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

I. Silver Complexes

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The thermodynamics of the complex formation between silver(I) and the triphenyl compounds Ph_3X ($X=N$, P, As, Sb or Bi) has been studied in dimethyl sulfoxide (DMSO) at 25 °C. The ionic strength of the solutions was maintained at 0.1 with ammonium perchlorate. The stability constants have been determined potentiometrically, using silver electrodes, and the enthalpy changes calorimetrically.

The stability constants found confirm quantitatively the affinity sequence $N \ll P > As > Sb > Bi$ previously inferred from largely qualitative observations on complex formation between soft acceptors and ligands coordinating *via* group V donor atoms. In the phosphine, arsine and stibine systems coordination of up to three ligands is found in solution, the mono- and tris(ligand) complexes predominating strongly over their neighbours. Coordination of a fourth ligand cannot be detected in solution, although solids of composition $[Ag(Ph_3X)_4]ClO_4$ ($X=P$, As or Sb) precipitate at high ligand concentrations. In the case of the amine and bismuthine systems, the complex formation is so weak that only the mono-complex is detected.

All the strong complexes are heavily enthalpy stabilized whereas the entropy contributions counteract the complex formation, generally quite strongly. The enthalpy and entropy changes for the consecutive steps in the various systems vary in a most interesting manner which apparently reflects a gradual change in the character of the donor to acceptor bond.

As is evident from numerous preparative studies,[1] ligands coordinating *via* phosphorus, arsenic and antimony behave as typically soft donors in that they form strong complexes with typically soft acceptors while their affinities for other acceptors are quite weak. Quantitative studies of equilibria involving such ligands are rare, however, for several reasons. Unlike ammonia and the simple amines, the homologous compounds of phosphorus, arsenic and antimony are extremely sensitive to oxidation. They are also increasingly thermally unstable in the order mentioned [2] and are moreover often highly toxic. In these respects, however, the trialkyl and triaryl derivatives have the least unfavourable properties, the triphenyl compounds in particular being easy to handle. At ordinary temperatures the latter are stable non-volatile solids. This is also the case for triphenyl bismuthine, so that this donor can also be included in the investigation. Unfortunately the triphenyl compounds are essentially insoluble in water, a problem which has been a severe hindrance to quantitative equilibrium studies since the techniques used for such investigations have been developed primarily for aqueous media. Early approaches to this problem involved modifying the ligands so as to render them sufficiently soluble in water. In the case of the triphenyl compounds this can be achieved by sulfonation.[3] A related method which has been applied to triethylphosphine is the replacement of one alkyl group with an alcoholic substituent.[4] Interesting results have indeed been obtained by this type of approach [3–8] but modification of the ligands in this manner is a time-consuming and rather troublesome procedure which moreover does not lead to analogous compounds for all the various donor atoms. Still more unsatisfactory is the fact that no such modification has ever been achieved for antimony or bismuth. In addition, the solubilities attained are often too low for the calorimetric measurements which are necessary for a complete determination of the thermodynamics of the complex formation.

The other possible approach to this problem which has been adopted in the present investigation is to change the solvent to meet the needs of the systems of complexes to be investigated. The ligands to be used here are not soluble in water because the strong hydrogen bonding between the water molecules virtually prevents any solvation of the ligands. In a less well-structured solvent, on the other hand, where the specific interactions between the solvent molecules are much weaker, the formation of ligand solvates becomes possible. Many ligands which are not soluble in water will therefore be soluble in such solvents. A really useful solvent has, however, to possess a number of additional important properties: It must be a good solvent not only for the ligands but also for the metal ion acceptors to be investigated and for the complexes formed. Suitable inert salts must also be soluble in order to provide the necessary ionic medium. Generally, its dielectric constant ε must not be too low since otherwise the purely electrostatic interactions might overshadow the specific acceptor-donor interactions which are of prime interest; for the present ligands, which are uncharged and have low dipole moments, this condition should not be very critical, however. Finally the solvent should have a suitable liquid range and be reasonably easy to handle.

