Complexation of [ω-diphenylphosphinoalkyl]diphenylphosphine sulphides with AgNO₃

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Abstract

By reaction of [ω-diphenylphosphinoalkyl]diphenylphosphine sulphides $Ph_2P(CH_2)_nP(S)Ph_2$ ($n = 2–4$) ($L^1–L^3$) with $AgNO_3$ in CH_3CN crystalline complexes with the composition metal:ligand 1:1 [$Ag(L^1)NO_3$, $Ag(L^2)NO_3$, $Ag(L^3)NO_3$] and 1:2 [$Ag(L^1)_2NO_3$, $Ag(L^3)_2NO_3$] were isolated. According to the X-ray analysis data, the crystals of $Ag(L^1)NO_3$ are constructed from centrosymmetric dimeric molecules based on the 12-membered macrocycle $\overline{AgSPCH_2CH_2PAgSPCH_2CH_2P}$. Each of the neutral ligands L^1 is a bridge between two silver ions and each of the silver ions is coordinated by a chelating NO_3 group. According to the IR spectra, the other 1:1 complexes also have an analogous structure. In the 1:2 complexes the coordinated NO_3 groups of the 1:1 complexes are replaced by the phosphine sulphide ligand. The downfield shifts of the signals of P^{III} and P^V atoms in ^{31}P NMR spectra of 1:2 complexes in comparison with the free ligands L^1 and L^3 reflect a participation of the P^{III} atom and P=S group in complex formation. © 1997 Elsevier Science S.A.

1. Introduction

Diphosphine disulphides $Ph_2P(S)(CH_2)_nP(S)Ph_2$ are well-known as efficient ligands for various metals ions [1]. In particular the complexes of bis(diphenylthiophosphoryl)methane with silver and copper ions were studied in detail [2–4]. In recent years the mixed bidentate ligands $Ph_2P(CH_2)_nX$ ($n = 1,2$; $X = NR_2$, SR, R_2PO) [5–9] have been a subject of special interest. The complexes of these ligands with 'soft' transition metals [Rh(I), Pt(II), Ru(II)] are found to be effective catalysts. For example, the complexes of rhodium are used for hydroformylation of alkenes [8], aldehydes [6] and carbonylation of methanol [7]. As for phosphine–phosphine sulphide ligands, only the compounds $RR'PCH_2P(S)Ph_2$ with a methylene group between the phosphorus atoms were obtained earlier [10]. Their complexes with carbonyls of Group VI metals were

investigated [11]; both donor centres of the ligand took part in coordination giving a five-membered cycle. The rhodium complex of the diphenylphosphino-substituted compound $Ph_2PCH_2P(S)Ph_2$ was found to be an effective catalyst for carbonylation of methanol [12]. In this work 1:1 and 1:2 complexes of $AgNO_3$ with phosphine–phosphine sulphides $Ph_2P(CH_2)_nP(S)Ph_2$ ($n = 2–4$) ($L^1–L^3$) [13] were obtained and investigated by IR spectroscopy and X-ray analysis.

2. Experimental section

Synthesis of the ligands $L^1–L^3$ was described earlier [13]. IR spectra of ligands and their complexes were recorded on a UR-20 spectrophotometer (400–3700 cm⁻¹) with use of KBr pellets four ligands and vaseline oil suspension for complexes. ^{31}P NMR spectra were obtained on a Bruker WP-200 SY instrument (81.01 MHz, 85% H_3PO_4 as the external standard). Concentration of $CHCl_3$ solutions 0.1–0.2 M.

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2.1. 1:1 complexes

Complex Ag(L^1)NO$_3$ (1). The solutions of ligand L^1 (0.2496 g, 0.580 mmol) and AgNO$_3$ (0.0989 g, 0.580 mmol) in CH$_3$CN were mixed; after 24 h the crystals formed were separated, dried in vacuo. 0.3117 g (90%) of complex (1) was obtained. Anal. Calcd. for C$_{26}$H$_{24}$AgNO$_3$P$_2$S: Ag, 18.0; P, 10.3. Found: Ag, 18.4; P, 10.2. Similarly the other 1:1 complexes were obtained.

Complex Ag(L^2)NO$_3$ (2). Yield 72%. Anal. Calcd. for C$_{27}$H$_{26}$AgNO$_3$P$_2$S: C, 51.9; H, 4.3 N, 2.3; P, 10.2. Found: C, 52.2; H, 4.1; N, 2.2; P, 9.9.

