

The Stability of Metal Halide Complexes in Aqueous Solution

VII. The Chloride Complexes of Copper(I)

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The chloride complexes of copper(I) have been studied by solubility and potentiometric techniques. The measurements have been performed at 25°C in a medium containing 0.1 M acid, at a constant ionic strength of 5 M. Stability constants for the first three mononuclear complexes have been determined, and also the solubility product for CuCl. Even for the highest ligand concentration reached (≈ 4.2 M), the fourth complex is not formed. On the other hand, strong evidence has been obtained for polynuclear species with a charge of -2 . Considering the simplest complex of this kind, *i.e.* $\text{Cu}_2\text{Cl}_4^{2-}$, to be the one most plausibly formed, a value for β_{24} has been estimated.

Copper(I) seems to be the only non-zero valent oxidation state of a first row transition element that shows typical class (*b*), or soft, acceptor properties.¹ At least as far as metal ion acceptors are concerned, such properties are found only for those possessing a large number of easily dislocated *d*-electrons. A suitable measure of the ease of dislocation is provided by the polarizability which has to be high enough in order that (*b*)-properties should ensue. A high polarizability alone is on the other hand not enough; it has to be combined with a well populated *d*-shell which should moreover preferably be unshielded.²

The obvious conclusions are that soft metal ions coordinate ligands by bonds which are markedly covalent and that the *d*-electrons are essential for the formation of these bonds.

The polarizability of metal ions decreases so sharply with the number of electron shells that, as already mentioned, copper(I) is the only ionic acceptor in the first row still displaying (*b*)-properties. Owing to the low charge, the polarizability is still fairly high, and the unshielded d^{10} configuration is evidently quite favourable for covalent bond formation.

Copper(I) is thus in a unique position and its solution chemistry should therefore be of special interest. In fact, however, relatively little has been done in this field, on account of the experimental difficulties. Solutions of copper(I) often tend to disproportionate into copper(II) and metallic copper,

and they are also often very sensitive to oxidation, *e.g.* by air. As a result, even simple copper(I) systems, such as the halides, are very incompletely known, at least in comparison with the analogous silver(I) systems. To start with, a reinvestigation of the copper(I) chloride system seemed worthwhile.

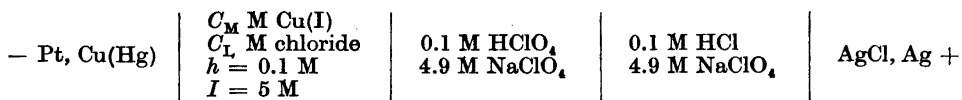
In most of the previous studies, the solubility of copper(I) in equilibrium with CuCl(s) has been measured as a function of the chloride concentration. This method cannot distinguish between complexes of different nuclearity; the number of entities CuCl present in a complex of a certain charge remains undetermined.^{3,4} The few measurements carried out by potentiometric methods have not been very extensive.

In his classical investigation of 1902, Bodländer⁵ was able to interpret his results reasonably well by postulating the formation of the complexes CuCl_2^- and CuCl_3^{2-} . These complexes are undoubtedly prominent, and later authors⁶ have as a rule also found it possible to interpret their data on the basis of these two species, or at least one of them. The time seems now due, however, to look for the first and fourth complex, and also for polynuclear species, the existence of which seems quite likely considering the complexes found in solutions of silver halides.⁷⁻⁹

Both potentiometric and solubility measurements have been employed in the present investigation. Potentiometrically, the concentration of Cu^+ in chloride solutions can be found by means of a copper amalgam electrode, provided that the standard potential of the $\text{Cu}^{2+}/\text{Cu}(\text{Hg})$ electrode (against the same reference electrode) and also the constant for the disproportionation equilibrium $\text{Cu}(\text{Hg}) + \text{Cu}^{2+} \rightleftharpoons 2 \text{Cu}^+$ are known. These have therefore been determined in separate experiments. All measurements refer to a medium of a total ionic strength $I=5 \text{ M}$, with sodium perchlorate as inert electrolyte. The acidity, h , has been kept $=0.1 \text{ M}$, and the temperature at 25°C .

DERIVATION OF STABILITY CONSTANTS FROM THE EMF MEASUREMENTS

The emf of the following cell (I)



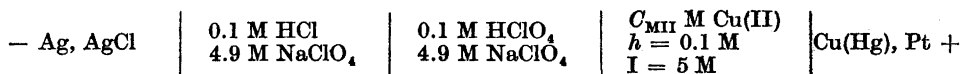
can be written as ($[\text{M}]=[\text{Cu}^+]$):

$$E_I = e_{\text{RE}} - e_{01} - (RT/F) \ln [\text{M}] = E_I^\circ - (RT/F) \ln [\text{M}] \quad (1)$$

where e_{RE} = electrode potential of the reference half-cell (including liquid junction potentials) and e_{01} = standard potential of the $\text{Cu}^+/\text{Cu}(\text{Hg})$ electrode.

On account of the disproportionation of copper(I) taking place in solutions which do not contain a stabilizing ligand, the value of the constant difference E_I° cannot be found in the usual way, *i.e.* by direct measurement of E_I for known values of $[\text{M}]$. Instead the following procedure has to be adopted.

The emf of the following cell (II)



can be written as ($[M]_{II} = [Cu^{2+}]$):

$$E_{II} = e_{02} + (RT/2F)\ln[M]_{II} - e_{RE} = E_{II}^{\circ} + (RT/2F)\ln[M]_{II} \quad (2)$$

where e_{02} = standard potential of the $Cu^{2+}/Cu(Hg)$ electrode. From measurements of E_{II} for known values of $[M]_{II}$, E_{II}° can easily be found.