All these conditions are fulfilled by dimethyl sulfoxide, DMSO. In this aprotic solvent, in which there is no hydrogen bonding, the triphenyl compounds Ph_3X ($X = N$, P, As Sb or Bi) are all soluble. The reactions of a complete series of analogous ligands coordinating *via* group V donor atoms can thus be compared. Furthermore, all the metal ions which have been investigated so far are adequately solvated by DMSO. The solvation is in fact without exception considerably stronger than in water.[9-12] This also applies [10,11] to Ag^+ which has been selected as the first acceptor to be studied in the present series of investigations. The silver complexes formed by the present ligands are soluble in DMSO except for the fact that the species $Ag(Ph_3X)_4^+$ ($X = P$, As or Sb), which are formed at high ligand concentrations, are all precipitated as perchlorates in the medium used. These perchlorates are also precipitated from ethanol and diethyl ether media and they appear in fact to have low solubility in most solvents.[13,14] Other non-complexing anions, *e.g.* BF_4^-, NO_3^- and BrO_3^-, also give salts of low solubility with these cations.[13,14] The physical properties of DMSO are favourable. Its melting point is 18.55 °C and it is thus suitable for measurements at the standard temperature of 25 °C at which it has a vapour pressure of only 0.599 Torr.[15] The boiling point of DMSO is 189 °C at 760 Torr and the dielectric constant ε is quite high, *viz.* 46.4 at 25 °C.[16]

The stability of a complex is the net result of many different interactions between the various species involved. These are reflected in changes in both the enthalpy and the entropy of the system when the complex is formed. In order to elucidate as far as possible the various factors influencing the reaction it is necessary to find out how the changes in enthalpy and entropy contribute to the net free energy change.[12,17,18] This is achieved by determination of both the stability constant, K_j, and the heat of formation, ΔH_j°, for each consecutive step, thereby permitting the calculation of all the thermodynamic functions according to eqn. (1).

$$-RT \ln K_j = \Delta G_j^\circ = \Delta H_j^\circ - T\Delta S_j^\circ \qquad (1)$$

For the present systems, K_j and ΔH_j° have been determined in separate measurements. The values of K_j have been found potentiometrically, using silver electrodes, whereas the values of ΔH_j° have been measured calorimetrically. The results obtained by the use of these two separate methods are generally both more accurate and more precise than those obtained from measurements of the variation of K_j with temperature.[19-21] Provided that certain conditions are fulfilled it is possible in principle to determine both K_j and ΔH_j° from calorimetric measurements.[22,23] For simple systems, the precision of such determinations is generally good.[24,25] For more complex systems, however, the thermodynamic conditions have to be rather exceptional if reasonable precision is to be achieved.[26–28] The present systems are not well suited to such simultaneous determination of K_j and ΔH_j° and consequently only the results of the separate determinations are tabulated and discussed here.

The ionic strength in the present measurements was maintained at 0.1 using ammonium perchlorate. This medium has been used in other investigations of metal complex equilibria in DMSO.[12] The use of media of the same ionic strength containing the related tetraethylammonium perchlorate is also common.[12] A perchlorate medium of ionic strength much higher than 0.1 was not suitable in the present case since it tends to bring about the precipitation of the rather insoluble $Ag(Ph_3X)_4ClO_4$ species at an early stage of the complex formation.

EXPERIMENTAL

Chemicals. The silver and ammonium perchlorates, triphenylamine, -phosphine, -arsine, -stibine and -bismuthine were commercial products of analytical grade and were used without further purification. The ammonium perchlorate was dried at 110 °C and the other reagents were dried at room temperature *in vacuo* over 4 Å molecular sieves.

The DMSO was purified by distillation under reduced pressure over calcium hydride and the distillate was stored in a dark bottle over molecular sieves. This solution contained less than 0.05 % water as determined by a modified Karl Fischer titration method.[29]

Solutions. The silver perchlorate solutions were prepared from anhydrous $AgClO_4$ and DMSO and the ionic strength adjusted to 0.1 M with anhydrous ammonium perchlorate. The exact silver content was determined by potentiometric titration with chloride. The solutions were stable for several weeks.

The ligand solutions were prepared by weighing an exact amount of the ligand and adding ammonium perchlorate (to give ionic strength 0.1 M) and anhydrous DMSO. These solutions were prepared daily since the ligands are slowly oxidized by DMSO. The stability of the Ph_3X ligands in this medium decreases in the sequence P, As, Sb and Bi. A solution of Ph_3Bi was only stable for about one hour but even the Ph_3P solutions deteriorated markedly in a few days, contrary to what has been reported in the literature.[30]

Unfortunately, molecular sieves could not be added to minimise water contamination of these solutions since they caused concentration changes as a result of adsorption. Consequently the water concentration was somewhat higher than in the pure solvent, typically 0.3 %.

