Organometallic Chemistry

Complexation of (carbamoylmethyl)diphenylphosphine sulfide with silver nitrate. The structure of the polymeric complex $[Ag_2\{Ph_2P(S)CH_2C(O)NH_2\}_2(NO_3)_2]_n$

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The reaction of (carbamoylmethyl)diphenylphosphine sulfide with $AgNO_3$ yields the polymeric complex $[Ag_2\{Ph_2P(S)CH_2C(O)NH_2\}_2(NO_3)_2]_n$. Its structure was established by X-ray diffraction analysis. The coordination environments about both Ag^+ cations are formed by five donor atoms, two of which are bonded to the metal atom substantially more weakly than the remaining three atoms. The compositions of the coordination polyhedra are different: ($\{AgSO'(C)O(N)O_2(N')\}$ and $\{AgS'SO(C)O_2(N)\}$). The coordinated ligands differ in their functions: one ligand chelates the metal cation and its sulfur atom is additionally bonded to the second cation, while the second ligand acts as a bridge between the two different cations. The structure of the complex and the character of the interaction between the ligand and $AgNO_3$ are substantially affected by the network of hydrogen bonds.

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

The interactions and the structures of complexes of bifunctional ligands that contain phosphoryl (thiophosphoryl) and carbamoyl groups as donor centers with cations of various metals have some peculiarities[1–6] compared to the complexes of classical chelating bis(phosphine oxides) and bis(phosphine sulfides). Although most (carbamoylmethyl)dialkylphosphine oxides, like bis(phosphine oxides), form chelate complexes with heavy metal cations,[1,2] the tridentate $(Pr^iO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ ligand is coordinated by the Er^{3+} cation only through the phosphoryl group in its complex with $Er(NO_3)_3$,[3] whereas in the $[MoO_2Cl_2\{(EtO)_2P(S)CH_2C(O)NEt_2\}_2]$ complex, only one carbonyl group is coordinated.[4] Unlike bis(diphenylthiophosphoryl)methane $Ph_2P(S)CH_2P(S)Ph_2$ (L-1), which forms the bisligand chelate complex $[Ag(L\text{-}1)_2]NO_3$ (**1**)[5] with the "thiophilic" silver cation, (*N,N*-diethylcarbamoylmethyl)diphenylphosphine sulfide, $Ph_2P(S)CH_2C(O)NEt_2$ (L-2), gives a complex of composition 1 : 1, $[Ag(L\text{-}2)NO_3]_2$ (**2**), which

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is a centrosymmetric dimer with a bridging S atom, namely, $\{AgS_2O(C)O(NO_2)\}$.[6] We have synthesized[7] the analog of L-2, namely, (carbamoylmethyl)diphenylphosphine sulfide, $Ph_2P(S)CH_2C(O)NH_2$ (L-3), containing a primary amide $C(O)NH_2$ group instead of a diethylamide $C(O)NEt_2$ fragment.

In this work, we studied complexation of the ligand L-3 with $AgNO_3$ at various metal—ligand ratios (M : L) in coordinating and noncoordinating solvents (under conditions of preparation of complex **2**)[6] by X-ray structural analysis and IR and UV spectroscopy.

Experimental

The synthesis of compound L-3 has been described previously.[7] The IR spectra were recorded on a UR-20 spectrometer. Cells of KBr or CaF_2 were used for solutions. The spectra of solutions of the ligand in $CHCl_3$ and MeCN were obtained at concentrations of 0.2, 0.1, 0.008, 0.003, and 0.0001 mol L^{-1}. With the aim of destroying associates and determining absorption bands corresponding to the free molecule L-3, the solution was repeatedly diluted. The cell length was chosen in relation to dilution. Solid samples were analyzed as KBr pellets (the initial compound) or as Nujol mulls (the initial compound and complexes).

The UV spectra of ligands L-1, L-2, and L-3 and of the complexes in MeCN (provided they were soluble) were recorded on a Specord UV-VIS M-40 spectrophotometer with the use of 0.1-cm quartz cells. A solution of the ligand (C_L = 0.0005 mol L^{-1}) was titrated (using 0.1 mol. equiv. portions) with a solution of $AgNO_3$ with a known concentration.

Preparation of the complex of ligand L-3 with $AgNO_3$. Solutions of the ligand (0.0507 g in 10 mL) and $AgNO_3$ (0.0313 g in 10 mL) in MeCN were mixed to give an equimolar ratio (C = 0.02 mol L^{-1}). A white finely dispersed precipitate was obtained after 1—2 h. The mixture was filtered, and the solid product was washed with Et_2O and dried in air. A white powdered compound was obtained in a yield of 0.053 g

Table 1. Atomic coordinates (×10^4, ×10^3 for H atoms) and their isotropic equivalent ($U_{eq} \cdot 10^3/Å^2$), isotropic for H atoms ($U_{iso} \cdot 10^3/Å^2$) thermal factors in the structure of $[Ag_2(Ph_2P(S)CH_2CONH_2)_2(NO_3)_2]$