Further, at equilibrium between $Cu(Hg)$, $Cu(I)$, and $Cu(II)$, the following relations hold:

$$e_{01} + (RT/F)\ln[M] = e_{02} + (RT/2F)\ln[M]_{II} \quad (3)$$

and

$$[M]^2/[M]_{II} = K \quad (4)$$

Hence

$$e_{01} = e_{02} - (RT/2F)\ln K \quad (5)$$

and, from (1), (2), and (5):

$$E_I^{\circ} = (RT/2F)\ln K - E_{II}^{\circ} \quad (6)$$

To find the unknown quantity E_I° , the disproportionation constant K has to be known besides E_{II}° . This has been determined, for the prevailing conditions, as described below.

Once E_I° is known, $[M]$ can be determined for any solution by measurements of E_I . Provided that so much of the stabilizing ligand is present that no disproportionation occurs, C_M is known from the amount of $Cu(I)$ added, and hence the function $C_M/[M]$. In the general case, this function takes the form

$$C_M/[M] = 1 + \sum_{n=1}^N \beta_n [L]^n + \sum_{m=1}^M \sum_{n=1}^{N'} \beta_{m,n} [M]^m [L]^n \quad (7)$$

where the double sum refers to the polynuclear complexes possibly present. By determining $C_M/[M]$ as a function of C_L for a number of different C_M and extrapolating to $C_M=0$, the value of

$$(C_M/[M])_{C_M=0} = X = 1 + \sum_{n=1}^N \beta_n [L]^n \quad (8)$$

can be determined as a function of $(C_L)_{C_M=0} = [L]$. Hence the mononuclear constants β_n can be found by established methods.^{10,11}

If only mononuclear complexes are present, the value of the ligand number $\bar{n} = (C_L - [L])/C_M$ will be equal to the slope of the straight (C_L, C_M) -lines of constant $C_M/[M]$ used for the extrapolation to $C_M=0$, as in such a case $[L]$, and hence

$$\bar{n} = \bar{n}_0 = \sum_{n=1}^N n \beta_n [L]^n X \quad (9)$$

are constant along each line, as is evident from (7). If polynuclear complexes also exist, however, this will no longer be true. The lines will not be straight

any more, and their slopes in the points ($[L]$, 0) of interaction with the C_T -axis can be shown¹⁰ to be $< \bar{n}_0$. By comparing the slopes k with the values of \bar{n}_0 found from (9), it is thus possible to decide whether polynuclear complexes are formed or not.

EMF MEASUREMENTS, EXPERIMENTAL

Chemicals. *Copper(I) chloride*, Merck p.a. was purified and dried according to Keller and Wycoff.¹² The product obtained was analyzed by electrolytic reduction of samples which had previously been oxidized to copper(II) by perchloric acid. The amount of copper found was about 98 % of that calculated from the formula $CuCl$. The stock solutions of *copper(II) perchlorate*, G. F. Smith, were also analyzed by electrodeposition. *Copper powder*, Merck p.a., was used without further purification. *Oxygen free water* was prepared by refluxing deionized water, through which a steady stream of pure nitrogen was passed, for about one hour. After distillation, the water obtained was stored under nitrogen.

Copper amalgam. An amalgam containing approximately 3% copper by weight was prepared by electrolyzing copper(II) perchlorate solution with a mercury pool as cathode. The exact composition is unimportant, as a two-phase amalgam is formed at room temperature for copper concentrations between 0.0032 and 24.1 %, as shown by Tammann *et al.*^{13,14} Between these limits, the potentials of a copper amalgam electrode should thus be independent of the copper concentration. Already before Tammann, Cohen *et al.*¹⁵ had in fact found that this is true at least for amalgams containing between 1 and 16 % copper. Prior to use, the amalgam was washed with dilute perchloric acid, to remove traces of copper(II), and finally with water.

Silver-silver chloride electrodes were prepared according to Brown.¹⁶

Determination of the disproportionation constant K . In glass-stopped bottles, filled with pure nitrogen, portions of the copper amalgam were shaken with copper(II) solutions of various concentrations, all with $h=0.1$ M and $I=5$ M. Shaking for six days provided ample time for the attainment of equilibrium. Prolonged shaking resulted in the formation of a greyish deposit on the glass walls, presumably mercury(II) oxide.

For comparison, samples of pure copper powder were equilibrated with copper(II) solutions in the same manner.

The concentration of copper(I) in the equilibrium solutions was determined spectrophotometrically by neocuproine (2,9-dimethyl-1,10-phenanthroline).¹⁷ Samples were withdrawn in a glove-box, filled with nitrogen or carbon dioxide. In the amalgam series, these samples were pipetted direct into a centrifuge tube containing a known volume of a 0.2 % ethanol solution of the reagent; in the copper powder series the samples were first filtered. A portion of sodium acetate solution, sufficient to give a pH between 5 and 6, was then added, and the complex formed extracted twice with isoamylalcohol, of a total volume similar to that of the solution to be extracted.

For the spectrophotometric calibration, previously analyzed solutions of copper(II) were completely reduced by hydroxylamine hydrochloride and the neocuproine complex then extracted with isoamylalcohol. A maximum absorptivity of $\epsilon=7970 \pm 110 \text{ cm}^{-1}\text{M}^{-1}$ was found for $\lambda=454$ nm, in good agreement with previous results.^{17,18} The actual samples were therefore measured at this wavelength, and the concentrations calculated by means of this value of ϵ . While very constant absorbance values were found for the solutions used for the calibration, those of the samples changed slowly with time. The values chosen for the calculations are those found by extrapolation to zero mixing time.

