Thermodynamic and Spectroscopic Studies on the Complexation of Silver(I) by Mixed Phosphorus–Sulfur Compounds in Propylene Carbonate. Crystal and Molecular Structure of a Silver(I)–Thiophosphine Complex†

Plinio Di Bernardo,[a] Marilena Tolazzi *,[b] and Pierluigi Zanonato[a]

[a] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, I-35131 Padova, Italy*

[b] *Dipartimento di Scienze e Tecnologie Chimiche, Via del Cotonificio 108, I-33110 Udine, Italy*

The thermodynamic parameters for complexation of silver(I) with the mixed-donor compounds Ph_2PCH_2SPh and $Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph) have been determined by potentiometric and calorimetric techniques in propylene carbonate at 25 °C and 0.1 mol dm^{-3} ionic strength (NEt_4ClO_4). Within the silver(I) concentration range investigated, Ph_2PCH_2SPh forms three successive mononuclear complexes whereas also polynuclear species are formed by the other thiophosphines. All the complexes are strongly enthalpy stabilized, the entropy changes being unfavourable. The ligands behave as either monodentate (through P) or bidentate, depending upon the length of the aliphatic chain between the donor atoms and on the stoichiometry of the species formed. The influence of R on the stabilities of the complexes is discussed. The crystal structure of the 1:1 Ag–$Ph_2P(CH_2)_2SEt$ complex has been determined: monoclinic, space group $P2_1/c$, $a = 8.924(2)$, $b = 9.620(1)$, $c = 44.797(6)$ Å, $\beta = 93.41(1)°$ and $Z = 4$. Phosphorus-31 NMR studies have also been performed to obtain additional information on the nature and structure of the species formed. Comparison of the thermodynamic data for formation of the silver(I) complexes with the same ligands in dimethyl sulfoxide evidences a different behaviour of the ligands in the two media: the results are discussed in terms of the different physicochemical properties of the two solvents.

In recent years transition-metal complexes with ligands containing dissimilar donor atoms such as phosphorus and nitrogen, phosphorus and oxygen, and phosphorus and sulfur have been widely investigated primarily for their applications as hydrogenation catalysts.[1–6] We have carried out studies on the thermodynamics of complex formation between the monovalent d^{10} acceptor silver(I) and mixed-donor compounds of the type $Ph_2P(CH_2)_nSR$ (n = 1 or 2; R = Me, Et or Ph) in the aprotic solvent dimethyl sulfoxide (dmso).[7] The results evidenced that, with these compounds, silver(I) forms only mononuclear complexes in which the thiophosphines co-ordinate only through the phosphorus atom. As thioether groups are known to have a moderately strong affinity for silver(I)[8] and be stronger donors than dmso,[9,10] these results were interpreted as due to a larger activity of the solvent which compensates for the slightly stronger donor properties of the thioether groups. The determinant influence of the solvent on the complex formation is clearly seen in this example.

Specific solvent effects can be studied by using solvents with different donating powers. In particular, a medium with weaker solvating properties toward silver(I) than those of dmso should show up the ability of thioether groups to co-ordinate. In the present study the thermodynamic functions for the formation of silver(I) complexes with mixed P,S-donors, in the aprotic solvent propylene carbonate (pc) (4-methyl-1,3-dioxolan-2-one) are reported, and the results compared with those previously obtained for the same systems in dmso.[7] The donor compounds investigated, which possess different basicities and steric properties, are diphenylphosphino(phenylsulfanyl)methane, Ph_2PCH_2SPh, and 1-(diphenylphosphino)-2-(methylsulfanyl)ethane, -2-(ethylsulfanyl)ethane and -2-(phenylsulfanyl)ethane of general formula $Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph). Propylene carbonate (donor number = 15.1)[11] was chosen as a solvent for its weaker solvating properties toward silver(I) than those of dmso[12] (donor number = 29.8).

Potentiometric and calorimetric measurements have been employed to obtain respectively the free energy and enthalpy of the reactions. Further information on the nature and co-ordination geometry of the species formed has been obtained, in solution, by means of ^{31}P NMR spectroscopy and, in the solid state, by a crystallographic study of a complex containing silver(I) perchlorate and $Ph_2P(CH_2)_2SEt$ in equimolar ratio. As in the previous study,[7] all measurements have been performed at 25 °C and in a 0.1 mol dm^{-3} ionic medium with NEt_4ClO_4.

Experimental

Chemicals.—Anhydrous silver perchlorate was obtained from $AgClO_4 \cdot H_2O$ (Fluka puriss) as described previously.[13] Propylene carbonate (Fluka > 99%) was purified by distillation as described elsewhere.[14] The silver(I) perchlorate solutions were prepared from anhydrous $AgClO_4$ and freshly distilled pc. The silver content was checked by potentiometric titrations with chloride. The background salt NEt_4ClO_4 was recrystallized from methanol and dried at 110 °C. The donor compounds were prepared according to reported methods[15] and doubly recrystallized from CH_2Cl_2–EtOH. Their purity was checked by measuring melting points on a Buchi 512 apparatus and by ^{31}P-{^1H} NMR spectroscopy. Solutions were prepared by dissolving weighed amounts of the thiophosphines in anhydrous pc and adding NEt_4ClO_4 to give an ionic strength of 0.1 mol dm^{-3}. These solutions were prepared afresh before each titration in a glove-box under an atmosphere of dry, oxygen-

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

free, nitrogen to exclude moisture and prevent oxidation. Infrared and ^{31}P NMR measurements, performed after each titration, did not reveal a significant presence of phosphine oxide within 24 h. The water content in the solutions, typically 10–20 ppm, was determined by a Metrohm 684 KF coulometer.

