

Thermodynamics and Structures of Complexes in Solvents Coordinating through Nitrogen. III. Equilibrium and Enthalpy Measurements on the Copper(I) and Silver(I) Chloride, Bromide, Iodide and Thiocyanate Systems in Pyridine

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The thermodynamics of formation of copper(I) and silver(I) halide and thiocyanate complexes in pyridine have been determined by potentiometric and calorimetric measurements. In the copper(I) systems, the first two mononuclear complexes were formed within the range of concentrations used. The complexes were strongly entropy-stabilized; the reactions were all endothermic. In the silver(I) systems, the complex formation proceeded with a third mononuclear complex in the case of chloride and bromide. Further, in all the silver(I) systems, the dinuclear complex Ag_2L^+ was formed even at the low silver concentrations used here (≤ 20 mM). The silver complexes were also strongly entropy-stabilized. The enthalpy terms were more favourable than for the copper(I) complexes, however, being generally around zero. It was inferred that strong entropy stabilization is a general characteristic of complexes formed in soft solvents between soft acceptors and halides, or pseudohalides. However, the entropy terms throughout were less favourable for the pseudohalides where conformational entropies act against the predominating desolvation entropies.

In the soft solvent pyridine, with strong electron donating properties, complex formation reactions between the soft acceptor Hg^{2+} and halide or thiocyanate ions display many remarkable features.¹ It is therefore of great interest to extend such studies to other soft acceptors, primarily of the electron configuration d^{10} . In the present paper, results referring to the monovalent acceptors Cu^+ and Ag^+ are reported.

By comparison with the conditions prevailing in aqueous solution, copper(I) is favoured relative to both copper(II) and copper(0) in aprotic

solvents. This applies especially if oxygen is exchanged for nitrogen as donor atom. In such solvents, Cu^+ is much more strongly solvated than in aqueous solution. The increase is more marked than for Cu^{2+} , so that the constant $K_D = [\text{Cu}^{2+}]/[\text{Cu}^+]^2$ of the disproportionation reaction $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu(s)}$ decreases from $\approx 10^6 \text{ M}^{-1}$ in water to $\approx 10^{-21} \text{ M}^{-1}$ in acetonitrile.^{2,3} In pyridine also, K_D is so small that virtually no disproportionation occurs, as is shown below. The stronger solvation of copper(I) further causes the neutral halide and thiocyanate complexes, slightly soluble in water, to become readily soluble. Consequently, the formation of copper(I) halide and thiocyanate complexes can be followed in its entire course in these solvents,² which is not possible in aqueous solutions.^{3,4} The strong stabilization of copper(I)

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relative to copper(II) further facilitates such measurements by making the solutions of copper(I) much less sensitive to air oxidation.

For an accurate, and precise, determination of the thermodynamics of the complex formation reactions, calorimetric determinations of the enthalpy changes involved are wanted. Such measurements demand concentrations of at least a few mM. For silver(I), the low solubility of the neutral halide and thiocyanate complexes in all solvents used so far, including acetonitrile,⁵ have heretofore precluded such investigations. In pyridine, however, these silver(I) species are so strongly solvated that they become sufficiently soluble for calorimetric measurements. In spite of the low dielectric constant of pyridine, $\epsilon = 12.3$, potentiometric measurements are feasible in this solvent, as has been proved in the case of the mercury(II) halide and thiocyanate systems.¹ Analogous measurements turned out to be possible also for copper(I) and silver(I) by means of copper amalgam and silver metal electrodes, respectively. All measurements were performed, as before, in a medium containing 0.1 M tetraethylammonium, Et_4N^+ , ions, perchlorate was used as the supplementary salt, the temperature was 25°C.

Experimental

The copper(I) tetrasolvate $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_4]\text{ClO}_4$ was prepared by treating the acetonitrile solvate $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ with pyridine. Copper analysis was made by EDTA titration: found 13.2%, calc. 13.3%. The copper(II) tetrasolvate $\text{Cu}(\text{C}_5\text{H}_5\text{N})_4(\text{ClO}_4)_2$ was prepared according to Penner-Hahn *et al.*⁶ The anhydrous silver perchlorate, AgClO_4 *p.a.*, was dried at 100°C under vacuum and used without further purification. The tetraethylammonium salts, and the pyridine solvent, all of *p.a.* quality, were treated as described before.¹ The two-phase copper amalgam, containing $\approx 3\%$ copper, was prepared as described before⁴ and stored under 0.1 M aqueous perchloric acid. Immediately before use, it was washed repeatedly with water then dried in a stream of dry nitrogen.