Emf measurements, procedure. The initial solutions for the left hand half-cell of cell I were prepared by treating $CuCl(s)$ with solutions of a concentration high enough to ensure a ready dissolution. To remove every trace of copper(II), these solutions were then shaken with copper amalgam under nitrogen until they were completely colourless. The absence of copper(II) was confirmed by the negative reaction shown by a sample of this solution towards cuprizone (*cf.* below). A suitable volume of the pure copper(I) solution was then transferred to the electrode vessel, the initial emf of the cell read, and C_T then varied by additions, from a burette, of further chloride solution, 1 M or 5 M. During all operations, air was carefully excluded by oxygen-free nitrogen. Constant

values of the emfs were attained within 2 min; they were reproducible within 0.4 mV. For each series, an aliquot of the original solutions was withdrawn for analytical determination of $C_M (=C_M')$. This was done by oxidation to copper(II) by perchloric acid and subsequent spectrophotometric analysis by means of the ammine complex, *i.e.* by the method also applied in the solubility measurements (*cf.* below p. 166).

The right hand half-cell of cell II initially contained, besides the amalgam, only the acid perchlorate solution. Copper(II) perchlorate was then added, and the emf read after each addition. The potentials were rapidly reached, remained stable, and were reproducible within 0.2 mV.

Table 1 A. The disproportionation constant.

C_{MII} mM	Amalgam		Metal	
	[M] mM	pK	[M] mM	pK
478	0.68	5.99 ± 0.05	0.68	5.99 ± 0.05
97.0	0.33	5.94 ± 0.07	0.33	5.94 ± 0.04
48.0	0.24	5.93 ± 0.05	0.24	5.93 ± 0.04

Table 1 B. Comparison of determinations of the disproportionation constant K .

Metal phase	Medium	M	$t^\circ\text{C}$	pK	Ref.
Amalgam	(Cu,Na,H)ClO ₄	5	25	5.95	^a
	Cu(ClO ₄) ₂	0.1	20	5.91	10
	(Cu,Na)NO ₃	0.1	20	6.25	23
	(Cu,K)NO ₃	1.0	22	6.26	24
Metal	(Cu,Na,H)ClO ₄	5	25	5.95	^a
	(Cu,H)ClO ₄	var.	25	6.23	22
	(Cu,H)ClO ₄	var.	25	5.96	20
	ClO ₄	1.13	25	6.25	21
	ClO ₄	1.13	30	6.00	21
	(Cu,H)SO ₄	var.	25	6.08	22
	(Cu,H)SO ₄	var.	25	6.08	20
	SO ₄	1.13	30	6.11	21
	ClO ₄	→ 0	25	5.94	25

^a This work.

EMF MEASUREMENTS, RESULTS

In Table 1 A, the results of the determination of K are presented. Each value is the mean of, as a rule, a triplicate determination. Copper(II) concentrations significantly lower than those actually used will result in copper(I) concentrations too low for a reasonably accurate analysis. The amalgam and the powder give, within the limits of random error, the same value, *viz.* $pK = 5.95 \pm 0.05$. From the emf of the cell $-\text{Cu(s)}|\text{Cu}^{2+}|\text{Cu(Hg)}+$ which has been reported ^{6,19} to be between 3 and 6 mV (with a preferred value ¹⁹ of

5.1 mV), one would expect that the amalgam value would be 0.1–0.2 (preferably 0.17) log units lower than that found for the copper powder. The expected difference thus seems to be just outside the experimental error.

A direct comparison with the values of pK determined previously is rendered somewhat difficult by the differences in medium, and as far as the amalgam measurements are concerned, also in temperature, Table 1 B. No measurements exist of the temperature coefficient dpK/dT for the equilibrium involving copper amalgam, and it does not seem advisable to use, not even as an approximation, the values found by Heinerth²⁰ and Miller²¹ for the metallic copper equilibrium (which are both close to -0.05 units/degree).

For metallic copper, our result agrees with that found by Heinerth, and by Endicott and Taube,²⁵ for a perchlorate medium at the same temperature. The value calculated by Heinerth²⁰ from measurements of Fenwick²² differs on the other hand considerably, *viz.* by ≈ 0.3 log units. The variation between the numbers found from the various determinations performed by Fenwick is so large, however, that even this difference may be more apparent than real. This suspicion is strengthened by the fact that Fenwick's measurements in sulphate medium yield a lower value of pK though sulphate ions should rather tend to stabilize copper(II) relative to copper(I) and thus cause an increase of pK relative to perchlorate medium, as is also found by Heinerth and by Miller. The values found by Miller are, however, throughout higher than those of Heinerth for the same temperature.

Like Frønes¹⁰ we have seen no sign of the chloride ion formation claimed by Heinerth to occur in perchlorate solutions.

In Table 2, the result of the determination of E_{II}° is reported, resulting in a mean of 107.1 ± 0.4 mV. The value of E_I° is thus calculated to be -283.1 mV.*

Table 2. Determination of E_{II}° .

$[M]_{II}$ mM	E_{II} mV	E_{II}° mV	$[M]_{II}$ mM	E_{II} mV	E_{II}° mV
1.30	21.6	107.0	11.45	49.5	106.9
2.00	27.0	106.8	16.2	54.3	107.3
3.07	32.5	106.8	22.9	58.9	107.4
4.87	38.6	107.0	28.0	61.5	107.4
8.11	45.1	107.0	32.1	63.2	107.4

In Tables 3 and 4, the function $C_M/[M]$ has been calculated from the main measurements (cell I). For the extrapolation to $C_M=0$, $\log C_M/[M]$ was plotted against C_L for each initial value of C_M' . The lines were cut at suitable values of $\log C_M/[M]$. For each point of intersection, C_L was read, while C_M was found from the known values of C_L , C_L' , and C_M' by a graphical procedure.¹¹ The (C_L, C_M) -lines of constant $C_M/[M]$ were then extrapolated to $C_M=0$, yielding corresponding values of $[L]$ and X , Table 5.

