

Thermodynamics of Metal Complex Formation in Aqueous Solution. XII. Equilibrium Measurements on the Copper(I) Bromide, Iodide and Thiocyanate Systems

STEN AHRLAND and BERNT TAGESSON

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden

The bromide, iodide and thiocyanate complexes of copper(I) have been studied in aqueous solution at 25 °C, in a sodium perchlorate medium of ionic strength $I=5$ M. Both potentiometric and solubility measurements have been performed. At low metal concentrations, mononuclear complexes predominate. The solubilities of the complexes decrease and the stabilities increase in the order bromide, iodide, thiocyanate. For iodide and thiocyanate, but not for bromide, a fourth complex is formed within the available concentration range. At higher metal concentration, polynuclear complexes exist in appreciable concentrations.

Copper(I) seems to be the only oxidation state of a first row transition element showing typical class (b) behaviour, characterized *inter alia* by the halide affinity sequence $F^- \ll Cl^- < Br^- < I^-$ in aqueous solution.^{1,5} The complex formation of an acceptor in such a unique position is of special interest. The hydrated copper(I) ion disproportionates almost completely, except at extremely low concentrations. Copper(I) is therefore stable in aqueous solution only in the presence of ligands forming strong complexes. The thiocyanate ion and all the halide ions with the exception of the fluoride ion belong to this group, see *e.g.* Ref. 3. Their complex formation has in fact been studied since the beginning of the century⁴ but due to the severe experimental difficulties many points have nevertheless remained obscure. It therefore seemed worthwhile to reinvestigate the systems. The first results of these studies, concerning copper(I) chloride, were published some years

ago.⁵ In this paper, the bromide, iodide and thiocyanate equilibria are discussed.

The chief method of measurement was the potentiometric determination of the free central ion concentration $[Cu^+]$ by means of a copper amalgam electrode. From these measurements both the stability constants and the solubility products were obtained. To check these results some solubility measurements have also been performed.

In the present systems, complexes beyond the second one are formed in appreciable amounts only at fairly high ligand concentrations. In order to cover also these equilibria, a medium of high ionic strength has to be used. The measurements have therefore been performed at $I=5$ M with sodium perchlorate as supplementary neutral salt. This choice also allows a direct comparison with the previous measurements of copper(I) chloride,⁵ silver(I) halide⁶⁻⁹ and silver(I) thiocyanate¹⁰ complexes performed in the same, or almost the same, medium.

The lower limit of the ligand concentration is set by the low solubility of the neutral complexes CuL . As soon as these constitute an appreciable part of the copper(I) present in the solution, the total solubility becomes too low for potentiometric measurements. Even when solubility measurements are used, solutions containing much of the copper(I) as CuL are difficult to reach. The final lower limit for the ligand concentration is determined by the disproportionation reaction (*cf.* Ref. 5).

On account of this disproportionation, the potentiometric determination of the equilibrium

constants of the copper(I) system cannot take place according to the standard procedure. The formal standard potential E°_I of the couple $\text{Cu}^+/\text{Cu}(\text{Hg})$ cannot be directly measured. It has to be calculated *via* the disproportionation constant K and the formal standard potential E°_{II} of the couple $\text{Cu}^{2+}/\text{Cu}(\text{Hg})$. The latter quantity can be directly measured only in acidic solutions where the hydrolysis of copper(II) does not interfere. For the chloride system measured previously, and also for the present bromide measurements, an 0.1 M acid medium has therefore been chosen, brought about by an appropriate substitution of perchloric acid for sodium perchlorate. On account of the decomposition of acid thiocyanate solutions, and the rapid oxidation of acid iodide solutions, an acid medium is unsuitable in these cases. Neutral solutions have therefore been used, and the appropriate value of E°_{II} found by an extrapolation procedure; cf. Procedure. All measurements have been performed at 25 °C.

CALCULATIONS

Potentiometric measurements. The emf of the cell (I) given in Scheme 1 can be written ($[\text{M}] = [\text{Cu}^+]$):

$$E_I = E^\circ_I - (RT/F) \ln [\text{M}] \quad (1)$$

As has already been pointed out, E°_I cannot be measured directly, on account of the disproportionation of Cu^+ taking place in solutions without a stabilizing ligand. The value of E°_I can be found, however, from the formula:⁵

$$E^\circ_I = (RT/2F) \ln K - E^\circ_{II} \quad (2)$$

where K is the disproportionation constant:

$$K = [\text{M}]^2/[\text{M}]_{II} \quad ([\text{M}]_{II} = [\text{Cu}^{2+}]) \quad (3)$$

which is known for the medium used,⁵ while E°_{II} is determined by means of the cell (II) given in Scheme 1 with the emf:

$$E_{II} = E^\circ_{II} + (RT/2F) \ln [\text{M}]_{II} \quad (4)$$

As $[\text{M}]_{II}$ is known, E°_{II} can be calculated, and hence E°_I from eqn. (2). From eqn. (2), $[\text{M}]$ is then found, and as C_M is known from the added amount of copper(I), the function $C_M/[\text{M}]$ needed for the preliminary graphical evaluation of the stability constants can be calculated.