The value of the disproportionation constant, K_D , was found from the standard potentials E_{01}° and E_{12}° of the couples $\text{Cu}(\text{s})/\text{Cu}^+$ and $\text{Cu}^+/\text{Cu}^{2+}$, respectively, according to the formula $\ln K_D = (E_{01}^\circ - E_{12}^\circ)/RTF^{-1}$. Actually, E_{01}° (am) of the amal-

gam couple $\text{Cu}(\text{Hg})/\text{Cu}^+$ was measured and the value of E_{01}° then calculated from $E_{01}^\circ = E_{01}^\circ(\text{am}) - E_1$ where $E_1 = 10.2$ mV. In all the measurements, a silver reference electrode was used, containing 10 mM silver perchlorate in 0.1 M tetraethylammonium perchlorate. As already found in the previous investigation,¹ this electrode gives very stable and well reproducible potentials. That silver electrodes generally work well in pyridine solutions has long been known.^{7,8} In the following, the copper potentials are referred to the standard silver electrode in the same medium (experimentally not to be realized!) which is 118.3 mV more positive than the reference electrode actually used.

For the determination of E_{01}° , three cells, with $[\text{Cu}^+]$ varying from 10 to 25 mM, were measured. For the determination of E_{12}° , a solution of the copper(II) perchlorate, with an initial $[\text{Cu}^{2+}] = 0.979$ mM, was titrated with a solution of the copper(I) perchlorate, so that the ratio $[\text{Cu}^{2+}]/[\text{Cu}^+]$ was varied between ≈ 1 and $\approx 1/15$ (see Fig. 1). Once E_{01}° and E_{12}° were known, the standard potential E_{02}° of the couple $\text{Cu}(\text{s})/\text{Cu}^{2+}$ could be calculated according to $E_{02}^\circ = (E_{01}^\circ + E_{12}^\circ)/2$.

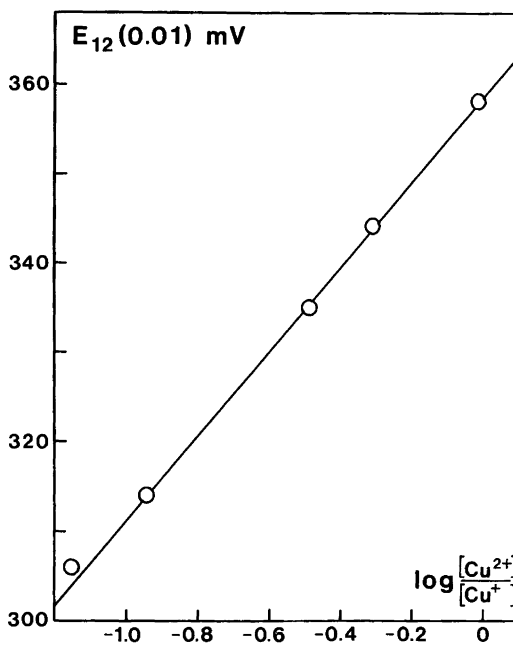


Fig. 1. Slope of the $\text{Cu}^+/\text{Cu}^{2+}$ electrode, ≈ 48 mV, and determination of E_{12}° .

For potentiometric measurements, solutions containing initially 3, 6 or 12 mM copper(I) perchlorate, or 5, 10 or 20 mM silver(I) perchlorate were titrated with solutions of the appropriate ligand. These solutions were 50, 24, 15 and 100 mM in chloride, bromide, iodide and thiocyanate, respectively. As to the bromide and iodide, these concentrations were as high as the solubilities of the respective tetraethylammonium salts in a medium of $[\text{Et}_4\text{N}^+] = 0.1 \text{ M}$ permitted. The same silver reference electrode as before was used. The emfs generally reached their final values in a few minutes and then stayed constant for hours. The reproducibility was generally within 1 mV. For values close to the equivalence points, the reproducibility was lower, but still within $\approx 3 \text{ mV}$. The titrations were performed in a carefully dried glove box. From the emfs found, the values of the overall stability constants $\beta_{ji} = [\text{M}_i\text{L}_j]/[\text{M}]^i [\text{L}]^j$ for the reactions $i\text{M} + j\text{L} \rightleftharpoons \text{M}_i\text{L}_j$ (charges omitted) were calculated by means of the program EMK, as modified for systems where polynuclear complexes are formed.⁹

Calorimetric measurements were made using the same calorimeter as for the mercury(II) systems previously reported.¹ An initial volume of 50 ml metal perchlorate solution was titrated with a ligand solution, the concentrations chosen the same as in the potentiometric measurements. The heats evolved were corrected for the heats of dilution: for the ligands, they have been determined previously;¹ for Ag^+ , they are very small; for Cu^+ , completely negligible. From the corrected heat values, the overall enthalpy changes $\Delta H_{\beta_{ji}}^\circ$ for the formation of the complexes M_iL_j were calculated by means of the program MAINKA, developed in order to allow for other systems where polynuclear complexes are formed.⁹ In these calculations, the stability constants β_{ji} from the potentiometric measurements were used as fixed parameters (cf. Ref. 1).

