

COMPLEX FORMATION IN PROTIC AND APROTIC MEDIA

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Abstract - Complex formation between a metal ion and a ligand occurs in competition with solvation reactions. In protic solvents, hydrogen-bonding ligands are especially strongly solvated and therefore not as amenable to complex formation as in aprotic solvents. Relative to complexes of ligands forming no hydrogen bonds, the complexes of hydrogen-bonding ligands should therefore be much more stable in aprotic than in protic solvents. This inference has been borne out by comparisons between the halide and thiocyanate complexes formed by zinc(II), cadmium(II), mercury(II) and copper (I) in the protic solvent water and the aprotic solvent dimethylsulfoxide (DMSO). Especially the chloride but also the bromide complexes are much more stable in DMSO than in water, while the stabilities of the iodide and the thiocyanate complexes do not differ very much between the two solvents. Considering the stronger solvation of the metal ions, and also of the iodide ion in DMSO, the high absolute stabilities found in this solvent are not self-evident. They are due to the fact that entropy changes are much more favourable in the fairly structureless DMSO than in the well-structured water. Also in this respect, the hydrogen-bonding properties of the protic solvent are evidently very important.

The thermodynamic functions of the complex formation reactions also allow conclusions about changes of the configuration around the metal ion as the coordination of halide or thiocyanate ions proceeds. Especially in the mercury(II) systems, it has been possible to verify these conclusions by direct determinations of the structures present in solution.

The lack of structure in DMSO also makes it a good solvent for many substances which cannot break the water structure and therefore are virtually insoluble in this solvent. Among these are simple phosphine, arsine, stibine and bismuthine ligands, as well as their complexes with various metal ions. By measurements in DMSO, it has therefore been possible to determine quantitatively, for the first time, the relative affinities of such donors for some representative acceptors, viz., copper(I), silver(I) and mercury(II). The results definitely verify the sequence $N \ll P \gg As \gg Sb \gg Bi$ postulated earlier for soft acceptors from largely qualitative evidence. Especially on account of the strict conformational demands connected with formation of these complexes, the influence of entropy and enthalpy on their stabilities follows a very complicated pattern.

SOLVATION AND HYDROGEN BONDING

Protic solvents form hydrogen bonds while aprotic solvents do not. In protic solvents containing donor atoms prone to hydrogen bonding, strong intermolecular bonds therefore exist. Such solvents are therefore much more structured than aprotic solvents where such bonds cannot be formed. Solvation of a chemical species in a protic solvent thus involves breaking strong intermolecular hydrogen bonds, while solvation in an aprotic solvent does not. The heats of solvation, ΔH_{sv}° , of most species, ions as well as neutral molecules, are therefore likely to be more exothermic in aprotic than in protic solvents of comparable donor properties. Species that are themselves able to form strong hydrogen bonds are exceptions to this general rule. They should be favoured by protic solvents and their heats of solvation consequently more exothermic in these solvents than in the aprotic ones.

Heats of solvation for ions of various types in solvents with different characteristics are compared in Table 1. The protic solvents chosen are water, forming strong hydrogen bonds via two protons, and methanol, forming weaker hydrogen bonds via only one proton. The aprotic solvents are propylene carbonate, PC, and dimethylsulfoxide, DMSO. Of these, DMSO has considerably stronger donor properties than PC. In DMSO both oxygen and sulfur can act as donor atoms. Most cations are coordinated via oxygen, however (11-15). This applies even to very

soft acceptors such as Ag^+ and Hg^{2+} . Only some very soft acceptors (none of them listed in Table 1), are coordinated via sulfur (11,16).

TABLE 1. Hydration enthalpies^a (ΔH_h^0) and enthalpies of transfer ($\Delta H_{tr}^0(\text{W}\rightarrow\text{S})$) between water and solvents of different solvating properties for some representative cations and anions (kJ mol^{-1}). A set of internally consistent crystallographic ionic radii^b ($r_c/\text{\AA}$).

	r_c	$-\Delta H_h^0$	Meth ^c	PC ^d	DMSO ^d
			$\Delta H_{tr}^0(\text{W}\rightarrow\text{S})^e$		
H^+		1103		43.9	-25.5
Li^+	0.93	533	-18.9	3.1	-26.4
Na^+	1.17	417	-20.4	-10.2	-27.7
K^+	1.49	333	-20.0	-21.9	-34.9
Rb^+	1.64	307	-19.7	-24.6	-33.5
Cs^+	1.83	289	-15.9	-26.8	-30.0
Ag^+	1.12	483	-21.3	-16.7	-54.0
Zn^{2+}	0.75	2063			-60
Cd^{2+}	0.95	1830			-67
Hg^{2+}	1.02	1940			-76
Et_4N^+	2.7	127	5.9	0.7	-2.8
Ph_4P^+	4.15	46		-13.4	-9.3
Ph_4As^+	4.3	42	<u>3.3</u>	<u>-14.6</u>	<u>-11.9</u>
F^-	1.16	502			
Cl^-	1.64	366	7.9	26.4	18.8
Br^-	1.80	335	3.8	13.6	3.5
I^-	2.04	294	-1.6	-3.3	-12.8
CF_3COO^-			10	32.6	
ClO_4^-	2.3		-4.6	-16.4	-19.2
BPh_4^-	4.05	47	<u>3.3</u>	<u>-14.6</u>	<u>-11.9</u>

^a Calculated on the basis of $\Delta H_h^0(\text{H}^+) = 1103 \text{ kJ mol}^{-1}$ suggested in (1). Values for alkali and halide ions from (1), for Ag^+ from (1) + (2), for Zn^{2+} , Cd^{2+} and Hg^{2+} from (3). For Et_4N^+ , Ph_4P^+ , Ph_4As^+ and BPh_4^- , values have been calculated as described in (4, Table III A).

^b For alkali and halide ions from (1), for Zn^{2+} , Cd^{2+} and Hg^{2+} from (5). For other ions, values have been calculated as described in (4, Table III A).

^c From (6), except for Ag^+ where the value has been taken from (7), and for CF_3COO^- where the value has been calculated by combining data from (6) and (8).

^d From (9), except for H^+ and Ag^+ where the values have been taken from (10) and (7), respectively, and for Zn^{2+} , Cd^{2+} and Hg^{2+} , where they have been taken from (3).

^e Values assumed to be equal (7) are underlined.

As expected, the heats of solvation for most ions are more exothermic in a strongly coordinating aprotic solvent, such as DMSO, than in a strongly coordinating protic solvent such as water. This is evident from the enthalpies of transfer, $\Delta H_{tr}^0(\text{W}\rightarrow\text{S})$, listed in Table 1. In almost all cases, the transfer of an ion from water to DMSO is a rather strongly exothermic reaction. Also as expected, however, the hydrogen-bonding Cl^- is an exception, with a fairly strongly endothermic value of $\Delta H_{tr}^0(\text{W}\rightarrow\text{S})$. Also for Br^- , $\Delta H_{tr}^0(\text{W}\rightarrow\text{S})$ is endothermic, though only weakly so, whereas the value for I^- , with little capacity for hydrogen bonding, is exothermic, i.e., follows the general pattern. For F^- , no value of $\Delta H_{tr}^0(\text{W}\rightarrow\text{S})$ is available as fluorides are generally only very slightly soluble in aprotic solvents. This is evidently because the value of $-\Delta H_{sv}^0$ is relatively low in such solvents while the lattice enthalpies of fluorides are high. In order to be at all soluble, fluorides must have that extra contri-

bution to $-\Delta H_{sv}^{\circ}$ that is provided by their strong hydrogen bonding to protic solvent molecules.

For the less strongly coordinating PC, the values of $\Delta H_{tr}^{\circ}(W \rightarrow S)$ are generally less exothermic, or more endothermic (Table 1). Even for this solvent, however, the values stay exothermic for most of the cations, and also for I^{-} . For Cl^{-} , the value is again strongly endothermic, and this is also the case for CF_3COO^{-} , another strongly hydrogen-bonding ion. For H^{+} , the change of $\Delta H_{tr}^{\circ}(W \rightarrow S)$ is much larger than for the monovalent alkali ions. Evidently, H^{+} is relatively poorly solvated in PC. A similar tendency, though less marked, is also observed in the case of Ag^{+} .

For methanol, not as markedly protic as water, the values of $\Delta H_{tr}^{\circ}(W \rightarrow S)$ follow similar trends as found for the aprotic solvents but they are, just as expected, much less marked. The solvation properties of methanol should, on the whole, be intermediate between those found for water and those found for aprotic solvents.

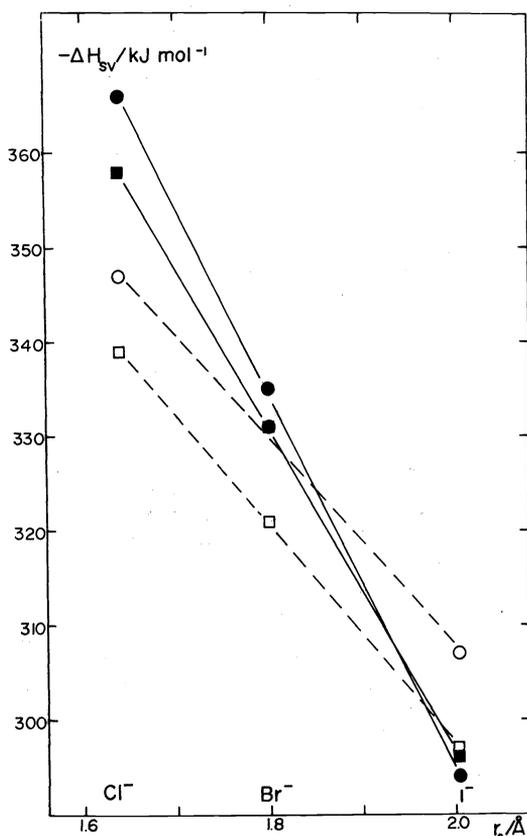


Fig. 1. Solvation enthalpies of the halide ions as a function of their ionic radii, in water (● —), methanol (■ —), DMSO (○ - - -) and PC (□ - - -).