Complex Ag(L^3)NO$_3$ (3). Yield 71%. Anal. Calcd. for C$_{28}$H$_{28}$AgNO$_3$P$_2$S: Ag, 17.7; P, 9.8. Found: Ag, 17.6; P, 9.7.

Complexes (1–3) are insoluble in most organic solvents (CHCl$_3$, CH$_3$CN, ethanol, acetone and others).

2.2. 1:2 complexes

Complex Ag(L^1)$_2$NO$_3$ (1a) was obtained by mixing of CH$_3$CN solutions of AgNO$_3$ (0.0246 g, 0.145 mmol) and of ligand L^1 (0.15 g, 0.348 mmol); after evaporation of some solvent and dry ether addition the precipitate formed was separated and dried in vacuo; 0.1289 g (86%) of crystalline complex (1a) was produced. Anal. Calcd. for C$_{52}$H$_{48}$AgNO$_3$P$_4$S$_2$: C, 60.6; H, 4.7; N, 1.3. Found: C, 60,6; H, 4.3; N, 1.3.

The 1:2 complex with ligand L^3 was obtained in a similar way.

Complex Ag(L^3)$_2$NO$_3$ (3a). Yield 73%. Anal. Calcd. for C$_{56}$H$_{56}$AgNO$_3$P$_4$S$_2$: C, 61.9; H, 5.2; N, 1.3. Found: C, 61.9; H, 5.3; N, 1.4.

The complexes 1a and 3a are soluble in CHCl$_3$ and CH$_3$CN.

2.3. Preparation of the single crystal and X-ray diffraction study of [Ag(L^1)NO$_3$]$_2$

The solutions of the components in CH$_3$CN were mixed; the solution of the ligand was taken in slight excess. The resultant clear mixture was left to stand in the dark for a day and the colourless plate-like crystals of complex (1) precipitated. The crystals of [A g(P h $_2$ P C H $_2$ C H $_2$ P(S)P h $_2$)]$_2$(N O $_3$)$_2$ (C$_{52}$H$_{48}$Ag$_2$N$_2$O$_6$P$_4$S$_2$; M = 1200.66) are monoclinic, at 20 °C a = 21.657(3), b = 10.837(2), c = 21.587(4) Å, β = 100.6(1)°, V = 4979(1) Å^3, D_c = 1.602 g cm^{-3}, Z = 4, space group $C2/c$ The unit cell parameters and intensities of 8351 reflections were measured with a Syntex P2$_1$ diffractometer (T = 293 K, MoKα radiation, λ = 0.71073 Å, θ–2θ scan technique, θ < 32°,

Table 1

Atomic coordinates ($\times 10^4$; for H atoms $\times 10^3$) and equivalent isotropic displacement parameters (U_{eq}, Å$^2 \times 10^3$; for H atoms isotropic displacement parameters U_{iso}, Å$^2 \times 10^3$) for (1)