Potentiometric Measurements.—The experimental data for the calculation of the stability constants of the silver(I) thiophosphine complexes were obtained from potentiometric determination of the equilibrium concentrations of the silver ion in solutions obtained by adding a thiophosphine to a known volume of silver(I) perchlorate of initial concentration, $c^0{}_{Ag}$, ranging from 2 to 10 mmol dm^{-3}. The galvanic cell and other experimental details were previously described.[13] Titrations were performed with at least three different initial silver(I) concentrations. A few titrations were also carried out in duplicate. The electrode response, periodically checked in the concentration range $10^{-5} < [Ag^+] < 10^{-2}$ mol dm^{-3}, did not show significant deviations from Nernst's law. The potential measurements were made with a PHM 84 Radiometer potentiometer, equipped with a Metrohm 6.0328.000 silver electrode as a working electrode and a Metrohm 6.0718.000 silver electrode as a reference The stability constants were calculated using the computer program SUPERQUAD.[16]

Calorimetric measurements.—A Tronac model 87-558 precision calorimeter was used to determine the heats of reaction. The calorimeter titrations were performed as described previously.[14] For each system, silver ion solutions of concentration $c^0{}_{Ag}$ ranging between 2 and 10 mmol dm^{-3} were titrated with thiophosphine solutions of concentration $40 < c^0{}_L < 80$ mmol dm^{-3}. The heats of dilution of the metal ion and of the thiophosphine solutions were so small that no corrections of the experimental heat changes were necessary. The program LETAGROP-KALLE[17] was employed for the determination of the reaction enthalpies.

^{31}P *NMR Measurements.*—The ^{31}P-{^{1}H} NMR spectra were recorded between 298 and 224 K on a Bruker AM400 unlocked spectrometer equipped with a VT 1000 variable-temperature probe operating at 161.978 MHz in the Fourier-transform mode. Power-gated decoupling was used. Chemical shifts are referenced to external 85% H_3PO_4 with downfield positive shifts. Measurements were performed on 10^{-2} mol dm^{-3} silver(I) solutions, where the ratio $R_c = c_L/c_{Ag}$ varied in the range 0.2–3.0 : 1. All the solutions were prepared afresh by dissolving the anhydrous reagents in pc.

Crystal Structure Determination.—*Preparation of the crystalline compound.* To an anhydrous pc solution containing $AgClO_4$ and $Ph_2P(CH_2)_2SEt$ in a 1 : 1 molar ratio, diethyl ether was added slowly and an oil was initially obtained. The oil was isolated, dissolved in the minimum volume of pc and white crystals were then grown by slow diffusion of diethyl ether vapours in the pc solution.

Crystal data. $C_{32}H_{38}Ag_2Cl_2O_8P_2S_2$ (Found: C, 40.00; H, 4.05; Ag, 22.60. Calc.: C, 39.90; H, 4.00; Ag, 22.40%), M = 963.36, monoclinic, space group $P2_1/c$, a = 8.924(2), b = 9.620(1), c = 44.797(6) Å, β = 93.41(1)°, U = 3839.0 Å^3, Z = 4, D_c = 1.67 Mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 13.82 cm^{-1}, F(000) = 1936, room temperature, crystal dimensions 0.3 × 0.3 × 0.4 mm, R = 0.0893 (R' = 0.0990) with 238 refinable parameters, maximum shift/error ratio equal to 0.55 : 1.

Data collection and processing. 6081 Reflections were measured on a CAD-4 diffractometer with ω scan in the range $6 < 2\theta < 48°$ ($\pm h,k,l$ octants; maximum hkl 10,10,50): of these 1355 were considered observed having $I > 2\sigma(I)$. Three standard reflections were periodically monitored over the data collection time (89.8 h), a steady intensity decrease being detected up to 7.5%. Observed intensities were corrected for the loss in intensity and for Lorentz and polarization factors. No experimental absorption correction was applied due to the difficulty in finding suitable reflections for ψ-scan measurements; instead a computational correction was evaluated according to the method of Walker and Stuart[18] with a computer program written by Ugozzoli.[19]

The small number of observed reflections, in spite of the low acceptance limit adopted, is due to the poor quality of the crystals. The impossibility of obtaining crystals of better quality, in spite of numerous attempts, might be related to the presence of a polymeric species within the crystal lattice. This is surely a severe drawback for the accuracy of the refined structural model and is responsible for the rather high final R value, but does not invalidate the overall features of the structure, in particular the atomic connectivity showing the copresence of a dimer and a polymer constituted by the same repeat unit.

Structure analysis and refinement. The structure was solved with SHELXS 86,[20] adopting the direct methods approach, and refined with SHELX 76.[21] Hydrogen atoms were located at calculated posission andin the last cycles, after the absorption correction, only the two independent Ag atoms were allowed to refine with an an sotropic thermal parameter. Unit weights were adopted throughout the refinement procedure.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

The best fit of the potentiometric data for each system was obtained when the species reported in Table 1 were taken into account. The overall stability constants for the reactions $m\mathrm{Ag}^+ + j\mathrm{L} \rightleftharpoons [\mathrm{Ag}_m\mathrm{L}_j]^{m+}$ and the corresponding error limits are also listed. The distribution of silver(I) between the different complexes, as a function of the ligand-to-metal ratio, $R_c = c_L/c_{Ag}$, for the different systems is given in Fig. 1.

The heats of reaction per mole of metal ion, Δh_v, are reported in Fig. 2 as a function of c_L/c_{Ag}. These data and the overall stability constants were used in the minimizing program to obtain the overall enthalpy changes reported in Table 1 together with the free energy and entropy changes. The calculated Δh_v values for the various systems (solid lines in Fig. 2) fit the experimental data quite well indicating that the systems are satisfactorily described by the parameters reported in Table 1. For comparison, the thermodynamic data for the system silver(I)–triphenylphosphine previously determined in pc[14] are also given in the same table.

The most important ^{31}P NMR data for the investigated species are collected in Table 2. Fig. 3 shows, as an example, the spectra at 298 and 224 K of solutions containing silver(I) and the thiophosphine $Ph_2P(CH_2)_2SEt$ at various ratios.

X-Ray analysis on the crystal adduct shows the copresence of polymeric species and cyclic dimers within the same lattice so that the cell content is composed of two independent units: unit (a) which is part of the polymeric species and may be denoted as $\frac{1}{n}[(AgL)_n(ClO_4)_n]$ and unit (b) which is part of a cyclic dimer and may be denoted as $\frac{1}{2}[(AgL)_2(ClO_4)_2]$. Figs. 4 and 5 show arbitrary views of these crystal units along with the labelling scheme. Final atomic coordinates for these crystal units are listed in Table 3, selected interatomic distances, angles and torsion angles in Table 4.

