Complexation of (*N*,*N*-diethylthiocarbamoylmethyl)diphenylphosphine sulfide with silver nitrate. The structure of the $[Ag\{Ph_2P(S)CH_2C(S)NEt_2\}_2]NO_3$ complex

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(*N*,*N*-Diethylthiocarbamoylmethyl)diphenylphosphine sulfide, $Ph_2P(S)CH_2C(S)NEt_2$, forms a distorted tetragonal bisligand complex $[AgL_2]NO_3$ with Ag^+. The stability constant of the complex in acetonitrile was estimated by spectrophotometry ($\log K = 3.7$).

Key words: silver complexes, organothiophosphorus compounds, IR and UV spectra, X-ray structural analysis.

(Carbamoylmethyl)phosphine oxides, which form complexes with heavy metal cations, are widely used as organophosphorus ligands whose properties are studied well.[1] It is also known that many sulfur-containing compounds form stable complexes with thiophilic metal cations, in particular, with silver.[2,3] In our studies aimed at the development of procedures for the synthesis of organothiophosphorus compounds in conditions of phase transfer catalysis, we have obtained three thio analogs of (carbamoylmethyl)phosphine oxides, namely, (*N*,*N*-diethylcarbamoylmethyl)diphenylphosphine sulfide $Ph_2P(S)CH_2C(O)NEt_2$[4] (L-1), (carbamoylmethyl)diphenylphosphine sulfide $Ph_2P(S)CH_2C(O)NH_2$[4] (L-2), and (*N*,*N*-diethylthiocarbamoylmethyl)diphenylphosphine sulfide $Ph_2P(S)CH_2C(S)NEt_2$ (L-3). Previously,[5,6] we have studied the complexes of ligands L-1 and L-2 with $AgNO_3$, namely, $[Ag(L\text{-}1)NO_3]_2$ (**1**) and $[Ag_2(L\text{-}2)_2(NO_3)_2]_n$ (**2**). In this work, we studied the interaction of L-3 with $AgNO_3$ by X-ray structural analysis and IR and UV spectroscopy.

Experimental

Synthesis of compound L-3. A mixture of (*N*,*N*-diethylcarbamoylmethyl)diphenylphosphine sulfide (L-1) (2.5 g, 7.5 mmol) and the Lawesson's reagent (1.8 g, 4.4 mmol) in anhydrous MeCN (40 mL) was refluxed for 6 h. $CHCl_3$ (70 mL) was added to the reaction mixture, which was washed three times with ice-cold water. The organic layer was dried with Na_2SO_4, and the solvents were removed *in vacuo*. The residue was crystallized from an ether—hexane mixture. The product was obtained in a yield of 2.1 g (81%), m.p. 139—141 °C (acetone—hexane). Found (%): C, 61.74; H, 6.37; N, 3.56; S, 18.29. $C_{18}H_{22}NPS_2$. Calculated (%): C, 61.85; H, 6.92; N, 4.00; S, 18.34. $^{31}P\text{-}\{^1H\}$ NMR (CH_2Cl_2), δ: 40.1 (s). ^1H NMR ($CDCl_3$), δ: 0.95 and 1.16 (both t, 6 H, 2 Me, $^3J_{H,H} = 7$ Hz); 3.67 and 3.80 (both q, 4 H, 2 CH_2N, $^3J_{H,H} = 7$ Hz); 4.30 (d, 2 H, CH_2P, $^2J_{P,H} = 14.4$ Hz); 7.43 and 8.00 (both m, 10 H, C_6H_5).

The IR spectra were recorded on a UR-20 spectrometer. Cells of KBr or CaF_2 were used for solutions. Solid samples were analyzed as KBr pellets (the initial compound) or as Nujol mulls (the initial compound and complexes).

The UV spectra of solutions of ligand L-3 and the complexes in MeCN were recorded on a Specord UV-VIS M-40 spectrophotometer with the use of 0.1-cm quartz cells. The stability constant of the $[Ag(L\text{-}3)_2]^+$ complex was determined by titration of a solution of the ligand ($C_L = 0.0005$ mol L^{-1}) with a solution of $AgNO_3$ in MeCN with a known concentration.

Preparation of a complex of the ligand L-3 with $AgNO_3$. Solutions of the ligand (0.0935 g) and $AgNO_3$ (0.023 g) in MeCN were mixed to give an M : L ratio of 1 : 2 ($C_L = 0.02$ mol L^{-1}). A white finely crystalline product was precipitated upon addition of Et_2O. The yield was ~60%, m.p. 170—173 °C (with decomp.). Found (%): C, 48.95; H, 5.06; Ag, 12.60; N, 4.72; P, 6.90. $C_{36}H_{44}AgN_3O_3P_2S_4$ (M : L=1 : 2). Calculated (%): C, 50.00; H, 5.09; Ag, 12.50; N, 4.87; P, 7.18.

An analogous complex was prepared in $CHCl_3$ with a not less than twofold excess of the ligand. When the reagents were taken in an equimolar ratio, the complex did not form in $CHCl_3$, MeCN, or EtOH. Judging from the darkening of the solution followed by the formation of a black precipitate, the starting compound decomposed.