The information about the composition and the stability of the complexes obtained by this graphical treatment is then fed into the computer program EMK (cf. Ref. 11) which yields the final refined values of the equilibrium constants.

The formulas used for the graphical evaluation have been derived before^{12,13} and only a brief summary will be given here. If only mononuclear complexes are formed, $C_M/[\text{M}]$ will be a function of the free ligand concentration $[\text{L}]$ only:

$$C_M/[\text{M}] = X = 1 + \sum_{j=1}^N \beta_j [\text{L}]^j \quad (5)$$

In this case, the functions $C_L(C_M)$ for constant X are straight lines with the intercepts $C_L = [\text{L}]$ and the slopes equal to the ligand number $\bar{n} = (C_L - [\text{L}])/C_M$. X is thus obtained as a function of $[\text{L}]$ and from this function the stability constants can be calculated.

If polynuclear complexes are formed as well, the curves $C_L(C_M)$ are no longer straight lines with the slopes \bar{n} . Extrapolation to $C_M = 0$ will nevertheless yield corresponding values of $[\text{L}]$ and X and hence the mononuclear constants β_j , just as before.¹² The slopes at the point of intersection, i.e. at $C_M = 0$, are $< \bar{n}$,

(I)

$-\text{Cu}(\text{Hg})$	$\begin{array}{l} C_M \text{ M Cu(I)} \\ C_L \text{ M ligand} \\ 0.1 \text{ M HClO}_4 \\ I = 5.00 \text{ M (NaClO}_4\text{)} \end{array}$	$\begin{array}{l} 0.1 \text{ M HClO}_4 \\ 4.9 \text{ M NaClO}_4 \end{array}$	$\begin{array}{l} 0.1 \text{ M HCl} \\ 4.9 \text{ M NaClO}_4 \end{array}$	$\text{Ag, AgCl} +$
-------------------------	---	--	---	---------------------

(II)

$-\text{Ag, AgCl}$	$\begin{array}{l} 0.1 \text{ M HCl} \\ 4.9 \text{ M NaClO}_4 \end{array}$	$\begin{array}{l} 0.1 \text{ M HClO}_4 \\ 4.9 \text{ M NaClO}_4 \end{array}$	$\begin{array}{l} [\text{M}]_{II} \text{ M Cu(II)} \\ 0.1 \text{ M HClO}_4 \\ I = 5.0 \text{ M (NaClO}_4\text{)} \end{array}$	$\text{Cu(Hg)} +$
--------------------	---	--	---	-------------------

Scheme 1.

however, and the difference is often very considerable. This is so in the case of copper(I) iodide and thiocyanate which certainly indicates that appreciable amounts of polynuclear complexes are formed in these systems.

The program EMK in the version used here is able to compute simultaneously both mononuclear and dinuclear complexes. When polynuclear complexes are indicated by the graphical evaluation, various plausible dinuclear complexes, or combinations of such complexes, have been fed into the program, beside the mononuclear complexes already identified. The best values are found by minimizing the error square sum

$$U(\beta_{j,k}) = \sum_{i=1}^N w_i (E_{M,i,calc} - E_{M,i})^2 \quad (6)$$

$$\text{where } E_M = (RT/F) \ln C_M/[M] \quad (7)$$

and the weighting term $w_i = 1$.

For both iodide and thiocyanate, the introduction of one single dinuclear complex makes $U(\beta_{j,k})$ so low that the deviations between measured and calculated values of E_M are clearly within the experimental error. A more sophisticated interpretation of the experimental data is therefore neither necessary nor possible.

Solubility measurements. In order to extend the potentiometric measurements to as low values of \bar{n} as possible some series were performed in such a way that the value of $[L]$ decreased during the series until finally a precipitate CuL formed. As indicated by the attainment of a constant emf, equilibrium between the solution and the solid phase was reached within a few hours; *cf.* Procedure. From these solutions, the total solubilities S of the various copper(I) systems, as a function of $[L]$, could be determined, as could also the solubility products K_s of $CuL(s)$. By combining these determinations, several of the constants β_j can be calculated from measurements which are independent of the previously measured emf's.

The values of S were found from analyses of the equilibrium solutions, as described in Procedure. The corresponding values of $[L]$ were calculated from

$$[L] = C_L - (\bar{n} - 1)S - C_M \quad (8)$$

where C_L and C_M denote the stoichiometric concentrations added, whether still in solution or precipitated. As the correction term $(\bar{n} - 1)S$ never exceeds a few per cent of C_L , a sufficiently accurate value of \bar{n} can be estimated from the potentiometric measurements. It also turns out that the values of $[L]$ thus obtained are not changed appreciably if \bar{n} is instead calculated from the solubility function, as described previously.⁵ As $[M]$ is directly measured (eqn. 1),

$$K_s = [M][L] \quad (9)$$

can be calculated once $[L]$ is known.

From the solubility function $S([L])$ it cannot be discerned whether polynuclear complexes are formed or not, for the inherent reason that the method does not allow various values of C_M (*i.e.* S) for a fixed value of C_L . In these systems where the solid phases are composed CuL , the number of such entities present in the complexes remains unknown.^{13,14} Generally, the evaluation of $S([L])$ would only yield sums of constants for complexes of the same charge. For the present systems, however, the potentiometric measurements prove that only mononuclear complexes exist in appreciable amounts in the concentration range where the solubility measurements are performed. Consequently, $S([L])$ is of the simple form

$$S = K_s[L]^{-1}X \quad (10)$$

At first, the constants $K_s\beta_j$ are obtained and from these β_j can be found as K_s is known. The evaluation is performed numerically by a least-squares program.