Discussion

The data in Table 1 show that a common feature of all the thiophosphines is the formation of successive mononuclear complexes $[AgL_j]^+$, j = 1–3. Moreover, in the Ag^+–$Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph) systems a very stable dinuclear species $[Ag_2L]^{2+}$ is formed when the metal-to-ligand ratio is still fairly large; in addition with $Ph_2P(CH_2)_2SR$ (R = Me or

Table 1 Overall stability constants and thermodynamic functions for silver(I)–thiophosphine systems in pc at 25 °C and I = 0.1 mol dm^{-3}; ΔG°_j and ΔH°_j in kJ mol^{-1}, ΔS°_j in J K^{-1} mol^{-1}

Ligand	Complex	log β_j	$-\Delta G^{\circ}_j$	$-\Delta H^{\circ}_j$	$-\Delta S^{\circ}_j$
PPh_3*	$[AgL]^+$	9.95(3)	56.8(2)	70.5(7)	46
	$[AgL_2]^+$	17.17(3)	98.0(2)	122.3(6)	82
	$[AgL_3]^+$	21.41(4)	122.2(3)	167(2)	150
Ph_2PCH_2SPh	$[AgL]^+$	10.05(9)	57.4(5)	73.2(5)	53
	$[AgL_2]^+$	16.48(8)	94.1(4)	114.3(6)	68
	$[AgL_3]^+$	20.65(7)	117.9(4)	157(8)	131
$Ph_2P(CH_2)_2SMe$	$[AgL]^+$	12.08(10)	68.9(6)	87(3)	61
	$[AgL_2]^+$	21.70(8)	123.9(4)	152(1)	94
	$[AgL_3]^+$	24.43(9)	139.4(5)	182(4)	143
	$[Ag_2L]^{2+}$	15.09(20)	86(1)	105(3)	64
	$[Ag_2L_2]^{2+}$	26.79(23)	152.9(7)	201(9)	161
$Ph_2P(CH_2)_2SEt$	$[AgL]^+$	12.15(10)	69.3(6)	88(3)	63
	$[AgL_2]^+$	21.86(9)	124.8(5)	152(1)	91
	$[AgL_3]^+$	24.57(8)	140.2(5)	179(3)	130
	$[Ag_2L]^{2+}$	15.4(3)	88(2)	106(3)	60
	$[Ag_2L_2]^{2+}$	27.1(2)	155(1)	200(5)	151
$Ph_2P(CH_2)_2SPh$	$[AgL]^+$	10.90(9)	62.2(5)	78(2)	53
	$[AgL_2]^+$	19.48(18)	111(1)	137(1)	87
	$[AgL_3]^+$	22.8(3)	130(2)	177(2)	158
	$[Ag_2L]^{2+}$	13.43(12)	76.7(6)	100(5)	78

* Ref. 14.

Table 2 Phosphorus-31 NMR data

Ligand	R_c = c_L/c_{Ag}	δ 298 K	δ 224 K	$J(^{31}P-^{107}Ag)$/ Hz
Ph_2PCH_2SPh	1.0	14.9	12.8	570
	2.0	≈6	4.1	515
	3.0	3.0	0.9	325
$Ph_2P(CH_2)_2SMe$	0.2	6.8		
	1.0	2.4		
	2.0	≈0	−0.5	407
	3.0	−2.9	≈ −1.4	≈300*
$Ph_2P(CH_2)_2SEt$	0.2	6.4		
	1.0	2.6		
	2.0	≈0	−0.4	401
	3.0	−2.8	≈ −1.4	≈300*
$Ph_2P(CH_2)_2SPh$	0.2	6.5		
	1.0	2.4		
	2.0	≈1	0.4	451
	3.0	−2.3	−0.9	295

* May be interpreted as the average of the $^{31}P-^{107,109}Ag$ coupling constants, which therefore can be estimated as 280 and 320 Hz, respectively [$J(^{31}P-^{109}Ag) = 1.15 \times J(^{31}P-^{107}Ag)$].

Et) the dinuclear complex $[Ag_2L_2]^{2+}$ is the prevalent species at R_c = 1 : 1 (Fig. 1).

From the analysis of the ΔH°_j and ΔS°_j values it is seen that the silver(I) complexes with thiophosphines are all formed in exothermic reactions and that their stabilities depend only on the enthalpy terms as the entropy terms are all negative. This is a consequence of the formation of strong metal-to-ligand bonds and the weak solvation of the reagents in pc.[12]

Ph_2PCH_2SPh *Complexes*.—The thermodynamic parameters for all the complexes of silver(I) with this thiophosphine are of the same order of magnitude as those for the complexes with unidentate triphenylphosphine in the same solvent.[14] This feature and the consideration that with this ligand bidentate co-ordination would lead to the formation of highly strained four-membered chelate rings exclude the co-ordination of both donor atoms to the metal ion and suggest that only the more basic phosphorus atom[22] is bonded to silver(I); ^{31}P NMR spectroscopy confirms this observation (see below).

In spite of the not negligible affinity of thioether groups for silver(I),[8] Ph_2PCH_2SPh does not form the dinuclear complex $[Ag_2L]^{2+}$. This can be explained as due on the one hand to the low basicity of the sulfur atom of this compound[22] (on the contrary, the diphosphine $Ph_2PCH_2PPh_2$ forms in pc only polynuclear species[14]) and on the other to the strong repulsion that would occur if two silver cations were simultaneously co-ordinated to its donor centres.

$Ph_2P(CH_2)_2SR$ (R = Me, Et *or* Ph) *Complexes*.—The $[AgL]^+$ complexes of $Ph_2P(CH_2)_2SR$ are more stable than the corresponding complex of PPh_3. Further, their enthalpies and entropies of formation are respectively more exothermic and more negative than the corresponding ΔH°_1 and ΔS°_1 of the silver(I) complex with the unidentate phosphine. This indicates formation of chelate complexes in which both P and S atoms are co-ordinated to the silver ion.