Preparation of single crystals of the $[Ag(L\text{-}3)_2]NO_3$ complex (3). A weighed sample of the ligand (0.090 g) was dissolved in EtOH (5 mL) with boiling. A weighed sample of $AgNO_3$ (0.022 g, M : L = 1 : 2) was dissolved in EtOH with the use of an ultrasonic stirrer. The hot solution of the ligand was mixed with a solution of the salt. After one day, crystals precipitated, m.p. 170—172 °C (with decomp.). Found (%): C, 49.63; H, 4.94; Ag, 12.92; N, 4.65.

Colorless isometric crystals of bis[μ_2-2-(*N*,*N*-diethylthiocarbamoylmethyl)diphenylphosphinesulfido]silver(+1) ni-

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trate, $[Ag(L\text{-}3)_2]NO_3$ (**3**), $C_{36}H_{44}AgN_3O_3P_2S_4$ (mol. weight 864.79), are monoclinic: at 20 °C, a = 9.213(2), b = 21.331(1), c = 19.818(4) Å, β = 93.63(3)°, V = 3887(1) Å^3, d_{calc} = 1.478 g cm^{-3}, Z = 4, space group $P2_1/c$. The unit cell parameters and intensities of 8034 independent reflections were measured on an automated CAD-4 Enraf Nonius diffractometer (Mo-Kα radiation, θ/(5/3θ)-scanning technique, μ = 8.55 cm^{-1}, θ > 26.5°).

The structure was solved by the direct method and refined on F^2 by the full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms. All H atoms were located from difference electron density syntheses and refined isotropically. The final values of the R factors are as follows: wR_2 = 0.0902 based on a total of 8034 reflections used in the refinement, R_1 = 0.0303 (using 5798 observed reflections with $I > 2\sigma(I)$). The number of refinable parameters was 645. All calculations were carried out using the SHELXTL PLUS 5 program package (the gamma version). The atomic coordinates are given in Table 1. The bond lengths and bond angles are listed in Table 2.

Table 1. Atomic coordinates (×10^4 for nonhydrogen atoms and ×10^3 for hydrogen atoms) and equivalent isotropic ($U_{eq}\cdot10^3$/Å^2) and isotropic (for hydrogen atoms, $U_{iso}\cdot10^3$/Å^2) thermal factors in the structure of $[Ag(Ph_2P(S)CH_2C(S)NEt_2)_2]NO_3$

