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Thermodynamics of the complex formation between silver(I) and mixed phosphorus–sulfur ligands in dimethyl sulfoxide

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Abstract

The thermodynamics of complex formation between silver(I) and the ligands Ph_2PCH_2SR (R = Me, Ph) and $Ph_2P(CH_2)_2SR$ (R = Et, Me, Ph) has been determined in dimethyl sulfoxide (dmso) at 25 °C and in a medium of ionic strength 0.1 mol dm^{-3} by potentiometric and calorimetric measurements. Within the silver and ligand concentration ranges investigated, three mononuclear complexes have been determined. All the complexes are strongly enthalpy stabilized while the entropy changes are unfavourable. The ligands all behave as monodentate, coordinating the silver ion through the phosphorus atom. The influence of the length of the aliphatic chain between the donor atoms as well as of the nature of R on the stabilities of the complexes formed are discussed.

Introduction

Thermodynamic and spectroscopic studies on the complexation of the monovalent d^{10} acceptor silver(I) with phosphorus donor ligands in dimethyl sulfoxide (dmso) solution showed that the potentially bidentate ligands of the type $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) may form a variety of complexes in which such ligands are bidentate chelating or bidentate bridging in behaviour [1]. The investigation also showed that ligand electronic effects in addition to steric factors determine the coordination behaviour of the phosphine ligands in these complexes as well as the stability and stereochemistry of the complexes formed in solution.

In recent years ligands with dissimilar donor sites have assumed considerable interest and importance in the formation of homogeneous and heterogeneous catalyst systems [2–7]. The ligands included phosphines which also contained nitrogen [2, 3] and oxygen [4] donor sites.

Potentially bidentate ligands containing P and S as donor atoms have not been so extensively investigated as have other mixed donor ligands.

No thermodynamic studies in solution have been previously reported for the complex formation of silver(I) with these ligands. The only thermodynamic data available concern the complexation of silver(I) with simple phosphines in water [8], dimethyl sulfoxide [9], and pyridine [10, 11] and with polyphosphines in dmso [1].

In the present paper we report potentiometric and calorimetric studies of complexation of silver(I) with a series of ligands containing P and S as donor atoms. The ligands investigated are: diphenylphosphino(methylthio)methane and diphenylphosphino(phenylthio)methane, of general formula Ph_2PCH_2SR (R = Me, Ph) and 1-(thiomethyl)-2-(diphenylphosphino)ethane, 1-(thioethyl)-2-(diphenylphosphino)ethane, 1-(thiophenyl)-2-(diphenylphosphino)ethane, of general formula $Ph_2P(CH_2)_2SR$ (R = Me, Et, Ph).

Among the considerations that prompted this investigation was to ascertain whether phosphine and thioether functions are both coordinated to silver(I)

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in solution and compare the thermodynamic data obtained with those reported earlier for analogous silver complexes with P–P bidentate ligands [1].

The stability constants of the complexes have been determined by potentiometry by using the silver electrode, the enthalpies of formation by calorimetry.

As in the previous study [1], this investigation has been performed at 25 °C. The ionic strength of the solutions was adjusted at 0.1 M with tetraethylammonium perchlorate.

Experimental

Chemicals

Silver(I) perchlorate, $AgClO_4 \cdot H_2O$ (Fluka), was dried under vacuum at 50 °C for several days and used as such. Stock solutions of silver(I) perchlorate in dmso were prepared and standardized as previously described [12]. The dmso and tetraethylammonium perchlorate were purified as described elsewhere [12].

The ligands Ph_2PCH_2SPh and $Ph_2P(CH_2)_2SR$ (R = Me, Et, Ph) were prepared according to methods reported in the literature [13] and were doubly recrystallized from CH_2Cl_2–EtOH. The purity of the ligands was checked by elemental analysis and confirmed by measuring their melting points on a Buchi 512 apparatus.

$Ph_2PCH_2SCH_3$ was prepared and purified as described elsewhere [14]. The purity of the obtained colorless oil was checked by $^{31}P\{^1H\}$ NMR.

Dimethyl sulfoxide solutions of the ligands were prepared by dissolving weighted amounts of anhydrous thiophosphines in freshly distilled solvent containing tetraethylammonium perchlorate 0.1 mol dm^{-3} as supporting electrolyte. In order to prevent possible oxidation of the ligands to phosphine oxides, the ligand solutions were prepared afresh after each set of titrations in a glove-box under nitrogen atmosphere. IR and ^{31}P NMR spectra of the ligand solutions revealed that no formation of phosphine oxides occurred within 24 h. Spectroscopic measurements were also performed after each potentiometric and calorimetric titration to ascertain that no phosphine oxide was present.