The values of the stability constants of the $[Ag\{Ph_2P(CH_2)_2SR\}_2]^+$ complexes, close to the formation constant value of the chelate complex $[Ag(dppe)_2]^+$ [log $\beta_{1,2}$ = 21.94,[14] dppe = $Ph_2P(CH_2)_2PPh_2$], and their heats of formation, intermediate between those of $[Ag(dppe)_2]^+$ ($-\Delta H^{\circ}_{1,2}$ = 173 kJ mol^{-1})[14] and of $[Ag(PPh_3)_2]^+$ ($-\Delta H^{\circ}_{1,2}$ = 122 kJ mol^{-1}), suggest that also in these complexes both ligands are bidentate. The crystal structure of the crystalline compound $[Ag\{Ph_2P(CH_2)_2SEt\}_2][ClO_4]$,[23] in which the silver atom is co-ordinated in a slightly distorted tetrahedral configuration to both the donor atoms of the ligands, supports this hypothesis. The heats of formation of the thiophosphine chelates, less exothermic than that of the bis(dppe) silver complex, and the shorter distance between the metal ion and the phosphorus atom (2.456 Å) as compared with that between silver and sulfur (2.694 Å) in the above-mentioned compound, confirm that, when the thiophosphines are bidentate, the thioether functions bond more weakly to the silver ion than do the phosphine groups.[22]

The abrupt decrease in the stepwise stability constants for the formation of the 1 : 3 complexes indicates that a rearrangement of the ligands around the metal ion must occur when these complexes are formed. Thermodynamic data and ^{31}P NMR measurements, which show three equivalent P atoms co-ordinated when R_c = 3 : 1, support the conclusion that in these complexes the three ligands are monodentate through the P atom.

From the potentiometric data treatment it is found that the presence of the $[Ag_2L_2]^{2+}$ complex is essential to obtain a good

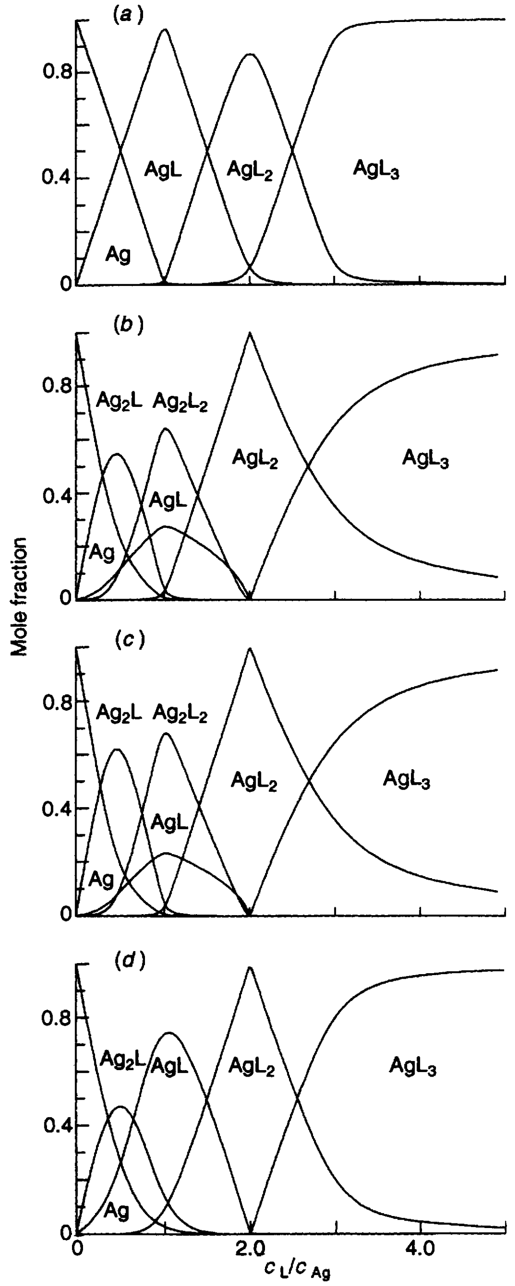
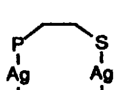


Fig. 1 Distribution curves for the silver(I)–thiophosphine systems in propylene carbonate at c^0_{Ag} = 10 mmol dm^{-3}. (*a*) Ph_2PCH_2SPh, (*b*) $Ph_2P(CH_2)_2SMe$, (*c*) $Ph_2P(CH_2)_2SEt$ and (*d*) $Ph_2P(CH_2)_2SPh$



I

II

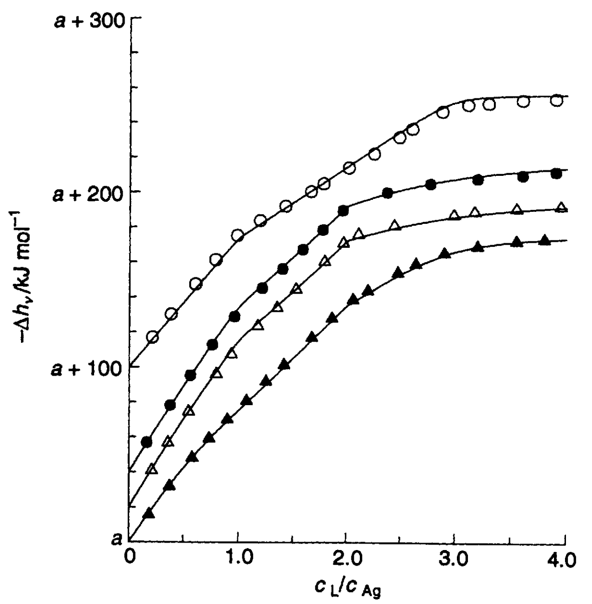


Fig. 2 The total molar enthalpy changes, Δh_v, as a function of $R_c = c_L/c_{Ag}$ for silver(I)–thiophosphine systems in propylene carbonate at c^0_{Ag} = 5.0 mmol dm^{-3}. (○) $a = -100$ for Ph_2PCH_2SPh, (●) $a = -40$ for $Ph_2P(CH_2)_2SMe$, (△) $a = -20$ for $Ph_2P(CH_2)_2SEt$ and (▲) $a = 0$ for $Ph_2P(CH_2)_2SPh$. The solid lines have been calculated from the values of β_j and $\Delta H^\circ{}_j$ in Table 1

