902. *Some Copper*(II) *Complexes with Bases.*

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The relative stabilities of copper(II) complexes with a number of ligands are compared by means of electrometric titrations. It is considered that monoethanolamine (mea) normally gives the complex ion $Cu(mea)_4^{2+}$, but that at high pH values an uncharged species $Cu(NH_2\cdot C_2H_4\cdot O)_2$ is formed.

When a sulphonic acid exchange resin in the form of its copper salt is exposed to a solution of ammonia or ethylenediamine, the base is taken up by the resin to form a copper complex. When monoethanolamine is used, however, a large proportion of the copper is released from the resin to form a deep-blue solution. Since electroneutrality must be preserved in the resin, the reaction

$$x NH_2\cdot C_2H_4\cdot OH + 2H_2O + \overline{Cu^{2+}} \longrightarrow 2\overline{NH_3\cdot C_2H_4\cdot OH^+} + Cu^{2+} + 2OH^- + (x-2)NH_2\cdot C_2H_4\cdot OH \quad (1)$$

must have proceeded extensively (where the barred symbols denote the ions in the resin phase); to learn more of the nature of the soluble copper complex, electrometric measurements have been made on the system and, for comparison, on copper hydroxide–ethylenediamine systems.

Experimental.—The three mixtures for which titration curves are shown in Figs. 1 and 2 had the following compositions (quantities of compounds in mmoles): (A) $CuSO_4$ 0·5, ethylenediamine (en) 1·115, NaOH 1·021, in 122 ml. of solution; (B) $CuSO_4$ 0·5, en 0·669, NaOH 1·021, in 121·2 ml. of solution; and (C) $CuSO_4$ 0·5, monoethanolamine (mea) 2·213, NaOH 1·021, in 122·2 ml. of solution. These were made up from the pure reagents and deionised water. The conductimetric titrations were carried out in a thermostat-bath at $25° \pm 0·01°$ in a cylindrical cell of about 200 ml. capacity. For the potentiometric titrations an Alki glass electrode and Cambridge pH-meter were used. Accurate end-points were obtained from $\Delta pH/\Delta v$ curves.

Results and Discussion.—Fig. 1 shows the results of conductimetric titration of the mixtures against 0·5309N-hydrochloric acid. Curve A shows the presence of a strong base, the slope of the first branch corresponding to the replacement of hydroxide ion by chloride ion, and that of the second to the formation of ethylenediamine hydrochloride. The end-point corresponds to the whole of the sodium hydroxide added. In this mixture there was sufficient ethylenediamine to bind, as complex, the whole of the copper in the form $Cu\,en_2^{2+}$ ion, and as the formation constants for en-complex formation are far higher than those for hydroxide-complexing (see below) no hydroxide ion is bound by the copper (the quinquevalent complex $Cu\,en_2OH^+$, reported by Jonassen, Reeves, and Segal[1] to have a formation constant of 0·73, would not be detected at this low hydroxide-ion concentration). The potentiometric titration shown in curve A of Fig. 2 confirms this. The first end-point corresponds to the whole of the sodium hydroxide added; the remainder of this titration, in which the ethylenediamine is neutralised, is strongly buffered around pH 5 and illustrates the great stability of the cupric–ethylenediamine complexes, and the reason why dilute solutions of this base (in contrast to ammonia) do not precipitate copper hydroxide from solutions of cupric salts.

Mixture B was studied to obtain information about the dissociation constant of any mixed amine-hydroxy-complex. Jonassen and Dexter[2] state that, if sodium hydroxide is added to the mono(ethylenediamine)–copper complex, one-half of the total copper ion is precipitated by the reaction: $2Cu\,en^{2+} + 2OH^- = Cu\,en_2^{2+} + Cu(OH)_2$. We find,

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[1] Jonassen, Reeves, and Segal, *J. Amer. Chem. Soc.*, 1955, **77**, 2748.