That this is indeed so, is very clearly illustrated by the values of ΔH_{sv}° of the three heavier halide ions in the various solvents discussed. These are compared in Fig. 1. Owing to the large variation in hydrogen-bonding capacity, the differences between the values of ΔH_{sv}° are quite large in water. In the aprotic DMSO where hydrogen bonding does not exist, the differences are much smaller, little more than half of those found in water. As might be expected, much the same differences as in DMSO are found in the other aprotic solvent PC. On account of the weaker donor properties of PC, however, all the values are lower in this solvent than in DMSO. For methanol, less markedly protic than water, the differences are indeed, as expected, intermediate between those found for water and those found for the aprotic solvents.

SOLVATION AND COMPLEX FORMATION

The formation of inner-sphere complexes involves a competition between the solvent and the complex-forming ligand for the coordination sites of the acceptor. As not only the acceptors but also the ligands are solvated, there is also a competition between the solvent and the acceptor. Evidently, the complexes will tend to be more stable the weaker the solvation of the acceptor and the ligand, and vice versa. To some extent, however, the effect of these

changes is offset by simultaneous changes in the solvation of the complexes formed. The resulting enthalpy changes are also influenced by the differences in the electrostatic work released as complexes are formed in solvents of different dielectric properties.

Besides being influenced by the various enthalpy terms, the stabilities are also much determined by entropy changes. Very important among these are the desolvation entropies, i.e. the entropies gained as the solvate structures of the acceptor, and the ligand, break up as complexes are formed. The net gain in this process depends very much upon the structural properties of the bulk solvent, as will be further discussed below. For ligands of low symmetry, the conformational entropies also become important. If the coordinated ligands have to conform to very strict structural requirements, the entropy losses might become very large.

If complex formation only involves the stepwise substitution of a solvent molecule in the solvate shell by a ligand, the desolvation entropies decrease monotonously for each step (17). If, on the other hand, the configuration around the acceptor changes at a certain step, striking anomalies often occur, owing to the sudden change of solvation. As many acceptors form octahedral solvates but prefer lower coordination numbers in their complexes, such anomalies are quite common. In many instances they clearly indicate the step where the change of coordination takes place, as will be discussed below.

Also the enthalpy change for this step is generally anomalous, as the desolvation enthalpy becomes especially high at a step where the coordination number is reduced.

Under favourable circumstances, such changes of coordination can be directly verified via determinations of the structures actually present in the various solutions, by means of X-ray diffraction measurements. In these studies, such measurements have been feasible in some cases. They have throughout provided a very gratifying confirmation of the conclusions drawn from thermodynamics.

RELATIVE AFFINITIES OF LIGANDS IN PROTIC AND APROTIC SOLVENTS

For the halide ions, where differences between the heats of solvation decrease considerably from protic to aprotic solvents, the affinities for metal-ion acceptors must change accordingly. Relative to iodide complexes, chloride and, to a lesser extent, bromide complexes must become more stable as the halide systems are transferred from a protic to an aprotic solvent. In the following, this postulate has been tested by a comparison between the stabilities in water and DMSO of some suitably chosen halide systems.

In water, the formation of halide complexes has been very extensively investigated. As a main result, two opposite affinity sequences have been established, viz., (a) $F^- > Cl^- > Br^- > I^-$ and (b) $F^- < Cl^- < Br^- < I^-$. The first sequence is displayed by acceptors coordinating via bonds of a predominantly electrostatic character, the second by acceptors coordinating via bonds that are markedly covalent, i.e., by hard and soft acceptors, respectively (18).

If the postulate advanced above is correct, (a)-sequences should be more marked when the systems are transferred from water to DMSO while (b)-sequences should be more or less levelled, or, if they are not very marked in water, even turned into (a)-sequences in DMSO.

It should be stressed that the argument only refers to relative changes of stabilities. Whether the complexes will generally be more, or less, stable in DMSO than in water cannot be easily foreseen. The higher values of $-\Delta H_{SV}^{\circ}$ found for most species should, as pointed out above, tend to lower the stabilities. On the other hand, the lower dielectric constant of DMSO should act in the opposite direction. Also desolvation entropies must differ considerably between solvents that are structurally as different as water and DMSO. It is evident that only experiments can decide the net result of these various influences.

Obviously, determination of stabilities alone gives only a very incomplete picture of the various influences involved. Much more information can be obtained if the enthalpy and entropy contributions to the free energy changes are known. In latter years such data have become available for many complexes formed in aqueous solution, though data pertaining to other solvents have been scarce. In the present work, however, heats of reaction have been determined as well as stabilities for all the systems investigated in DMSO. From the values of the free energy changes ΔG_j° and enthalpy changes ΔH_j° thus found for the consecutive steps of the complex formation, the corresponding entropy changes ΔS_j° are calculated.

For groups of donor atoms with little or no ability to form hydrogen bonds, changes of relative affinities are of course not to be expected between water and DMSO. Thus, in the case of the heavier donor atoms of the nitrogen group, the sequence $P > As > Sb > Bi$, valid for both hard and soft acceptors (18), certainly stays unchanged if the complexes are transferred from water to DMSO. Further it is characteristic of soft acceptors that, in an equivalent atomic arrangement, the affinity of N in water is much lower than that of P. Considering the fairly weak hydrogen bonding of N, this will certainly not change when the systems are trans-

ferred to DMSO.

CHOICE OF SYSTEMS FOR INVESTIGATION

For the present study, the halide and thiocyanate systems of zinc(II), cadmium(II) and mercury (II) have been chosen in the first instance. The thermodynamic functions of these systems in aqueous solution are already well known. These divalent d^{10} -ions display very different affinity sequences. Zinc(II) is an (a)-acceptor while cadmium(II) has a mild and mercury(II) a strong (b)-character. The various changes expected on a transfer to DMSO can thus all be tested and, in addition, an extensive comparison of all the thermodynamic characteristics of the complex formation in water and DMSO should be possible.

In water, investigation of the bromide and especially the iodide system of mercury(II) presents difficulties on account of the low solubilities of the neutral complexes HgL_2 . Like the ion Hg^{2+} (Table 1), the complexes HgL_2 are much more strongly solvated in DMSO than in water, as will be more fully discussed below. As a consequence they become very soluble in DMSO, which much facilitates the thermodynamic measurements.

For all these systems, the stabilities can be conveniently determined via measurements of the free metal ion concentration $[M^{2+}]$. Amalgam electrodes are used for Zn^{2+} and Cd^{2+} , and a pure mercury electrode for Hg^{2+} .

In the last case, the disproportionation reaction $Hg_2^{2+} \rightleftharpoons Hg(l) + Hg^{2+}$ has to be taken into account. In both water and DMSO, this equilibrium is far to the left, though the disproportionation constant is somewhat higher in DMSO (Table 2) undoubtedly due to a more favourable solvation of Hg^{2+} relative to Hg_2^{2+} in this solvent. The formation of halide complexes strongly stabilizes mercury(II) relative to mercury(I). The mercury electrode can therefore be used as long as $[Hg^{2+}]$ is negligible compared with the concentration of halide complexes. In this respect the situation is evidently more favourable in DMSO than in water.

TABLE 2. Disproportionation constants $K_d(Hg) = [Hg^{2+}]/[Hg_2^{2+}]$ and $K_d(Cu) = [Cu^{2+}]/[Cu^+]^2$ (M^{-1}) in DMSO and water, at 25°C.

	DMSO ^a		Water ^b	
I ^c	0.15	1	0	0.15
$K_d(Hg) \times 10^3$	29	42	11.4	9.5
I ^c	0.1	1	0	5
$K_d(Cu)$	1.5	4.4	9×10^5	9×10^5

^a Refs. (19) and (20) for Hg and Cu, respectively.

^b Refs. (21) and (22) for Hg and Cu, respectively.

^c Ionic strength (I/M) brought about by adding NH_4ClO_4 in DMSO and $NaClO_4$ in water.

For the calculation of $[Hg^{2+}]$, it is necessary to know the standard potential $E_{O_2}^0$ of the couple $Hg^{2+}/Hg(l)$ in DMSO, related to some convenient reference electrode. Owing to formation of Hg_2^{2+} , $E_{O_2}^0$ cannot be directly determined, but is calculated from the experimentally accessible standard potentials E_{12}^0 and E_{01}^0 of the couples Hg^{2+}/Hg_2^{2+} and $Hg_2^{2+}/Hg(l)$ according to $E_{O_2}^0 = (E_{12}^0 + E_{01}^0)/2$. From these standard potentials, the disproportionation constant K_d of Table 2 can also be calculated from the relationship $\ln K_d = (E_{01}^0 - E_{12}^0) / RTF^{-1}$. The value of K_d has also been determined by analysis of equilibrium solutions prepared either from $Hg_2(ClO_4)_2 \cdot 3DMSO(s)$, or from $Hg(ClO_4)_2 \cdot 4DMSO$ and $Hg(l)$. The results agree completely with that found potentiometrically, though the precision is somewhat lower (19).

As well, the halide systems of the d^{10} acceptor copper (I) have been investigated. In contrast to the divalent zinc(II) of the same period, this monovalent acceptor is soft. In aqueous solution, strong halide complexes are formed which display a rather marked (b)-sequence (23). A complete investigation of these systems has not been possible, however, for two reasons. Firstly, the disproportionation $2Cu^+ \rightleftharpoons Cu(s) + Cu^{2+}$ is practically complete in water (Table 2). Secondly, the neutral complexes CuL are very slightly soluble. In DMSO, these conditions are drastically different. The disproportionation is much less extensive (Table 2) certainly due to a more favourable solvation of Cu^+ relative to Cu^{2+} in this solvent. In DMSO, dilute ($\leq 10mM$) solutions of copper(I) perchlorate are in fact disproportionated only to an insignificant extent. Also the neutral complexes are much more strongly

solvated in DMSO and, consequently, quite soluble (20,24). The formation of copper(I) halide complexes can therefore be very completely investigated in this solvent. For these systems also, the stabilities have been measured potentiometrically by means of a copper amalgam electrode.