Potentiometric measurements

The potentiometric data were collected by means of the apparatus described elsewhere [1]. The emfs were measured by means of a PHM 84 Radiometer equipped with a Metrohm EA 282/2 silver electrode and a Metrohm 440 silver electrode as reference. Other details were as reported previously [1]. Data for the calculation of stability constants were obtained by titration of silver(I) solutions with solutions of the ligand concerned. The initial silver(I) concentration, C_M^0, was within the range $2 \leqslant C_M^0 \leqslant 10$ mmol dm^{-3}, the ligand concentration, C_L^0, in the range $50 \leqslant C_L^0 \leqslant 120$ mmol dm^{-3}. Titrations were performed with at least three different initial silver (I) concentrations. Each titration was carried out at least in duplicate. The reproducibility was better than 0.2 mV for low values of C_L/C_M and better than 0.3 mV for higher ones. The electrode couple was periodically checked in solutions containing no coordinating ligands: in the concentration range $10^{-5} \leqslant [Ag^+] \leqslant 10^{-2}$ mol dm^{-3}, the e.m.f. values varied with the metal ion concentration according to Nernst's law. All measurements were carried out at 25.0 ± 0.1 °C.

The computer program Superquad [15] was used for the calculation of the stability constants.

Calorimetric measurements

The enthalpies of complexation of silver(I) by various ligands were determined by using an automated titration calorimeter Tronac Model 450. The calorimetric titrations were performed by adding to a silver(I) solution ($5.00 \leqslant C_M^0 \leqslant 20.00$ mmol dm^{-3}) known volumes of ligand solution. The heats of dilution, determined in separate runs, were negligible in the concentration range of silver(I) and ligands used. All experiments were performed at 25.000 ± 0.001 °C. The least-squares computer program Letagrop Kalle [16] was used for the calculation of the enthalpy changes.

Results

Within the ranges of metal and ligand concentration studied, the best fit of the experimental data, for all the systems investigated, was obtained when only mononuclear complexes were assumed to be present in solution. The general reactions studied in this research were therefore

$$Ag^+ + nL = = AgL_n{}^+$$

where L = thiophosphines and $n = 1$–3.

The stability constants are defined by

$$\beta_n = [AgL_n{}^+]/[Ag^+][L]^n$$

The overall stability constants, as calculated from potentiometric data, are collected in Table 1. The enthalpies of complexation, ΔH_n°, for the above reactions are also collected in Table 1. These values were computed from the experimental data obtained directly from the calorimetric measurements. Observed heat changes are plotted in Fig. 1 as Δh_v, the heat evolved per mol silver(I), as a function of

TABLE 1. Overall stability constants and thermodynamic functions for Ag(I)–thiophosphine systems in dmso at 25 °C and $I=0.1$ mol dm^{-3}. ΔG_n° and ΔH_n° in kJ mol^{-1}; ΔS_n° in J K^{-1} mol^{-1}.
Figures in parentheses correspond to three standard deviations.

		$\log \beta_n$	$-\Delta G_n^\circ$	$-\Delta H_n^\circ$	$-\Delta S_n^\circ$
PPh_3[a]	ML	6.58	37.6	51.8	48
	ML_2	10.73	61.3	89.9	96
	ML_3	13.17	75.2	126.2	171
Ph_2PCH_2SMe	ML	6.57(3)	37.5(2)	48.4(1.5)	37
	ML_2	10.48(4)	59.8(2)	80.0(2.1)	68
	ML_3	12.69(11)	72.4(6)	110(3)	126
Ph_2PCH_2SPh	ML	6.26(5)	35.7(3)	47.4(9)	39
	ML_2	10.21(6)	58.3(3)	82.3(1.2)	80
	ML_3	12.78(12)	72.9(7)	110.9(1.8)	127
$Ph_2P(CH_2)_2SMe$	ML	7.18(3)	41.0(1)	54.5(2.1)	45
	ML_2	12.68(3)	72.4(1)	104(3)	106
	ML_3	15.31(9)	87.4(5)	137(4)	166
$Ph_2P(CH_2)_2SEt$	ML	7.40(1)	42.2(1)	55.9(1.8)	46
	ML_2	12.99(3)	74.1(1)	105.9(2.1)	107
	ML_3	15.5(3)	88.5(1.8)	139(4)	169
$Ph_2P(CH_2)_2SPh$	ML	7.00(3)	40.0(2)	53.5(1.5)	45
	ML_2	11.77(5)	67.2(3)	96.5(2.1)	98
	ML_3	14.41(12)	82.2(7)	134(4)	174

[a] Ref. 9.

the ratio C_L/C_M, for all the systems investigated. The fit of the experimental data with the curves calculated by means of the values of β_n and ΔH_n° reported in Table 1 (solid line in Fig. 1), is quite satisfactory. Table 1 also lists the values calculated for the changes in free energy, ΔG_n°, and entropy, ΔS_n°. For comparison, the thermodynamic data for the system silver(I)–triphenylphosphine previously determined [9] are also given in Table 1.

