The Copper(II)–Hydroxide–*NNN'N'*-Tetramethylethylenediamine System in Aqueous Solution: log *K*, Δ*H*, and Δ*S*

By **E. Arenare** and **P. Paoletti,*** Istituto di Chimica Generale dell'Università, Via I. Nardi, 39 Florence, Italy
A. Dei and **A. Vacca,** Laboratorio per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R., Florence, Italy

The system copper(II)–*NNN'N'*-tetramethylethylenediamine has been investigated over a wide range of pH at 25° in 0·5M-KNO_3. Mixtures of copper salt and amine, the ratio varying from 1 : 1 to 1 : 9, containing nitric acid were titrated with KOH solution using a glass electrode calomel (0·1M-KCl) couple. The range of total copper-ion concentration studied was 0·0008—0·0072M. Evaluation of the potentiometric data was carried out with a new program on an IBM 1130 computer. The formation constants of the species $[CuL]^{2+}$, $[Cu(OH)L]^{+}$, $[Cu_2(OH)_2L]^{2+}$, $[Cu_2(OH)_2L_2]^{2+}$, $[Cu_3(OH)_4L_2]^{2+}$, and $[Cu(OH)_2L]$ were determined. No evidence was found for $[CuL_2]^{2+}$ and $[Cu_2(OH)_4L_2]$ or for the presence of the species formed by hydrolysis of the aqueous copper(II) ion itself, that is $Cu(OH)^{+}$, $Cu_2(OH)_2^{2+}$, and $Cu_3(OH)_4^{2+}$. The heats of formation of the predominant species, $[CuL]^{2+}$, $[Cu(OH)L]^{+}$, $[Cu_2(OH)_2L_2]^{2+}$, $[Cu_3(OH)_4L_2]^{2+}$, and $[Cu(OH)_2L]$ were determined using a titration calorimeter. The mechanism of formation of the hydroxo-complexes agrees with the scheme of successive polymerisation which has been proposed for the alkaline hydrolysis of the copper ion.

IT has long been known that in the reactions of copper(II) ions with sufficiently basic ligands in aqueous solution, large amounts of hydroxo-complexes are formed.[1]

Until recently, the study of these equilibria presented considerable difficulties because of the large number of species present at equilibrium. For this reason the analysis of the experimental data, usually carried out by graphical methods, was limited to the identification and the determination of the formation constants of the dominant species, ignoring the formation of lesser species. The use of computers allows a more accurate and complete analysis of the data, and the application

---

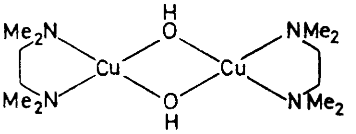
[1] L. G. Sillèn and A. E. Martell, 'Stability Constants,' Special Publication No. 17, The Chemical Society, London, 1964.

of methods capable of determining, on the basis of a rigorous statistical treatment, the stoicheiometry and the formation constants of the species present at equilibrium.

Here we report the results of a thermodynamic study of the equilibria in aqueous solution between the copper(II) ion and *NNN'N'*-tetramethylethylenediamine (tmen), undertaken to examine the mechanism of hydrolysis of complexes of copper(II) with aliphatic diamines and to determine the influence of complex formation on the hydrolysis of copper(II).

Perrin and Sharma [2] have shown that the results obtained from a study of the Cu^{II}–hydroxide–ethylenediamine system were unsatisfactory because of the great stability of the complex $[Cu(en)_2]^{2+}$. The disproportionation of $[Cu(en)]^{2+}$ to $[Cu(en)_2]^{2+}$ and Cu^{2+}, becomes so important that precipitation of insoluble hydroxides occurs before any appreciable amount of the mixed copper–hydroxide–ligand complexes has been formed.

Because of the appreciable steric hindrance in complexes of tmen, it seemed reasonable to suppose that the complex $[Cu(tmen)_2]^{2+}$ would not be very stable so that at high pH, large amounts of hydroxo-complexes could be formed. This supposition is confirmed by the isolation and characterisation [3] in the solid state of the compound containing the binuclear ion (I).



