

Thermodynamics of Complex Formation in Dimethyl Sulfoxide with Ligands Coordinating *via* N, P, As, Sb or Bi.

II. Copper(I) and Mercury(II) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The thermodynamics of the complex formation between the metal ions Cu^+ and Hg^{2+} and the ligands Ph_3X (Ph=phenyl; X=N, P, As, Sb, Bi) has been studied in dimethyl sulfoxide (DMSO) at 25 °C, in an ammonium perchlorate medium of ionic strength 0.1 M. Stability constants have been determined potentiometrically, by copper amalgam and mercury electrodes, and enthalpy changes calorimetrically.

For copper(I), the stabilities follow the affinity sequence $\text{N} \ll \text{P} > \text{As} > \text{Sb} > \text{Bi}$, i.e. the same as for silver(I). For mercury(II), measurements are feasible only when X=N, P, As, as the ligands Ph_3Sb and Ph_3Bi are rapidly oxidized. For the systems measured, the same sequence is again found: $\text{N} \ll \text{P} > \text{As}$. As to the first two steps, the affinities of a certain ligand Ph_3X (X=P, As) for the acceptors investigated increase in the order $\text{Cu}^+ < \text{Ag}^+ < \text{Hg}^{2+}$ while the tendency to form a third complex is strongest for Ag^+ .

All complexes are strongly enthalpy stabilized. The entropy changes counteract the complex formation, except for the first step in the mercury(II) systems where an entropy stabilization is found. The very negative, and hence strongly destabilizing, entropy changes generally found for the latter steps are no doubt due to the strict conformational demands connected with the formation of these complexes.

Jannik Bjerrum and his school have contributed greatly to our knowledge of the complex-forming

properties of ligands coordinating *via* phosphorus by their investigations in aqueous solution of the complexes formed between the water-soluble diphenylphosphinobenzene-*m*-sulfonate, Dpm, and soft metallic centers of various oxidation states and electron configurations. The metallic centers included Pt(II) and Pd(II)¹ (d^8); Cu(I)², Au(I)³ and Hg(II)⁴ (d^{10}); and Bi(III)⁵ ($d^{10}s^2$), of which Pd(II), Hg(II) and Bi(III) were the aquo metal ions. Disproportionation reactions precluded the use of aquo Cu(I) and Au(I), so that in these cases the complex formation was referred to the chloro and the thiocyanato complexes respectively. At that time the aquo Pt^{2+} had not yet been prepared,⁶ so for Pt(II) the diammine complexes (*cis*- and *trans*-) were used. In a related investigation the complexes formed by Ag^+ and HgCl_2 with triphenylarsine were studied.⁷ This ligand, like the other non-substituted triphenyl compounds of the nitrogen group donor atoms (Ph_3X ; X=N, P, As, Sb, Bi) is not soluble in water so that the measurements were performed in a mixed water/methanol solvent.

Jannik Bjerrum has stated⁸ that his great interest in these complexes was inspired by the remarkable complex formation observed between Ag^+ and the phosphine ligand Dpm.⁹ In marked contrast to the conditions prevailing in most silver(I) systems,¹⁰ the first and the third complex predominate strongly over a large range of ligand concentration, while the second one possesses a

fairly narrow range of existence. In the studies referred to above similar unusual features were found in various degrees also for gold(I)³ and mercury(II).⁴

It is evidently of interest to investigate the complexes formed by these metallic centers with the analogous arsine, stibine, and bismuthine ligands. Attempts to prepare these have so far been abortive. Sulfonation of triphenylarsine gives a trisulfonate⁹ in which arsenic is likely to have donor properties which are markedly different from those found in a monosulfonate. The higher anionic charge presumably also influences the complex formation. The sulfonation of triphenylstibine or triphenylbismuthine has so far not been achieved.

The large influence exerted on the donor properties of the ligand atom by its environment is demonstrated by the complex-forming properties of the aliphatic and uncharged phosphine diethyl- β -hydroxyethylphosphine, Dop.¹¹ Due to its alcoholic group this ligand is sufficiently water-soluble to be used in aqueous solution. Both the absolute and the relative stabilities of the consecutive complexes differ considerably from those found for Dpm.^{8,11} Perhaps most important, the complexes formed by Dop are generally more stable, reflecting the stronger donating properties of phosphorus in the aliphatic environment.