Atom	x	y	z	U_{eq}/U_{iso}
Ag(1)	1980(1)	4006(1)	952(1)	60(1)
S(1)	1528(1)	4960(1)	1672(1)	54(1)
S(2)	4652(1)	4166(1)	769(1)	48(1)
S(3)	1388(1)	2923(1)	1654(1)	51(1)
S(4)	445(1)	3573(1)	−25(1)	54(1)
P(1)	3458(1)	5064(1)	2152(1)	35(1)
P(2)	2642(1)	2444(1)	1081(1)	36(1)
N(1)	6939(2)	4420(1)	1580(1)	41(1)
N(2)	348(3)	2444(1)	−552(1)	51(1)
N(3)	5414(4)	3447(2)	4026(2)	68(1)
O(1)	5993(25)	3647(13)	3594(11)	167(11)
O(2)	4233(13)	3308(5)	4133(10)	105(4)
O(3)	5194(25)	3296(7)	4559(7)	126(6)
O(11)	6135(15)	3321(9)	4546(7)	211(8)
O(12)	4307(10)	3273(4)	3627(5)	115(3)
O(13)	6222(13)	3782(8)	3757(7)	116(4)
C(1)	4657(3)	4368(1)	2141(2)	39(1)
C(2)	5522(3)	4327(1)	1523(1)	36(1)
C(3)	2539(3)	2661(2)	180(1)	38(1)
C(4)	1072(3)	2845(1)	−145(1)	41(1)
C(5)	801(5)	1792(2)	−704(2)	71(1)
C(6)	−107(6)	1312(2)	−394(3)	88(2)
C(7)	−988(4)	2647(2)	−944(2)	73(1)
C(8)	−628(8)	2990(3)	−1582(3)	100(2)
C(9)	7815(3)	4348(2)	983(2)	51(1)
C(10)	7922(5)	4949(2)	596(3)	75(1)
C(11)	7790(3)	4622(2)	2193(2)	50(1)
C(12)	8632(4)	4094(2)	2546(2)	58(1)
C(13)	4460(3)	5714(1)	1834(1)	37(1)
C(14)	4053(4)	5970(2)	1210(2)	57(1)
C(15)	4822(5)	6475(2)	975(2)	69(1)
C(16)	5982(5)	6718(2)	1349(2)	65(1)
C(17)	6414(4)	6458(2)	1960(2)	55(1)
C(18)	5654(3)	5958(1)	2208(2)	44(1)
C(19)	3270(3)	5210(1)	3036(1)	38(1)
C(20)	3076(3)	5812(1)	3279(2)	45(1)
C(21)	2848(4)	5903(2)	3955(2)	54(1)
C(22)	2824(4)	5407(2)	4388(2)	62(1)
C(23)	2992(4)	4807(2)	4149(2)	65(1)
C(24)	3204(4)	4707(2)	3476(2)	53(1)
C(25)	2318(3)	1605(1)	1118(1)	41(1)
C(26)	1143(4)	1362(2)	1434(2)	55(1)
C(27)	971(4)	714(2)	1467(2)	66(1)
C(28)	1942(4)	319(2)	1199(2)	62(1)
C(29)	3122(4)	557(2)	892(2)	56(1)
C(30)	3306(3)	1202(2)	848(2)	47(1)
C(31)	4549(3)	2543(1)	1336(1)	38(1)
C(32)	5634(3)	2509(2)	884(2)	47(1)
C(33)	7082(3)	2581(2)	1125(2)	57(1)
C(34)	7421(4)	2664(2)	1798(2)	63(1)
C(35)	6357(4)	2695(2)	2242(2)	62(1)
C(36)	4916(3)	2640(2)	2017(2)	47(1)
H(11)	535(3)	442(2)	256(2)	64(10)
H(12)	402(3)	402(1)	214(1)	38(7)
H(301)	312(3)	300(2)	15(1)	44(8)
H(302)	295(3)	235(2)	−6(2)	44(8)
H(51)	82(3)	170(1)	−124(1)	33(7)
H(52)	170(5)	174(2)	−58(2)	79(13)
H(61)	9(7)	93(3)	−55(3)	147(24)
H(62)	−117(5)	135(2)	−51(2)	96(14)
H(63)	−1(7)	137(3)	18(4)	174(26)
H(71)	−154(4)	292(2)	−64(2)	61(10)
H(72)	−141(4)	230(2)	−105(2)	64(11)
H(81)	−34(8)	270(4)	−191(4)	185(33)
H(82)	−166(8)	316(3)	−177(3)	176(26)
H(83)	−4(6)	331(3)	−154(3)	117(21)
H(91)	741(3)	397(1)	71(2)	43(8)
H(92)	876(3)	424(1)	115(1)	40(8)
H(101)	817(4)	531(2)	88(2)	84(14)
H(102)	708(4)	506(2)	39(2)	69(12)
H(103)	858(6)	477(2)	20(3)	123(17)
H(111)	848(4)	493(2)	207(2)	58(10)
H(112)	712(4)	482(2)	250(2)	60(10)
H(121)	929(4)	427(2)	286(2)	77(12)
H(122)	800(5)	380(2)	275(2)	97(15)
H(123)	923(4)	386(2)	223(2)	85(13)
H(14)	323(4)	579(2)	94(2)	56(9)
H(15)	448(4)	663(2)	55(2)	81(12)
H(16)	638(4)	707(2)	120(2)	77(12)
H(17)	708(5)	663(2)	222(2)	100(16)
H(18)	593(3)	579(2)	263(2)	51(9)
H(20)	305(3)	619(2)	299(2)	49(8)
H(21)	271(4)	632(2)	411(2)	66(10)
H(22)	282(4)	546(2)	481(2)	66(11)
H(23)	297(4)	447(2)	445(2)	70(11)
H(24)	333(4)	436(2)	333(2)	53(10)
H(26)	52(3)	164(2)	162(2)	47(9)
H(27)	14(4)	60(2)	168(2)	82(12)
H(28)	175(4)	−12(2)	121(2)	83(12)
H(29)	376(4)	26(2)	70(2)	70(11)
H(30)	408(3)	137(1)	62(1)	43(8)
H(32)	544(3)	243(1)	43(2)	36(7)
H(33)	769(4)	256(2)	82(2)	67(11)
H(34)	844(5)	266(2)	196(2)	86(12)
H(35)	657(4)	278(2)	271(2)	71(11)
H(36)	419(3)	271(1)	232(2)	46(8)

Table 2. Bond lengths (*d*) and bond angles (ω) in the structure of $[Ag(Ph_2P(S)CH_2C(S)NEt_2)_2]NO_3$