(I)

The stability constants were calculated from the potentiometric data using a new computer method and the enthalpies of formation of the more important species were determined calorimetrically.

A determination of the formation constant of the 1 : 1 complex formed by Cu^{II} with tmen appeared recently.[4] A previous study [5] concerned with the hydrolytic tendency of this complex was reported before the introduction of the computer in the treatment of potentiometric data.

EXPERIMENTAL

All the details concerning the preparation and standardisation of the amine and KOH solutions have been reported elsewhere.[6] The copper(II) nitrate solution was prepared using the solid salt (RP-ACS Erba) and decarbonated water and the copper(II) content was analysed periodically by electrolysis. To prevent hydrolysis the solution was slightly acidified with nitric acid and the acidity was determined potentiometrically.

E.m.f. Measurements.—The apparatus and procedure have been described.[6] Experimental details of the potentiometric measurements are given in Table 1.

TABLE 1

Experimental details of the potentiometric measurements

Curve	Approx. Cu : L ratio	Initial concentration ($mol\ l^{-1} \times 10^2$) $Cu(NO_3)_2$	tmen	HNO_3	pH range
(1)	1 : 1	0·722	0·732	1·895	2·4—7·7
(2)	1 : 2	0·388	0·734	1·909	2·4—9·9
(3)	1 : 9	0·080	0·732	1·909	2·4—10·5
(4)	1 : 5	0·153	0·736	1·914	2·4—10·3
(5)	1 : 1	0·165	0·164	0·476	2·8— 8·7
(6)	1 : 3	0·286	0·842	1·858	2·6—10·2
(7)	1 : 2	0·082	0·178	0·485	2·5—10·6

Calorimetric Measurements.—The apparatus and method have been described.[7] The results of the calorimetric measurements are shown in Table 2. In calculating the enthalpies of formation of the copper complexes account was taken of the heats associated with the simultaneous secondary reactions, that is the protonation reaction of the ligand and the dissociation of water. Values of the basicity constants of the ligand and the ionic product of water and the corresponding heats have been published elsewhere.[6]

Calculations.—Each point on a titration curve represents an equilibrium state between a number of species of general formula $M_pH_qL_r$ (for details on this symbolism, see ref. 8). The concentration of the species $M_pH_qL_r$ at each point is given by

$$[M_pH_qL_r] = \beta_{pqr}[M]^p[H]^q[L]^r$$

where β_{pqr} is the formation constant of the species under consideration and [H], [M], and [L] are the concentrations of the hydrogen ion, of the free metal, and of the free ligand respectively.

For each data point, the mass balance equations are

$$T_M = [M] + \Sigma p\beta_{pqr}[M]^p[H]^q[L]^r$$
$$T_H = [H] + \Sigma q\beta_{pqr}[M]^p[H]^q[L]^r$$
$$T_L = [L] + \Sigma r\beta_{pqr}[M]^p[H]^q[L]^r$$

where T_M, T_H, and T_L are the analytical concentration of metal ion, acid, and ligand, respectively. The unknown quantities are [M] and [L] for each point and the stability constants β_{pqr}. The values of [H] are obtained from the potentiometric measurement. In the present method, the error square sum defined as

$$U = \sum_i (\Delta T^2{}_M + \Delta T^2{}_H + \Delta T^2{}_L)_i$$

where ΔT_M, ΔT_H, and ΔT_L are the differences between the calculated and experimental values of the analytical concentrations of metal ion, hydrogen ion, and ligand respectively for the *i*th point, is minimised with respect to all the unknown parameters, [M] and [L] for each point and β_{pqr}. The Newton–Raphson least-squares method, with the optimisation of the calculated shifts,[9] is used.

---

[2] D. D. Perrin and V. S. Sharma, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1271.

[3] (*a*) D. W. Meek and S. A. Ehrardt, *Inorg. Chem.*, 1965, **4**, 584; (*b*) T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Cryst.*, 1970, **B26**, 2096.