As a consequence of these difficulties the measurements so far performed in aqueous solution have failed to confirm the stability sequence $N \ll P > As > Sb > Bi$ which as early as 1958 was postulated to be generally valid for soft acceptors on the basis of scarce and largely qualitative evidence.¹²

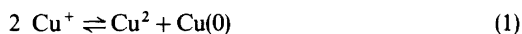
Moreover, even for the sulfonated ligands and their complexes, the solubilities in water are still too low to allow precise calorimetric measurements. Consequently, the complete thermodynamics of the complex formation reactions cannot be determined. This is indeed a serious drawback, as important conclusions about the structure and bonding of the complexes formed can be drawn from the enthalpy and entropy changes involved.^{13,14}

In the present series of investigations we have therefore chosen another approach. By changing the solvent from water to dimethyl sulfoxide (DMSO) where the simple triphenyl compounds, Ph_3X , and in most cases also their complexes, are readily soluble, a comparative study of the affinities of all the nitrogen group donor atoms towards various acceptors becomes possible. Moreover the

influence on the stabilities of the enthalpy and the entropy terms can be precisely determined.

In the first paper of this series,¹⁵ the thermodynamic functions of the silver(I) complexes formed with all the ligands Ph_3X were determined. As a result the affinity sequence stated above was quantitatively confirmed, seemingly for the first time. The present paper deals with the corresponding copper(I) and mercury(II) complexes. Like silver(I), these acceptors have both d^{10} configurations, but while copper(I) differs from silver(I) only by one electron shell, mercury(II) also possesses one additional ionic charge.

Relative to water, DMSO has the further advantage that not only silver(I) and mercury(II) but also copper(I) can exist in the solution as the solvated ions. This of course much facilitates the comparison between the complex forming properties of the acceptors. The disproportionation constant referring to the reaction



is so much lower in DMSO than in water^{16,17} that copper(I) perchlorate solutions of a concentration as high as ≈ 15 mM (which are used in the present investigation) only disproportionate to $\approx 2\%$ in DMSO while the disproportionation would be virtually complete, $\approx 99\%$ in water. This drastic change is connected with the changes of the solvation enthalpies for Cu^+ and Cu^{2+} from water to DMSO, which bring about a very considerable stabilization of Cu^+ relative to Cu^{2+} as the system is transferred from water to DMSO.¹⁸

Also the relative stabilities of mercury(I) and mercury(II) according to the reaction



are different in water and in DMSO. In this case, however, the transfer to DMSO favours the divalent oxidation state relative to the monovalent one.¹⁹ The equilibrium change is much smaller than for copper but is nevertheless advantageous for the measurements described below, where mercury electrodes are employed. In DMSO such measurements can be extended to higher concentrations of solvated mercury(II) than would be possible in water.

For both systems the stability constants have been determined potentiometrically, by means of copper amalgam and mercury electrodes, respec-

tively. The enthalpy changes have been determined calorimetrically, applying in the calculations the stability constants already determined. From the changes of free energy and enthalpy thus found, the entropy changes have been calculated.

As in the previous study, the measurements refer to a medium of ionic strength 0.1 M, maintained by ammonium perchlorate, and a temperature of 25 °C.

EXPERIMENTAL

Chemicals. Dimethyl sulfoxide was purified and analyzed for water as described before.¹⁵ Ammonium perchlorate was dried at about 110 °C. Triphenylamine, -phosphine, -stibine and -bismuthine were recrystallized from a mixture of 1:1 ether/ethanol^{20,21} and triphenylarsine from ethanol.²² All ligands were dried *in vacuo* at room temperature. Ligand solutions were not kept longer than two days because of their limited stability. The ligands are oxidized to Ph₃XO with concomitant reduction of DMSO to (CH₃)₂S, which is easily detected by its characteristic smell.²³ The solvates Cu(ClO₄)₂·4DMSO, Hg(ClO₄)₂·4DMSO and [Cd(DMSO)₆](ClO₄)₂ were prepared and analyzed as described previously.^{16,24–26} The copper amalgam, and the cadmium amalgam used for the reference electrodes, were prepared according to standard methods.^{16,27} Solutions of copper(I) perchlorate in DMSO were prepared by reducing copper(II) perchlorate with copper foil at 60 °C. Because of the disproportionation of copper(I), no solution of copper(I) concentration >0.02 M was prepared.¹⁶