Potentiometric measurements. The silver electrodes were prepared as follows: platinum wire electrodes were immersed in an aqueous suspension of freshly prepared hydrated silver oxide. The electrodes were then placed in an electric oven and heated gradually to ≃400 °C over a period of 2 h. They were maintained at that temperature for 6 h and then cooled slowly to room temperature.[31]

Electrode vessels of the Ingold type were used for the electrode solutions: one for the reaction vessel and two for the reference electrodes. The solutions were maintained at a temperature of 25.0 ± 0.1 °C by the flow of water from a pumping thermostat through outer jackets around the vessels. Potential measurements were made with an Eldorado 1820 potentiometer.

The manipulations and measurements were performed in a dry box containing molecular sieves (4 Å) to remove traces of water. Dry, oxygen free nitrogen saturated with DMSO vapour, was bubbled through the solutions in the electrode vessels in order to exclude moisture and prevent oxidation. The gas stream also provided efficient stirring in the vessels.

Procedure. The reaction vessel initially contained V cm³ silver perchlorate solution of concentration C_M'. The reference electrode vessel also contained this solution. To the reaction vessel were added portions of ligand solution, of concentration C_L. The emf measured is associated both with the complex formation and the dilution of the silver solution in the reaction vessel.[3] When v cm³ of ligand solution have been added the total silver concentration has decreased to $C_M = C_M' V/(V+v)$. If the concentration of free silver ions is denoted by $[M]$, the emf E in this point may be expressed as eqn. (2), where the first term

$$E = \frac{RT}{F}\log_e\frac{C_M}{[M]} + \frac{RT}{F}\log_e\frac{V+v}{v} \tag{2}$$

is associated with the complex formation and the second with the dilution. In the phosphine, amine and stibine systems, where strong complexes are formed, the dilution term is small relative to the term for complex formation.

Owing to the limited stability of the triphenylbismuthine ligand in DMSO measurements on this system were made using fresh solutions for each point instead of the titration technique.

Two electrodes in the reaction solution and two reference electrodes were used. When the same potential within 0.1 mV was read between the electrodes pairwise it was taken as an indication that equilibrium had been reached. This was normally achieved within 15 min.

Titration series were performed for 3 or 4 values of C_M' and each series was repeated at least twice. The reproducibility was generally better than 0.2 mV except at the highest values of $\bar{n}$ where it was $\simeq 1$ mV.

The calculation of the stability constants was performed using a least squares computer program described previously.[32]

Calorimetric measurements. A titration calorimeter of the isothermal jacket type described by Ots[33] was employed. To allow work with DMSO solutions, the experimental arrangement was modified so that all parts in contact with the solvent were made of gold, glass, teflon or silicone rubber. The inner gold vessel, which holds 100 cm^3, was inserted in an outer can completely immersed in an LKB precision thermostatted water bath, maintaining the temperature at 25.000 ± 0.001 °C. For shorter periods, however, the temperature normally remained constant within $\pm 2 \times 10^{-4}$ °C. The room temperature was maintained at 25.0 ± 0.1 °C.

Procedure. The calorimetric titrations were performed as described by Ahrland and Björk.[27] For each system, 5 – 10 titration series were performed. In most of these, ligand solutions T with $C_L = 100$ mM were titrated into silver ion solutions S with C_M' varying from $\simeq 2$ mM to $\simeq 10$ mM. In other series silver ion solutions T of $\simeq 40$ mM were titrated into ligand solutions S of $\simeq 25$ mM or $\simeq 100$ mM.

The experimental heat changes were corrected for heats of dilution which were determined separately.[27] The latter were quite small for both the silver perchlorate and the ligand solutions.

The least squares program "KALORI"[34,35] was employed for the enthalpy and entropy calculations.

RESULTS

The quantities calculated directly from the potentiometric and calorimetric measurements are β_j and $\Delta H_{\beta j}°$, respectively, referring to the overall reactions $Ag^+ + jL \rightleftharpoons AgL_j^+$. The values found are listed in Table 1, with errors corresponding to three times the standard deviations as given by the computer. The precision is much better for β_j than for $\Delta H_j°$. Within the three systems where extensive complex formation takes place, the magnitude of the errors generally increases in the order $P < As < Sb$. This may reflect the decreasing stability of the ligand in solution. In all cases, however, the values obtained permit the calculation of reasonably precise values of the stability constants and the thermodynamic functions referring to the consecutive steps. These quantities are listed in Table 2. The full experimental data can be obtained from the authors upon request. Previously studied silver(I) systems involving modified phosphine or arsine ligands in aqueous solution[3,4] are also included in the table for comparison purposes.

