

## Thermodynamics of the Copper(I) Halide and Thiocyanate Complex Formation in Acetonitrile

STEN AHRLAND, KARIN NILSSON and BERNT TAGESSON \*

Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund, Sweden

Potentiometric and calorimetric measurements have been performed to determine the stability constants and enthalpy changes of the copper(I) halide and thiocyanate complex formation in acetonitrile. As ionic media 0.1 M tetraethylammonium perchlorate and tetrafluoroborate have been used. Much the same results have been obtained in the two media. In the halide systems two mononuclear complexes are formed in endothermic reactions. For both steps the stabilities decrease in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . In the thiocyanate system, three mononuclear complexes are formed. The enthalpy change is exothermic for the first and the third step and endothermic for the second one. For all the complexes formed, the entropy changes are large and positive.

The constant for the disproportionation  $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}(\text{Hg})$  has been determined potentiometrically. The value found,  $K_D = [\text{Cu}^{2+}]/[\text{Cu}^+]^2 = 10^{-21} \text{ M}^{-1}$ , is very low which is ascribed to the strong solvation of  $\text{Cu}^+$  relative to  $\text{Cu}^{2+}$  in acetonitrile.

The thermodynamics of copper(I) halide complex formation has previously been investigated in water,<sup>1-3</sup> dimethylsulfoxide<sup>4</sup> (DMSO) and, recently, in pyridine.<sup>5</sup> In aqueous solution, copper(I) disproportionates completely in copper(II) and metallic copper if ligands stabilizing the monovalent state are not present in sufficiently high concentrations. This makes the investigation of copper(I) in aqueous solution fairly difficult. In aprotic solvents, copper(I) is much more favoured. Dilute solutions in DMSO are only

slightly disproportionated<sup>4</sup> and in pyridine the disproportionation is negligible at all concentrations.<sup>5,6</sup> This must be due to a stronger solvation of copper(I) relative to copper(II) in aprotic solvents.

In the aprotic solvent acetonitrile (AN), copper(I) is even more favoured relative to copper(II). The monovalent oxidation state is quite stable, with no tendency to disproportionation. Nor is the solution readily oxidized by air, in strong contrast to the conditions in DMSO.<sup>4</sup> The divalent oxidation state is, on the other hand, a powerful oxidizing agent in AN<sup>7</sup> where it has even been used as an analytical oxidant.<sup>8</sup> The easy reduction of copper(II) in AN has also been utilized for electrolytic regeneration of copper.<sup>9,10</sup>

The aim of this investigation has been to study the thermodynamics of the formation of the copper(I) halides and thiocyanate complexes in AN. The stability constants were determined potentiometrically and the enthalpy changes calorimetrically. The formation entropies were then calculated from these quantities. The extreme stability of the solvated copper(I) ion has, moreover, been quantitatively established by determination of the disproportionation constant for the reaction  $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}(\text{Hg})$ . The temperature in all experiments has been 25 °C.

Both tetraethylammonium perchlorate and tetrafluoroborate have been used as ionic media in the present investigation. Perchlorates have sometimes been found to react very violently in AN, causing dangerous explosions.<sup>11,12</sup> This seemingly does not happen to copper(I) solutions, nor to the solid solvate  $\text{Cu}(\text{AN})_4\text{ClO}_4$ , but

\* Present address: Alfa Laval AB, Thermal Division, P.O. Box 1008, S-221 03 Lund, Sweden.

if the investigations are to be extended to other metals it seems safer to use a non-oxidizing medium anion. As such, the tetrafluoroborate ion has been chosen as it presumably interferes as little with the complex formation as does the perchlorate ion. The disadvantage hampering the use of the tetrafluoroborate ion in aqueous solutions, that it is readily hydrolyzed, is of course not felt in an aprotic solvent. The postulate that perchlorate and tetrafluoroborate media behave in much the same way must, however, be tested. This has been done by the present comparison.

