Complexes of (ω-diphenylphosphinoalkyl)diphenylphosphine sulfides with silver nitrate in pyridine

E. I. Matrosov,[*] *Z. A. Starikova, A. I. Yanovsky, D. I. Lobanov, I. M. Aladzheva, O. V. Bykhovskaya, T. A. Mastryukova, and M. I. Kabachnik*[†]

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: mastr@ineos.ac.ru

The behavior of the phosphine-phosphine sulfide complexes of silver, $[Ph_2P(S)(CH_2)_nPPh_2]_m \cdot AgNO_3$ (n = 2 or 4; m = 1 or 2), in pyridine was studied. Dissolution of the 1 : 1 complexes in pyridine leads to destruction of their dimeric structures $Ag_2[Ph_2P(S)(CH_2)_nPPh_2]_2(NO_3)_2$ (A) to form the complexes $Ag_{Py}{}^+{-}P(Ph_2)(CH_2)_nPh_2P{=}S$ and $Ag_{Py}{}^+{-}S{=}PPh_2(CH_2)_nPPh_2$. The solid complexes isolated from pyridine restore dimeric structure A. According to the data of X-ray diffraction analysis, the 1 : 2 complex isolated from pyridine has the structure $[S{=}P(Ph_2)(CH_2)_2(Ph_2)P{-}(NO_3)Ag(Py){-}P(Ph_2)(CH_2)_2(Ph_2)P{=}S]Py$. According to the data of IR spectroscopy, dissolution of this complex in chloroform leads to the formation of the dimeric structure $Ag_2[Ph_2P(S)(CH_2)_2PPh_2]_4(NO_3)_2$.

Key words: silver complexes, phosphine-phosphine sulfides; IR spectra; ^{31}P NMR spectra; X-ray structural analysis.

Complexation in nonaqueous media is often accompanied by the formation of solvate complexes.[1] These complexes are clearly manifested in electronic and vibrational spectra of salts of different metals in coordinating solvents.[1–4] In particular, the formation of pyridine complexes of $CoCl_2$ in various solvents has been studied,[1] and complexes containing the $Co(Py)_nCl_2$ fragments (n = 1 or 2) were detected in acetone.

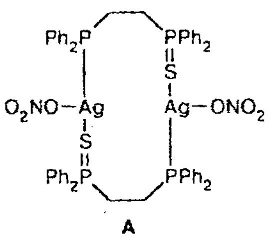
In this connection, we noticed that 1 : 1 phosphine-phosphine sulfide complexes of silver, which we have studied previously[5] and which are insoluble in the usual organic solvents, are readily soluble in pyridine. It was believed that dissolution of these complexes in pyridine is also associated with the formation of solvate complexes.

Therefore, in this work we studied the behavior of the complexes of $AgNO_3$ with phosphine-phosphine sulfides $Ph_2P(S)(CH_2)_nPPh_2$ (n = 2 (L^1) or 4 (L^2)) by ^{31}P NMR and IR spectroscopy and by X-ray diffraction analysis.

Results and Discussion

1 : 1 Complexes. Previously, the complex $Ag(L^1)NO_3$ (**1**) was studied[5] by X-ray diffraction analysis, and it was demonstrated that **1** has dimeric structure **A**.

In this structure, the P=S group and the P^{III} atom are involved in coordination to silver. In agreement with this fact, the IR spectrum of solid complex **1** has a band corresponding to the coordinated P=S group at 595 cm^{-1} ($\Delta\nu$ = 20 cm^{-1}) and two bands corresponding to the coordinated NO_3 groups at 1390 and 1295 cm^{-1}.[6]



A

With the aim of revealing the effect of the solvent on the structures of the 1 : 1 complexes, we dissolved complexes **1** and $Ag(L^2)NO_3$ (**2**) in pyridine and immediately isolated them in the solid state. Like the spectra of the initial complexes **1** and **2**, the IR spectra of the resulting complexes have an absorption band of the coordinated P=S group at 595 cm^{-1} and bands of the coordinated NO_3 group at 1390 and 1300 cm^{-1} (Table 1). The data of elemental analysis of the resulting and initial complexes coincide. Consequently, complexes that are analogous in structure and composition to the initial compounds were isolated from freshly prepared solution of the complexes of 1 : 1 composition.

The IR spectra of solutions of complexes **1** and **2** in pyridine were examined, and the results were compared with the spectra of these compounds in the solid state (see Table 1). The IR spectra of solutions of complexes **1** and **2** in pyridine have a band at 615 cm^{-1} corresponding to the free P=S group along with a band at 595 cm^{-1} corresponding to the coordinated P=S. The intensities of these bands are approximately equal. One absorption band of free NO_3 groups[7] (1355 cm^{-1}) in the spectra of solutions of the complexes in pyridine corresponds to intense absorption bands of coordinated NO_3 groups[6] (1390, 1385, 1310, and 1295 cm^{-1}) in the spectra of the solid complexes. From these data it may be concluded that the

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[†] Deceased.

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Table 1. Vibration frequencies of the P=S and NO_3 groups in the IR spectra of complexes **1** and **2** in the solid phase and in pyridine

Complex	Phase	ν(P=S)	ν(NO_3)
		cm^{-1}	
$Ag(L^1)NO_3$ (**1**)	Solid	595	1390, 1295
	Solution in pyridine	615, 595	1355
$Ag(L^2)NO_3$ (**2**)	Solid	595	1385, 1310
	Solution in pyridine	615, 595	1355

Note. $L^1 = Ph_2P(S)(CH_2)_2PPh_2$,
$L^2 = Ph_2P(S)(CH_2)_4PPh_2$.

partial (structure **B**) or complete cleavage of dimeric ring **A** occurs in pyridine to form monomeric complexes of types **C** and **D** accompanied by the replacement of coordinated NO_3 groups by solvent molecules. Because the initial complexes **1** and **2** were isolated from pyridine, the conversion of the 1 : 1 complexes can be represented by Scheme 1 (the Ph groups in structures **C** and **D** and hereinafter are omitted for clarity).