Immediate information about the predominating complexes is obtained from the slopes of the solubility curves $\log S(\log [L])$ which for the present solid phases of the composition CuL are $\bar{n} - 1$ (*cf.* Ref. 14).

EXPERIMENTAL

Chemicals and analysis. Copper(I) bromide, copper(I) iodide and copper(I) thiocyanate (BDH) were used without further purification. Traces of copper(II) present (<2 %) were reduced by treating the copper(I) solutions with copper amalgam.

Sodium perchlorate (Fluka) was purified by recrystallisation between 140 °C and 110 °C. The crystals were dried at 140 °C.

Sodium bromide (Malinckrodt *p.a.*), sodium iodide (Merck *p.a.*) and sodium thiocyanate (Malinckrodt *p.a.*) were used without further purification. The stock solutions were analyzed argentometrically, with dichlorofluorescein as indicator.

Copper amalgam containing $\approx 3\%$ copper was prepared by electrolyzing a copper(II) perchlorate solution with a mercury pool as cathode. At room temperature, a two-phase amalgam is formed between 0.0032 and 24.1 % copper.^{15,16} Within this range, the potential will be independent of the composition, and the exact concentration of copper is therefore unimportant.⁵ A high copper content should be avoided, however, as the amalgam then becomes inconveniently stiff. The amalgam was stored under 0.1 M perchloric acid. Prior to use it was washed with dilute perchloric acid to remove traces of copper(II).

Analysis. The copper(I) solutions were oxidized and the concentration of copper(II) then determined spectrophotometrically by means of the cuprizone complex.¹⁷ For bromide and iodide, the oxidation was brought about by concentrated perchloric acid. The samples were then evaporated to dryness in order to remove the halide and the excess acid. A maximum molar absorptivity $\epsilon = 16\,360\text{ M}^{-1}\text{ cm}^{-1}$ was found at 600 nm, as compared with $\epsilon = 16\,520\text{ M}^{-1}\text{ cm}^{-1}$ quoted in the original investigation.¹⁷ For thiocyanate this technique was not possible due to the decomposition of thiocyanate in acid solution. Instead the samples were diluted and then oxidized by air. The analysis was then carried out in 0.5 M sodium thiocyanate solution, where slight variations in the thiocyanate concentration did not influence the absorbance. For this solution a maximum absorbance of $\epsilon = 16\,550\text{ M}^{-1}\text{ cm}^{-1}$ was found at 600 nm.

Apparatus. The emf's were measured by means of a "Norma Präz. Kompensationsapp. Mod 54" combined with a Kipp galvanometer allowing a precision of 0.01 mV. The silver-silver chloride electrodes were prepared according to Brown.¹⁸ The electrode solutions, in vessels of the Ingold type, were kept at $25.0 \pm 0.1^\circ\text{C}$ by means of water circulating in an outer jacket. The ligand solutions were added from a Methrohm piston burette.

Procedure. The measurements for determination of E°_{II} were arranged as titrations where a copper(II) solution was titrated into the initial sodium perchlorate solution. The measurements for the iodide and thiocyanate systems had to be performed in neutral solutions where, however, the value of E°_{II} cannot be directly measured; cf. Introduction. Instead it was obtained by measuring cell II at different acidities in the right hand half-cell and subsequent extrapolation to zero acidity. For $[\text{H}^+] = 0.1\text{ M}$, $E^\circ_{\text{II}} = 107.2 \pm 0.4\text{ mV}$, while for $[\text{H}^+] = 0.01\text{ M}$ the value of E°_{II} was 2.6 mV higher. Hence for a neutral solution $E^\circ_{\text{II}} =$

$110.1 \pm 0.4\text{ mV}$. These values are the mean of about 15 determinations of E°_{II} within the range $0.5 \lesssim [\text{M}]_{\text{II}} \lesssim 25\text{ mM}$. The values of E°_{II} could be reproduced within $\pm 0.3\text{ mV}$, and they did not depend upon $[\text{M}]_{\text{II}}$, which means that the copper amalgam electrodes behaved according to Nernst's law.

With the value of E°_{II} thus found and with $K = (1.13 \pm 0.13) \times 10^{-8}\text{ (M)}$, eqn. (2) yields $E^\circ_{\text{I}} = -286.0 \pm 1.5\text{ mV}$ for neutral solution and $E^\circ_{\text{I}} = -283.1 \pm 1.5\text{ mV}$ for $[\text{H}^+] = 0.1\text{ M}$.

In the main measurements, solutions of the left half-cell of cell I were obtained by adding $v\text{ cm}^3$ of a solution T to $V_0\text{ cm}^3$ of a solution S. Two different titration series were performed on each system using either (a) $T' = 4.9\text{ M NaBr}$, 0.1 M HClO_4 , or 5 M NaI if $L = \text{I}$ or SCN ; or (b) $T'' = 4.9\text{ M NaClO}_4$, 0.1 M HClO_4 (if $L = \text{Br}$), or 5 M NaClO_4 (if $L = \text{I}$ or SCN).

