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Thermodynamic and spectroscopic studies on the complexation of silver(I) by mixed phosphorus–nitrogen ligands in dimethyl sulfoxide and propylene carbonate

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Received 29th September 1998, Accepted 19th January 1999

The results of a thermodynamic study concerning Ag(I) complexation in dimethyl sulfoxide (dmso) and propylene carbonate (4-methyl-1,3-dioxolan-2-one, pc) with the mixed P–N ligands: 1-(diphenylphosphino)-2-(dimethylamino)ethane (Me_2Npe), 1-(diphenylphosphino)-2-(dimethylamino)benzene (Me_2Npph), 1-(diphenylphosphino)-3-(dimethylamino)propane (Me_2Npp) and 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye) are reported. Potentiometric and calorimetric measurements have been performed to obtain, respectively, free energy and enthalpy data for the reactions at 298 K and 0.1 mol dm^{-3} ionic strength (NEt_4ClO_4). A common feature of the different ligands is the formation of successive mononuclear complexes $[AgL_j]^+$ (j = 1–3) both in dmso and pc. In the former solvent Me_2Npph gives only the first two species. Me_2Npe, Me_2Npp and ppye also form appreciable amounts of the dinuclear species $[Ag_2L]^{2+}$ and $[Ag_2L_2]^{2+}$ in pc. All the complexes are strongly enthalpy stabilized, the entropy changes being unfavourable. The ligands behave as P donors in dmso, while are normally chelating or bridging in behaviour in pc, depending on the stoichiometry of the species formed. The results are discussed in terms of the steric requirements of the species and of the different donor properties of the solvents. $^{31}P-\{^1H\}$ and ^1H NMR studies and FT-IR investigations have also been performed to obtain additional information on the nature of the species in solution.

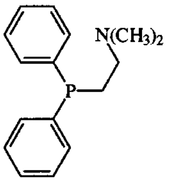
In the last years much effort has been devoted to the synthesis of transition metal complexes with P-containing hybrid ligands, mainly bidentate of the type P–X (X = O or N). The importance of such species depends on the relative ease of dissociation of the metal–X bond, which has prompted their use in homogeneous catalysis.[1] Recently, the preparation of chiral P–X compounds has initiated the application of their transition metal complexes to asymmetric catalysis.[2]

Growing interest in P–X ligands also concerns inorganic medicinal chemistry. It is known that metals of Group 11 form complexes with ditertiary phosphines (P–P) that exhibit high cytotoxic and antitumour activity.[3] The availability of analogous complexes with P–X ligands may offer the opportunity to enlarge the area of potential anticancer drugs. Indeed, very recently, Cu(I), Ag(I) and Au(I) complexes with two different (2-aminophenyl)phosphines were reported and preliminary studies have shown them to be active against tumours in mice.[4] On the other hand, Pt(II) complexes with coordinating P–N ligands, related to *cis*-platin, exhibit promising cytotoxic activity.[5]

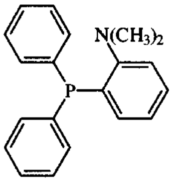
In this context, despite its usefulness, little work has been done in order to obtain thermodynamic data concerning complexation of silver(I) by these classes of ligands. Some coordinate thermodynamic and spectroscopic studies on the complexation of Ag(I) with diphosphines[6,7] $[Ph_2P(CH_2)_nPPh_2$ (n = 1–3)] and with P–S ligands[8,9] of general formula $Ph_2P(CH_2)_nSR$ (n = 1 or 2; R = Me, Et or Ph) have been carried out in the aprotic solvents dimethyl sulfoxide (dmso) and propylene carbonate (pc). The investigations have shown that composition and stability of the complexes are highly influenced by both the donor atoms present in the ligand (either P–P or P–S) and the solvent concerned.

No thermodynamic studies in solution have been reported till now for the complex formation of Ag(I) with P–N ligands. Nevertheless, some Ag(I)–P–N complexes have been prepared and characterized by spectroscopic and X-ray investigations.[10–15]

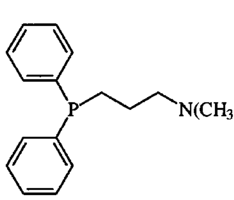
In this paper we report the results of a study on Ag(I) complexation in dmso and pc with the following P–N ligands, suitably chosen for their different electronic and steric properties: 1-(diphenylphosphino)-2-(dimethylamino)ethane (Me_2Npe), 1-(diphenylphosphino)-2-(dimethylamino)benzene (Me_2Npph), 1-(diphenylphosphino)-3-(dimethylamino)propane (Me_2Npp) and 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye). The primary aim of this work was to study how the nature of the solvent and the properties of the ligands influence complex formation.



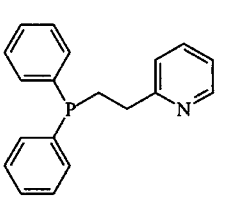
Me_2Npe



Me_2Npph



Me_2Npp



ppye

Table 1 Overall stability constants and thermodynamic functions for the reaction $m\mathrm{Ag}^+ + j\mathrm{L} \rightleftharpoons \mathrm{Ag}_m\mathrm{L}_j^{m+}$ in dmso and pc at 298 K and $I = 0.1$ mol dm^{-3}. The errors quoted correspond to three standard deviations