Bond	*d*/Å	Angle	ω/deg
Ag(1)—S(4)	2.5010(10)	S(4)—Ag(1)—S(2)	116.46(4)
Ag(1)—S(2)	2.5345(9)	S(4)—Ag(1)—S(1)	128.89(3)
Ag(1)—S(1)	2.5350(9)	S(2)—Ag(1)—S(1)	99.69(3)
Ag(1)—S(3)	2.7700(10)	S(4)—Ag(1)—S(3)	87.76(3)
S(1)—P(1)	1.9753(11)	S(2)—Ag(1)—S(3)	114.05(3)
S(2)—C(2)	1.686(3)	S(1)—Ag(1)—S(3)	110.03(3)
S(3)—P(2)	1.9583(11)	P(1)—S(1)—Ag(1)	100.77(4)
S(4)—C(4)	1.678(3)	C(2)—S(2)—Ag(1)	108.18(10)
P(1)—C(19)	1.799(3)	P(2)—S(3)—Ag(1)	90.13(4)
P(1)—C(13)	1.801(3)	C(4)—S(4)—Ag(1)	105.57(10)
P(1)—C(1)	1.852(3)	C(19)—P(1)—C(13)	106.93(13)
P(2)—C(31)	1.811(3)	C(19)—P(1)—C(1)	104.13(13)
P(2)—C(25)	1.815(3)	C(13)—P(1)—C(1)	107.06(13)
P(2)—C(3)	1.841(3)	C(19)—P(1)—S(1)	110.48(9)
N(1)—C(2)	1.318(3)	C(13)—P(1)—S(1)	112.57(10)
N(1)—C(11)	1.469(4)	C(1)—P(1)—S(1)	115.05(10)
N(1)—C(9)	1.481(4)	C(31)—P(2)—C(25)	105.27(12)
N(2)—C(4)	1.327(4)	C(31)—P(2)—C(3)	103.33(13)
N(2)—C(7)	1.478(4)	C(25)—P(2)—C(3)	106.84(14)
N(2)—C(5)	1.488(5)	C(31)—P(2)—S(3)	111.96(10)
N(3)—O(1)	1.12(2)	C(25)—P(2)—S(3)	112.74(10)
N(3)—O(3)	1.134(12)	C(3)—P(2)—S(3)	115.76(10)
N(3)—O(2)	1.159(11)	C(2)—N(1)—C(11)	126.1(2)
N(3)—O(13)	1.183(10)	C(2)—N(1)—C(9)	120.2(2)
N(3)—O(11)	1.219(14)	C(11)—N(1)—C(9)	113.7(2)
N(3)—O(12)	1.304(9)	C(4)—N(2)—C(7)	120.0(3)
O(2)—O(3)	1.18(2)	C(4)—N(2)—C(5)	126.2(3)
C(1)—C(2)	1.506(4)	C(7)—N(2)—C(5)	113.7(3)
C(3)—C(4)	1.512(4)	O(1)—N(3)—O(3)	160(2)
C(5)—C(6)	1.480(7)	O(1)—N(3)—O(2)	137(2)
C(7)—C(8)	1.517(8)	O(3)—N(3)—O(2)	62.2(10)
C(9)—C(10)	1.500(5)	O(13)—N(3)—O(11)	100.9(10)
C(11)—C(12)	1.513(5)	O(13)—N(3)—O(12)	112.8(9)
C(13)—C(14)	1.383(4)	O(11)—N(3)—O(12)	144.4(9)
C(13)—C(18)	1.388(4)	N(3)—O(2)—O(3)	57.9(8)
C(14)—C(15)	1.385(5)	N(3)—O(3)—O(2)	59.9(9)
C(15)—C(16)	1.364(6)	C(2)—C(1)—P(1)	113.8(2)
C(16)—C(17)	1.368(5)	N(1)—C(2)—C(1)	119.6(2)
C(17)—C(18)	1.383(4)	N(1)—C(2)—S(2)	121.3(2)
C(19)—C(24)	1.387(4)	C(1)—C(2)—S(2)	119.1(2)
C(19)—C(20)	1.387(4)	C(4)—C(3)—P(2)	117.9(2)
C(20)—C(21)	1.383(4)	N(2)—C(4)—C(3)	119.5(3)
C(21)—C(22)	1.364(5)	N(2)—C(4)—S(4)	121.2(2)
C(22)—C(23)	1.377(5)	C(3)—C(4)—S(4)	119.1(2)
C(23)—C(24)	1.377(5)	C(6)—C(5)—N(2)	112.9(4)
C(25)—C(30)	1.385(4)	N(2)—C(7)—C(8)	111.2(4)
C(25)—C(26)	1.385(4)	N(1)—C(9)—C(10)	112.2(3)
C(26)—C(27)	1.392(5)	N(1)—C(11)—C(12)	113.3(3)
C(27)—C(28)	1.362(6)	C(14)—C(13)—C(18)	119.3(3)
C(28)—C(29)	1.377(5)	C(14)—C(13)—P(1)	120.1(2)
C(29)—C(30)	1.388(5)	C(18)—C(13)—P(1)	120.6(2)
C(31)—C(32)	1.386(4)	C(13)—C(14)—C(15)	119.5(3)
C(31)—C(36)	1.386(4)	C(16)—C(15)—C(14)	120.9(3)
C(32)—C(33)	1.396(4)	C(15)—C(16)—C(17)	120.0(3)
C(33)—C(34)	1.361(5)	C(16)—C(17)—C(18)	120.1(3)
C(34)—C(35)	1.360(5)	C(17)—C(18)—C(13)	120.1(3)
C(35)—C(36)	1.379(4)	C(24)—C(19)—C(20)	119.1(3)
		C(24)—C(19)—P(1)	119.3(2)
		C(20)—C(19)—P(1)	121.4(2)
		C(21)—C(20)—C(19)	119.9(3)
		C(22)—C(21)—C(20)	120.6(3)
		C(21)—C(22)—C(23)	119.9(3)
		C(24)—C(23)—C(22)	120.2(3)
		C(23)—C(24)—C(19)	120.3(3)
		C(30)—C(25)—C(26)	119.5(3)
		C(30)—C(25)—P(2)	118.9(2)
		C(26)—C(25)—P(2)	121.5(3)
		C(25)—C(26)—C(27)	119.2(4)
		C(28)—C(27)—C(26)	121.1(3)
		C(27)—C(28)—C(29)	120.0(3)
		C(28)—C(29)—C(30)	119.8(4)
		C(25)—C(30)—C(29)	120.4(3)
		C(32)—C(31)—C(36)	119.7(3)
		C(32)—C(31)—P(2)	122.7(2)
		C(36)—C(31)—P(2)	117.5(2)
		C(31)—C(32)—C(33)	119.1(3)
		C(34)—C(33)—C(32)	120.3(3)
		C(35)—C(34)—C(33)	120.7(3)
		C(34)—C(35)—C(36)	120.3(4)
		C(35)—C(36)—C(31)	119.9(3)