* The difference calculated from the values of e_{RH} and e_{01} valid at $I=0$ is -295.9 .^{19,26}

Table 3. Determination of $C_M/[M]$ using 1 M chloride as titrant.

$C_M' = 5.43 \text{ mM}$				$C_M' = 12.76 \text{ mM}$			
C_L mM	C_M mM	E_I mV	$C_M/[M]$ $\times 10^{-5}$	C_L mM	C_M mM	E_I mV	$C_M/[M]$ $\times 10^{-5}$
206	5.43	128.7	0.50	313	12.76	130.5	1.25
259	5.07	143.7	0.83	359	11.91	140.5	1.72
305	4.75	155.0	1.21	399	11.17	149.0	2.24
346	4.47	163.8	1.60	434	10.51	155.9	2.76
382	4.22	171.8	2.06	466	9.92	161.7	3.27
444	3.80	183.6	2.94	519	8.93	171.7	4.30
537	3.17	199.7	4.59	599	7.44	185.3	6.14
603	2.72	210.7	6.05	657	6.38	195.1	7.72
673	2.24	222.4	7.84	717	5.25	205.7	9.59
722	1.90	230.7	9.19	760	4.47	213.4	11.00
786	1.46	242.3	11.10	815	3.44	224.6	13.10
861	0.95	258.4	13.50	880	2.23	240.4	15.70

Table 4. Determination of $C_M/[M]$ using 5 M chloride as titrant.

$C_M' = 8.02 \text{ mM}$				$C_M' = 13.34 \text{ mM}$				$C_M' = 47.85 \text{ mM}$			
C_L M	C_M mM	E_I mV	$C_M/[M]$ $\times 10^{-4}$	C_L M	C_M mM	E_I mV	$C_M/[M]$ $\times 10^{-5}$	C_L M	C_M mM	E_I mV	$C_M/[M]$ $\times 10^{-5}$
208	8.02	117.1	4.64	313	13.34	129.0	1.24	817	47.85	151.3	1.05
341	7.80	146.9	14.4	443	12.97	150.2	2.73	876	47.18	156.4	1.26
467	7.59	166.4	30.1	566	12.62	166.1	4.95	933	46.52	161.2	1.51
700	7.20	192.8	79.6	794	11.97	189.0	11.4	1043	45.26	169.2	2.00
807	7.02	202.9	115	899	11.67	197.7	15.6	1147	44.07	176.5	2.58
909	6.85	211.2	155	999	11.39	205.2	20.4	1246	42.94	182.7	3.20
1054	6.60	221.7	225	1140	10.99	214.7	28.5	1472	40.36	195.7	5.00
1188	6.38	230.5	305	1272	10.61	222.8	37.8	1595	38.95	202.1	6.18
1314	6.17	238.0	396	1395	10.26	229.7	47.7	1747	37.22	209.6	7.90
1469	5.91	246.4	528	1546	9.83	236.8	60.3	1918	35.26	217.2	10.1
1646	5.61	255.2	704	1719	9.34	245.6	80.5	2072	33.50	223.8	12.4
1951	5.10	268.9	1090	2017	8.49	258.8	122	2338	30.45	234.5	17.0
2205	4.68	279.4	1500	2266	7.78	268.8	166	2560	27.91	243.0	21.6
2604	4.01	294.0	2280	2657	6.67	283.2	249	2909	23.93	255.6	30.4
3027	3.30	308.8	3340	3070	5.49	297.7	359	3278	19.70	268.7	41.8
3475	2.55	324.3	4700	3509	4.24	313.0	505	3669	15.23	283.0	56.4
3882	1.87	339.2	6170	3906	3.11	327.7	655	4024	11.17	297.4	72.5
4161	1.40	350.7	7230	4180	2.33	339.4	774	4268	8.37	308.7	84.1

In solutions of low C_L , only low values of C_M could be chosen, because of the low solubility of copper(I) in such solutions. The value of C_M can therefore not be varied very much. This does not detract from the accuracy of the determination of $[L]$, but the slopes become rather uncertain. At high

values of C_L , high values of C_M can also be chosen, but in this range $[L]$ is anyway close to C_L and the slope will therefore still not be very accurately determined.

From $X([L])$, the functions X_1 (Table 5) and X_2 are computed.^{10,11} The former passes through the origin which means that the first complex is not present in appreciable amounts within the range of $[L]$ studied. The function X_2 (Fig. 1) has a straight lined portion extending to $[L] \approx 2.5$ M which yields

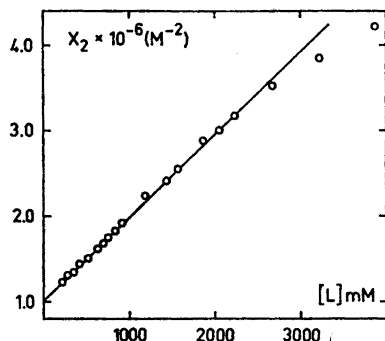


Fig. 1. Evaluation of β_2 and β_3 from the potentiometric measurements.

$\beta_2 = (1.00 \pm 0.05) \times 10^6 \text{ M}^{-2}$ and $\beta_3 = (0.97 \pm 0.05) \times 10^6 \text{ M}^{-3}$, and hence $K_3 = \beta_3/\beta_2 = 0.97 \text{ M}^{-1}$. For $[L] > 2.5$ M, the function bends more and more downwards. This is most likely due to variations in the activity conditions caused by the very extensive exchange of perchlorate for chloride. Such an exchange is known to have a marked influence also upon the silver chloride system, as is shown, *e.g.*, by the variation of the value of the solubility product³ for AgCl with $[\text{Cl}^-]$. The formation of a fourth complex, CuCl_4^{3-} which would have been indicated by an upward bend of X_2 is not found.