Atoms	x	y	z	U_{eq} / U_{iso}
Ag(1)	1355(1)	2822(1)	4641(1)	26(1)
S(1)	1282(1)	3272(1)	3514(1)	27(1)
P(1)	1843(1)	1945(1)	3299(1)	20(1)
P(2)	3741(1)	2961(1)	4346(1)	19(1)
N(1)	1941(2)	5337(3)	4899(1)	32(1)
O(1)	2141(2)	6394(3)	4898(2)	74(1)
O(2)	1405(1)	5110(3)	4988(2)	55(1)
O(3)	2299(1)	4445(3)	4833(1)	37(1)
C(1)	2601(1)	1905(3)	3826(1)	21(1)
C(2)	2971(1)	3106(3)	3825(1)	20(1)
C(3)	2011(1)	2149(3)	2521(1)	25(1)
C(4)	1775(2)	3146(3)	2146(2)	33(1)
C(5)	1920(2)	3282(4)	1549(2)	45(1)
C(6)	2301(2)	2440(4)	1329(2)	48(1)
C(7)	2546(2)	1443(4)	1702(2)	43(1)
C(8)	2399(2)	1287(4)	2294(2)	33(1)
C(9)	1503(1)	431(3)	3313(1)	24(1)
C(10)	1111(2)	−23(3)	2774(2)	33(1)
C(11)	824(2)	−1152(4)	2789(2)	41(1)
C(12)	919(2)	−1841(4)	3329(2)	43(1)
C(13)	1305(2)	−1416(4)	3870(2)	38(1)
C(14)	1599(2)	−276(3)	3866(2)	29(1)
C(15)	4167(1)	1870(3)	3942(1)	21(1)
C(16)	4681(2)	1251(3)	4288(2)	30(1)
C(17)	5019(2)	400(3)	3995(2)	37(1)
C(18)	4835(2)	143(3)	3365(2)	34(1)
C(19)	4329(2)	751(3)	3016(2)	31(1)
C(20)	3994(1)	1615(3)	3300(1)	26(1)
C(21)	4112(1)	4452(3)	4278(1)	22(1)
C(22)	3861(2)	5492(3)	4511(2)	31(1)
C(23)	4133(2)	6642(3)	4477(2)	36(1)
C(24)	4653(2)	6756(3)	4193(2)	36(1)
C(25)	4909(2)	5727(4)	3961(2)	40(1)
C(26)	4644(2)	4574(3)	4003(2)	32(1)
H(101)	255(2)	169(4)	424(2)	51(13)
H(102)	284(2)	118(3)	370(2)	26(9)
H(201)	275(2)	375(3)	399(2)	23(9)
H(202)	305(2)	330(3)	340(2)	24(9)
H(4)	150(2)	375(4)	227(2)	34(10)
H(5)	174(3)	401(5)	132(3)	70(16)
H(6)	242(2)	254(5)	90(3)	58(14)
H(7)	282(2)	95(4)	155(2)	49(13)
H(8)	253(2)	57(4)	258(2)	44(12)
H(10)	106(2)	41(3)	240(2)	21(9)
H(11)	58(2)	−142(5)	241(2)	52(13)
H(12)	74(2)	−258(4)	331(2)	47(13)
H(13)	143(2)	−190(4)	421(2)	31(10)
H(14)	187(2)	−0(3)	421(2)	21(8)
H(16)	480(2)	147(4)	475(2)	50(12)
H(17)	541(3)	−5(5)	423(2)	68(16)
H(18)	506(2)	−46(4)	316(2)	37(11)
H(19)	419(2)	58(4)	258(2)	46(12)
H(20)	365(2)	205(4)	307(2)	40(12)
H(22)	355(2)	539(4)	472(2)	42(12)
H(23)	399(2)	736(5)	462(2)	55(14)
H(24)	483(3)	747(5)	418(3)	63(15)
H(25)	529(2)	583(4)	380(2)	50(13)
H(26)	480(2)	388(4)	383(2)	37(11)

Table 2
Bond lengths (Å) and angles (deg) for (1)

Ag(1)–P(2')	2.3906(8)	Ag(1)–S(1)	2.4574(9)
Ag(1)–O(2)	2.587(3)	S(1)–P(1)	1.9920(10)
P(1)–C(3)	1.798(3)	P(1)–C(9)	1.801(3)
P(1)–C(1)	1.817(3)	P(2)–C(15)	1.818(3)
P(2)–C(21)	1.822(3)	P(2)–C(2)	1.838(3)
P(2)–Ag(1')	2.3906(8)	N(1)–O(1)	1.225(4)
N(1)–O(2)	1.236(4)	N(1)–O(3)	1.264(4)
C(1)–C(2)	1.529(4)	C(3)–C(4)	1.389(5)
C(3)–C(8)	1.404(5)	C(4)–C(5)	1.390(5)
C(5)–C(6)	1.373(7)	C(6)–C(7)	1.393(7)
C(7)–C(8)	1.382(5)	C(9)–C(10)	1.397(4)
C(9)–C(14)	1.401(5)	C(10)–C(11)	1.376(5)
C(11)–C(12)	1.367(6)	C(12)–C(13)	1.383(6)
C(13)–C(14)	1.391(5)	C(15)–C(16)	1.394(4)
C(15)–C(20)	1.394(4)	C(16)–C(17)	1.398(5)
C(17)–C(18)	1.374(5)	C(18)–C(19)	1.377(5)
C(19)–C(20)	1.394(4)	C(21)–C(22)	1.386(4)
C(21)–C(26)	1.395(4)	C(22)–C(23)	1.386(5)
C(23)–C(24)	1.383(5)	C(24)–C(25)	1.380(6)
C(25)–C(26)	1.386(5)		

