

Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. VII. Thermodynamics of Copper(I) Halide and Copper(II) Bromide Complex Formation

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The copper(I) ion, and its complexes, are strongly solvated by dimethylsulfoxide (DMSO) and therefore fairly stable in this solvent. Therefore, it has been possible to study extensively the thermodynamics of copper(I) halide complex formation in DMSO. The measurements have been performed in a medium of the ionic strength $I=1$ M, maintained by ammonium perchlorate, at 25 °C. The stabilities of the first complexes CuL vary only slightly in the sequence $\text{Cl}^- > \text{Br}^- < \text{I}^-$. For the second complex, the stabilities decrease in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. With I^- , dinuclear species are presumably also formed. The formation of CuL is exothermic and increasingly so in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$. For the second step the opposite trend is observed. Only the formation of CuCl_2^- is exothermic while CuBr_2^- and CuI_2^- are formed in slightly endothermic reactions. The entropy changes are all large and positive.

The copper(II) bromide system has also been investigated under the same conditions. The first two complexes are both formed in endothermic reactions but due to the favorable entropy changes, they are still fairly stable.

The disproportionation constant $K_D = [\text{Cu}^{2+}]/[\text{Cu}^+]^2$ has been determined in ammonium perchlorate media of both $I=1$ M and 0.1 M, at 25 °C.

The formation of metal complexes in solution is much influenced by the solvation of the species involved.^{1,2} The effect can be studied by investigating the formation of complexes between the same acceptors and donors in different solvents. As to halide systems, large differences are expected, and found, on account of the possibilities of hydrogen bonding in protic solvents. As the capacity for hydrogen bonding sharply decreases in the se-

quence $\text{Cl}^- > \text{Br}^- > \text{I}^-$, the chloride ion is much more strongly solvated than the iodide ion in protic solvents. In aprotic solvents where no hydrogen bonding occurs, this difference is much smaller.¹⁻³ Consequently, the chloride complexes should be much stronger relative to the iodide ones in aprotic solvents than they are in protic solvents.

The change of solvent does not only affect the solvation of the various species present, however. Profound changes also occur in the character of the bonding between the solvent molecules. In protic solvent, intermolecular hydrogen bonds are apt to bring about a much more well-ordered solvent structure than found in aprotic solvents where this ordering influence is lacking.

In order to disentangle the effects due to the various influences at work, it is necessary to determine not only the stabilities of the complexes but also the enthalpy and entropy changes accompanying their formation.^{1,2}

The primary aim of the present investigation is to determine the thermodynamics of complex formation for the copper(I) halide systems in an aprotic solvent. These systems have been studied in water,^{4,5} the most important of the protic solvents. As a representative aprotic solvent, dimethylsulfoxide (DMSO) has been chosen, for several reasons. Firstly, this solvent generally solvates ions quite strongly which of course is necessary if systems of metal ion complexes should at all be soluble.¹⁻³ Further, its physical properties are favourable, allowing the solutions to be handled rather easily. In the last few years, numerous investigations employing this solvent have therefore been performed. Results obtained for copper(I) can thus be

compared with those found for several other systems.^{1,2}

Due to the strong solvation of copper(I) in DMSO, this oxidation state is very markedly stabilized relative to copper(II) and metallic copper. In water,⁶ the disproportionation $2 \text{Cu(I)} \rightleftharpoons \text{Cu(II)} + \text{Cu(s)}$ is very complete in the absence of ligands stabilizing copper(I), with a value of the constant $K_D = [\text{Cu}^{2+}]/[\text{Cu}^+]^2 \approx 10^6 \text{ M}^{-1}$. Much the same value of K_D is found for the disproportionation in contact with a two-phase copper amalgam.⁶ In DMSO, a value $\approx 2 \text{ M}^{-1}$ has been found for 0.1 M LiClO_4 or Et_4NClO_4 media.⁷ Values of K_D of the same order of magnitude have been found in the present study for 0.1 and 1 M NH_4ClO_4 media, cf. below. The disproportionation evidently increases with the concentration, but for the most concentrated copper(I) perchlorate solutions used in the complex formation measurements, $C_M = 20 \text{ mM}$, it is nevertheless only $\approx 8 \%$. In water, it would be virtually complete, viz. $\approx 99.9 \%$. The strong solvation of copper(I) by DMSO moreover makes the neutral halides CuL quite soluble. The conditions for the investigation of copper(I) halide complexes in solution are thus much more favourable in DMSO than in water.