Table 5. Evaluation of $[L]$, and subsequent calculation of X_1 .

log X	[L] mM	$X_1 \times 10^{-3}$ M^{-1}	$X_2 \times 10^{-4}$ M^{-2}	log X	[L] mM	$X_1 \times 10^{-3}$ M^{-1}	$X_2 \times 10^{-4}$ M^{-2}
	0	0	1.00	6.20	908	17.4	1.92
4.75	214	2.63	1.23	6.50	1190	26.6	2.24
5.00	277	3.61	1.31	6.70	1440	34.8	2.42
5.20	342	4.62	1.35	6.80	1573	40.1	2.55
5.40	417	6.02	1.45	7.00	1865	53.6	2.88
5.60	514	7.74	1.51	7.10	2045	61.6	3.01
5.80	624	10.1	1.62	7.20	2235	70.7	3.17
5.90	686	11.6	1.69	7.40	2674	93.9	3.52
6.00	754	13.3	1.76	7.60	3220	124	3.85
6.10	828	15.2	1.83	7.80	3870	163	4.22

For the range of $[L]$ where CuCl_2^- and CuCl_3^{2-} are the only mononuclear species existing in appreciable amounts, the ligand number \bar{n}_0 can be calculated from a simplified version of (9):

$$\bar{n}_0 = (2 + 3K_3[L]) / (1 + K_3[L]) \quad (10)$$

This has been done for $[L] > 100$ mM, and the result entered in Fig. 3, together with values of the slope k , as far as these have been possible to estimate with reasonable accuracy. They are throughout much lower which strongly indicates a formation of polynuclear complexes in the solutions.

DERIVATION OF STABILITY CONSTANTS FROM THE SOLUBILITY

As has just been shown, polynuclear complexes are also most probably formed in the present system. The solubility S of copper(I) in contact with CuCl(s) should then be written as:⁴

$$S = \sum_i (\sum_m m K_s^m \beta_{mn}) [L]^{-i} \quad (11)$$

where $i = -(n - m)$ = the charge of the complex formed and K_s = the solubility product of CuCl(s) . If S is known as a function of $[L]$, it is evidently possible to compute, by standard methods, the sum $\sum m K_s^m \beta_{mn}$ for each value of i . This means that each parameter found is a sum, contributed to by all complexes carrying a certain charge. As mentioned in the introduction, the method cannot decide how many neutral units CuCl that are present in the complex. In a range of $[L]$ where only mononuclear complexes are assumed, or known, to exist, eqn. (11) is, for solid phases of the present type, simplified to:

$$S = K_s [L]^{-1} X \quad (12)$$

In this case, the constants found are simply $K_s \beta_n$.

Besides the directly measured quantity S , $[L]$ has to be found. For systems of very low solubility, $[L] \simeq C_L$,* but as far as the present system is concerned this approximation is not good enough for any values of C_L . A perceptible proportion of the ligand ions is always bound in the complexes, i.e. the term $(\bar{n} - 1)S$ in the expression

$$[L] = C_L - (\bar{n} - 1)S \quad (13)$$

is never negligible. If only mononuclear complexes are formed, a good estimation of this quantity can be obtained from the slope of the solubility curve,⁴ i.e. from a plot of $\log S$ against $\log [L]$, or, in the first approximation, $\log C_L$. By combining eqn. (12) with the Bodländer equation $d \log X / d \log [L] = \bar{n}$ we obtain

$$d \log S / d \log [L] = \bar{n} - 1 \quad (14)$$

* In the solubility measurements, C_L means the concentration of ligand added, not including that present as, or coming from, CuCl(s) .

The values of $\bar{n}-1$ obtained from $d \log S/d \log C_L$ are used to calculate values of $[L]$ according to eqn. (13), these are inserted in eqn. (14) to give better values of $\bar{n}-1$, and so on until constant values of $[L]$, $\bar{n}-1$ are reached.

These final values are reached after one or two iterations if the values of C_L and $[L]$ are reasonably close, *i.e.* if $S \ll C_L$, as is the case for low values of C_L in the present system. As C_L is increased, however, the solubility S becomes very high, and, consequently, the approximation $d \log S/d \log C_L = \bar{n}-1$ becomes a very poor one. Many iterations will then be necessary before a constant value of $[L]$ is reached, and it is even found that for high values of S , the series will never converge. It can in fact be proved that the series will become divergent if the ratio S/C_L exceeds a certain value, the magnitude of which depends upon \bar{n} .²⁷

For the present system, the calculation of $[L]$ according to the method outlined may fail also because polynuclear complexes are presumably present in appreciable amounts, at least when the copper(I) concentration, *i.e.* S , is high. In such a case, the slope of the solubility curve, even if it could be properly determined, will not be $\bar{n}-1$, as stated in eqn. (14), but $-\bar{i}$, where \bar{i} = the average charge of the complexes formed, defined by⁴

$$\bar{i} = \frac{\sum_{m,i} mi[M_m L_n^i]}{\sum_{m,i} m[M_m L_n^i]} \quad (15)$$

If the complexes formed are, on the average, anionic, then $-\bar{i} > 0$, whereas if they are cationic, $-\bar{i} < 0$. Only if the system is mononuclear is $-\bar{i} = \bar{n}-1$.