		$\log \beta_{m,j}$		$-\Delta G°_{m,j}$/kJ mol^{-1}		$-\Delta H°_{m,j}$/kJ mol^{-1}		$-T\Delta S°_{m,j}$/kJ mol^{-1}	
Ligand	Complex	dmso	pc	dmso	pc	dmso	pc	dmso	pc
PPh$_3$[a,b]	$[\mathrm{AgL}]^+$	6.58	9.95	37.6	56.8	51.8	70.5	14.2	13.7
	$[\mathrm{AgL}_2]^+$	10.73	17.17	61.3	98.0	89.9	122.3	28.6	24.3
	$[\mathrm{AgL}_3]^+$	13.17	21.41	75.2	122.2	126.2	167	51.0	44.8
Me$_2$Npe	$[\mathrm{AgL}]^+$	7.48 ± 0.05	12.87 ± 0.30	42.7 ± 0.3	73.5 ± 1.7	52.4 ± 0.9	94 ± 6	9.7	20.5
	$[\mathrm{AgL}_2]^+$	12.91 ± 0.06	22.09 ± 0.03	73.7 ± 0.3	126.1 ± 0.2	98.3 ± 0.9	152 ± 3	24.6	25.9
	$[\mathrm{AgL}_3]^+$	15.01 ± 0.18	24.45 ± 0.15	85.7 ± 1.0	139.6 ± 0.8	126 ± 2	184 ± 8	40.3	44.4
	$[\mathrm{Ag}_2\mathrm{L}]^{2+}$		15.74 ± 0.15		89.8 ± 0.9		107 ± 4		17.2
	$[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$		28.66 ± 0.21		163.6 ± 1.2		215 ± 5		51.4
Me$_2$Npph	$[\mathrm{AgL}]^+$	6.39 ± 0.3	10.90 ± 0.09	36.5 ± 0.1	62.1 ± 0.5	46 ± 2	73 ± 2	9.5	10.9
	$[\mathrm{AgL}_2]^+$	11.01 ± 0.3	19.49 ± 0.20	62.8 ± 0.2	111.2 ± 1.2	88 ± 1	125 ± 2	25.2	13.8
	$[\mathrm{AgL}_3]^+$		22.04 ± 0.21		125.8 ± 1.2		183 ± 5		57.2
Me$_2$Npp	$[\mathrm{AgL}]^+$	7.55 ± 0.02	13.4 ± 0.4	43.1 ± 0.1	76.5 ± 2.2	56.1 ± 0.8	95 ± 2	13.0	18.5
	$[\mathrm{AgL}_2]^+$	12.46 ± 0.02	20.87 ± 0.06	71.1 ± 0.1	119.1 ± 0.4	98.7 ± 0.9	142.4 ± 0.6	27.6	23.3
	$[\mathrm{AgL}_3]^+$	14.95 ± 0.06	24.02 ± 0.05	85.3 ± 0.4	137.1 ± 0.3	128.7 ± 0.9	174.6 ± 0.2	43.4	37.5
	$[\mathrm{Ag}_2\mathrm{L}]^{2+}$		16.80 ± 0.21		95.9 ± 1.2		108 ± 3		12.1
	$[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$		31.1 ± 0.4		177.5 ± 2.3		223 ± 6		45.5
ppye	$[\mathrm{AgL}]^+$	7.28 ± 0.02	13.10 ± 0.27	41.6 ± 0.1	74.8 ± 1.5	53.2 ± 0.5	91 ± 1	11.6	16.2
	$[\mathrm{AgL}_2]^+$	12.22 ± 0.03	20.91 ± 0.03	69.7 ± 0.2	119.4 ± 0.1	92.9 ± 0.6	142 ± 1	23.2	22.6
	$[\mathrm{AgL}_3]^+$	14.87 ± 0.08	24.08 ± 0.05	84.9 ± 0.4	137.4 ± 0.1	121 ± 2	174 ± 2	36.1	36.6
	$[\mathrm{Ag}_2\mathrm{L}]^{2+}$		15.57 ± 0.03		88.9 ± 0.3		107 ± 9		18.1
	$[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$		30.18 ± 0.08		172.3 ± 0.4		214 ± 3		41.7
dppe[b,c]	$[\mathrm{AgL}]^+$	7.73	13.75	44.1	78	87	114	42.9	36
	$[\mathrm{AgL}_2]^+$	13.91	21.94	79.4	125.2	149	173	69.6	47.8
	$[\mathrm{Ag}_2\mathrm{L}]^{2+}$	11.91	18.01	68.0	102.8	110	144	42	41.2
	$[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$	18.28	30.63	104.3	175	186	233	81.7	58
dppp[b,c]	$[\mathrm{AgL}]^+$	8.65	14.1	49.4	80	95	120	45.6	40
	$[\mathrm{AgL}_2]^+$	14.39	21.83	82.1	124.6	162	198	79.9	73.4
	$[\mathrm{Ag}_2\mathrm{L}]^{2+}$	12.37	18.15	70.6	103.6	115	147	44.4	43.4
	$[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$	20.13	32.63	114.9	186	195	253	80.1	67.0
PSMe[d,e]	$[\mathrm{AgL}]^+$	7.18	12.08	41.0	68.9	54.5	87	13.5	18.1
	$[\mathrm{AgL}_2]^+$	12.68	21.70	72.4	123.9	104	152	31.6	28.1
	$[\mathrm{AgL}_3]^+$	15.31	24.43	87.4	139.4	137	182	49.6	42.6
	$[\mathrm{Ag}_2\mathrm{L}]^{2+}$		15.09		86		105		19
	$[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$		26.79		152.9		201		48.1

[a] Ref. 16. [b] Ref. 7. [c] Ref. 6. [d] Ref. 8. [e] Ref. 9.

Potentiometric and calorimetric measurements have been used to obtain, respectively, free energy and enthalpy data for the reactions. Further information on the coordination of the species formed in solution has been obtained by means of NMR and FT-IR spectroscopies. In the case of pc, NMR spectra have also been collected at low temperatures. As in previous studies,[6–9] all measurements have been performed at 298 K and in an ionic medium (0.1 mol dm^{-3}) with $\mathrm{NEt_4ClO_4}$ as neutral salt.

Results

The best fit of the potentiometric data for each system studied both in dmso and pc was obtained when the species reported in Table 1 were taken into account. The overall stability constants and free energies of formation, with the limits of error indicated, are listed for the reactions: $m\mathrm{Ag}^+ + j\mathrm{L} \rightleftharpoons \mathrm{Ag}_m\mathrm{L}_j^{m+}$ (where L is a P–N, P–P or P–S ligand). A common feature of the different ligands is their ability to form successive mononuclear complexes $[\mathrm{AgL}_j]^+$ (j = 1–3) both in pc and in dmso. Yet, in the latter solvent Me$_2$Npph gives only the first two mononuclear species. In addition, Me$_2$Npe, Me$_2$Npp and ppye also form appreciable amounts of dinuclear species such as $[\mathrm{Ag}_2\mathrm{L}]^{2+}$ and $[\mathrm{Ag}_2\mathrm{L}_2]^{2+}$ in pc. The distribution of silver(I) between the different complexes as a function of the ligand-to-metal ratio, R_c, for all the systems studied is plotted in Fig. 1.

The total heats of reaction per mole of metal ion, Δh_v, are reported as a function of R_c in Figs. 2 and 3 for dmso and pc, respectively. The dotted lines in Fig. 2 refer to the values of enthalpy per mole of added metal, $\Delta h'_v$, obtained by the "reverse" titrations in dmso. $\Delta h'_v$ is equal to Δh_v at $R_c \geq 2$ only for the Ag(I)–Me$_2$Npph system. Hence, the calorimetric "reverse" titrations confirm the formation of only 1 : 1 and 1 : 2 complexes for this system. The experimental heats of reaction and the overall stability constants in Table 1 were used to calculate the full lines in Figs. 2 and 3. The fit of the experimental data is quite good indicating that all the systems are satisfactorily described.

