Equilibrium and Enthalpy Measurements of the Complex Formation between Silver(I) and Ligands Coordinating via N, P, As, Sb or Bi in Pyridine Solution

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The stabilities and heats of formation of silver(I) triphenylphosphine, -arsine and -stibine complexes have been determined in pyridine by means of potentiometric and calorimetric measurements. Within the range of concentrations available, the first three mononuclear complexes were formed with triphenylphosphine, but only the first one with triphenylarsine and -stibine. No complex formation could be proved with triphenylamine or -bismuthine in pyridine. The entropy terms were very similar for all three steps in the phosphine system and also for the first step in the three systems studied, indicating that the complex formation involves the substitution of a pyridine molecule in the silver(I) solvate by a ligand and that no appreciable steric hindrance exists when the complexes are formed.

Soft acceptors display the affinity sequence N ≪ P > As > Sb > Bi for ligands coordinating via donor atoms of the nitrogen group.[1-4] In the case of typically soft acceptors, e.g. silver(I), the affinity for phosphorus is indeed very strong; but complexes coordinating through arsenic and antimony are also quite stable. On the other hand, the affinities of these donor atoms for hard, and even for borderline acceptors, are quite weak.[1,4-6] Suitable ligands for the investigation of these affinities are the triphenyl compounds Ph_3X (X = N, P, As, Sb, Bi). In water, these compounds are insoluble but, at least in the N, P and As compounds, sulfonate groups can be introduced in the aromatic rings to make the ligands sufficiently soluble for thermodynamic measurements in aqueous solutions. Such sulfonated ligands were employed in the first quantitative study of silver(I) complexes involving this group of donor atoms.[7] Later on, it was found that the compounds Ph_3X, as well as their silver(I) complexes, are easily soluble in aprotic solvents such as dimethyl sulfoxide (DMSO). In this solvent, the affinity sequence quoted above could be fully sub-

stantiated.[2,3] The aim of the present investigation was to investigate the same systems in an aprotic solvent of donor properties fairly different from those of DMSO, namely pyridine.

In this solvent, solvating through nitrogen, the solvation of the silver ion is much stronger than in DMSO, as evident from the heats of solvation, ΔH°_{sv}, which are −594 and −539 kJ mol^{-1} for pyridine and DMSO, respectively.[8] Silver(I) complexes should therefore generally tend to be less stable in pyridine than in DMSO. The decrease of stability due to the less favourable enthalpy terms should be counteracted by more favourable entropy terms, however, arising from the circumstances that, in pyridine, the solvate is more well ordered, and the bulk structure less well ordered, than in DMSO.[9] These inferences have been confirmed by investigations of the halide complex formation in the two solvents.[9,10]

The ligands Ph_3X are solvated mainly through London forces.[11] The heats of solvation are small, with the values of $-\Delta H^\circ_{sv}$ increasing slightly in the order N < P < As < Sb < Bi for both pyridine and DMSO, evidently due to the increasing size

Table 1. Overall stability constants (β_i/M^{-j}) for the complexes formed between silver(I) and Ph_3X ligands in pyridine solution at 25 °C. Ionic medium 0.1 M Et_4NClO_4. The limits of error refer to three standard deviations; NP denotes the number of observations (emfs measured) for each system.

X→	N	P	As	Sb	Bi
β_1	<0.1	$(2.06\pm0.05)\cdot10^4$	27.7 ± 0.7	12.4 ± 0.4	<0.1
β_2		$(2.87\pm0.12)\cdot10^6$			
β_3		$(3.91\pm0.39)\cdot10^7$			
NP	144	248	339	342	1

and polarizability of X. The values of $-\Delta H^\circ_{sv}$ range from 74 to 90 kJ mol^{-1} in pyridine and from 70 to 85 kJ mol^{-1} in DMSO. For a given ligand, the values of ΔH°_{sv} differ only by 4 to 8 kJ mol^{-1} between the two solvents; as might be expected, the character of the solvent donor atom is of little importance for the solvation of the ligands. The change of ligand solvation evidently influences the stabilities of the complexes only slightly.