The tetraethylammonium ion has been chosen as the medium cation because not only the perchlorate and tetrafluoroborate, but also the tetraethylammonium halides and thiocyanate are sufficiently soluble in AN to allow an ionic medium of reasonably high concentration. The perchlorate and tetrafluoroborate are most probably completely dissociated in AN.<sup>13</sup> This means a high conductivity which makes the emf measurements very accurate. Also in tetraethylammonium iodide and thiocyanate solutions, the dissociation is seemingly complete,<sup>14,15</sup> while a slight association is indicated for bromide<sup>13</sup> and, especially, chloride.<sup>16</sup> This is much the same behaviour as found for ammonium halides in DMSO.<sup>17,18</sup>

In the partly associated chloride and bromide systems, the activity of the halide ions, and hence the complex formation with other cations, should depend strongly on the concentration of the tetraethylammonium ion, more than would be expected from the change of the ionic strength alone. Such effects have previously been found just for DMSO solutions containing ammonium salts.<sup>17,18</sup> The concentration of ammonium ions exerts an abnormally large influence on the stabilities of the metal bromide and, especially, chloride complexes formed in the solution. In such cases, an approximately constant medium is best achieved if the total concentration of medium cation is kept at the same level. Under the circumstances, this is more adequate than to aim at constant ionic strength, or a constant anion concentration. Obviously, the "free" ligand concentrations formally denoted [L] which enter the expression for the formation of complexes, are in these media the sums of the concentrations of the solvated ligand L and its associate with the medium cation. The constants

reported in this study all refer to the standard states thus defined. The total concentration of tetraethylammonium ions has been 0.1 M in all solutions.

Referred to a standard state where the chloride and bromide medium electrolytes are completely dissociated, the values of the constants  $K_j$  would be slightly higher than the present ones, presumably by about 0.1 or 0.2 log units.<sup>18</sup>

## EXPERIMENTAL

*Chemicals.* Acetonitrile (Baker Analyzed) was purified by fractional distillation over calcium hydride and stored over 3 Å molecular sieves. The residual water content was about 0.01 %, as determined by Karl Fischer titration.

$Cu(CH_3CN)_4BF_4$  was prepared as described previously.<sup>19</sup> The salt was stored in a carbon dioxide atmosphere. When exposed to air a blue-green discolouration, indicating oxidation to copper(II), is noticed after  $\approx 1$  hr. For analysis, the salt was oxidized with nitric acid. After dilution, AN was removed by heating the solution to boiling point. After cooling, the copper content was determined by EDTA titration, with murexide as indicator (found 20.1 %, calc. 20.2 %).

$Cu(CH_3CN)_4ClO_4$  was prepared analogously and analyzed for copper by the same procedure (found 19.3 %, calc. 19.4 %).

$Cu(CH_3CN)_4(BF_4)_2$  was prepared by oxidation of copper with nitrosyl tetrafluoroborate, according to the method of Hathaway *et al.*<sup>20</sup> The solvate was analyzed by EDTA-titration (found 16.2 %, calc. 15.8 %). Elementary analysis was performed for carbon (found 22.3 %, calc. 24.0 %). Evidently, the solvate contains somewhat less than four AN molecules per copper atom.

*Tetraethylammonium tetrafluoroborate and perchlorate* were dried in vacuum at 80 °C.

*Tetraethylammonium chloride, bromide, iodide* (Merck) and *thiocyanate* (Fluka) were dried at 100 °C and the halide or thiocyanate content determined titrimetrically.

*Copper amalgam*, containing  $\approx 3$  % Cu, was prepared as previously described.<sup>1</sup>

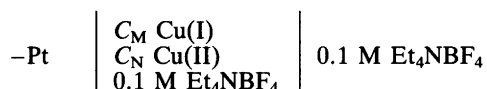
*Determination of the disproportionation constant  $K_D$ .* The value of  $K_D$  has been found from the standard potentials  $E_{01}^0$  and  $E_{12}^0$  of the couples  $Cu(Hg)/Cu^+$  and  $Cu^+/Cu^{2+}$ , respectively, according to the formula  $\ln K_D = (E_{01}^0 - E_{12}^0) / RTF^{-1}$ . The measurements have been carried out in 0.1 M tetrafluoroborate medium. The disproportionation is much too small to allow a check of



Scheme 1.

the value of  $K_D$  found by chemical analysis of the solutions, as was possible e.g. for the mercury(I) disproportionation in DMSO.<sup>21</sup>