When polynuclear complexes are formed, $-\bar{i} = \bar{n}-1$ only for $\bar{i} = 0$, when $\bar{n} = 1$. For lower values of \bar{n} , $-\bar{i} < \bar{n}-1$, *i.e.* < 0 . For $\bar{n} > 1$, $-\bar{i} > \bar{n}-1$. The difference may grow quite large, with the consequence that not even an approximately correct value of \bar{n} will be found from the slope of the solubility curve. As far as the ligand numbers calculated in this manner, \bar{n}_s , do coincide with those calculated from the mononuclear stability constants found potentiometrically, \bar{n}_o , it is certain, however, that no perceptible formation of polynuclear complexes occurs. On the other hand, once they grow apart polynuclear complexes have begun to form. If so, the solubility measurements will not allow the separation of all stability constants involved, as has already been pointed out.

SOLUBILITY MEASUREMENTS, EXPERIMENTAL

Portions of copper(I) chloride were shaken under nitrogen in glass stoppered bottles with chloride solutions of varying concentrations (all of $I = 5$ M and $h = 0.1$ M). To reduce any traces of copper(II) present, ≈ 0.1 g copper powder was also added. Equilibrium was reached within two days. After equilibration, the solids were allowed to settle, and the solution was then rapidly filtered through a polyvinylchloride membrane of pore size $0.8 \mu\text{m}$ (Gelman VM 4). Aliquots of this solution were repeatedly evaporated almost to dryness with concentrated perchloric acid, to remove all chloride and oxidize all copper to the divalent state. The copper was then estimated spectrophotometrically. For solutions of a copper(II) concentration > 1 mM, ammonia was used, in a concentration of 1 M, and at a constant perchlorate concentration of 1 M. The complexes formed under these conditions had a maximum absorptivity of $58.5 \pm 0.3 \text{ cm}^{-1} \text{ M}^{-1}$ at 610 nm (*cf.* Bjerrum²⁸). For more dilute solutions, cuprizone, *i.e.* bis-cyclohexanone-oxalyldi-

Table 6. The solubility measurements.

C_L mM	S mM	$[L]$ mM	\bar{n}_s	$S_1 \times 10^2$	C_L mM	S mM
7	0.313	6.70	1.96	4.37	1300	154
10	0.431	9.58	1.97	4.29	1500	199
30	1.27	28.7	2.04	4.36	1800	272
40	1.65	38.2	2.07	4.27	2000	327
50	2.15	47.6	2.10	4.48	2300	418
80	3.67	75.8	2.16	4.81	2500	482
90	4.09	85.2	2.17	4.78	2800	584
100	4.68	94.4	2.19	4.94	3000	658
200	10.7	186	2.29	5.74	3300	776
300	18.0	276	2.35	6.51	3500	854
400	26.1	360	2.46	7.20	3800	981
500	35.8	450	2.55	8.04	4000	1094
600	46.9	520	2.62	8.91	4300	1250
700	56.3	610	2.69	9.30	4500	1344
800	73.3	670	2.79	11.0	4800	1514
900	88.2	740	2.82	11.9	5000	1606
1000	102	810	2.85	12.6		

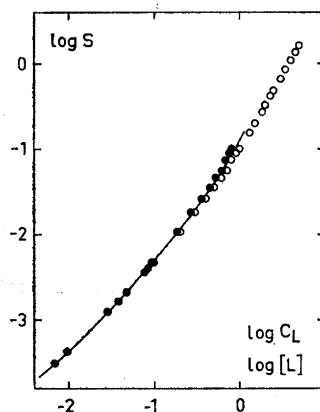


Fig. 2. The solubility curve. Open circles refer to $\log C_L$, filled circles to $\log [L]$. The curve has been calculated from the constants found, by means of eqn. (16).

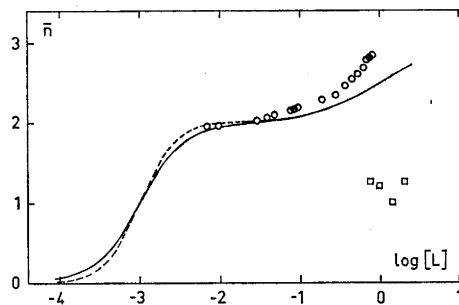


Fig. 3. The complex formation function. The full-drawn curve has been calculated from eqn. (9), or for $\log [L] > -1$ from eqn. (10), with the values of β_2 and β_3 found potentiometrically, and a value of $\beta_1 = 500 \text{ M}^{-1}$, estimated from the solubility measurements. The dashed curve has been calculated with the same values of β_2 and β_3 , and a value of $\beta_1 = 0$. Above $\log [L] = -1.5$, the curves coincide. Values of \bar{n}_s , found from the slope of the solubility curve, are represented by circles. The squares are the slopes k of the (C_L, C_M) -lines of constant $C_M/[M]$.

hydrazone, Merck *p.a.*, was used.¹⁹ In a medium of 0.5 M sodium perchlorate, the complex formed had its maximum absorptivity of $16\,630 \pm 300 \text{ cm}^{-1}\text{M}^{-1}$ at 595 nm.

Solubility values $> 5 \text{ mM}$ could be reproduced within $\pm 1 \%$, for lower values a maximum error of $\pm 4 \%$ was observed.

SOLUBILITY MEASUREMENTS, RESULTS

With increasing values of C_L , the solubility soon reaches very high values, Table 6, and for $C_L > 1000 \text{ mM}$, the iteration procedure for $[L]$ does not result in a converging series. For $C_L \leq 1000 \text{ mM}$, however, *i.e.* for ratios $S/C_L < 0.1$, values of $[L]$ can be calculated, at least formally, and hence the solubility curve $\log S(\log [L])$, Fig. 2. From the slope of this curve, values of \bar{n}_s have been calculated, Table 6. For high values of $[L]$, \bar{n}_s is significantly higher than \bar{n}_0 , Fig. 3. The existence of the polynuclear complexes indicated by the potentiometric measurements is thus confirmed. Consequently, the very calculation of $[L]$ by means of the slopes is somewhat objectionable. In the range where $[L]$ can at all be calculated, however, S is nevertheless so small that even a fairly wrong value of \bar{n} should not cause too large an error in $[L]$. The error will moreover decrease rapidly with S .