Potentiometry, copper(I) systems. The potentiometric titrations were performed in a glove box in dry carbon dioxide atmosphere as described in Ref. 16. In addition a stream of purified nitrogen was bubbled through the solution. The emf of the cell in Scheme 1 was measured. Initially the right hand half cell contained only copper(I) perchlorate of a C_M between 3 and 15 mM (*I* = 0.1 M). When a stable initial potential had been reached, portions of ligand solutions of a C_L between 100 and 300 mM (*I* = 0.1 M) were added. Generally three titrations were performed for every value of C_M and C_L. The emf's could be reproduced within ≈1 mV. In the

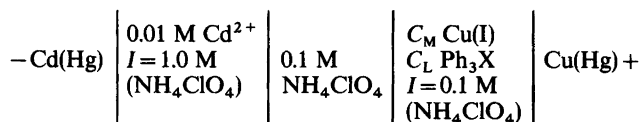
phosphine system the reproducibility was not as good for $\bar{n} > 2$, viz. ≈3 mV. From the potential difference measured the constants β_j were calculated according to the procedure described before.^{15,16}

Generally a slight oxidation of Cu(I) by traces of O₂ could not be avoided, but the products formed were again rapidly reduced by Cu(Hg). The overall result is an increase of C_M. In the phosphine system the decrease of the concentration of free copper(I) ions [Cu⁺] at $\bar{n}=1$ and $\bar{n}=2$ was steep enough to allow the calculation of C_M. This was not the case with the arsine and stibine systems, where C_M had to be determined separately by EDTA titration.¹⁶ It was then necessary to extract most of the ligand with ether as the point of equivalence was approached. The precision was ≈1 %. For some samples the final C_M was also measured by atomic absorption spectrophotometry. The results agreed well with those found by EDTA titration, but the precision was lower.

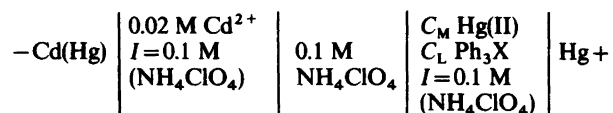
In the phosphine titrations it was observed that the oxidation rate was perceptible when $\bar{n} < 1$, i.e. when [Cu⁺] is relatively high. For $\bar{n} > 2$ the solutions were very stable, giving emf's which did not change appreciably overnight. Therefore C_M had only to be corrected in the first part of the titrations. For the arsine and stibine systems the highest values of \bar{n} reached were 1.9 and 1.5, respectively. In these systems where only the initial and final value of C_M were determined it was therefore considered adequate to calculate the intermediate values of C_M by a linear interpolation. If C_M increased >5 %, the titration was discarded.

Potentiometry, mercury systems. To exclude moisture, the potentiometric measurements were performed in a glove box as described before,^{15,16,28} and dry nitrogen was bubbled through the electrode solutions. The emf of cell in Scheme 2 was measured. In the absence of stabilizing ligands, solutions of mercury(II) perchlorate in DMSO are reduced by metallic mercury according to eqn. (2). In the present medium,¹⁹ the reproporationation constant $K_r = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}] = 35 \pm 5$. In 1 M NH₄ClO₄, a value of $K_r = 24 \pm 3$ has been determined¹⁹ which is again not very different from $K_r = 40$ recently found for another 1 M perchlorate medium.²⁹ The earlier value determined indirectly in 0.1 M Et₄NClO₄ disagrees very markedly, however.³⁰

The value of K_r found for DMSO implies, as



Scheme 1.



Scheme 2.

already stated, a stabilization of Hg(II) relative to Hg(I) as compared with aqueous solution. Evidently, this stabilization is not large enough, however, to allow any considerable concentration of Hg^{2+} in equilibrium with the mercury electrode. The titrations were therefore conducted from higher to lower values of \bar{n} and interrupted when reproporation became perceptible; the initial solution thus contained an excess of ligand. To this solution portions of mercury(II) perchlorate solution of the same concentration C_M were added. Consequently only C_L decreased during the titration, while C_M remained constant. Using this procedure it is necessary to determine independently the emf referring to a non-complex solution containing only free Hg^{2+} of a known concentration. The potential of a standard mercury half-cell $1 \text{ M Hg}^{2+}/\text{Hg(I)}$ relative to the cadmium reference cell used here has been found to be 1192.65 mV under the present conditions.¹⁹ As the potential of the reference electrode is easily reproducible within 0.5 mV and remains constant for about three days, this procedure is quite adequate.