Results and Discussion

The structure of the $[Ag(L\text{-}3)_2]NO_3$ complex (3). The crystal of **3** consists of isolated $[Ag(L\text{-}3)_2]^+$ cations and NO_3^- anions. The structure of the cation is shown in Fig. 1. The independent ligands L′ and L″* are η^2-bidentate. They coordinate the Ag atom through both S atoms and form six-membered chelate rings. The coordination environment about the Ag atom is a distorted tetrahedron in which the S(3)Ag(1)S(4) and S(1)Ag(1)S(4) angles are the smallest (87.76(3)°) and the largest (128.89(3)°), respectively. The dihedral angle between the S(1)Ag(1)S(2) and S(3)Ag(1)S(4) planes is 84.0°. The Ag—S bonds also differ substantially in that one of them (Ag(1)—S(3)) is significantly longer (2.771(1) Å) than the three other bonds (Ag(1)—S(1), Ag(1)—S(2), and Ag(1)—S(4) bond lengths are 2.535(1), 2.533(1), and 2.500(1) Å, respectively).

The chelate rings are nonplanar and have irregular conformations (the torsion angles are given in Table 3). The $CH_2C(=S)N$ fragments of every ligand are planar. In the L′ ligand, deviations of the Ag(1), P(1), and S(1) atoms from the S(2)C(2)C(1)N(1) plane are −0.060(4), 1.596(4), and 1.763(5) Å, respectively. In the L″ ligand, deviations of the Ag(1), P(2), and S(3) atoms from the S(4)C(4)C(3)N(2) plane are −0.549(4), −1.566(4), and −2.747(4) Å, respectively. To a first approximation, the overall conformation of the rings can be described as boat-like: the "bottom" of the boat is formed by the

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* Hereinafter, index 3 in the notations of the ligands (L-3)′ and (L-3)″ is omitted for simplicity.

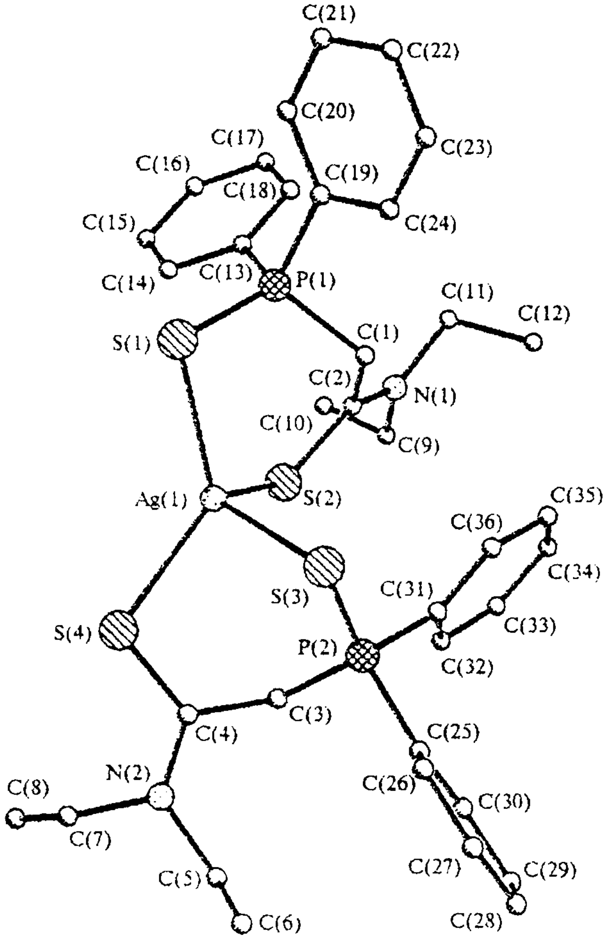
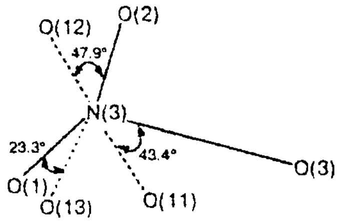


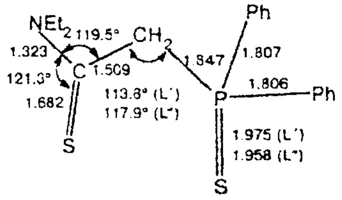
Fig. 1. Structure of the $[Ag(L\text{-}3)_2]^+$ cation in complex **3**.