[2] Jonassen and Dexter, *J. Amer. Chem. Soc.*, 1949, **71**, 1553.

however, that, although this reaction occurs initially, hydroxide ion is taken up without precipitation by a solution containing Cu en^{2+} and Cu $en_2{}^{2+}$ in suitable proportions, to form a soluble hydroxy-complex. Some light on this behaviour is thrown by the known [3] stability constants of the Cu–en complexes, which are: $\log K_1 = 10{\cdot}72$, for Cu en^{2+} formation, and $\log K_2 = 9{\cdot}31$, for Cu $en_2{}^{2+}$. When the second is divided by the first, $\log [\text{Cu en}_2{}^{2+}][\text{Cu}^{2+}]/[\text{Cu en}^{2+}]^2 = -1{\cdot}41$, so that in a solution of Cu $enSO_4$, one-seventh of the copper will be present as free cupric ions and the solution will be unstable with respect to copper hydroxide at fairly low pH values. If, however, sufficient ethylenediamine were added to the solution to give: $[\text{Cu en}_2{}^{2+}] = [\text{Cu en}^{2+}]$, then $[\text{Cu}^{2+}] = 0{\cdot}04[\text{Cu en}^{2+}]$, and only 2% of the total copper would not be bound as complex. A correspondingly higher pH would be required for precipitation, and, in fact, added hydroxide ions are taken up by another process and the hydroxide concentration for precipitation is not established.

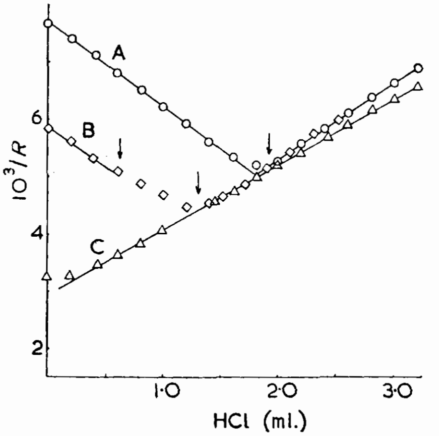

FIG. 1. Conductimetric titration of mixtures A, B, and C (see text) with HCl.

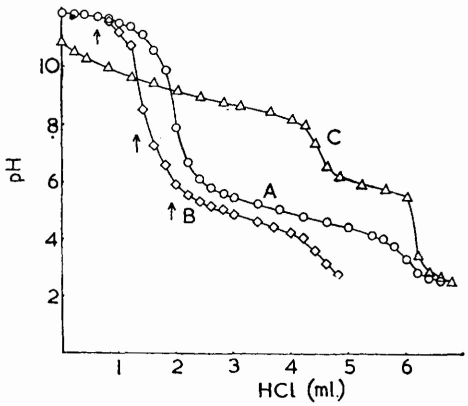

FIG. 2. Potentiometric titration of mixtures A, B, and C (see text) with HCl.

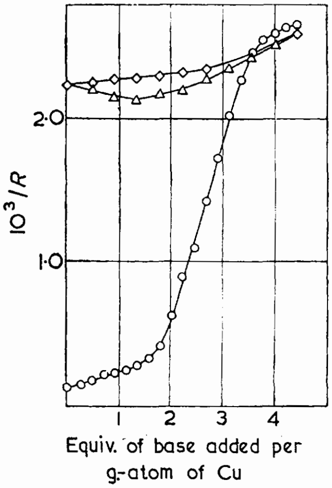

FIG. 3. Effect of organic bases on the conductance of copper salts:

(A) -○-○- $CH_2(CO_2)_2Cu$ + en.
(B) -△-△- $CuSO_4$ + mea.
(C) -◇-◇- $CuSO_4$ + en.

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[3] Sutton *et al.*, "Stability Constants," Part I, p. 5, *Chem. Soc. Special Publ.* No. **11**, **1957**.