Scheme 1

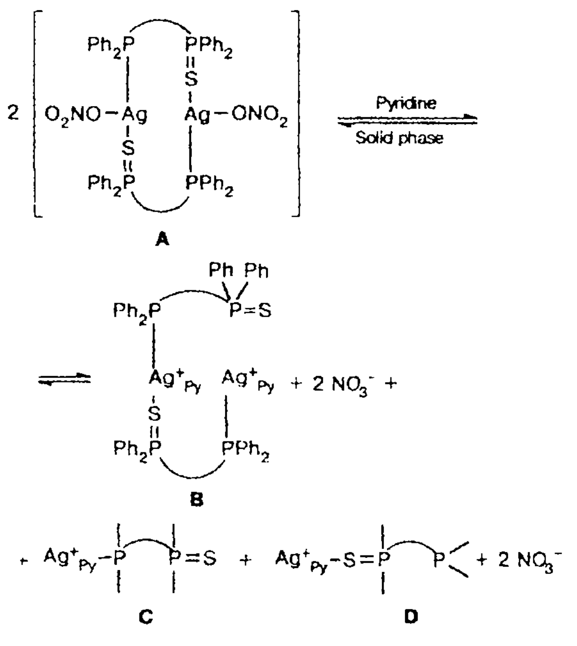


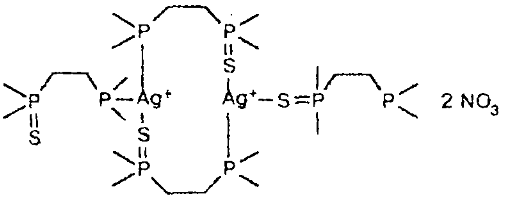
Table 2. ^{31}P NMR spectra of the ligands and their 1 : 1 complexes with $AgNO_3$ in pyridine

Compound	δP^{III}	$\Delta\delta$	δP^{V}	$\Delta\delta$	J_{PP}/Hz
$Ph_2P(S)(CH_2)_2PPh_2$ (L^1)	−13.23	—	44.83	—	49.7
$Ag(L^1)NO_3$ (**1**)	+8.39	21.62	45.28	0.45	41.7
$Ph_2P(S)(CH_2)_4PPh_2$ (L^2)	−16.03	—	42.74	—	0
$Ag(L^2)NO_3$ (**2**)	+2.51	18.54	44.07	1.33	0
$Ag(L^2)NO_3$ + 2 L^2	−0.85	15.18	43.49	0.75	0

The ^{31}P NMR spectra of solutions of the free ligands L^1 and L^2 in pyridine, like those in CH_2Cl_2,[8] show two narrow signals. The first signal (at δ −13.23 and −16.03 for L^1 and L^2, respectively) corresponds to P^{III}, and the second signal (at δ 44.83 and 42.74, respectively) corresponds to P^V (Table 2). In the spectrum of the ligand L^1, the doublet splitting of the signals for P^{III} and P^V with the spin-spin coupling constant J_{PP} = 49.7 Hz is observed. In the spectra of complexes **1** and **2** in pyridine, the signals are shifted downfield: $\Delta\delta$ = 21.62 and 18.54 (P^{III}) and $\Delta\delta$ = 0.45 and 1.33 (P^V) for **1** and **2**, respectively. This indicates that the P^{III} atom and the P=S group are involved in coordination to Ag^+ ions. This fact coupled with the data of IR spectroscopy indicate that various complexes of types **B**, **C**, and **D** containing the $Ag^+—P^{III}$ and $Ag^+—S=P$ coordination bonds are present in pyridine solutions.

In complexes **C** and **D**, only one coordination center of the ligand (P^{III} or P=S) is coordinated to the Ag atom. In the ^{31}P NMR spectra of solutions of complexes **1** and **2** in pyridine, signals for the free P=S group and for the free P^{III} atom are absent, which may be associated with the ligand exchange in the complexes in solutions. To confirm this suggestion, we measured the ^{31}P NMR spectrum of a mixture of complex **2** and two equivalents of the ligand L^2 in pyridine. The spectrum has two narrow signals at δ −0.85 (P^{III}) and 43.49 (P=S) (see Table 2), which are slightly shifted upfield compared to those in the spectrum of the initial complex **2**. In the spectrum of the mixture, signals of the free ligand are absent, which is indicative of the rapid ligand exchange in the systems under study.

1 : 2 Complexes. Previously,[5] it has been demonstrated that the formation of 1 : 2 complexes is associated with the replacement of two NO_3 groups in structure **A** by two ligand molecules. Thus, compared to the spectrum of complex **1**, the IR spectrum of the solid complex $Ag_2(L^1)_4(NO_3)_2$ (**4**) (Table 3, see Table 1) has a low-intensity band at 615 cm^{-1}, which corresponds to free P=S groups, along with a band at 595 cm^{-1} corresponding to coordinated P=S groups. Vibrations of the NO_3 groups in the spectrum of complex **4** are represented by one intense band at 1380 cm^{-1} typical of free NO_3^- anions.[7] These spectral data suggest an unsymmetrical coordination of the "outer" ligands in complex **4** (structure **E**).