The entropy changes are unfavourable in DMSO.[2] This applies especially to the third step, presumably on account of a severe steric hindrance for the formation of the third complex. The fact that the effect increases with the size of the ligand also speaks in favour of this interpretation. A DMSO molecule is much more bulky than a flat pyridine molecule. Therefore, if the second complex is still appreciably solvated, and the formation of the third complex is an associative process, the steric hindrance should be less in pyridine and the entropy changes consequently less unfavourable than in DMSO.

In the present investigation, 0.1 M tetraethylammonium perchlorate was used as a supporting electrolyte. The measurements were carried out at 25 °C.

Experimental

Chemicals. The silver and tetraethylammonium perchlorates, the ligands Ph_3X and the solvent (all Fluka) were of analytical grade and used without further purification. The silver perchlorate was dried at 80 °C over P_2O_5 under vacuum. The tetraethylammonium perchlorate was dried at 80 °C and the Ph_3X ligands at room temperature over silica gel under vacuum. The pyridine was stored in a dark bottle over 3Å molecular sieves. It contained less than 0.1 % water, determined by the Karl Fischer method. The pyridine

solutions of the ligands (all containing 0.1 M Et_4NClO_4) did not keep very well, their stabilities decreasing in the order N > P > As > Sb > Bi, Triphenylphosphine solutions were stable for some days but deteriorated markedly after one week, while the triphenylstibine solutions were stable for only about 24 h.

Potentiometric measurements. Electrode vessels of Ingold type were used for the electrode solutions; three as reaction vessels, two for the reference electrodes and one as a connecting salt bridge. Every measuring electrode was measured against both reference electrodes. The electrodes were thick silver foils, with an area of about 2 cm^2. The reaction vessels initially contained 10.0 ml silver(I) perchlorate of a concentration C_M = 3, 6 or 12 mM. The same solutions were used for the reference electrodes. To the reaction vessels, ligand solutions of concentration C_L were added portionwise. Solutions with C_L = 500 mM Ph_3N, 40 and 100 mM Ph_3P, 40 and 300 mM Ph_3As, 100 and 500 mM Ph_3Sb and 500 mM Ph_3Bi were used. The potentials were measured with an Eldorado 1820 digital potentiometer. The input resistance over the voltmeter was at least 500 times larger than the resistance over a cell. All measurements were carried out in a dry box containing 3Å mo-
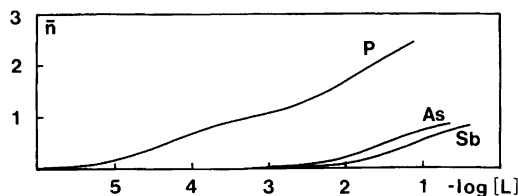

Fig. 1. Complex formation functions of the systems Ag^+-Ph_3X, X = P, As and Sb, in pyridine. Medium 0.1 M Et_4NClO_4, 25 °C.
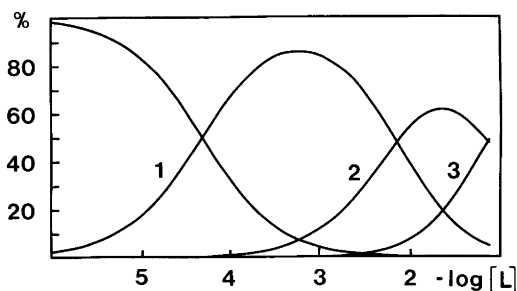
Fig. 2. Distribution of silver(I) between the species Ag^+, AgL^+ (1), AgL_2^+ (2) and AgL_3^+ (3) for the phosphine system in pyridine as a function of the free ligand concentration.

lecular sieves and phosphorous pentoxide to remove traces of water. The stability constants β_j were calculated from the emfs measured by the least-squares program EMK.[12]