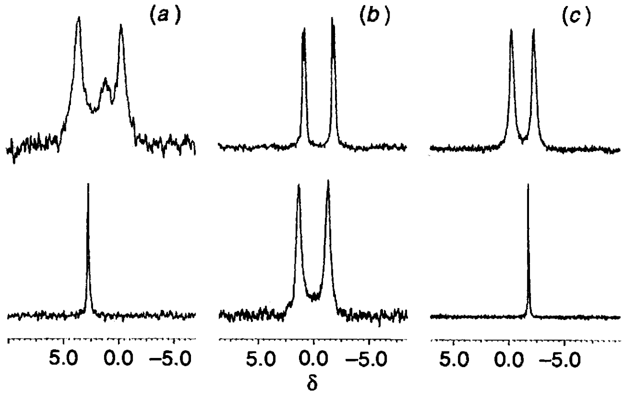


Fig. 3 The ^{31}P-{^1H} NMR spectra obtained at 298 (below) and 224 K (above) for the Ag^I–$Ph_2P(CH_2)_2SEt$ system at R_c = 1.0 (*a*), 2.0 (*b*) and 3.0 : 1 (*c*)

fit of the experimental data for the Ag–$Ph_2P(CH_2)_2SR$ (R = Me or Et) systems. It is not easy to draw conclusions on the structure of this species as the crystals obtained from 1 : 1 solutions of Ag^+ and $Ph_2P(CH_2)_2SEt$ show the copresence of both a cyclic dimer I and a polymer II indicating that neither structure is particularly favoured in the solid state. Moreover, the NMR measurements (see below) do not improve the description of the probable structure. A reasonable hypothesis can be derived from the thermodynamic data. The enthalpy of formation of $[Ag_2L]^{2+}$ complexes formed by $Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph) ($\Delta H^\circ{}_{2,1}$ = −105, −106 and −100 kJ mol^{-1} respectively) as compared with $\Delta H^\circ{}_{2,1}/2$ for the formation of the corresponding dppe complex (−72 kJ mol^{-1})[14] indicates that about 31 kJ mol^{-1} are evolved for each Ag–S bond. Formation of the cyclic dimer I should involve two Ag–P and two Ag–S bonds with ΔH_I = −210 kJ mol^{-1}, whereas to the linear dimer II should complete two Ag–P and one Ag–S bond and ΔH_{II} = 2(−72) + (−31) = −175 kJ mol^{-1}. The enthalpy of formation of the $[Ag_2L_2]^{2+}$ complex (about −200 kJ mol^{-1}) is slightly less exothermic than that calculated for I and much more exothermic than that established for II: this fact, together with the observation that in the cyclic dimer a certain strain is present in the solid state (see below), suggests that the formation of species I in solution is at least more probable than of II. This seems also to be confirmed by recent detailed thermodynamic and spectroscopic studies on the interaction of silver(I) with $Ph_2P(CH_2)_2PPh_2$, a structural analogue of the thiophosphines considered here, which have established the formation, in dmso[24] and pc,[14] of a similar annular structure.

In contrast with what is observed for the Ag–Ph_2PCH_2SPh

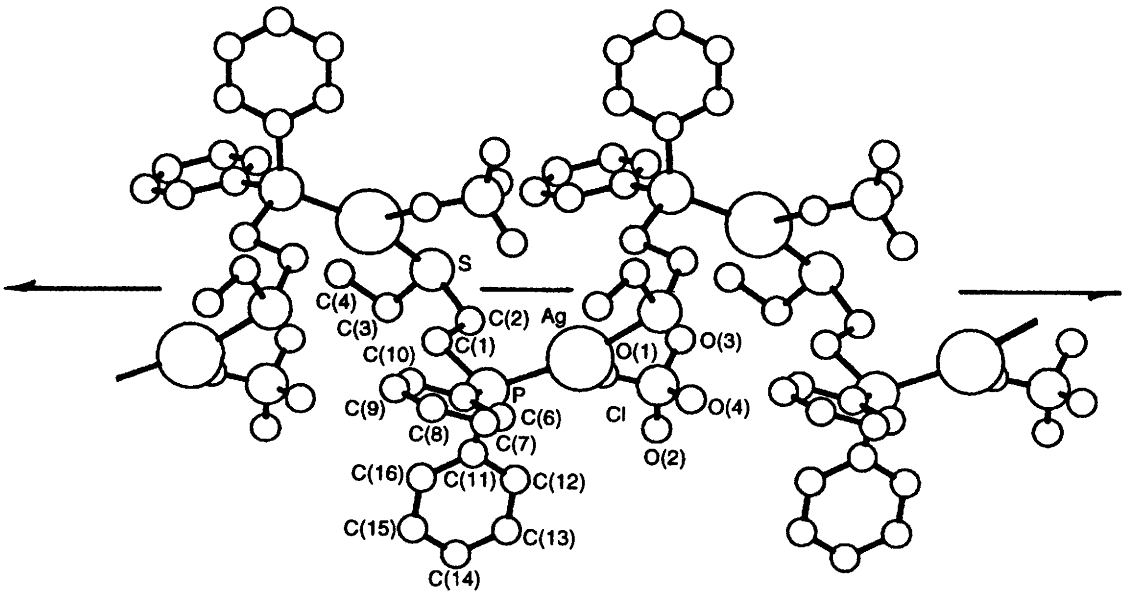


Fig. 4 Arbitrary view of unit (a)

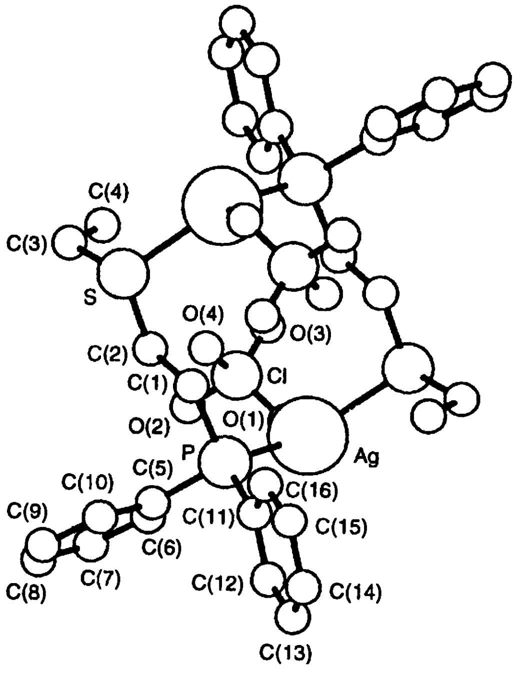


Fig. 5 Arbitrary view of unit (b)

system, the dinuclear $[Ag_2L]^{2+}$ complex is a fairly important species for all the other thiophosphine systems. Evidently, the insertion of one more CH_2 group between the phosphorus and the sulfur atoms gives rise to a larger separation between the donor atoms thus weakening the repulsion between the two co-ordinated silver ions.