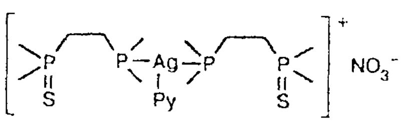


E

Table 3. Vibration frequencies of the P=S and NO_3 groups in the IR spectra of complexes **3** and **4** in the solid phase, in pyridine, and in chloroform

Complex	Phase	ν(P=S)	ν(NO_3)
		cm^{-1}	
$Ag[Ph_2P(S)(CH_2)_2PPh_2]_2NO_3Py$ (**3**)	Solid	615	1390, 1310
	Solution in pyridine	615, 595 (w)	1380
	Solution in $CHCl_3$	615 (w), 590	1350
$Ag_2[Ph_2P(S)(CH_2)_2PPh_2]_4(NO_3)_2$ (**4**)	Solid	615 (w), 595	1380
	Solution in pyridine	615, 595 (w)	1380
	Solution in $CHCl_3$	615 (w), 590	1350

In this work, the crystal structure of the complex $\{Ag[Ph_2P(S)(CH_2)_2PPh_2]_2NO_3Py\}Py$ (**3**), which was isolated from a pyridine solution, was established by X-ray diffraction analysis (Fig. 1). The complex consists of $[Ag(L^1)_2Py]^+$ cations, NO_3^- anions, and pyridine molecules of solvation. The anions and cations are linked in isolated contact ion pairs **F** through weak Ag...O(NO_3^-) interactions.



F

Unlike the structure of the dimer $[Ag_2(L^1)_2](NO_3)_2$ **A** studied previously[5] in which the Ag atoms are coordi-

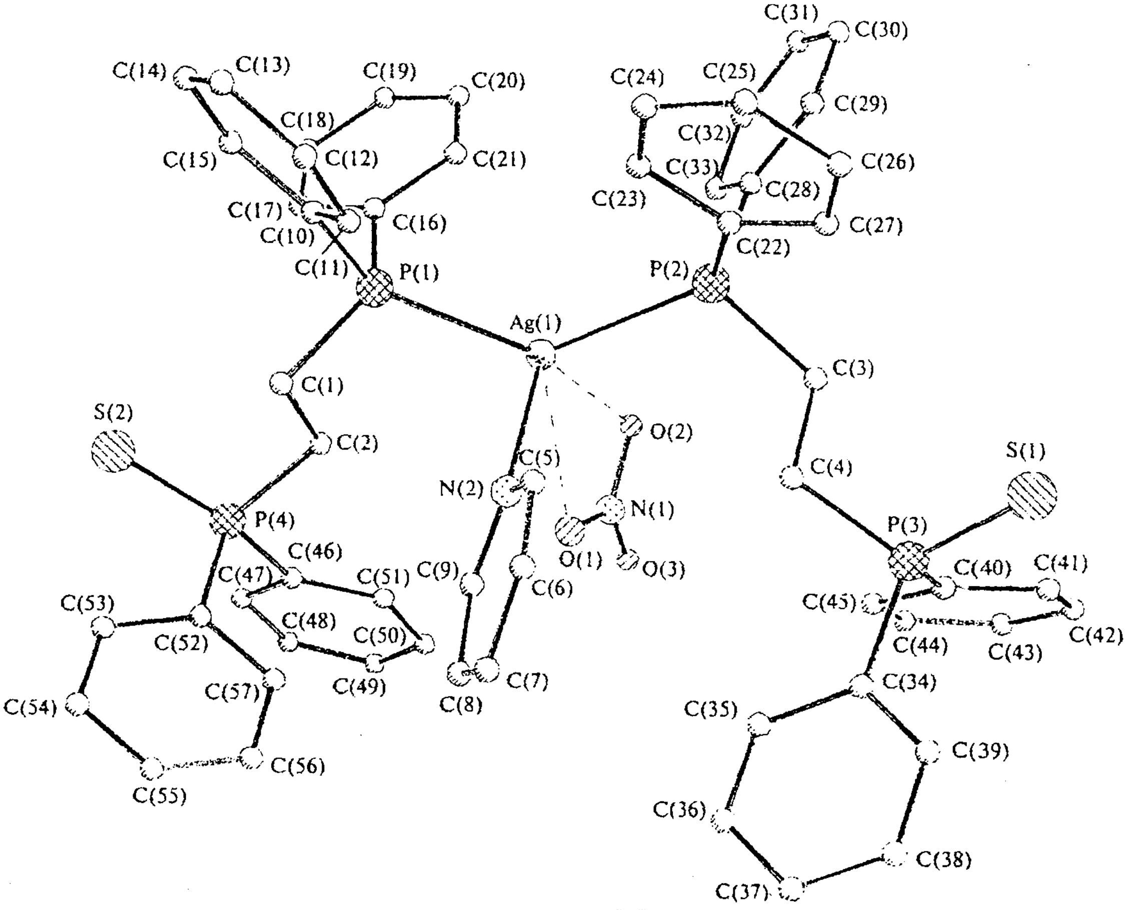
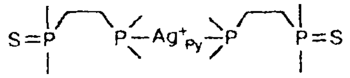


Fig. 1. Structure of the complex $\{Ag[Ph_2P(S)(CH_2)_2PPh]_2NO_3Py\}Py$ (**3**); the pyridine molecule of solvation is omitted.