In mixture B the ethylenediamine is sufficient to provide 0·169 mmole of Cu en_2^{2+}; the remaining 0·331 mmole of monoamino-complex could bind a maximum of 0·662 mmole of hydroxide to give Cu en(OH)_2, leaving a residue of 0·359 mmole of " free " hydroxide ion; that some hydroxide ion is bound by the complex is shown by the much lower initial conductivity. On curves B in Figs. 1 and 2 the first arrow marks the point at which the " free " hydroxide ion has been neutralised; up to this point curves B are similar to curves A. From there on the added acid is utilised in the reactions: (*a*) Cu $\text{en(OH)}_2 \longrightarrow$ Cu enOH,Cl (terminating at the second arrow), and (*b*) Cu enOH,Cl $\longrightarrow$ Cu enCl_2, terminating at the third. Fig. 1 shows that in the first of these stages a fairly strong but not completely dissociated base is being titrated, and that the second stage corresponds to the neutralisation of a weak base. Fig. 2 confirms this, and four measurements on the relevant section of the curve, ranging from 20% to 68% conversion into Cu enOH^+, give calculated values for $K = [\text{Cu en}^{2+}][\text{OH}^-]/[\text{Cu enOH}^+]$ of $\log K = -6{\cdot}82, -6{\cdot}76, -6{\cdot}76$, and $-6{\cdot}66$. The conductivity and pH data therefore point to the formation of the species Cu enOH^+, though the possibility of dimerisation to Cu $\text{en}_2(\text{OH})_2^{2+}$ is not excluded.

It is of interest to compare the pK value just reported with the value obtained for the hydrated copper ion[4] from hydrolysis data. If we omit co-ordinated water molecules the equations are:

$$\text{Cu enOH}^+ \rightleftharpoons \text{Cu en}^{2+} + \text{OH}^-;\ \log K = -6{\cdot}7 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

$$\text{CuOH}^+ \rightleftharpoons \text{Cu}^{2+} + \text{OH}^-;\ \log K = -6{\cdot}47 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

so that even after allowance for a statistical factor the strength of binding of the hydroxide group is not greatly affected by the presence of the ethylenediamine molecule.

Equation (2) may be combined with Bjerrum and Nielsen's constant[5] for the reaction:

$$\text{Cu en}^{2+} + \text{en} \rightleftharpoons \text{Cu en}_2^{2+};\ \log K = 9{\cdot}31 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

to give

$$\text{Cu enOH}^+ + \text{en} \rightleftharpoons \text{Cu en}_2^{2+} + \text{OH}^-;\ \log K = 2{\cdot}61 \quad . \ . \ . \ . \ . \ . \quad (5)$$

The ethylenediamine molecule is greatly the preferred ligand, and only in the presence of much strong alkali could an appreciable amount of the hydroxy-complex be formed.

The curves for the ethanolamine mixture provide a complete contrast. The initial conductivity contains no contribution from the added hydroxide ions, and it is clear that these have all reacted with the copper ion for form a non-conducting species. This explains the release of copper from a resin by ethanolamine; the ions on the right-hand side of equation (1) are combined to form an uncharged substance which will not be retained by the resin. Curve C of Fig. 2 differs from curves A and B both in the location of the end-points and in its position on the pH scale. The first end-point corresponds to the conversion of the whole of the ethanolamine into the hydrochloride, and the second part of the curve corresponds to the neutralisation of the copper hydroxide present; some incipient precipitation occurred during the titration but did not interfere with its smoothness of reproducibility. The position of the curve is interesting because (once the free hydroxide ion has been neutralised) it lies above curves A and B on the pH scale although ethylenediamine is a stronger base than ethanolamine. The reason for this is that the stability of the copper–ethanolamine complexes is much less than that of the copper–ethylenediamine complexes.