For a better understanding and for the aim of comparison, the thermodynamic functions relative to 1:1 complexes reported in Table 1 are visualized in Fig. 2, together with the analogous data obtained previously [1] for the system Ag(I)–$Ph_2P(CH_2)_2PPh_2$ also in dmso.

Discussion

The thermodynamic parameters of complexation of silver(I) by the ligands studied in this work show that the stabilities of the complexes are due only to the enthalpy terms as the entropy terms are all negative. Further, an analysis of the data in Fig. 2 shows that the stabilities of silver(I) complexes with the ligands Ph_2PCH_2SR are much lower than those established for analogous complexes with a series of bidentate P–P ligands [1] and are rather of the same magnitude as the complexes formed by silver(I) with the unidentate ligand triphenylphosphine, which means that bidentation can be presumably excluded.

On the other hand the stabilities of the complexes with the ligands $Ph_2PCH_2CH_2SR$ are intermediate between the ones relative to unidentate and P–P bidentate ligands: from ΔG° values only, one might conclude that the coordination of both donor atoms to the metal ion occurs. A glance at enthalpy and entropy values relative to the complex formation of Ag^+ with the thiophosphines and those relative to the complex formation with $Ph_2PCH_2CH_2PPh_2$ enables us to discard this hypothesis. The enthalpy terms are in fact considerably less exothermic for the thiophosphines while the values of ΔS_n° are all very negative but throughout smaller than for the diphosphines. Moreover, these values are very similar to those found for the silver(I)–PPh_3 system. As the diphosphines were described as forming bidentate chelate rings [1], we can conclude that the thiophosphines behave all as monodentate.

It seems reasonable that, in spite of the moderately strong affinity of the thioether donors for silver(I) [17], these ligands are bonded to silver(I) through phosphorus. It is known, in fact, that these ligands may form complexes in which they are either monodentate or bidentate chelating in behaviour: when they act as monodentate, the coordination occurs generally through phosphorus whereas when they are bidentate the thioether function is always more labile than the phosphine [13].

On the other hand, previous studies have shown that the thioether groups are stronger donors for silver(I) than dmso [18, 19]: the reason why these groups do not coordinate silver(I) in dmso solution is most likely to be found in a larger activity of the solvent which compensates for the slightly stronger donor properties of the thioether functions and therefore no coordination of these groups takes place with silver(I). For the same reasons, thiophosphines cannot form polynuclear complexes.

As stressed above, all silver(I) complexes with thiophosphines are strongly enthalpy stabilized, which is to be expected from the strongly covalent Ag–P bonds formed [20]. The enthalpy changes for each consecutive step decrease smoothly reflecting a gradual weakening of the Ag–P bonds as the number of coordinated ligands increases. The entropy changes, on the other hand, are much the same for all ligands which means that the complexes are all formed in quite similar processes. The entropy trend for the different steps indicates that, in these systems,