The stability constants of the complexes have been determined potentiometrically, by means of the copper amalgam electrode. The enthalpy changes accompanying their formation have been measured calorimetrically. By combining the stability and enthalpy data, the entropy changes are finally found.

Our original intention was to study the thiocyanate complexes as well. In this system, however, the solubility of the neutral complex CuSCN is too low even in DMSO, only $\approx 2 \text{ mM}$, to allow precise calorimetric measurements.

Also the copper(II) bromide system has been studied, primarily in order to determine the influence of the small amounts of copper(II) that are inevitably present in the copper(I) solutions. Only calorimetric measurements were performed. For the first two complexes, these yielded not only the enthalpy changes but also the stability constants with fair precision. For higher ligand concentrations, however, an unexpected reaction took place, as indicated by a slow but persistent evolution of heat between the additions of ligand solution. As will be further discussed below, an oxidation of the gold vessel by copper(II) takes place, brought about by the strong affinity of both gold(I) and

copper(I) for bromide ions.

The complex formation measurements have been performed in the same medium, $I = 1 \text{ M}$, maintained by NH_4ClO_4 , as used in the previous studies of cadmium⁸ and zinc⁹ halides in DMSO. The standard potentials E_{01}° and E_{12}° of the Cu(Hg)/Cu^+ and $\text{Cu}^+/\text{Cu}^{2+}$ couples which yield the standard potential E_{02}° of the couple Cu(Hg)/Cu^{2+} and the disproportionation constant K_D in contact with copper amalgam have been determined in NH_4ClO_4 media of both $I = 1 \text{ M}$ and 0.1 M . All measurements have been done at 25°C .

EXPERIMENTAL

Chemicals. Dimethyl sulfoxide was purified and analyzed for water as described before.¹⁰ The water content was $< 0.04 \%$. $\text{Cu(ClO}_4)_2 \cdot 5\text{DMSO}$ was prepared according to the method used by Selbin *et al.*¹¹ who found, however, that a tetrasolvate was formed. Our preparation was analyzed for copper by EDTA titration with murexide as indicator, and for sulfur by elementary analysis. Found: Cu 9.60, S 24.3; calc. Cu 9.73, S 24.4%. A fairly sharp melting point was obtained at $183\text{--}185^\circ \text{C}$, while the solvate of Selbin *et al.* exploded on heating. Our tetrasolvate $\text{Cu(ClO}_4)_2 \cdot 4\text{DMSO}$ was prepared according to Cotton and Francis.¹² The copper analysis gave Cu 11.03; calc. 11.05 (in Ref. 12 Cu 11.17%). The sulfur analysis failed as the substance exploded. This solvate does not melt sharply but liquifies in the range $180\text{--}210^\circ \text{C}$. The tetrasolvate is also formed from the pentasolvate by evaporation of DMSO *in vacuo* at 75°C for about two days. Both solvates have been used in the present investigation, with the same results. The two-phase copper amalgam, containing $\approx 3 \%$ Cu, was prepared and stored as described previously.⁴ Before use, it was carefully washed with DMSO.

Copper(I) perchlorate solutions in DMSO. These were prepared by reducing copper(II) perchlorate solutions at 60°C with copper foil.¹³ During this process, it was most important to prevent oxidation by air. A steady stream of carbon dioxide was therefore passed through the solution. Carbon dioxide was preferred to nitrogen, as it keeps air out more efficiently. The ammonium perchlorate making up the ionic medium was added after the reduction, as it tended to oxidize the heated solutions. The final concentrations of copper(I) and copper(II) were found from the initial copper(II) concentration and the total concentration of copper present after reduction. These were both determined by EDTA titration. Contact with air during the EDTA titration is sufficient to oxidize copper(I) completely.

At least two days were needed to achieve a reduction close to the equilibrium given by K_D .

Potentiometry. In the complex formation titrations, a copper(I) perchlorate solution S, of a concentration C_M between 3 and 16 mM, with $I=1$ M, by means of NH_4ClO_4 , was first introduced in the copper amalgam electrode vessel. This half-cell was then connected with a reference electrode, either $\text{Ag(s)}/10$ mM Ag^+ or, in the later series, $\text{Cd(Hg)}/10$ mM Cd^{2+} , both containing 1 M NH_4ClO_4 . When a stable initial emf E' had been reached, portions of a ligand solution T, of $C_L=100$ mM and $I=1$ M by NH_4ClO_4 was added and the emf E measured after each addition. The cadmium reference electrode yields the more reproducible emf's and is therefore to be preferred. For each ligand, titrations were generally performed with three values of C_M , and each titration was run three times.

