Organometallic Chemistry

The complexation of (*N,N*-diethylcarbamoylmethyl)diphenylphosphine sulfide with silver nitrate

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The crystalline complex $[Ag(L^1)NO_3]_2$ (**A**) was isolated by the interaction of (*N,N*-diethylcarbamoylmethyl)diphenylphosphine sulfide $Ph_2P(S)CH_2C(O)NEt_2$ (L^1) with $AgNO_3$ in different solvents at the ratios of metal:ligand = 1:1 and 1:2. According to the X-ray data, complex **A** is a center-symmetric dimer with bridge sulfur atoms. The cations of the metal are in a tetrahedral environment formed by two S atoms and the O atoms of CO and NO_3 groups. The interaction of L^1 with $AgNO_3$ was studied in solution by IR spectroscopy, and the structures of the complexes formed are discussed.

Key words: silver complexes, organothiophosphorus compounds, vibration spectra, X-ray analysis.

It is known that diphosphine sulfides $R_2P(S)(CH_2)_nP(S)R_2$ are efficient chelating agents of complex formation with ions of various metals, and this is a primary concern of bis (diphenylthiophosphinyl) methane $Ph_2P(S)CH_2P(S)Ph_2$ (**L**). For the latter, the interaction with ions of transition and nontransition metals has been studied the most comprehensively.[1] In particular, the complexation of **L** with silver and copper salts[2–4] has been studied, the structure of the isolated complexes has been established, and the extraction constants from aqueous solutions have been determined for silver ions, and turned out to be rather high.[4] However, the possibility of using compound **L** is restricted by the absence of convenient methods of its synthesis. From this viewpoint, the more readily available (*N,N*-diethylcarbamoylmethyl)diphenylphosphine sulfide $Ph_2P(S)CH_2C(O)NEt_2$ (L^1), a ligand with one thiophosphoryl group and one carbamoyl group, is of great interest. It was shown previously[5] that the ability of the ligand $Ph_2P(S)CH_2C(O)NEt_2$ to form complexes remains sufficiently high when one phosphoryl group is similarly replaced by the carbamoyl group in the dioxide $Ph_2P(O)CH_2C(O)Ph_2$. The method developed for the preparation of organothiophosphorus compounds under conditions of phase-transfer catalysis[6] was used for the synthesis of ligand L^1.

The present work deals with the study of the interaction of L^1 with $AgNO_3$ in different solvents and at various ratios of the reagents.

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Experimental

The synthesis of compound **L**^{1} has been described previously.[6] IR spectra of free ligand **L**^{1} and its complexes in solutions and the crystalline state were obtained on UR-20, 400—3700 cm^{-1} and Specord M-40, 200—1800 cm^{-1} spectrophotometers using KBr pellets (only for the ligand, because the ionic exchange with KBr occurred in the molding of complexes with Ag$^+$) and as a suspension in Vaseline oil between plates of CsI. The spectra of the solutions were obtained using cuvettes of KBr, CaF_2, and KRS-5 (the exchange of Ag$^+$ and K$^+$ ions took place when cuvettes of KBr were used).

Raman spectra of crystalline samples were obtained on a JOBIN IVON spectrometer, λ = 5145 Å.

Complex L^1 with AgNO$_3$. Solutions of ligand L^1 (0.1615 g) and $AgNO_3$ (0.0830 g) in CH_3CN were mixed at the equimolar ratio of the components, c_L = 0.2 *M*. A precipitate as a fine suspension formed immediately. The mixture was kept in the dark for 2—3 h, then filtered off, the precipitate was washed with ether and dried, and 0.16 g (67%) of a white crystalline substance, m. p. 128—130 °C (with decomposition) was obtained. The data of the elemental analysis of the isolated complex correspond to the composition metal:ligand (M:L), 1:1. Found (%): Ag, 21.0; P, 6.1. $C_{18}H_{22}AgN_2O_4PS$. Calculated (%): Ag, 21.5; P, 6.19.

After 1 day, no new precipitate formed in the mother liquor and the IR spectrum did not change. An additional 0.03 g of the complex was obtained after the addition of ether to the mother liquor.