Results

Disproportionation constant and standard potentials of the $\text{Cu(s)}-\text{Cu}^+-\text{Cu}^{2+}$ system. From the Cu(Hg)/Cu^+ measurements, a value of E_{01}° (am) = -576.2 mV was obtained; hence, $E_{01}^\circ = -586.4 \text{ mV}$. The Nernst slope was close to the theoretical value. In the measurements of E_{12}° , on the other hand, the slope was considerably lower than the

theoretical value, though still fairly constant, (Fig. 1). For $[\text{Cu}^{2+}]/[\text{Cu}^+] = 1$, an emf of $358.7 \pm 0.4 \text{ mV}$ was found, corresponding to $E_{12}^\circ = 240.4 \text{ mV}$. Hence, $K_D = 1.06 \times 10^{-14} \text{ M}^{-1}$ which means, of course, that no perceptible disproportionation of Cu^+ takes place in pyridine. For Cu(s)/Cu^{2+} , a value of $E_{02}^\circ = -173.0 \text{ mV}$ was found. An earlier determination of K_D in pyridine resulted in a small, but nevertheless considerably larger value, namely $1.4 \times 10^{-9} \text{ M}^{-1}$ (at 18°C).⁸ This value was calculated from measurements in chloride media of varying concentrations, however. The strong complex formation in such media (a main theme of the present paper!) means, of course, that the conditions are very different from those of the present measurements.

Stability measurements. The overall stability constant β_j of the copper(I) complexes are listed in Table 1. Within the ranges of total metal and ligand concentrations (C_M and C_L , respectively) used here, only the two mononuclear complexes CuL and CuL_2^- were formed. For the iodide system, the highest free ligand concentration $[\text{L}]$ attainable was only $\approx 10 \text{ mM}$, on account of the low solubility of Et_4NI ; the second complex was therefore barely formed. This is also reflected in the complex formation curve in Fig. 2; it does not exceed $\bar{n} = 1$. As a consequence, the error in β_2 is quite large. In the bromide system also, the second complex never became very prominent in the restricted range of $[\text{L}]$ available on account of the fairly low solubility of Et_4NBr . Even for the chloride system which is the most stable one and where a value of $[\text{L}] \approx 30 \text{ mM}$ was attained, the value of \bar{n} did not quite reach 2. As is immediately clear from Fig. 2, all copper(I) halide complexes are considerably less stable in pyridine than in AN^2 , or DMSO .¹⁰ Moreover, the marked (a) sequence of stabilities, $\text{Cl}^- > \text{Br}^- > \text{I}^-$, found in these solvents (except for the first step of the iodide system in DMSO) is very much compressed in pyridine. Between the bromide and iodide systems, the stability difference is in fact marginal; the thiocyanate also follows a very similar course (Fig. 2).

The overall stability constants β_{ji} of the silver(I) complexes are also listed in Table 1. Within the ranges of C_M and C_L investigated, the third mononuclear complex AgL_3^{2-} was also found in the chloride and bromide systems. An important difference from the copper(I) systems is further

Table 1. Overall stability constants (β_i/M^{-i+1}) of the copper(I) and silver(I) halide and thiocyanate complexes in pyridine. Medium 0.1 M Et_4NClO_4 ; temperature 25 °C. The limits of error refer to three standard deviations; NP denotes the number of observations (emfs measured) for each system.

Ligand \rightarrow	Cl^-	Br^-	I^-	SCN^-
Copper(I)				
β_1	1229 ± 38	602 ± 12	495 ± 12	416 ± 9
β_2	$(9.92 \pm 0.43)10^4$	$(7.5 \pm 1.2)10^3$	$(3.9 \pm 1.9)10^3$	$(6.79 \pm 0.37)10^3$
NP	331	304	250	286
Silver(I)				
β_{11}	$(8.92 \pm 0.26)10^4$	$(1.07 \pm 0.04)10^5$	$(7.48 \pm 0.20)10^6$	$(4.34 \pm 0.08)10^3$
β_{21}	$(3.60 \pm 0.10)10^8$	$(2.74 \pm 0.12)10^8$	$(1.19 \pm 0.06)10^{10}$	$(3.62 \pm 0.13)10^5$
β_{31}	$(3.49 \pm 0.69)10^9$	$(3.91 \pm 0.54)10^{10}$		
β_{12}	$(8.31 \pm 1.25)10^6$	$(4.81 \pm 1.05)10^6$	$(1.33 \pm 0.15)10^9$	$(1.83 \pm 0.22)10^5$
NP	382	406	498	353