Two independent reference electrodes were used, and the emf was taken as the average of the values measured between the mercury electrode in the reaction vessel and each of the reference electrodes. The equilibrium emf was normally reached within 20 min and remained constant for more than 5 h. Titration series were generally performed for three values of C_M and each series were made at least three times. In the arsine system, the emf values were readily reproduced within 2 mV. The same reproducibility was found in the phosphine system except for solutions that contained a large excess of ligand or had values of C_L/C_M around 2.

Contrary to this, no reproducible emf values at all were established in the stibine and the bismuthine systems. The values decreased rapidly, signifying a fast decrease of Hg^{2+} . Very likely, this decrease is due to a reduction of Hg(II) by the ligands although another possibility is that Hg(II) catalyzes an oxidation of the ligands by DMSO, resulting in a formation of dimethyl sulfide which would strongly sequester Hg^{2+} .

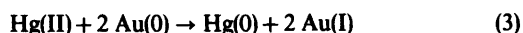
The least-squares programme EMK was used to calculate the stability constants from the potential measurements.²⁸

Calorimetry, copper(I) systems. The calorimeter is described in Ref. 16. To prevent oxidation of

Cu(I) a steady stream of CO_2 was bubbled through the solutions. Initially the calorimeter contained pure perchlorate solutions of $C_M \approx 10 \text{ mM}$, which were titrated with ligand solutions of a C_L between 100 and 300 mM ($I=0.1 \text{ M}$). The heats measured were reproduced within $\approx 0.1 \text{ J}$. Corrections were introduced for the heats of dilution. These were slightly positive for the ligand solutions and negligible for the copper(I) solutions. At high ligand concentrations traces of copper(II) tended to oxidize the gold vessel. This was prevented by placing a piece of copper wire in the vessel. By weighing the the copper wire before and after the measurement the increase of copper(I) during the experiment could be determined. Assuming that this increase took place during the first part of the phosphine titrations, but continuously in the arsine and stibine ones, the actual values of C_M were calculated (*cf.* potentiometry, copper(I) systems).

The least-squares program KALORI^{31,32} was used for the numerical treatment of the experimental data yielding $\Delta H^\circ_{\beta_i}$. The stability constants found in the potentiometric measurements were applied.

Calorimetry, mercury systems. The calorimeter used was the same as described in the first paper of this series.^{15,33} In the present measurements, however, the inner gold vessel was oxidized by the mercury(II) as triphenylphosphine was added. Metallic mercury seemingly precipitated, and by analysis it was found, that for each mol of mercury reduced, 2 mol of gold metal had been dissolved, in accordance with



This reaction must be due to a very strong affinity between Au(I) and the phosphine ligand. The complexes formed are evidently so thermodynamically stable that not only did they compete successfully with the Hg(II) complexes, but also the oxidation potential of the couple Au(I)/Au(0) was changed so much that the metallic gold was oxidized. This complication was avoided by coating electrolytically the gold with a $3 \mu\text{m}$ rhodium layer.

The calorimetric measurements could then be performed in the conventional manner.³⁴ For each system 6–15 titrations were made. In most of these, ligand solutions of $\approx 100 \text{ mM}$ were titrated into mercury(II) perchlorate solutions of C_M varying from ≈ 2 to $\approx 10 \text{ mM}$. In other series, mercury(II)

Table 1. Overall stability constants (β_j in M^{-1}) and enthalpy changes ($\Delta H_{\beta_j}^\circ$ in kJ mol^{-1}) calculated for the complexes formed between copper(I) and mercury(II) and the ligands Ph_3X in DMSO at 25 °C and ionic strength $I=0.1\text{ M}$ (NH_4ClO_4). The errors given (for β_j in the last digit(s)) are three times the standard deviation given by the computer.