Calorimetric measurements. The measurements were performed in the automated titration calorimeter system described previously.[13] Initially, the reaction vessel contained 80 ml of a silver(I) solution, with C_M ranging from 5 to 25 mM. To these solutions, aliquots of ligand solution were added until a total volume of 100 ml was reached. The values of C_L used were 25, 100 and 200 mM Ph_3P, 30 and 500 mM Ph_3As and 500 mM Ph_3Sb. If the ligand concentration in the calorimeter was to be further increased, a volume of 20 ml was withdrawn and the titration continued. Heats of dilution for silver(I) and the ligands were determined. These were so small, however, that no corrections were necessary. The enthalpy changes were calculated by means of the least-squares program KALORI.[12]

Results

The overall stability constants β_j obtained from the potentiometric measurements are listed in Table 1. Three silver(I)-triphenylphosphine complexes were formed even at fairly low concentrations of free ligand. Within the concentration range of free ligand available for triphenylarsine and triphenylstibine in pyridine, ≤ 160 mM, only the first complex was formed. No complex formation between silver(I) and Ph_3N or Ph_3Bi could be detected, even at a free ligand concentration of 300 mM. The complex formation func-

tions are shown in Fig. 1, and the distribution of the silver(I) triphenylphosphine complexes in Fig. 2. The stepwise stability constants, K_j, are summarized in Table 3.

The overall enthalpy changes, $\Delta H_{\beta j}$, obtained from the calorimetric measurements are listed in Table 2. The quantity found directly from these measurements, the heat evolved per mol silver(I), Δh_v, is plotted as a function of the ligand number $\bar{n}$ in Fig. 3. The thermodynamic functions ΔG_j°, ΔH_j° and ΔS_j° were calculated and are listed in Table 3. Under certain conditions, the overall stability constants β_j can be determined from the calorimetric measurements though in most cases this means considerably larger errors than if the constants are determined potentiometrically in a separate measurement.[14,15] Thus, in the present case, the values of β_j found calorimetrically were compatible with the potentiometrically determined ones, but the random errors were about 10 times larger.

Discussion

As expected, the stabilities of the complexes followed the same sequence in pyridine as in DMSO (Table 3). They are considerably weaker in pyridine, however, due to the stronger solvation of the silver(I) ion in this solvent. The donor properties of Ph_3As and Ph_3Sb are only slightly stronger than those of pyridine and obviously not strong enough to form complexes higher than the first one. Ph_3N and Ph_3Bi are evidently too weak donors to substitute a pyridine in the tetrakispyridinesilver(I) solvate existing in the noncomplexing solutions.[16]

Table 2. Overall enthalpy changes ($\Delta H_{\beta j}^0$/kJ mol^{-1}) for the complex formation between silver(I) and Ph_3X ligands in pyridine solution at 25 °C. Ionic medium 0.1 M Et_4NClO_4. The limits of error refer to three standard deviations; NP denotes the number of observations (aliquots added) for each system.

X→	P	As	Sb
$\Delta H_{\beta 1}^0$	−(34.4±0.5)	−(15.6±0.6)	−(11.6±0.4)
$\Delta H_{\beta 2}^0$	−(56.4±1.2)		
$\Delta H_{\beta 3}^0$	−(72.2±3.3)		
NP	194	120	129