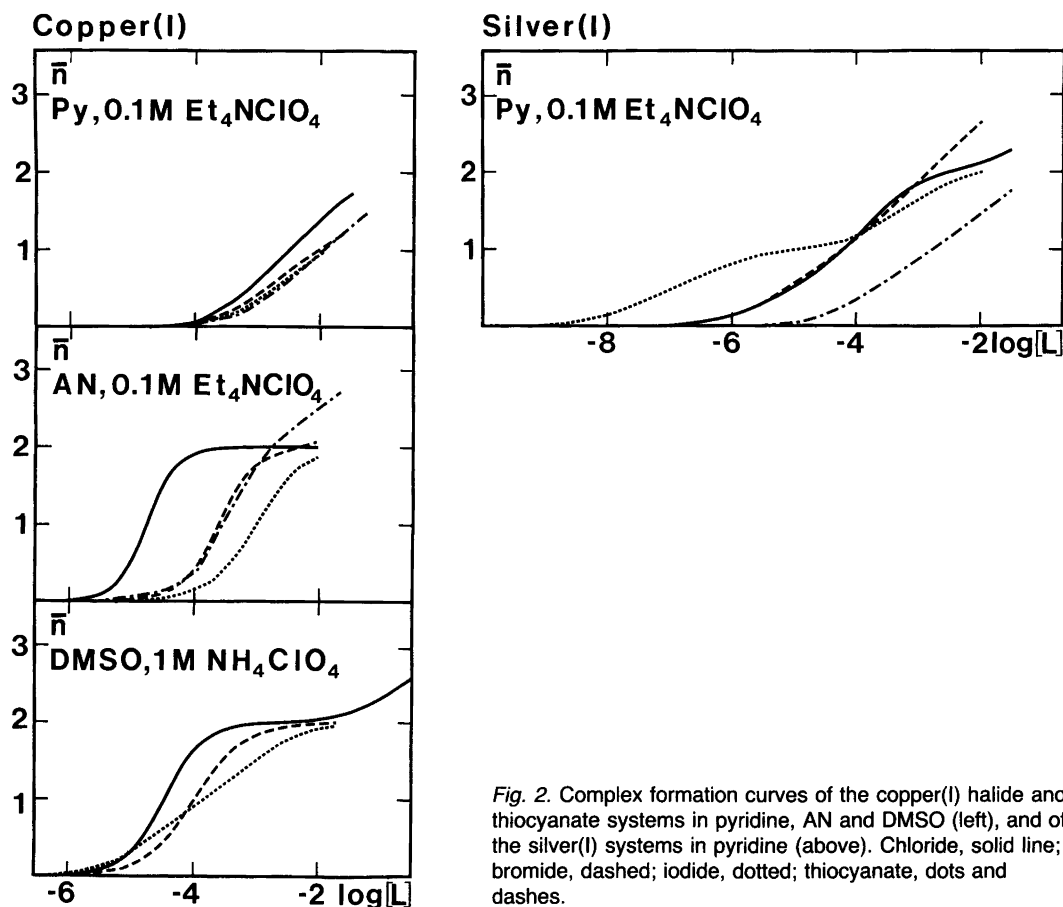


Fig. 2. Complex formation curves of the copper(I) halide and thiocyanate systems in pyridine, AN and DMSO (left), and of the silver(I) systems in pyridine (above). Chloride, solid line; bromide, dashed; iodide, dotted; thiocyanate, dots and dashes.

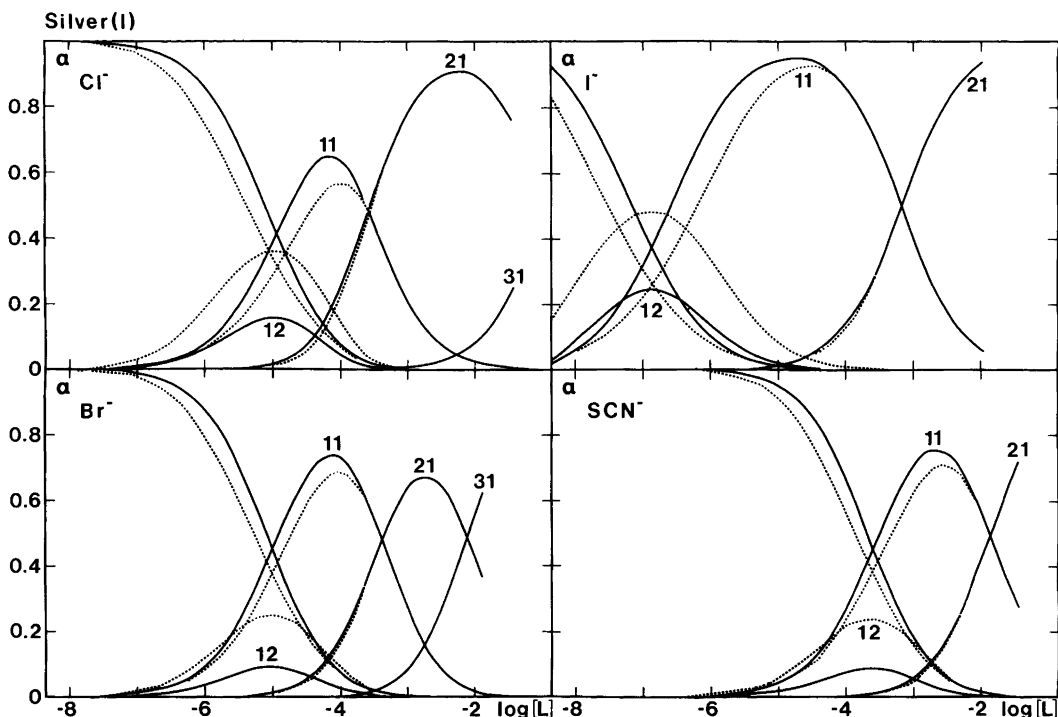


Fig. 3. Distribution of silver(I) halide and thiocyanate complexes in pyridine. The curves refer to the complexes $\text{Ag}_j\text{L}_i^{+i-j}$, denoted for each curve by the subscripts ji ; the first curves to the left refer to the solvated ion Ag^+ . Full-drawn and dotted curves refer to initial silver(I) concentrations of 5 and 20 mM, respectively.