$\{S_2PC(NEt_2)\}$ atoms, and the Ag and $C(H_2)$ atoms deviate from the plane of the "bottom" of the boat in the same direction (by 1.012(4) and 0.846(6) Å, respectively, in the Ag(1)S(1)P(1)C(1)C(2)S(2) ring and by 1.764(4) and 0.547(6) Å, respectively, in the Ag(1)S(3)P(2)C(3)C(4)S(2) ring).

The O atoms of the NO_3^- anion are distributed between two positions with occupancies of 0.4 (the O(1), O(2), and O(3) atoms) and 0.6 (the O(11), O(12), and O(13) atoms). The dihedral angle between the N(3)O(1)O(2)O(3) and N(3)O(11)O(12)O(13) planes is 21(1)°. Apparently, it is more proper to describe the disorder of the NO_3^- ion as a whole (rather than to describe the disorder as the rotation of O atoms about the threefold pseudoaxis passing through the N(3) atom) because the N(3) atom deviates from the O(1)O(2)O(3) and O(11)O(12)O(13) planes by −0.04(1) and 0.093(7) Å, respectively. However, we failed to locate an alternative position of the N(3) atom, apparently because it is close to the first position of N(3).



The geometric parameters of the independent ligands L′ and L″ in complex **3** are close within the experimental error, except for the P=S bond lengths and CCP bond angles. The average values are given in the scheme (both individual values are given only for the parameters that differ substantially):



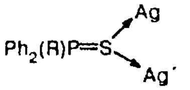
The C=S and C—N bond lengths in the noncoordinated $S{=}C{-}NMe_2$ groups of the thiocarbamides studied previously are 1.678(5) and 1.334(6) Å,[7] 1.676(6) and 1.334(7) Å,[8] 1.674(3) and 1.326(4) Å,[9] and 1.666(4) and 1.339(4) Å,[10] respectively. A comparison of these data with the bond lengths obtained for complex **3** demonstrated that the thiocarbonyl group in the complex with ligand L-3 remains virtually unchanged upon coordination with the Ag atom. Analogous values of the C=S (1.674(7) Å) and C—N (1.322(8) Å) bond lengths have been reported for the coordinated $(Bu_2NC(S)CH_2OCH_2)_2$ ligand (L-4), which also contains a thiocarbonyl group, in the $[Cd_2Cl_4(L\text{-}4)]$ complex (**4**).[11]

The P=S bond length changes upon coordination of the $Ph_2P{=}S$ group by the Ag atom. The difference in the

Table 3. Torsion angles (τ) in the chelate rings of the $[Ag(L\text{-}3)_2]^+$ cation of complex **3**

Angle	τ/deg
Ag(1)S(4)C(2)C(1)	−1.6(2)
Ag(1)S(3)C(4)C(3)	−15.6(2)
S(4)C(2)C(1)P(1)	−70.1(3)
S(3)C(4)C(3)P(2)	−80.0(3)
C(2)C(1)P(1)S(1)	85.7(2)
C(4)C(3)P(2)S(2)	−37.0(3)
C(1)P(1)S(1)Ag(1)	−39.1(1)
C(3)P(2)S(2)Ag(1)	−17.5(1)
P(1)S(1)Ag(1)S(4)	−30.95(5)
P(2)S(2)Ag(1)S(3)	71.51(4)
S(1)Ag(1)S(4)C(2)	47.7(1)
S(2)Ag(1)S(3)C(4)	−50.7(1)

Table 4. Selected geometric parameters and ν(PS) stretching frequencies of the P=S bond in the fragments $Ph_2(R)P{=}S\rightarrow Ag$ (*A*) and



$Ph_2(R)P{=}S\begin{matrix}\nearrow Ag \\ \searrow Ag'\end{matrix}$ (*B*)

Complex	Fragment *A*					
	R	ν(PS) /cm^{-1}	*d*/Å P=S	*d*/Å Ag—S	ω/deg, P—S—Ag	Coordination number and composition of the polyhedron
2 [6]	CH_2	600	1.979(1)	2.449(1)	104.38(7)	3+2 $\{S_2O+O_2\}$
3	CH_2	580, 620*	1.975(1), 1.958(1)	2.535(1), 2.770(1)	110.77(4), 90.13(4)	3+1 $\{S_4\}$
5 [3]	CH_2	605, 585	1.962(3), 1.969(3), 1.974(3), 1.974(3)	2.634(3), 2.637(3), 2.584(2), 2.584(3)	95.9(1), 99.7(1), 101.2(1), 98.0(1)	4 $\{S_4\}$
6 [13]	CH_2	595	1.992(1)	2.457(1)	99.03(4)	2+2 $\{SP+O_2\}$
7 [14]	—		1.999(3), 1.990(3), 1.991(3)	2.585(2), 2.639(3), 2.667(2)	97.3(1), 97.7(1), 96.2(1)	4 $\{S_3P\}$

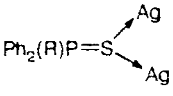
Complex	Fragment *B*						
	R	ν(PS) /cm^{-1}	*d*/Å P=S	*d*/Å S—Ag	*d*/Å S—Ag′	*d*/Å Ag—Ag′	Coordination number and composition of the polyhedron
2 [6]	CH_2	585	2.005(2)	2.464(1)	2.558(1)	3.541	3+2 Ag: $\{S,O_2+O_2\}$ Ag′: $\{S_2,O+O_2\}$
1 [5]	CH_2	565, 595	2.010(1)	2.571(1)	2.722(1)	3.241	4 $\{S_2,O_2\}$

* Average value of the frequency (see the text).