An aprotic solvent like DMSO further opens up new possibilities for the investigation of complexes of ligands coordinating via such donor atoms as P, As, Sb, Bi. On account of the strong hydrogen bonds joining the water molecules, simple phosphines, arsines, etc. are not soluble in water. The only possibility tried so far to investigate the affinities of these donor atoms has been to make the ligands water-soluble by sulphonation or by introduction of an alcoholic group (25,26). Even then, however, the solubilities achieved are not very high, and for some donor atoms, e.g., Sb and Bi, such modifications appear to be difficult, or impossible. The lack of specific forces between the DMSO-molecules makes this solvent much less discriminating. Unsubstituted phosphines, arsines, stibines and bismuthines are therefore easily soluble in DMSO, as are also many of their metal complexes. For the present study, the simple triphenyl derivatives have been selected as being easiest to handle. The acceptors so far investigated have been copper(I), silver(I), and mercury(II), all typically soft (27,28).

The stabilities of the copper(I) and mercury(II) complexes have been determined by copper amalgam and mercury electrodes, as for the halide systems. For silver(I), porous silver electrodes, prepared by heating Ag_2O , have been used.

For all the systems investigated, heats of reactions have been determined calorimetrically. This direct method is generally both faster and more precise than calculations of ΔH_j° via the temperature-dependence of the stability constants.

In principle, calorimetric measurements allow a simultaneous determination of the enthalpy changes ΔH_j° and the stability constants K_j of the consecutive steps, provided that K_j is not so large that the reaction is virtually complete. Once this is the case, any sufficiently high value of K_j will of course satisfy the measurements. In practice, however, the values of ΔH_j have to vary considerably between consecutive steps if both ΔH_j and K_j are to be determined simultaneously with reasonable precision (29,30). Generally, therefore, a separate determination of K_j is much to be preferred. In cases where such determinations are difficult or impossible, however, a calorimetric determination of K_j may nevertheless be of great service, provided that the system is reasonably well conditioned. In this work, the cadmium bromide system has been studied by this method in media which attack the amalgam electrode.

THERMODYNAMICS AND STRUCTURES OF THE ZINC(II), CADMIUM(II) AND MERCURY(II) HALIDE AND THIOCYANATE COMPLEXES IN WATER AND DMSO

Zinc(II) Complexes. In water, the halide complexes of zinc(II) are very weak (Table 3). The (a)-sequence is nevertheless quite evident. In DMSO, the complexes are all stronger, and the stability increase is, as expected, much larger for chloride than for iodide, while bromide is intermediate. The (a)-sequence thus becomes more marked than in water. Also as expected, the stability of the thiocyanate complexes increases at much the same rate as for the iodide complexes. The conditions are illustrated by the complex formation curves of Fig. 2, which give the average number of ligands, \bar{n} , per metal ion, as a function of the free ligand ion concentration $[L]$. In the chloride and bromide systems, these curves also show that the third complex is very stable relative to the fourth one. The latter is in fact not formed at all, in spite of the almost complete formation of the third complex at the highest values of $[L]$ reached.

The values of ΔH_j° and ΔS_j° reveal that the complex formation is not a simple step-by-step substitution of solvent molecules by ligands. For iodide and thiocyanate in DMSO, as well as for chloride and bromide in water, the values of ΔS_2° and ΔH_2° are abnormally positive, signifying an additional desolvation. In both DMSO and water, Zn^{2+} most probably exists as an octahedral hexasolvate (30). On the other hand, all trihalido and tetrahalido complexes so far found in solid phases contain discrete tetrahedral units (33). The coordination of halide and presumably also thiocyanate ions thus provokes a switch from octahedral to tetrahedral structure which should be accompanied by abnormally high values of ΔS_j° and ΔH_j° . For the systems mentioned, this switch must mainly take place at the coordination of the second ligand. For chloride and bromide in DMSO, already the values of ΔS_1° and ΔH_1° are extremely high. In these systems, the switch thus seems to take place mainly as the first ligand enters the sphere of coordination.

In DMSO, the interplay between the enthalpy and entropy terms causes a very marked suppression of the first complex for all the halide systems, as indicated by the very low values of the ratio K_1/K_2 . This common trait occurs in spite of the change of coordination taking place at different steps for chloride and bromide, on the one hand, and for iodide on the other. This clearly illustrates that a complete knowledge of all the thermodynamic functions is indeed necessary if a true insight is to be gained into the nature of the complex formation.

TABLE 3. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\ mol^{-1}$; $\Delta S_j^\circ/J\ K^{-1}\ mol^{-1}$) for the stepwise formation of zinc(II) halide and thiocyanate complexes in DMSO and water, at 25°C.

	DMSO ^a				Water ^b				
	NH ₄ ClO ₄		1 M		NaClO ₄		3 M		1 M
	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	
log K ₁	1.94	0.84	-0.70	1.38	-0.19	-0.57	-1.5	0.71	
log K ₂	3.89	2.89	1.41	1.41	-0.40	-0.8		0.34	
log K ₃	2.26	1.34	0.15	2.40	0.75	0.5		0.15	
log K ₄				1.65				0.32	
K ₁ /K ₂	0.011	0.009	0.008	0.9	1.6	2		2.3	
K ₂ /K ₃	43	35	18	0.10	0.07	0.05		1.6	
K ₃ /K ₄				5.6				0.7	
-ΔG ₁ ^o	11.1	4.8	-4.0	7.9	-1.1	-3.3		4.0	
-ΔG ₂ ^o	22.2	16.5	8.0	8.1	-2.4	-4.7		1.9	
-ΔG ₃ ^o	12.9	7.7	0.9	13.7	4.3	3		0.8	
-ΔG ₄ ^o				9.4				1.9	
-ΔH ₁ ^o	-22.3	-27.8	-19.0	-5.5	-5.5	-1.5		5.8	
-ΔH ₂ ^o	-0.8	-9.1	-29.4	-23.5	-38	-42		2	
-ΔH ₃ ^o	10.2	4.2	-12.7	17.8	0	8		1	
-ΔH ₄ ^o				10.7				8	
ΔS ₁ ^o	112	110	50	45	15	-6		-6	
ΔS ₂ ^o	77	85	127	105	120	125		0	
ΔS ₃ ^o	9.1	12	45	-13	8	-17		0	
ΔS ₄ ^o				-4				-20	

^a Ref. (30).

^b Refs. (31) for the halides, (32) for the thiocyanate.

Cadmium(II) Complexes. In water, the halide complexes of cadmium(II) display a mild (b)-sequence (Table 4). The complexes are also much stronger than those formed by zinc(II), and this also applies to the thiocyanate systems. A transfer to DMSO again increases the stabilities more the lighter the halide ion, with the result that the (b)-sequence found in water turns into an (a)-sequence in DMSO. Again, thiocyanate behaves much like iodide. The changes are also illustrated by the complex formation curves of Fig. 3.

Also in the cadmium(II) halide systems, a change of coordination is indicated by the values of ΔS_j° and ΔH_j° found for the consecutive steps. In DMSO, the values of ΔS_2° and ΔH_2° are abnormally positive, in water the values of ΔS_3° and ΔH_3° . The increase is admittedly less marked in water (and is completely absent for ΔH_3° of the iodide system), but no doubt an extensive additional desolvation takes place in both water and DMSO at the formation of the third and second complex of each halide, respectively.

In both solvents, Cd²⁺ exists as an octahedral solvate if complexing ligands are absent, as has been shown by X-ray diffraction studies of such solutions (15,36,37). In both solvents, the highest complex formed in the halide systems is the fourth one, CdL₄²⁻ (29,34). Again by X-ray diffraction, CdI₄²⁻ has been proved to be tetrahedral in both solvents (37,38) and no doubt the same is true for CdCl₄²⁻ and CdBr₄²⁻. Thus, a change from octahedral to tetrahedral structure takes place as halide ions are coordinated. The thermodynamics clearly indicates that the switch occurs mainly as the second complex is formed in DMSO, but as the third complex is formed in water.

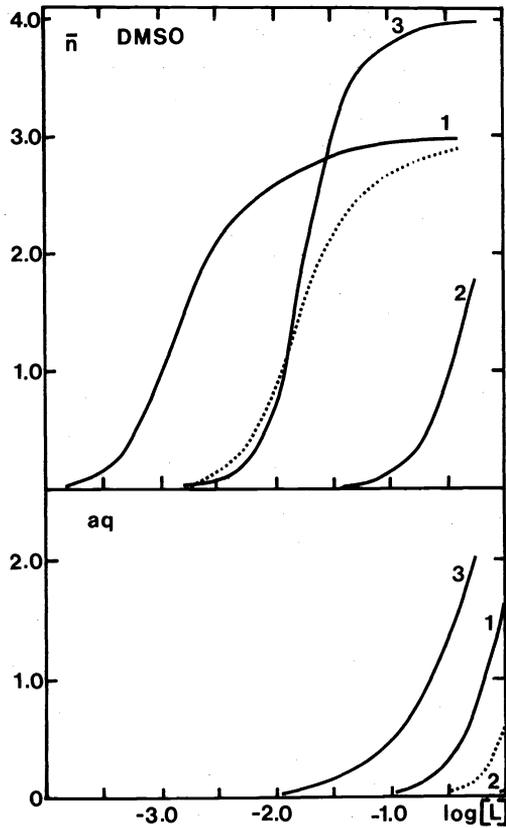


Fig. 2. Complex formation curves in DMSO and water of the zinc(II) chloride (1 —), bromide (·····), iodide (2 —) and thiocyanate (3 —) systems, in the media stated in Table 3.