The same complex was obtained by the interaction of equimolar amounts of the reagents in EtOH. However, an unstable, rapidly darkening product formed in $CHCl_3$ when ligand L^1 and $AgNO_3$ were mixed in equimolar ratio. At the ratio of L:M = 2:1, a complex of the composition 1:1 identical to that described above by the data of the element analysis, m. p., and spectral parameters was isolated from EtOH, CH_3CN, and $CHCl_3$ (in the latter case, a suspension of $AgNO_3$ was mixed with a ligand solution).

Preparation of the monocrystal [Ag(L^1)NO$_3$]$_2$ (complex A). Dilute solutions of L^1 (0.1192 g) and $AgNO_3$ (0.0612 g) in ethanol (c_L = 0.01 *M*) were mixed at an equimolar ratio of the components. The transparent solution obtained was kept in the dark for about a day, during which crystals with m. p. 128—130 °C (with decomposition) were grown in the solution. A monocrystal in the form of a colorless transparent prism with approximate sizes 0.8 × 0.4 × 0.2 mm was chosen for the X-ray study. The parameters of the elementary cell and intensity of 4428 independent reflections with $I > 3\sigma(I)$ were measured on a Siemens P3/PC four-circle automatic diffractometer (λ Mo-Kα-radiation, graphite monochromator, θ/2θ-scanning, θ < 27°). The structure was solved by the direct method and refined by the full-matrix least-square method in anisotropic approximation for nonhydrogen atoms and in isotropic approximation for hydrogen atoms up to *R* 0.052, R_w 0.062. All calculations were performed by the SHELXTL PLUS program (version for PC) on an IBM PC/AT-286.

Results and Discussion

Structure of the complex [Ag(L^1)NO$_3$]$_2$ (A) (Fig. 1, Tables 1—3). The crystals that form at the equimolar ratio of metal:ligand are triclinic with the space group $P\bar{1}$; at 25 °C *a* = 9.634(3), *b* = 10.234(3), *c* = 10.738(3) Å, α = 90,75(2), β = 103.45(2), γ = 97.99(2)°, *V* = 1018.6(5) Å^3, *Z* = 2, d_{calc} = 1.634 g/cm^3, μ =1.196 mm^{-1}, σF(000) 508.

In the center-symmetric dimeric molecules, the Ag atoms located at a distance of 3.241(1) Å from each other are in distorted tetrahedral surroundings formed by two bridge sulfur atoms of the thiophosphoryl groups (Ag—S 2.722(1) and 2.571(1) Å), and oxygen atoms O(1) of the carbonyl group (Ag—O (1) 2.494(3) Å), and O(4) of the monodentate NO_3-group (Ag—O(4) 2.418(4) Å). The angles at the silver atom are 86.9(1)—135.9(1)°.

The six-membered AgO(1)C(14)C(13)PS cycle has the conformation of a butterfly, and the angle between the AgSPO(1) and O(1)C(14)C(13)P planes is 141.6°. The AgSAg'S' cycle is in the form of a slightly distorted rhombus and forms the following angles with the planar fragments of the molecule: Ag'S'PO(1) 82.6°, O(1)C(14)C(13)P 59.6°, phenyl groups 24.0° and 91.4°, NO_3-group 118.1°. The angle between the planes of the phenyl groups is 82.6°.

The P atom is in a tetrahedral configuration; the angles are 106.0(1)—112.6(1)° and the bond lengths are: P—S 2.010(1), P—C 1.808(3), 1.809(4) Å. The C(14) atom is in a planar configuration; the angles are 117.9(3)°—122.1(3)° and the bond length of C(13)—O(1) is 1.246(4) Å. The nitrate group is almost planar (with accuracy of 0.01 Å). Due to the participation of the O(4) atom in coordination with the silver atom, the corresponding O—N distance (1.257(4) Å) is somewhat greater than the two other O—N distances (1.220(5) and 1.237(5) Å).

The other interatomic distances and valent angles are typical of the corresponding groups and are listed in Tables 2, 3.