In Table 1 are also reported, for comparison, the stability constants and the thermodynamic functions for the complexation reactions of Ag(I) by the ligands PPh$_3$, 1,2-(diphenylphosphino)ethane (dppe), 1,3-(diphenylphosphino)propane (dppp) and 1-(diphenylphosphino)-2-(sulfanylmethyl)ethane (PSMe), previously determined in dmso[6,8,16] and pc.[7,9]

^{1}H NMR spectra have been collected in dmso-d$_6$ solution at 298 K for free Me$_2$Npe and for the Ag(I)–Me$_2$Npe system at different $R_c = c_L/c_M$ values. In Fig. 4 the $\Delta\delta$ values relative to NMe$_2$ protons are reported as a function of R_c ($\Delta\delta$ represents the difference between the chemical shifts of coordinated and free ligand).

The most significant ^{31}P-{^{1}H} NMR results obtained in dmso and pc solutions are collected in Tables 2 and 3, respectively. In dmso solution, unresolved ^{31}P-{^{1}H} spectra have been obtained at 298 K. In the few cases in which the spectrum showed two broad signals, their separation being consistent with a rough average of $^1J(^{31}\mathrm{P}–^{107}\mathrm{Ag})$ and $^1J(^{31}\mathrm{P}–^{109}\mathrm{Ag})$, coupling constants have been estimated.[7] The freezing point of dmso (291.7 K)[17] did not allow us to run spectra at low temperature. On the contrary, in pc, which freezes at 224.4 K,[17] the temperature range explored was extended down to 228 K. At this temperature, the slow-exchange limiting spectrum was obtained for each system except for Ag(I)–Me$_2$Npph at $R_c = 1.0$ and 3.0 and Ag(I)–Me$_2$Npe at $R_c = 1.0$.

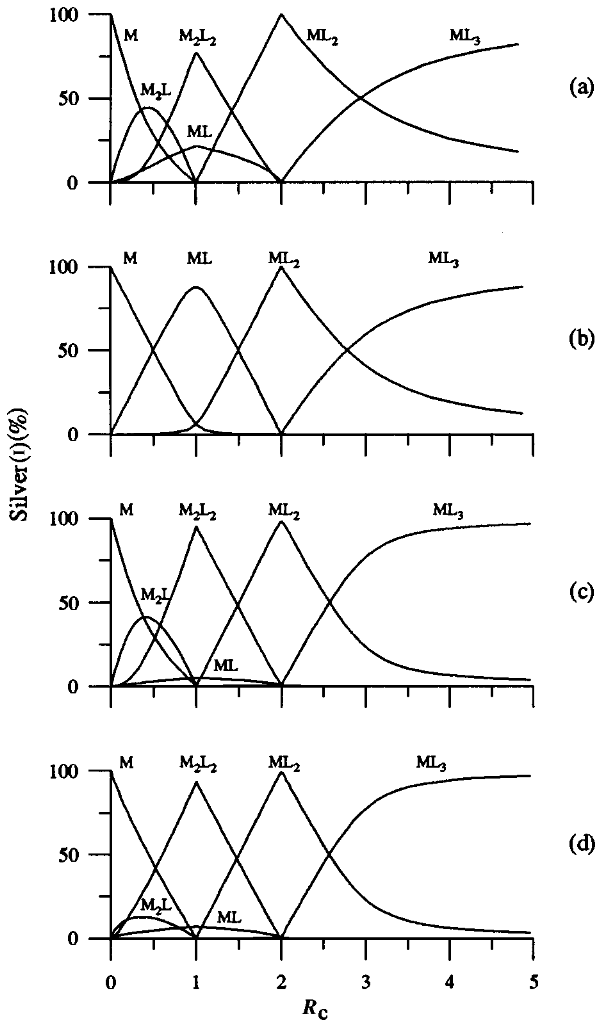


Fig. 1 The percent distribution of the metal ion in the silver(I)–P–N systems in pc at $c^{\circ}_{Ag} = 10$ mmol dm^{-3}. (a) Me$_2$Npe; (b) Me$_2$Npph; (c) Me$_2$Npp; (d) ppye.

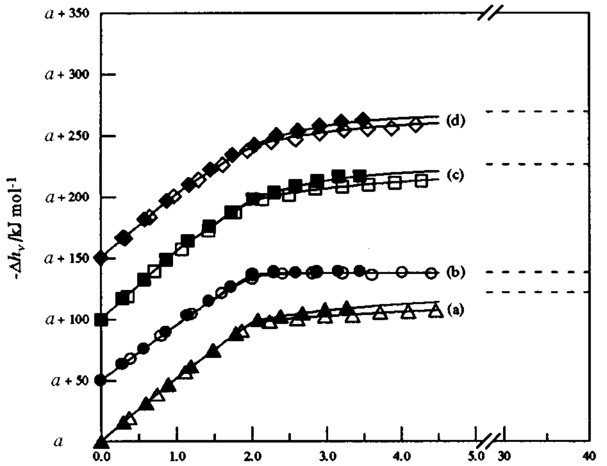


Fig. 2 The total molar enthalpy changes, Δh_v, as a function of R_c for silver(I)–P–N systems in dmso. (a) $a = 0$ for Me$_2$Npe: (△) 2.075, (▲) 6.977 mmol dm^{-3} in Ag$^+$; (b) $a = -50$ for Me$_2$Npph: (○) 1.892, (●) 7.011 mmol dm^{-3} in Ag$^+$; (c) $a = -100$ for Me$_2$Npp: (□) 1.953, (■) 7.234 mmol dm^{-3} in Ag$^+$; (d) $a = -150$ for ppye: (◇) 2.220, (◆) 7.159 mmol dm^{-3} in Ag$^+$. The solid lines have been calculated from the values of $\beta_{m,j}$ and $\Delta H^{\circ}_{m,j}$ in Table 1. The dashed lines represent the "reverse" titrations (see text for details).