DISCUSSION

Stabilities of complexes examined. The affinity of the soft acceptor Ag+ for the present group V donors generally follows the sequence $N \ll > P > As > Sb > Bi$ (Table 2). This indeed confirms the stability sequence postulated as early as 1958 on the basis of the rather few and largely qualitative data then available.[36] The evidence in the case of Sb was at that time very sparse, and for Bi no complexes containing Bi as donor atom had in fact ever been prepared. Since then further preparative work has been done,[2] including the preparation[14] of the perchlorate of the silver(I) bismuthine complex $AgPh_3Bi^+$. This work has certainly strengthened

Table 1. Overall stability constants (β_j/M^{-j}) and enthalpy changes ($\Delta H_{\beta j}°$/kJ mol^{-1}) calculated for the complexes formed between silver(I) and ligands Ph_3X in DMSO. The errors correspond to three standard deviations. Ionic medium 0.1 M NH_4ClO_4; 25 °C.

X→	N	P	As	Sb	Bi
log β_1	0.19(14)	6.58(2)	3.56(1)	3.16(2)	0.80(8)
log β_2		10.73(3)	5.37(3)	4.62(11)	
log β_3		13.17(2)	6.68(6)	6.06(12)	
$-\Delta H_{\beta_1}°$	1(1)	51.8(7)	34.1(8)	32.1(10)	0.5(5)
$-\Delta H_{\beta_2}°$		89.9(10)	52.4(23)	40.7(45)	
$-\Delta H_{\beta_3}°$		126.2(14)	98.8(37)	97.8(35)	

Table 2. Equilibrium constants (K_j/M^{-1}) and thermodynamics for the stepwise formation of complexes between silver(I) and ligands coordinating *via* N-group donors in DMSO and in water, at 25 °C (C (Dop 22 °C). $\Delta G_j°$, $\Delta H_j°$/kJ mol^{-1}; $\Delta S_j°$/JK^{-1} mol^{-1}.

	DMSO; ligands Ph_3X; 0.1 M NH_4ClO_4					Water		
X→	N	P	As	Sb	Bi	Dpm[a]	Dop[b]	Asm[a]
log K_1	0.19	6.58	3.56	3.16	0.80	8.15	11.83	5.36
log K_2		4.15	1.81	1.45		5.95	9.02	
log K_3		2.44	1.31	1.45		5.40	4.86	
K_1/K_2		269	56	51		160	650	
K_2/K_3		52	3.2	1.0		3.5	14500	
$-\Delta G_1°$	1.1	37.6	20.3	18.1	4.6	46.5	66.8	30.6
$-\Delta G_2°$		23.7	10.4	8.3		34.0	51.0	
$-\Delta G_3°$		13.9	7.5	8.3		30.8	27.4	
$-\Delta H_1°$	1	51.8	34.5	32.1	0.5		80.8	
$-\Delta H_2°$		38.1	19.4	8.6			69.0	
$-\Delta H_3°$		36.3	44.5	57.1			38.1	
$-\Delta S_1°$	0	48	48	47	-14		47	
$-\Delta S_2°$		48	30	1			60	
$-\Delta S_3°$		75	124	164			36	
$-\Delta G_{\beta_3}°$		75.2	38.1	34.6		111.3	145.2	
$-\Delta H_{\beta_3}°$		126.2	98.4	97.8			187.9	
$-\Delta S_{\beta_3}°$		171	202	212			143	

[a] Ref. 3; Dpm = $Ph_2PC_6H_4SO_3^-$(*m*-); 0.1 M $NaClO_4$; Asm = $As(C_6H_4SO_3^-)_3^{3-}$(*m*-); 0.2 M $NaClO_4$. [b] Ref. 4; Dop = $Et_2PCH_2CH_2OH$; 1 M KNO_3.

the view that the above affinity sequence is valid generally for soft acceptors but the present study seems to provide the first quantitative confirmation of these observations.