Special care had to be taken to prevent the oxidation of copper(I) by oxygen. The titrations were performed in a glove box under carbon dioxide atmosphere, and all stock solutions were also deaerated by this gas. Moreover, a stream of especially purified nitrogen gas was passed through the copper(I) solution in the electrode vessel. This gas had first been passed over finely divided copper at 200 °C and then through a 5 mM copper(I) solution, containing ≈ 4 mM ammonium chloride, and in contact with pieces of copper foil. In this solution, the traces of oxygen left reacted momentarily, with the formation of copper(II), water and ammonia. The ammonium ions provided the protons necessary for the formation of water and prevented that formation of ill-defined oxidation products which otherwise is apt to take place.¹⁴ The copper(II) formed was again reduced to copper(I) by the metallic copper. As already pointed out, this reduction is quite slow in solutions containing only the solvated ions. The halide complexes are rapidly reduced, however, and a fast reduction is therefore achieved in the presence of the chloride ions. On the other hand, concentrations appreciably higher than 4 mM should not be used, as copper(I) will then be stabilized to an extent which will impair its rapid oxidation by oxygen. The ammonia formed was slowly carried away with the nitrogen gas which was therefore subsequently led through two wash-bottles containing copper(II) perchlorate solution. In these, the ammonia was absorbed and thus prevented from reaching the solution in the electrode vessel.

Especially for the highest copper concentrations used, a sizable repropotionation takes place during the titration, leading to an increase of the concentration of copper(I). Further, in spite of all precautions, a slight oxidation by air occurred in most experiments. As the copper(II) formed was rapidly

reduced by the amalgam, also this reaction leads, somewhat paradoxically, to an increase of the copper(I) concentration C_M . In the chloride and bromide titrations the resulting increase of C_M could be directly observed during the titrations as the formation of the second complex, *i.e.* the attainment of the ligand number $\bar{n}=2$, is accompanied by a clearly marked equivalence point at a ratio of $C_L/C_M=2$. The values of C_M thus found were higher than those calculated from C_M' . The final value of C_M was always determined at the end of each experiment, by EDTA titration as described above. This method worked well also at the fairly high ligand concentrations present in the final solutions. The EDTA analyses showed that practically all air oxidation occurred at $\bar{n}<2$, before copper(I) had become protected by the complex formation. A similar behaviour has also been observed for the copper(I) triphenylphosphine system, though the more extensive complex formation in this case provides an even better protection towards oxidation.¹⁵ For the halides, the emf's changed appreciably overnight even at large excesses of ligand, $C_L/C_M > 4$, while they stayed constant if excess phosphine had been added.

To minimize the oxidation by air, all titrations were completed within one day. During this time, this reaction generally caused an increase of C_M that was $< 3\%$. If it was $> 5\%$, the titration was discarded. If it was lower, the intermediate values of C_M were corrected by linear interpolation.

The initial values E' varied with C_M as expected from the law of Nernst. From the values of E' found, the electrode potential E_{01}° of $\text{Cu(Hg)}/\text{Cu}^+$ can be calculated. $\text{Cd(s)}/\text{Cd}^{2+}$ has been chosen as a suitable standard electrode. In the present measurements cadmium amalgam electrodes are used. The difference between the electrode potentials of $\text{Cd(Hg)}/\text{Cd}^{2+}$ and $\text{Cd(s)}/\text{Cd}^{2+}$ is well-known, however, *viz.* 50.5 mV.¹⁶

The value of E_{01}° has also been determined for a 0.1 M NH_4ClO_4 medium. The pure medium was titrated with a ≈ 20 mM solution of copper(I) perchlorate of $I=0.1$ M, by NH_4ClO_4 . The law of Nernst was obeyed in the range $2 \leq C_M \leq 15$ mM. In this case, also the reference electrode solution was kept at $I=0.1$ M.

For the determination of the electrode potentials E_{12}° of $\text{Cu}^+/\text{Cu}^{2+}$ in the two media used, a copper(I) perchlorate solution was titrated with copper(II) perchlorate, and the emf's measured by means of a platinum electrode, relative to the cadmium amalgam reference electrode.

From the values of E_{01}° and E_{12}° thus found, E_{02}° of the couple $\text{Cu(Hg)}/\text{Cu}^{2+}$ has been calculated according to $E_{02}^\circ = (E_{01}^\circ + E_{12}^\circ)/2$, and K_D according to $\ln K_D = (E_{01} - E_{12})/RTF^{-1}$.