P=S bond lengths in the crystallographically independent ligands L-3 (L′ and L″) in complex **3** is attributable to the fact that the S(3) atom in L″, unlike the S(1) atom in L′, forms a very weak bond with the Ag(1) atom (*d* = 2.770(1) Å). Therefore, the interaction between the P(2)=S(3) bond and the Ag atom has no noticeable effect on this bond: its length is equal to the P=S bond length in the noncoordinated molecules (1.954 Å),[12] whereas the C(4)—C(3)—P(2) angle in the chelate ring formed by the L″ ligand is substantially more "expanded" (117.9(2)°) than the analogous C(2)—C(1)—P(1) angle (113.8(2)°) in the L′ ligand.

Although in the complexes with ligands L-1, L-2, and L-3 studied the P=S and Ag—S bond lengths differ substantially, there is no distinct correlation between the P=S and Ag—S (Ag—S=P) bond lengths in these structures. Selected characteristics of the fragments

$Ph_2(R)P{=}S\rightarrow Ag$ and



$Ph_2(R)P{=}S\begin{matrix}\nearrow Ag \\ \searrow Ag\end{matrix}$

in complexes with ligands L-1 (**1**), L-2 (**2**), and L-3 (**3**), in complexes with $Ph_2P(S)CH_2P(S)Ph_2$ (L-5), ($[Ag(L\text{-}5)_2]NO_3$ (**5**)),[3] and $Ph_2PCH_2CH_2P(S)Ph_2$ (L-6), ($[Ag_2(L\text{-}6)_2](NO_3)_2$ (**6**)),[13] and in the $[(Bu_3P)Ag^+\{S{=}PPh_2)_3C^-\}]$ complex (**7**)[14] are given in Table 4. As can be seen from Table 4, the strongest Ag—S bonds occur in complexes **2** and **6**. Two of these bonds are formed by terminal S atoms (2.449 and 2.457 Å), and the third bond is formed by the bridging S atom (2.464 Å). It seems reasonable to expect that the P=S bond is the longest when the Ag—S bond is the shortest. However, the shortest Ag—S bond (2.449 Å) corresponds to the P=S bond with the length (1.979 Å) close to the average value of those listed in Table 4 (1.958—2.010 Å). Apparently, the absence of the above-mentioned correlation is indicative of different degrees of participation of both the lone electron pair of the S atom and the electrons of the π orbital of the P=S bond in the formation of each particular Ag←S=P bond.

IR spectra of ligand L-3 and complex 3. Table 5 gives the absorption bands of ligand L-3, whose frequencies are changed by coordination.

As in the case of the related compounds L-1 [5] and L-2 [6], the bands at 615 and 635 cm^{-1} may be attributed to the ν(P=S) vibration of the thiophosphoryl bond of the free L-3 molecule. In the spectrum of complex **3**, a

Table 5. Frequencies of vibrations (ν/cm^{-1}) of (*N*,*N*-diethylthiocarbamoylmethyl)diphenylphosphine sulfide (L-3) that change upon coordination in the [Ag_2(L-3)]NO_3 complex (3)

Solid sample		Solution in $CHCl_3$		Assignment
Free ligand	Complex	Free ligand	Complex	
553 m	535 m	550 w	550 w	Deformation vibrations
590 m	557 m	585 w		
615 w	580 s	615 w	580 s	ν(P=S)
635 s	610 m	635 s	615 w	
	625 m	625 w		
	630 m			
890 m	885 s	Absorption of the solvent		
1235 m	1190 m			ν((N)CS), ν(NC(S))
1280 m	1220 w			
	1240 m			
1520 n.s	1525—1530 s.d	1520 s	1530—1540 m.br	ν(N—C(S))

band at 580 cm^{-1} appears instead of the band at 635 cm^{-1}. However, in the 610—630 cm^{-1} region, medium-intensity absorption bands persist. Each of these bands can correspond to the ν(P=S) vibration. This spectral pattern can be related to the data of X-ray structural analysis, according to which the P=S bond in the L′ ligand is longer than in the free molecule (ν(P=S) at 580 cm^{-1} corresponds to this bond), whereas in the L″ ligand this bond remains virtually unchanged (ν(P=S) is 610—630 cm^{-1}). However, this assignment requires that the ν(P=S) vibration be highly characteristic, which is not generally recognized.[15] In Table 4, the P=S bond lengths in various complexes correlate with the frequencies of vibrations. Although each complex under consideration contains two coordinated ligands, whose vibrations can be coupled and cause splitting of the bands, a certain correlation is observed: it can be noted that in complex 3 with the shortest P=S bond (1.958 Å), the highest ν(P=S) frequency (610—630 cm^{-1}) is observed, whereas the lowest frequency (565 cm^{-1}) corresponds to the longest bond, which is in complex 1 (2.010 Å). A comparison of ν(P=S) in compounds L-1—L-3 under study and also in L-5 and L-6 and the changes in these frequencies upon coordination suggests that the shape of the ν(P=S) vibration is rather characteristic.