The value of  $E_{01}^{\circ}$  was established by measuring the emf's of the cell (Scheme 1) at varying concentrations of copper(I) tetrafluoroborate,  $C_M$ . For the silver reference electrode, the readily available anhydrous  $\text{AgClO}_4$  was used as a source of  $\text{Ag}^+$ . As  $\text{AgBF}_4$  is only slightly soluble in AN, a perchlorate medium was used in this half-cell. The value of  $E_{01}^{\circ}$  determined thus includes the liquid junction potential perchlorate/tetrafluoroborate which, however, should be small. Simultaneously,  $E_{12}^{\circ}$  was determined by varying the ratio  $C_N/C_M$  in the half cell



connected with the same reference half-cell. The variation of  $C_N/C_M$  could not be effected by the usual procedure of titration, as a solution of copper(II) in AN, prepared by dissolving  $\text{Cu(AN)}_4(\text{BF}_4)_2(\text{s})$ , is spontaneously reduced to copper(I). This has been observed spectrophotometrically, with 2,9-dimethyl-1,10-phenanthroline (neo-cuproine) as complexing agent.<sup>22</sup> In AN, the absorption maximum of the copper(I) neo-cuproine complex is at 457 nm, with an extinction coefficient of  $7800 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$ . At the same wavelength the extinction coefficient of the copper(II) neo-cuproine complex is only  $\approx 100 \text{ M}^{-1} \text{ cm}^{-1}$ . In an AN solution, originally containing only  $\text{Cu(AN)}_4(\text{BF}_4)_2$ , the absorption continuously increases due to increasing copper(I) concentration. The variation of the ratio  $C_N/C_M$  has instead been brought about by dissolving various portions of the copper(II) solvate in copper(I) solutions of known concentrations, the emf measured as soon as possible (after  $\approx 3$  min), and then observed for about two hours. During this period, the drift was  $\approx 3$  mV. By linear extrapolation to zero time, the emf for the known initial ratio  $C_N/C_M$  could thus be determined with good precision. The standard electrode potentials found for the two copper couples relative to the reference electrode actually used have been recalculated so as to refer to a standard silver electrode of unit silver ion

activity.

From  $E_{01}^{\circ}$  and  $E_{12}^{\circ}$ , it is also possible to calculate  $E_{02}^{\circ}$ , according to  $E_{02}^{\circ} = (E_{01}^{\circ} + E_{12}^{\circ})/2$ . The value of  $K_D$  is, of course, independent of the reference electrode chosen.

**Potentiometric measurements.** Data for the calculation of the stability constants were obtained by titrations of copper(I) solutions with solutions of the ligand concerned. All solutions contained the appropriate ionic medium. The emf's were measured with a copper amalgam electrode in the copper(I) solution within the concentration range  $0.7 < C_M < 10$  mM. An amalgam electrode  $\text{Cu(Hg)}/10 \text{ mM Cu}^+$ , or, in the later series a silver electrode  $\text{Ag(s)}/C_{\text{Ag}} \text{ Ag}^+$ , with  $3 \text{ mM} < C_{\text{Ag}} < 10$  mM, were used as reference electrodes in the appropriate ionic medium. In this manner the liquid junction potentials were minimized. Aliquots of the ligand solution were added, concentration range  $0.2 < C_L < 24$  mM. The emf's measured were generally reproducible within 2 mV for the halides and within 5 mV for the thiocyanate. In solutions containing no ligands the emf varied with the copper concentration according to Nernst's law.

To exclude moisture, the titrations were performed in a glove box, with silica gel as the main drying agent. The last traces of moisture were removed by phosphorus pentoxide. The solutions were kept free from moisture, and stirred, by a stream of oxygen-free nitrogen which had been dried by passing through concentrated sulfuric acid. The gas was saturated with AN of the proper vapour pressure by passing through a wash-bottle containing the ionic medium used. Each titration was completed in a day. During this time, no sign of oxidation of copper(I) could be discovered.

**Calorimetric measurements.** The calorimeter employed has been described previously.<sup>23-25</sup> The calibration constant,  $\epsilon_v$ , depends upon the volume,  $V$  ml, according to  $\epsilon_v = a + b(V - 80) \text{ J ohm}^{-1}$  where  $a = 0.8 \pm 0.3 \text{ J ohm}^{-1}$  and  $b = (0.98 \pm 0.08) \times 10^{-2} \text{ J ohm}^{-1} \text{ ml}^{-1}$ . The calorimeter vessel initially contained 80 ml copper(I) solution, of a concentration  $3 < C_M < 10$  mM. Aliquots of ligand solutions were added. The concentrations of the ligand solutions were  $C_L = 100$  mM for the halides, and 50 mM for the thiocyanate which is not soluble enough for the higher concentration.

Table 1. Standard electrode potentials ( $E_{01}^{\circ}$ ,  $E_{12}^{\circ}$ ,  $E_{02}^{\circ}/\text{mV}$ ) and disproportionation constant ( $K_D/M^{-1}$ ), present and previous measurements in acetonitrile at 25 °C.