P(2')–Ag(1)–S(1)	167.32(3)	P(2')–Ag(1)–O(2)	94.71(9)
S(1)–Ag(1)–O(2)	95.02(9)	P(1)–S(1)–Ag(1)	99.03(4)
C(3)–P(1)–C(9)	106.30(14)	C(3)–P(1)–C(1)	105.83(14)
C(9)–P(1)–C(1)	107.05(14)	C(3)–P(1)–S(1)	111.48(11)
C(9)–P(1)–S(1)	112.69(10)	C(1)–P(1)–S(1)	113.01(10)
C(15)–P(2)–C(21)	105.54(13)	C(15)–P(2)–C(2)	104.21(13)
C(21)–P(2)–C(2)	103.79(13)	C(15)–P(2)–Ag(1')	110.19(10)
C(21)–P(2)–Ag(1')	120.17(10)	C(2)–P(2)–Ag(1')	111.59(9)
P(2')–Ag(1)–O(3)	106.61(9)	S(1)–Ag(1)–O(3)	86.00(8)
O(3)–Ag(1)–O(2)	48.21(9)	O(1)–N(1)–O(2)	122.0(4)
O(1)–N(1)–O(3)	119.4(4)	O(2)–N(1)–O(3)	118.6(3)
N(1)–O(2)–Ag(1)	97.8(2)	C(2)–C(1)–P(1)	113.1(2)
C(1)–C(2)–P(2)	110.0(2)	C(4)–C(3)–C(8)	119.6(3)
C(4)–C(3)–P(1)	121.6(2)	C(8)–C(3)–P(1)	118.8(3)
C(3)–C(4)–C(5)	120.0(4)	C(6)–C(5)–C(4)	120.3(4)
C(5)–C(6)–C(7)	120.3(3)	C(8)–C(7)–C(6)	120.1(4)
C(7)–C(8)–C(3)	119.7(4)	C(10)–C(9)–C(14)	119.2(3)
C(10)–C(9)–P(1)	119.7(3)	C(14)–C(9)–P(1)	121.0(2)
C(11)–C(10)–(9)	120.1(4)	C(12)–C(11)–C(10)	120.5(4)
C(11)–C(12)–C(13)	120.8(4)	C(12)–C(13)–C(14)	119.7(4)
C(13)–C(14)–C(9)	119.7(3)	C(16)–C(15)–C(20)	118.6(3)
C(16)–C(15)–P(2)	118.8(2)	C(20)–C(15)–P(2)	122.6(2)
C(15)–C(16)–C(17)	120.5(3)	C(18)–C(17)–C(16)	120.1(3)
C(17)–C(18)–C(19)	120.0(3)	C(18)–C(19)–C(20)	120.4(3)
C(19)–C(20)–C(15)	120.3(3)	C(22)–C(21)–C(26)	119.2(3)
C(22)–C(21)–P(2)	118.9(2)	C(26)–C(21)–P(2)	121.9(2)
C(21)–C(22)–C(23)	120.8(3)	C(24)–C(23)–C(22)	119.5(3)
C(25)–C(24)–C(23)	120.2(3)	C(24)–C(25)–C(26)	120.4(3)
C(25)–C(26)–C(21)	119.9(3)		

The primed atoms used the following symmetry transformations to generate equivalent atoms: $- x + \frac{1}{2}$, $- y + \frac{1}{2}$, $- z + 1$.

$\mu(\lambda\text{Mo}\,K\alpha) = 10.51\,\text{cm}^{-1}$, no absorption correction was applied). The structure was solved by direct methods and refined by the full-matrix least squares technique in the anisotropic approximation. All H atoms were located in the difference Fourier synthesis and included in the refinement with isotropic temperature factors. Final discrepancy factors are: $R1 = 0.046$ (on F

for 5880 observed reflections with $I > 2\sigma(I)$), $wR2 = 0.1035$ (on F^2 for all 8153 unique reflections used for the refinement of 403 parameters). All calculations were carried out on an IBM PC with the help of SHELXTL PLUS 5 (gamma version) program. Atomic coordinates and their thermal parameters are given in Table 1, bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. The structure of $[Ag(L^1)NO_3]_2$ (1)