As already mentioned, within the same class of ligands $Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph), the stability and the favourable enthalpy of formation of the silver complexes increase in the order Ph $\ll$ Me < Et, consistent with a higher nucleophilicity of the ethyl thioether group as compared with the methyl and phenyl ones.[25] In addition to the lower nucleophilicity of the SPh group, also the steric hindrance of the phenyl group might be responsible for both the lower stability and exothermicity of $[Ag\{Ph_2P(CH_2)_2SPh\}_n]^+$ ($n = 1$ or 2) chelate complexes (with respect to the other chelates) and for the inability of $Ph_2P(CH_2)_2SPh$ to form in a detectable amount the annular $[Ag_2L_2]^{2+}$ complex.

Recent studies[7] have demonstrated that in dmso the present thiophosphines form complexes with silver(I) where they bond only through the phosphorus atoms. In pc these compounds are prevalently bidentate and also form polynuclear complexes. Such a different behaviour in the two solvents is mainly to be attributed to the weaker solvation of silver(I) in pc than in dmso, as indicated by the very endothermic heat of transfer of Ag^+ between dmso and pc, $\Delta H^{\circ}_{\mathrm{tr(dmso \longrightarrow pc)}} = 37.3$ kJ mol^{-1}.[12] As the co-ordination of a donor atom to a metal ion in solution occurs in competition with solvation of the species involved,[12] the weaker solvation of Ag^+ in pc favours co-ordination of the thioether groups and makes easier the formation of chelate complexes and of polynuclear species. An additional factor that should favour in particular the formation of polynuclear species in pc with respect to dmso is the different relative permittivities of the two solvents ($\varepsilon = 46.4$ and 64.4 for dmso and pc respectively[12]). The stronger electrostatic interactions in dmso should make the formation of polynuclear species, where two or more charged metal ions are close to each other, less easy in this solvent than in pc.

That solvation plays an important role in the formation and stabilization of the species in solution is further confirmed by a comparison of the thermodynamic functions for species common to the two solvents where the ligands behave in the same way (namely for the species $[AgL_3]^+$). The higher stability of the complexes and the more exothermic values of the heats of reaction in propylene carbonate are undoubtedly a consequence of the stronger solvation of the central metal ion in dmso than in propylene carbonate.

^{31}P *NMR Studies*.—In order to gain information on structural aspects of the species in solution, variable-temperature $^{31}P\text{-}\{^1H\}$ NMR measurements were made in solutions containing silver(I) and the thiophosphines in appropriate ratios. The ligand-to-silver ratios, $R_c = c_L/c_{Ag}$, were 0.2, 1.0, 2.0 and 3.0:1 depending on the species to be studied in each system. The temperature range explored, owing to the freezing point of propylene carbonate (224 K),[12] was limited to 298–224 K.

A peculiar characteristic of the ^{31}P NMR spectra of silver(I) complexes containing magnetically equivalent phosphorus atoms is the two doublets arising from coupling of the P atom to each of the spin $I = \frac{1}{2}$ silver isotopes (^{107}Ag and ^{109}Ag with 51.82 and 48.18% natural abundance, respectively). Sharp singlets, due to rapid exchange equilibria, were normally observed at room temperature for each thiophosphine and R_c

Table 3 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms of units (a) and (b)

	Unit (a)			Unit (b)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ag	958(4)	5 527(42)	2 098(8)	7 085(4)	529(5)	4 833(8)
P	425(12)	3 211(12)	1 933(2)	8 076(13)	9 466(16)	4 411(3)
S	−2 526(12)	2 347(12)	2 672(3)	12 309(13)	7 581(12)	4 801(3)
C(1)	−460(31)	2 136(29)	2 220(7)	10 111(29)	9 088(35)	4 488(8)
C(2)	−1 599(44)	3 104(36)	2 361(7)	10 327(27)	7 855(35)	4 706(8)
C(3)	−4 093(33)	1 395(36)	2 494(8)	12 236(59)	6 096(38)	5 050(9)
C(4)	−4 772(48)	326(44)	2 704(11)	11 430(56)	6 255(56)	5 342(10)
C(5)	2 118(37)	2 345(37)	1 843(8)	7 312(47)	7 810(46)	4 298(10)
C(6)	3 150(44)	2 995(44)	1 718(9)	6 059(49)	7 292(50)	4 450(10)
C(7)	4 591(44)	2 446(44)	1 655(9)	5 622(53)	5 943(52)	4 363(11)
C(8)	4 854(49)	1 103(47)	1 712(10)	6 095(59)	5 315(57)	4 110(12)
C(9)	3 799(38)	254(39)	1 846(8)	7 313(59)	5 781(62)	3 975(12)
C(10)	2 378(40)	921(40)	1 918(8)	7 833(46)	7 098(46)	4 062(10)
C(11)	−757(49)	2 983(51)	1 606(10)	7 948(44)	502(49)	4 081(9)
C(12)	−1 482(52)	4 200(54)	1 472(11)	6 624(59)	726(65)	3 932(13)
C(13)	−2 384(50)	4 075(48)	1 193(10)	6 424(64)	1 546(61)	3 678(13)
C(14)	−2 588(52)	2 873(55)	1 092(11)	7 818(61)	2 236(59)	3 592(12)
C(15)	−2 006(55)	1 690(56)	1 209(12)	9 060(67)	2 098(67)	3 734(14)
C(16)	−1 011(56)	1 775(57)	1 462(12)	9 201(68)	1 254(63)	3 978(14)
Cl	1 917(12)	2 982(12)	2 984(3)	6 479(13)	8 063(12)	5 397(3)
O(1)	1 625(29)	1 557(14)	2 916(6)	5 737(38)	9 180(30)	5 241(7)
O(2)	3 120(30)	3 080(31)	3 207(6)	7 916(21)	7 846(39)	5 282(7)
O(3)	2 316(36)	3 688(26)	2 720(5)	5 603(39)	6 829(26)	5 359(9)
O(4)	605(26)	3 604(28)	3 092(8)	6 659(37)	8 394(37)	5 707(3)

investigated, except for $R_c = 2.0:1$ where two large resonances appeared (Fig. 3, for example).