Atom	x	y	z	U_{eq}/U_{iso}
Ag(1)	13225(1)	1328(1)	1268(1)	50(1)
Ag(2)	9609(1)	900(1)	883(1)	52(1)
S(1)	8006(1)	−75(1)	284(1)	36(1)
S(2)	11364(1)	2158(1)	689(1)	34(1)
P(1)	7550(1)	−1070(1)	817(1)	27(1)
P(2)	10781(1)	3171(1)	1201(1)	27(1)
N(1)	4393(6)	−874(4)	1664(3)	56(2)
N(2)	7553(6)	2815(5)	2104(3)	61(2)
N(3)	14026(5)	2028(3)	2480(2)	48(1)
N(4)	10919(5)	−7(3)	2018(2)	45(1)
O(1)	5080(4)	350(3)	1208(2)	56(1)
O(2)	8117(4)	1965(3)	1372(2)	61(1)
O(3)	14727(5)	1983(4)	2052(2)	84(2)
O(4)	12832(5)	1696(4)	2425(2)	95(2)
O(5)	14513(6)	2343(3)	2946(2)	87(2)
O(6)	11384(6)	−453(3)	2437(2)	91(2)
O(7)	9833(5)	456(3)	2040(2)	77(1)
O(8)	11549(4)	1(3)	1558(2)	52(1)
C(1)	6847(6)	−719(4)	1506(2)	35(1)
C(2)	5359(5)	−367(4)	1448(2)	31(1)
C(3)	9968(5)	2828(4)	1861(2)	31(1)
C(4)	8461(5)	2496(4)	1758(2)	33(1)
C(5)	6206(5)	−1776(3)	454(2)	27(1)
C(6)	5386(5)	−1421(4)	−16(2)	33(1)
C(7)	4355(5)	−1945(4)	−318(2)	40(1)
C(8)	4139(6)	−2816(4)	−145(3)	41(2)
C(9)	4919(6)	−3166(4)	332(3)	47(2)
C(10)	5954(6)	−2653(4)	628(3)	42(1)
C(11)	9092(5)	−1751(3)	1040(2)	30(1)
C(12)	9049(6)	−2418(4)	1471(2)	41(1)
C(13)	10244(7)	−2919(5)	1629(3)	50(2)
C(14)	11466(7)	−2764(5)	1361(3)	57(2)
C(15)	11522(6)	−2116(5)	931(3)	51(2)
C(16)	10328(6)	−1617(4)	774(3)	38(1)
C(17)	12280(5)	3862(3)	1447(2)	29(1)
C(18)	12134(6)	4547(4)	1856(2)	41(1)
C(19)	13273(7)	5085(4)	2030(3)	51(2)
C(20)	14550(7)	4941(5)	1802(3)	62(2)
C(21)	14703(7)	4272(5)	1403(4)	68(2)
C(22)	13569(6)	3736(4)	1221(3)	45(2)
C(23)	9530(5)	3892(3)	792(2)	29(1)
C(24)	8818(6)	4551(4)	1087(3)	40(1)
C(25)	7912(6)	5140(4)	777(3)	48(2)
C(26)	7729(6)	5066(4)	175(3)	50(2)
C(27)	8415(6)	4416(4)	−118(3)	42(1)
C(28)	9328(6)	3830(4)	187(2)	34(1)
H[C(1A)]	692(4)	−126(3)	177(2)	27(12)
H[C(1B)]	741(4)	−34(3)	161(2)	9(12)
H[C(3A)]	1046(4)	237(3)	200(2)	6(11)
H[C(3B)]	1004(4)	335(3)	213(2)	24(12)
H[N(1A)]	457(5)	−131(3)	177(2)	5(13)
H[N(1B)]	338(7)	−71(4)	165(3)	67(19)
H[N(2A)]	677(8)	262(5)	210(3)	99(30)
H[N(2B)]	775(6)	314(4)	233(3)	46(22)
H(6)	552(4)	−85(3)	−15(2)	16(12)
H(7)	382(5)	−168(3)	−65(2)	36(14)
H(8)	347(5)	−316(3)	−34(2)	37(14)
H(9)	470(6)	−370(4)	47(2)	51(18)
H(10)	641(5)	−291(3)	96(2)	33(14)
H(12)	827(5)	−247(3)	169(2)	20(12)
H(13)	1009(6)	−338(4)	189(3)	56(19)
H(14)	1222(7)	−311(4)	145(3)	66(20)
H(15)	1243(6)	−201(4)	74(2)	51(16)
H(16)	1039(5)	−123(3)	53(2)	30(17)
H(18)	1127(5)	464(3)	202(2)	34(14)
H(19)	1319(6)	555(4)	230(2)	53(17)
H(20)	1524(7)	528(5)	195(3)	89(25)
H(21)	1550(6)	417(4)	127(2)	46(17)
H(22)	1374(5)	329(4)	94(2)	40(15)
H(24)	901(6)	460(4)	148(3)	52(18)
H(25)	753(6)	555(4)	104(3)	69(21)
H(26)	708(5)	549(4)	0(2)	46(15)
H(27)	825(6)	436(4)	−57(3)	58(17)
H(28)	978(4)	345(3)	1(2)	13(13)

(65%), m.p. 132—135 °C (with decomp.). Found (%): C, 37.53; H, 3.14; Ag, 23.84; N, 6.14; P, 6.78. $C_{14}H_{14}AgN_2O_4PS$ (M : L = 1 : 1). Calculated (%): C, 37.70; H, 3.15; Ag, 24.27; N, 6.29; P, 6.97. The reaction in $CHCl_3$ was carried out using a weighed sample of $AgNO_3$, which was added to a solution of the ligand to give a M : L ratio of 1 : 1 or 1 : 2. The mixture was stirred with an ultrasonic stirrer. After 30—40 min, a complex analogous to that described above precipitated.

Preparation of the finely crystalline complex $[Ag_2(L\text{-}3)_2(NO_3)_2]_n$ (3). Equimolar amounts of ligand L-3 (0.0243 g) and $AgNO_3$ (0.015 g) were dissolved in MeOH (5 mL each) with the use of an ultrasonic stirrer. The solutions were mixed. After ~1 day, colorless crystals precipitated, m.p. 132—135 °C (with decomp.). Found (%): C, 37.66; H, 3.04; N, 6.16.

The IR spectrum of a single-crystalline sample (as Nujol mulls) was identical to the spectra of powdered complexes isolated from MeCN and $CHCl_3$.