This study shows, on the other hand, that the affinity differences between two consecutive group V donors with a given acceptor vary greatly as one descends in group V. The phosphine complexes are far more stable than the arsine complexes, while the latter do not differ very much in stability from the stibine complexes. An exception to the general sequence is the fact that the value of K_3 is somewhat higher for the stibine than for the arsine system. Between the stibine and the bismuthine complex the difference in stability is again very large. The affinity of Ph_3Bi for Ag^+ is, like that of Ph_3N, so low that only the mono(ligand) complex is formed even at the highest ligand concentrations obtainable.

A very interesting feature displayed by all the three systems in which the complex formation proceeds beyond the first step is that the mono- and tris(ligand) complexes are particularly stable relative to their neighbours. The bis(ligand) complex, which is so prominent in most silver(I) systems both in protic and aprotic solvents,[12,37] plays a rather subordinate part here. No appreciable amounts of the tetrakis(ligand) complexes are formed in any of the systems within the range of ligand concentrations used.

The above features are clearly illustrated by the complex formation curves drawn in Fig. 1. These functions give the ligand number, $\bar{n}$, defined as the average number of ligands per acceptor ion, as a function of the free ligand concentration, [L]. The wide range of existence of the mono-complex is evident from the marked

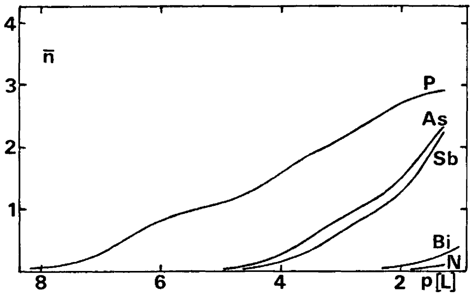

Fig. 1. The complex formation curves of the systems $Ag^+ - Ph_3X$, X = N, P, As, Sb, Bi, in DMSO. Medium 0.1 M NH_4ClO_4; 25 °C.

inflexions at $\bar{n}=1$ for the three systems in which strong complexes are formed. Only for the phosphine system can an inflexion at all be discerned at $\bar{n}=2$. For this system, $\bar{n}$ seems to approach a limiting value of 3 without any visible tendency to exceed this value.

These features are also reflected in the values of the ratios K_j/K_{j+1} (Table 2). If the complex formation were statistical, the ratios between the consecutive stability constants would be (if tetrahedral coordination ($N=4$) is assumed):[38] $K_1/K_2=8/3$; $K_2/K_3=9/4$ and $K_3/K_4=8/3$. For systems such as the present ones, for which specific interactions are clearly prominent, the actual ratios are generally far from the statistical ones. The values of K_1/K_2 are indeed much larger, and also much larger than K_2/K_3. In this respect, as in others, the phosphine system stands out from the arsine and stibine systems in having much larger values of both the ratios mentioned. Again, the differences between the arsine and stibine systems seem slight. Since no values of K_4 can be determined the ratios K_3/K_4 cannot be calculated. On the reasonable assumption, however, that in the phosphine system a concentration of the tetrakis-complex amounting to $\simeq 10\ \%$ of the total would at least be detected, the value of K_3/K_4 must be $\gtrsim 270$, *i.e.* at least as large as K_1/K_2. For the amine and stibine systems, for which $\bar{n}$ reaches only 2.4 and 2.3, respectively, an analogous estimate is of little significance.

As already mentioned, perchlorates of composition $Ag(Ph_3X)_4ClO_4$ ($X=P$, As or Sb) are precipitated on addition of excess ligand, the arsine and stibine species being precipitated rather more easily than the phosphine compound. Preliminary structural investigations of the precipitates show that they are all isostructural,[39] the ligands being tetrahedrally coordinated to Ag^+. This does not mean, however, that the ligands are also tetrahedrally disposed in the preceding complexes. The marked stop at $\bar{n}=3$ found in the phosphine system might well be indicative of a change of coordination geometry accompanying the formation of the tetrakis complex. A trigonal planar configuration for the complex $(Tol_3P)_3Ag^+$ (Tol = *p*-tolyl) has in fact been inferred[40] from NMR measurements on dichloromethane solutions. Moreover, in solid phosphine halido complexes of copper(I)[41] and gold(I),[42] *viz.* $(Ph_3P)_2CuBr$ and $(Ph_3P)_2AuCl$ (both of which crystallize with 1/2 C_6H_6), this configuration has been unequivocally demonstrated by full X-ray structure determinations. The same is true also for the complex $(Ph_3P)_3Pt$ formed by the d^{10} acceptor platinum(0).[43] It is therefore probable that the complex $(Ph_3P)_3Ag^+$ in DMSO solution has the same configuration. The same may also apply to the corresponding arsine and stibine complexes, although in the absence of structural data for analogous systems of this type this prediction is less well-founded.