Calorimetry. The titration calorimeter described

before¹⁷ has been modified in order to make work with DMSO possible. Teflon is now used for all plastic parts. Similar precautions as before⁵ have to be taken in order to prevent the oxidation of copper(I) by air. A stream of nitrogen, presaturated with DMSO (by passing through a solution of 1 M NH_4ClO_4 in DMSO), was bubbled through the calorimeter solution during the measurements. As oxygen penetrates teflon, all joints were made glass to glass, and the short teflon ligatures were covered with pieces of PVC tubing.

In the copper(I) titrations, solid ammonium perchlorate was first placed in the calorimeter vessel, in order to provide the ionic medium. The copper(I) solution was then transferred, in carbon dioxide atmosphere. The ammonium perchlorate was dissolved within 30 min and after equilibration for about 2 h the titration series were started and run as described before.⁵

For the copper(II) bromide titrations, the calorimeter vessel initially contained copper(II) perchlorate in 1 M ammonium perchlorate.

For each system seven or eight series were performed, with initial concentrations C_M between 5 and 20 mM. Ligand solutions of $C_L = 200$ and 500 mM were used in the copper(I) and the copper(II) titrations, respectively.

The heats of dilution of Cu^+ and Cu^{2+} were negligible within the range of C_M used. Additions of 200 mM ligand solution to 1 M ammonium perchlorate gave a slight endothermic effect for chloride, at most 0.1 J ml^{-1} , an even smaller effect for bromide, at most 0.025 J ml^{-1} , and a negligible one for iodide.

Calculations. The simple EMK program used previously^{8,9} allows the calculation of the stability constants β_j for a series of mononuclear complexes ML_j . In the present measurements, this turns out to be adequate for the chloride and bromide systems. For iodide, however, the values of β_j computed increased strongly with C_M , indicating that polynuclear complexes are probably formed. The program was modified so that also such complexes could be accounted for. The various sets of stability constants were used, with the calorimetric data measured, as input values in the program KALORI,^{18,19} to compute the enthalpy changes. Also this program was modified so that polynuclear complexes could be incorporated.

RESULTS AND DISCUSSION

Electrode potentials and disproportionation of copper(I). The electrode potentials E_{01}° , E_{12}° and E_{02}° of the couples Cu(Hg)/Cu^+ , $\text{Cu}^+/\text{Cu}^{2+}$ and Cu(Hg)/Cu^{2+} , relative to the Cd(s)/Cd^{2+} standard

Table 1. Electrode potentials (E°/mV) of the couples Cu(Hg)/Cu^+ , $\text{Cu}^+/\text{Cu}^{2+}$ and Cu(Hg)/Cu^{2+} in DMSO, and in water, relative to the Cd(s)/Cd^{2+} electrode, and the disproportionation constant $K_D = [\text{Cu}^{2+}]/[\text{Cu}^+]^2$ (M^{-1}). Media of $I = 0.1 \text{ M}$ and 1 M , by NH_4ClO_4 ; 25°C . The errors indicated are the maximum deviations from the means listed which have been observed in the individual points.

Medium	0.1	1	Water: $I = 0$
E_{01}°	783.8 ± 2	795.8 ± 1	931
E_{12}°	773.0 ± 1	757.8 ± 1	561
E_{02}°	778.4 ± 1.5	776.8 ± 1	746
K_D	1.52 ± 0.15	4.4 ± 0.4	1.8×10^6

electrode, are listed in Table 1, together with the values of K_D for the disproportionation $2 \text{ Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu(Hg)}$ in the two media used. For comparison, values referring to aqueous solution have also been entered. In this solvent, the disproportionation is so extensive that direct determinations of E_{01}° or E_{12}° are not feasible. On the other hand, E_{02}° can be measured directly, and also K_D , though not very precisely.⁶ From the values of E_{02}° and K_D found, the values of E_{01}° and E_{12}° are then calculated according to $E_{01}^\circ = E_{02}^\circ + (RT/2F) \ln K_D$ and $E_{12}^\circ = E_{02}^\circ - (RT/2F) \ln K_D$. Careful scrutiny^{20,21} has shown that, at $I = 0$, probable values of E_{02}° are 338.4 mV for Cu(s)/Cu^{2+} and 343.5 mV for Cu(Hg)/Cu^{2+} . As $E_{02}^\circ(\text{Cu(Hg)}) - E_{02}^\circ(\text{Cu(s)}) = (RT/2F) \ln [K_D(\text{Cu(Hg)})/K_D(\text{Cu(s)})]$, this difference of 5.1 mV in E_{02}° (which of course can be directly measured) means a difference of 0.17 log units in K_D . A value of $\log K_D(\text{Cu(s)}) = 6.08$ has been assumed,^{20,21} hence $\log K_D(\text{Cu(Hg)}) = 6.25$. The same value has later also been found by a direct measurement at low I (0.1 M), though at 20°C .²² With a value²¹ of $E^\circ = -402.5 \text{ mV}$ for the couple Cd(s)/Cd^{2+} , the set of values listed in Table 1 is then obtained.