The solution S had the composition: $C_{\text{M}}\text{ M Cu(I)ClO}_4$; $C_{\text{L}}\text{ M NaL}$, $L = \text{Cl, Br or SCN}$; $I = 5\text{ M}$ by means of NaClO_4 , or, if $L = \text{Br}$, $\text{NaClO}_4 + 0.1\text{ M HClO}_4$. The S-solutions were prepared by dissolving copper(I) halide or thiocyanate in a ligand solution of a concentration high enough to ensure complete dissolution. Before adding the copper(I) halide, or thiocyanate, the solutions were made free from oxygen by nitrogen bubbling for about 30 min. Traces of copper(II) in this solution were reduced by shaking the solution overnight with copper amalgam under nitrogen. Before the transfer to the Ingold vessel the absence of copper(II) was checked by a negative cuprizone test. At the same time samples were withdrawn which after oxidation were used to determine the total copper concentration by cuprizone, as outlined in Analysis. Oxygen-free nitrogen was continuously bubbling through the left half-cell of cell I, in order to mix the solutions and prevent oxidation. The T-solutions were also freed from oxygen by nitrogen bubbling. In order to obtain the right vapour pressure, the nitrogen was passed through 5 M NaClO_4 before entering the solutions.

Titration series with solution T' were performed with at least three different initial concentrations of copper(I), ranging from 1 to 20 mM, in the S-solutions. Constant values of the emf's were reached within 5 min. Each series was repeated at least once, and the reproducibility was found to be within $\pm 0.3\text{ mV}$. At the end of some series, samples were withdrawn for direct analytical determination by cuprizone both of copper(II) and total copper content. In no case was copper(II) found and the total copper concentration had not changed significantly from that calculated from the initial one, from which follows that no oxidation of copper(I) or copper amalgam had taken place.

The titration series with solutions T'' were performed with at least five different initial copper(I) concentrations, ranging from 1 to 25 mM. These titrations were performed in the

same way as the T' titrations until copper(I) halide, or thiocyanate, began to precipitate. Equilibrium between the saturated copper(I) ligand solution and the precipitated solid CuL was attained about four hours after the precipitate had started to form, as indicated by the establishment of a stable emf. The equilibrium potentials remained very constant drifting $\lesssim 0.3$ mV in two days. Due to the fairly slow attainment of the heterogeneous equilibrium, the titrations were not continued once a precipitate had formed. When equilibrium had been reached, samples were taken to determine the solubility S . The samples were filtered through a glass filter G4 and then analyzed by the cuprizone method.

MEASUREMENTS AND RESULTS

Potentiometric measurements. The emf's for a random selection of points are shown in Figs. 1, 2 and 3. Complete potentiometric data are obtainable from the authors.

The stability constants calculated from the potentiometric data by means of the least-squares EMK program are shown in Table 1. The mononuclear constants found by the graphical evaluations of the bromide, iodide and thiocyanate systems did not deviate significantly from the numerical constants listed in Table 1.

Copper(I) chloride. The constants of the chloride system have been recalculated by means of the EMK program. The new values, of β_2 and β_3 , differ from the previous ones, evaluated graphically,⁵ by amounts just outside

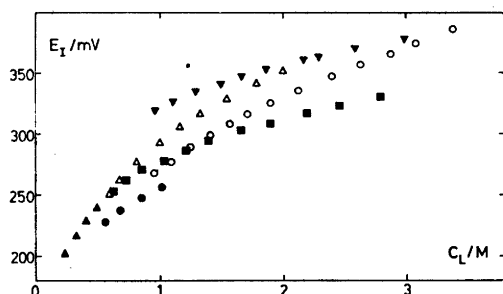


Fig. 1. Copper(I) bromide. A random selection of the measured emfs E_I . Filled and open symbols refer to titrations with 5.0 M sodium perchlorate (emf decreasing) and 5.0 M sodium halide (emf increasing), respectively. The initial and final copper(I) concentrations are (mM): ∇ 5.25, 1.70; Δ 5.67, 3.85; \blacktriangle 6.19, 3.02; \circ 12.7, 5.08; \bullet 22.9, 12.7; \blacksquare 27.9, 6.00.

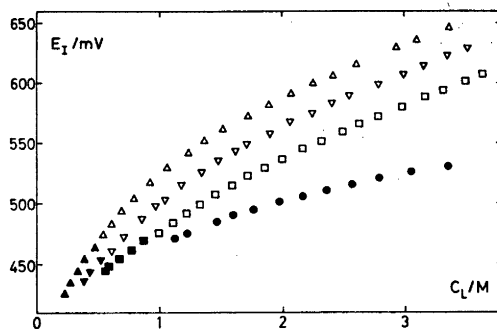


Fig. 2. Copper(I) iodide. A random selection of the measured emfs E_I (cf. Fig. 1). The initial and final copper(I) concentrations are (mM): \blacktriangle 0.72, 0.34; \triangle 0.71, 0.26; \blacktriangledown 1.50, 1.08; \triangledown 1.76, 0.59; \blacksquare 4.00, 2.56; \square 4.56, 1.52; \bullet 23.8, 7.93.