With decreasing values of $[L]$ the values of \bar{n}_s approaches the complex formation curve calculated from the potentiometrically determined values of β_2 and β_3 . At $[L] \approx 30 \text{ mM}$, practically the same ligand number $\bar{n} = \bar{n}_0 = 2$ is obtained by both methods. This would mean that, even in a saturated solution, the only complex of a charge $i = -1$ is the mononuclear CuCl_2^- , while polynuclear complexes of a charge $i = -2$ exist, besides the mononuclear CuCl_3^{2-} . For very low values of $[L]$, the uncharged complex CuCl may be formed; due to the extremely low solubility in this region (and hence low values of $[M]$) the existence of uncharged polynuclear complexes is most improbable.

As the solubility curve of Fig. 2 is monotonically increasing, it is further evident that no terms with $-i < 0$ (referring to the free central ion, or to complexes such as M_2L) are of any great consequence. For the present calculations, eqn. (11) can thus be simplified to

$$S = K_s\beta_1 + K_s\beta_2[L] + \sum_m mK_s^m\beta_{m,m+2}[L]^2 + \sum_m \sum_{i=-3}^{i'} mK_s^m\beta_{m,m-i}[L]^{-i} \quad (16)$$

As far as only complexes with a negative charge ≤ 2 are formed, the function S_1 should be linear:

$$S_1 = (S - K_s\beta_1)/[L] = K_s\beta_2 + \sum_m mK_s^m\beta_{m,m+2}[L] + \sum_m \sum_{i=-3} mK_s^m\beta_{m,m-i}[L]^{-i-1} \quad (17)$$

Extrapolation of S to $[L] = 0$ indicates a value of $K_s\beta_1 \approx 2 \times 10^{-5} \text{ M}$. With this value of $K_s\beta_1$ the linearity of S_1 for the lowest values of $[L]$ is also significantly better than if it is assumed that $K_s\beta_1$ is quite negligible. The linear part of S_1 yields $K_s\beta_2 = (4.2 \pm 0.2) \times 10^{-2}$ and $\sum_m mK_s^m\beta_{m,m+2} = (8.3 \pm 1.0) \times 10^{-2} \text{ M}^{-1}$, Fig. 4. It is doubtful whether the upward bend of S_1 for high values of $[L]$ is due to the formation of complexes with a negative charge higher than 2. More likely, it is caused by the circumstance that too low values

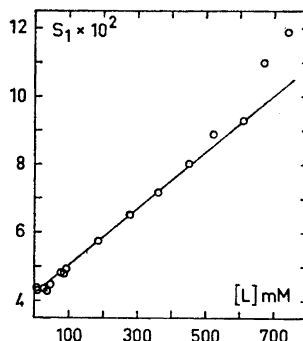


Fig. 4. Evaluation of $K_s \beta_s$ and $\sum m K_s^m \beta_{m,m+2}$ from the solubility measurements.

of $[L]$ result from the application of eqns. (14) and (13) when polynuclear complexes are present.

With the value of β_2 found from the potentiometric measurements, a value of $K_s = (4.2 \pm 0.3) \times 10^{-8} \text{ M}^{-2}$ is calculated. With the value of $K_s \beta_1$ estimated above this would mean $\beta_1 = K_1 \approx 500 \text{ M}^{-1}$, and hence $K_2 = \beta_2 / \beta_1 \approx 2000 \text{ M}^{-1}$. Combining K_s with the potentiometrically determined β_3 results in $K_s \beta_3 = (4.1 \pm 0.3) \times 10^{-2}$. On the simplest assumption conceivable that the only complex of charge -2 besides the mononuclear CuCl_3^{2-} is the dinuclear $\text{Cu}_2\text{Cl}_4^{2-}$, the stability constant of this complex is $\beta_{24} = (1.2 \pm 0.5) \times 10^{13} \text{ M}^{-5}$. For the dimerization $2 \text{CuCl}_2^- \rightleftharpoons \text{Cu}_2\text{Cl}_4^{2-}$ a constant $K_{d2} = \beta_{24} / \beta_2^2 = 12 \pm 6 \text{ M}^{-1}$ is then computed.

With decreasing $[L]$, the free central ion concentration $[M]$ will sooner or later become a perceptible part of S . Even if this part *per se* is small, it may imply a disproportionation of copper(I) which is not negligible. It is therefore of interest to calculate $[M]$ for the lowest values of $[L]$ used, and the accompanying disproportionation at equilibrium. In the range of $[L]$ considered, only mononuclear complexes exist, and therefore:

$$[M] = S / (1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3) \quad (18)$$

For the lowest value used, $[L] = 6.7 \text{ mM}$ (Table 6), $[M] = 6.3 \times 10^{-6} \text{ M}$, or close to 2 % of S . Once equilibrium is reached, the value of $[M]_{\text{II}}$ will be $3.5 \times 10^{-5} \text{ M}$, or about 10 % of S . Already for the next lowest value, $[L] = 9.58 \text{ mM}$, $[M]_{\text{II}}$ is only ≈ 3.5 % of S , and for all higher values of $[L]$ the disproportionation is completely negligible.