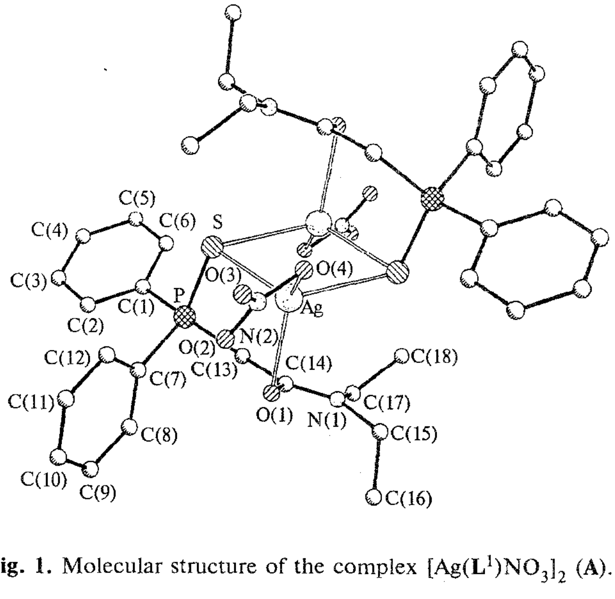


Fig. 1. Molecular structure of the complex [Ag(**L**^{1})NO$_3$]$_2$ (**A**).

Table 1. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic parameters of heat vibrations U_{eq} ($\times 10^3$ Å^2)

Atom	*x*	*y*	*z*	U_{eq}
Ag	3607(1)	9001(1)	9215(1)	54(1)
P	5386(1)	8256(1)	12584(1)	27(1)
S	4419(1)	9748(1)	11753(1)	38(1)
N(1)	7423(3)	7595(3)	9822(3)	37(1)
N(2)	2301(3)	6322(3)	8077(3)	42(1)
O(1)	7798(3)	9148(2)	11441(2)	37(1)
O(2)	1974(5)	7269(4)	7422(4)	91(2)
O(3)	1941(4)	5183(3)	7653(4)	76(1)
O(4)	3067(4)	6621(4)	9188(3)	67(1)
C(1)	4030(4)	7157(3)	13127(3)	32(1)
C(2)	4226(5)	6791(4)	14392(4)	51(1)
C(3)	3093(6)	6034(5)	14777(5)	64(2)
C(4)	1791(5)	5630(5)	13912(5)	58(2)
C(5)	1596(4)	5968(4)	12651(4)	50(1)
C(6)	2705(4)	6733(4)	12252(4)	40(1)
C(7)	6854(3)	8756(3)	13967(3)	34(1)
C(8)	7849(5)	7898(4)	14433(4)	50(1)
C(9)	8947(5)	8267(5)	15526(4)	60(2)
C(10)	9062(5)	9472(5)	16152(4)	60(2)
C(11)	8077(5)	10313(6)	15704(5)	65(2)
C(12)	6962(5)	9964(4)	14610(4)	51(1)
C(13)	6014(3)	7269(3)	11459(3)	29(1)
C(14)	7152(3)	8076(3)	10902(3)	29(1)
C(15)	8577(5)	8359(5)	9319(4)	49(1)
C(16)	10005(7)	7950(8)	9848(10)	98(4)
C(17)	6775(5)	6319(4)	9168(4)	47(1)
C(18)	5928(6)	6439(6)	7805(5)	64(2)
H(2)	5157(60)	6997(52)	14994(53)	66(15)
H(3)	3215(66)	5994(61)	15628(63)	85(18)
H(4)	1009(65)	5076(62)	14132(58)	79(17)
H(5)	515(70)	5575(63)	11925(62)	93(19)
H(6)	2625(42)	7006(39)	11434(41)	35(10)
H(8)	7887(58)	7147(57)	13950(53)	71(16)
H(9)	9625(47)	7689(43)	15945(42)	44(11)
H(10)	9833(69)	9741(62)	16903(60)	88(19)
H(11)	8404(89)	11078(80)	16130(83)	128(28)
H(12)	6223(54)	10608(50)	14219(48)	61(14)
H(13A)	6358(40)	6541(39)	11815(36)	30(9)
H(13B)	5198(44)	6907(38)	10858(37)	33(9)
H(15A)	8567(53)	9310(55)	9476(48)	61(14)
H(15B)	8204(60)	8190(55)	8522(57)	67(16)
H(16A)	9792(41)	7482(40)	9087(37)	22(9)
H(16B)	10675(75)	8507(67)	9259(62)	98(21)
H(16C)	10100(72)	6890(71)	9861(69)	98(21)
H(17A)	6164(48)	5882(44)	9584(41)	45(12)
H(17B)	7733(65)	5836(59)	9178(58)	85(18)
H(18A)	5348(66)	7077(64)	7830(57)	81(18)
H(18B)	6783(67)	6902(59)	7386(58)	81(17)
H(18C)	5389(78)	5607(77)	7228(71)	111(24)