From the decrease of the difference $E_{01}^\circ - E_{12}^\circ$, and of the constant K_D directly connected with this difference, it is obvious that the disproportionation equilibrium is shifted very much in favour of Cu^+ when the system is transferred from water to DMSO. Relative to Cd(s)/Cd^{2+} , the Cu(Hg)/Cu^+ couple becomes much less oxidizing, the Cu(Hg)/Cu^{2+} couple somewhat more oxidizing on a transfer from water to DMSO.

The large decrease of K_D between water and DMSO is certainly mainly due to the fact that the

Table 2. Overall stability constants (β_j/M^{-j}) and enthalpy changes ($\Delta H_{\beta_j}^\circ/kJ\ mol^{-1}$) for the copper(I) chloride and bromide and the copper(II) bromide complexes formed in DMSO. Medium $I=1\ M$, by NH_4ClO_4 ; $25\ ^\circ C$. The errors indicated are three times the standard deviation given by the computer.

	Copper(I) Cl ⁻		Copper(II) Br ⁻
$\log \beta_1$	4.37(4)	4.19(2)	1.55(13)
$\log \beta_2$	8.87(2)	7.94(2)	2.60(18)
$\log \beta_3$	9.45(12)	—	—
$-\Delta H_{\beta_1}^\circ$	6.38(27)	9.29(22)	-8.2(1.6)
$-\Delta H_{\beta_2}^\circ$	14.18(15)	7.23(21)	-14.7(2.8)

solvation enthalpies of the ions involved differ considerably between the two solvents. The values of ΔH_{tr}° ($W \rightarrow DMSO$) for Cu^+ and Cu^{2+} are admittedly not known but must be of much the same size as the values found² for Ag^+ and Cd^{2+} , respectively, i.e. -54 and $-67\ kJ\ mol^{-1}$. At a transfer from water to DMSO, such changes would bring about a displacement to the left of the equilibrium $2\ Cu^+ \rightleftharpoons Cu^{2+} + Cu(Hg)$, equivalent to $\approx 40\ kJ\ mol^{-1}$, i.e. K_D would decrease by a factor $\approx 10^7$. Considering that the values of $\Delta H_{tr}(W \rightarrow DMSO)$ are crude approximations, and that the entropy terms have been neglected, the value calculated is indeed not far from the actually observed 10^6 .

Copper(I) halides. In the range of copper(I) concentrations used, only mononuclear complexes are formed in the chloride and bromide systems. For the first two complexes, fairly precise values of β_j can be determined, Table 2. In the chloride system, the formation of a third complex is indicated at high ligand concentrations. The value of β_3 determined is not very precise, however. The calorimetric measurements therefore only allow the determination of $\Delta H_{\beta_1}^\circ$ and $\Delta H_{\beta_2}^\circ$. For both systems these quantities are listed in Table 2.

In the iodide system, polynuclear complexes are seemingly also formed. At the low values of C_M used they are nevertheless of minor importance. Higher values of C_M were not tried, on account of the difficulties due to the disproportionation. To interpret the present data, only dinuclear complexes were assumed. Table 3 presents the values of β_{ij} and $H_{\beta_{ij}}^\circ$ obtained for three alternatives, viz. only the mononuclear complexes CuI and CuI_2^- , the dinuclear complex Cu_2I^+ in addition to these, and finally with Cu_2I_2 as a further addition. On the

Table 3. Overall stability constants (β_{ij}/M^{1-i-j}) and enthalpy changes ($\Delta H_{\beta_{ij}}^\circ/kJ\ mol^{-1}$) for the various sets of copper(I) iodide complexes postulated. Medium $I=1\ M$, by NH_4ClO_4 ; $25\ ^\circ C$. Errors refer to three standard deviations.