The crystal of (1) is built of contact ion-pairs, which are made up of dimeric cations $[Ag(\mu_2\text{-}L^1)]_2^{2+}$ ($L^1 = Ph_2P(S)CH_2CH_2PPh_2$), occupying special positions in the crystallographic inversion centres and interacting with two NO_3^--anions. Each of the neutral L^1 ligands acts as a bridge between the two Ag atoms (Fig. 1). The 12-atom macrocycle is non-planar, the displacements of the four P atoms from the mean plane of all atoms of the cycle being equal to 0.939, 1.625, -0.486 and $0.610\,\text{Å}$; the latter plane forming the dihedral angles of $71.5°$, $125.7°$, $54.2°$ and $109.9°$ with the planes of the Ph rings C(3)–C(8), C(9)–C(14), C(15)–C(20) and C(21)–C(26) respectively. The configuration of the macrocycle may be approximated as the [3333] square (according to
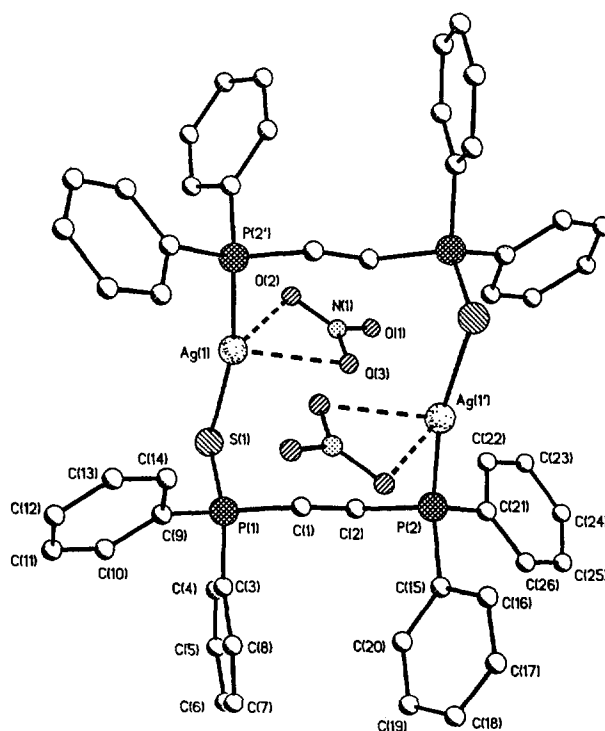

Fig. 1. The structure of complex $[Ag(Ph_2PCH_2CH_2P(S)Ph_2)]_2(NO_3)_2$ (1).

the notation suggested in Ref. [14]), which is limited by nearly planar fragments P(2)Ag(1)S(1)P(1)(Fr1), P(1)C(1)C(2)P(2)(Fr2) and their symmetry-derived P(2)Ag(1′)S(1′)P(1′)(Fr1′) and P(1′)C(1′)C(2′)P(2′)(Fr2′) counterparts. The mean planes of Fr1 and Fr2 form the dihedral angles of 68.5 and 71.6° with the mean plane of the macrocycle and the angle of 90.7° with each other. Thus, the macrocycle as a whole assumes the shape of a box without the upper and lower lids with the Fr1, Fr2, Fr1′ and Fr2′ fragments limiting it on the sides; the Fr1 · · · Fr1′, and Fr2 · · · Fr2′ distances between the opposite walls being equal to 4.097 Å and 4.010 Å respectively. The spaces corresponding to both upper and lower lids of the box are occupied by the NO_3^--groups, their planes being almost orthogonal to the plane passing through four P atoms of the macrocycle; the relevant dihedral angle is equal to 100.6°.

The NO_3^--anions act as bidentate η^2-ligands in respect to the Ag atoms so that the latter are involved in four-membered chelate rings. Such a mode of coordination of the NO_3^- anion by the metal atom is unexceptional and the inequality in the Ag–O and N–O distances [Ag(1)–O(2) 2.587(3), N(1)–O(1) 1.225(4) Å and Ag(1)–O(3) 2.671(3), N(1)–O(3) 1.264(4) Å] observed in the structure of (1) is quite typical of this type of coordination. The average Ag–O bond in (1), 2.629 Å, is significantly longer than the standard value, 2.555 Å, quoted in Ref. [15] and exceeds the sum of the ionic radii of Ag^+ (1.00 Å for coordination number equal to 4) and O^{2-} (1.40 Å) [16], which means that the Ag^+–NO_3^- interaction is rather weak, although it obviously exhibits definite directional preference and is responsible for the formation of isolated ion-pairs in the crystal.