Vibrational spectra of the ligand $\mathbf{L}^1$ and complex **A** are presented in Fig. 2. The 1640 cm^{-1} band of the ν(C=O) vibrations of the free ligand $\mathbf{L}^1$ (spectra *a* and *d*) shifts to 1610 cm^{-1} in complex **A** (spectrum *b*), which agrees well with the participation of the C=O group in coordination. The assignment of the ν(P=S) vibration of the P=S group is a more complicated problem, because this vibration is not very characteristic.[7] The P=S bond may make a noticeable contribution

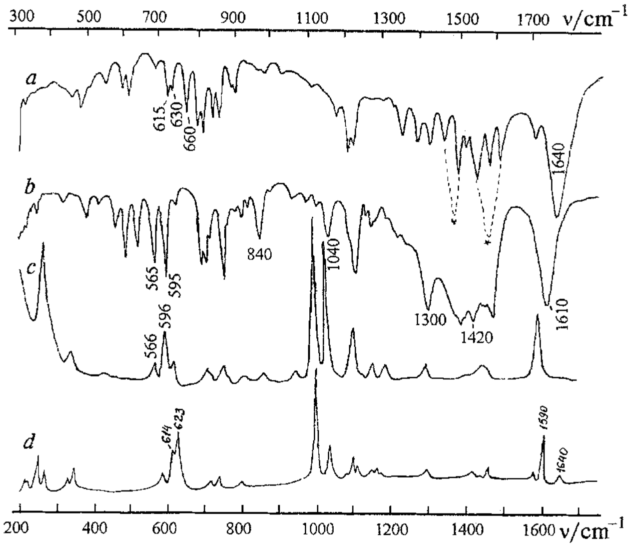


Fig. 2. IR and Raman spectra of (*N,N*-diethylcarbamoylmethyl)diphenylphosphine sulfide ($\mathbf{L}^1$) and complex $[\mathrm{Ag}(\mathbf{L}^1)\mathrm{NO_3}]_2$ (**A**):

a) IR spectrum of the free ligand (KBr in pellets and in suspension in Vaseline oil, absorption bands of the Vaseline oil are indicated by the dotted line);

b) IR spectrum of complex **A** (Vaseline oil);

c) Raman spectrum of complex **A**;

d) Raman spectrum of ligand $\mathbf{L}^1$.

Table 2. Bond lengths (*d*/Å)