597

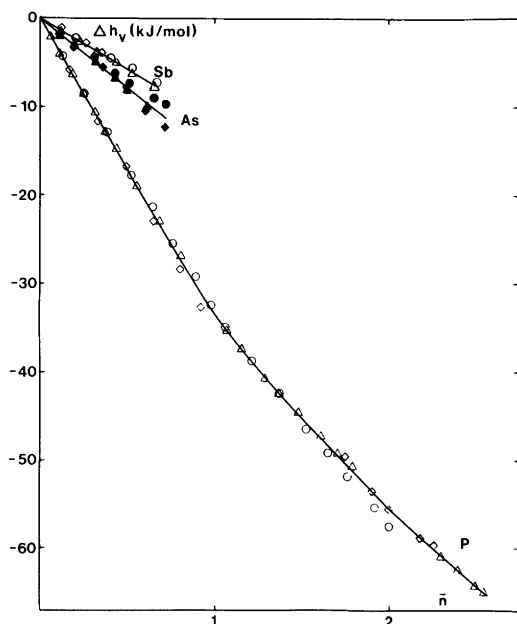*Fig. 3.* Total molar enthalpy changes Δh_v as a function of the ligand number $\bar{n}$ for the silver(I)-Ph_3X (X = P, As and Sb) systems in pyridine. The points refer to the values actually measured with initial values of C_M = 6,10 and 20 mM Ag^+ (squares, circles and triangles, respectively). The full-drawn curves have been calculated from the values of β_j and $\Delta H_{\beta_j}^0$ determined (Tables 1 and 2). Medium 0.1 M Et_4NClO_4; 25 °C.

The enthalpy changes are all negative in pyridine (Table 3). All entropy terms are also negative. All the complexes are thus enthalpy-stabilized. The formation reactions are much less exothermic than in DMSO, however, as expected from the difference in the desolvation enthalpies quoted above. The difference in $\Delta H_{\beta_3}^0$ between the silver(I) phosphine system in pyridine and DMSO was 53.7 kJ mol^{-1} (Table 3). This value is quite close to the difference of 55 kJ mol^{-1} between the desolvation enthalpies of silver(I) in

Table 3. Equilibrium constants, K_j/M^{-1}, and thermodynamic functions ΔG_j^o, $\Delta H_j^o/kJ$ mol^{-1}; $\Delta S_j^o/J$ mol^{-1} K^{-1}, for the stepwise formation of complexes between silver(I) and Ph_3X in pyridine and DMSO. In water, the ligands $(m-C_6H_4SO_3)Ph_2P^-$ and $(m-C_6H_4SO_3)_3As^{3-}$ are employed. Temperature 25 °C.

| X = | Pyridine, 0.1 M Et_4NClO_4 | | | DMSO, 0.1 M NH_4ClO_4[a] | | | | | Water | |
	P	As	Sb	N	P	As	Sb	Bi	P[b]	As[c]
$\log K_1$	4.31	1.44	1.09	0.19	6.58	3.56	3.16	0.80	8.15	4.96
$\log K_2$	2.14				4.15	1.81	1.45		5.95	1.7
$\log K_3$	1.14				2.44	1.31	1.45		5.40	
K_1/K_2	148				269	56	51		160	
K_2/K_3	10.2				52	3.2	1.0		3.5	
$-\Delta G_1^0$	24.6	8.2	6.2	1.1	37.6	20.3	18.1	4.6	46.5	28.3
$-\Delta G_2^0$	12.2				23.7	10.4	8.3		34.0	10
$-\Delta G_3^0$	6.5				13.9	7.5	8.3		30.8	
$-\Delta H_1^0$	34.4	15.6	11.6	1	51.8	34.5	32.1		71	31
$-\Delta H_2^0$	22.0				38.1	19.4	8.6		60	17
$-\Delta H_3^0$	16.1				36.3	44.5	57.1		64	
ΔS_1^0	−33	−25	−18	0	−48	−48	−47		−80	−10
ΔS_2^0	−33				−48	−30	−1		−91	−22
ΔS_3^0	−32				−75	−124	−164		−111	
$-\Delta G_{\beta_3}^0$	43.3				72.2	38.1	34.6		111.3	
$-\Delta H_{\beta_3}^0$	72.5				126.2	98.4	97.5		195	
ΔS_β^o	−98				−171	−202	−212		−282	

[a]Ref. 2. [b]Refs. 7,17; I=0.1 M $NaClO_4$. [c]Ref. 17; I=0.5 M $NaClO_4$.

the two solvents. As might be presumed, this term thus accounts for most of the enthalpy difference actually observed. It might be further inferred that the desolvation of silver(I) is almost complete in both solvents with the formation of the third phosphine complex.