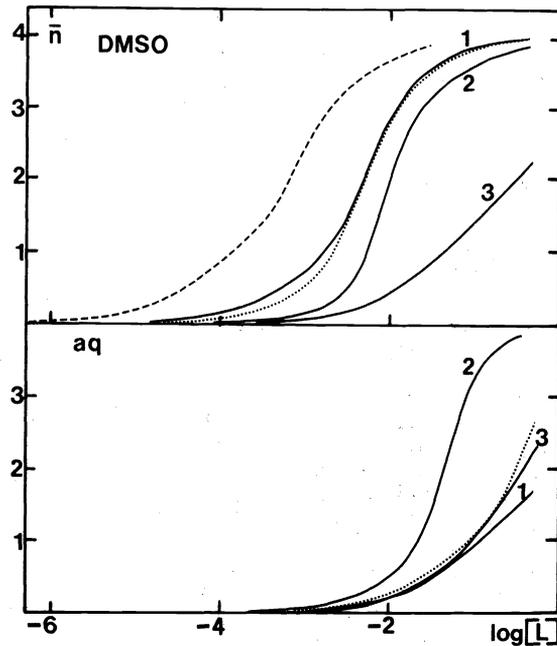


Fig. 3. Complex formation curves in DMSO (medium 1 M NH_4ClO_4) and water (medium 1 M NaClO_4 ; cf. ref. (4)) of the cadmium(II) chloride (1 —), bromide (·····), iodide (2 —) and thiocyanate (3 —) systems. The chloride curve pertaining to the medium 0.1 M NH_4ClO_4 in DMSO is also given (---).

TABLE 4. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\ mol^{-1}$, $\Delta S_j^\circ/J\ K^{-1}\ mol^{-1}$) for the stepwise formation of cadmium(II) halide and thiocyanate complexes in DMSO and water, at 25°C.

	DMSO ^a				Water ^b			
	NH ₄ ClO ₄		1M		NaClO ₄		3M	
	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻
log K ₁	3.23	2.92	2.18	1.81	1.59	1.76	2.08	1.39
log K ₂	1.98	1.91	1.40	0.91	0.64	0.59	0.70	0.59
log K ₃	2.57	2.75	2.93	0.20	0.18	0.98	2.14	0.60
log K ₄	1.75	1.68	1.17			0.38	1.60	
K ₁ /K ₂	18	10	6	7.9	8.8	15	24	6.3
K ₂ /K ₃	0.26	0.14	0.03	5	2.9	0.41	0.04	1.0
K ₃ /K ₄	7	12	58			4.0	3.4	
-ΔG ₁ ^o	18.4	16.7	12.5	10.3	9.0	10.0	11.9	8.0
-ΔG ₂ ^o	11.2	10.9	7.8	5.2	3.7	3.3	4.0	4.8
-ΔG ₃ ^o	14.7	15.7	16.8	1.2	1.0	5.6	12.2	1.3
-ΔG ₄ ^o	10.0	9.5	6.7			2.1	9.2	0.0
-ΔH ₁ ^o	6.3	3.9	-2.4	3.0	0.4	4.1	9.5	8.1
-ΔH ₂ ^o	-15	-17	-27	2.8	-0.1	2.4	0.8	7.2
-ΔH ₃ ^o	-1	-2	5	-4.2	-7.7	-7.2	3.1	6.6
-ΔH ₄ ^o	12.2	13	9.5			-1.3	15.9	4
ΔS ₁ ^o	41	43	50	25	29	20	8	0
ΔS ₂ ^o	88	94	117	8	13	3	10	-8
ΔS ₃ ^o	53	59	40	18	29	43	31	-18
ΔS ₄ ^o	-7	-12	-10			11	-23	-15

^a Ref. (29).

^b Refs. (34,35).

Most of the intermediate complexes in these systems are fairly unstable relative to their neighbours, as is evident from the generally quite low values of K_j/K_{j+1} of Table 4. They are therefore always relatively minor components in the solutions, which means that their structures cannot be determined by diffraction methods. This applies especially to the second complex which is more or less severely suppressed in all the halide systems (Table 4). Again, a general suppression of a certain complex appears in spite of the fact that its ultimate cause, the change of coordination, occurs at different steps in the various systems involved. This stresses once more the need for the determination of all the thermodynamic functions. The complex CdI^+ in water and CdI_3^- in DMSO are relatively stable, as is evident from the fairly high values of $K_1/K_2=24$ and $K_3/K_4=58$. It has therefore been feasible to determine their structures (38,39). These are octahedral and approximately tetrahedral, respectively, i.e., as expected from the thermodynamics.

The thermodynamic functions so far discussed for the formation of cadmium(II), and zinc(II), complexes in DMSO all refer to 1 M ammonium perchlorate medium. This medium was originally chosen as it allows the determination of stabilities by potentiometric measurements utilizing amalgams. Other media, e.g., anhydrous lithium perchlorate, attack these electrodes. Others are unsuitable for other reasons, e.g., sodium perchlorate which does not allow the investigation of chloride complexes on account of the limited solubility of sodium chloride in DMSO (40).

As so little is known about the influence of the medium on equilibria in DMSO, it is never-

theless very desirable to study some representative systems in various media. Preferably, the medium should be varied both quantitatively and qualitatively. The result of a rather profound quantitative change has been investigated by measuring the cadmium(II)halide systems in 0.1 M ammonium perchlorate, applying the same potentiometric and calorimetric methods as before (41). Qualitative changes have been brought about by changing the ammonium ion for tetraethylammonium (0.1 M), lithium (0.1 and 1 M) or sodium ion (1 M). In these media, only the cadmium bromide complexes have been studied (41). For this system, both the stability constants and the enthalpy changes can be determined simultaneously from calorimetry, and the difficulty connected with amalgam measurements in aggressive media thus avoided. Further, sodium bromide is fairly soluble in DMSO (40).

TABLE 5. 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 cadmium(II)^j complexes in various DMSO media, at 25°C (Ref. 41).

I/M	NH_4ClO_4			Et_4NClO_4	$LiClO_4$		$NaClO_4$
	0.1			0.1	0.1	1	1
	Cl^-	Br^-	I^-	Br^-	Br^-		Br^-
$\log K_1$	4.36	3.69	2.57	3.92	3.79	3.56	3.48
$\log K_2$	2.92	2.50	1.80	2.88	3.07	2.93	2.36
$\log K_3$	3.46	3.28	2.83	3.40	3.05	2.94	3.17
$\log K_4$	2.34	1.83	1.07	2.21	3.11	3.35	1.86
K_1/K_2	27	16	6	11	5.3	4.3	13
K_2/K_3	0.29	0.17	0.09	0.31	1.0	1.0	0.15
K_3/K_4	13	28	58	16	0.88	0.39	21
$-\Delta G_1^\circ$	24.9	21.0	14.7	22.4	21.6	20.3	19.9
$-\Delta G_2^\circ$	16.7	14.2	10.3	16.5	17.5	16.7	13.5
$-\Delta G_3^\circ$	19.7	18.7	16.2	19.4	17.4	16.8	18.1
$-\Delta G_4^\circ$	13.4	10.4	6.1	12.6	17.7	19.1	10.6
$-\Delta H_1^\circ$	4.9	0.9	-5.2	0.0	-0.3	0.3	2.8
$-\Delta H_2^\circ$	-12.5	-15.8	-21.5	-17.9	-4.0	-3.1	-13.6
$-\Delta H_3^\circ$	-6.5	-7.2	-6.6	-7.3	-27.5	-23.9	-6.6
$-\Delta H_4^\circ$	15.5	11.4	4.8	9.5	10.9	10.5	13.4
ΔS_1°	67	68	67	75	73	67	57
ΔS_2°	98	101	106	115	72	66	91
ΔS_3°	88	87	76	90	151	137	83
ΔS_4°	-7	-3	4	10	23	29	-9
$-\Delta G_{\beta 4}^\circ$	74.7	64.4	47.2	70.8	74.3	72.9	62.0
$-\Delta H_{\beta 4}^\circ$	1.5	-10.6	-28.5	-15.7	-20.8	-16.2	-4.0
$\Delta S_{\beta 4}^\circ$	245	252	254	290	319	299	221

The results of these measurements are in Table 5. A comparison between the 0.1 M ammonium perchlorate and the 1 M used previously, Table 4, shows a general increase of the values of K_j as the concentration NH_4^+ is decreased. The increase is largest for Cl^- (cf. also Fig. 3), smaller for Br^- , and fairly small for I^- . In the last case moreover, it is confined to the first two steps while the two later ones in fact show a slight decrease. Most probably, the pattern found is due to the fact that complexes are formed between NH_4^+ and Cl^- and, to a lesser extent, between NH_4^+ and Br^- . This implies a competition between NH_4^+ and Cd^{2+} for these ligands, which would considerably suppress the formation of the cadmium(II) complexes in solutions of high $[NH_4^+]$, just as found. On the other hand, the difference between the stabilities of the iodide complexes between the two media is hardly larger than expected from the difference in ionic strength. The values of ΔH_j° and ΔS_j° show that the stability increases

are due to more favourable entropy changes. This is also to be expected as the desolvation of, e.g., a free Cl^- should give a larger entropy contribution than if Cl^- is more or less tightly bonded to NH_4^+ .

It may be argued that these conditions again reflect the various tendencies for hydrogen bonding between the halide ions. In an aprotic solvent, such as DMSO, the hydrogens of NH_4^+ become attractive to Cl^- , and, though less, to Br^- , but hardly to I^- .

If this interpretation is correct, the stabilities of, e.g., bromide complexes could be even higher in media where hydrogen bonding is completely impossible. That this is indeed so is evident from a comparison between 0.1 M NH_4^+ and 0.1 M Et_4N^+ media. Also the values found in 0.1 M Li^+ medium are generally higher, though with this ion other factors also enter, as will be discussed below. In the 1 M Li^+ and 1 M Na^+ media, the cadmium(II) bromide complexes are also, as expected, throughout more stable than in 1 M NH_4^+ .

In 0.1 M NH_4^+ , the values of ΔS_3^0 are larger relative to ΔS_2^0 than is the case in 1 M NH_4^+ (Tables 4 and 5). The change of coordination is no longer so sharply indicated to take place at the second step. It is understandable that the desolvation is somewhat delayed by the decrease in concentration of other cations to be solvated. In 0.1 M Et_4N^+ the same picture emerges and also in 1 M Na^+ . In the Li^+ media, 0.1 M as well as 1 M, the switch definitely takes place mainly at the third step, as indicated by values of both ΔH_3^0 and ΔS_3^0 which are much more positive than the neighbouring values. Evidently, the differences in energy between different structures for a certain complex are fairly small. Not only the radical change of moving the system to a different solvent, but also changes in the ionic environment are sufficient to tip the balance in favour of one structure or the other.