that a dinuclear complex Ag_2L^+ was formed in all the systems even at the lowest silver(I) concentrations used here (initial value of $C_M = 5$ mM). This complex became, of course, more prominent the higher the value of C_M , as illustrated by the distribution curves given in Fig. 3. These also show that the dinuclear complex formation was most prominent in the iodide system. At its maximum, which occurs at the value of $[\text{L}]$ corresponding to $\bar{n} = 0.5$, close to half of the total silver concentration of 20 mM was in fact present as Ag_2I^+ (Fig. 3.). Somewhat surprisingly, the chloride system came next, while the formation of Ag_2L^+ was least prominent in the bromide and thiocyanate systems. These results are further discussed below.

The presence of dinuclear complexes also means that the complex formation curves became dependent on C_M in the range where these complexes existed in perceptible amounts, i.e. for $\bar{n} < 1$ (in the chloride system for $\bar{n} < 1.3$). On account of the character of the complex formation

function, the difference in \bar{n} for a given value of $[\text{L}]$ is not very large, however. For the iodide system where the effect is most marked, it amounted at most to 0.07 between the curves of $C_M = 5$ and 20 mM. For values of $\bar{n} < 0.5$, the value of \bar{n} were higher, the higher the value of C_M ; for $\bar{n} > 0.5$ the opposite was true. At $\bar{n} = 0.5$, the complex formation curves of different C_M crossed over.* The silver complex formation curves of Fig. 2 refer to the intermediate value of $C_M = 10$ mM. The silver complexes are all considerably more stable than those of copper and a value of $\bar{n} = 2$ was either exceeded, or at least approached, in all the systems. Consequently, the values of β_{21} could be much more precisely deter-

* At $\bar{n} = 0.5$, only the species Ag^+ , AgL and Ag_2L^+ existed in perceptible amounts, (Fig. 3). Hence, $\bar{n} = (C_L - [\text{L}])/C_M = 0.5 = (\beta_{11}[\text{L}] + \beta_{12}[\text{M}][\text{L}]) / (1 + \beta_{11}[\text{L}] + 2\beta_{12}[\text{M}][\text{L}])$ and $[\text{L}] = 1/\beta_{11}$, independent of the value of β_{12} .

Table 2. Overall enthalpy changes ($\Delta H_{\beta_i}^{\circ}/\text{kJ mol}^{-1}$) for the formation of the copper(I) and silver(I) halide and thiocyanate complexes in pyridine. Medium 0.1 M $\text{Et}_4\text{N}(\text{ClO}_4)$; temperature 25 °C. The limits of error refer to three standard deviations; NP denotes the number of observations (aliquots added) for each system.

Ligand \rightarrow	Cl^-	Br^-	I^-	SCN^-
Copper(I)				
$\Delta H_{\beta_1}^{\circ}$	13.0 ± 0.7	10.2 ± 0.4	8.5 ± 0.4	4.7 ± 0.1
$\Delta H_{\beta_2}^{\circ}$	30.4 ± 1.2	30.2 ± 3.6		11.6 ± 0.4
NP	88	62	58	86
Silver(I)				
$\Delta H_{\beta_{11}}^{\circ}$	1.0 ± 0.3	-3.3 ± 0.2	-12.3 ± 0.5	-1.5 ± 0.1
$\Delta H_{\beta_{21}}^{\circ}$	8.6 ± 0.3	3.3 ± 0.3	-8.5 ± 1.0	-1.4 ± 0.1
$\Delta H_{\beta_{31}}^{\circ}$	6.0 ± 5.6	2.1 ± 0.7		
$\Delta H_{\beta_{12}}^{\circ}$	3.0 ± 0.8	-1.6 ± 0.8	-13.0 ± 0.7	-1.1 ± 0.3
NP	121	138	142	144

mined. Even the values of β_{31} determined for the chloride and bromide systems were fairly precise.

Calorimetric measurements. The overall enthalpy changes, $\Delta H_{\beta_i}^{\circ}$, of all the systems investigated are listed in Table 2. The copper(I) complexes were all formed by endothermic reactions, the endothermicity decreasing in the order $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{SCN}^-$. In the silver(I) systems, the values throughout were more favourable for complex formation, increasingly so as the ligands became softer. These conditions are well illustrated by the course of Δh_n , the total heat change per mol copper(I) or silver(I) present as a function of \bar{n} , shown in Fig. 4. Obviously, the parameters calculated fit the experimental data very well. It should further be noted that the function Δh_n was not very sensitive to the formation of a dinuclear complex. In the silver systems, the points found for series of different initial values of C_M fell, within the limits of error, on the same curve. This curve was well fit by that calculated for $C_M = 10$ mM with the constants of Tables 1 and 2.