$R_c = 0.2$. All the silver(I)–thiophosphine systems (except Ag^I–Ph_2PCH_2SPh) were investigated with the purpose of obtaining information on the dinuclear complex $[Ag_2L]^{2+}$. The singlets observed at 298 K broadened with decreasing sample temperature, but even at 224 K very large signals were obtained. Thus, no information on these complexes could be obtained.

$R_c = 1.0$. The singlet observed at 298 K for the Ag–Ph_2PCH_2SPh system split into two well resolved doublets at 224 K. The spectrum indicates that only one species is present in solution. Moreover, the $J(^{31}P–^{107}Ag)$ value of 570 Hz is in the range expected when only one P atom is bonded to silver(I), as found for complexes with tertiary phosphines or phospholes.[14,26–29] This is in agreement with the thermodynamic data which show that the mononuclear species $[AgL]^+$ is the only complex formed in solution at $R_c = 1$.

For the Ag–$Ph_2P(CH_2)_2SR$ (R = Me, Et or Ph) systems, a splitting of the singlet was observed on lowering the temperature but even at 224 K the spectra were unresolved showing two (for R = Ph) or more than two (for R = Me or Et) broad signals. This spectral pattern is indicative of the presence of more than one species in solution for which the exchange processes are not frozen out even at low temperature. These species have already been identified in the elaboration of the thermodynamic data as $[Ag_2L]^{2+}$, $[AgL]^+$ and $[AgL_2]^+$ (for R = Ph) and as $[AgL]^+$ and $[Ag_2L_2]^{2+}$ (for R = Me or Et) (Fig. 1).

$R_c = 2.0$. For all the silver(I)–thiophosphine systems at 224 K ($[AgL_2]^+$ exclusively present) the typical two doublets expected for the slow-exchange limit spectrum were obtained [Fig. 3(*b*)]. The $J(^{31}P–^{107}Ag)$ values (from 401 to 515 Hz, see Table 2) agree well with literature data[26–29] concerning compounds where two P atoms are bonded to one silver ion. The increase in $J(^{31}P–^{107}Ag)$ values parallels the increase in phosphorus electron-withdrawing power, as already found in other silver(I)–phosphorus compounds.[29]

$R_c = 3.0$. Two well shaped doublets were shown by the low-temperature spectra for the two silver(I)–phenylsulfanylphosphine systems, whereas for the $Ph_2P(CH_2)_2SMe$ and $Ph_2P(CH_2)_2SEt$ systems the two resonances were still somewhat broad [Fig. 3(*c*)] but indicative of almost slow-exchange limit spectra. The spectral patterns suggest the presence of a largely predominant complex: as the separation between the signals (about 300 Hz) is in the range of values expected when three P atoms are bonded to one silver ion,[14,27–29] this species can be identified as $[AgL_3]^+$.[*] The presence of three magnetically equivalent phosphorus atoms in the low-temperature spectra enables us to conclude that in the $[AgL_3]^+$ complexes all the ligands are monodentate.

Description of the Structure.—The polymer propagates along the binary screw axis (Fig. 4) and the cyclic dimer presents a centre of symmetry (Fig. 5). No solvent molecules are present in the unit cell. This was also true in the crystal structure of the 1 : 2 chelate silver complex $[Ag\{Ph_2P(CH_2)_2SEt\}_2][ClO_4]$, obtained from a propylene carbonate solution containing 2 mol of the thiophosphine per mol of metal ion.[23] This is certainly due to the weak affinity of this solvent toward silver(I).[12]

In both units (a) and (b) the silver atoms show distorted trigonal geometry. Each ligand molecule connects two silver ions through the phosphorus and sulfur atoms. In the polymer this gives rise to a chain (Fig. 4), in the dimer to a cyclic structure (Fig. 5). The third co-ordination position is occupied in both cases by an oxygen atom of the perchlorate ion. The distances of the silver(I) ions from the plane defined by co-ordinated P, O and S atoms are of 0.11 and 0.34 Å in units (a) and (b) respectively, which reflect a slight distortion from planarity of the trigonal co-ordination of Ag^I.

Examples of three-co-ordinate silver have been reported in the literature.[30–32] In bis(tricyclohexylphosphine)silver(I) perchlorate[30] and in a series of bis(dialkylphosphinomethyl)benzo[*c*]phenanthrene complexes of Ag^I,[31,32] the Ag–P bond

---

[*] By application of the van't Hoff law, considering ΔH°_{j} constant in the temperature range investigated, one can show that when $R_c = 3.0:1$ the $[AgL_2]^+$ species never exceeds 6% of the total silver concentration at 224 K.

Table 4 Molecular dimensions (distances in Å, angles in °) for units (a) and (b)