Method <sup>a</sup>	Ref.el. <sup>a</sup>	$E_{01}^{\circ}(\text{Cu}(\text{Hg}))$	$E_{01}^{\circ}(\text{Cu}(\text{s}))$	$E_{12}^{\circ}$	$E_{02}^{\circ}$	$-\log K_D$	Ref.
0.1 M $\text{Et}_4\text{NBF}_4$							
Pot	SSE,AN	$-591 \pm 1$		$627 \pm 2$	$19 \pm 2$	20.6	This
Pot	SSE,AN		$-601 \pm 1$	$627 \pm 2$	$13 \pm 2$	20.8	work
0.006 to 0.03 M $\text{Et}_4\text{NClO}_4$							
Pot	SSE,AN	$-594.2 \pm 0.5$	$-604.4 \pm 0.5$				30
$\text{Et}_4\text{NClO}_4$ , ionic strength=0							
Pot	SSE,AN			$679 \pm 1$			35
0.1 M $\text{Et}_4\text{NClO}_4$							
Vol	Ag/AgCl,aq		450	1700		21.1	36
Vol	SSE,AN		-620	580		20.3	37
0.1 M $\text{NaClO}_4$							
Vol	SCE,aq		-260	1000		21.3	7
Medium unknown						20	9

<sup>a</sup>Methods: Pot=potentiometry, Vol=voltametry. SSE=standard silver electrode, SCE=saturated calomel electrode.

For  $\text{Cu}^+$ , the heat of dilution was negligible in the concentration range used. When ligand solutions were added to 80 ml of the pure perchlorate medium, small exothermic heats of dilution were found, viz.  $-0.08 \text{ J ml}^{-1}$  for chloride,  $-0.03 \text{ J ml}^{-1}$  for bromide and iodide, and  $-0.01 \text{ J ml}^{-1}$  for thiocyanate. In the tetrafluoroborate medium the

heats were even smaller, viz.  $-0.03 \text{ J ml}^{-1}$  for chloride and quite negligible for the other ligands.

*Calculations.* The numerical calculations of the stability constants were performed by means of the computer program EMMA.<sup>26</sup> The stability constants found were used as fixed parameters

Table 2. Overall stability constants ( $\beta_j/M^{-j}$ ) of the copper(I) halide and thiocyanate complexes in acetonitrile at 25 °C. The limits of error refer to three standard deviations; NP denotes the number of observations (emf's measured for each system).

Ligand	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$	$\text{SCN}^-$
Medium 0.1 M $\text{Et}_4\text{NClO}_4$				
$\beta_1$	$(1.05 \pm 0.07)10^4$	$(2.44 \pm 0.04)10^3$	$(1.34 \pm 0.02)10^3$	$(3.37 \pm 0.36)10^3$
$\beta_2$	$(3.57 \pm 0.05)10^9$	$(1.61 \pm 0.01)10^7$	$(0.93 \pm 0.02)10^6$	$(1.19 \pm 0.08)10^7$
$\beta_3$				$(1.34 \pm 0.19)10^9$
NP	122	119	119	183
Medium 0.1 M $\text{Et}_4\text{NBF}_4$				
$\beta_1$	$(2.23 \pm 0.10)10^4$	$(2.34 \pm 0.12)10^3$	$(1.34 \pm 0.04)10^3$	$(6.45 \pm 0.54)10^3$
$\beta_2$	$(4.95 \pm 0.09)10^9$	$(1.58 \pm 0.04)10^7$	$(1.05 \pm 0.02)10^6$	$(2.02 \pm 0.10)10^7$
$\beta_3$				$(0.87 \pm 0.17)10^9$
Np	106	141	141	235

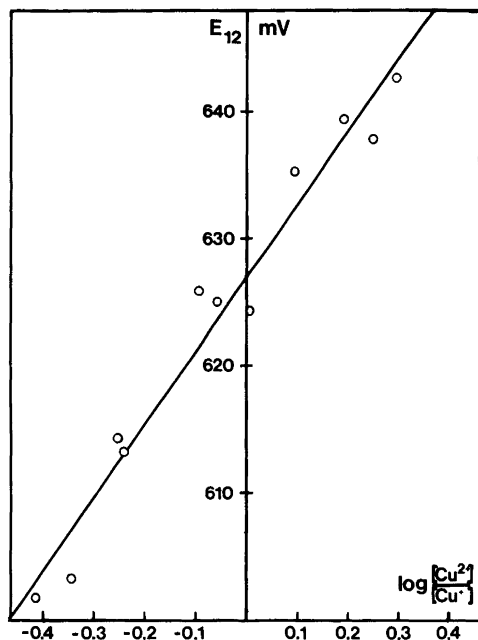
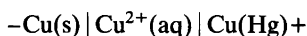