These observations agree with the general observation that fractional functions such as Δh_n (and also \bar{n}) are often not well suited for the investigation of polynuclear complex formation. In this respect, the polynomial $C_M/[M]$, as determined in the present potentiometric measurements, is much superior.

Discussion

The thermodynamic functions ΔG_j° , ΔH_j° and ΔS_j° for the consecutive formation reactions $\text{ML}_{j-1} + \text{L} \rightleftharpoons \text{ML}_j$, as calculated from the data of Tables 1 and 2, are listed in Table 3 which also gives the stepwise stability constants K_j , and the ratios K_j/K_{j+1} . For the silver systems, the data found for the formation of the dinuclear complexes according to $\text{AgL} + \text{Ag}^+ \rightleftharpoons \text{Ag}_2\text{L}^+$ are also listed.

The most striking thermodynamic feature of all complexes formed in pyridine is the very strong entropy stabilization, except for the formation of the third silver chloride complex. The same predominance of the entropy terms was also found for the mercury halide and thiocyanate complexes in pyridine.¹ Evidently, several factors combine to bring about this effect. Firstly, soft acceptors are strongly solvated in a typically soft solvent such as pyridine.^{11,12} As to Cu^+ and Ag^+ , tetrahedral solvates are formed⁶ which also exist in solid phases.^{13,14} As to Hg^{2+} , the structure of the solvate in solution is not yet established. Considering the structures of mercury(II) solvates in other solvents, an octahedral coordination seems likely.¹⁵ This surmise is also supported by the existence of a solid hexasolvate.¹⁶ Secondly, the coordination of halide or thiocyanate ions implies, at least initially, the formation of complexes where only two ligands are strongly bonded. This is evident from the complex formation curves which generally have a marked shelf

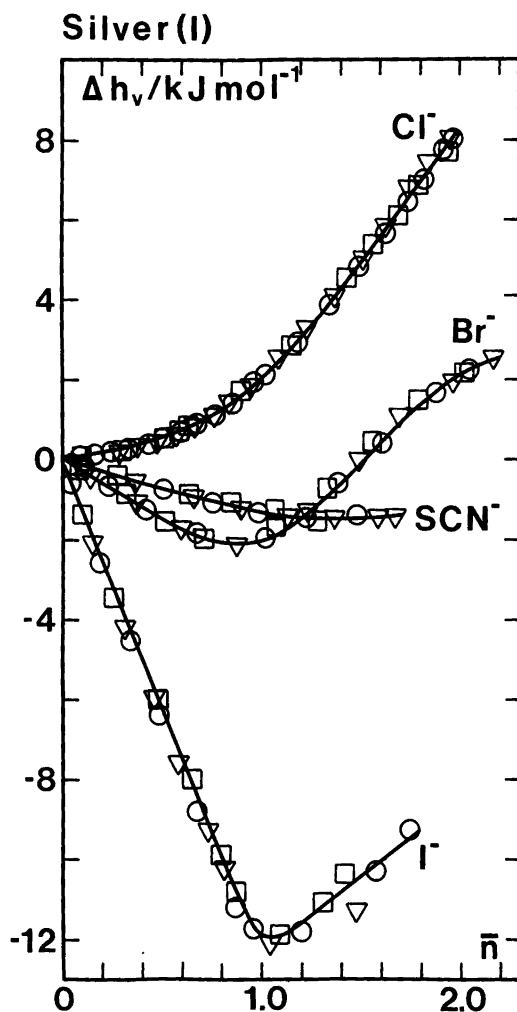
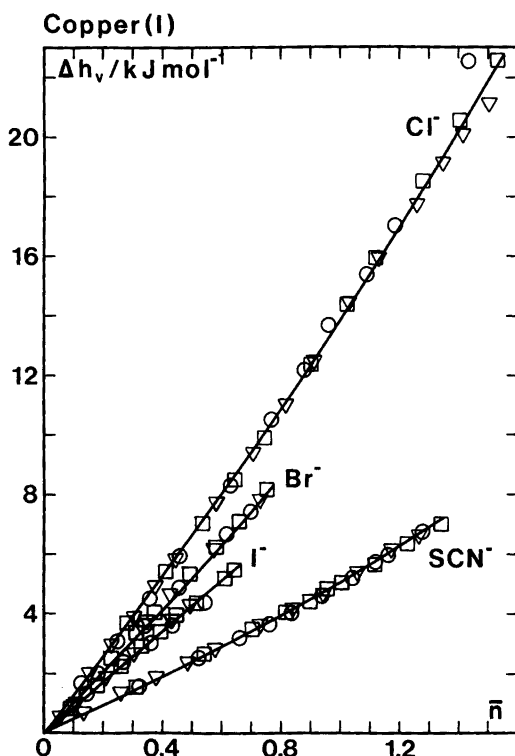


Fig. 4. The total molar enthalpy changes Δh_v as a function of the ligand number \bar{n} for the formation of halide and thiocyanate complexes of copper(I) (left) and silver(I) (right) in pyridine. The points refer to the values actually measured, with initial concentrations of 3, 6 and 12 mM for copper(I) and 5, 10 and 20 mM for silver(I) (circles, squares, and triangles, respectively). The full-drawn curves have been calculated from the values of β_1 and ΔH_{β_1} listed in Tables 1 and 2.