Colorless isometric crystals of [μ_2-2-(carbamoylmethyl)diphenylphosphinesulfido]-[η^2,μ_2-2-(carbamoylmethyl)diphenylsulfido]-disilver(+1) nitrate, $[Ag_2(L\text{-}3)_2(NO_3)_2]$ (3), $C_{28}H_{28}Ag_2N_4O_8P_2S_2$ (mol. weight 890.34) are monoclinic, at 20 °C, a = 9.4805(11), b = 14.829(2), c = 22.868(3) Å, V = 3208.0(7) Å^3, Z = 4, d_{calc} = 1.843 g cm^{-3}, space group $P2_1/c$. The unit cell parameters and intensities of 3959 independent reflections were measured on an automated Siemens P3/PC diffractometer (Mo-Kα radiation, θ/2θ scanning technique, μ = 15.06 cm^{-1}, θ > 22°). The structure was solved by the direct method and refined based on F^2 by the full-matrix least-squares method with anisotropic thermal factors for nonhydrogen atoms. All H atoms were located from the difference electron density syntheses and refined isotropically. The final R factors are as follows: R_1 = 0.0332 for 3116 observed reflections with $\langle I \rangle > 2\sigma(I)$, wR_2 = 0.1346 based on a total of 3946 reflections included in the refinement. The number of refinable parameters was 527. 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 2. Bond lengths (d) and bond angles (ω) in the structure of $[Ag_2(Ph_2P(S)CH_2CONH_2)_2(NO_3)_2]$

Bond	d/Å	Angle	ω/deg
Ag(1)—O(1)′	2.291(4)	O(1)′—Ag(1)—O(3)	83.2(2)
Ag(1)—O(3)	2.418(4)	O(1)′—Ag(1)—S(2)	144.06(11)
Ag(1)—S(2)	2.4635(13)	O(3)—Ag(1)—S(2)	124.33(14)
Ag(2)—O(2)	2.441(4)	O(2)—Ag(2)—S(1)	106.34(9)
Ag(2)—S(1)	2.4491(13)	O(2)—Ag(2)—S(2)	90.61(10)
Ag(2)—S(2)	2.5576(14)	S(1)—Ag(2)—S(2)	136.08(5)
S(1)—P(1)	1.979(2)	P(1)—S(1)—Ag(2)	104.38(7)
S(2)—P(2)	2.005(2)	P(2)—S(2)—Ag(1)	105.97(6)
P(1)—C(5)	1.808(5)	P(2)—S(2)—Ag(2)	103.74(7)
P(1)—C(11)	1.821(5)	Ag(1)—S(2)—Ag(2)	89.65(4)
P(1)—C(1)	1.826(5)	C(5)—P(1)—C(11)	109.6(2)
P(2)—C(17)	1.812(5)	C(5)—P(1)—C(1)	105.9(2)
P(2)—C(3)	1.812(5)	C(11)—P(1)—C(1)	104.4(2)
P(2)—C(23)	1.811(5)	C(5)—P(1)—S(1)	109.0(2)
N(1)—C(2)	1.306(7)	C(11)—P(1)—S(1)	112.5(2)
N(2)—C(4)	1.296(7)	C(1)—P(1)—S(1)	115.2(2)
N(3)—O(3)	1.221(6)	C(17)—P(2)—C(3)	105.6(2)
N(3)—O(5)	1.226(6)	C(17)—P(2)—C(23)	107.4(2)
N(3)—O(4)	1.233(6)	C(3)—P(2)—C(23)	107.2(2)
N(4)—O(6)	1.222(6)	C(17)—P(2)—S(2)	111.4(2)
N(4)—O(7)	1.241(6)	C(3)—P(2)—S(2)	115.2(2)
N(4)—O(8)	1.244(6)	C(23)—P(2)—S(2)	109.7(2)
O(1)—C(2)	1.217(6)	O(3)—N(3)—O(5)	121.7(5)
O(1)—Ag(1)″	2.291(4)	O(3)—N(3)—O(4)	116.2(5)
O(2)—C(4)	1.212(6)	O(5)—N(3)—O(4)	122.1(6)
C(1)—C(2)	1.502(7)	O(6)—N(4)—O(7)	121.6(5)
C(3)—C(4)	1.515(7)	O(6)—N(4)—O(8)	120.0(5)
C(5)—C(10)	1.384(7)	O(7)—N(4)—O(8)	118.4(5)
C(5)—C(6)	1.388(7)	C(2)—O(1)—Ag(1)″	132.1(3)
C(6)—C(7)	1.396(7)	C(4)—O(2)—Ag(2)	128.2(3)
C(7)—C(8)	1.370(8)	N(3)—O(3)—Ag(1)	106.9(3)
C(8)—C(9)	1.378(8)	C(2)—C(1)—P(1)	114.7(4)
C(9)—C(10)	1.383(8)	O(1)—C(2)—N(1)	122.4(5)
C(11)—C(16)	1.370(7)	O(1)—C(2)—C(1)	121.1(5)
C(11)—C(12)	1.399(7)	N(1)—C(2)—C(1)	116.4(5)
C(12)—C(13)	1.383(8)	C(4)—C(3)—P(2)	114.2(4)
C(13)—C(14)	1.365(9)	O(2)—C(4)—N(2)	121.6(5)
C(14)—C(15)	1.377(9)	O(2)—C(4)—C(3)	122.0(5)
C(15)—C(16)	1.381(8)	N(2)—C(4)—C(3)	116.4(5)
C(17)—C(22)	1.371(7)	C(10)—C(5)—C(6)	118.7(5)
C(17)—C(18)	1.393(7)	C(10)—C(5)—P(1)	122.8(4)
C(18)—C(19)	1.380(8)	C(6)—C(5)—P(1)	118.5(4)
C(19)—C(20)	1.366(9)	C(5)—C(6)—C(7)	120.6(5)
C(20)—C(21)	1.361(10)	C(8)—C(7)—C(6)	119.7(5)
C(21)—C(22)	1.378(8)	C(7)—C(8)—C(9)	120.0(5)
C(23)—C(28)	1.387(7)	C(8)—C(9)—C(10)	120.4(6)
C(23)—C(24)	1.388(7)	C(9)—C(10)—C(5)	120.4(5)
C(24)—C(25)	1.387(8)	C(16)—C(11)—C(12)	118.8(5)
C(25)—C(26)	1.380(9)	C(16)—C(11)—P(1)	119.3(4)
C(26)—C(27)	1.363(8)	C(12)—C(11)—P(1)	121.9(4)
C(27)—C(28)	1.383(7)	C(13)—C(12)—C(11)	120.1(6)
		C(14)—C(13)—C(12)	119.8(7)
		C(13)—C(14)—C(15)	120.8(6)
		C(14)—C(15)—C(16)	119.3(6)
		C(11)—C(16)—C(15)	121.1(6)
		C(22)—C(17)—C(18)	118.9(5)
		C(22)—C(17)—P(2)	120.4(4)
		C(18)—C(17)—P(2)	120.7(4)
		C(19)—C(18)—C(17)	120.3(6)
		C(20)—C(19)—C(18)	119.7(6)
		C(21)—C(20)—C(19)	120.4(6)
		C(20)—C(21)—C(22)	120.5(7)
		C(17)—C(22)—C(21)	120.3(6)
		C(28)—C(23)—C(24)	119.5(5)
		C(28)—C(23)—P(2)	121.2(4)
		C(24)—C(23)—P(2)	119.2(4)
		C(25)—C(24)—C(23)	120.0(6)
		C(26)—C(25)—C(24)	119.5(6)
		C(27)—C(26)—C(25)	120.9(6)
		C(26)—C(27)—C(28)	120.0(6)
		C(27)—C(28)—C(23)	120.1(6)