$Cu_iI_j^{i-j} \rightarrow$	CuI	CuI_2^-	Cu_2I^+	Cu_2I_2
$\log \beta_{ij}$	4.83(4)	7.64(7)		
$-\Delta H_{\beta_{ij}}^\circ$	13.5(4)	10.5(6)		
$\log \beta_{ij}$	4.71(6)	7.67(6)	6.5(2)	
$-\Delta H_{\beta_{ij}}^\circ$	13.6(3)	10.5(4)	10(1)	
$\log \beta_{ij}$	4.51(6)	7.49(5)	6.4(1)	9.6(1)
$-\Delta H_{\beta_{ij}}^\circ$	12.1(8)	10.3(4)	12(1)	120(19)

whole, the fit does improve by the introduction of Cu_2I^+ while Cu_2I_2 brings no further improvement. On the contrary, a quite improbable value of $\Delta H_{\beta_{ij}}^\circ$ is obtained for this complex. Nor is the situation improved by the introduction of further dinuclear complexes. The second alternative therefore provides the best interpretation of the data, though it must be admitted that the existence of Cu_2I^+ remains somewhat hypothetical. Its maximum share of the total copper(I) concentration (reached in the solutions of $C_M \approx 16\ mM$, for $\bar{n}=0.5$) would never exceed 20%. An indirect support for the existence of this complex is found in the ready formation of the analogous Ag_2I^+ in DMSO solutions, containing an excess of silver(I) nitrate.²³

The values of the stepwise mononuclear stability constants, K_j , and enthalpy changes, ΔH_j° , are listed in Table 4, together with the derived values of the free energy and entropy changes. For comparison, the results of earlier stability measurements in DMSO, referring to $0.1\ M\ Et_4NClO_4$ medium, have also been listed, as well as some stability data referring to aqueous solutions.

The relative stabilities of the complex CuL in water are not known, on account of their slight solubilities. Both for the first two steps combined, and for the third step, (b)-sequences $Cl^- < Br^- < I^-$ are found, however, though in the case of the first two steps the difference between the chloride and the bromide complex is rather small, Table 4. When the systems are transferred to DMSO, the expected increase of the stabilities of the chloride relative to the iodide complexes takes place. While the value of $-\Delta G_{\beta_2}^\circ$ increases considerably for $CuCl_2^-$, it decreases for CuI_2^- . Also for $CuBr_2^-$, an increase is found, though smaller than for $CuCl_2^-$.

Table 4. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\ mol^{-1}$; $\Delta S_j^\circ/JK^{-1}\ mol^{-1}$) for the stepwise formation of copper(I) halide and copper(II) bromide complexes in DMSO and in water, at 25 °C.

	Cu(I)			Cu(II)	Cu(I)			Cu(II)	
	Cl ⁻	Br ⁻	I ⁻	Br ⁻	Cl ⁻	Br ⁻	I ⁻	Cl ⁻	Br ⁻
DMSO, 1 M NH ₄ ClO ₄ ^a					DMSO, 0.1 M Et ₄ NClO ₄ ^b				
log K_1	4.37	4.19	4.71	1.55	6.0	5.0	5.5	6.0	3.4
log K_2	4.50	3.75	2.96	1.05	6.0	4.6	2.7	6.2	0.9
log K_3	0.58								
K_1/K_2	0.7	2.8	56	3.2	1	3	600	0.6	300
K_2/K_3	8000								
$-\Delta G_1^\circ$	24.9	23.9	26.9	8.8	34	29	31	34	19
$-\Delta G_2^\circ$	25.7	21.7	16.9	6.0	34	26	16	35	5
$-\Delta G_3^\circ$	3.3								
$-\Delta H_1^\circ$	6.4	9.3	13.6	-8.2					
$-\Delta H_2^\circ$	7.8	-2.1	-3.1	-6.5					
ΔS_1°	62	49	45	57					
ΔS_2°	60	78	67	42					
$-\Delta G_{\beta 2}^\circ$	50.6	45.6	43.8	14.9	68	55	47	69	24
$-\Delta H_{\beta 2}^\circ$	14.2	7.2	10.5	-14.7					
$\Delta S_{\beta 2}^\circ$	122	127	112	99					
Water, 5 M NaClO ₄ ^c					Water, $I = 0$ ^d				
$-\Delta G_{\beta 2}^\circ$	34.6	35.8	50		30.3	33.6	50.0		
$-\Delta G_3^\circ$	-0.7	6.7	10						
$-\Delta G_4^\circ$			-5.9						

^a This work. ^b Ref. 7, except the second set of values for copper(I) chloride which is from Ref. 13. ^c Ref. 4. ^d Ref. 20.