Table 2 ^{31}P-{^{1}H} NMR data in dmso solution[a]

Ligand	R_c[b]	δ[c] (ppm)	$J(^{31}P-^{107}Ag)$[d]/Hz
Me$_2$Npe	Free	−19.2	
	1.0	≈2 (br)	
	2.0	≈2 (br), ≈−3 (br)	≈430
	3.0	−4.1 (br)	
Me$_2$Npph	Free	−13.2	
	1.0	≈2 (br), ≈−7 (br)	≈680
	2.0	≈−2 (br), ≈−8 (br)	≈480
	3.0	*e*	
Me$_2$Npp	Free	−16.1	
	1.0	≈13 (br), ≈4 (br)	≈660
	2.0	≈6 (br)	
	3.0	2.0 (br)	
ppye	Free	−15.8	
	1.0	≈9 (br)	
	2.0	≈6 (br)	
	3.0	1.4 (br)	

[a] 10^{-2} mol dm^{-3} solutions at 298 K. [b] $R_c = c_L/c_M$. [c] br = broad signal. [d] Estimated values obtained from the separation of the two broad resonances, which has been roughly interpreted as the average of the ^{31}P–^{107,109}Ag coupling constants. [e] Asymmetric broad signal at ≈δ −7.

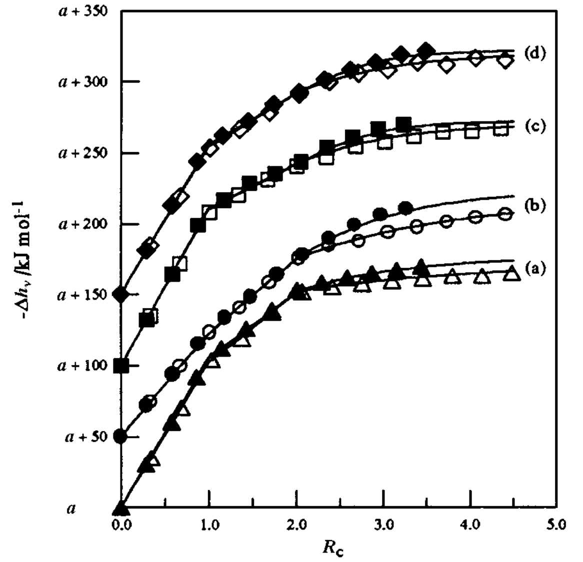


Fig. 3 The total molar enthalpy changes, Δh_v, as a function of R_c for silver(I)–P–N systems in pc. (a) $a = 0$ for Me$_2$Npe: (△) 1.985, (▲) 6.952 mmol dm^{-3} in Ag$^+$; (b) $a = -50$ for Me$_2$Npph: (○) 2.130, (●) 7.011 mmol dm^{-3} in Ag$^+$; (c) $a = -100$ for Me$_2$Npp: (□) 2.015, (■) 6.853 mmol dm^{-3} in Ag$^+$; (d) $a = -150$ for ppye: (◇) 1.913, (◆) 7.153 mmol dm^{-3} in Ag$^+$. The solid lines have been calculated from the values of $\beta_{m,j}$ and $\Delta H^{\circ}_{m,j}$ in Table 1.

From the resolved spectra collected at 228 K it was possible to calculate Garrou's ^{31}P Δ_R parameter[18] (Table 3), which represents a useful tool often employed to get more information on structural features of phosphino-complexes in solution. Owing to the structural analogies, PEtPh$_2$ has been used as reference ligand for Me$_2$Npe, Me$_2$Npp and ppye (all showing a Ph$_2$-PCH$_2$CH$_2$ moiety), while PPh$_3$ has been chosen for Me$_2$Npph. In the case of Me$_2$Npe, PMePh$_2$ has also been tested as reference ligand. ^{31}P-{^{1}H} NMR spectra have also been recorded for Ag(I)–dppe and –dppp systems for comparative purpose. In both cases PEtPh$_2$ has been used as reference ligand for the calculation of Δ_R.

Discussion

The analysis of the thermodynamic functions (Table 1) shows that the formation of Ag(I) complexes with P–N ligands both in dmso and in pc is always enthalpy controlled, as expected when covalent bonds are formed and the desolvation of the species is small.[19]

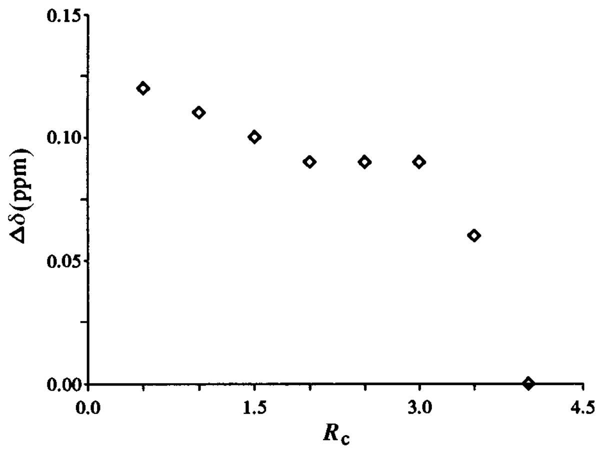


Fig. 4 $\Delta\delta$ values relative to methyl protons as a function of R_c for the Ag(I)–Me_2Npe system in dmso-d_6 solution at 298 K. For free Me_2Npe δ(Me) = 2.10.

Silver(I) complexes in dmso

The data reported in Table 1 show that the Ag(I)–P–N complexes have the same stoichiometry as the monodentate complexes of silver(I) with PPh_3 or PSMe. In particular it is worth noting that in all systems no polynuclear complexes are formed, in contrast to what occurs in Ag(I)–dppe and −dppp systems.[6] Moreover, it can be observed that the stabilities of the first two complexes of the P–N ligands are lower than those of mononuclear species formed by the bidentate dppe and dppp and, most important, the enthalpy terms for the Ag(I)–P–N complexation are much less exothermic and the entropy values always less negative than for the diphosphines and similar to those found for PPh_3 and PSMe. These values, together with the absence of polynuclear species, give a concrete indication that the P–N ligands all behave as P-bound monodentate in dmso. The low increase of stability and exothermicity of the silver(I) complexes with ppye, Me_2Npe and Me_2Npp, with respect to the values found for PPh_3, can be ascribed to a bland +I effect of the aliphatic chain[20] which improves the P donor properties toward the metal centre.

Since in previous works[21,22] it was found that primary and secondary nitrogens are able to bond silver(I) in dmso, NMR and IR measurements have been carried out in order to confirm the thermodynamic indications.

The ^{31}P-{^1H} NMR data reported in Table 2 show a regular decrease of the δ values on increasing R_c from 1.0 to 3.0, which reflects the decreasing value of the Ag–P bond strength as the number of coordinated ligands increases.[23] The calculated coupling constants for R_c = 1.0 and 2.0 are in agreement with those obtained when only one[7,9,14,15,23–29] or two[7,9,11,23–31] P atoms are coordinated to Ag(I), respectively.