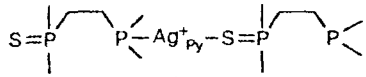
nated by the P=S group and the P^{III} atom, the Ag atom in complex **3** is coordinated only by the P^{III} atoms (see Fig. 1) The Ag(1)—P(1) and Ag(1)—P(2) bond lengths (2.431(2) and 2.455(2) Å, respectively) agree with the mean value of the Ag—PPh_2Me bond (2.438 Å).[9] The Ag(1)—N(2) bond length (2.489(5) Å) is larger than the mean value of the Ag—N(Py) bond length (2.228—2.331 Å)[9] but it is similar to the mean length of the bond between the Ag atom and secondary amines NHR_2 (2.483 Å). The Ag atom forms two weak Ag—O(NO_3^-) contacts. The Ag(1)—O(1) and Ag(1)—O(2) distances are 2.664(13) and 2.780(12) Å, respectively. The Ag(1) atom is located at the vertex of the substantially flattened trigonal pyramid. The Ag(1) atom deviates from the P(1)P(2)N(2) plane toward the NO_3^- ion by 0.490(2) Å. The Ag...NO_3^- interaction in complex **3** is rather weak; the Ag—O distance is substantially larger than the mean value for the η^2-coordinated NO_3^- ion (2.555 Å)[9] and is somewhat larger than the corresponding distances in structure **A** (2.587 and 2.671 Å) in which the analogous η^2-coordination of the NO_3^- ion is observed. However, as in the case of other complexes in which the widely occurring bidentate-chelate mode of coordination of the NO_3^- anion is realized, the above-mentioned interaction involves, apparently, a certain contribution of a partially covalent directed interaction. Therefore, the formation of the contact ion pair in the structure of **3** is beyond doubt. The NO_3^- ion is located above the Ag(1) atom (the dihedral angle between the plane of this ion and the P(1)P(2)N(2) plane is 82.4(7)°) and is oriented so that the O(1) and O(2) atoms are located above the Ag(1)—N(2) and Ag(1)—P(2) bonds, respectively.

Both independent ligands L^1 (L′ and L″) adopt very similar conformations. Only slight differences in the torsion angles are observed: the Ag(1)—P(1)—C(1)—C(2), P(1)—C(1)—C(2)—P(4), and C(1)—C(2)—P(4)—S(2) angles in the ligand L′ are 60.1(5)°, 169.9(4)°, and −54.8(6)°, respectively, and the analogous Ag(1)—P(2)—C(3)—C(4), P(2)—C(3)—C(4)—P(3), and C(3)—C(4)—P(3)—S(1) angles in the ligand L″ are 50.2(6)°, 163.6(4)°, and −64.5(6)°, respectively. In the $[Ag(L^1)_2Py]^+$ cation, the ligands L′ and L″ are related to each other by a twofold pseudoaxis passing through the Ag(1) atom and the midpoints of the P(1)...P(2) and P(3)...P(4) distances. The symmetry is distorted mainly due to slight differences in the angles of rotation of the Ph rings about the P—C(Ph) bonds. The dihedral angles between the Ag(1)P(1)C(1) plane and the planes of the C(10)—C(15) and C(16)—C(21) rings in the ligand L′ are 67.6° and 51.2°, respectively. The angles between the Ag(1)P(2)C(3) plane and the C(28)—C(32) and C(22)—C(27) rings in the ligand L″ are 77.8° and 48.4°, respectively. Analogously, the orientations of the Ph rings with respect to the PSC plane in both ligands are slightly different. The dihedral angles between the P(4)S(2)C(2) plane and the C(46)—C(51) and C(52)—C(57) rings are 51.2° and 64.0° in L′ and 53.9° and 55.5° in L″, respectively. These differences, like the differences in the conformations of the ligands, are apparently due to the packing effects determined primarily by steric requirements of the arrangement of the coordinated NO_3^- ions and pyridine molecules in the cavity between the ligands.

Complex **3** is readily soluble in pyridine and chloroform. The IR spectra of complex **3** in these solvents were examined, and the results were compared with the spectra of the complex $Ag_2(L^1)_4(NO_3)_2$ (**4**) (see Table 3). The IR spectrum of complex **3** in pyridine, unlike the spectrum of the solid sample, has a low-intensity band at 595 cm^{-1} corresponding to the coordinated P=S group. One band at 1380 cm^{-1} corresponding to the free NO_3 group[7] is observed in the spectrum of the solution instead of two intense bands at 1390 and 1310 cm^{-1} corresponding to the coordinated NO_3 group,[6] which are observed in the spectrum of the solid sample. These data indicate that dissolution of complex **3** in pyridine is accompanied by its dissociation so that complex **F** is converted into complex **G**, and unsymmetrical complex **H** is formed due to the ligand exchange in the solution.



G



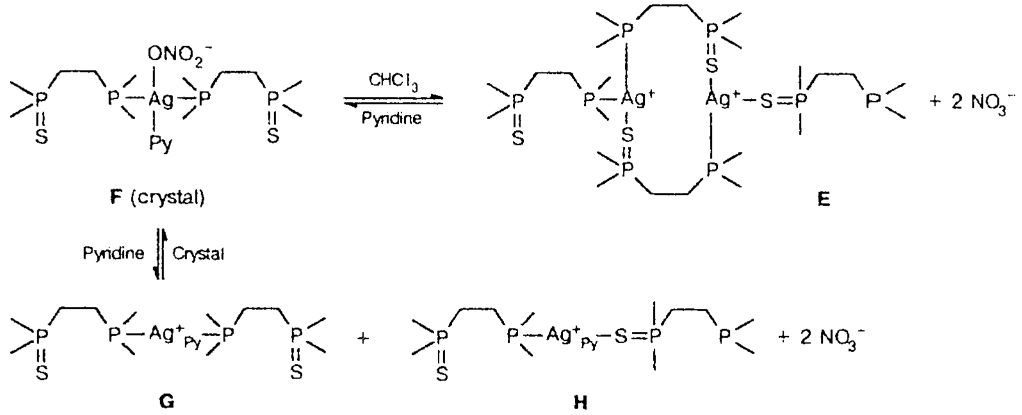
H

The IR spectra of solid complexes **3** and **4** are different but the spectra of their solutions in pyridine are identical. From this fact it follows that dissolution of complex **4** in pyridine is accompanied by destruction of dimeric structure **E** to form complexes **G** and **H**.