For the first two complexes combined, the net result of the transfer will therefore be a switch to an (a)-sequence Cl⁻ > Br⁻ > I⁻.

In DMSO, the two consecutive steps behave very differently, however. For both the media investigated, the first step, in fact, displays a hybrid sequence Cl⁻ > Br⁻ < I⁻, with a minimum at Br⁻. As a consequence, a very marked (a)-sequence is found for the second step. This also means that the stability of the first complex relative to the second one increases markedly from chloride to iodide, as reflected in the increasing values of K_1/K_2 . These conditions are well illustrated by the complex formation curves of Fig. 1. The curves become less steep in the sequence Cl⁻ > Br⁻ > I⁻, and the iodide curve crosses over the other two, displaying a marked bend towards $\bar{n} = 1$. The increasing im-

portance of the intermediate complex CuL is also shown by the distribution curves of Fig. 2.

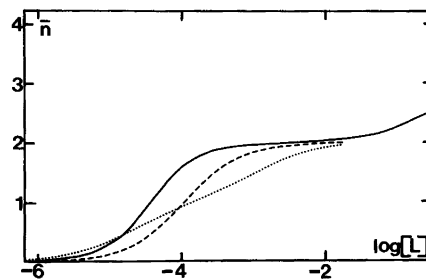


Fig. 1. The complex formation curves of the copper(I) chloride (—), bromide (---) and iodide (···) systems in DMSO. Medium 1 M NH₄ClO₄; 25 °C.

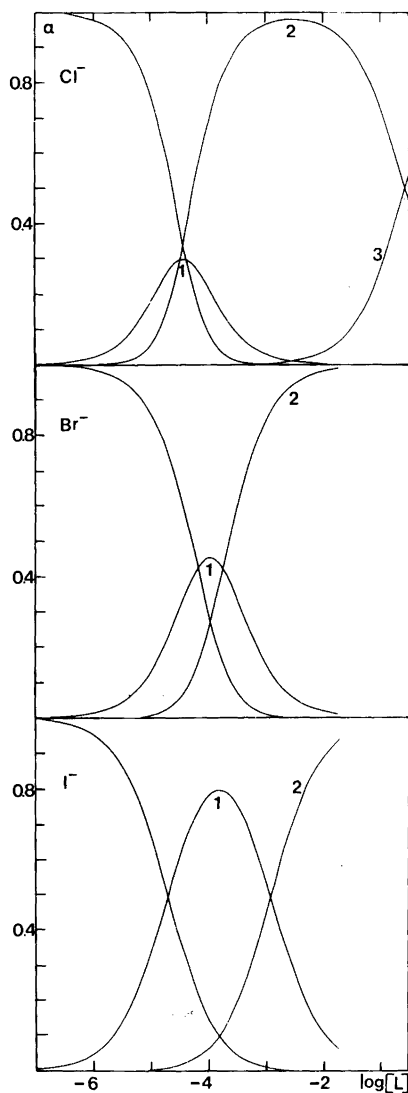


Fig. 2. The distribution of copper(I) between the species Cu^+ , CuL (1), CuL_2 (2) and CuL_3 (3) for the halide systems, as a function of the concentration of free ligand.

These trends in the stabilities are brought about by very marked trends in the heats of reaction, while the entropy changes are less specific, Table 4. The values of ΔH_1° are all exothermic, and more so in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The values of ΔH_2° show the opposite trend, with the values endothermic for Br^- and I^- . The values of ΔS_j° are

all large and positive, implying a strong entropy stabilization of the complexes. This is a common feature of halide complex formation in aprotic solvents, such as DMSO, which are relatively, unstructured. Consequently, the break-up of the solvate structures imply a much larger loss of order than in the more well-structured protic solvents.^{1,2,8,9,24}

The trend found for ΔH_1° is the one expected for halide complexes of typically soft metal ions, both in protic and aprotic solvents, on account of the strengthening of the coordinate bond, and the weakening of the ligand solvation, from Cl^- to I^- . For Hg^{2+} , all ΔH_j° also vary in this manner.^{2,24}

The unexpected trend found for ΔH_2° is presumably connected with the desolvation of relatively strongly solvated complexes CuBr and CuI . An unusually strong solvation of these complexes is further indicated by the circumstance that $\Delta S_2^\circ > \Delta S_1^\circ$.