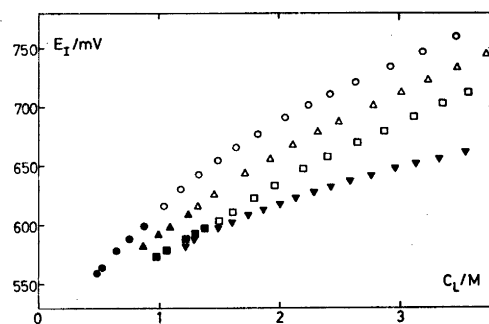


Fig. 3. Copper(I) thiocyanate. A random selection of the emfs E_I (cf. Fig. 1). The initial and final copper(I) concentrations are (mM): \bullet 0.96, 0.54; \circ 0.92, 0.35; \blacktriangle 2.48, 1.71; \triangle 2.44, 0.83; \blacksquare 5.63, 3.98; \square 6.18, 2.47; \blacktriangledown 18.3, 6.23.

the random errors; Table 1. The value of the dinuclear constant β_{42} , previously determined by a combination of potentiometric and solubility measurements,⁵ has been nicely confirmed by the present calculation which involved only the potentiometric data.

Copper(I) bromide. The functions $C_M/[M](C_L)$ calculated from the family of functions $E_I(C_L)$ plotted in Fig. 1 do not vary significantly between the series of different copper(I) concentrations. Consequently, within the limits of random errors, $[L] \approx C_L$. For the further calculations, the mean of the C_L -values found for each $C_M/[M]$ was therefore taken as $[L]$. From this follows that the curves $C_L(C_M)$ ($C_M/[M] = \text{constant}$) have no defined slopes.

Table 1. The overall stability constants β_i and the solubility products K_s for the copper(I) systems. The limits of error correspond to three standard deviations, as obtained by the computer or as estimated.

	Chloride Graphical	Chloride Numerical	Bromide	Iodide	Thiocyanate
A. Potentiometric measurements					
β_2/M^{-2}	$(1.00 \pm 0.05) \times 10^6$	$(1.14 \pm 0.06) \times 10^6$	$(1.89 \pm 0.25) \times 10^6$	$(4.8 \pm 3.7) \times 10^8$	
β_3/M^{-3}	$(0.97 \pm 0.05) \times 10^6$	$(0.87 \pm 0.04) \times 10^6$	$(2.80 \pm 0.05) \times 10^7$	$(2.70 \pm 0.11) \times 10^{10}$	$(4.01 \pm 0.15) \times 10^{11}$
β_4/M^{-4}				$(2.50 \pm 0.30) \times 10^9$	$(10.51 \pm 0.12) \times 10^{11}$
β_{23}/M^{-5}	$(12 \pm 5) \times 10^{13}$	$(8.8 \pm 3.5) \times 10^{13}$			
β_{24}/M^{-7}				$(10.0 \pm 1.2) \times 10^{21}$	$(2.17 \pm 0.30) \times 10^{24}$
K_d/M^{-1}	12 ± 6^a	7 ± 4^a		14 ± 2^b	14 ± 2^b
B. Solubility measurements					
K_s/M^3	$(4.2 \pm 0.3) \times 10^{-8}$		$(1.30 \pm 0.06) \times 10^{-9}$	$(1.92 \pm 0.06) \times 10^{-13}$	$(1.71 \pm 0.16) \times 10^{-15}$
β_2/M^{-2}			$(1.5 \pm 1.0) \times 10^6$		
β_3/M^{-3}			$(3.0 \pm 0.5) \times 10^7$	$(2.8 \pm 0.4) \times 10^{10}$	$(5.4 \pm 1.6) \times 10^{11}$
β_4/M^{-4}				$(7.9 \pm 7.4) \times 10^9$	$(10.8 \pm 1.6) \times 10^{11}$

^a $K_d = \beta_{23}/\beta_2^2$ is the constant for dimerization according to $2 \text{ Cu}_2\text{L}_3^{2-} \rightleftharpoons \text{Cu}_4\text{L}_6^{4-}$.

^b $K_d = \beta_{24}/\beta_2^2$ is the constant for dimerization according to $2 \text{ Cu}_2\text{L}_3^{2-} \rightleftharpoons \text{Cu}_4\text{L}_6^{4-}$.