Mercury(II) Complexes. In water, the halide complexes of mercury(II) are very strong and display a marked (b)-sequence (Table 6). A transfer to DMSO again implies a strong increase in the stabilities of the chloride complexes relative to the bromide and, especially the iodide complexes. The (b)-sequence is so marked in water, however, that even the large changes of the relative affinities that occur do not result in an (a)-sequence in DMSO. The levelling effect of this solvent is nevertheless considerable (Table 6). Thiocyanate again behaves in a similar way to iodide, which means a large decrease in stability of the thiocyanate complexes relative to the chloride and bromide ones. The changes discussed are illustrated by the complex formation curves of Fig. 4.

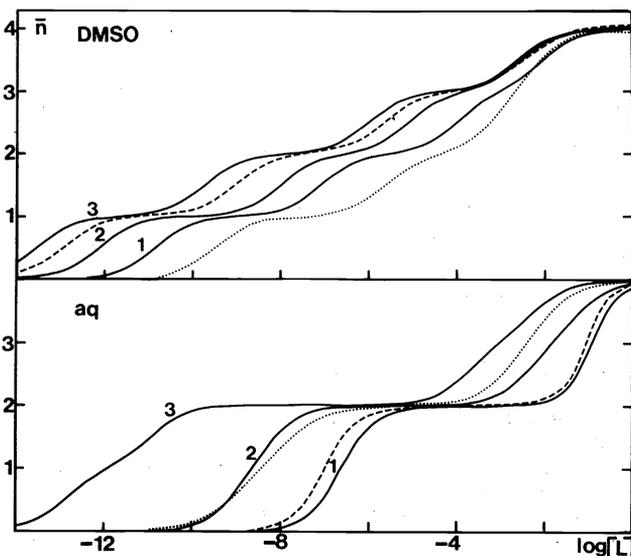


Fig. 4. Complex formation curves in DMSO and water of the mercury(II) chloride (1 —), bromide (2 —), iodide (3 —) and thiocyanate (.....) systems, in the media stated in Table 6. The bromide curve pertaining to 0.1 M NH_4ClO_4 in DMSO (---) (42) and the chloride curve pertaining to 3 M NaClO_4 in water (---) (56) are also given.

A very striking feature of these curves is their wavy appearance in DMSO. Every complex (except the third one in the thiocyanate system) is formed almost completely before the next one appears. These conditions are further illustrated by the distribution curves plotted in Fig. 5, and are also evident from the high values of the ratios K_j/K_{j+1} in Table 6. In water, only the second complexes have a really extended range of existence, though a slight tendency

is also found for the first iodide complex (Fig. 4 and Table 6). The reasons for these differences and similarities between the complex formation in water and DMSO are clearly discerned from a combination of the thermodynamic and structural evidence now available.

TABLE 6. 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 mercury(II) halide and thiocyanate complexes in DMSO and water, at 25°C.

	DMSO ^a				Water ^b			
	NH ₄ ClO ₄		1M		NaClO ₄		0.5M	1M
	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻
log K ₁	10.87	12.14	13.52	9.52	6.74	9.05	12.87	9.08
log K ₂	7.10	8.06	9.76	5.63	6.48	8.28	10.95	7.78
log K ₃	3.99	5.14	6.01	3.12	0.85	2.41	3.78	2.84
log K ₄	2.08	2.54	2.62	2.19	1.00	1.26	2.23	1.97
K ₁ /K ₂	5930	12100	5810	7660	1.8	5.9	83	20
K ₂ /K ₃	1270	830	5540	320	4x10 ⁵	7x10 ⁵	1.5x10 ⁷	9x10 ⁴
K ₃ /K ₄	82	400	2450	9	0.7	14	35	7
-ΔG ₁ ^o	62.0	69.3	77.2	54.3	38.5	51.7	73.5	51.8
-ΔG ₂ ^o	40.5	46.0	55.7	32.1	37.0	47.3	62.5	44.4
-ΔG ₃ ^o	22.8	29.3	34.3	17.8	5.4	13.8	-	16.2
-ΔG ₄ ^o	11.9	14.5	15.0	12.5	6.0	7.2	-	11.2
-ΔH ₁ ^o	20.4	24.8	33.3	28.1	24.7	42.2	75.3	49.7
-ΔH ₂ ^o	28.6	32.2	39.2	31.2	28.9	44.8	67.8	50.4
-ΔH ₃ ^o	19.5	27.3	27.6	9.9	9.2	12.6	-	20.4
-ΔH ₄ ^o	13.3	18.0	20.3	16.1	-0.4	17.2	-	21.0
ΔS ₁ ^o	140	149	147	88	46	32	-6	7
ΔS ₂ ^o	40	46	55	3	27	8	-18	-20
ΔS ₃ ^o	11	7	22	26	-13	4	-	-14
ΔS ₄ ^o	-5	-12	-18	-12	21	-33	-	-33

^a Ref. (42).

^b Refs. (43-45) for Cl⁻; (43,46) for Br⁻; (43,47) for I⁻; (32,48) for SCN⁻.

In water the first two steps are strongly exothermic and, moreover, to about the same degree (Table 6). This evidently reflects the formation of the digonal neutral complexes HgL₂, well-known from gaseous and solid phases (33). Not even the solubility of HgCl₂ is high enough, however, to allow a structure determination in aqueous solution by X-ray diffraction (49). The third step involves the breakup of these digonal structures. Mononuclear complexes HgBr₃ and HgI₃ are formed, with the ligands in approximately tetrahedral positions (50). Complexes HgCl₃, of presumably the same structure, are formed in dilute mercury(II) solutions (43) but at the high concentrations (≥ 0.5 M) that have to be used in the structure determinations polynuclear complexes predominate at mole ratios Cl/Hg around 3. For all the halides, the highest complex formed is the regularly tetrahedral ML₄²⁻ (49,50). The last two steps are much less exothermic than the first ones, indicating that the tetrahedral Hg-L bonds are considerably weaker than the digonal ones. The values of ΔS_j^o (except ΔS₃^o) rapidly become smaller in the sequence Cl⁻ > Br⁻ > I⁻ which reflects the steep decrease of the hydration enthalpies of the halide ions (Table 1). For Cl⁻ and, though less, for Br⁻, the entropy changes are fairly positive for the first two steps, indicating a fairly extensive desolvation. This is indeed to be expected, as Hg²⁺ exists in aqueous solution as an octahedral hydrate (15,51) while the solvation of the complexes HgL₂ is quite weak (3), as will be further discussed below. For Cl⁻, the relative magnitudes of the values of ΔS₃^o and ΔS₄^o are hard to interpret. This point merits a further check.

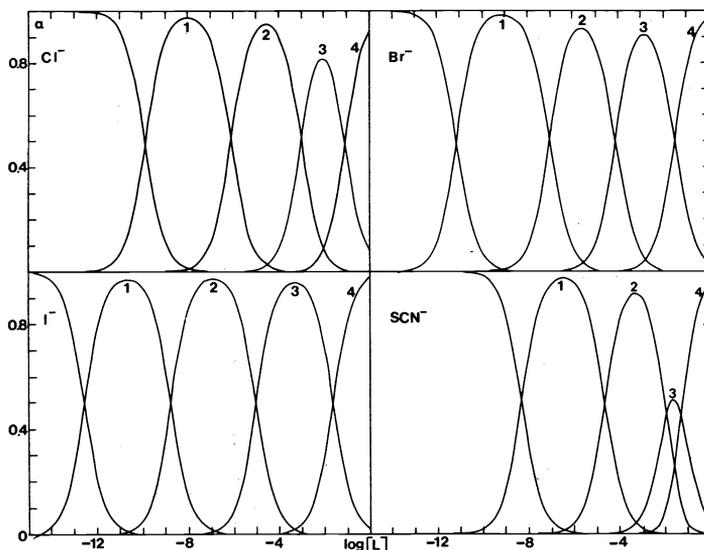


Fig. 5. Distribution curves for the consecutive complexes HgL_j^{2-j} ($L = \text{Cl}^-$, Br^- , I^- , SCN^- ; $j = 1 - 4$) in DMSO; medium 1 M NH_4ClO_4 .

In DMSO, the conditions for both structural and thermodynamic measurements are much more favourable than in water. For structure determinations by X-ray diffraction the situation is in fact almost ideal, as sufficiently concentrated solutions containing virtually only the complex to be investigated can be prepared for all the halide and thiocyanate complexes except $\text{Hg}(\text{SCN})_3$. Also the thermodynamic measurements, especially the calorimetric ones, are much favoured by the increased solubility of the neutral complexes.

As in water, Hg^{2+} exists as an octahedral solvate in DMSO (15) (See Fig. 6). In spite of the soft character of Hg^{2+} , the DMSO molecules are coordinated via oxygen. Also the solid $\text{Hg}(\text{DMSO})_6(\text{ClO}_4)_2$ contains discrete octahedral solvate ions, with DMSO coordinated via oxygen (14), as has in fact been inferred earlier from IR-measurements (13). As to the first step, HgI^+ , only the iodide complex has so far been investigated (52). Already in this complex, the octahedral structure has been changed to a digonal one. The DMSO molecule trans to the iodide ligand is now markedly closer to the central atom ($\text{Hg-O} = 2.30 \text{ \AA}$) than in the solvate $\text{Hg}(\text{DMSO})_6^{2+}$, while the other DMSO in the solvate sphere are too far out to be discerned. Presumably, the other complexes HgL^+ have similar structures. With the formation of the digonal neutral complexes HgL_2 , the last closely attached DMSO is expelled (53). In contrast to what has been found in gaseous and solid phases, the complexes HgL_2 seem to be slightly bent in DMSO (Fig. 6). The solvation, though weak, is evidently still able to modify the structure to some extent. The Hg-I distance is longer than in HgI^+ , indicating a weakening of the Hg-I bond on the coordination of a further ligand (sc. below).