at $\bar{n} = 2$. For Hg^{2+} in pyridine, this conclusion has further been directly confirmed by structure determinations of the HgL_2 complexes.^{17,18} Both in solution and in solid phase, pseudolinear complexes are formed with angles $\text{L}-\text{Hg}-\text{L}$ between 141° and 150° . Two pyridine molecules complete a very distorted tetrahedron with angles $\text{N}-\text{Hg}-\text{N}$ only slightly larger than 90° . Further, the distances $\text{Hg}-\text{N}$ are long, ≈ 0.245 nm, compared with 0.212 nm in the cation of the solid¹⁹ $[\text{Hg}(\text{py})_2][\text{CO}_2\text{CF}_3]_2$.

The preponderance of the entropy terms also applies to the formation of halide and thiocyanate complexes of copper(I) in acetonitrile where

the conditions are analogous to those described above.² The complex formation implies that a tetrahedral solvate (also existing in crystalline solids²⁰) is replaced by two-coordinated halide or thiocyanate complexes. In all these cases, the initial steps of the complex formation thus mean an extensive desolvation of the central ion, accompanied by a lowering of the coordination number in the inner sphere. The solvents leaving the strictly ordered solvates are, moreover, transferred to a bulk solvent which is not very ordered. The molecules of the solvents are admittedly fairly polar (dipole moment $\mu = 2.23$ and 3.92 D for pyridine and acetonitrile, respec-

tively), but the values of the dielectric constant ϵ are nevertheless comparatively low. The ratios ϵ/μ are only 5.5 and 9.2 D⁻¹, respectively, as against 42.4 D⁻¹ for water and 19.2 D⁻¹ for methanol, which certainly indicates that the dipoles do not line up very orderly in the nitrogen donor solvents.² The desolvation entropy therefore becomes very positive. This gain is by far not compensated for by the loss of entropy, due to the coordination of a much smaller number of ligands, especially as the desolvation of the ligands on coordination means another gain of entropy. The net outcome of the complex formation is, therefore, a large gain of entropy.

In pyridine, the entropy increases are much the same for the copper(I) and silver(I) systems. Neither do they differ much between the different halides. For the thiocyanate complexes, they are considerably lower than for the halides, however.

Evidently, this is due to the lower symmetry of the thiocyanate ion which is reflected in an unfavourable conformational entropy. For all the copper(I) and silver(I) systems, the entropies are much lower than for the analogous mercury (II) systems.¹ This is to be expected; the divalent Hg²⁺ is much more strongly solvated than the monovalent ions, and the coordination number of the solvate certainly higher than for Cu²⁺ and Ag⁺. Extensive desolvation consumes much energy, not always fully compensated for by the energy gain from complex formation. Consequently, the enthalpy changes tended to be unfavourable, (Table 3). This applies especially to the copper(I) systems whereas the values of the silver(I) systems were more favourable. Evidently, the heat of complex formation is more favourable relative to the heat of desolvation for silver(I) than for copper(I), reflecting the lower

Table 3. Equilibrium constants (K_i/M^{-1}) and thermodynamic functions (ΔG_i° ; $\Delta H_i^\circ/kJ\ mol^{-1}$; $\Delta S_i^\circ/JK^{-1}mol^{-1}$) for the stepwise formation of copper(I) and silver(I) halide and thiocyanate complexes in pyridine, at 25°C. Medium 0.1 M Et₄NClO₄.

	Copper(I)				Silver(I)			
	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻
logK ₁	3.09	2.78	2.69	2.62	4.95	5.03	6.87	3.64
logK ₂	1.91	1.10	~0.9	1.21	3.61	3.41	3.20	1.92
logK ₃					0.99	2.16		
logK ₋₂					1.97	1.65	2.25	1.63
K ₁ /K ₂	15	48	~60	26	22	42	4.7·10 ³	52
K ₂ /K ₃					420	18		
K ₁ /K ₋₂					960	2.4·10 ³	4.2·10 ⁴	103
K ₂ /K ₋₂					43	57	8.9	2.0
-ΔG ₁ ^o	17.6	15.9	15.4	15.0	28.3	28.7	39.2	20.8
-ΔG ₂ ^o	10.9	6.3	~5	6.9	20.6	19.5	18.3	11.0
-ΔG ₃ ^o					5.6	12.3		
-ΔG ₋₂ ^o					11.2	9.4	12.8	9.3
-ΔH ₁ ^o	-13.0	-10.2	-8.5	-4.7	-1.0	3.3	12.3	1.5
-ΔH ₂ ^o	-17.4	-20.0		-6.9	-7.6	-6.7	-3.8	-0.1
-ΔH ₃ ^o					2.6	1.2		
-ΔH ₋₂ ^o					-2.0	-1.8	0.6	0.4
ΔS ₁ ^o	103	87	80	66	98	85	90	65
ΔS ₂ ^o	95	88		46	95	88	74	37
ΔS ₃ ^o					10	37		
ΔS ₋₂ ^o					44	38	41	33
-ΔG _{β2} ^o	28.5	22.1	~20	21.9	48.8	48.2	57.5	31.7
-ΔH _{β2} ^o	-30.4	-30.2		-11.6	-8.6	-3.3	8.5	1.4
-ΔS _{β2} ^o	198	175		112	193	173	164	102