Consequently, no information can be obtained about the possible existence of polynuclear complexes. The graphical evaluation indicated that the second and the third mononuclear complex were formed within the range covered. These were also the only complexes found in the subsequent numerical calculation. For the stability constant of the first complex no significant value was found, $\beta_1 = (0 \pm 0.13) \times 10^6 \text{ M}^{-1}$. As expected from the graphical evaluation, tests with dinuclear complexes, *viz.* $\text{Cu}_2\text{Br}_2^{2-}$ and $\text{Cu}_2\text{Br}_4^{4-}$, did not give a better fit. This difference from the other systems might, however, at least partly be due to the fact that the random errors are evidently somewhat larger for the bromide system. *Per se*, a formation of polynuclear complexes is of course plausible also in this system, though probably to a lower degree than for iodide or thiocyanate, *cf.* the corresponding silver(I) systems.⁷⁻¹⁰

Copper(I) iodide. For this system the functions $C_M/[M](C_L)$ calculated from the family of functions $E_I(C_L)$, Fig. 2, varied significantly with C_M . The functions $C_L(C_M)(C_M/[M] = \text{constant})$ were fairly well-defined lines, yielding, [L] by extrapolation to $C_M = 0$. Their slopes were negative, however, varying between -1 and -8 . These values are evidently much lower than \bar{n} , indicating that polynuclear complexes are formed in appreciable amounts. Graphically,

the second, third and fourth mononuclear complexes are indicated. In the numerical calculation, various dinuclear complexes have been introduced besides the mononuclear ones. The best fit is found with $\text{Cu}_2\text{I}_6^{4-}$, with an error square sum $\approx 25\%$ of that found by the calculation involving only mononuclear complexes.

Copper(I) thiocyanate. Also in this system the functions $C_M/[M](C_L)$ calculated from $E_I(C_L)$, Fig. 3, varied significantly with C_M . The functions $C_L(C_M)(C_M/[M] = \text{constant})$ are again well-defined lines, yielding [L] by extrapolation. The slopes are ≈ 1 , *i.e.* much higher than in the iodide system: Still they are evidently much lower than \bar{n} , indicating the formation of considerable amounts of polynuclear complexes also in this system. Graphically, only the third and fourth mononuclear complexes were found. This was confirmed by the numerical calculations which yielded $\beta_2 = (0 \pm 0.21) \times 10^{11} \text{ M}^{-2}$. Introduction of the dinuclear complex $\text{Cu}_2(\text{SCN})_6^{4-}$, in addition to CuL_3^{2-} and CuL_4^{2-} , reduces the error square sum to $\approx 16\%$ of that obtained for only mononuclear complexes. Introduction of $\text{Cu}_2(\text{SCN})_7^{5-}$ results in an even better fit ($\approx 13\%$ of the mononuclear sum). A value of $\beta_{72} = (9.8 \pm 1.1) \times 10^{24}$ was obtained while β_3 and β_4 remained much the same as in Table 1A.

Considering the rather unlikely configuration of a complex $\text{Cu}_2(\text{SCN})_7^{4-}$ and the slight difference in fit between the two dinuclear complexes tried, we think $\text{Cu}_2(\text{SCN})_6^{4-}$ the most plausible alternative, especially as the analogous $\text{Cu}_2\text{I}_6^{4-}$ seems the best one to adopt in the iodide system.

Solubility measurements. From the corresponding values of S and $[\text{L}]$ determined as described in Procedure, the solubility curves $\log S(\log [\text{L}])$ presented in Fig. 4 have been calculated for the systems investigated. The potentiometric measurements indicate that for no point in the solubility measurements have the amounts of polynuclear complexes exceeded 5 % of the total copper(I) concentration. For most points the figure is in fact $< 2\%$. Consequently, eqn. (10) applies within the limits of error, and the constants directly found are $K_s\beta_j$. The slopes of the solubility curves confirm that for the bromide system only the second and third complexes, for the iodide and thiocyanate systems only the third and fourth complexes, are present in appreciable amounts. With the values of K_s determined as described in Solubility measurements, the values of β_j can be found immediately, Table 1B. For the bromide and iodide systems only the values of β_3 are in fact significant, while for the thiocyanate system a value of β_4 is also obtained. This is to be expected, as the third complex strongly predominates in the concentration ranges used for the bromide and iodide measurements, while large amounts of the fourth complex are present in the case of the thiocyanate,

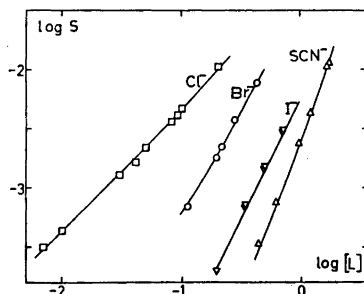


Fig. 4. The solubility curves of the copper(I) halide and thiocyanate systems. The points refer to the solubilities directly measured, while the full drawn curves have been calculated from the stability constants and the solubility products listed in Table 2.

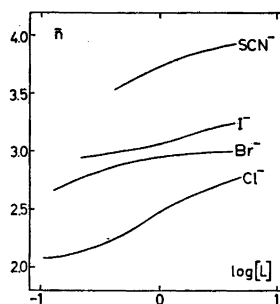


Fig. 5. The complex formation functions of the copper(I) systems, as calculated from the constants listed in Table 2.

cf. Fig. 5. In so far as significant values of β_j are obtained from the solubility measurements, they agree very well with those obtained potentiometrically which are thus confirmed; cf. Table 1. The precision is far better with the latter method, however, as is evident from the random errors of β_j listed. This is why those values have been used in the following discussion. The differences between these values and a weighted mean of the constants found by the two methods are in any case insignificant.

COMPARISON WITH PREVIOUS WORK, DISCUSSION

In Table 2, the results of the present studies are compared to those found in earlier investigations. The table also lists the constants found for the analogous silver systems.