[4] R. Nasanen, M. Koskinen, M. Alatalo, L. Adler, and S. Koskela, *Suomen Kem.*, 1967, *B* **40**, 124.

[5] R. L. Gustafson and A. E. Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 525.

[6] P. Paoletti, R. Barbucci, A. Vacca, and A. Dei, *J. Chem. Soc.* (*A*), 1971, 310.

[7] R. Barbucci, P. Paoletti, and A. Vacca, *J. Chem. Soc.* (*A*), 1970, 2202.

[8] A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, 1966, **5**, 1384.

[9] T. G. Strand, D. A. Kohl, and R. A. Bonham, *J. Chem. Phys.*, 1963, **39**, 1307.

A Fortran IV program for the IBM 1130 computer has been written. The calculation of the constants, for the present system, was carried out on 151 data points deriving from seven different titration curves* (Table 1).

As shown below, the calculation of the constants was carried out on the assumption that the complex species present were $[CuL]^{2+}$, $[Cu(OH)L]^{+}$, $[Cu_2(OH)_2L_2]^{2+}$, and $[Cu(OH)_2L]$. Other species were tried in the calculation one at a time. When one of these new hypothetical species was tried in the program, one of the following types of behaviour was observed: (*a*) the value of the constant converged in successive cycles to a positive value, greater than three times the corresponding standard deviation, the value of the function *U* decreasing simultaneously; (*b*) the constant for the new species decreased progressively until it became negative, whilst the value of the function *U* did not decrease appreciably; (*c*) a positive value of the constant was obtained which was however smaller than three times the relative standard deviation. Only when type (*a*) behaviour was found, was the new species retained for successive cycles.

TABLE 2

Calorimetric results for the copper(II)–hydroxide–*NNN'N'*-tetramethylethylenediamine system in 0·5M-KNO_3 at 25 °C

Calorimetric Ampoule				$Cu(NO_3)_2$ added [a]		
H^+ [c] (mmol)	$Cu(NO_3)_2$ (mmol)	tmen (mmol)	Volume (ml)	Volume (ml)	mmol	Q [b] (cal)
1·1003	0·0320	1·7566	88·51	2·00	0·6404	3·663
1·1015	0·6724	1·7566	90·51	2·00	0·6404	2·876
1·1026	1·3128	1·7566	92·51	2·00	0·6404	0·183
1·0311	0·0320	1·7529	87·78	2·00	0·6404	3·642
1·0323	0·6724	1·7529	89·78	2·00	0·6404	3·074
1·0334	1·3128	1·7529	91·78	2·00	0·6404	0·204
1·0130	0·0320	1·8029	92·83	2·00	0·6404	3·634
1·0142	0·6724	1·8029	94·83	2·00	0·6404	3·356
1·0153	1·3128	1·8029	96·83	2·00	0·6404	0·347
0·5617	0·0320	1·8506	89·62	2·00	0·6404	3·288
0·5629	0·6724	1·8506	91·62	2·00	0·6404	4·271
0·5640	1·3128	1·8506	93·62	2·00	0·6404	1·900
−1·2470	0·0320	2·2525	91·58	2·00	0·6404	7·182
−1·2458	0·6724	2·2525	93·58	2·00	0·6404	5·869
−0·4988	0·0320	2·5828	86·47	1·45	0·4643	4·449
−0·4979	0·4963	2·5828	87·92	1·50	0·4803	2·770
−0·4970	0·9766	2·5828	89·42	1·50	0·4803	2·538
−0·4961	1·4569	2·5828	90·92	1·50	0·4803	3·175
−1·9952	0·0320	0·4527	89·06	1·50	0·4803	5·594
−1·9943	0·5123	0·4527	90·56	1·50	0·4803	5·381
−1·9934	0·9926	0·4527	92·06	1·50	0·4803	5·028

[a] Molarity of titrant was 0·3202 mol l^{-1} in $Cu(NO_3)_2$ and 0·0006 mol l^{-1} in HNO_3. [b] Corrected for heat of dilution. [c] Negative values are referred to OH^- mmol.