These results make it very unlikely that Cu–en–OH and the Cu–mea–OH complexes have analogous structures. A comparison of equations (2) and (3) suggests that the binding of hydroxide ion by copper is not greatly affected by the nature of the other groups with which the copper is co-ordinated. If this were true of the ethanolamine system the compound Cu $\text{mea}_2(\text{OH})_2$ would be expected to behave as a semi-strong base. That it

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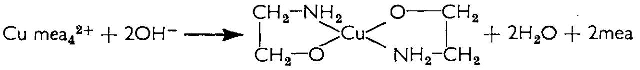
[4] Davies, *J.*, 1951, 1256.

[5] Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, 2, 307.

behaves, in fact, as a non-electrolyte suggests that at high pH values the following reaction takes place:



$$\mathrm{Cu\,mea_4^{2+} + 2OH^- \longrightarrow \begin{matrix} CH_2{-}NH_2 \\ | \\ CH_2{-}O \end{matrix} {>}Cu{<} \begin{matrix} O{-}CH_2 \\ | \\ NH_2{-}CH_2 \end{matrix} + 2H_2O + 2mea} \quad . . . . . . (6)$$

the monoethanolamine behaving under these conditions as a bidentate ligand. This work, therefore, supports and supplements the views of J. L. Hall and his colleagues,[6] who have been led to a similar suggestion based on the formulæ of solid compounds and on spectrophotometric studies. It also parallels the recent observations by Reeves and Bragg [7] on the amminehydroxocopper(II)–diolate reaction, which proceeds by a similar mechanism and leads to a closely analogous product.

In the present work some supplementary observations of interest were made. These are illustrated in Fig. 3, which shows the effect on the conductivity of some copper salt solutions of adding base. Curve C refers to the addition of ethylenediamine to 0·01N-copper sulphate. Although the mobility of the $\mathrm{Cu\,en_2^{2+}}$ ion is likely to be markedly lower than that of the hydrated copper ion, the conductance of the solution shows a 16% increase when the Cu : en ratio reaches 1 : 2, and the only simple explanation for this is that the ion-pairing that occurs in copper sulphate is completely, or almost completely, prevented by complex-formation of the copper with ethylenediamine; the conductance rise is much greater in the second half of the titration than in the first, as would be expected if ion-pairing to give $\mathrm{Cu\,enSO_4}$ could still be shown by the mono-complex but was prevented when the four main co-ordination sites of the copper ion are occupied by ethylenediamine. Some writers have considered that ion association in aqueous metal sulphate solutions occurs between the sulphate ion and the fully hydrated metal ion, but if this were the case a more uniform rise would be looked for in curve 1; the two-step curve accords better with the process: $\mathrm{(Cu,3H_2O,SO_4) \longrightarrow (Cu\,en,H_2O,SO_4) \longrightarrow Cu\,en_2^{2+} + SO_4^{2-}}$.

Curve B shows the addition of monoethanolamine to 0·01N-copper sulphate. Ethanolamine is a much weaker ligand for copper than ethylenediamine, and in the early part of the curve it is competing with hydroxide ion on more or less equal terms; the solution is unstable in this part of the titration. However, at higher concentrations the hydroxide ion is displaced, and when four equivalents of base have been added the solute appears to be entirely converted into $\mathrm{Cu\,mea_4^{2+} + SO_4^{2-}}$.

Curve A refers to the addition of ethylenediamine to copper malonate. The latter is extremely weakly dissociated, but ethylenediamine is an even stronger ligand for copper than the malonate ion, and when the ratio added ligand : copper is 2 : 1 the conductance has increased twenty-fold and obviously corresponds with the formation of the strong salt $\mathrm{Cu\,en_2^{2+},CH_2(CO_2)_2^{2-}}$. Again the curve has a two-step character, in accordance with the formation, at first, of the weakly dissociating salt $\mathrm{CH_2(CO_2)_2Cu\,en}$.

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[6] Fisher and Hall, *Analyt. Chem.*, 1962, **9**, 1094; Bolling and Hall, *J. Amer. Chem. Soc.*, 1953, **75**, 3953.

[7] Reeves and Bragg, *J. Amer. Chem. Soc.*, 1962, **84**, 2491.