 150° in an electric oven. The benzene, over sodium, in flask *A* was boiled, and the first few drops of distillate watched carefully. If these were cloudy the benzene had to be dried before use. This test was only necessary when several days had elapsed since the previous determination, or when a fresh batch of benzene was used. The cell tube was removed from the oven, the bottom 2 inches cooled by immersion in water, and a known weight of complex introduced by using a weighing tube attached to a rod to avoid touching the sides. The tube was clamped in position, and the rest of the apparatus assembled, whilst hot, as quickly as possible. The gas inlet and outlet lines, which were kept permanently in place, were connected with rubber tubing so that glass touched glass, and taps *T*1 and *T*4 were opened. A mercury trap was used between the water-pump and *T*1 to minimise back diffusion of damp air. When the benzene, at room temperature, began to boil and the pressure in the apparatus reached a steady minimum, the valve of the gas cylinder was opened and the rate of flow adjusted, the mercury trap at *T*4 being used as indicator. After a few moments *T*1 and then *T*4 were closed and *T*3 opened, admitting gas into the apparatus at *B*, atmospheric pressure being attained in 3—4 min. The rate of gas flow was then reduced until one bubble escaped from the bottom of the manometer every 10 seconds, and *T*4 was opened as safety valve. Tap *T*3 was closed, *T*1 opened, and the benzene distilled slowly into the larger flask *C*. Just before the heating was stopped, *T*1 and *T*4 were closed and *T*3 and *T*2 opened so that the apparatus filled with gas on cooling. The measured volume of benzene was introduced into the cell, and the complex was dissolved, by careful warming if necessary. The solution could be stirred by using the gas stream obtained by closing *T*3. An oil-filled thermostat was raised around the cell tube and controlled the temperature to $\pm 0{\cdot}05°$. The gas used to fill the apparatus was usually nitrogen dried by passing through a trap at $-80°$ and then through two phosphoric oxide tubes.

The current passed by the cell when connected to an H.T. battery was measured by use of a Tinsley galvanometer of sensitivity 1960 mm./microamp. The simple d.c. method of measuring conductivity is satisfactory as long as the cell resistance is greater than 10^5 ohms. In this work it was of the order of 10^{10} ohms, usually more. All wires were covered by narrow Polythene tubing and suspended freely as far as possible. The battery and galvanometer stood on Polythene strips on a Polythene sheet. In order to avoid glavanometer zero changes, the circuit was made by connecting a lead from the cell to the galvanometer, none of the other wiring being touched. The potential was measured by a voltmeter when the cell circuit was open. The current was measured at approximately 24, 48, 72, 96, and 120 v and the results plotted to ensure that Ohm's law was obeyed.

The effect of moisture on the conductivity was investigated in the cases of tetrakis(methyldiphenylarsine)copper(I) perchlorate, bisdodecylaminecopper(II) chloride, and *cis*-triethylphosphineplatinous chloride by passing air saturated with water vapour through a solution of known conductivity for about an hour. The conductivity rose slowly by about 5%, and subsequent addition of a drop of water caused little or no further change.

In some cases heating the solutions caused partial decomposition so that on cooling the conductivity remained above its previous value at that temperature. By working quickly it was usually possible to obtain accurate figures up to about 45°, the rate of decomposition being slow below this. When it was necessary to work above that temperature separate solutions were used for each temperature, the benzene being warmed in the measuring flask before being tipped into the cell containing the compound.

Cupric chloride complexes with amines decomposed on warming in this way and the rate of decomposition was increased in the presence of the electric field, the effect being most noticeable at higher concentrations. Ohm's law was obeyed below about 72 v, but above this the current passing was too high and on reduction of the voltage it remained above the previous values until the cell was shaken vigorously to disturb the solution between the electrodes. After some hours at the higher temperatures it was possible to detect traces of the salt $(R{\cdot}NH_3)_2CuCl_4$, but addition of this salt to a fresh solution of the complex did not cause any appreciable rise in conductivity and neither did small quantities of dry amine hydrochloride. It seems likely that the increase in conductivity is due, not to the almost completely insoluble end-product, but to an intermediate of the reaction, probably hydrogen chloride. This is suggested by the fact that in the presence of excess of amine the rise in conductivity is small. The great effect of the formation of hydrogen chloride during decomposition is shown by the fact that a 10^{-3}M-solution of bistributylphosphinepalladous chloride in benzene, after being sealed in a glass tube in an atmosphere of air and stored for 2 weeks at 45°, had about the same conductivity as the fresh solution, while a sample stored similarly in an atmosphere of hydrogen contained hydrogen chloride above the liquid and had a conductivity so large that it could not be measured in this apparatus.

A few of the tributylphosphinepalladous complexes such as the thiocyanato- and the nitro-compound exhibited the reverse phenomenon, and in very dilute solutions (*ca.* 10^{-4}M) the conductivity slowly fell and after several days became almost zero. This phenomenon was not explained, and the values given are those obtained within a few hours of making up the solution. They are reproducible and gave a smooth curve when log c was plotted against log $\sigma/\sqrt{c}$.