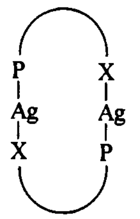
^{31}P NMR data do not directly show if N coordination would occur or not. Conversely, the chemical shift of the methyl protons of the NMe_2 group would be a good probe of the behaviour of the nitrogen arm of the ligand upon complexation. In particular, ^1H NMR spectra have been run on the Ag(I)–Me_2Npe system as the ligand concerned is potentially the most prone to give chelates. A small increase in chemical shift is observed upon coordination of Me_2Npe (from $R_c = 0$ to $R_c = 0.5$) while δ values remain practically unchanged on increasing R_c from 0.5 to 3.0 (Fig. 4). This means that no drastic variation occurs at the neighbour to the methyl protons on changing R_c in this range. If coordination of the N atom occurred in $[Ag(Me_2Npe)_j]^+$ complexes (j = 1 or 2), a remarkable change of the corresponding $\Delta\delta$ values would be expected with respect to that observed for R_c = 3.0 where reasonably only P-bound ligands are present in $[Ag(Me_2Npe)_3]^+$.

For the Ag(I)–ppye system, a definitive proof that the nitrogen atom of the ligand is uncoordinated in dmso comes from the IR spectra. At all R_c values (R_c = 1.0, 2.0 and 3.0) the observed pyridine-ring stretching absorption at 1594 cm^{-1} is close to that measured for the free ligand (1593 cm^{-1}), whereas values above 1598 cm^{-1} are expected when N-coordination occurs.[11,14]

The lower basicity of the tertiary amino group (or pyridyl) as compared with the basicity of primary and secondary nitrogens,[32,33] is likely the reason why the nitrogen atom of these P–N ligands is not able to compete with dmso for coordination to the metal center. Certainly, the steric demand of the ligands is also to be considered, in particular for the bulkiest Me_2Npph.[34] Its steric crowding is probably responsible for the fact that the formation of $[Ag(Me_2Npph)_3]^+$ is prevented.

Silver(I) complexes in pc

A common feature of all the systems investigated in pc at R_c = 1.0 [except Ag(I)–Me_2Npph, which is discussed separately] is the simultaneous formation of $[AgL]^+$ and $[Ag_2L_2]^{2+}$, complexes, the latter always being the prevalent species (Fig. 1). Formation of dinuclear complexes is frequent in the coordination chemistry of silver(I). In particular, several Ag(I) complexes bearing P–P,[6,7,25,35–46] P–N[12,14,15] or P–S[9] ligands are known to possess the dinuclear head-to-tail core structure **1** (X = P, N or S).



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Simple considerations concerning the enthalpies of formation of the dimers $[Ag_2(P\text{–}N)_2]^{2+}$ suggest that the annular arrangement is also characteristic for these complexes. For example, it is reasonable that the enthalpy value associated with the formation of one Ag–P bond in these complexes corresponds to one half of the enthalpy gain observed for the formation of $[Ag_2(dppe)]^{2+}$ (−144 kJ mol^{-1} in Table 1; *i.e.* $\Delta H_{Ag\text{–}P} \approx$ −72 kJ mol^{-1}).[7] Moreover, the difference {−107 − [−72] = −35 kJ mol^{-1}} between the enthalpy of formation of $[Ag_2(Me_2Npe)]^{2+}$, where one Ag–P and one Ag–N bond is formed, and $\Delta H_{Ag\text{–}P}$ can be ascribed to the formation of one Ag–N bond. Hence, formation of the annular dimer with two Ag–P and two Ag–N bonds should give a total of 214 kJ mol^{-1}, which is very close to the experimental value. Similar calculations for the Ag(I)–Me_2Npp system [which can be compared with Ag(I)–dppp] leads to a theoretical enthalpy gain for dimer formation of 216 kJ mol^{-1}, close to the reported value of 223 kJ mol^{-1}.

The coordination hypothesis formulated for the annular $[Ag_2L_2]^{2+}$ complexes is strengthened by NMR and IR measurements on the systems Ag(I)–Me_2Npp and –ppye at R_c = 1.0. In fact: *(i)* the ^{31}P-{^1H} NMR spectra for these long-bite ligands (at 298 and 228 K for Me_2Npp and ppye, respectively) show the typical two doublets arising from spin–spin coupling of equivalent P atoms to $^{107,109}Ag$ atoms and the $^1J(^{31}P\text{–}^{107}Ag)$ values are indicative of only one P bound to each silver(I);[7,9,14,15,23–29] *(ii)* the formation of a non-annular dimer of the type $[N\text{–}P\text{–}Ag\text{–}N\text{–}P\text{–}Ag]^{2+}$ can be safely excluded as in this case the P atoms should not be equivalent; *(iii)* the IR solution spectrum of the Ag(I)–ppye system at R_c = 1.0 shows the pyridine-ring stretching absorption at 1606 cm^{-1}, close to that (1607 cm^{-1}) measured in Nujol mull for the annular complex $[Ag_2(ppye)_2][PF_6]_2\cdot 2(CH_3)_2CO$.[14]

Despite the fact that the percent formation of $[AgL]^+$ com-

Table 3 ^{31}P-{^{1}H} NMR data in pc solution[a]