Note. Primed and doubly primed atoms are generated from the basis atoms by the symmetry operations $x+1$, y, z and $x-1$, y, z, respectively.

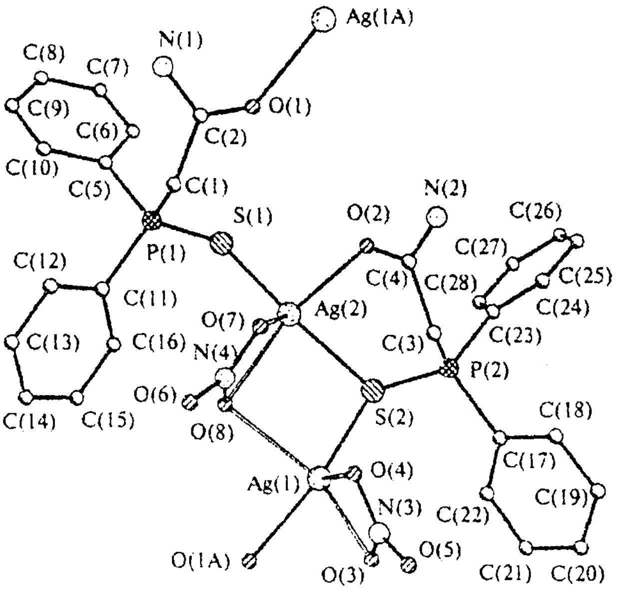


Fig. 1. Fragments of the chain in the structure of the complex [Ag_2(L-3)$_2$(NO_3)$_2$]$_n$ (3).

Results and Discussion

The reactions of ligand L-3 with $AgNO_3$ taken in M : L ratios of 1 : 1 and 1 : 2 in $CHCl_3$, MeCN, and MeOH yield insoluble 1 : 1 adducts with identical spectral parameters (complex 3). In the case of an excess of the ligand, the IR spectra of the mother liquors show the presence of the free ligand. A twofold excess of the ligand was necessary for the preparation of the monoligand complex 2 by the reaction of ligand L-2 studied previously[6] with $AgNO_3$ in $CHCl_3$. When the reagents were taken in an equimolar ratio, compound L-2 decomposed. It is also noteworthy that complexation with ligand L-3 proceeded more slowly than with ligand L-2. Complex 3 is insoluble in most organic solvents. However, according to the data of IR spectroscopy, the complex changed when it was dissolved in pyridine (apparently, the solvent molecule replaced the ligand and was incorporated into the coordination sphere).

Structure of {Ag_2(L-3)$_2$(NO_3)$_2$}$_n$ (3). Crystals of complex 3 consist of infinite chains {Ag_2(L-3)$_2$(NO_3)$_2$}$_n$ (Figs. 1 and 2) running along the *a* axis. The coordination environments about independent silver ions Ag(1) and Ag(2) are formed by five donor atoms, two of which are bonded to the metal atom substantially more weakly than the other three atoms. In the {Ag(1)S(2)O(1A)O(3)O(4)O(8)} polyhedron, the S(2), O(1A), and O(3) atoms form strong bonds (the Ag(1)—S(2), Ag(1)—O(1A), and Ag(1)—O(3) bond lengths are 2.464(1), 2.291(4), and 2.418(4) Å, respectively). The Ag(1) atom deviates from the plane through the above-mentioned atoms by 0.368(2) Å. The fourth position of the "pseudotetrahedral" environment about the Ag(1) atom is simultaneously occupied by two atoms, namely, O(4) and O(8) (the O(4)...O(8) distance is 2.083 Å), which are bonded to Ag(1) substantially more weakly (the Ag(1)—O(4) and Ag(1)—O(8) distances are 2.750(5) and 2.642(4) Å, respectively). In the {Ag(2)S(1)S(2)O(2)O(7)O(8)} polyhedron, the O(7) and O(8) atoms form weak bonds typical of Ag—O bonds with the participation of η^2-coordinated NO_3^- ions (the Ag(2)—O(7) and Ag(2)—O(8) distances are 2.677(4) and 2.642(4) Å, respectively). The Ag(2)S(1)S(2)O(2) fragment in which the bonds are rather strong (the Ag(2)—S(1), Ag(2)—S(2), and Ag(2)—O(2) bond lengths are 2.449(1), 2.559(1), and 2.441(4) Å, respectively) is a flattened trigonal pyramid with the Ag(2) atom at the vertex (Ag(2) deviates from the S(1)S(2)O(2) plane by 0.712(2) Å). The O(7) and O(8) atoms (the O(7)....O(8) distance is 2.135 Å) occupy the fourth position of the