Nevertheless, in the solutions of the lowest chloride concentrations, the copper possibly present in the divalent state may be a substantial part of S , in spite of the fact that the values of \bar{n} are still fairly high in these solutions. The reason is that the first complex is so unstable, that perceptible amounts of Cu^+ is formed as soon as \bar{n} is significantly below 2, and consequently a significant disproportionation becomes possible even for solutions of \bar{n} close to 2. This disproportionation may partly, or even wholly, account for the effect ascribed above to the formation of the complex CuCl . Therefore, β_1 , may in fact have any value between 0 and $\approx 500 \text{ M}^{-1}$. In Fig. 3, the complex formation curve has been calculated from eqn. (9) for these two limits of β_1 .

Even if β_1 is assumed to be at the upper limit, the first complex is evidently not of much consequence in this system.

Table 7. Comparison of some mononuclear stability constants reported for the copper(I) and silver(I) chloride systems.

<i>t</i> °C	<i>I</i> M	log K_n				log β_n			p K_s	Ref.
		1	2	3	4	2	3	4		
copper(I)										
25	5	2.70	3.30	-0.01	<-1.3	6.00	5.99	<4.7	7.38	^a
18	var.					4.60			5.92	5
18	var.			0.2		5.5	5.7			5,20,30
25	0					5.31			6.50	31,32
25	1			-0.35						33
25	4			-0.04						34
20	0			0.2		5.5	5.7			35
25	6.5			-0.06	-0.4	6.04	5.98	5.6		36
25	14			-0.22	-0.4	6.30	6.08	5.7		37
silver(I)										
25	5	3.08	2.32	0.75	-0.85	5.40	6.15	5.30	10.10	3,38
25	0	3.04	2.00	0.00	0.26	5.04	5.04	5.30	9.75	3,38

^a This work.

COMPARISON WITH PREVIOUS WORK, CONCLUSIONS

In Table 7, the results of some previous investigations of the copper(I) chloride system have been compared with those now found. The most direct comparison should be possible with the solubility study of Vestin *et al.*³⁴ In the notation of the present paper, they report $K_s\beta_2=4.47 \times 10^{-2}$ and $\sum m K_s^m \beta_{m,m+2}=4.05 \times 10^{-2} \text{ M}^{-1}$. The value of $K_s\beta_2$ agrees with our value, but $\sum m$ the sum pertaining to complexes of charge -2 is only about half of what we have found. As only solubility measurements have been performed, it is not possible to decide whether polynuclear complexes are formed. The authors have tacitly assumed that only mononuclear complexes exist. On this assumption, the sum above has been identified with the product $K_s\beta_3$, and hence the value of K_3 entered in Table 7 has been obtained. This value is very close to our value of K_3 , obtained after due correction for the polynuclear complexes which have been shown to exist in our solutions. This is most plausibly explained by assuming that polynuclear species do exist also in the medium used by Vestin *et al.* (4 M acid) but that the constants of the complexes of charge -2 have values markedly different from those found for our medium.

Recently, Sukhova *et al.*^{36,37} have performed fairly extensive potentiometric investigations, using ammonium nitrate media of $I=6.5$ and 14 M. They also find that polynuclear complexes are very important constituents of the system. We have not been able to confirm their conclusion, however, that such complexes exist even with a charge of -1 . It is not excluded that the authors have in fact rather strained their experimental material in order to calculate the very large number of polynuclear constants which are finally reported. As to the mononuclear complexes, the values of β_2 and β_3 are quite consistent with our results while that of β_4 is at least one power of ten higher than the highest value compatible with our measurements (Table 7).

The main conclusion from most previous investigations^{5,30,33-35} is that CuCl_2^- and CuCl_3^{2-} are predominant species within a wide range of chloride concentrations. This has been confirmed. The species CuCl_4^{3-} is certainly not formed in appreciable amounts for $[\text{L}] < 2.5$ M, presumably not for $[\text{L}] < 5$ M. This would mean that the value of β_4 is in any case $< 5 \times 10^4 \text{ M}^{-4}$; *i.e.* $K_4 < 0.05 \text{ M}^{-1}$. For values of $[\text{L}] < 0.01$ M, on the other hand, the uncharged complex CuCl may possibly be formed. The existence of polynuclear complexes of charge -2 has been established beyond doubt, by combination of potentiometric and solubility measurements.

As seen already from the well-developed inflexion of the complex formation curve around $\bar{n}=2$, Fig. 3, the third complex is only reluctantly formed from the second one. The second complex has a very wide range of existence, as is also reflected by the very high value of the ratio K_2/K_3 . With $K_2 \approx 2000 \text{ M}^{-1}$ which, as pointed out above, should be regarded as a minimum, $K_2/K_3 \approx 2000$ which would mean that the second complex would attain a maximum share of 96 % of the total copper(I) concentration, at $\bar{n}=2$ (*cf.* Ref. 10, p. 30). If K_2 is in fact larger which is very probable, the maximum share would be still higher, reaching well over 98 % for the lower limit of $\beta_1=0$.

Even for the upper limit of $K_1=500 \text{ M}^{-1}$, the maximum share of CuCl (at $\bar{n}=1$) would not be higher than 20 % which further illustrates the low stability of the first complex.

In Table 7, data for the silver(I) chloride system^{3,38} have also been entered for comparison. Both obvious similarities and striking differences are observed between the systems. The second complex is preferred in both cases, but much more strongly for copper(I). The wider range of existence of CuCl_2^- relative to AgCl_2^- depends on a higher value of K_2 , and, at least as far as solutions of $I=5$ M are concerned, also on a lower value of K_3 , resulting in a much higher value of the crucial ratio K_2/K_3 for the copper(I) system. The high solubility of copper(I) in chloride solutions as compared with silver(I) depends mainly upon that the value of K_s is much higher for CuCl(s) than for AgCl(s) .

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