The silver atom, taking into account both coordination and ionic bonds, has a strongly distorted tetrahedral environment, one of the bond angles in the coordination tetrahedron being considerably increased and the opposite angle substantially decreased as compared to the remaining four angles, which are close to the ideal tetrahedral value (P(2′)Ag(1)S(1) 167.32(3)°, P(2′)Ag(1)O(2) 106.61(9)°, P(2′)Ag(1)O(3) 94.71(9)°, S(1)Ag(1)O(2) 95.02(9)°, S(1)Ag(1)O(3) 86.00(8)°, O(2)Ag(1)O(3) 48.21(9)°). The dihedral angle formed by the S(1)Ag(1)P(2′) and O(2)Ag(1)O(3) planes is equal to 79.2°. The Ag(1)–P(2′) bond in the structure of (1) is rather short and its length (2.391(1) Å) almost coincides with the lower limits of the ranges, quoted in Ref. [15] for the Ag–P(PPh₂Me), Ag–P(μ_2–Ph₂PCH₂CH₂PPh₂) and Ag–P(PPh₃) bonds (2.406 Å, 2.406 Å and 2.388 Å respectively; the mean values of these bond lengths are noticeably greater, viz. 2.438 Å, 2.427 Å, and 2.419 Å [15]). The Ag(1)–S(1) bond, 2.457(1) Å, is significantly shorter than the Ag–S=P distances, observed in the (Bu₃P)Ag⁺[(S=PPh₂)₃C] complex, which has the structure of the (B) type [17], wherein the silver atom is involved in the three Ag–S=P

bonds (Ag–S 2.585, 2.639 and 2.670 Å). At the same time the P=S bond lengths in the structures of both types, A and B, are in fact identical, the corresponding values being 1.992(1) Å (for the P(1)–S(1) bond in (1)) and 1.993 Å (the average value for the above-mentioned tributylphosphine complex) respectively. Thus, one may believe that the Ag–P and the Ag–S bonds in the A-type structure are stronger than in the analogous compounds.

The studies of the nature of bonding in the complexes involving the 2,11-bis(diphenylphosphinomethyl)-benzo[c]phenanthrene ligand (L^4), viz. $[M(L^4)]^+X^-$ or $[M(L^4)X]$ (M = Cu, Ag, Au, X = Cl), have led to the assumption [18], that in such complexes, wherein the metal atom forms two M–P bonds and one M^+–X^- bond, the increase of the ionic character of the M^+–X^- bond is accompanied by the increase of the P–M–P bond angle, i.e. the value of the P–M–P angle may be considered the quantitative measure of the ionic character of the M–X bond. Further pursuing these studies, the authors of Ref. [19] have shown on the basis of the X-ray structural as well as spectroscopic results that the increase of the P–Ag–P bond angle (140.7 → 151.5°) and the simultaneous decrease of the average Ag–P bond length (2.435 → 2.409 Å) in the series of complexes [Ag(L^4)X] (X = Cl, SnCl₃, NO₃, ClO₄) are correlated with the weakening of the Ag^+–X^- interaction. The certain analogy between the donor–acceptor P–Ag–P bonds in the $[M(L^4)X]$ complexes and S–Ag–P moiety in (1) allows one to anticipate the correlation between the increase of the S–Ag–P bond angle, the shortening of the Ag–S and Ag–P bonds and the weakening of the Ag^+–O(NO_3^-) interaction. Such a correlation is indeed observed in the structure of (1), which is characterized by a large value of the S–Ag–P angle [167.32(3)°], shortened Ag–S and Ag–P bonds and rather weak (vide supra) ionic Ag^+–NO_3^- interaction.

The geometric parameters of the L^1 ligand (Table 2) in each of its halves, Ph₂PCH₂ and CH₂P(S)Ph₂, are close to the corresponding values observed in complexes with analogous groups coordinated to various metals: according to Ref. [15] the average P–C(Ph) and P–C(CH₂) bond lengths in complexes with the Ph₂PCH₂CH₂PPh₂ ligands are equal to 1.827 Å and 1.845 Å respectively, the P–S bond lengths in the phosphinesulphides η^1-SPR₃ and dithiophosphinates η^2-S₂PR₂ complexes span the range of 2.000–2.007 Å. There is, however, a distinct difference between the P–C(CH₂) and the P–C(Ph) bonds in the Ph₂PCH₂ and in the CH₂P(S)Ph₂ halves of the ligand, both distances being shorter in the latter moiety (1.817(3) Å and 1.800(3) Å respectively) than in the former (1.838(3) Å and 1.820(3) Å respectively). Thus, the presence of both Ph₂PCH₂ and CH₂P(S)Ph₂ moieties in one molecule makes possible the quantitative assessment of the influence of the electronegative sulphide substituent on the
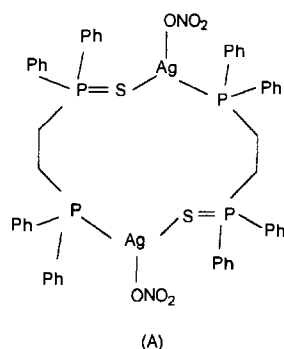
lengths of the P–C bonds. This influence is manifested in the shortening (by approximately 0.020 Å) of the P–C bonds and in the slight increase of the C(CH$_2$)PC(Ph) and C(Ph)PC(Ph) angles in the sulphur-containing CH$_2$P(S)Ph2 moiety (106.4(1)° and 106.3(1)° respectively) as compared to the corresponding angles (104.0(1)° and 105.5(1)°) in the CH$_2$PPh$_2$ fragment.