The desolvation accompanying these structural changes is very strikingly reflected in the thermodynamics (Table 6). The extensive break-up of the solvate shell that occurs on the formation of the first complex brings about a huge entropy gain, of much the same magnitude for all the halides. This levelling relative to water must at least partly be due to the smaller differences between the strengths of the halide solvate bonds in DMSO, cf. Table 1. Also the expulsion of the last strongly bonded DMSO with the formation of the second complex brings about a fairly large entropy gain. The formation of the strong Hg-L bonds makes the reactions strongly exothermic, but owing to the exceptionally large desolvation enthalpy spent in the first step, the second step is in fact the more exothermic one. The reactions become more exothermic in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, but at a much lower rate than in water (Table 6). This is obviously also due to the smaller differences between the strength of solvation of the halide ions in DMSO.

The formation of the third complex again involves a change of structure, though the configuration of HgL_3 differs somewhat between the three halides (53). The complex HgI_3 has a pyramidal structure, though the angle $\text{I-Hg-I} = 112^\circ$ is considerably larger than the tetrahedral angle of 109.5° (Fig. 6), HgBr_3 is still more flattened, with the angle $\text{Br-Hg-Br} = 116^\circ$, and HgCl_3 is trigonal planar. The complexes finally formed, HgL_4^{2-} , are all regular tetrahedra (53). The bonds Hg-L become longer for each ligand coordinated (Fig. 6); in HgI^+ the distance is only 2.56 \AA (52). The bond strength evidently decreases as the bonding capacity of the central atom is divided between more ligands.

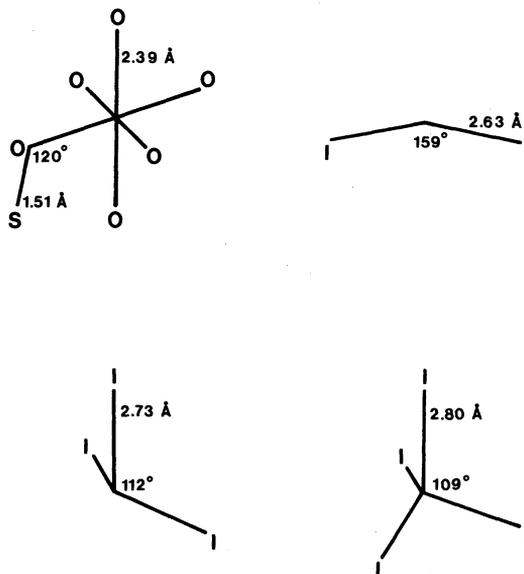


Fig. 6. Schematic structures of the species $\text{Hg}(\text{DMSO})_6^{2+}$, HgI_2 , HgI_3^- and HgI_4^{2-} in DMSO.

The weak solvation of the second and third complexes is reflected in the small values of ΔS_2° and ΔS_3° (Table 6). The latter is even slightly negative, indicating that the entropy gained by the desolvation cannot compensate for the entropy lost by the coordination of the ligand. On the other hand, the desolvation enthalpies are certainly low. The values of $-\Delta H_2^\circ$ should therefore decrease from the second step on, reflecting the decreasing strength of the bond formed. This is in fact found, Table 6.

Thermodynamics of the formation of zinc(II), cadmium(II) and mercury(II) complexes of analogous structures. As has been stated repeatedly, the complexes investigated are generally more stable in DMSO than in water. Exceptions are found for a few steps, however (Tables 4 and 6). This is not surprising, as the thermodynamic functions of the individual steps are much affected by the desolvation processes, and this leads to different structures in the two solvents, e.g., for the complexes CdL_2 . A comparison between such complexes would tend to obscure the more general effects of the change of solvent. To find these, reactions involving similar structures should be compared. At first thought, the reactions $\text{M}^{2+} + 4\text{L}^- \rightleftharpoons \text{ML}_4^{2-}$ seem suitable. In both DMSO and water, they mean a transformation of an octahedral solvate into a tetrahedral complex. Moreover, this applies also to the mercury complexes, so the comparison can be extended to analogous reactions of different acceptors. Unfortunately, a fourth complex is not formed in all the systems, even at the highest ligand concentrations available. Therefore the reactions $\text{M}^{2+} + 3\text{L}^- \rightleftharpoons \text{ML}_3^-$ are also considered. This should be permissible as the structures of the complexes ML_3^- are probably not fundamentally different even if slight variations occur, e.g., between the complexes HgI_3^- . The important point is that the octahedral and digonal structures prevailing at the lower steps are now all gone. In this way, the comparison can be extended also to the zinc halide systems in DMSO. In water, however, the complexes formed between zinc and halide ions are too unstable to warrant a meaningful discussion. All functions to be compared have been collected in Table 7.

The large increases in stabilities of the chloride and bromide complexes of mercury(II) and cadmium(II) in passing from water to DMSO are evident. The iodide and thiocyanate systems are, on the other hand, of much the same stability in both solvents. These conditions are, however, the net results of a rather complicated interplay between the enthalpy and entropy terms.

In the chloride systems, the values of ΔH_2° are about the same in DMSO and water. Evidently, the increase of $-\Delta H_{\text{sv}}^\circ$ for M^{2+} , and decrease of $-\Delta H_{\text{sv}}^\circ$ for Cl^- (Table 1) between water and DMSO approximately cancel each other out. In the iodide systems, on the other hand, the values of ΔH_2° are much more unfavourable in DMSO than in water. This is to be expected, as in this case $-\Delta H_{\text{sv}}^\circ$ increases also for the ligand. Also as expected, the bromide systems show an intermediate behaviour.

Obviously, the enthalpy changes occurring between water and DMSO very much favour the chloride and, to a lesser extent, the bromide systems relative to the iodide ones. They are not responsible for the large stability increases of the chloride and bromide complexes, however. On the contrary, the enthalpy changes alone would not appreciably change the stabilities of the chloride complexes but depreciate those of the bromide and, especially, the iodide complexes.

TABLE 7. Cumulative changes of free energy, enthalpy and entropy over the first three or four steps in the halide and thiocyanate systems of zinc(II), cadmium(II) and mercury(II) in DMSO and water, at 25°C (ΔG° , $\Delta H^\circ/\text{kJ mol}^{-1}$, $\Delta S^\circ \text{ JK}^{-1} \text{ mol}^{-1}$).

	Zn^{2+}				Cd^{2+}				Hg^{2+}			
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
DMSO, NH_4ClO_4 , 1 M												
$-\Delta G_{\beta 3}^\circ$	46	29	5	30	44	43	37	17	125	145	167	104
$-\Delta G_{\beta 4}^\circ$				39	54	52	44		137	159	182	117
$-\Delta H_{\beta 3}^\circ$	-13	-33	-61	-11	-10	-15	-24	2	68	84	100	69
$-\Delta H_{\beta 4}^\circ$				0	2	-2	-14		82	102	120	85
$\Delta S_{\beta 3}^\circ$	198	207	222	137	182	196	207	51	191	202	225	118
$\Delta S_{\beta 4}^\circ$				133	175	184	197		186	190	207	106
Water, NaClO_4^a												
$-\Delta G_{\beta 3}^\circ$					14	19	28	14	81	113		112
$-\Delta G_{\beta 4}^\circ$						21	37	14	87	120	171	124
$-\Delta H_{\beta 3}^\circ$					-7	-1	13	22	63	99		121
$-\Delta H_{\beta 4}^\circ$						-2	29	26	62	116	185	142
$\Delta S_{\beta 3}^\circ$					71	66	49	-26	60	46		-27
$\Delta S_{\beta 4}^\circ$						77	26	-41	81	13	-49	-60

^a Ionic medium 3 M for Cd^{2+} , 0.5 M for Hg^{2+} halides, 1 M for Hg^{2+} thiocyanate.

These trends are strongly counteracted by the entropy changes, however. For all the complexes, these are much more favourable in DMSO than in water (Table 7). For the chloride and bromide systems, the strong entropy stabilization in DMSO results in the large stability increases observed relative to water. For the iodide and thiocyanate systems, it so happens that the entropy gains just about compensate for the less favourable enthalpy changes in DMSO.

The reason why the entropy changes are so much more favourable in DMSO is certainly the following. In water, the desolvation implies that water molecules leave a hydrate structure and enter another fairly well-ordered structure, viz. that of bulk water. The result is a modest entropy gain, or even a net loss if the entropy change connected with the coordination of the ligand is sufficiently unfavourable. In DMSO, on the other hand, solvent molecules leave a solvate structure which very probably is more strictly ordered than the corresponding hydrate and enter a bulk solvent that is fairly unstructured. The result is a very large entropy gain.

Evidently, this solvent effect will be found for all systems of complexes. Moreover, not only DMSO, but all strongly coordinating solvents of low internal order should behave in the same manner. Any complex-formation reaction where a desolvation process is important should generally display a more favourable entropy change in such solvents than in aqueous solution. Only for steps where the desolvation is abnormal, on account of structure changes, may exceptions from this rule be found.

In DMSO, the values of $\Delta S_{\beta 3}^\circ$ and $\Delta S_{\beta 4}^\circ$ for a certain halide do not vary much between the acceptors. This is not surprising, as both the initial solvates and the complexes finally formed have much the same structures for these acceptors. For all the halides, the variations observed follow the order of solvation enthalpies of the ions M^{2+} , i.e., $\text{Zn}^{2+} > \text{Cd}^{2+} < \text{Hg}^{2+}$ (Table 8). This is also understandable as the solvate should be more ordered and hence the entropy gain larger, the stronger the solvate bonds.

The values of $\Delta H_{\beta 3}^\circ$ and $\Delta H_{\beta 4}^\circ$, on the other hand, become rapidly more favourable in the sequence

$Zn^{2+} < Cd^{2+} < Hg^{2+}$ (Table 7) reflecting the increasing strength of the covalent bonding $M^{2+} - L^{-}$ in that order. The difference is especially large between Cd^{2+} and Hg^{2+} .