Dissolution of complex **3** in $CHCl_3$ leads to a decrease in the intensity of the absorption band of free P=S groups (615 cm^{-1}) and to the appearance of the band of coordinated P=S groups (590 cm^{-1}) (see Table 3). One band at 1350 cm^{-1} corresponding to free NO_3 groups[7] is observed in the IR spectrum of the solution of **3** instead of two intense bands at 1390 and 1310 cm^{-1}, which are observed in the IR spectrum of solid complex **3**. On the whole, the spectrum of complex **3** in $CHCl_3$ is similar to the spectrum of complex **4** (see Table 3). In addition, a solution of complex **3** in $CHCl_3$ yielded a solid complex whose IR spectrum is identical to that of complex **4**. Therefore, complex **3** in $CHCl_3$ restores dimeric structure **E**. Conversions of the 1 : 2 complexes that occur when the aggregative state or the solvent is changed can be represented by Scheme 2.

The ^{31}P NMR spectra of solutions of the ligand L^1 in $CHCl_3$ and pyridine are little different. They have narrow signals at δ −13 and 45 for P^{III} and P^V, respectively. The signals occur as doublets with the spin-spin coupling constant J_{PP} = 49.5 Hz (Table 4). Upon for-

Scheme 2



mation of complex **3** in pyridine, both signals are shifted downfield with retention of the doublet splitting (J_{PP} = 38.5 Hz). In the spectra of complexes **3** and **4** in $CHCl_3$, the signals for P^{III} and P^V are also shifted downfield. However, the doublet splitting of the signals is retained only for P^V (J_{PP} = 16.1 (**3**) and 21.7 Hz (**4**)), while one signal with the value $\Delta_{1/2} \approx 180$ Hz is observed for P^{III} (see Table 4). Apparently, this broadening of the signals for P^{III} is due to the "outer" ligand exchange in structure **E**. Interestingly, in the spectrum of complex **3** in pyridine, the signal for P^V is shifted by 0.63 ppm, while in the spectrum of complex **3** in $CHCl_3$, this signal is shifted by 1.56 ppm (see Table 4). This difference in the values of $\Delta\delta$ reflects the change in the structure of the complex in pyridine (structures **G** and **H**) and in $CHCl_3$ (structure **E**).

In conclusion, it should be noted that the characteristic feature of the complexes under study is that they have different structures depending on the nature of the solvent and the aggregative state. Apparently, these changes are associated with the unsymmetrical structures of the ligands containing different-valence phosphorus atoms. In addition, the 1 : 1 and 1 : 2 complexes in pyridine form different structures in which the Ag^+ atom is coordinated both to the P^{III} atom and to the P=S group. From this it follows that the P^{III} atom and the P=S group are comparable in their ability to form dπ-bonds with the Ag^I atom.

Experimental

The IR spectra of the complexes were measured on an UR-20 spectrophotometer (400—3700 cm^{-1}) as Nujol mulls and in pyridine solutions (l = 0.07 mm, $C \approx 0.2$ mol L^{-1}). The $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker WP-200SY instrument (81.01 MHz) with a 85% H_3PO_4 solution as the external standard. The concentrations of the solutions were 0.1—0.2 mol L^{-1}.

Isolation of the 1 : 1 complexes from pyridine. The complex $Ag(L^1)NO_3$ (**1**) (0.11 g, 0.065 mmol) was dissolved in pyridine (1 mL) upon heating to 40—45 °C. The solution was cooled, and anhydrous ether was gradually added until a precipitate formed. The precipitate was filtered off and thoroughly dried *in vacuo*. The yield of complex **1** was 0.09 g (82%). Found (%): C, 52.2; H, 4.1; N, 2.5; P, 9.7. $C_{26}H_{24}AgNO_3P_2S$. Calculated (%): C, 52.1; H, 4.0; N, 2.3; P, 10.3. The data of elemental analysis correspond to the metal : ligand composition of 1 : 1.

The complex $Ag(L^2)NO_3$ (**2**) was prepared as described above; the yield was 61%. Found (%): C, 54.0; H, 4.4; N, 2.3; P, 9.7. $C_{28}H_{28}AgNO_3P_2S$. Calculated (%): C, 53.5; H, 4.5; N, 2.3; P, 9.9.

Synthesis of {Ag[$Ph_2P(S)(CH_2)_2PPh_2$]$_2NO_3$Py}Py (3). The ligand L^1 (0.579 g, 0.1765 mmol) was added to a solution of $AgNO_3$ (0.015 g, 0.082 mmol) in pyridine (1.5 mL) so that the metal : ligand ratio was approximately 1 : 2 with a small excess of the ligand. The reaction solution was kept in the dark. Crystals of **3** were isolated after approximately one month. Found (%): C, 62.7; H, 4.9; N, 3.5. $C_{62}H_{58}AgN_3O_3P_4S_2$. Calculated (%): C, 62.6; H, 4.9; N, 3.5.