3.2. Investigation of IR spectra

Ligands L^1–L^3 have two possible coordination sites: the P^{III} atom and the P=S group. For characterizing the complexes the positions of bands corresponding to the P=S group were used. It is known that the P=S group vibrations are not completely definitive [20] and that complicates their assignment. The IR spectra of the free ligands have two bands in the region above 600 cm^{-1} and at 625 and 615 cm^{-1}. Only the band 615 cm^{-1} is shifted on complexation and this band is assigned to the P=S group vibrations.

3.2.1. 1:1 complexes (1–3)

The P=S band 595 cm^{-1} is present in IR spectra of these complexes. It is displaced towards lower frequencies by 20 cm^{-1} as compared with the free ligand and corresponds to the coordinated P=S group (P=S · · · Ag$^+$). The assignment of the NO$_3^-$ group vibrations presents some difficulties because of the superposition of the vaseline oil bands. By subtraction of these latter bands the spectra of solid complexes were obtained. The NO$_3^-$ group vibrations give rise to two intense bands: ν_{as} 1390–1335 cm^{-1} and ν_s 1310–1295 cm^{-1}. A small band separation ($\Delta\nu$ 80–90 cm^{-1}) correlated with the weak Ag$^+$ · · · NO$_3^-$ interaction [21]. IR spectra of all 1:1 complexes (1–3) are similar and correspond to structure A derived from the X-ray analysis data.
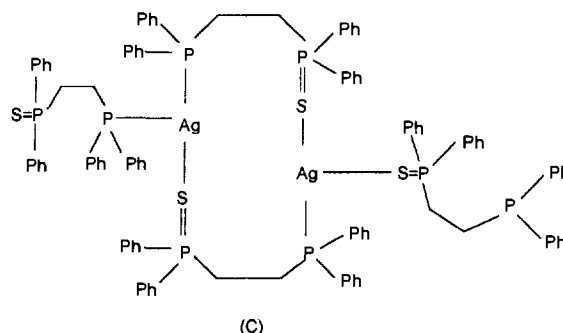
with AgNO$_3$, recently investigated by us, is also a centrosymmetric dimer [Ag(L^5)NO$_3$]$_2$ but of a different type [22].

(B)
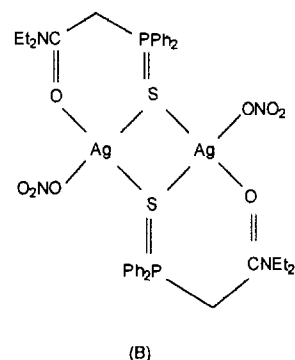
3.2.2. 1:2 complexes (1a,3a)

These complexes in the solid state contain in their IR spectra two bands for the P=S group vibrations, at 615 and 595 cm^{-1}, associated with the free and coordinated P=S groups respectively. As to the NO$_3^-$ group vibrations, there is only one band corresponding to a free NO$_3^-$ group. In CHCl$_3$ solution spectra of 1:2 complexes are changed insignificantly, only for 3a is increasing of intensity of the free P=S group band observed. A comparison of IR spectra of 1:1 and 1:2 complexes allows one to conclude that 1:2 complex formation is due to replacing of two NO_3^- groups in structure A by two ligand molecules. The formation of various structures of 1:2 complexes satisfying the requirements $I_{P=S,coord.} > I_{P=S,free}$ is possible.

(1) The last two ligand molecules are attached by different means to 12-membered macrocycle: the first by the P^{III} atom, the second by the sulphur atom. The complex is built from the identical asymmetric molecules (structure C).