A direct comparison between the various results presupposes, of course, that the constants have been determined under the same, or at least similar, conditions. For the copper(I) chloride system this was the case in some instances. A reasonable agreement was indeed found, at least for the principal constants.⁵ For the bromide system, only one investigation¹⁰ has been performed under conditions somewhat similar to ours. If the presently determined value of K_s is applied, the values of β_2 and β_3 resulting from that investigation agree reasonably well with the present ones, Table 2. Moreover, polynuclear complexes have been proved not to exist in the solutions studied which is also in accordance with our result. No less than three investigations²⁰⁻²²

Table 2. Mononuclear halide and thiocyanate complexes of copper(I) and silver(I). Stepwise (K_j) and overall (β_j) stability constants of the complexes ML_j , and solubility products (K_s) of the solids ML .

L	log K_j				log β_j			pK_s	t (°C)	I (M)	Ref.
	1	2	3	4	2	3	4				
<i>Copper(I)</i>											
Cl ⁻			-0.12		6.06	5.94		7.38	25	5	5
Br ⁻			1.17		6.28	7.45		8.89			a
I ⁻			~1.7	-1.03	~8.7	10.43	9.40	12.72			a
SCN ⁻				0.43		11.60	12.03	14.77			a
Cl ⁻					5.31			6.50	25	0	3
Br ⁻					5.04			7.38	19	var.	4
					5.92			8.28	25	0	3
			1.01		6.47 ^b	7.48 ^b			25	2	19
I ⁻					8.19			11.30	19	var.	4
					8.85			11.96	25	0	3
				0.35		9.38	9.73		25	5	20
			0.71		9.03	9.74		12.03	20	0.6	21
							9.85		20	4	21
					9.68		9.44		20	3.9	22
SCN ⁻								13.40	25	0	3
				0.18		9.90	10.09	12.73	20	var.	28
			-0.10	-0.42	11.00	10.90	10.48		25	5	20
<i>Silver(I)</i>											
Cl ⁻	3.08	2.32	0.75	-0.85	5.40	6.15	5.30	10.10	25	5	6
Br ⁻	4.22	3.00	1.88	0.11	7.22	9.10	9.21	12.62	25	5	7
I ⁻			2.85	0.72	10.35	13.20	13.92	16.35	25	4	8,9
	6.58	5.16	1.94	-0.6	11.74	13.68	~13.1	16.60	18	0	27
SCN ⁻	4.59	3.70	1.77	1.20	8.29	10.06	11.26	12.11	25	4	10

^a This study. ^b Calculated from their $K_s\beta_j$ -values by means of our $pK_s = 8.89$.

of the iodide system have been performed at conditions similar to ours, all by means of solubility measurements. The results of these investigations do not agree very well, nor have they been confirmed by the present measurements. One reason for this is certainly that the earlier investigators have not taken polynuclear complexes into account in solutions where they exist in considerable amounts, another that values of K_s have been applied that are not valid in the medium actually used. As to the thiocyanate system, one investigation has been performed under conditions similar to ours (though in a nitrate medium), by mean of solubility measurements.²⁰ The results seem doubtful for the same reasons as quoted in the case of the iodide system. Evidently they do not agree with the present ones.

The values of K_s presently found for $I = 5$ M are throughout considerably smaller than those

valid at $I = 0$, Table 2. The difference is about the same for all the halides and seemingly somewhat larger for the thiocyanate.

The typical (*b*)-behaviour is certainly the most prominent feature of the halide complex formation of copper(I); Table 2. All the stability constants increase in the order $Cl^- < Br^- < I^-$. The differences between the various halides are throughout smaller than for silver(I), however. As might be expected from its position in a higher period, this acceptor has an even stronger (*b*)-character than copper(I).²⁴

With copper(I), thiocyanate forms complexes which are even stronger than the iodide complexes, in striking difference to silver(I), where the iodide complexes are considerably stronger than the thiocyanate ones. The complexes formed by copper(I) with the latter ligand are even more stable than the corresponding silver complexes. Being typical (*b*)-acceptors, both copper(I) and silver(I) certainly coordinate

the thiocyanate ion *via* its sulfur end.^{25,26} Evidently, copper(I) prefers the heavy chalcogen sulfur as donor atom in relation to the heavy halides in a much higher degree than does silver(I).

For both copper(I) and silver(I), the solubility products decrease as the stability constants increase. The increase of the latter is not sufficient to compensate for the decrease of the former, however, so in solutions of a certain solubility *S* of copper(I) the proportion of higher complexes increases strongly in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{SCN}^-$. At the lowest solubilities measured here, the second complex predominated in the chloride and is still prominent in the bromide system while for iodide it can just be proved to exist. In the thiocyanate system, no complex below the third one can be discerned.

For the silver(I) halide systems, the solubility products are throughout smaller relative to the stability constants than for copper(I). Consequently, the solubilities are even lower. A rather complete determination of the stability constants has nevertheless been possible by solubility measurements, as even very low solubilities of silver(I) can be measured radiometrically.^{6,7,9,27} For copper such measurements are not feasible as no suitable active isotope exists.