Naturally the values of *U* calculated on the same set of data, depend on the chemical model adopted (type and number of the species considered in the calculation) and on the values of the stability constants. All the constants were varied simultaneously until the best agreement between the experimental and calculated data was obtained, *i.e.* until the minimum value of *U* was found consistent with a realistic chemical model. The enthalpies of formation were obtained from the calorimetric data using a previously published method.[7]

RESULTS AND DISCUSSION

Stability Constants (*Curve Fitting*).—For the copper(II)–tmen system in aqueous solution one would predict the formation of a large number of complexes over a wide range of pH. The complexes $[CuL]^{2+}$, $[Cu(OH)L]^{+}$, $[Cu(OH)_2L]$, and $[Cu_2(OH)_2L_2]^{2+}$ have already been characterised.[5] The latter has also been isolated in the solid state and its structure determined.[3b] This shows that the two metal ions are joined by the two hydroxo-bridges. This unit represents one of the fundamental species involved in the alkaline hydrolysis of the cupric ion, together with two others, $Cu(OH)^+$ and $Cu_3(OH)_4{}^{2+}$. It seemed to us that, starting with these basic units, it would be possible to form a whole series of complexes with tmen. We thought that the following complex species might be formed in this system: $[CuL]^{2+}$, $[Cu(OH)L]^{+}$, $[Cu(OH)_2L]$, $[Cu_2(OH)_2L]^{2+}$, $[Cu_2(OH)_2L_2]^{2+}$, $[Cu_3(OH)_4L_2]^{2+}$, $[CuL_2]^{2+}$, $[Cu_2(OH)_4L_2]$, $[Cu(OH)]^{+}$, $[Cu(OH)_2]$, $[Cu_2(OH)_2]^{2+}$. As it will be seen below, the first six species were in part characterised, whilst the others were not.

The calculation of the complex formation constants was started, assuming that the four species already reported in the literature were formed. Using this chemical model (trial 1, Table 3) the agreement between the experimental and calculated values is already fairly good for all the curves except those with metal : ligand ratio 1 : 2. In these curves appreciable and systematic differences between the calculated and experimental values were observed in the region of rapid pH change and high pH values. Introducing the complex $[CuL_2]^{2+}$ did not lead to any improvement and within a few

---

* The program, computer output and 151 data points are deposited with the National Lending Library in SUP. 20299 (17 pp. 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

TABLE 3

Values (logarithmic units) of the formation constants in the successive trials,[a] $\beta_{pqr} = \frac{[Cu_pH_qL_r]}{[Cu]^p[H]^q[L]^r}$ for negative values of q the formula $[Cu_p(OH)_{-q}L_r]$ is substituted for $[Cu_pH_qL_r]$ [b]

Trial	$\beta_{0,1,1}$ CuL	$\beta_{1,-1,1}$ Cu(OH)L	$\beta_{2,-2,2}$ $Cu_2(OH_2)L_2$	$\beta_{1,-2,1}$ $Cu(OH)_2L$	$\beta_{2,-2,1}$ $Cu_2(OH)_2L$	$\beta_{3,-4,2}$ $Cu_3(OH)_4L_2$	$\beta_{2,-4,2}$ $Cu_2(OH)_4L_2$	U.10[c]
1	7·377(1)	−0·377(35)	2·622(15)	−10·789(22)				0·8890
2	7·377(1)	−0·806(138)	2·688(15)	−10·815(17)	−3·727(72)			0·5124
3	7·375(1)	−0·278(24)	2·421(28)	−10·913(29)		−8·080(64)		0·6086
4	7·376(1)	−0·659(75)	2·590(18)	−10·908(20)	−3·648(53)	−8·149(64)		0·3036
5	7·376(1)	−0·644(101)	2·550(28)		−3·613(74)	−7·927(56)	−18·572(38)	0·5691
6	7·378(2)		2·684(9)	−10·908(23)	−3·450(30)	−8·173(83)		0·3842