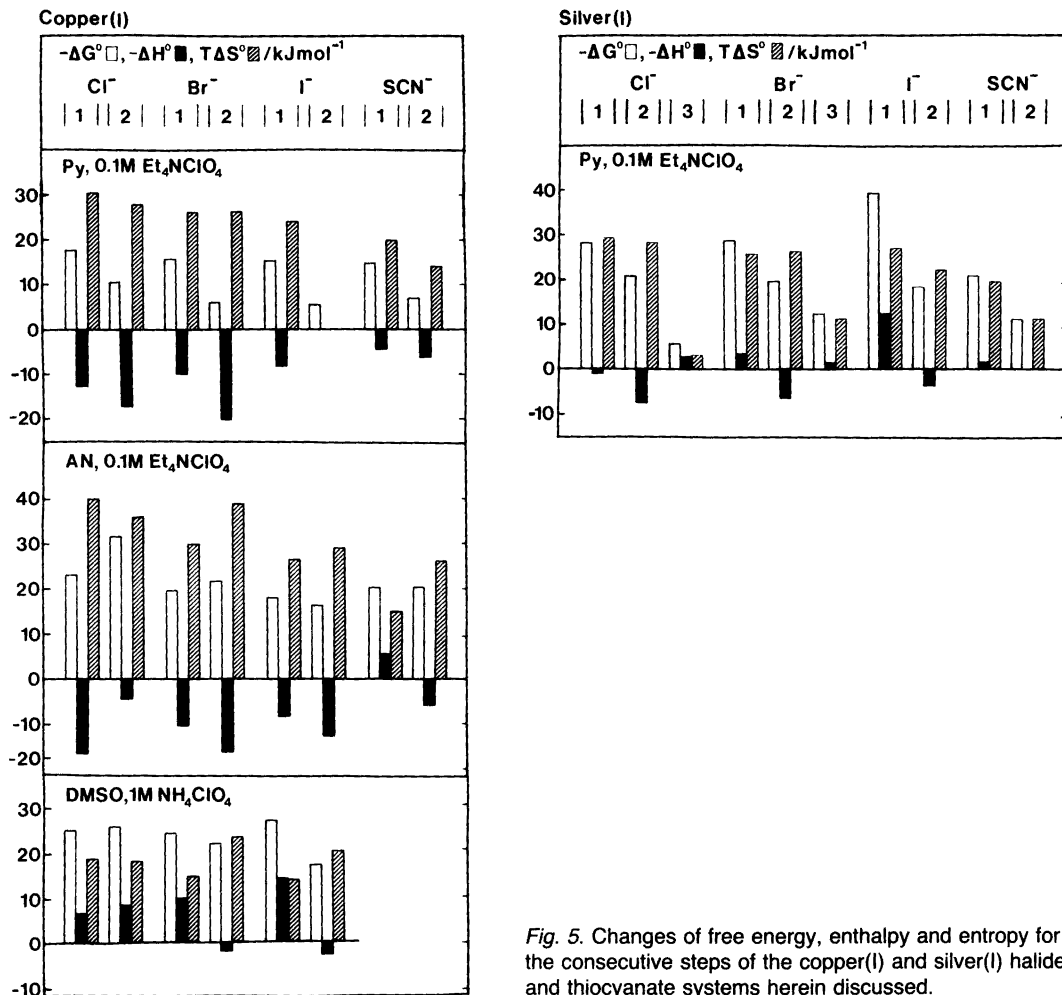


Fig. 5. Changes of free energy, enthalpy and entropy for the consecutive steps of the copper(I) and silver(I) halide and thiocyanate systems herein discussed.

charge density of silver(I) and the more covalent character of its halide bonds.

The enthalpy and entropy contributions to the free energy changes are illustrated in Fig. 5. The paramount importance of the entropy changes for the stability of all the complexes investigated is evident. For the reasons just discussed, this must be a general feature for interactions between halides, or pseudohalides, and soft metal ions in soft solvents, at least for the initial steps of complex formation. The degree of predominance of the entropy terms depends upon the character of the solvent. For copper(I) it is more marked in pyridine, and in acetonitrile,² than in DMSO.¹⁰

The reasons are, firstly, that Cu⁺ is less strongly solvated in DMSO^{11,12} and, secondly, that DMSO is a more structured solvent. For the same reasons, the entropy stabilization is more marked in pyridine than in DMSO for the mercury(II) systems.¹ For these, the functions pertaining to the complex formation in water are also known. Not surprisingly, in this highly structured solvent, where, moreover, the solvation of mercury(II) is weaker than in the aprotic solvents, the complexes are strongly *enthalpy*-stabilized.¹

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