	Copper(I) X=P	X=As	X=Sb	Mercury(II) X=P	X=As
$\log \beta_1$	6.57(2)	2.65(2)	1.26(3)	11.06(1)	6.77(2)
$\log \beta_2$	10.43(3)	4.04(2)	1.79(5)	17.62(1)	8.97(3)
$\log \beta_3$	11.83(10)				
$-\Delta H_{\beta_1}^\circ$	46.9(0.7)	22.3(0.4)	10.6(0.8)	56.8(1.2)	34.0(1.3)
$-\Delta H_{\beta_2}^\circ$	87.9(1.0)	56.0(1.2)	35.4(4.1)	107.7(2.0)	61.3(2.0)
$-\Delta H_{\beta_3}^\circ$	112.3(3.7)				

Table 2. Equilibrium constants (K_j in M^{-1}) and thermodynamic functions (ΔH_j° , ΔG_j° in kJ mol^{-1} , ΔS_j° in $\text{JK}^{-1}\text{mol}^{-1}$) for the stepwise formation of complexes between copper(I), silver(I) and mercury(II) and ligands Ph_3X in DMSO, at 25 °C and $I=0.1\text{ M}$ (NH_4ClO_4).

	Copper(I) ^a			Silver(I) ^b			Mercury(II) ^a	
	X=P	X=As	X=Sb	X=P	X=As ^c	X=Sb	X=P	X=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	32 000	38 000
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 This work. ^b Ref. 15. ^c From Table 1, Ref. 15, slightly different values of ΔH_j° are calculated for the arsine system. The present values, taken from Table 2, Ref. 15, are to be preferred, however.

perchlorate solutions of $C_M \approx 40\text{ mM}$ were titrated into ligand solutions of $C_L \approx 60\text{ mM}$. Each series was run at least twice with a reproducibility generally better than 0.1 J. The experimental heat changes were corrected for heats of dilution. The calculations were performed as for copper(I).

RESULTS

The measurements yield the overall stability constants β_j and enthalpy changes $\Delta H_{\beta_j}^\circ$ listed in Table 1. Complex formation is neither observed between copper(I) and the ligands Ph_3N or Ph_3Bi , nor be-

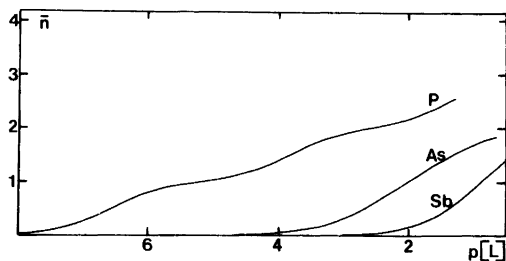


Fig. 1. The complex formation curves of the systems $\text{Cu}^+ - \text{Ph}_3\text{X}$, $\text{X} = \text{P}, \text{As}, \text{Sb}$, in DMSO. Medium $0.1 \text{ M } \text{NH}_4\text{ClO}_4$; 25°C .

tween mercury(II) and Ph_3N . The redox reactions discussed above preclude the investigation of the Ph_3Sb and Ph_3Bi complexes of mercury(II).

From the data of Table 1, the values of the stepwise stability constants K_j and thermodynamic functions ΔG_j° , ΔH_j° and ΔS_j° are calculated, Table 2.

Within the range of ligand concentrations available (indicated on Figs. 1 and 2), a third complex is formed with certainty only between copper(I) and Ph_3P , Tables 1 and 2. A corresponding complex is presumably formed also by mercury(II), but in this case the results of the potentiometric and calorimetric measurements are difficult to reconcile. Potentiometrically, a value of $K_3 = 1.7 \pm 0.3 \text{ M}^{-1}$ is found. With this value of K_3 , the calorimetric data yield the quite improbable value $\Delta H_3^\circ = -240 \pm 75 \text{ kJ mol}^{-1}$. If, on the other hand, K_3 and ΔH_3° are both calculated from the calorimetric data, $K_3 = 35 \pm 32 \text{ M}^{-1}$ and $\Delta H_3^\circ = -26 \pm 21 \text{ kJ mol}^{-1}$ are found, i.e. values which are quite reasonable, but unfortunately very imprecise. Evidently the measurements are not able to provide any reliable values for these quantities.

DISCUSSION

Stabilities of the complexes. Both copper(I) and, within the limits of our measurements, mercury(II) follow the same affinity sequence $\text{N} \ll \text{P} > \text{As} > \text{Sb} > \text{Bi}$ as found previously for silver(I). This early postulated sequence can thus now be considered as well confirmed by quantitative data for soft acceptors.