Bond	*d*	Bond	*d*
Ag—S	2.722(1)	Ag—O(4)	2.418(4)
Ag—S'	2.571(1)	Ag—O(1')	2.494(3)
P—S	2.010(1)	P—C(1)	1.809(4)
P—C(7)	1.808(3)	P—C(13)	1.823(4)
N(1)—C(14)	1.348(5)	N(1)—C(15)	1.479(6)
N(1)—C(17)	1.461(5)	N(2)—O(2)	1.237(6)
N(2)—O(3)	1.220(5)	N(2)—O(4)	1.257(4)
O(1)—C(14)	1.246(4)	C(1)—C(2)	1.391(5)
C(1)—C(6)	1.406(4)	C(2)—C(3)	1.395(7)
C(2)—H(2)	0.970(48)	C(3)—C(4)	1.383(6)
C(3)—H(3)	0.896(68)	C(4)—C(5)	1.378(7)
C(4)—H(4)	0.955(64)	C(5)—C(6)	1.389(6)
C(5)—H(5)	1.163(60)	C(6)—H(6)	0.915(43)
C(7)—C(8)	1.401(6)	C(7)—C(12)	1.387(6)
C(8)—C(9)	1.392(6)	C(8)—H(8)	0.931(60)
C(9)—C(10)	1.376(7)	C(9)—H(9)	0.978(45)
C(10)—C(11)	1.377(8)	C(10)—H(10)	0.967(54)
C(11)—C(12)	1.399(6)	C(11)—H(11)	0.881(75)
C(12)—H(12)	1.057(53)	C(13)—C(14)	1.519(5)
C(13)—H(13A)	0.911(40)	C(13)—H(13B)	0.921(36)
C(15)—C(16)	1.481(9)	C(15)—H(15A)	0.988(57)
C(15)—H(15B)	0.852(57)	C(16)—H(16A)	0.908(41)
C(16)—H(16B)	1.113(73)	C(16)—H(16C)	1.101(74)
C(17)—C(18)	1.517(6)	C(17)—H(17A)	0.894(48)
C(17)—H(17B)	1.104(68)	C(18)—H(18A)	0.920(70)
C(18)—H(18B)	1.085(66)	C(18)—H(18C)	1.044(73)

Table 3. Valent angles (ω/degree)

Angle	ω	Angle	ω	Angle	ω
S—Ag—O(4)	104.1(1)	P—C(13)—H(13A)	112.4(26)	C(2)—C(3)—C(4)	120.7(5)
O(4)—Ag—Ag'	130.5(1)	P—C(13)—H(13B)	105.7(28)	C(4)—C(3)—H(3)	123.5(40)
O(4)—Ag—S'	124.1(1)	H(13A)—C(13)—H(13B)	102.4(33)	C(3)—C(4)—H(4)	122.9(35)
S—Ag—O(1')	95.6(1)	N(1)—C(14)—C(13)	117.9(3)	C(4)—C(5)—C(6)	119.8(4)
Ag'—Ag—O(1')	92.3(1)	N(1)—C(15)—C(16)	112.2(5)	C(6)—C(5)—H(5)	120.7(34)
S—P—C(1)	106.9(1)	C(16)—C(15)—H(15A)	113.0(27)	C(1)—C(6)—H(6)	116.3(23)
C(1)—P—C(7)	107.2(2)	C(16)—C(15)—H(15B)	117.3(42)	P—C(7)—C(8)	120.2(3)
C(1)—P—C(13)	106.0(1)	C(15)—C(16)—H(16A)	82.3(26)	C(8)—C(7)—C(12)	119.5(3)
Ag—S—P	104.3(1)	H(16A)—C(16)—H(16B)	74.7(42)	C(7)—C(8)—H(8)	120.8(32)
P—S—Ag'	102.0(1)	H(16A)—C(16)—H(16C)	61.9(45)	C(8)—C(9)—C(10)	120.3(4)
C(14)—N(1)—C(17)	125.7(3)	N(1)—C(17)—C(18)	113.1(4)	C(10)—C(9)—H(9)	115.2(24)
O(2)—N(2)—O(3)	122.0(4)	C(18)—C(17)—H(17A)	106.9(26)	C(9)—C(10)—H(10)	120.7(41)
O(3)—N(2)—O(4)	122.6(4)	C(18)—C(17)—H(17B)	110.8(31)	C(10)—C(11)—C(12)	120.9(5)
Ag—O(4)—N(2)	103.4(3)	C(17)—C(18)—H(18A)	107.0(36)	C(12)—C(11)—H(11)	131.0(57)
P—C(1)—C(6)	118.3(3)	H(18A)—C(18)—H(18B)	105.2(54)	C(7)—C(12)—H(12)	118.1(26)
C(1)—C(2)—C(3)	119.4(4)	H(18A)—C(18)—H(18C)	112.8(54)	P—C(13)—C(14)	111.9(2)
C(3)—C(2)—H(2)	119.3(36)	S—Ag—Ag'	50.2(1)	C(14)—C(13)—H(13A)	109.7(26)
C(2)—C(3)—H(3)	114.5(37)	S—Ag—S'	104.5(1)	C(14)—C(13)—H(13B)	114.3(26)
C(3)—C(4)—C(5)	120.3(5)	Ag'—Ag—S'	54.4(1)	N(1)—C(14)—O(1)	122.1(3)
C(5)—C(4)—H(4)	116.7(35)	O(4)—Ag—O(1')	135.9(1)	O(1)—C(14)—C(13)	120.0(3)
C(4)—C(5)—H(5)	119.4(34)	S'—Ag—O(1')	86.9(1)	N(1)—C(15)—H(15A)	108.7(32)
C(1)—C(6)—C(5)	120.3(4)	S—P—C(7)	114.5(1)	N(1)—C(15)—H(15B)	98.1(39)
C(5)—C(6)—H(6)	123.4(24)	S—P—C(13)	112.6(1)	H(15A)—C(15)—H(15B)	106.4(48)
P—C(7)—C(12)	120.2(3)	C(7)—P—C(13)	109.2(2)	C(15)—C(16)—H(16B)	101.4(37)
C(7)—C(8)—C(9)	120.0(4)	Ag—S—Ag'	75.5(1)	C(15)—C(16)—H(16C)	119.1(34)
C(9)—C(8)—H(8)	118.4(32)	C(14)—N(1)—C(15)	117.5(3)	H(16B)—C(16)—H(16C)	112.8(58)
C(8)—C(9)—H(9)	124.3(24)	C(15)—N(1)—C(17)	116.5(3)	N(1)—C(17)—H(17A)	110.9(28)
C(9)—C(10)—C(11)	119.8(4)	O(2)—N(2)—O(4)	115.3(4)	N(1)—C(17)—H(17B)	102.0(28)
C(11)—C(10)—H(10)	119.4(41)	C(14)—O(1)—Ag'	111.7(2)	H(17A)—C(17)—H(17B)	113.3(44)
C(10)—C(11)—H(11)	107.1(55)	P—C(1)—C(2)	122.1(3)	C(17)—C(18)—H(18B)	100.1(30)
C(7)—C(12)—C(11)	119.4(4)	C(2)—C(1)—C(6)	119.4(3)	C(17)—C(18)—H(18C)	121.6(40)
C(11)—C(12)—H(12)	122.5(26)	C(1)—C(2)—H(2)	121.1(36)	H(18B)—C(18)—H(18C)	108.4(54)