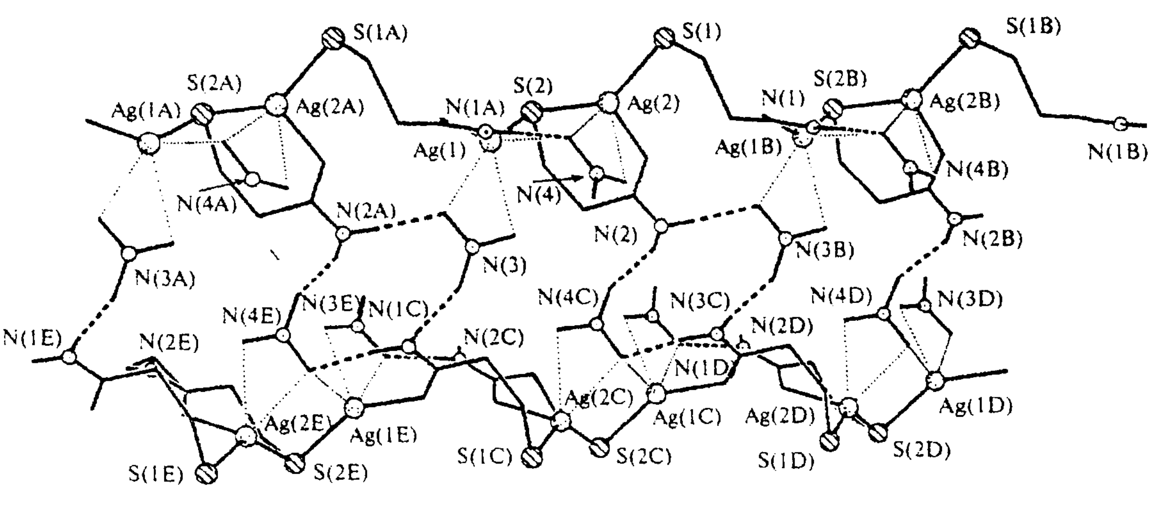


Fig. 2. Fragments of the bilayer in the structure of the complex [Ag_2(L-3)$_2$(NO_3)$_2$]$_n$ (3).

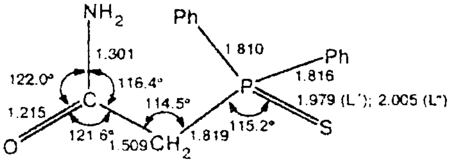
"pseudotetrahedral" environment about the Ag(2) atom.

In the crystal of 3, the functions of the neutral ligands (L′ and L″)* are different. One ligand, μ_2-L′, acts only as a bridge and links two Ag atoms through the O(1) and S(1) atoms. The second chelate-bridging ligand, μ_2,η^2-L″, is coordinated by the Ag(2) atom to form the six-membered chelate ring, and its S(2) atom is additionally coordinated by the second silver atom Ag(1). The chelate ring has an irregular conformation. To a first approximation, it can be described as a boat with the O(2)C(4)P(2)S(2) fragment (planar to within 0.2 Å) as the "bottom". The "corners" Ag(2) and C(3) deviate from this plane by 0.55 and 0.79 Å, respectively.

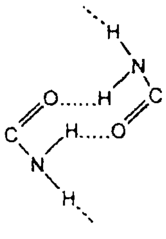
The endocyclic torsion angles of rotation about the Ag(2)—O(2), O(2)—C(4), C(4)—C(3), C(3)—P(2), P(2)—S(2), and S(2)—Ag(2) bonds are −50.4(5), 22.5(8), 46.3(7), −74.8(4), 29.2(2), and 13.2(1)°, respectively.

The NO_3^- ions are coordinated in different fashions. One of them, $N(3)O_3^-$, is involved in a four-membered chelate ring Ag(1)O(3)N(3)O(4) with a very short Ag(1)—O(3) bond (2.418(4) Å) and a long Ag(1)—O(4) bond (2.750(4) Å). The second chelate-bridging ion, $N(4)O_3^-$, is involved in the chelate ring Ag(2)O(7)N(4)O(8) and is bonded to the Ag(1) atom (Ag(1)—O(8) is 2.642(4) Å) as well. In the coordination "pseudotetrahedra" about the Ag atoms, the $N(4)O_3^-$ ion (the O(7) and O(8) atoms) occupies the vertex of the "pseudotetrahedron", whereas the $N(3)O_3^-$ ion (the O(3) and O(4) atoms) "contract" the edge of the "pseudotetrahedron" about the Ag(1) atom.

Most of the geometric parameters of the independent ligands L′ and L″ in complex 3 are close to each other (to within the experimental error). Their average values are given below.



A substantial difference is observed only in the P=S bond lengths, which are 1.979(2) and 2.005(2) Å in L′ and L″, respectively. The unusually short C=O and C—N bond lengths in the amide group of the coordinated ligand are also noteworthy. These bonds are somewhat shorter than the mean values for noncoordinated amide groups (C=O is 1.234 Å, and C—NH_2 is 1.325 Å).[8,9] However, it should be remembered that in the crystalline state, amides are generally self-associated through hydrogen bonds,[10] which cause elongation of interatomic C=O distances.



Based on the data of IR spectra (see below), compound L-3 is no exception. The vibration frequency of the C=O bond, ν(CO), of the free ligand L-3 in the crystalline state appears at 1690 cm^{-1}. Dissociation of associates in a dilute solution leads to an increase in ν(CO) to 1700—1720 cm^{-1}, *i.e.*, to shortening of the bond, whereas ν(CO) is lowered to 1670 cm^{-1} upon formation of complex 3, which is indicative of a regular weakening (elongation) of the C=O bond compared not only to the monomeric molecule, but to an H-associate as well. However, its length in the complex is closer to the mean C=O bond in ketones (1.210 Å)[8] than to that in amides.