Table 4. ^{31}P NMR spectra of the 1 : 2 complexes (**3** and **4**) in pyridine and chloroform

Compound	Solvent	δP^{III}	$\Delta\delta$	J_{PP}/Hz	δP^V	$\Delta\delta$	J_{PP}/Hz
$Ph_2P(S)(CH_2)_2PPh_2$ (L^1)	Pyridine	−13.23	0	49.5	44.83	0	49.7
	$CHCl_3$	−12.88	0	49.3	44.32	0	49.5
$Ag(L^1)_2NO_3Py$ (**3**)	Pyridine	+5.13	18.36	38.4	45.46	0.63	38.5
	$CHCl_3$	+4.52	17.40	0[a]	45.88	1.56	16.1
$Ag_2(L^1)_4(NO_3)_2$ (**4**)	$CHCl_3$	+5.28	18.16	0[b]	45.89	1.57	21.7

[a] $\Delta\nu_{1/2}$ = 175 Hz.
[b] $\Delta\nu_{1/2}$ = 185 Hz.

Table 5. Atomic coordinates (×10^4; for H atoms, ×10^3) and isotropic (equivalent for nonhydrogen atoms) temperature factors (U_{eq}/U_{iso}×10^3) in the structure of 3

Atom	x	y	z	U_{eq}/U_{iso}/Å^2
Ag(1)	−9415(1)	2188(1)	5170(1)	56(1)
N(1)	−6564(6)	2455(2)	4159(6)	71(1)
N(2)	−11087(6)	2483(2)	3291(5)	69(1)
O(1)	−7675(12)	2373(9)	3638(13)	266(12)
O(2)	−6527(12)	2405(7)	5224(12)	211(8)
O(3)	−5493(9)	2509(4)	3805(10)	149(4)
S(1)	−9590(2)	4537(1)	5563(2)	74(1)
S(2)	−8329(3)	120(1)	2326(2)	88(1)
P(1)	−9799(1)	1350(1)	5157(1)	46(1)
P(2)	−9226(2)	2825(1)	6665(1)	52(1)
P(3)	−8802(2)	4096(1)	4548(1)	51(1)
P(4)	−8024(2)	782(1)	2093(1)	57(1)
C(1)	−9740(6)	1064(3)	3699(5)	55(1)
C(2)	−8270(7)	1141(3)	3386(5)	59(1)
C(3)	−8410(8)	3364(3)	6202(6)	57(2)
C(4)	−9172(7)	3497(2)	4899(6)	60(1)
C(5)	−12275(8)	2727(3)	3338(7)	72(2)
C(6)	−13141(11)	2925(4)	2348(9)	96(3)
C(7)	−12747(13)	2885(5)	1227(9)	105(3)
C(8)	−11578(15)	2636(6)	1169(9)	105(4)
C(9)	−10768(11)	2443(4)	2216(8)	90(2)
C(10)	−11601(6)	1205(2)	5405(5)	52(1)
C(11)	−12639(6)	1551(3)	5244(6)	67(2)
C(12)	−14006(8)	1466(3)	5478(8)	82(2)
C(13)	−14338(8)	1041(3)	5851(7)	78(2)
C(14)	−13335(9)	693(3)	5981(8)	80(2)
C(15)	−11974(8)	767(3)	5760(7)	71(2)
C(16)	−8538(6)	1016(2)	6288(5)	48(1)
C(17)	−8097(7)	560(2)	6095(6)	61(1)
C(18)	−7097(9)	331(3)	6992(8)	77(2)
C(19)	−6530(9)	546(3)	8079(7)	81(2)
C(20)	−6951(10)	991(4)	8295(7)	85(2)
C(21)	−7935(8)	1224(3)	7399(5)	64(2)
C(22)	−10946(7)	3001(3)	7005(5)	62(1)
C(23)	−11959(10)	2639(4)	7024(8)	88(2)
C(24)	−13245(11)	2734(5)	7337(12)	114(4)
C(25)	−13606(11)	3183(5)	7620(10)	108(3)
C(26)	−12656(12)	3547(5)	7569(10)	107(3)
C(27)	−11320(9)	3451(3)	7258(8)	82(2)
C(28)	−8107(7)	2713(2)	8183(6)	63(2)
C(29)	−8412(12)	2893(4)	9236(7)	102(3)
C(30)	−7551(13)	2795(5)	10369(8)	112(3)
C(31)	−6391(10)	2496(4)	10443(8)	92(3)
C(32)	−6065(10)	2328(5)	9422(10)	101(3)
C(33)	−6914(8)	2426(3)	8273(7)	78(2)
C(34)	−9589(7)	4160(2)	2933(6)	60(1)
C(35)	−9698(17)	3799(3)	2094(8)	121(4)
C(36)	−10313(22)	3854(4)	894(10)	142(6)
C(37)	−10853(13)	4281(4)	476(9)	104(3)
C(38)	−10792(12)	4639(4)	1249(8)	96(3)
C(39)	−10192(10)	4572(3)	2468(8)	80(2)
C(40)	−6863(7)	4140(2)	4705(6)	62(2)
C(41)	−6142(10)	4532(4)	5240(10)	96(3)
C(42)	−4652(14)	4575(7)	5363(14)	137(6)