Fig. 1. The electrode potential of the couple  $\text{Cu}^+/\text{Cu}^{2+}$  referred to the standard silver electrode, as a function of the concentration ratio. Medium 0.1 M  $\text{Et}_4\text{NBF}_4$ ; 25 °C.

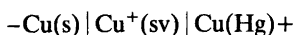
for the calculation of the enthalpy changes by means of a modernized version of the program KALORI.<sup>27</sup>

## RESULTS

The standard potential  $E_{01}^{\circ}$  ( $\text{Cu}(\text{Hg})$ ) from the copper(I) titrations with  $\text{Cu}(\text{Hg})$  electrode is listed in Table 1. The amalgamation makes the copper somewhat more noble. The emf  $E_{\text{II}}$  of the cell



with the cell reaction  $\text{Cu}(\text{s}) \rightarrow \text{Cu}(\text{Hg})$  has been reported to be 5.1 mV.<sup>28,30</sup> This value is independent of the copper(II) concentration, and of the solvent used. From  $E_{\text{II}}$ , the free energy change of the cell reaction,  $\Delta G = 2FE_{\text{II}} = -0.98 \text{ kJ mol}^{-1}$  is calculated, and also the activity of copper in the amalgam,  $a(\text{Cu}(\text{Hg})) = 0.67$ . For the cell



involving the same cell reaction, the emf would thus be  $E_1 = -\Delta G/F = 10.2 \text{ mV}$ . The  $E_{01}^{\circ}(\text{Cu}(\text{s}))$  in Table 1 has been calculated accordingly.

The values of  $E_{12}$  found for various ratios  $[\text{Cu}^{2+}]/[\text{Cu}^+]$  have been plotted in Fig. 1. The intersection with the  $E_{12}$  axis gives the value of  $E_{12}^{\circ}$  listed in Table 1. The values of  $K_{\text{D}}$  and  $E_{02}^{\circ}$  hence calculated are reported in Table 1. The extremely low value of  $K_{\text{D}}$  means, of course, that no disproportionation whatever of  $\text{Cu}^+$  occurs in AN solutions.

In several previous investigations voltammetric half-wave potentials,  $E_{1/2}$ , have been measured for the reductions  $\text{Cu}^{2+} \rightarrow \text{Cu}^+$  and  $\text{Cu}^+ \rightarrow \text{Cu}(\text{s})$  in AN. From  $E_{1/2}$ , approximate values of  $E_{01}^{\circ}$  and  $E_{12}^{\circ}$ , referred to the reference electrode actually used, may be found. For the couples  $\text{Cu}^+/\text{Cu}^{2+}$ ,  $E_{12}^{\circ} \approx E_{1/2}$ ; for  $\text{Cu}(\text{s})/\text{Cu}^+$ ,  $E_{01}^{\circ} \approx E_{1/2} - RTF^{-1} \ln C_{\text{M}}/2$  (the activity coefficient = 1). The values of  $K_{\text{D}}$  calculated from the  $E_{01}^{\circ}$  and  $E_{12}^{\circ}$  thus obtained are not very different from that found presently, Table 1. Also another value of  $K_{\text{D}}$  quoted in the literature is of much the same order of magnitude.<sup>9</sup>

The overall stability constants,  $\beta_1$ , are listed in Table 2. The same values, within the limits of error, are found in the perchlorate and tetrafluoroborate media for the bromide and iodide systems. For chloride and thiocyanate, however, the constants are slightly different in the two media. Within the metal and ligand concentration ranges studied, all the halides form two mononuclear complexes, while for thiocyanate a third complex is also formed. The values found agree rather well with those of previous investigations.<sup>29-31</sup>

The overall enthalpy changes,  $\Delta H_{\beta_1}$  (Table 3), are endothermic for all the halide complexes. For thiocyanate,  $\Delta H_{\beta_1}$  is slightly exothermic, while  $\Delta H_{\beta_2} \approx 0$ . Because of the difficulty to reach sufficiently high values of  $[\text{L}]$  in the calorimetric measurements, no accurate value of  $\Delta H_{\beta_3}$  could be calculated for the thiocyanate system though a third complex is undoubtedly formed. Except for chloride, where considerably more endothermic values are found in the perchlorate medium, the values of  $\Delta H_{\beta_1}$  are almost the same in the two media used.