It would appear reasonable that the longer C=O(Ag) bond would correspond to a stronger Ag—O(C) bond. However, this relationship is not observed in complex 3. Although the Ag—O bonds in complex 3 are substantially different (2.291(4) and 2.441(4) Å), the C(2)—O(1) and C(4)—O(2) bond lengths are virtually identical (1.217(6) and 1.212(6) Å). The average length of the C—N bonds in molecules L′ and L″ approximates the mean length of the double $C(sp^2)=N$ bond (1.279 Å),[8] which also seems unusual because both H atoms of the NH_2 group, as in the case of associated amide molecules, are involved in H bonding. Therefore, the bond lengths in complex 3 and in amides should have similar values.

Such an anomaly is absent[6] in complex 2 in which the C=O bond in the coordinated amide group $CONEt_2$ is longer (1.246(4) Å) than that in the noncoordinated group. The C—N bond length in compound 2 (1.348(5) Å) coincides with the mean bond length in the noncoordinated $O=C-NR_2$ group (1.346 Å).[8] Apparently, a possible increase in the contribution of the bipolar resonance structure $H_2N^+=C-O^-$ (along with $H_2N-C=O$) upon coordination of ligand L-3 by the Ag atom should be taken into account. Apparently, an additional positive charge on the atoms of the NH_2 group favors the formation of $NH_2^+...ONO_2^-$ H bonds in complex 3.

Coordination of the $Ph_2P=S$ group by the Ag atom produces a change in the P=S bond length. Apparently, the difference in the P=S bond lengths in the two independent ligands L′ and L″ in 3 is caused by the fact that the S(1) atom in L′ forms one bond with the metal atom (Ag(2)—S(1)), whereas the S(2) atom in L″ acts as a bridge and forms two bonds (Ag(1)—S(2) and Ag(2)—S(2)).

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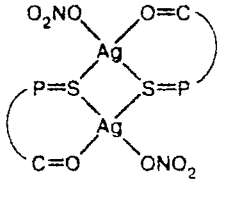
* Hereinafter, the index 3 in the notations of the ligands (L-3)′ and (L-3)″ is omitted for simplicity.

There is a substantial difference in the Ag—O=C bond lengths in complex **3**: the Ag(2)—O(2) bond (2.441(4) Å) in the chelate ring is 0.150 Å longer than the nonchelate Ag(1)—O(1A) bond (2.291(4) Å). The analogous "chelate" Ag—O=C bond length in compound **2** is 2.494(3) Å.[6] Close values of the Ag—O=C bond lengths were observed previously in complexes with β-alanine $[Ag_2(C_3H_7NO_2)_2](NO_3)_2$[11] (Ag—O is 2.20(2) Å) and glutarimide $[Ag_2(C_5H_6NO_2)_2]$[12] (Ag—O are 2.288(4) and 2.429(4) Å). In both complexes, an excess negative charge occurs on the O atoms.

In the structure of complex **3**, NH_2 groups of both independent ligands form H bonds with O atoms of NO_3^- ions (see Fig. 2): O(5′)...HN(1A)—N(1)—HN(1B)...O(8″) and O(6′)...HN(2B)—N(2)—HN(2A)...O(3″) (atoms generated from the basis atoms by the symmetry operation $-x+2$, $y-0.5$, $0.5-z$ are primed, and atoms generated by the operation $x-1$, y, z are doubly primed). The parameters of the H bonds are as follows: the O(5′)...N(1), O(8″)...N(1), O(6′)...N(2), and O(3″)...N(2) distances are 2.957(8), 2.987(7), 2.926(8), and 2.945(8) Å, respectively; the N(1)—HN(1A), N(1)—HN(1B), N(2)—HN(2A), and N(2)—HN(2B) distances are 0.71(4), 0.99(6), 0.80(6), and 0.73(6) Å, respectively; the O(5′)...HN(1A), O(8″)...HN(1B), O(6′)...HN(2B), and O(3″)...HN(2A) distances are 2.25(5), 2.04(6), 2.30(6), and 2.15(6) Å, respectively; and the angles at the HN(1A), HN(1B), HN(2B), and HN(2A) atoms are 170(9), 162(5), 147(6), and 175(6)°, respectively. In the crystal, chains of molecules are linked in double layers parallel to the *ab* plane through H bonds, and all H bonds are located inside the double layer. The outer surface of this bilayer is formed by phenyl rings and S atoms. There are only pure van der Waals interactions between the bilayers. The shortest contacts are as follows: S...S (3.876 and 4.085 Å) and Ag(2)...S(1) (3.812 Å).

In complex **3**, the function of the hydrogen bonds is not limited to the formation of a layer structure of the crystal. It is believed that H bonds determine also the mode of coordination of ligand L-3 to the Ag atom. This conclusion follows from a comparison of the structures of complexes **2** and **3**. Both complexes have the identical dimeric composition, namely, $[Ag_2L_2(NO_3)_2]$. The only difference is that ligand L-3 contains one nonsubstituted amide fragment, whereas ligand L-2 contains an amide fragment with ethyl substituents. However, this difference leads to basically different structures of complexes **2** and **3**. In **2**, centrosymmetric dimers are formed,[6] whereas the crystal of **3** consists of chains.