For copper(I), the first phosphine complex is as thermodynamically stable as the corresponding silver(I) complex and also the second and the third complexes are comparatively stable, Table 2. The arsine, and even more the stibine complexes are all much weaker for copper(I), however. A third complex is not even formed at the highest ligand concentrations which we are able to attain. As has already been stated ammine and bismuthine complexes do not exist under our conditions. The second complex has a wider range of existence in the copper(I) systems as is evident from those values of K_2/K_3 which can be calculated or estimated. The first complex has a remarkably wide range of existence for the phosphine system only. The ratio K_1/K_2 is even higher than for the corresponding silver(I) system. These features are well illustrated by the complex formation curves of the copper(I) systems, Fig. 1. The phosphine curve is markedly deflected at $\bar{n} = 1$ as well as at $\bar{n} = 2$, while the arsine curve is only deflected at $\bar{n} = 2$.

A still much higher ratio K_1/K_2 has been found for the complex formation between copper(I) and the aliphatic phosphine Dop in aqueous solutions, Table 3. In this system, the ratio K_2/K_3 is moreover quite low implying a narrow range of existence for the second complex. The constants measured for the ligand Dpm refer, as stated, to a chloride solution. Their recalculation to equilibria referred to the hydrated ion cannot be carried out for the first two steps, so the ratios K_1/K_2 and K_2/K_3 remain unknown for this system.

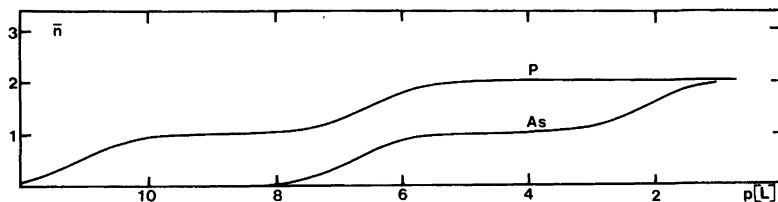


Fig. 2. The complex formation curves of the systems $\text{Hg}^{2+} - \text{Ph}_3\text{X}$; $\text{X} = \text{P}, \text{As}$, in DMSO. Medium $0.1 \text{ M } \text{NH}_4\text{ClO}_4$; 25°C .

Table 3. Stability constants (β_i in M^{-i}) and ratios K_i/K_{i+1} for the complex formation in water between copper(I) and mercury(II) and two substituted phosphines, one aliphatic (Dop^a) and one aromatic (Dpm^b).

	Copper(I) Dop	Dpm ^c	Dpm ^d	Mercury(II) Dop	Dpm ^e
$\log \beta_1$	12.60	5.76			14.3
$\log \beta_2$	20.34	11.20		37.30	24.6
$\log \beta_3$	27.0	16.12	22.0	42.5	29.7
$\log \beta_4$		19.92	25.8		33.0
K_1/K_2	72 400				10 000
K_2/K_3	12				160 000
K_3/K_4					60

^a Ref. 11. Dop = Et₂PCH₂CH₂OH; $I = 1 M$ (KNO₃), 22 °C. ^b Ref. 2 and 4. Dpm = Ph₂PC₆H₄SO₃⁻ (*m*-); 25 °C. ^c Referred to the actual chloride medium, 1 M LiCl. ^d Referred to the copper(I) aquo ion, Cu⁺. ^e Medium 1 M KNO₃.

As has also been found for silver(I),¹⁵ the overall stability of phosphine complexes of copper(I) is much higher in water than in DMSO, Tables 1 and 3. Most probably, this is mainly due to the stronger solvation of these acceptors in DMSO which implies that the ligands have to undergo a stronger competition in this solvent.

For mercury(II), the first phosphine and arsine complexes are considerably stronger than the corresponding copper(I) and silver(I) complexes, Table 2. The same trend, though less marked, also prevails during the formation of the di-ligand complexes. At the third step, however, the trend is reversed. If formed at all, the mercury(II) complexes are considerably weaker. These changes in the relative stability of the consecutive complexes mean that both the first and the second mercury(II) complex have much wider ranges of existence than the corresponding copper(I) or silver(I) complexes. This is expressed by much higher ratios K_1/K_2 and K_2/K_3 and, even more strikingly, by the extended plateaus at $\bar{n} = 1$ and 2 characterizing the complex formation curves of these systems, Fig. 2. The ranges of existence of the mono-ligand complexes are even wider than for the mono-Dpm complex formed in aqueous solution, the first mercury(II) complex to display this feature.⁴ For the present systems, ratios $K_1/K_2 \approx 3 \times 10^4$ are found and can be compared with 10^4 for the Dpm system, Tables 2 and 3. Recently, ratios K_1/K_2 of similar magnitude have also been found for the mercury(II) halide and thiocyanate systems in DMSO.³⁵