The decrease in $-\Delta H_j^\circ$ for each consecutive step in the phosphine system (Table 3) certainly reflects a successive weakening of the Ag-P bond as more ligands are coordinated, while the decrease in $-\Delta H_1^\circ$ in the order P > As > Sb is due to the lowering of the strength of the Ag-X bonds in that order. Also, as might be expected, the en-

tropy terms are less unfavourable in pyridine than in DMSO (Table 3 and Fig. 4). In the phosphine system, the entropy changes are, moreover, about the same for the three steps. This means that the complexes are presumably formed by the substitution of a ligand for a solvent molecule; any switch of coordination accompanied by an extensive desolvation evidently does not take place (cf. e.g. Ref. 9). Also, the third complex is formed without any special steric hindrance, very much in contrast to what has been found for DMSO (cf. Fig. 4).

In water, where the early stability measurements involving sulfonated ligands were later completed with calorimetric determinations of the heats of reaction,[17] the enthalpy changes for the phosphine complexes are even more favourable than in DMSO (Table 3). This is evidently due to the still weaker solvation of the silver ion in aqueous solution,[8] $\Delta H_{sv}^\circ = -488$ kJ mol^{-1}. The entropy changes are, on the other hand, even more unfavourable in water, as expected for a more well-structured solvent.[8,10] The net result is, however, that the phosphine complexes are more stable in aqueous solution than in any of the softer solvents.

The arsine complexes behave differently, having about the same enthalpy changes in water and DMSO, and less negative entropy changes in water (Table 3). It should be remembered, however, that in this case, the data determined in aqueous solution refer to a ligand of high charge: 3−. The neutralization taking place on complex formation should tend to make the entropy changes less unfavourable than for the uncharged arsine employed in DMSO. Further, the arsine measurements in aqueous solution refer to a much higher ionic strength (0.5 M) than that used in the other measurements (0.1 M), which obviously makes a direct comparison difficult.

To sum up, the variation in the complex-formation thermodynamics of the systems studied between the solvents employed very faithfully reflects the differences in donor properties and structural order between these solvents.
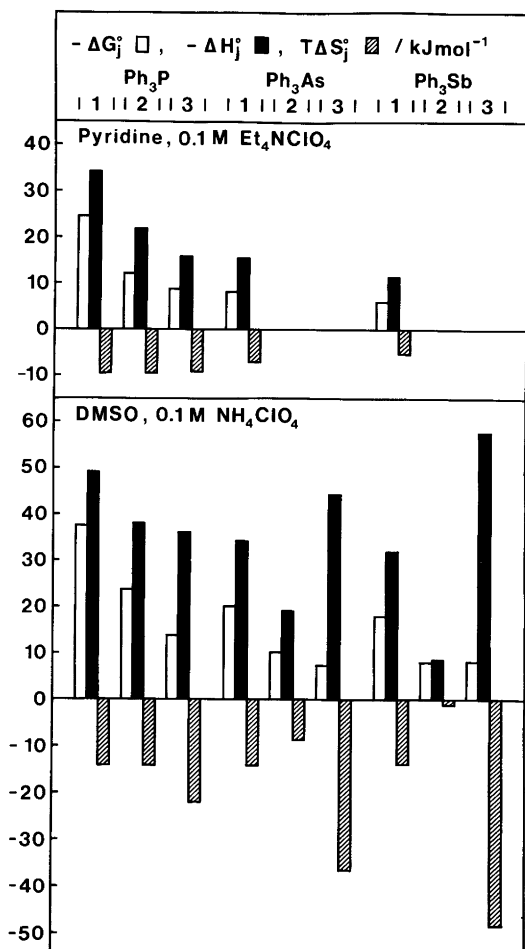
Fig. 4. Changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the Ag$^+$−Ph$_3$X (X = P, As and Sb) systems in pyridine and DMSO, at 25 °C.

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