C(43)	−3873(12)	4241(9)	4983(14)	135(6)
C(44)	−4535(15)	3849(8)	4501(14)	141(6)
C(45)	−6039(10)	3788(4)	4348(10)	99(3)
C(46)	−6199(7)	939(3)	1894(5)	67(2)
C(47)	−5369(10)	601(4)	1468(8)	92(3)
C(48)	−4018(12)	722(7)	1268(10)	124(5)
C(49)	−3463(10)	1161(6)	1499(9)	112(4)
C(50)	−4262(8)	1497(5)	1942(8)	93(3)
C(51)	−5632(8)	1376(3)	2154(7)	79(2)
C(52)	−9295(6)	1025(2)	783(5)	54(1)
C(53)	−10379(8)	752(3)	126(7)	76(2)
C(54)	−11362(11)	931(5)	−854(8)	93(3)
C(55)	−11270(9)	1378(4)	−1201(7)	85(2)
C(56)	−10188(11)	1658(3)	−577(8)	87(2)
C(57)	−9189(9)	1480(3)	433(7)	73(2)
C(58)*	−4882(26)	4115(11)	−414(31)	214(13)
C(59)*	−4912(29)	4166(11)	734(31)	206(10)
C(60)*	−5844(26)	4395(9)	1193(19)	170(7)
C(61)*	−7074(27)	4512(11)	340(36)	214(11)
C(62)*	−7221(30)	4443(11)	−870(34)	208(12)
C(63)*	−6111(40)	4219(12)	−1224(19)	195(10)
H(101)	−1001(7)	77(3)	380(6)	51(16)
H(102)	−1058(8)	118(3)	300(7)	72(20)
H(201)	−790(10)	142(4)	334(8)	87(27)
H(202)	−756(10)	102(3)	409(8)	83(24)
H(301)	−740(7)	325(2)	614(5)	45(14)
H(302)	−854(6)	356(2)	663(5)	33(14)
H(401)	−883(6)	328(2)	433(5)	37(13)
H(402)	−1028(9)	359(3)	479(7)	73(21)
H(5)	−1254(8)	279(3)	398(8)	68(21)
H(6)	−1381(13)	314(5)	246(11)	120(38)
H(7)	−1331(13)	298(4)	57(11)	120(36)
H(8)	−1162(16)	248(5)	79(13)	120(36)
H(9)	−991(10)	233(3)	216(8)	86(27)
H(11)	−1252(10)	181(4)	476(9)	95(26)
H(12)	−1483(12)	174(4)	554(10)	121(34)
H(13)	−1532(10)	100(3)	605(8)	86(24)
H(14)	−1339(10)	39(4)	628(9)	101(29)
H(15)	−1121(8)	54(3)	590(7)	69(20)
H(17)	−855(11)	41(4)	526(10)	100(28)
H(18)	−687(9)	2(3)	69(7)	78(22)
H(19)	−587(15)	41(5)	874(12)	135(43)
H(20)	−658(9)	114(3)	895(9)	79(23)
H(21)	−821(6)	154(2)	757(5)	45(14)
H(23)	−1162(11)	234(4)	665(10)	106(32)
H(24)	−1393(13)	263(4)	758(11)	114(35)
H(25)	−1450(13)	320(4)	788(11)	121(36)
H(26)	−1283(11)	389(4)	780(9)	96(28)
H(27)	−1069(11)	374(4)	723(9)	101(30)
H(29)	−926(10)	313(3)	911(8)	89(25)
H(30)	−792(10)	293(4)	1105(9)	97(27)
H(31)	−588(9)	243(3)	1118(8)	73(21)
H(32)	−561(9)	213(3)	914(8)	73(26)
H(33)	−669(7)	227(3)	756(6)	59(17)
H(35)	−868(19)	348(7)	288(16)	200(71)
H(36)	−894(35)	393(12)	9(32)	262(170)
H(37)	−1105(9)	427(3)	−24(8)	68(21)
H(38)	−1124(11)	495(4)	78(10)	107(30)
H(39)	−970(14)	480(5)	291(11)	124(42)
H(41)	−672(11)	478(4)	570(9)	99(29)
H(42)	−436(13)	487(4)	559(11)	111(35)
H(43)	−265(14)	444(5)	525(11)	128(38)
H(44)	−403(16)	351(6)	411(13)	160(49)
H(45)	−676(8)	355(3)	393(6)	57(17)
H(47)	−592(12)	34(4)	140(10)	103(37)
H(48)	−386(16)	31(5)	117(13)	145(46)
H(49)	−255(12)	119(4)	132(9)	98(29)
H(50)	−398(15)	195(5)	192(13)	155(49)
H(51)	−636(9)	163(3)	257(8)	86(24)
H(53)	−1038(9)	48(4)	42(8)	75(24)
H(54)	−1180(9)	74(3)	−115(8)	69(25)
H(55)	−1201(10)	160(4)	−191(9)	104(29)
H(56)	−1029(12)	201(5)	−68(11)	127(39)
H(57)	−847(14)	168(5)	74(12)	139(43)