(A)

(C)

It should be mentioned, that the complex of (N,N-di-ethylcarbamoylmethyl)diphenylphosphine sulphide [L^5]

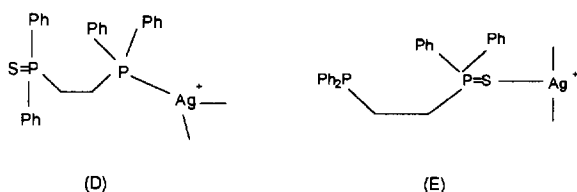(2) Both of the last two molecules of the ligand are coordinated either to the P^{III} atom or to the P=S group

Table 3
^{31}P NMR spectra data of ligands L^1, L^3 and their 1:2-complexes with AgNO$_3$

| Compounds	$\delta_{P^{III}}$ (ppm)	$\Delta\delta$ (ppm)	J_{PP} (Hz)	$\delta_{P=S}$ (ppm)	$\Delta\delta$ (ppm)	J_{PP} (Hz)
Ph$_2$P(S)(CH$_2$)$_2$PPh$_2$ (L^1)	−12.88	—	49.5	44.32	—	49.3
Ag(L$^1_2$)NO$_3$ (1a)	+5.28 [a]	18.16	0	45.89	1.57	21.7
Ph$_2$P(S)(CR$_2$)$_4$PPh$_2$ (L^3)	−16.10	—	0	42.60	—	0
Ag(L$^3_2$)NO)$_3$ (3a)	+0.23 [b]	16.33	0	44.36	1.76	0

[a] $\Delta\nu_{1/2} = 175\,Hz$.
[b] $\Delta\nu_{1/2} = 184\,Hz$.

giving the mixture of two types of the symmetric complexes (structure fragments D and E).

(D)   (E)

(3) The last two molecules of the ligand are always attached by the P^{III} atoms which are known to form more strong coordination bonds with metal ions. However, there are two different conformations of the molecules attached owing to rotation about the C–C bond. One of them is with the 'screwed out' P=S group (structure fragment F) and another with the P=S group turned to the Ag$^+$ ion. In the latter conformation an additional coordination Ag$^+$ · · · S=P can arise and a six-membered cycle with a four-coordinated Ag$^+$ ion is formed (structure fragment G).

(F)   (G)
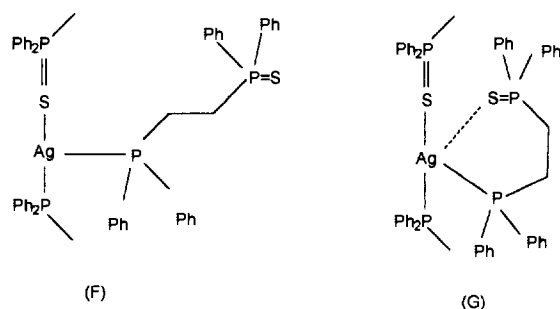
Unfortunately, the IR spectra data do not allow a choice between the structures being discussed. But we suppose that the structures F and G are more probable. In the 1:2 complexes solutions the exchange of 'outer' ligands of structures D, E, F and G is possible.

3.3. ^{31}P NMR spectra of 1:2 complexes

^{31}P NMR spectra of free ligands L^1 and L^3 (Table 3) contain two narrow signals in the region −16 to −12 ppm (P^{III}) and 42–44 ppm (P^V). The signals of

ligand L^1 are doublets with the coupling constant J_{PP} 49.4 Hz. By formation of complexes 1a and 3a all the signals are shifted downfield owing to decreasing electron density on the phosphorus atoms by coordination [23]. Naturally, the shift of P^{III} signal ($\Delta\delta$ 16–18 ppm) is greater than that of P^V, as the P^{III} atom immediately takes part in coordination with Ag$^+$. Along with the shift, their broadening was observed which was especially pronounced for P^{III} signals. So, in the spectrum of the complex 1a a doublet splitting of the P^{III} signal disappeared. The broadening of P^{III} signals may be associated with the exchange of the 'outer' ligands.

4. Conclusion

Thus, the reaction of phosphine–phosphine sulphide ligands with AgNO$_3$ leads to formation of the complexes based on the centrosymmetric macrocyclic dimer. The structure of the complexes does not depend essentially on the length of the methylene chain between two phosphorus atoms.

Acknowledgements

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