Ligand	R_c[b]	δ[c] (ppm)	J[d]/Hz	T/K	Δ_C[e] (ppm)	Δ_R[f] (ppm)
Me_2Npe	Free	−19.8 (s)		298		
		−21.9 (s)		228		
	1.0	≈6 (br)		298		
		≈9 (br), ≈1 (br)	≈650[g]	228		
	2.0	≈0 (br), ≈−6 (br)		298		
		−4.0 (dd)	436	228	17.9	−7.9, −6.7[h]
	3.0	−5.5 (br)		298		
		−4.5 (dd)	311	228	17.4	−2.3, −2.4[h]
Me_2Npph	Free	−13.1 (s)		298		
		−15.1 (s)		228		
	1.0	≈−5 (br)		298		
		≈−2 (br), ≈−11 (br)	≈680[g]	228		
	2.0	≈−3 (br), ≈−9 (br)		298		
		−8.0 (dd)	489	228	7.1	−11.9
	3.0	−7.3 (br)		298		
		i		228		
Me_2Npp	Free	−16.3 (s)		298		
		−18.2 (s)		228		
	1.0	13.1 (dd)	655	298		
		12.9 (dd)	655	228	31.1	2.4
	2.0	≈2 (br), ≈7 (br)		298		
		3.7 (dd)	439	228	21.9	−3.9
	3.0	2.1 (br)		298		
		2.0 (dd)	312	228	20.2	0.5
ppye	Free	−16.2 (s)		298		
		−18.0 (s)		228		
	1.0	≈18 (br), ≈9 (br)		298		
		12.3 (dd)	652	228	30.3	1.6
	2.0	≈8 (br), ≈3 (br)		298		
		4.8 (dd)	430	228	22.8	−3.0
	3.0	≈2 (br)		298		
		1.8 (dd)	302	228	19.8	0.1
$PMePh_2$	Free	−27.1 (s)		298		
		−28.2 (s)		228		
	1.0	−3.3 (dd)	719	228	24.9	
	2.0	3.6 (dd)	521	228	24.6	
	3.0	−8.4 (dd)	325	228	19.8	
$PEtPh_2$	Free	−11.9 (s)		298		
		−13.6 (s)		228		
	1.0	15.1 (dd)	737	228	28.7	
	2.0	12.2 (dd)	503	228	25.8	
	3.0	6.1 (dd)	318	228	19.7	
	4.0	4.2 (dd)	229	228	17.8	
PPh_3	Free	−5.1 (s)		298		
		−6.8 (s)		228		
	2.0	12.2 (dd)	497	228	19.0	
	3.0	9.7 (dd)	319	228	16.5	
dppe	Free	−14.7 (s)		228		
	2.0	2.0 (dd)	232	228	16.7	−1.1
dppp	Free	−19.5 (s)		228		
	1.0	7.3 (dd)	512	228	26.8	1.0
	2.0	−6.1 (dd)	219	228	13.3	−4.5

[a] 10^{-2} mol dm^{-3} pc solutions, unless otherwise stated. [b] $R_c = c_L/c_M$. [c] Multiplicity given in parentheses by s = singlet, dd = two doublets, br = broad singlet. [d] $^1J(^{31}P–^{107}Ag)$. [e] $\Delta_C = \delta(P_{coord.}) - \delta(P_{free})$. [f] $\Delta_R = \Delta_C - [\delta(P\{PPh_3\}_{coord.}) - \delta(P\{PPh_3\}_{free})]$ for Me$_2$Npph, $\Delta_R = \Delta_C - [\delta(P\{PEtPh_2\}_{coord.}) - \delta(P\{PEtPh_2\}_{free})]$ for Me$_2$Npe, Me$_2$Npp and ppye. [g] Estimated value obtained from the separation of the two broad resonances, which has been roughly interpreted as the average of the $^{31}P–^{107,109}Ag$ coupling constants. [h] $\Delta_R = \Delta_C - [\delta(P\{PMePh_2\}_{coord.}) - \delta(P\{PMePh_2\}_{free})]$. [i] Asymmetric broad multiplet in the range δ −2 to 8.

plex in solution is low, this species is always essential for obtaining the best fit of potentiometric and calorimetric data. In the case of the Ag(I)–Me$_2$Npe system the percentage of [AgL]$^+$ in solution is about 20%, while for ppye and, even more, for Me$_2$Npp that value decreases below 10% (Fig. 1).

The [AgL]$^+$ complexes in pc are much more stable than the corresponding complexes of PPh$_3$ and their enthalpies and entropies of formation are close to those of the [Ag(PSMe)]$^+$ chelate complex. This agrees with coordination of both P and N atoms to silver(I).

It must be noted that NMR signals relative to the formation of [AgL]$^+$ complexes, always present in solutions at $R_c = 1.0$, were never observed in the NMR spectra of Ag(I)–Me$_2$Npp and –ppye systems. This is because, at the temperature where well defined spectra were obtained, the four-line spectrum expected for a "frozen" [AgL]$^+$ species is too low in intensity to be detectable[7] under the adopted experimental conditions [<5% for Ag(I)–Me$_2$Npp system at 298 K and about 1% for Ag(I)–ppye at 228 K †].

The values of the thermodynamic parameters of the [Ag(P–N)$_2$]$^+$ complexes are similar to those previously found for [Ag(PSMe)$_2$]$^+$ in pc, where both phosphinothioethers act as bidentate ligands (Table 1). ^{31}P-{^{1}H} NMR spectra recorded at 228 K for all Ag(I)–P–N systems at $R_c = 2.0$ show two doublets and $^{31}P–^{107}Ag$ coupling constants (430–439 Hz) are indicative

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† By application of the van't Hoff law, considering $\Delta H°_{m,j}$ **to be** constant in the temperature range investigated, when $R_c = 1.0$ the [Ag(ppye)]$^+$ species does not exceed 1% of the total silver concentration at 228 K.

of two equivalent P atoms coordinated to the metal ion.[7,9,11,23–31] In addition, IR solution spectroscopy on $[Ag(ppye)_2]^+$ shows the pyridine-ring stretching absorption at 1599 cm^{-1}, practically coincident with that at 1598 cm^{-1} observed both in Nujol mull and in dichloromethane for the bis-chelate $[Ag(ppye)_2][PF_6]_2$ complex.[11] Thus all of the results obtained at $R_c = 2.0$ suggest that in $[Ag(P–N)_2]^+$ the ligands also behave as bidentate.

The abrupt decrease of K_3 and the values of the thermodynamic functions associated with the formation of the third complex might be due to a rearrangement of the ligands around the metal ion when ML_3 complexes are formed,[19] which implies rupture of previously formed Ag–N bonds and formation of a Ag–P bond. The spectroscopic data confirm this hypothesis. The two doublets in the $^{31}P-\{^1H\}$ NMR spectra recorded at 228 K and $R_c = 3.0$ for all Ag(I)–P–N systems are indicative of the presence of a single compound with three equivalent P atoms bound to Ag(I) $[^1J(^{31}P–^{107}Ag) \approx 300$ Hz].[7,9,11,15,23,26–30,47,48] Moreover, the IR spectrum run in pc solution for $[Ag(ppye)_3]^+$ is diagnostic of only P-bound ligands (pyridine ring stretching absorption at 1595 cm^{-1}), very close to that observed for the three-coordinated $[Ag(ppye)_3]PF_6$ complex in dichloromethane.[11]

As far as Me_2Npph is concerned, it is reasonable to admit that this ligand also behaves as bidentate in the first two steps of complexation. Nevertheless, the stability constants of the first two mononuclear complexes are intermediate between those of Me_2Npe, which can give five-membered chelate rings, and those of PPh_3. On the other hand, the enthalpy terms relative to the formation of the first two complexes are close to those of PPh_3, while the entropy terms are less unfavourable. A great desolvation of the reagents, a consequence of the steric demand that this rigid ligand imposes on the closure of the chelate rings, might be a rationale for this observation.