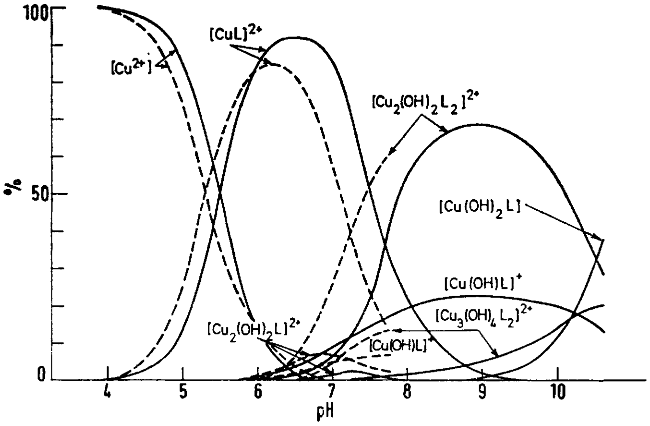
[a] Standard deviations in parentheses. [b] The charges of ions are omitted. [c] Ref. 7.

cycles its constant had become negative. We conclude that this complex is not formed.

On the other hand, introducing the complex $[Cu_2(OH)_2L]^{2+}$ led to a decrease in the value of U (see Table 3, trial 2) together with a reasonable and fairly accurate value for the corresponding constant. Although the introduction of this species improved the agreement in the region of rapid pH change, there was no corresponding agreement at high pH.

For this reason the species $[Cu_3(OH)_4L_2]^{2+}$ was introduced in place of the species $[Cu_2(OH)_2L]^{2+}$. In this case (Table 3, trial 3), there was a net improvement in the agreement compared with the initial set (trial 1), but, although the agreement was very good in the region of high pH, it was not so good in the region of rapid pH change. At this point it seemed obvious that both the above species should be introduced and this led to a decisive improvement (trial 4) compared with the initial set.

From an examination of the distribution curves (see the Figure) it is clear that the complex formed predominantly at high pH is the neutral species $[Cu(OH)_2L]$. If we suppose that the formation of hydroxo-complexes involves a polymerisation process it seems odd that the final species should be a monomer. We therefore decided to substitute the dimeric species $[Cu_2(OH)_4L_2]$ for the monomer (Table 3, trial 5) but the value of U increased considerably. An attempt to retain both species was also unsuccessful as after only one cycle the dimer constant became negative.



Distribution curves for system copper(II)–*NNN′N′*-tetramethylethylenediamine; % = $p[Cu_pH_qL_r]/T_M$; dotted lines, molar ratio Cu : L = 1 : 1, initial concentration of copper(II) 7·22 × 10^{-3}M (Curve 1, Table 1); solid lines, molar ratio Cu : L = 1 : 2, initial concentration of copper(II) 0·82 × 10^{-3}M (Curve 7, Table 1)

It is worth noting that the calculated constants did not vary much in the various trials except in the case of the complex $[Cu(OH)L]^+$. For trial 6 therefore this complex was removed and as can be seen the agreement obtained is only slightly worse than that found in the best case (trial 4) and the constants do not vary appreciably. If we take account of the fact that in the hydrolysis of the Cu^{2+} ion the species $[Cu(OH)]^+$ is only present in negligible amounts, then the existence of the complex $[Cu(OH)L]^+$ in our system is open to doubt.

At this point in the calculation it seemed logical to consider the presence in our system of hydroxo-species which do not contain the organic ligand. Therefore one cycle of calculation was carried out using the literature values of the constants for the species $[Cu_2(OH)_2^2]^+$ and $[Cu_3(OH)_4]^{2+}$. None of the distribution curves revealed any trace of these complexes.

The Figure shows the distribution curves for the potentiometric curves (1) and (7) of Table 1. One fact stands out: except in the initial highly buffered region where only one complex, $[CuL]^{2+}$, is present, there are always several complexes present simultaneously.

Thermodynamic Functions.—Table 4 gives the thermodynamic data for complex formation. It was only possible to measure the heats of formation for those complexes formed in appreciable amounts.