The silver(I) complexes formed by the ligands Ph_3P and Ph_3As in DMSO are considerably less stable than those formed by the sulfonated phosphine, Dpm, and sulfonated arsine, Asm, in water (see Table 2), in spite of the fact that the sulfonation would be expected to weaken the donor properties of the ligands. This lower stability in DMSO is undoubtedly due mainly to the stronger solvation of Ag^+ in this solvent, reflected in the very negative value of the enthalpy of transfer for Ag^+ between water and DMSO,[11] ΔH_{tr}° (W→DMSO) $= -54$ kJ mol^{-1}. Owing to the stronger donating properties of the aliphatic phosphine Dop, the silver(I) complex formed by this ligand in aqueous solution are even stronger than those formed by the aromatic Dpm.

As in the present system, the mono- and tris(ligand) complexes predominate in the sulfonated aromatic phosphine system in aqueous solution. No tetrakis-complex is detected within the range of [L] available, which implies that $K_3/K_4 \gtrsim 4000$. For the sulfonated arsine Asm, the mono-complex has an even wider range of existence, no further complex formation being detected. This indicates that $K_1/K_2 \gtrsim 20\,000$. The aliphatic phosphine, Dop, behaves similarly in so far as both the mono- and the tris-complex have unusually wide ranges of existence with a ratio $K_3/K_4 \gtrsim 4000$. In this latter system, however, the bis(ligand) complex is predominant, and the qualitative picture is thus reminiscent of that for most other silver(I) systems.

Thermodynamic functions. The formation of phosphine, arsine and stibine complexes of silver(I) is strongly exothermic, both in DMSO and in aqueous solution (Table 2). This is to be expected in view of the strong covalency of the

Ag − X bond (X = P, As, Sb) and the weak solvation, especially of the ligands. The weak solvation also results in unfavourable entropy contributions, however, so that the stabilities of the complexes are lower than would be expected *per se* in view of the very considerable enthalpy decreases. The value of $-\Delta H_{\beta_3}{}^\circ$ referring to the formation of the highest complex actually found in the solutions, decreases in the order P > As > Sb, reflecting decreasing strength of the Ag − X bond, while the value of $-\Delta S_{\beta_3}{}^\circ$ increases in the same order, reflecting the increasing steric restrictions on the ligands as they become more bulky. For both $\Delta H_{\beta_3}{}^\circ$ and $\Delta S_{\beta_3}{}^\circ$, however, the really significant jump is between P and As, while the differences between the As and Sb systems are quite small, especially in the case of $\Delta H_{\beta_3}{}^\circ$.

Whereas the formation of the highest complexes from the solvated Ag^+ ion and Ph_3X are characterized by thermodynamic functions which can be fairly easily interpreted in terms of bond strength, solvation and conformation, this is not the case for the individual complex formation steps. For these, a very intricate but also very consistent pattern is found (Table 2). Most interesting is the observation that the very similar stabilities of the triphenylarsine and -stibine complexes in DMSO are the net result of very different enthalpy and entropy contributions which largely compensate each other. Moreover, for both these ligands, the second step is characterized by enthalpy contributions which are less favourable and by entropy terms which are more favourable than those for the neighbouring steps. This trait is particularly apparent for the stibine system. A gradual change in the covalent character of the Ag − X bond with the donor atom X is undoubtedly one of the main causes of the variations observed. At present, however, it seems wise to postpone any elaborate interpretation until experimental data have also been gathered for other acceptors which are capable of coordinating these donors.

The weak complex formation between silver(I) and the ligands Ph_3N and Ph_3Bi is characterized by low values of both $\Delta H_1{}^\circ$ and $\Delta S_1{}^\circ$ (Table 2). Evidently, these reactions involve only very modest changes in bond strength and structural ordering.