IR spectra of ligand L-3 and complex 3. Figure 3 shows the spectrum of the free ligand L-3 in the solid state (spectrum *b*), the spectra of its solutions in MeCN and $CHCl_3$ at various concentrations (spectra *c*—*e*), and the spectrum of the crystalline complex **3** (spectrum *a*). Some absorption bands of the ligand are changed in going from the solid state to a dilute solution, which is indicative of the existence of intermolecular H bonds between the C=O and NH_2 groups. Thus, in the spectrum of the solid sample of ligand L-3, a series of absorption bands corresponding to associated NH_2



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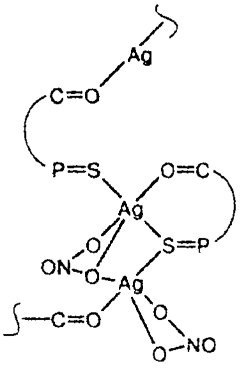

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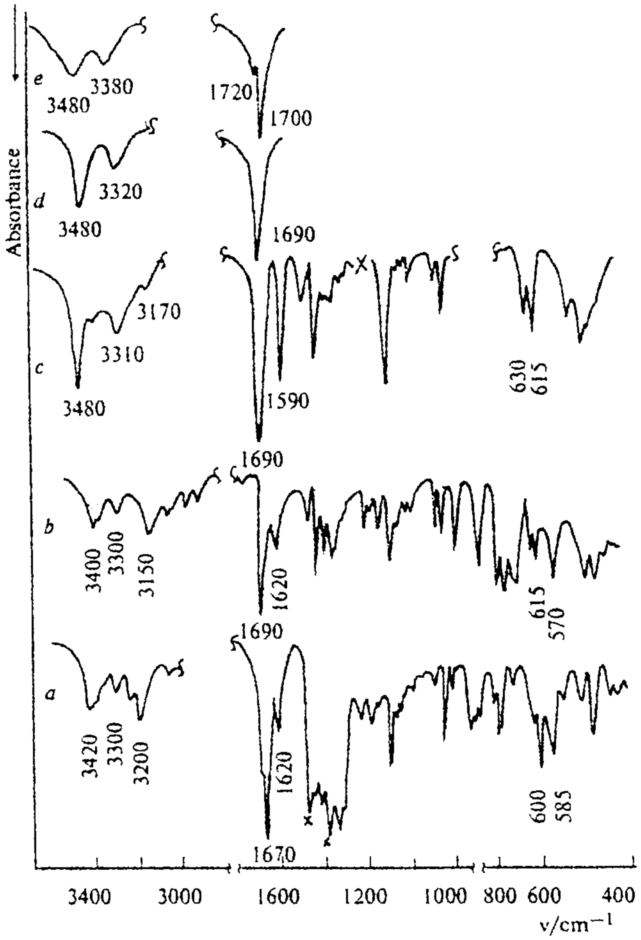

Fig. 3. IR spectra of (carbamoylmethyl)diphenylphosphine sulfide (L-3) and the complex $[Ag_2(L\text{-}3)_2(NO_3)_2]_n$ (**3**): *a*, crystalline complex **3** (as Nujol mulls, whose absorption is marked with an asterisk); *b*, ligand L-3 (as KBr pellets); *c* and *d*, solutions of the ligand in $CHCl_3$, C = 0.2 and 0.001 mol L^{-1}, respectively; and *e*, a solution of the ligand in MeCN, C = 0.001 mol L^{-1}.

groups[10] are observed in the region of stretching vibrations $\nu(NH_2)$. The highest intensity bands are observed at 3150 and 3400 cm^{-1}. A lower intensity band occurs at 3300 cm^{-1}. The "amide I" absorption band[10] (the vibration of the carbonyl bond of the N—C=O group, $\nu(CO)$) occurs at 1690 cm^{-1}. In the spectra of concentrated solutions of the ligand in $CHCl_3$ and MeCN, bands of both free (3480 cm^{-1}) and associated (3310 cm^{-1}) NH bonds are observed. The $\nu(CO)$ absorption band appears at 1690 cm^{-1}. Dimers do not dissociate when the solution in $CHCl_3$ is diluted as evidenced by the fact that absorption bands of associated NH_2 groups persist (see Fig. 3, *d*). In a dilute acetonitrile solution, dimers partly dissociate: the absorption bands of free NH_2 and CO groups appear at 3380 and 3480 cm^{-1} ($\nu(NH_2)$) and 1700—1720 cm^{-1} ($\nu(CO)$), respectively (see Fig. 3, *e*).

Therefore, in the crystalline state, ligand L-3, which contains an amide fragment, like most amides, exist as associates, namely, as dimers linked in chains. In concentrated solutions, the chains are partly broken. In a dilute $CHCl_3$ solution, the chains are completely broken, but dimers persist, and only in a very dilute MeCN solution do the dimers partly dissociate. In this case, the absorption bands of the nonassociated solvated L-3 molecule are observed. This molecule is characterized by a very high (for amides) vibration frequency of the C=O bond (~1720 cm^{-1}), which corresponds to its small length (for comparison, in the compound L-2, $\nu(C=O)$ occurs at 1640 cm^{-1}).

In the spectra of concentrated solutions, the "amide II" absorption band is observed at 1590 cm^{-1}, which corresponds to the deformation vibration $\delta(NH_2)$.[10] In the spectrum of the solid sample of the ligand, this band is shifted (due to the formation of chain associates) to 1620 cm^{-1}. The absorption bands at 615 and 630 cm^{-1} (or one of these bands), which are analogous to those observed in the spectra of ligand L-2,[6] are assigned to the vibration of the thiophosphoryl group $\nu(P=S)$.