Solvation enthalpies of the free zinc(II), cadmium(II) and mercury(II) ions, and of their neutral halide complexes. The interpretation of the thermodynamics in DMSO postulates that the neutral halide complexes ZnL_2 and CdL_2 are tetrahedral and consequently have two DMSO closely attached to the central atom while in the digonal complexes HgL_2 , no DMSO is very close to Hg. The latter postulate has been verified by the structure determination referred to above, while no such direct proof can be brought in the case of ZnL_2 and CdL_2 (15). Independent evidence on this point would therefore be valuable.

Closely attached solvent molecules are held by stronger bonds than more distant ones. Consequently, if the gaseous complexes ZnL_2 and CdL_2 are solvated by two DMSO which enter into close contact with the central atoms, completing tetrahedral structures, their solvation enthalpies must be much higher than those of the complexes HgL_2 , where such close contacts are not established between DMSO and the central atom.

The solution enthalpies of the neutral complexes can be determined without any extrathermodynamic assumptions. For HgL_2 , they are very simple to find, as the differences between the solution and the sublimation enthalpies. For ZnL_2 and CdL_2 , which in solution do not remain exclusively as neutral complexes, the distribution between different complexes and the complex formation enthalpies have to be known as well (3).

For HgL_2 and CdL_2 , values of ΔH_{Sv}° can be determined both in DMSO and water. For ZnL_2 , the measurements have to be confined to DMSO, on account of the low stability of the neutral complex in water.

These measurements also allow the thermodynamic evaluation of the sum $\Delta H_{Sv}^{\circ}(M, 2L) = \Delta H_{Sv}^{\circ}(M^{2+}) + 2\Delta H_{Sv}^{\circ}(L^{-})$ for $M=Zn, Cd$ and Hg in both DMSO and water. As the values of $\Delta H_{Sv}^{\circ}(L^{-})$ have been fixed by means of reasonable extrathermodynamic assumptions (Table 1) the values of $\Delta H_{Sv}^{\circ}(M^{2+})$ can be computed (3).

TABLE 8. Solvation enthalpies ($-\Delta H_{Sv}^{\circ}/kJmol^{-1}$) of free metal ions M^{2+} and neutral complexes ML_2 ($M=Zn, Cd, Hg$) in water and DMSO, at 25°C.

M ⁺	DMSO			Water		
	Zn	Cd	Hg	Zn	Cd	Hg
M ²⁺	2123	1898	1921	2063	1831	1845
MCl ₂	219	221	104		194	69
MBr ₂	221	209	101		170	64
MI ₂	225	191	96		141	62

As seen in Table 8, the solvation enthalpies of ZnL_2 and CdL_2 do not differ much, but are all much higher than those of HgL_2 , as expected from the different structures postulated. The main point is thus well confirmed.

Both for CdL_2 and HgL_2 , the solvation is much stronger in DMSO than in water. For HgL_2 , the increases of $-\Delta H_{Sv}^{\circ}$ are $\approx 35kJ$, corresponding to a solubility increase of $\approx 10^6$. The very high solubilities of the complexes HgL_2 in DMSO are therefore not surprising.

For CdL_2 and HgL_2 , the values of $-\Delta H_{Sv}^{\circ}$ decrease in the order $MCl_2 > MBr_2 > MI_2$, while for ZnL_2 the trend is slightly in the opposite order (Table 8). No doubt this reflects the difference in bonding character. In CdL_2 and HgL_2 , the bonding is markedly covalent. Therefore, the halide giving the most extensive orbital overlap, i.e., I^{-} , brings about the most extensive compensation of the cationic charge on M^{2+} and hence the lowest value of $-\Delta H_{Sv}^{\circ}$. In ZnL_2 , on the other hand, the bonding is mainly electrostatic. In this case, the ligand with the highest charge density, i.e., Cl^{-} , brings about the most extensive compensation of the cationic charge and hence the lowest $-\Delta H_{Sv}^{\circ}$.

In contrast to the solvation enthalpies of the neutral molecules, those of the free metal ions are all of the same order of magnitude as expected for ions of the same charge forming solvates of the same structure. Naturally they are also very much larger than for the neutral molecules. The values of $-\Delta H_{Sv}^{\circ}(M^{2+})$ vary in the order $Zn^{2+} > Cd^{2+} < Hg^{2+}$, with the minimum at Cd^{2+} more marked in DMSO than in water (Table 8).

As the ionic radius increases monotonously with the period (Table 1), the solvate bond M - O must have a partially covalent character which increases as the acceptor becomes softer, and is more marked in DMSO than in water. Evidently, the relatively high values of $-\Delta H_{S_1}^{\circ}$ for Zn^{2+} and Hg^{2+} must be due to strong electrostatic and covalent interactions, respectively, while Cd^{2+} , a second on both counts, ends up with a lower total than any of its neighbours.

THERMODYNAMICS OF THE COPPER(I) HALIDE COMPLEXES IN WATER AND DMSO

In aqueous solution, the slightly soluble complexes CuL are never present in appreciable concentrations. Only with the formation of the complexes CuL_2^- do the solubilities of copper(I) become high enough to allow investigations of the equilibria existing in the solutions. To reach these solubilities, fairly high concentrations of halide ions are needed. Even at the highest concentrations available, the ligand number \bar{n} does not exceed 2.8, 3.0 and 3.2 for $L=Cl, Br$ and I , respectively (23). In the chloride and bromide systems, only CuL_2^- and CuL_3^{2-} are formed in appreciable amounts. In the iodide system, even CuL_2^- is never present in more than minor amounts while, on the other hand, CuL_4^{3-} is fairly prominent. The possibilities to perform calorimetric measurements are even more restricted (55). The only thermodynamic functions available for comparison with the conditions in DMSO have therefore been some free energy changes, in the first instance the cumulative functions $\Delta G_{\beta 2}^{\circ}$, referring to the reactions $Cu^+ + 2L^- \rightleftharpoons CuL_2^-$. Except in the medium presently used, 5 M $NaClO_4$, these functions are also known for $I=O$ (Table 9). The magnitude does not differ very much between the two media. In both, a (b)-sequence is found though the difference between chloride and bromide is unusually small, especially in 5 M $NaClO_4$. A much larger difference between chloride and bromide is found for ΔG_3° .

TABLE 9. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG° , $\Delta H^{\circ}/kJ\ mol^{-1}$, $\Delta S^{\circ}/JK^{-1}\ mol^{-1}$) for the formation of copper(I) halide complexes in DMSO and water, at 25°C.

	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
	1 M NH_4ClO_4 ^a			0.1 M Et_4NClO_4 ^b		
DMSO						
$\log K_1$	4.37	4.19	4.71	6.0	5.0	5.5
$\log K_2$	4.50	3.75	2.96	6.0	4.6	2.7
$\log K_3$	0.58					
K_1/K_2	0.7	2.8	56	1	3	600
K_2/K_3	8000					
$-\Delta G_1^{\circ}$	24.9	23.9	26.9	34	29	31
$-\Delta G_2^{\circ}$	25.7	21.7	16.9	34	26	16
$-\Delta G_3^{\circ}$	3.3					
$-\Delta H_1^{\circ}$	6.4	9.3	13.6			
$-\Delta H_2^{\circ}$	7.8	-2.1	-3.1			
ΔS_1°	62	49	45			
ΔS_2°	60	78	67			
$-\Delta G_{\beta 2}^{\circ}$	50.6	45.6	43.8	68	55	47
$-\Delta H_{\beta 2}^{\circ}$	14.2	7.2	10.5			
$\Delta S_{\beta 2}^{\circ}$	122	127	112			
Water	5 M $NaClO_4$ ^c			$I = O$ ^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			
$-\Delta G_4^{\circ}$			-5.8			

^a Ref. (20). ^b Ref. (24). ^c Ref. (23). ^d Ref. (54).

In DMSO, a complete determination of the thermodynamic functions is possible, as has been stated above. As for the acceptors discussed earlier, the chloride and, to a lesser extent, the bromide complexes are much more stable in DMSO than in water. The iodide complexes are, on the other hand, considerably less stable. For the complexes CuL_2 , these changes result in a rather unique hybrid stability sequence, with a minimum at Br^- (Table 9). For the second step, on the other hand, a marked (a)-sequence is found in DMSO. These sequences are found both in the medium 1 M NH_4ClO_4 presently used (20), and in 0.1 M Et_4NClO_4 (24). The ratio K_1/K_2 consequently increases considerably in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$. The conditions are also illustrated by the complex formation curves (Fig. 7) which cut across each other in a rather unusual manner.

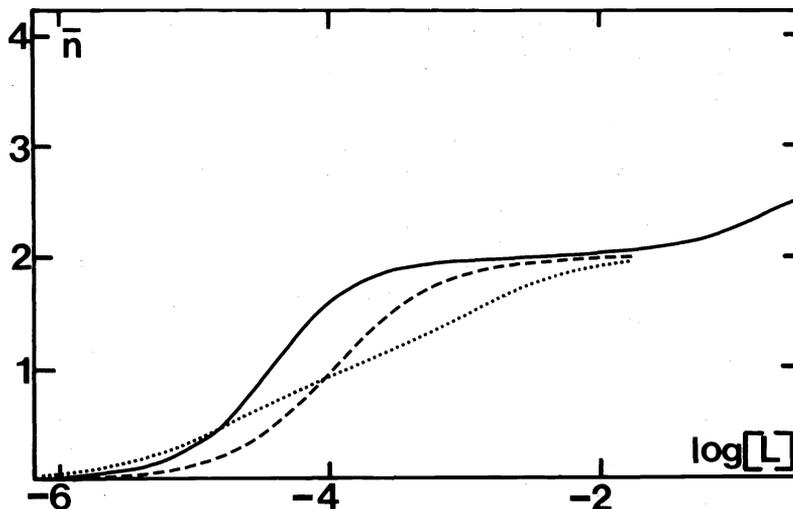


Fig. 7. Complex formation curves in DMSO (medium 1 M NH_4ClO_4) of the copper(I) chloride (—), bromide (---) and iodide (·····) systems.