simultaneously into several vibrations of the molecule, mixing with the frequency of the deformational vibrations of the frame. In the studied case, the group of bands observed in the IR and Raman spectra in the range higher than 600 cm^{-1}, that is,thebands at 615, 630 cm^{-1} (in the Raman spectra 614, 623 cm^{-1}) and, perhaps, the band at about 660 cm^{-1} in the IR spectrum, can be assigned to a vibration involving the P=S bond. The formation of complex **A** is accompanied by the disappearance of these bands (residual peaks in the range of 620 cm^{-1} are likely to be related to the ν(P=S) vibration and were masked by them in the spectra of the ligand) and the appearance of bands in a lower frequency range: at 595 and 565 cm^{-1}. This assignment agrees with the spectral data of related compounds.[2,8] For example, diphosphine disulfide **L** and triphenylphosphine sulfide have the same ν(P=S) vibration frequencies as L^1, and the bands at 567 and 565 cm^{-1} are assigned[2] to ν(P=S) of the complexes $[Ag(L)_2]ClO_4$ and $[Ag(L)NO_3] \cdot 2H_2O$, respectively. The bands at 605, 586 cm^{-1} (IR) and 617, 586 cm^{-1} (Raman) were observed in the IR and Raman spectra of the complex $[Ag(L)_2NO_3]$, whose synthesis and structure have been described.[4] The absorption of the Vaseline oil in the IR spectrum of complex **A** and the superposition of the δ(CH) bands make it difficult to observe the frequencies of the vibrations of the NO_3-group. However, the appearance in the spectrum of the complex of the band in the range of 1300 cm^{-1}, which relates to $\nu_s(NO_2)$ of the monodentately coordinated NO_3-group, cannot be questioned. One can also note the appearance of the absorption in the range of 1420 ($\nu_{as}(NO_2)$) and 1040 cm^{-1} (ν(NO)). The line in the Raman spectrum at 1037 cm^{-1} corresponds to the latter.[9]