The heat of formation for the complex $[CuL]^{2+}$ is the lowest yet determined for a copper complex with an aliphatic polyamine. This is undoubtedly due to the considerable steric hindrance caused by the four methyl groups. The high positive value of ΔS is indicative of the extent of dehydration occurring on complex formation.

Now let us consider the complexes obtained by allowing the amine ligand to react with the hydroxo-species as outlined in the following scheme:

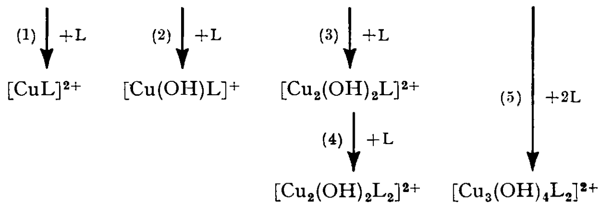


TABLE 4

Thermodynamic functions of complex formation in 0·5M-KNO_3 at 25·0 °C for the copper(II)–hydroxide–*NNN'N'*-tetramethylethylenediamine (L) system [a]

Reaction	log *K*	ΔH (kcal mol^{-1})	ΔS (cal deg^{-1} mol^{-1})
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	7·376 ± 0·001	−6·15 ± 0·02	13·1 ± 0·1
$Cu^{2+} + L + H_2O \rightleftharpoons [Cu(OH)L]^+ + H^+$	−0·66 ± 0·07	3·3 ± 0·8	8·0 ± 3·0
$Cu^{2+} + L + 2H_2O \rightleftharpoons [Cu(OH)_2L] + 2H^+$	−10·91 ± 0·02	15·00 ± 0·07	0·4 ± 0·3
$2Cu^{2+} + 2L + 2H_2O \rightleftharpoons [Cu_2(OH)_2L_2]^{2+} + 2H^+$	2·59 ± 0·02	4·70 ± 0·14	27·6 ± 0·6
$3Cu^{2+} + 2L + 4H_2O \rightleftharpoons [Cu_3(OH)_4L_2]^{2+} + 4H^+$	−8·15 ± 0·06	17·7 ± 0·7	22·1 ± 2·7
$2Cu^{2+} + L + 2H_2O \rightleftharpoons [Cu_2(OH)_2L]^{2+} + 2H^+$	−3·65 ± 0·05		

[a] Uncertainty intervals associated with all values are standard deviations.

Using the values −8·0, −10·7, and −21 for the formation constants[1] (log units) of the species $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, and $Cu_3(OH)_4^{2+}$ respectively, the appropriate constants for the addition of one or two molecules of the organic ligand can be readily calculated. For reactions (2) and (3) in the scheme above values of 7·3 and 7·1 were obtained which are very close to the value of 7·38 found for reaction 1 (Table 4). The addition of a second molecule of ligand (reaction 4) leads to a value of 6·2, slightly lower than that for the first molecule as is usually found in stepwise reactions. The sum of these two constants, 13·3, is very close to the value (12·8) found for the direct addition of two molecules (reaction 5). From the data in Table 4 it is also possible to obtain the thermodynamic quantities for the following reactions:

(1′) $[CuL]^{2+} + OH^- \rightleftharpoons [Cu(OH)L]^+$
(2′) $[CuL]^{2+} + 2OH^- \rightleftharpoons [Cu(OH)_2L]$
(3′) $2[Cu(OH)L]^+ \rightleftharpoons [Cu_2(OH)_2L_2]^{2+}$

The values found for log *K*, ΔH (kcal mol^{-1}), ΔS (cal deg^{-1} mol^{-1}) were respectively 5·67, −3·9, 12·8 for reaction (1′), 9·13, −5·62, 22·9 for reaction (2′), and 3·91, −2·0, 11·2 for reaction (3′). The agreement with published data for the constants[5] can be considered satisfactory, whilst the discrepancies between the present values of ΔH and ΔS and previous values[5] can be attributed to the limitations of the method, which makes use of the temperature dependence of the equilibrium constants.

We thank the Italian C.N.R. for financial assistance.

[1/1099 *Received*, 30*th June*, 1971]