In order to demonstrate the effects of possible sources of error in measuring the conductance, the following experiments may be mentioned. When benzene alone was used, no galvanometer deflection was detectable after the initial kick on connecting the circuit. About 0·1 g. of tri-*n*-butylphosphine, distilled into a thin-walled glass tube, sealed and broken in the conductivity cell, gave a benzene solution of negligible conductivity. Dodecylamine behaved similarly, and in each case traces of water caused little change. After 20 hr. over anhydrous cupric chloride or platinous chloride in the conductivity cell, a sample of dry benzene showed zero conductivity. A solution of bisoctadecylaminecupric chloride prepared at 60° had a considerable conductivity as indicated by the results for this compound, but on cooling to 15°, at which temperature the substance is almost insoluble, the conductance was almost zero. This was true as long as no decomposition of the type mentioned above had occurred.

The degree of ionisation of the complexes studied was compared with that of organic compounds which kinetic studies show to behave as though they ionise in solution, by measurements on *tert.*-butyl bromide. This was purified by fractionation and showed zero conductivity both alone and in benzene solution. Even after some time and the acquisition of a distinct brown colour, this compound did not have a conductivity large enough to be measured in this apparatus.

Materials.—The *n*-octadecylamine and *n*-dodecylamine were obtained from Armour and Co. Ltd. and were fractionated in a high vacuum several times until the whole of a 10-g. sample in a sealed tube melted over a 0·1° range. Cupric chloride, acetate, and methyl succinate complexes were prepared as described previously (*J.*, 1950, 122).

Cupric chloroacetate complexes. Cupric mono-, di-, and tri-chloroacetate were prepared by dissolving cupric oxide in rather more than the theoretical quantity of the acid in a very little water. The salts were very soluble, giving syrups, but good crystals were obtained on seeding with particles obtained by drying a drop of solution over calcium chloride and keeping the residue at −80° for some days. The crystals were filtered off and washed with a little ice-cold water. They were dried (P_2O_5) until all water of crystallisation was removed. The amine complexes were prepared by heating the anhydrous salt with very slightly more than 2 equivs. of amine in light petroleum (b. p. 60—80°). The hot solution was filtered under gravity and cooled on ice, and the blue solid filtered off, dried, and carefully recrystallised from a little benzene. The following were obtained: *bisdodecylaminecupric monochloroacetate* (Found: C, 53·6; H, 9·4; Cl, 11·2; Cu, 10·3. $C_{28}H_{58}O_4N_2Cl_2Cu$ requires C, 54·1; H, 9·4; Cl, 11·4; Cu, 10·2%), *bisoctadecylaminecupric monochloroacetate* (Found: C, 60·0; H, 10·3; Cl, 8·9, 9·0; Cu, 8·1. $C_{40}H_{82}O_4N_2Cl_2Cu$ requires C, 60·8; H, 10·5; Cl, 9·0; Cu, 8·05%), *bisdodecylaminecupric dichloroacetate* (Found: C, 49·9, 50·3; H, 8·3, 8·5; Cl, 19·8, 19·6, 18·9; Cu, 9·3, 9·3. $C_{28}H_{56}O_4N_2Cl_4Cu$ requires C, 48·7; H, 8·2; Cl, 20·55; Cu, 9·2%), *bisoctadecylaminecupric dichloroacetate* (Found: C, 56·9, 56·6; H, 9·8, 9·6; Cl, 16·4, 16·0, 15·8; Cu, 7·5, 7·6. $C_{40}H_{80}O_4N_2Cl_4Cu$ requires C, 55·95; H, 9·4; Cl, 16·5; Cu, 7·4%), *bisdodecylaminecupric trichloroacetate* (Found: C, 45·0, 45·6; H, 7·2, 7·5; Cl, 27·6, 27·3, 26·8; Cu, 8·4, 8·45. $C_{28}H_{54}O_4N_2Cl_6Cu$ requires C, 44·3; H, 7·2; Cl, 28·0; Cu, 8·4%), and *bisoctadecylaminecupric trichloroacetate* (Found: C, 52·8, 53·7; H, 8·7, 8·6; Cl, 22·6, 22·4, 21·9; Cu, 6·9, 6·9. $C_{40}H_{78}O_4N_2Cl_6Cu$ requires C, 51·8; H, 8·5; Cl, 22·9; Cu, 6·85%).

The author thanks Dr. J. Chatt for helpful discussions and for supplying certain of the palladous complexes and some samples of *cis*-triethylphosphineplatinous chloride, and Dr. R. S. Nyholm for supplying the complex cuprous salts used in this work.

THE UNIVERSITY, SOUTHAMPTON.
[Present address: ROYAL SCHOOL OF MINES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W.7.]

[*Received, July 27th,* 1953.]