Vibrations of the second functional (thioamide) group of the L-3 molecule are not characteristic. Analysis of vibrations of molecules containing an N—C=S fragment have demonstrated[16] that the absorption bands corresponding to mixed vibrations of the C—N and C=S bonds with a larger contribution of ν(C=S) and to skeletal deformations are observed in the 500—700 cm^{-1} region. Mixed ν(N—C=S) vibrations occur in the 950—1100 cm^{-1} region. Bands with a substantial contribution of the vibration of the C—N bond, which are most sensitive to coordination of the S atom,[17] are observed in the 1400—1600 cm^{-1} region. In complexation of tetraethylthiuram disulfide, {$Et_2NC(S)$}$_2S_2$, with various ions, coordination of the S atom of the C=S group is accompanied by a shift of the ν(C—N) band at 1495 cm^{-1} to the high-frequency region and by the disappearance of the ν(C=S) band at 1000 cm^{-1}, *i.e.*, the S=C—N group transforms into a bipolar $^{-}$S—C=N^{+} group.[18] The bands in the 700 cm^{-1} region, which are shifted to the low-frequency region after coordination of the S atom, are also assigned to the ν(C=S) vibration.[19]

The bands at 1235 and 1280 cm^{-1} are shifted to the low-frequency region after coordination of ligand L-3, which may be associated with the coordination of the C=S group. However, the coordination of this group is best characterized by a shift of the band at 1520 cm^{-1} to the high-frequency region, which confirms the fact that this band corresponds to the vibration of the (S)C—N bond, whose order increases regularly as the C=S bond length increases. Note that analogous spectral changes have been observed in the formation of complexes of *N*-arylthiobenzamides.[19] A single intense absorption band at 1340 cm^{-1} (ν_e) was observed in the spectrum of complex 3. This band is characteristic of a nitrate anion with nondistorted D_{3h} symmetry[15] and indicates that the NO_3^- ion is not involved in the coordination polyhedron. Therefore, the spectrum of ligand L-3 is consistent with coordination of both functional groups, and unambiguous assignment of the band of the degenerate ν_e vibration of the free nitrate anion is indirect evidence that the silver ion is chelated by two ligands.

The spectra of a solution of complex 3 and solutions containing metal-ligand mixtures in a ratio of 1 : 2 are analogous to the spectra of the crystalline sample (see Table 5) and, therefore, the structure of the complex of ligand L-3 with $AgNO_3$ obtained at this component ratio in a solution is identical to that observed in the crystal.

UV spectra of solutions of ligand L-3 and complex 3 in MeCN. The free ligand gives an absorption band λ_{max} at 287 nm, ε = 10400. This band was not observed[6] in the spectra of the ligands L-1, L-2, and L-5 studied previously. This band is characteristic of many compounds containing a thioamide group,[20,21] and therefore it may be associated with the presence of this group in the molecule. An analogous band was observed in the spectra of metallocomplexes of *N*-arylthiobenzamides,[17] and it was assigned to the n→π* transition in molecules with the C=S bond.

In the spectrum of the bisligand complex 3, λ_{max} of the C=S-band is observed at 298 nm.

In the course of titration of a solution of the ligand with a solution of $AgNO_3$, a change typical of an equilibrium "free ligand—complex" transition is observed in the spectrum. Once the M : L ratio becomes equal to 1 : 2, the band corresponding to complex 3 (λ_{max} = 299 nm) is not shifted any longer. In addition, in the course of titration, the absorption at ~250 nm (in the region of the manifestation of the P=S-band[6]) increases gradually, which is indicative of coordination of the thiophosphoryl group.

The stability constant of the $[Ag(L\text{-}3)_2]^+$ complex in MeCN was determined according to the standard procedure,[21] $\log K = 3.7(1)$.

Thus, when silver nitrate reacts with the thiophosphoryl-thioamide ligand L-3, the $[Ag(L\text{-}3)_2]NO_3$ complex, whose structure is analogous to the structure of the silver bis(diphenylthiophosphoryl)methane complex (5) is formed.[3]

Studies of the interactions of the three related compounds, L-1, L-2, and L-3, with $AgNO_3$ demonstrated that all of them form complexes through coordination of both donor centers with an Ag^+ ion. However, the structures of these complexes are different: in the case of L-1, the centrosymmetric $[Ag(L\text{-}1)NO_3]_2$ dimer forms;[5] in the case of L-2, the polymeric $[Ag_2(L\text{-}2)_2(NO_3)_2]_n$ complex forms;[6] and in the case of the ligand L-3, the soluble $[Ag(L\text{-}3)_2]NO_3$ complex forms. Ligand L-3 is the closest analog of bis(diphenylthiophosphoryl)methane (L-5). Because L-5 is characterized by high extraction constants of silver ions from aqueous solutions,[3] it can be suggested that ligand L-3 is also a good extractive agent with respect to silver ions.

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