The overall stabilities of phosphine complexes are for the mercury(II) system considerably higher in

water than in DMSO, Tables 2 and 3. The reason is once more that the acceptor is more strongly solvated in DMSO than in water. This applies even more for mercury(II) than for silver(I) (and copper(I)) as is evident from the enthalpies ΔH_{tr}° (W → DMSO) found for the transfer of the acceptors from water to DMSO. These are -54 and -76 kJ mol⁻¹ for Ag⁺ and Hg²⁺, respectively.¹⁸

Thermodynamics of the complex formation. Just as for silver(I), all the complexes are formed in exothermic reactions, Table 2. As already stated, this is a natural consequence of the formation of strong metal to ligand bonds and the weak solvation of the ligands involved.¹⁵ On the other hand, the weak solvation, together with the strict conformational demands imposed upon the ligands as the complexes are formed, generally result in unfavourable entropy terms, Table 2. In several instances, the entropy changes are indeed heavily counteracting the complex formation. Extreme examples are the second step in the copper(I) arsine and stibine systems where the effects of quite large negative enthalpies are almost vitiated by the huge entropy losses. The only favourable entropy terms are found in the first step of the mercury(II) systems. Here the desolvation of the strongly solvated divalent Hg²⁺ brings about a net gain of entropy. This desolvation must be very extensive as even the second steps are characterized by large entropy losses. Relative to the di-Ph₃X complexes, the mono-Ph₃X ones are thus strongly entropy stabilized which causes their remarkably wide range of existence.

In the silver(I) systems, the values of ΔS_j° vary be-

tween different steps in a manner which is highly individual for each ligand, Table 2. From the silver data alone, these variations are indeed very difficult to interpret. Comparison with data pertaining to other suitably chosen acceptors may make this possible, however. In fact, the values of ΔS_1° now determined for the copper(I) and mercury(II) systems seem to present some features that can be utilized in order to rationalize the existing body of entropy data.

In the formation of the mono- Ph_3X complexes, the conformational entropies should be of relatively little importance as the structural requirements are still not very severe. The values of ΔS_1° should thus largely be determined by the desolvation entropies which depend mostly on the solvation of the acceptor. The solvation generally becomes stronger and the desolvation entropies consequently more favourable the smaller the radius and the higher the charge of the acceptor. In accordance with this, the values of ΔS_1° for the smaller copper(I) are less negative *i.e.* more favourable than for the larger silver(I). On the other hand, they are not as favourable as for the larger mercury(II) where the higher charge brings about an even stronger solvation, resulting in $\Delta S_1^\circ > 0$.

As higher complexes are formed, however, the structural requirements become stricter and, consequently, the conformational entropies become very important. These should moreover increase as the size of the acceptor decreases. In accordance with this, the values of ΔS_2° for copper(I) are all more negative, *i.e.* less favourable than for silver(I). In the silver(I) systems, ΔS_2° is moreover less negative than ΔS_1° (or, in the phosphine case, of the same value) which would not be possible should the values of ΔS_2° be determined mainly by the desolvation entropies. The evidence thus strongly indicates that the conformational entropies are indeed of decisive importance from the second step onwards.

The values of ΔS_3° for the silver(I) systems become extremely unfavourable, and increasingly so in the order $\text{P} < \text{As} < \text{Sb}$. This is indeed to be expected as the conformational demands should be severe when three ligands are to be accommodated, and moreover to an increasing degree as the ligands become larger. For the smaller copper(I), the conformational entropies involved in the coordination of the large arsine and stibine ligands may become even more unfavourable, which is probably the reason why

these complexes are in fact not formed in perceptible amounts.

The results now available thus allow rather extensive conclusions about the nature of the complex formation. Quite a few features are still difficult to interpret, however, *e.g.* why the values of ΔS_2° found in the silver(I) systems become more favourable in the order $\text{P} < \text{As} < \text{Sb}$. Investigations of the thermodynamics of the complex formation between the ligands Ph_3X and further acceptors may hopefully clarify the situation, especially if the thermodynamic data can be combined with structural information.

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