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REFERENCES

1. McAuliffe, C. A., Ed., *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*, Macmillan, London and Basingstoke 1973.
2. Doak, G. O. and Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York 1970.
3. Ahrland, S., Chatt, J., Davies, N. R. and Williams, A. A. *J. Chem. Soc.* (1958) 276.
4. Meier, M. *Phosphinokomplexe von Metallen*, Diss., Nr. 3988, Eidgenössische Technische Hochschule, Zürich 1967.
5. Salvesen, B. and Bjerrum, J. *Acta Chem. Scand. 16* (1962) 735.
6. George, R. and Bjerrum, J. *Acta Chem. Scand. 22* (1968) 497.
7. Hawkins, C. J., Mønsted, O. and Bjerrum, J. *Acta Chem. Scand. 24* (1970) 1059.
8. Chang, J. C. and Bjerrum, J. *Acta Chem. Scand. 26* (1972) 815.
9. Krishnan, C. V. and Friedman, H. L. *J. Phys. Chem. 73* (1969) 3934.
10. Le Démézet, M. *Bull. Soc. Chim. Fr.* (1970) 4550.
11. Cox, B. G. and Parker, A. J. *J. Am. Chem. Soc. 95* (1973) 402.
12. Ahrland, S. In Lagowski, J. J., Ed., *The Chemistry of Non-aqueous Solvents*, Academic, London and New York, Vol. 5, Chapter 1. *In press.*
13. Cotton, F. A. and Goodgame, D. M. L. *J. Chem. Soc.* (1960) 5267.
14. Nuttall, R. H., Roberts, E. R. and Sharp, D. W. A. *J. Chem. Soc.* (1962) 2854.
15. Lam, S. Y. and Benoit, R. L. *Can. J. Chem. 52* (1974) 718
16. Martin, D. and Hauthal, H. G. *Dimethyl Sulphoxide*, van Nostrand Reinhold, Wokingham, Berks. 1975.
17. Ahrland, S. *Struct. Bonding (Berlin) 15* (1973) 167.
18. Schwarzenbach, G. *Pure Appl. Chem. 24* (1970) 307.
19. McAuley, A. and Nancollas, G. *J. Chem. Soc.* (1963) 989.

20. Carvalho, R. G. and Choppin, G. R. *J. Inorg. Nucl. Chem. 29* (1967) 737.
21. Choppin, G. R. and Schneider, J. K. *J. Inorg. Nucl. Chem. 32* (1970) 3283.
22. Christensen, J. J., Ruckman, J., Eatough, D. J. and Izatt, R. M. *Thermochim. Acta 3* (1972) 203.
23. Eatough, D. J., Christensen, J. J. and Izatt, R. M. *Thermochim. Acta 3* (1972) 219.
24. Eatough, D. J., Izatt, R. M. and Christensen, J. J. *Thermochim. Acta 3* (1972) 233.
25. Ahrland, S. and Kullberg, L. *Acta Chem. Scand. 25* (1971) 3677.
26. Ahrland, S., Avsar, E. and Kullberg, L. *Acta Chem. Scand. A 28* (1974) 855.
27. Ahrland, S. and Björk, N.-O. *Acta Chem. Scand. A 30* (1976) 257.
28. Ahrland, S., Björk, N.-O. and Portanova, R. *Acta Chem. Scand. A 30* (1976) 270.
29. Karlsson, R. and Karrman, K. J. *Talanta 18* (1971) 459.
30. Amonoo-Neizer, E. H., Ray, S. K., Shaw, R. A. and Smith, B. C. *J. Chem. Soc.* (1965) 4296.
31. Lewis, G. N. *J. Am. Chem. Soc. 28* (1906) 154.
32. Trinderup, P. *Acta Chem. Scand. A 30* (1976) 47.
33. Ots, H. *Acta Chem. Scand. 26* (1972) 3810.
34. Karlsson, R. and Kullberg, L. *Chem. Scr. 9* (1976) 54.
35. Kullberg, L. *Acta Chem. Scand. A 28* (1974) 829.
36. Ahrland, S., Chatt, J. and Davies, N. R. *Q. Rev. Chem. Soc. 12* (1958) 265.
37. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-ion Complexes*, Spec. Publ. Nos. 17 and 25, Chemical Society, London 1964, 1971.
38. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, Diss., Københavns Universitet, Copenhagen 1940.
39. Cassel, A. *Personal communication.*
40. Muetterties, E. L. and Alegranti, C. W. *J. Am. Chem. Soc. 92* (1970) 4114.
41. Davis, P. H., Belford, R. L. and Paul, I. C. *Inorg. Chem. 12* (1973) 213.
42. Baenziger, N. C., Dittemore, K. M. and Doyle, J. R. *Inorg. Chem. 13* (1974) 805.
43. Albano, V., Bellon, P. L. and Scatturin, V. *Chem. Commun.* (1966) 507.

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