The above-mentioned absorption bands belonging to vibrations of the functional groups of the ligand change during complexation (see Fig. 3, *a*). The absorption bands at 600 and 585 cm^{-1} can be assigned to vibrations of coordinated P=S bonds. The maximum of the "amide I" absorption band with the shoulder at 1690 cm^{-1} is shifted to 1670 cm^{-1} in coordination of the carbonyl group. The splitting of this band may be caused by the mixed character of the vibration of the amide group. Based on the data of X-ray structural analysis, the bipolar resonance structure $H_2N^+=C-O^-$ makes a substantial contribution to this amide group in the complex (possible interaction between the vibrations of the two ligands L′ and L″ must not be ruled out). Therefore, the absorption band of the carbonyl group is shifted ~40 cm^{-1} lower by coordination (if $\nu(C=O)$ of the free ligand in the solution is 1720 cm^{-1}), which corresponds to stronger Ag—O coordination in the case of ligand L-3 than in the case of ligand L-2 (30 cm^{-1}).[6] This agrees with the results of X-ray diffraction analysis. The absorption bands of stretching vibrations of the NH_2 groups of complex 3 (see Fig. 3, *a*) indicate that these groups are involved in H bonding. The intense bands at 1300, 1340, and 1420 cm^{-1} belong to stretching vibrations of nonequivalent NO_3 groups coordinated in different fashions.[13]

Therefore, the analysis of the IR spectra demonstrated that under the reaction conditions of complexation of the ligand L-3 with $AgNO_3$, the ligand is self-associated, and its carbonyl group is blocked. Therefore, dissociation of the dimer is necessary for its coordination. This could be responsible for the difference in the character of the interaction of $AgNO_3$ with ligands L-2 and L-3 (the rate of complexation, required molar ratios, *etc.*).

UV spectra. The analysis of the UV spectra obtained in the course of titration of solutions of ligands L-1, L-2, and L-3 in MeCN with solutions of $AgNO_3$ (Fig. 4, the spectrum of ligand L-1 is not shown in the figure because it is analogous to the spectrum of L-2 and changes in a

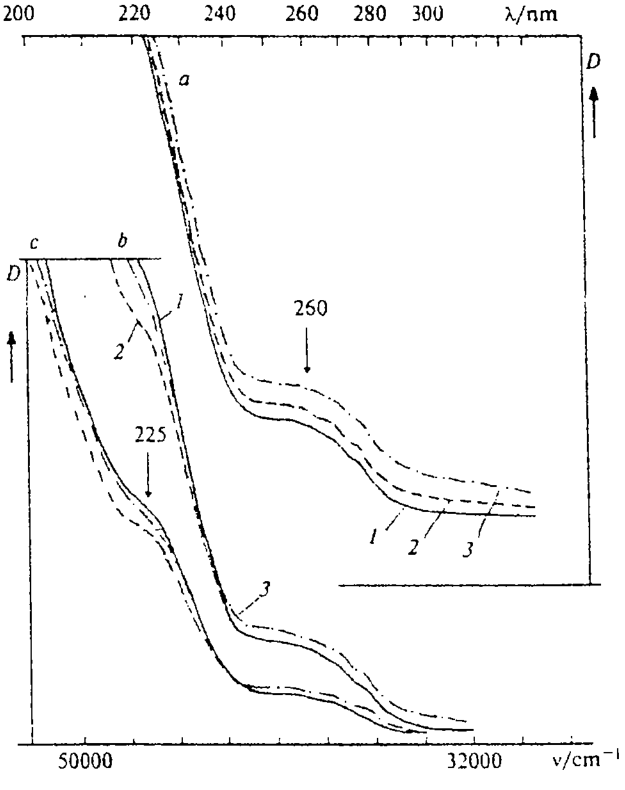

Fig. 4. UV spectra of solutions of (*N,N*-diethylcarbamoylmethyl)diphenylphosphine sulfide (L-2) and (carbamoylmethyl)diphenylphosphine sulfide (L-3) in MeCN, which are changed when titrated with a solution of $AgNO_3$ (C_L = 0.0005 mol L^{-1}). *a*, L-2; *b* and *c*, L-3 (spectrum *c* was recorded with double contraction of the ordinate): *1* is the initial solution of the ligand, *2* is the solution after addition of 0.1 mol equiv. of $AgNO_3$, *3* is the solution after addition of 0.2 mol. equiv. of $AgNO_3$.

similar fashion in the titration) demonstrated a difference in the course of the reaction of $AgNO_3$ with ligand L-3 from that with ligand L-2. In the spectra of all three ligands, an absorption band at 260 nm is observed (see Fig. 4, *a—c*, spectrum *1*). When a solution of $AgNO_3$ is added to solutions of ligands L-1 or L-2, the sulfur atom becomes coordinated,[5,6] and this band changes (see Fig. 4, *a*, spectra *2* and *3*), which makes it possible to assign this band to the P=S group. Unlike ligands L-1 and L-2, ligand L-3 has absorption as a shoulder in the region of 220—230 nm in addition to the above-mentioned band (see Fig. 4, *b*, *c*, spectrum *1*). According to the published data,[14,15] this shoulder can be attributed to the NH_2 group. After the addition of the first portion of a solution of $AgNO_3$ (0.1 mol. equiv.) to a solution of ligand L-3, the short-wavelength shoulder (see Fig. 4, *c*, *b*, spectrum *2*) rather than the band corresponding to the P=S group (as was observed in the case of ligands L-1 and L-2) immediately changes, and only thereafter does the band of the P=S bond change. It is impossible to observe the spectrum after further titration because of the formation of insoluble complex **3**.

Based on the above-mentioned spectral changes, we suggested that at the initial stage of the reaction of ligand L-3 with $AgNO_3$, H bonds are formed between the proton of the NH_2 group of the ligand and the NO_3 anion, which leads to destruction of self-associates of the ligands. Apparently, this stage slows down the reaction of ligand L-3 with $AgNO_3$, and this reaction appears to be "softer" than the analogous reaction of ligand L-2.

Therefore, ligand L-3, which contains a primary amide group, like the diethylamide ligand L-2, forms a dimeric complex with $AgNO_3$. However, the character of the interaction and the structure of the complex formed substantially differ from those of ligand L-2. These differences are, apparently, caused by H bonds. In the free ligand L-3, HNH...O=C associates lead to dimerization of molecules. In the reaction of L-3 with $AgNO_3$, the $HNH...ONO_2$ H bonds, apparently, promote dissociation of dimers and, therefore, make possible the coordination of the C=O group by the silver ion. In complex **3** formed, the $HNH...ONO_2$ H bonds stabilize the polymeric structure.

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