These differences between the halide systems are mainly caused by the unusual trends of the functions ΔH_1^0 (Table 9). The values of ΔH_1^0 become more exothermic the softer the ligand, as is generally the rule for typically soft acceptors (Table 6, and refs. 17,55). The values of ΔH_2^0 show the opposite trend, however. The latter trend is also found for ΔH_1^0 and ΔH_2^0 of the cadmium halide systems in DMSO (Table 4), but it might be premature to draw far-reaching conclusions from this parallel.

Though copper(I) is reluctant to form digonal complexes in solid phases, it is nevertheless probable that the complexes CuL_2 have such structures both in water and DMSO (33). Unfortunately, direct structure determinations have so far not been attempted. The values of ΔS_{12}^0 are very high, however, considering that the cation involved is only singly charged, cf. the values found for CdL_2 (Table 4). They indicate that the desolvation accompanying the first two steps must be much more extensive for copper(I). Admittedly, the pattern followed by ΔS_1^0 and ΔS_2^0 is not the same for copper(I) as for mercury(II) where the formation of the digonal complexes is beyond doubt. This difference might very likely be due to different solvate structures however.

THERMODYNAMICS OF THE COPPER(I), SILVER(I) AND MERCURY(II) COMPLEXES FORMED IN DMSO WITH NITROGEN GROUP DONORS

In the case of copper(I) and silver(I), the complex formation with the complete series of triphenyl derivatives Ph_3X , X = N, P, As, Sb, Bi can be investigated. The results referring to Ph_3P , Ph_3As and Ph_3Sb are listed in Table 10. For Ph_3N , and Ph_3Bi , only one weak complex ($\log K_1 = 0.19$ and 0.80 , respectively) is found with silver(I), and no appreciable complex formation at all with copper(I), (27,28). In the case of mercury(II), measurements involving Ph_3Sb and Ph_3Bi are not feasible, as these ligands are rapidly oxidized. The other ligands are stable, though complexes are not formed in appreciable amounts by Ph_3N . The data obtained for Ph_3P and Ph_3As are in Table 10.

Obviously the stability sequence for copper(I) and silver(I) is $\text{N} << \text{P} > \text{As} > \text{Sb} > \text{Bi}$. These are seemingly the first instances where this sequence, postulated quite early from largely qualitative data, has indeed been quantitatively verified (18). The stability differences between the arsine and stibine systems are not very large, however, especially not for silver(I) where even a slight reversal is observed in the third step.

For both acceptors, the phosphine complexes are by far the most stable ones. A striking feature of the three silver systems, and of the copper(I) phosphine, is that the first

complex is very stable relative to the second one. This is indeed in contrast to the behaviour of these acceptors in most systems, though a parallel has just been found in the copper(I) iodide in DMSO (Fig. 7). The wide range of existence of the complexes ML^+ is clearly discernible in the complex formation curves (Fig. 8). It is also evident that in the silver(I) phosphine system, the third complex is quite stable relative to the fourth one.

TABLE 10. 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 complexes between copper(I), silver(I) and mercury(II) and ligands Ph_3X in DMSO, at 25°C and $I = 0.1 M (NH_4ClO_4)$

X →	Copper(I) ^a			Silver(I) ^b			Mercury(II) ^a	
	P	As	Sb	P	As	Sb	P	As
log K_1	6.57	2.65	1.25	6.58	3.56	3.16	11.06	6.77
log K_2	3.87	1.40	0.54	4.15	1.81	1.45	6.55	2.20
log K_3	1.40			2.44	1.31	1.45		
K_1/K_2	510	18	5	269	56	51	32000	38000
K_2/K_3	300			52	3.2	1		
$-\Delta G_1^\circ$	37.5	15	7	37.6	20.3	18.1	63.2	38.6
$-\Delta G_2^\circ$	22.0	8	3	23.7	10.4	8.3	37.4	12.5
$-\Delta G_3^\circ$	8			13.9	7.5	8.3		
$-\Delta H_1^\circ$	47	23	11	51.8	34.5	32.1	57	34
$-\Delta H_2^\circ$	41	32	25	38.1	19.4	8.6	51	27
$-\Delta H_3^\circ$	25			36.3	44.5	57.1		
ΔS_1°	-32	-27	-13	-48	-48	-47	20	15
ΔS_2°	-64	-80	-74	-48	-30	-1	-47	-49
ΔS_3°	-57			-75	-124	-164		

^a Ref. (28).

^b Ref. (27).

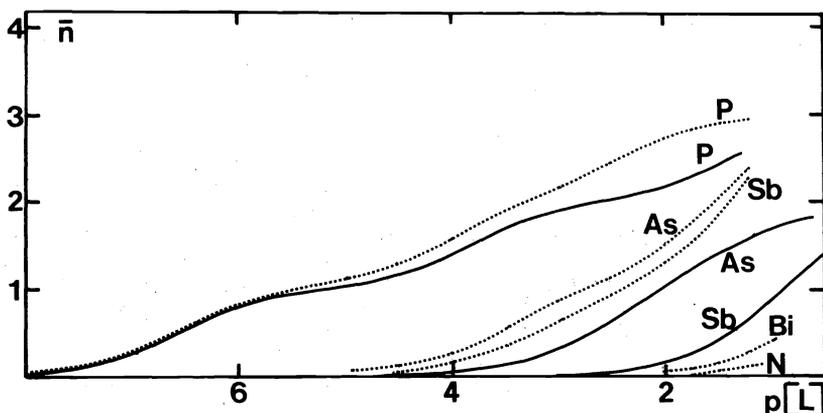


Fig. 8. Complex formation curves in DMSO (medium 0.1 M NH_4ClO_4) of the copper(I) (—) and silver(I) (·····) systems of complexes formed with the ligands Ph_3X ($X = N, P, As, Sb, Bi$).

These trends are the net result of a quite complicated interplay of enthalpy and entropy terms (Table 10). Common traits are, however, that all complexes are enthalpy-stabilized while the entropy terms are all counteracting the reactions and generally quite strongly so.

The favourable enthalpy changes are certainly to be expected for reactions where the desolvation enthalpies are small for both the acceptor and, even more, for the donor, and where strong coordinate bonds of a markedly covalent character are formed. On the other hand, the formation of complexes of this type involves large conformational entropy losses which are not compensated by any large gains due to desolvation. Consequently, the entropy terms become generally very unfavourable. The conformational entropies should further be different for the consecutive steps and also for the different donors and acceptors which explains the very individual behaviour of the various systems.

The conformational demands should be smallest for the formation of the first complex, and the functions pertaining to this step should therefore be easiest to rationalize. For corresponding complexes, the values of ΔH_1^0 are throughout more exothermic for silver(I) than for copper(I), as is to be expected on account of the softer character of silver(I). For both acceptors, the values moreover become less exothermic in the sequence $P > As > Sb$, i.e., with decreasing capacity for covalent bonding. The trend is more marked for copper(I). This is understandable as this acceptor should have larger difficulties than the softer silver(I) to make up for deficiencies in the covalent bonding capacity of the ligand. As copper(I) is presumably more strongly solvated than silver(I), the values of ΔS_1^0 should be more favourable for the former acceptor, as is in fact found.

The mercury systems that can be investigated follow the same stability pattern as copper(I) and silver(I) (Table 10). Especially the first phosphine and the first arsine complex are much more stable than the corresponding silver(I) and copper(I) complexes. This is very much due to favourable values of $\Delta S_1^0 > 0$, owing certainly to the larger desolvation enthalpy of the divalent Hg^{2+} . Already the values of ΔS_2^0 are quite unfavourable, however. The differences in stability between the complexes HgL_2^{2+} and HgL_3^{2+} therefore become quite large, and the complex formation curves display long plateaus at $\bar{n} = 1$ (Fig. 9). A third complex is not formed at all within the range of [L] available. At least in the phosphine system, this means that the second complex is very stable relative to the third one.

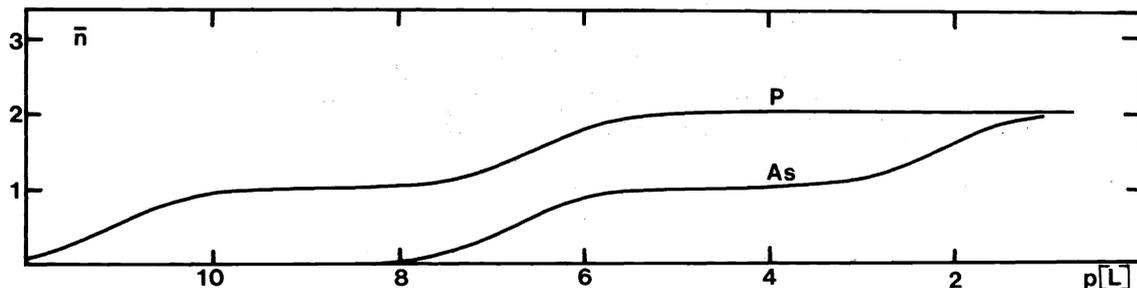


Fig. 9. Complex formation curves in DMSO (medium 0.1 M NH_4ClO_4) of the mercury(II) systems of complexes formed with the ligands Ph_3P and Ph_3As .

It cannot be decided whether the large differences found between ΔS_1^0 and ΔS_2^0 are due to an especially heavy desolvation in the first step, as is the case in the halide system, or to conformational entropy losses in the second step. This illustrates clearly the difficulties inherent in the interpretation of the thermodynamics of reactions involving ligands of strong conformational demands.

Acknowledgements - The work of the inorganic solution chemistry group at the Chemical Center of the University of Lund is supported by the Swedish Natural Science Research Council. Part of the work has been done at the H. C. Ørsted Institute of the University of Copenhagen. I am much indebted to my friend Jannik Bjerrum for his help and hospitality over the years. We have also had a most fruitful cooperation with Georg Johansson and Magnus Sundström, of the structural chemistry group, Royal Institute of Technology, Stockholm. My sincere thanks are finally due to my able and

conscientious coworkers Torsten Berg, Nils-Olof Björk, Peter Bläuenstein, Lennart Kullberg, Ingmar Persson, Roberto Portanova, James Rawsthorne, Bernt Tagesson, Per Trinderup and Dinko Tuhtar.

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