For the formation of the Cu_2I^+ according to $\text{CuI} + \text{Cu}^+ \rightleftharpoons \text{Cu}_2\text{I}^+$, values of $\log K = 1.8$ and $\Delta H^\circ \approx 4 \text{ kJ mol}^{-1}$ are calculated, and hence $\Delta S^\circ \approx 45 \text{ JK}^{-1} \text{ mol}^{-1}$. The enthalpy and entropy changes of this reaction would thus be of much the same magnitude as for $\text{CuI} + \text{I}^- \rightleftharpoons \text{CuI}_2^-$.

Copper(II) bromide. The calorimetric investigation of this system yielded the values of β_j and $\Delta H_{\beta_j}^\circ$ listed in Table 2. From these values, the quantities pertaining to the consecutive steps have been calculated, Table 4. In this table, the values of K_j obtained in an earlier potentiometric investigation,⁷ performed in 0.1 M Et_4NClO_4 , have also been entered. The difference between the values of K_1 found in the two investigations seems too large to be explained by the difference in medium.

As might be expected, the complexes are much more stable in DMSO than in water.^{1,21} For both steps, the complex formation is endothermic. For Cu^{2+} , the considerable amount of energy spent on desolvation is evidently larger than the energy gained by the formation of the acceptor to donor bond. This is most probably due to the relatively hard character of Cu^{2+} which means that less energy is to be gained by covalent bond formation. The complexes are thus entropy stabilized. The entropy terms are of much the same magnitude as for the copper(I) halide systems which, of course, implies that the stabilities of the complexes are much lower.

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REFERENCES

1. Ahrland, S. In Lagowski, J. J., Ed., *The Chemistry of Non-Aqueous Solvents*, Academic, New York and London 1978, Vol. 5 A, Chapter 1.
2. Ahrland, S. *Pure Appl. Chem.* 51 (1979) 2019.
3. Criss, C. M. and Salomon, M. In Covington, A. K. and Dickinson, T., Eds., *Physical Chemistry of Organic Solvent System*, Plenum, London and New York 1973, Chapter 2. Part 4.
4. Ahrland, S. and Tagesson, B. *Acta Chem. Scand. A* 31 (1977) 615.
5. Ahrland, S., Tagesson, B. and Tuhtar, D. *Acta Chem. Scand. A* 31 (1977) 625.
6. Ahrland, S. and Rawsthorne, J. *Acta Chem. Scand.* 24 (1970) 157.
7. Foll, A., Le Démézet, M. and Courtot-Coupez, J. *J. Electroanal. Chem.* 35 (1972) 41.
8. Ahrland, S. and Björk, N.-O. *Acta Chem. Scand. A* 30 (1976) 249, 257.
9. Ahrland, S., Björk, N.-O. and Portanova, R. *Acta Chem. Scand. A* 30 (1976) 265, 270.
10. Ahrland, S. and Björk, N.-O. *Acta Chem. Scand. A* 28 (1974) 823.
11. Selbin, J., Bull, W. E. and Holmes, L. H., Jr. *J. Inorg. Nucl. Chem.* 16 (1961) 219.
12. Cotton, F. A. and Francis, R. *J. Am. Chem. Soc.* 82 (1960) 2986.
13. Suarez, T. E., Iwamoto, R. T. and Kleinberg, J. *Inorg. Chim. Acta* 7 (1973) 292.
14. Rainoni, G. and Zuberbühler, A. D. *Chimia* 28 (1974) 67.
15. Ahrland, S., Berg, T. and Bläuenstein, P. *Acta Chem. Scand. A* 32 (1978) 933.
16. Parks, W. G. and LaMer, V. K. *J. Am. Chem. Soc.* 56 (1934) 90.
17. Grenthe, I., Ots, H. and Ginstrup, O. *Acta Chem. Scand.* 24 (1970) 1067.
18. Karlsson, R. and Kullberg, L. *Chem. Scr.* 9 (1976) 54.
19. Kullberg, L. *Acta Chem. Scand. A* 28 (1974) 829.
20. Berecki-Biedermann, C., Biedermann, G. and Sillén, L. G. *Report to Analytical Section, IUPAC, Stockholm 1953.*
21. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-Ion Complexes*, Chemical Society, Special Publication No. 17, London 1964.
22. Anderegg, G. *Helv. Chem. Acta* 46 (1963) 2397.
23. Luehrs, D. C. and Abate, K. *J. Inorg. Nucl. Chem.* 30 (1968) 549.
24. Ahrland, S., Persson, I. and Portanova, R. *To be published.*

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