	Unit (a)	Unit (b)
Ag–P	2.387(12)	2.369(13)
Ag–S	2.433(11)	2.485(12)
Ag–O(1)	2.506(25)	2.592(32)
P–C(1)	1.864(31)	1.864(28)
P–C(5)	1.792(36)	1.793(46)
P–C(11)	1.795(48)	1.779(44)
S–C(2)	1.815(38)	1.814(26)
S–C(3)	1.815(33)	1.814(41)
C(1)–C(2)	1.540(56)	1.540(49)
C(3)–C(4)	1.540(55)	1.540(66)
S–Ag–O(1)	103.4(5)	89.7(8)
P–Ag–O(1)	101.3(6)	123.9(8)
P–Ag–S	154.5(4)	139.9(5)
Ag–P–C(1)	112.9(10)	110.0(12)
Ag–P–C(5)	110.4(13)	117.1(16)
Ag–P–C(11)	118.1(17)	114.3(16)
C(1)–P–C(5)	107.2(15)	103.2(18)
C(1)–P–C(11)	104.3(18)	106.1(16)
C(5)–P–C(11)	103.1(20)	105.0(20)
Ag–S–C(2)	109.7(13)	102.7(11)
Ag–S–C(3)	103.4(12)	100.7(14)
C(2)–S–C(3)	103.9(17)	100.9(19)
P–C(1)–C(2)	105.3(20)	110.6(18)
S–C(2)–C(1)	114.4(23)	110.2(17)
S–C(3)–C(4)	113.0(24)	118.6(30)
P–C(5)–C(6)	120.9(31)	118.0(34)
P–C(5)–C(10)	121.3(26)	121.5(34)
P–C(11)–C(12)	118.2(35)	121.0(36)
P–C(11)–C(16)	125.6(39)	122.6(35)
Torsion angles		
Ag–P–C(11)–C(12)	−6.6(4.4)	−71.9(4.3)
Ag–P–C(5)–C(6)	−37.4(3.6)	5.9(4.1)
Ag–P–C(1)–C(2)	41.1(2.2)	73.2(2.2)
C(5)–P–C(1)–C(2)	162.9(2.2)	−52.5(2.7)
C(11)–P–C(1)–C(2)	−88.3(2.3)	−162.7(2.4)
C(11)–P–C(5)–C(10)	−92.8(3.3)	53.5(4.2)
Ag–S–C(3)–C(4)	48.5(2.6)	43.2(3.6)
Ag–S–C(2)–C(1)	24.8(2.7)	76.9(2.1)
C(2)–S–C(3)–C(4)	163.2(2.6)	−62.2(3.7)
C(3)–S–C(2)–C(1)	−85.2(2.6)	−179.4(2.4)
P–C(1)–C(2)–S	−175.4(1.8)	−175.7(1.6)

lengths were found in the range 2.46–2.39 Å and compare well with the values in the present work. The Ag–S bond lengths are longer than the Ag–P ones, as expected on the basis of the weaker Ag–S bond strength.[22] These values are within the expected range, being comparable with those observed in other silver(I) compounds.[33–36]

The bond angles (Table 4) around the silver centre in the polymer are larger than in the dimer: this is consistent with the dimeric species being more constrained than the polymeric one.

Acknowledgements

Support of this work by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica is gratefully acknowledged. We are grateful to Professor S. Bruckner and Dr. A. Del Zotto for helpful discussion, to Dr. P. Martinuzzi and Mr. P. Polese for technical assistance.

References

1 J. P. Farr, M. M. Olmstead, C. H. Lindsay and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 1182.
2 J. P. Farr, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1986, **102**, 6654.
3 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
4 G. K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.
5 A. Del Zotto, A. Mezzetti, P. Rigo, M. Bressan, F. Morandini, A. Morvillo, *Inorg. Chim. Acta*, 1989, **158**, 151 and refs. therein.
6 S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365.
7 P. Di Bernardo, P. Zanonato, M. Tolazzi and G. Tomat, *Inorg. Chim. Acta*, 1990, **177**, 25.
8 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
9 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, 1987, **127**, 15.
10 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, 1987, **127**, 25.
11 V. Guttmann, *Coordination Chemistry in Non-aqueous Solution*, Springer, Wien, 1968.
12 S. Ahrland, in *The Chemistry of Non-aqueous Solvents*, ed. J. J. Lagowsky, Academic Press, New York, 1978, vol. 5a.
13 A. Cassol, P. Di Bernardo, P. Zanonato, R. Portanova and M. Tolazzi, *J. Chem. Soc., Dalton Trans.*, 1987, 657.
14 A. Del Zotto, P. Di Bernardo, M. Tolazzi, G. Tomat and P. Zanonato, *J. Chem. Soc., Dalton Trans.*, 1993, 3009.
15 A. R. Sanger, *Can. J. Chem.*, 1983, **61**, 2214.
16 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1995.
17 R. Arnek, *Ark. Kemi*, 1970, **32**, 81.
18 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
19 F. Ugozzoli, ABSORB, *Comput. Chem.*, 1987, **11**, 109.
20 G. M. Sheldrick, SHELXS 86, *Program for Crystal Structure Determination*, University of Göttingen, 1986.
21 G. M. Sheldrick, SHELX 76, *Program for Crystal Structure Determination*, University of Cambridge, 1976.
22 H. Maskill, in *The General Basis of Organic Chemistry*, Oxford University Press, Oxford, 1985, ch. 5.
23 P. Di Bernardo, M. Tolazzi and P. Zanonato, *Inorg. Chim. Acta*, 1994, **215**, 199.
24 P. Di Bernardo, G. Dolcetti, R. Portanova, M. Tolazzi, G. Tomat and P. Zanonato, *Inorg. Chem.*, 1990, **29**, 2589.
25 M. Charton, *J. Org. Chem.*, 1964, **29**, 1222.
26 R. G. Goel and P. Pilon, *Inorg. Chem.*, 1978, **17**, 2876.
27 S. M. Socol and J. G. Verkade, *Inorg. Chem.*, 1984, **23**, 3487.
28 E. C. Alyea, J. Malito and J. H. Nelson, *Inorg. Chem.*, 1987, **26**, 4294.
29 S. Attar, N. W. Alcock, G. A. Bowmaker, J. S. Frye, W. H. Bearden and J. H. Nelson, *Inorg. Chem.*, 1991, **30**, 4166.
30 M. Camalli and F. Caruso, *Inorg. Chim. Acta*, 1988, **144**, 205 and refs. therein.
31 M. Camalli and F. Caruso, *Helv. Chim. Acta*, 1984, **67**, 1603.
32 M. Barrow, H.-B. Burgi, M. Camalli, F. Caruso, E. Fisher, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.*, 1983, **22**, 2356.
33 A. Muller, H. Bogge and U. Shimanski, *Inorg. Chim. Acta*, 1983, **69**, 5.
34 D. D. Heinrich, J. P. Fackler, jun., and P. Lahuerte, *Inorg. Chim. Acta*, 1986, **116**, 15.
35 M. G. B. Drew, R. J. Hobson, P. P. E. M. Mumba and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1987, 1569.
36 I. G. Dance, L. J. Fitzpatrick, D. C. Craig and M. L. Scudder, *Inorg. Chem.*, 1989, **28**, 1853.

Received 25th *October* 1994; *Paper* 4/06528J