The higher halide complexes in the copper(I) systems are formed only reluctantly so that even at the highest halide concentrations available a fourth complex does not exist at all in the chloride and bromide systems, and only in relatively minor amounts in the iodide system. In contrast to this, the fourth complex is the most prominent species in the whole range of thiocyanate concentrations employed and at the highest concentration it is completely predominating. These conditions are clearly illustrated by the complex formation curves drawn in Fig. 5.

In the silver(I) halide systems the highest complexes are formed much more readily. The values of K_3 and K_4 are throughout considerably higher for the silver(I) systems; Table 2. This applies also to the chloride system where the lower complexes are less stable than the corresponding copper(I) complexes. A similar behaviour is also found for thiocyanate. While the value of β_3 is higher for copper(I)

than for silver(I), the opposite is true for K_4 . Within the same range of halide concentrations as in the present investigation, appreciable amounts of the fourth complex are formed in all the silver(I) systems.

The dinuclear complex $\text{M}_2\text{L}_6^{4-}$ postulated to exist in the copper(I) iodide and thiocyanate systems has also been found in the corresponding silver systems.^{9,10} In these, higher complexes of the series $\text{Ag}_n\text{L}_{2n+2}^{(n+2)-}$ are seemingly also formed, while no such complexes are indicated in the corresponding copper(I) systems. This may be because the concentrations of copper(I) in the present measurements never exceeded 25 mM, which is much less than the concentrations of silver(I) in those solutions, where the polynuclear silver complexes have been found. Also the existence of $\text{Ag}_2\text{Br}_6^{4-}$ has been claimed, although the stability constant could not be calculated.⁷ The corresponding copper(I) complex might well be found at higher concentrations of copper(I) than those used here.

Acknowledgement. This work is part of a program sponsored by the Swedish Natural Science Research Council whose support is most gratefully acknowledged.

REFERENCES

1. Ahrlund, S., Chatt, J. and Davies, N. R. *Chem. Rev.* 12 (1958) 265; also in Pearson, R. G., Ed., *Hard and Soft Acids and Bases*, Dowden, Hutchinson and Ross, Stroudsburg, Pa. 1973, p. 28.
2. Pearson, R. G. *J. Chem. Educ.* 45 (1968) 581, 643.
3. Latimer, W. M. *The Oxidation States of the Elements and their Properties in Aqueous Solutions*, 2nd Ed., Prentice-Hall, Englewood Cliffs, N. J. 1952, p. 183.
4. Bodländer, G. and Störbeck, O. *Z. Anorg. Chem.* 31 (1902) 1, 458.
5. Ahrlund, S. and Rawsthorne, J. *Acta Chem. Scand.* 24 (1970) 157.
6. Berne, E. and Leden, I. *Sven. Kem. Tidskr.* 65 (1953) 88.
7. Berne, E. and Leden, I. *Z. Naturforsch. Teil A* 8 (1953) 719.
8. Leden, I. and Parck, C. *Acta Chem. Scand.* 10 (1956) 535.
9. Leden, I. *Acta Chem. Scand.* 10 (1956) 540, 812.
10. Leden, I. and Nilsson, R. *Z. Naturforsch. Teil A* 10 (1955) 67.
11. Ahrlund, S. and Björk, N.-O. *Acta Chem. Scand. A* 30 (1976) 249.

12. Fronæus, S. In Jonassen, H. B. and Weissberger, A., Eds., *Technique of Inorg. Chem.*, Interscience, New York, London 1963, Vol. 1, Chapter 1.
13. Ahrland, S., Chatt, J., Davies, N. R. and Williams, A. A. *J. Chem. Soc.* (1958) 264.
14. Johansson, L. *Coord. Chem. Rev.* 3 (1968) 293.
15. Tammann, G. and Kollmann, K. *Z. Anorg. Chem.* 143 (1925) 357.
16. Tammann, G. and Stassfurth, T. *Z. Anorg. Chem.* 160 (1927) 246.
17. Wetlesen, C. U. *Anal. Chim. Acta* 16 (1957) 268.
18. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
19. Peters, D. G. and Caldwell, R. L. *Inorg. Chem.* 6 (1967) 1478.
20. Fridman, Ya.D. and Sarbaev, Dzh.S. *Russ. J. Inorg. Chem.* 4 (1959) 835.
21. Golub, A. M., Sazhienko, S. M. and Romanenko, *Ukrain. Khim. Zh.* 28 (1962) 561 (as cited in Ref. 23).
22. Gyunner, E. A. and Yakhkind, N. D. *Russ. J. Inorg. Chem.* 13 (1968) 1420 (as corrected in Ref. 23).
23. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-Ion Complexes*, Chemical Society, London 1964 and 1971 (Special Publications Nos. 17 and 25).
24. Ahrland, S. *Struct. Bonding (Berlin)* 1 (1966) 207.
25. Bailey, R. A., Kozak, S. L., Michelsen, T. M. and Mills, W. N. *Coord. Chem. Rev.* 6 (1971) 407.
26. Kullberg, L. *Acta Chem. Scand. A* 28 (1974) 979.
27. Lieser, K. H. *Z. Anorg. Chem.* 292 (1957) 97.
28. Golub, A. M. *Zh. Neorg. Khim.* 1 (1956) 2517 (as cited in Ref. 23).

Received May 11, 1977.