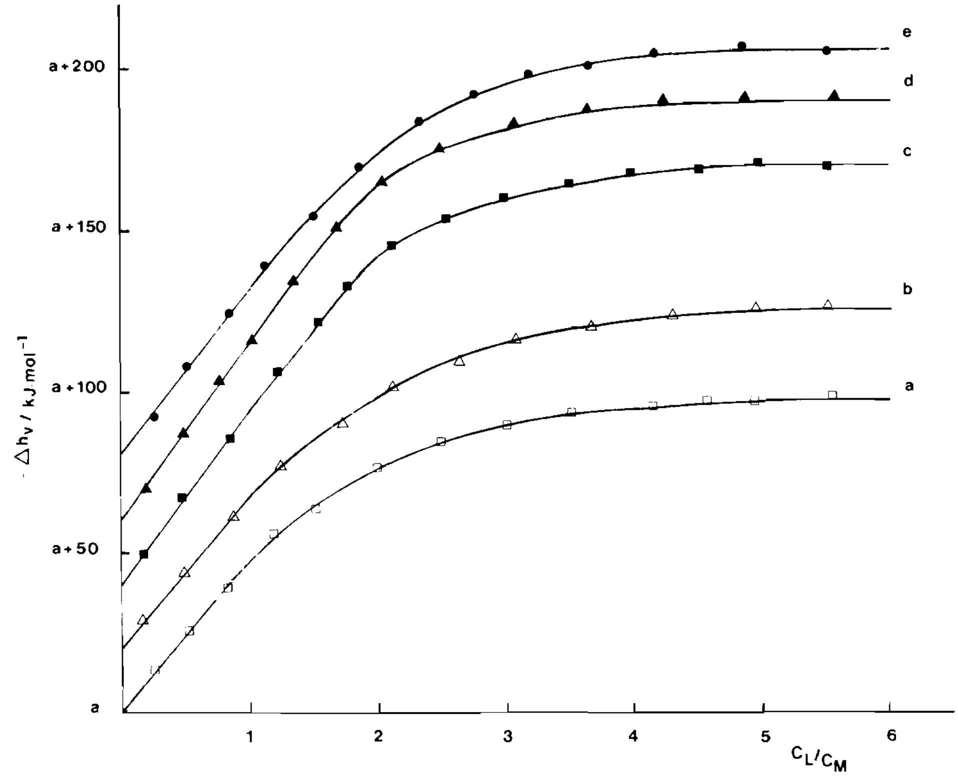

Fig. 1. The total molar enthalpy changes, ΔH_v, as a function of C_L/C_M for the silver(I)–Ph_2PCH_2SR systems (curve (a), R = Me (□); curve (b), R = Ph (△)) and silver(I)–$Ph_2P(CH_2)_2SR$ systems (curve (c), R = Me (■); curve (d), R = Et (▲); curve (e), R = Ph (●)) at $C^0_M = 5.00$ mmol dm^{-3} in dmso at 25 °C. For curve (a) $a = 0$, (b) $a = -20$, (c) $a = -40$, (d) $a = -60$, (e) $a = -80$. The full drawn curves have been calculated from the values of β_n and ΔH°_n reported in Table 1.

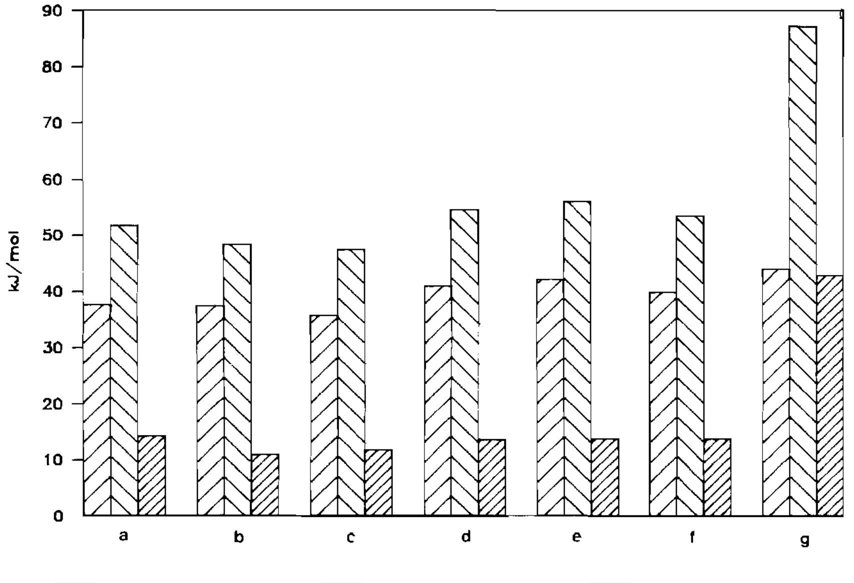

Fig. 2. Changes of free energy, enthalpy and entropy for the ML silver(I) complexes with the ligands: (a) Ph_3P, (b) Ph_2PCH_2SMe, (c) Ph_2PCH_2SPh, (d) $Ph_2P(CH_2)_2SMe$, (e) $Ph_2P(CH_2)_2SEt$, (f) $Ph_2P(CH_2)_2SPh$, (g) $Ph_2P(CH_2)_2PPh_2$ in dmso at 25 °C.

simple substitution reactions occur and that no extensive desolvation takes place at any step.

A point of interest in Table 1 is that the replacement of a phenyl group in PPh_3 with a $-CH_2SR$ group ($R = Me$ or Ph) does not significantly affect the donor properties of the phosphorus atom: the stability constants and the heat of formation of the silver(I) complexes with these ligands are in fact much of the same order of magnitude, which means that the electron withdrawing power of $-CH_2SR$ and phenyl groups is very similar.

The addition of one more methylene group in the central unit between P and S atoms, is by contrast accompanied by an increase in the stability and exothermicity of the complexes: the larger separation between the two donor atoms in addition to the +I effect of the aliphatic chain weakens the S withdrawing effect on the phosphorus atom, thus improving the P donor properties towards silver(I). The effect of the intervening $-CH_2-$ group on the stability of complexes was already proved for a series of aryl substituted benzoic, phenylacetic and 3-phenylpropionic acids in water [21].

Within each of the two classes of ligands, further variations arise depending on the substituent groups on the sulfur atom.

The increase in the stability of the complexes as well as more exothermic heats of reaction follow the order $Ph < Me < Et$: this is consistent with the ethyl thioether moiety being a better nucleophile than methyl and phenyl analogues [22].

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