Not unexpectedly, the thermodynamics of the reactions investigated are much the same in perchlorate and tetrafluoroborate media of the same concentration. Significant differences are

**Table 3.** Overall enthalpy changes ( $\Delta H_{\beta_i}/\text{kJ mol}^{-1}$ ) for the formation of the copper(I) halide and thiocyanate complexes in acetonitrile, at 25 °C. The limits of error refer to three standard deviations; NP denotes the number of observations for each system.

Ligand	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	SCN <sup>-</sup>
<b>Medium 0.1 M Et<sub>4</sub>NClO<sub>4</sub></b>				
$\Delta H_{\beta_1}$	16.8±1.4	10.5±0.7	8.5±0.4	-5.4±0.8
$\Delta H_{\beta_2}$	21.2±0.3	27.2±0.4	21.3±0.4	0.6±0.7
NP	68	67	78	36
<b>Medium 0.1 M Et<sub>4</sub>NBF<sub>4</sub></b>				
$\Delta H_{\beta_1}$	11.7±0.9	11.9±0.5	8.3±0.5	-5.1±0.5
$\Delta H_{\beta_2}$	18.4±0.3	27.4±0.3	19.9±0.5	-0.1±0.5
NP	57	64	56	53

**Table 4.** Equilibrium constants ( $K_i/\text{M}^{-1}$ ) and thermodynamic functions ( $\Delta G_i^\circ$ ,  $\Delta H_i^\circ/\text{kJ mol}^{-1}$ ;  $\Delta S_i^\circ/\text{J K}^{-1} \text{mol}^{-1}$ ) for the stepwise formation of copper(I) halide and thiocyanate complexes in acetonitrile (AN) and dimethylsulfoxide (DMSO) at 25 °C.

Ligand	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	SCN <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	SCN <sup>-</sup>
<b>AN, 0.1 M Et<sub>4</sub>NClO<sub>4</sub><sup>a</sup></b>					<b>AN, 0.1 M Et<sub>4</sub>NBF<sub>4</sub><sup>a</sup></b>			
log $K_1$	4.02	3.39	3.13	3.53	4.35	3.37	3.13	3.81
log $K_2$	5.53	3.82	2.84	3.54	5.35	3.82	2.89	3.50
log $K_3$				2.05				1.63
$K_1/K_2$	0.031	0.37	1.9	0.95	0.010	0.35	1.7	2.1
$K_2/K_3$				31				73
$-\Delta G_1^\circ$	23.0	19.3	17.9	20.2	24.8	19.2	17.9	21.7
$-\Delta G_2^\circ$	31.6	21.8	16.2	20.3	30.5	21.5	16.5	20.0
$-\Delta G_3^\circ$				11.7				9.3
$\Delta H_1^\circ$	16.8	10.5	8.5	-5.4	11.7	11.9	8.3	-5.1
$\Delta H_2^\circ$	4.4	16.7	12.8	6.0	6.7	15.5	11.6	5.0
$\Delta S_1^\circ$	133	100	89	50	122	104	88	56
$\Delta S_2^\circ$	121	129	97	88	125	125	94	84
$-\Delta G_{\beta_2}^\circ$	54.5	41.1	34.1	40.4	55.3	41.1	34.4	441.7
$\Delta H_{\beta_2}^\circ$	21.2	27.2	21.3	0.6	18.4	27.4	19.9	-0.1
$\Delta S_{\beta_2}^\circ$	254	229	186	137	247	230	182	140
<b>DMSO, 0.1 M Et<sub>4</sub>NClO<sub>4</sub><sup>b</sup></b>					<b>DMSO, 1 M NH<sub>4</sub>ClO<sub>4</sub><sup>c</sup></b>			
log $K_1$	6.0	5.0	5.5		4.37	4.19	4.71	
log $K_2$	6.0	4.6	2.7		4.50	3.75	2.96	
log $K_3$					0.58			
$K_1/K_2$	1	3	600		0.7	2.8	56	
$-\Delta G_1^\circ$	34	29	31		24.9	23.9	26.9	
$-\Delta G_2^\circ$	34	26	16		25.7	21.7	16.9	
$-\Delta H_1^\circ$					6.4	9.3	13.6	
$-\Delta H_2^\circ$					7.8	-2.1	-3.1	
$\Delta S_1^\circ$					62	49	45	
$\Delta S_2^\circ$					60	78	67	

<sup>a</sup> This work. <sup>b</sup> Ref. 38. <sup>c</sup> Ref. 4.