The thermodynamic data associated with the third step of complexation indicate that the three ligands all behave as monodentate. The high stepwise enthalpy gain and the high unfavourable entropy term associated with the formation of $[Ag(Me_2Npph)_3]^+$ agree with the hypothesis that desolvation of the reagents is primarily important when the first two steps of complexation are involved.

A striking feature of Me_2Npph is that this ligand does not form dinuclear species. A different behaviour of this ligand, if compared with other potentially bidentate ligands which gave primarily dinuclear species, has already been observed.[1a] A rationale of this behaviour can be found in the analysis of the space filling molecular model (CPK) of Me_2Npph in its unconstrained configurations. The model clearly shows that σ-donor orbitals of N and P atoms are convergent, thus not being suitable for the simultaneous binding of two metal centres.

^{31}P NMR Δ_R parameter applied to Ag(I)–P–N systems

From the analysis of the Δ_R values calculated for a long list of transition metal complexes bearing potentially bidentate phosphine ligands, Garrou[18] showed that when Δ_R is close to zero, *i.e.*, the coordination chemical shift resembles that of the reference complex, the lack of a ring-contribution to the observed chemical shift indicates that no chelation occurs. On the contrary, when the ligand is chelated to the metal centre, Δ_R values different from zero are found which are typically dependent on the size of the chelate ring.

In the cited review which focuses on Δ_R application, no examples pertinant to silver(I) complexes were reported, nor, to the best of our knowledge, in any other publication to date. Δ_R values have been calculated for silver(I) phosphine derivatives in pc (Table 3) to analyse whether some correlation can be found between this parameter and the coordinating mode adopted by the ligands.

As a preliminary premise to the following discussion, it is necessary to point out that generally Δ_C values differ very much according to the ligand coordinating mode, while in the present case the differences in Δ_C values are rather small (within a range of *ca.* 12 ppm). Consequently, Δ_R values are also within a narrow range, in particular for the chelating mode Δ_C is about one order of magnitude lower with respect to the literature data.

In the case of the ligands Me_2Npp and ppye, the calculated Δ_R values for $R_c = 3.0$ are close to zero in agreement with their monodentate binding through the P atom. On the contrary, Δ_R for the Ag(I)–Me_2Npe system at $R_c = 3.0$ is, unexpectedly, −2.3 ppm. This value seems to be anomalous as both spectral pattern and $^1J(^{31}P–^{107}Ag)$ unambiguously indicate that the three P atoms in $[Ag(Me_2Npe)_3]^+$ are equivalent and, reasonably, that the ligands act as monodentate. An inadequate choice of the reference monodentate ligand may be a possible explanation for such an anomaly.[18] However, the alternative choice of $PMePh_2$ as reference ligand instead of $PEtPh_2$ does not lead to an appreciable change in Δ_R (−2.4 ppm).

As both thermodynamic and spectroscopic data indicate that at $R_c = 2.0$ all ligands form chelate complexes, a tentative correlation between Δ_R and the coordinating mode adopted by the ligand must associate the formation of $[Ag(P–N)_2]^+$ derivatives with a negative sign of Δ_R. It should be noted that for several transition metal complexes with chelated dppe and dppp, which form five- and six-membered rings, respectively, different trends have been found. While dppe gives positive Δ_R values, for dppp smaller and negative Δ_R values are obtained.[18] To explain the anomalous results found here for Ag(I) derivatives, spectra at 228 K for both Ag(I)–dppe and Ag(I)–dppp systems have been collected at $R_c = 2.0$ in order to calculate the relative Δ_R values for $[Ag(P–P)_2]^+$ (P–P = dppe or dppp) bis-chelated[7] complexes. Also the results obtained with the diphosphines (Table 3) seem to confirm that chelation to Ag(I) is correlated with a negative Δ_R value, independent of the size of the chelate ring formed.

Finally, the positive Δ_R values obtained for $R_c = 1.0$ in the case of Me_2Npp and ppye could be related to the bridging coordination mode. As symmetric dinuclear annular species have been shown to exist in pc solution when R_c is 1.0 by both NMR and thermodynamic studies. Such coordinating mode/Δ_R correlation for $R_c = 1.0$ seems to be confirmed in the case of the Ag(I)–dppp system for which the formation of a dinuclear annular species has been proved.[7] In the case of the ligand dppe the slow-exchange limiting spectrum was not obtained at 228 K.

Conclusion

The results reported here evidence the different behaviour of the P–N ligands in the two solvents investigated. In dmso, like the previously studied phosphinothioethers,[9] the P–N ligands coordinate the silver(I) ion only through the soft P atom, while in pc the N atom also bonds to the metal ion in a chelating or bridging fashion. Thus, it is possible to conclude that P–X ligands give only mononuclear P-bound complexes in solvents with high donor number (DN) (DN = 15.1 and 29.8 for pc and dmso,[49] respectively). On the contrary, solvents with low DN greatly enhance the coordinating ability of these ligands, which in this case can give both mononuclear chelate and dinuclear complexes.

Such behaviour can be mainly attributed to the weaker solvation of silver(I) in pc than in dmso as evidenced by the parameters of transfer: $\Delta G^\circ_{tr\ pc\rightarrow dmso} = -37.1$, $\Delta H^\circ_{tr\ pc\rightarrow dmso} = -40.9$, $T\Delta S^\circ_{tr\ pc\rightarrow dmso} = -3.8$ kJ mol^{-1}.[50] The enthalpy of transfer of Ag(I) from pc to dmso is close to its free energy of transfer. This means that the transfer process causes a significant release of heat which accompanies only a modest increase of order. As the structural order in pure dmso and pc is almost the same,[19] the transfer parameters seemingly indicate that on going from pc to dmso the ion–solvent bond energy increases remarkably without significant changes of the ordering effect of metal ion towards solvent molecules. In other words, the transfer of Ag^+ from one solvent to another seems to involve mainly the solvent molecules in the immediate proximity of the metal ion, with the bulk solvent less involved. In line with this, the lower donor properties of pc favour coordination of the ligand's N atom with formation of either chelate or polynuclear species.

The mean of the differences between the heats of formation in the two solvents of the structurally similar $[AgL_3]^+$ complexes, where the ligands are monodentate and $L = PPh_3$, Me_2Npe, Me_2Npp, ppye and PSMe, is -49 ± 6 kJ mol^{-1}, close to the $\Delta H^\circ_{tr\ pc\rightarrow dmso}$ for the Ag(I) ion. Since the $[AgL_3]^+$ complexes in the two solvents are reasonably similar from a structural point of view, this result is in line with the hypothesis that the lower solvation of the cation is mainly responsible for the higher affinity of P–N ligands toward silver(I) in pc than in dmso.