In the Raman spectrum of complex **A**, the intense line at about 280 cm^{-1} is likely to relate to the vibration of the Ag—S bond, because it is absent in the spectrum of the ligand. However, its assignment needs additional study. The IR and Raman spectra of the powder-like products isolated from all of the solutions regardless of the solvent used or the ratio of the reagents coincided with the spectra of the monocrystalline dimeric complex **A**. This fact, together with the coincidence of melting points and the data of elemental analysis, indicates that any method of complex preparation results in the formation in the solid state of the same product, complex **A**.

In such a case when the initial ratio of the reagents L:M is 2:1, the free ligand remains in the supernatant solution, which should be manifested in the IR spectrum.

IR spectra of the supernatant liquids (Fig. 3). After precipitation of the solid complex, the acetonitrile solutions obtained at the reagent ratio L:M = 1:1 and 2:1 gave IR spectra (spectra *b*, *d*, respectively), which did not differ basically from one another but differed from the spectrum of the crystalline complex **A**. The ν(P=S) band in the spectra of all supernatant solutions is shifted relative to ν(P=S) of the free ligand (spectrum *a*) to 605 cm^{-1}, which attests to coordination of the P=S group in the soluble complexes but somewhat more weakly than in complex **A**. The ν(C=O) band is split into two components of almost equal intensities, 1640 and 1620 cm^{-1}, and the ratio of their intensities is almost independent of the ratio of the components in the initial mixture (spectra *b* and *d*) after spontaneous precipitation of complex **A**. Taking into account this fact as well as the circumstance that the ν(P=S) bands of the free ligand at 630, 615, and 670 cm^{-1} (spectrum *a*) are almost absent in the spectra of the supernatant liquids (spectra *b*, *c*) or are very weak (spectrum *d*), one may assume that ν(C=O) at 1640 cm^{-1} in the spectra of the supernatant solutions belongs to free C=O group of the ligand coordinated at the P=S group. The ν(C=O) band at 1620 cm^{-1} indicates that a complex coordinated at both of the donor groups (C=O and P=S) is formed in the solution as well. The intensity of this band increases relative to the band of the free C=O group after the additional precipitation of the solid complex (spectrum *c*). When there is a twofold excess of the ligand in the initial mixture (spectrum *d*), the band at about 670 cm^{-1} is somewhat more intense than that at the equimolar ratio of the reagents, which indicates an excess of the ligand in the final mixture. All absorption bands of the free ligand can be observed in the IR spectrum only after additional precipitation of the solid complex **A**.