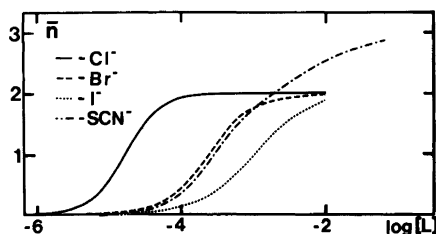


Fig. 2. The complex formation curves of the copper(I) halides and thiocyanate systems in acetonitrile. Medium 0.1 M  $\text{Et}_4\text{NClO}_4$ ; 25 °C.

observed only for the chloride and thiocyanate systems, and even in these cases they are fairly small.

The stepwise stability constants,  $K_j$ , and enthalpy changes,  $\Delta H_j$ , are listed in Table 4, with the values derived of the changes in free energy,  $\Delta G_j^\circ$ , and entropy,  $\Delta S_j^\circ$ .

The stabilities of the halide complexes follow an (a)-sequence  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . This is also illustrated by the complex formation curves of Fig. 2. The first two thiocyanate complexes are of much the same stability as the analogous bromide complexes. The formation of a third thiocyanate complex causes the formation curves of the two systems to deviate strongly at high ligand concentrations, however. The stability of the first complex relative to the second one increases from chloride to iodide, as seen from the increasing values of the ratio  $K_1/K_2$ . This change is also reflected in the decreasing steepness of the complex formation curves. Even more clearly, the increasing importance of the intermediate complex  $\text{CuL}$  is illustrated by the complex distribution curves of Fig. 3.

The values of  $\Delta H_1^\circ$  are endothermic for all the halides but less so in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ , Table 4. For  $\text{SCN}^-$ ,  $\Delta H_1^\circ$  is slightly exothermic. The values of  $\Delta H_2^\circ$  are endothermic for all the ligands. Remarkably enough, the most endothermic value is found for  $\text{Br}^-$ .

The endothermic values of  $\Delta H_j^\circ$  found for all the complexes except  $\text{CuSCN}$  counteract their formation. Only by large positive values of  $\Delta S_j^\circ$  do the complexes attain the fairly high stability which they, in fact, possess. Even in the case of  $\text{CuSCN}$ , formed in an exothermic reaction, the entropy term contributes by far most to the stability.

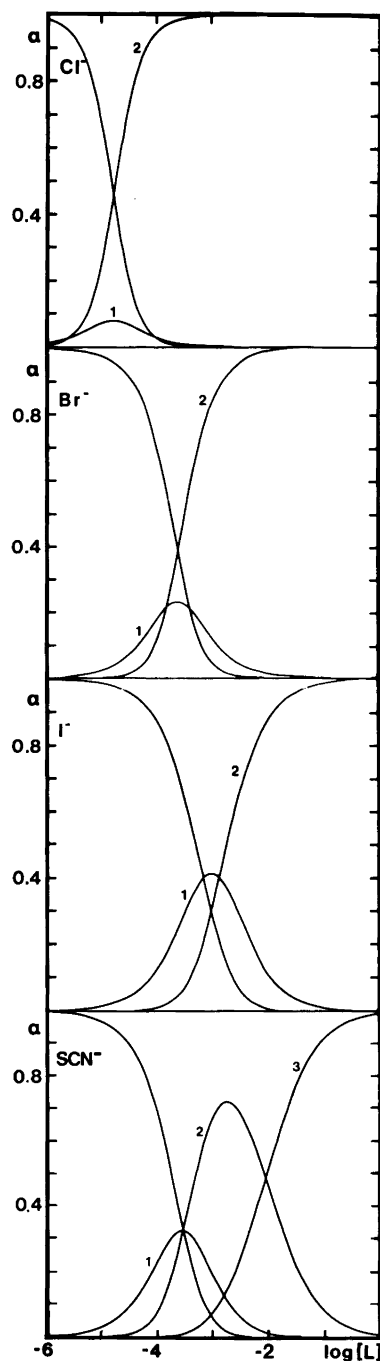


Fig. 3. The distribution of copper(I) between the species  $\text{Cu}^+$ ,  $\text{CuL}$  (1),  $\text{CuL}_2^-$  (2) and  $\text{CuL}_3^{2-}$  (3) for the halide and thiocyanate systems, as a function of the free ligand concentration. Medium 0.1 M  $\text{Et}_4\text{NClO}_4$ ; 25 °C.