The different relative permittivity ($\varepsilon = 46.4$ and 64.4 for dmso and pc,[19] respectively) are an additional factor which can explain the existence of polynuclear species only in pc. In fact, formation of polynuclear complexes necessarily requires approach of positively charged entities and the ε values point out that electrostatic repulsion between metal ions is stronger in dmso than in pc.

A comparison can also be made between the thermodynamic parameters found here for the complex formation of Ag(I) with Me_2Npe and those found for closely related P–P and P–S ligands, *i.e.* dppe and PSMe, previously studied in pc. The silver(I) complexes with Me_2Npe are more stable and more enthalpy stabilized than the analogous species formed by PSMe, while the opposite is true for the dppe complexes. Therefore, the stability sequence of silver(I) complexes with the ligands concerned in pc follows the order P–P > P–N > P–S.

The NMR investigations have always supported the conclusions drawn from the thermodynamic studies, thus confirming that the thermodynamic technique is an effective tool for the assessment of the metal–ligand bonding mode in solution. Furthermore, we have proved that the ^{31}P Δ_R criterion proposed by Garrou[18] can also be applied to silver(I) complexes but only with much care. As all Δ_R values are within a narrow range, the choice of the reference ligand may be determinant. It should also be stressed that no correlation between Δ_R (Δ_C) and chelate-ring size seems to be operative. Finally, the correlation found between the Δ_R values and the coordinating mode adopted by the ligand could be useful, but it must be supported by other data.

Experimental

Chemicals

Anhydrous silver perchlorate was obtained from $AgClO_4\cdot H_2O$ (Fluka puriss) as described previously.[7] Dimethyl sulfoxide and propylene carbonate (Fluka > 99%) were purified by distillation according to the described procedures[7,21] and stored over activated 4 Å molecular sieves. The salt NEt_4ClO_4 was recrystallized twice from methanol and dried at 110 °C. The ligands Me_2Npe,[51] Me_2Npph,[34] Me_2Npp[51] and ppye,[52] which were synthesized according to literature procedures, have been purified on neutral aluminium oxide (Me_2Npe and Me_2Npp) or silica gel (Me_2Npph and ppye) columns by using diethyl ether as eluent. Their purity (>99.5%) was checked by ^{31}P NMR spectroscopy.

The silver(I) solutions were prepared from anhydrous $AgClO_4$ and freshly distilled dmso or pc. The metal concentration in these solutions was checked by potentiometric titrations with chloride. Solutions of the ligands were prepared by dissolving weighed amounts in the appropriate solvent. NEt_4ClO_4 was used to obtain the required ionic strength. The water content in the solutions, typically 10–20 ppm, was determined by a Metrohm 684 KF coulometer. All the solutions were freshly prepared before each experiment in a glove box under an atmosphere of dry, oxygen free, nitrogen to avoid oxidation of the ligands.

Potentiometric measurements

All measurements were carried out under dry nitrogen in a thermostatted cell maintained at 298.0 ± 0.1 K. The experimental data required for the determination of the stability constants of the complexes were the equilibrium concentrations of the silver ion, which were obtained from potentiometric measurements. The galvanic cell and other experimental details were previously described.[6] The emf were measured by means of an Amel 338 pHmeter equipped with a Metrohm 6.0328.000 silver electrode as a working electrode and a Metrohm 6.0718.000 silver electrode as a reference. In general, a given experimental run consisted of collecting many equilibrium data points when solutions of silver perchlorate ($2 < c^\circ_M < 10$ mmol dm^{-3}) were titrated with solutions of the ligands ($10 < c^\circ_L < 100$ mmol dm^{-3}). Titrations were performed with at least three different initial silver(I) concentrations and some titrations were carried out in duplicate to verify the reproducibility of the system. The electrode couple was periodically checked in dmso or pc solutions containing no coordinating ligands. In the concentration range $10^{-5} < [Ag^+] < 10^{-2}$ mol dm^{-3}, the emf values varied with the metal ion concentration according to Nernst's law. The computer program Superquad[53] was used for the calculation of the stability constants.

Calorimetric measurements

A Tronac model 87-558 precision calorimeter was employed to measure the heats of reaction. The calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (tham) with a standard solution of HCl in water. The experimental value of the heat of neutralization of tham was found to be $\Delta H^\circ = -47.48$ kJ mol^{-1}, in good agreement with the accepted value of -47.53 ± 0.13 kJ mol^{-1}.[54]

The calorimetric titrations were performed at 298.00 ± 0.02 K by adding known volumes of ligand solutions ($30 < c^\circ_L < 120$ mmol dm^{-3}) to 20 ml of silver(I) solution ($2.00 < [Ag^+] < 10.00$ mmol dm^{-3}). In order to reach higher ligand-to-metal ratios, some "reverse" calorimetric titrations were carried out. In these titrations metal ion solutions ≈ 50 mmol dm^{-3} were added to solutions of ligand ≈ 100 mmol dm^{-3}. The heats of dilution of the reactants, determined in separate runs, were found negligible. The least squares computer program Letagrop Kalle[55] was used for the calculation of the enthalpy changes.

NMR and IR measurements

The NMR spectra were recorded on a Bruker AC 200 F QNP spectrometer equipped with a variable-temperature probe, temperatures were calibrated with methanol. ^{31}P-{^1H} spectra were obtained at 298 K (dmso) or in the range 298–228 K (pc). Positive ^{31}P chemical shifts are downfield from 85% H_3PO_4 external standard. Measurements were performed on 10^{-2} mol dm^{-3} Ag^+ solutions, where the ratio $R_c = c_L/c_M$ varied in the range 1.0–3.0. All solutions were freshly prepared by dissolving the anhydrous reagents in the solvent concerned. ^1H NMR spectra for the Ag(I)–Me_2Npe system were recorded at 298 K. Samples were prepared by adding neat Me_2Npe (8 portions of 5 µl) to a dmso-d_6 solution (0.5 ml) containing 8.4 mg of anhydrous $AgClO_4$. The ratio $R_c = c_L/c_M$ varied in the range 0.5–4.0.

The FT-IR difference spectra were recorded using a Nicolet Magna 550 spectrometer with a resolution of 1 cm^{-1}. A cell with barium fluoride windows (thickness 27 µm) was used.

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