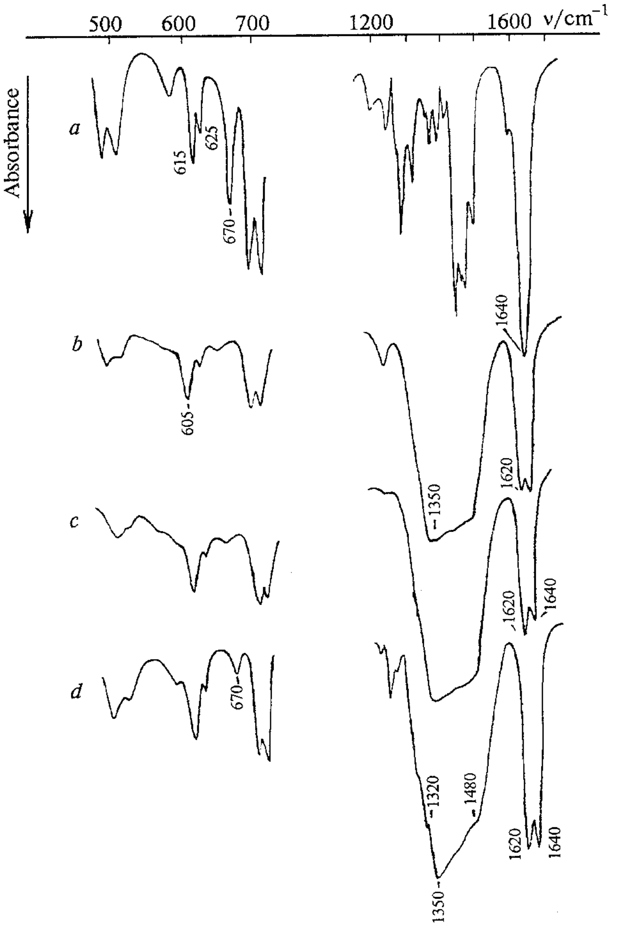


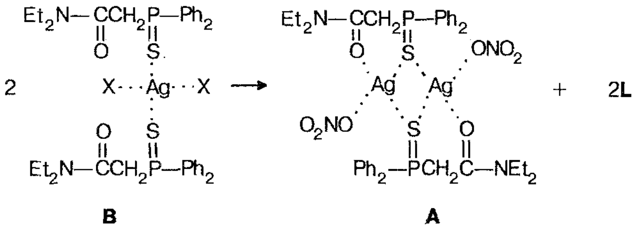
Fig. 3. IR spectra of the solution of the ligand L^1 and supernatant solutions of the complexes of L^1 with $AgNO_3$ (CH_3CN):
a) free ligand (CH_3CN, $c = 0.25$ *M*);
b) solution above the spontaneously precipitated complex **A** (CH_3CN, M:L = 1:1);
c) solution above the additionally precipitated complex **A** (CH_3CN, M:L = 1:1);
d) solution above the spontaneously precipitated complex **A** (CH_3CN, M:L = 1:2).

The broad absorption in the range of 1300—1500 cm^{-1} is caused by the superposition of several bands relating to the vibrations of NO_3-groups of different types. For example, the maximum in the range of 1350 cm^{-1} relates to $\nu_e(NO_3)$ of the noncoordinated nitrate ion. In addition, coordinated nitrate groups seem to exist in solution, and the maxima at about 1320 cm^{-1} ($\nu_s(NO_2)$ and 1480 cm^{-1} ($\nu_{as}(NO_2)$) are assigned to them; they can be seen in spectra *b—d*.[9] Similar spectra of the supernatant solutions were obtained with $CHCl_3$, however, in this case the absorption in the $\nu(NO_3)$ range manifested itself more structurally, which may be caused by the presence of coordinated nitrate groups in the noncoordinating solvent. Analyzing the spectra of the supernatant solutions and taking into account the fact that the formation of a stable complex in the noncoordinating solvent ($CHCl_3$) is possible only with excess ligand, one may assume that at first a bisligand complex with coordination of only the P=S groups (complex **B**) is formed in the solution. When the cation is in a tetrahedral configuration, the free coordination sites may be occupied by a solvent, if it is coordinating, or by a nitrate group. Then the coordination of the oxygen atom of the C=O-group occurs resulting in the rearrangement of the complex and formation of the insoluble dimer **A**. This may be represented by Scheme 1.

In addition, complex **C** is likely to be formed in a solution. In this complex, the coordination is performed by both of the donor groups: P=S (band at 605 cm^{-1}) and C=O (band at 1620 cm^{-1}), these bands remain in the solution spectrum after additional precipitations of complex **A** (spectrum *c*), but complex **C** is not isolated in the solid state.

Thus, the interaction of the ligand L^1 with $AgNO_3$ results in the formation of the complex $[Ag(L^1)NO_3]_2$, which is crystallized from various solvents, at different ratios of reagents, and its center-symmetric dimer **A**.

Scheme 1



X is the solvent molecule or NO_3-group.

Like diphosphine-disulfide **L**, phosphine sulfide with the carbamoyl group **L**^{1} is a bidentate chelating ligand towards the Ag^+ cation and, hence, may be used for silver fixation.

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