## DISCUSSION

In protic solvents, the ability to form hydrogen bonds makes the chloride ion much more strongly solvated than the iodide ion. In aprotic solvents where no hydrogen bonds can be formed, this difference is smaller. Consequently, the chloride complexes are stronger relative to iodide ones in aprotic solvents than in protic solvents. This is reflected in the change of order for the stability of the complexes formed. In water the stabilities of the copper complexes formed follows a (b)-sequence,  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . In aprotic solvents the (b)-sequence tends to switch to an (a)-sequence,  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . In the aprotic DMSO, coordinating *via* oxygen, the first complex formation step displays a hybrid sequence  $\text{Cl}^- > \text{Br}^- < \text{I}^-$ , but for the second step an (a)-sequence is found.<sup>4</sup> In AN the (a)-sequence is quite marked, Table 4. Pyridine, another nitrogen-donating solvent, also gives an (a)-sequence.<sup>5</sup>

The stabilities of the complexes formed are, of course, also strongly influenced by the solvation of all the metal species involved. For obvious reasons, however, the solvation of the central ion is always much stronger than that of any of the complexes. A strongly solvating solvent will therefore mean a large net desolvation enthalpy, counteracting the complex formation. In aprotic solvents,  $\text{Cu}^+$  is strongly solvated; consequently the overall enthalpy changes are generally not favourable. They are, moreover, much more unfavourable in AN than in DMSO, Table 4. This reflects the strong increase of the solvation enthalpy of  $\text{Cu}^+$  between DMSO and AN which is not at all counterbalanced by an equivalent increase for the complexes.<sup>32</sup> On the other hand, the breakup of the strong  $\text{Cu}^+$  solvate formed in AN will bring about a large increase of entropy, which tends to make the overall entropy change of the complex formation very favourable. The actual increase of entropy due to this desolvation does not depend solely on the state of order of the solvate, however, but also on the degree of order prevailing in the bulk solvent. The larger the difference in order between the solvate and the bulk solvent, the larger the entropy gain.

The structural order of a solvent should be fairly well reflected in the ratio between the dielectric constant and the dipole moment,  $\epsilon/\mu$ . The higher the value of  $\epsilon$  relative to that of  $\mu$ , the

more orderly the dipoles are lined up and, consequently, the more structured the solvent. By this criterion, AN is appreciably less ordered than DMSO.<sup>33</sup> Relative to DMSO, the desolvation in AN thus occurs from a more well-ordered solvate to a less well-ordered solvent. The considerably higher entropy gains found in AN are therefore just what to expect.

As is often found, even if the enthalpy and entropy changes of the formation of a certain complex differ widely between different solvents, these changes compensate each other extensively. Consequently, the free energy changes, and hence the stabilities, may not differ widely, in spite of the rather different characteristics of the reactions involved.

The difference in stability found for the chloride system between the two media used is essentially an enthalpy effect. For the thiocyanate system, on the other hand, the difference is mostly an entropy effect. Also for the bromide system, significant differences exist between the enthalpy and entropy changes in the two media, though these compensate each other completely. That the thermodynamics differ somewhat between different media is *per se* natural and also that various systems are influenced to various extents. At least presently, however, it does not seem fruitful to speculate about the details of the trends observed. The main conclusion is, however, that a change of perchlorate for tetrafluoroborate exerts only a marginal influence on the complex formation.

The very low value of  $K_D$  in AN reflects a strong stabilization of  $\text{Cu}^+$  relative to  $\text{Cu}^{2+}$ , as compared with DMSO and, even more, with water. This stabilization is directly connected with the free energies of transfer  $\Delta G_{\text{tr}}^0$  which favour  $\text{Cu}^+$  relative to  $\text{Cu}^{2+}$  especially between DMSO and AN.<sup>34</sup> The values of  $\Delta G_{\text{tr}}^0$  (DMSO→AN) are for  $\text{Cu}^+$   $-11.7 \text{ kJ mol}^{-1}$  and for  $\text{Cu}^{2+}$   $98.3 \text{ kJ mol}^{-1}$ . The relative contributions of the enthalpies and entropies of transfer are so far not known for these ions, however.

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