* The atoms of the pyridine molecule of solvation.

Table 6. Bond lengths (*d*) and bond angles (ω) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Ag(1)—P(1)	2.431(2)	P(4)—C(46)	1.836(7)	C(22)—C(23)	1.414(11)	C(43)—C(44)	1.34(3)
Ag(1)—P(2)	2.455(2)	C(1)—C(2)	1.516(8)	C(23)—C(24)	1.358(14)	C(44)—C(45)	1.40(2)
Ag(1)—N(2)	2.489(5)	C(3)—C(4)	1.528(9)	C(24)—C(25)	1.38(2)	C(46)—C(51)	1.368(12)
N(1)—O(1)	1.109(12)	C(5)—C(6)	1.352(12)	C(25)—C(26)	1.38(2)	C(46)—C(47)	1.392(11)
N(1)—O(3)	1.170(9)	C(6)—C(7)	1.39(2)	C(26)—C(27)	1.403(13)	C(47)—C(48)	1.38(2)
N(1)—O(2)	1.192(13)	C(7)—C(8)	1.33(2)	C(28)—C(29)	1.371(12)	C(48)—C(49)	1.37(2)
N(2)—C(9)	1.304(10)	C(8)—C(9)	1.37(2)	C(28)—C(33)	1.380(11)	C(49)—C(50)	1.38(2)
N(2)—C(5)	1.331(10)	C(10)—C(11)	1.379(9)	C(29)—C(30)	1.379(12)	C(50)—C(51)	1.405(11)
S(1)—P(3)	1.950(2)	C(10)—C(15)	1.386(9)	C(30)—C(31)	1.38(2)	C(52)—C(57)	1.372(10)
S(2)—P(4)	1.948(3)	C(11)—C(12)	1.389(10)	C(31)—C(32)	1.33(2)	C(52)—C(53)	1.371(10)
P(1)—C(16)	1.814(6)	C(12)—C(13)	1.347(13)	C(32)—C(33)	1.390(12)	C(53)—C(54)	1.375(13)
P(1)—C(10)	1.826(5)	C(13)—C(14)	1.362(13)	C(34)—C(39)	1.366(10)	C(54)—C(55)	1.35(2)
P(1)—C(1)	1.836(6)	C(14)—C(15)	1.373(11)	C(34)—C(35)	1.386(11)	C(55)—C(56)	1.367(14)
P(2)—C(22)	1.815(7)	C(16)—C(21)	1.385(9)	C(35)—C(36)	1.35(2)	C(56)—C(57)	1.403(11)
P(2)—C(28)	1.825(6)	C(16)—C(17)	1.402(9)	C(36)—C(37)	1.37(2)	C(58)—C(59)	1.30(4)
P(2)—C(3)	1.849(7)	C(17)—C(18)	1.387(10)	C(37)—C(38)	1.33(2)	C(58)—C(63)	1.34(4)
P(3)—C(40)	1.802(6)	C(18)—C(19)	1.366(13)	C(38)—C(39)	1.372(12)	C(59)—C(60)	1.29(3)
P(3)—C(34)	1.809(6)	C(19)—C(20)	1.374(13)	C(40)—C(41)	1.381(12)	C(60)—C(61)	1.38(4)
P(3)—C(4)	1.813(6)	C(20)—C(21)	1.383(10)	C(40)—C(45)	1.384(13)	C(61)—C(62)	1.35(4)
P(4)—C(52)	1.820(6)	C(22)—C(27)	1.381(12)	C(41)—C(42)	1.39(2)	C(62)—C(63)	1.36(4)
P(4)—C(2)	1.829(6)	Ag(1)—O(1)	2.664(13)	C(42)—C(43)	1.33(3)	Ag(1)—O(2)	2.780(12)

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
P(1)—Ag(1)—P(2)	136.75(5)	C(7)—C(8)—C(9)	119.5(11)	C(35)—C(34)—P(3)	123.7(5)
P(1)—Ag(1)—N(2)	105.3(2)	N(2)—C(9)—C(8)	123.8(10)	C(36)—C(35)—C(34)	122.4(9)
P(2)—Ag(1)—N(2)	105.3(2)	C(11)—C(10)—C(15)	118.3(6)	C(35)—C(36)—C(37)	119.6(11)
O(1)—N(1)—O(3)	129.5(11)	C(11)—C(10)—P(1)	118.2(5)	C(38)—C(37)—C(36)	120.3(9)
O(1)—N(1)—O(2)	108.8(11)	C(15)—C(10)—P(1)	123.4(5)	C(37)—C(38)—C(39)	119.1(9)
O(3)—N(1)—O(2)	120.7(10)	C(10)—C(11)—C(12)	120.6(7)	C(34)—C(39)—C(38)	123.3(9)
C(9)—N(2)—C(5)	116.3(7)	C(13)—C(12)—C(11)	120.2(8)	C(41)—C(40)—C(45)	117.6(9)
C(9)—N(2)—Ag(1)	121.3(6)	C(12)—C(13)—C(14)	119.7(7)	C(41)—C(40)—P(3)	119.6(7)
C(5)—N(2)—Ag(1)	122.1(5)	C(13)—C(14)—C(15)	121.4(8)	C(45)—C(40)—P(3)	122.7(7)
C(16)—P(1)—C(10)	105.5(3)	C(14)—C(15)—C(10)	119.7(7)	C(40)—C(41)—C(42)	120.7(13)
C(16)—P(1)—C(1)	104.1(3)	C(21)—C(16)—C(17)	117.4(6)	C(43)—C(42)—C(41)	121.4(14)
C(10)—P(1)—C(1)	103.8(3)	C(21)—C(16)—P(1)	118.7(5)	C(44)—C(43)—C(42)	119.4(11)
C(16)—P(1)—Ag(1)	116.3(2)	C(17)—C(16)—P(1)	123.8(5)	C(43)—C(44)—C(45)	121.6(14)
C(10)—P(1)—Ag(1)	111.5(2)	C(18)—C(17)—C(16)	120.6(7)	C(40)—C(45)—C(44)	119.3(13)
C(1)—P(1)—Ag(1)	114.5(2)	C(19)—C(18)—C(17)	120.4(8)	C(51)—C(46)—C(47)	119.2(8)
C(22)—P(2)—C(28)	102.6(3)	C(18)—C(19)—C(20)	120.2(7)	C(51)—C(46)—P(4)	122.1(5)
C(22)—P(2)—C(3)	105.6(4)	O(1)—Ag(1)—N(2)	75.9(5)	C(47)—C(46)—P(4)	118.7(8)
C(28)—P(2)—C(3)	102.4(3)	O(1)—Ag(1)—P(1)	107.7(4)	C(48)—C(47)—C(46)	119.0(12)
C(22)—P(2)—Ag(1)	114.3(2)	O(1)—Ag(1)—P(2)	108.9(4)	C(49)—C(48)—C(47)	121.9(10)
C(28)—P(2)—Ag(1)	116.5(2)	O(1)—Ag(1)—O(2)	40.1(9)	C(48)—C(49)—C(50)	119.7(9)
C(3)—P(2)—Ag(1)	113.9(3)	C(19)—C(20)—C(21)	119.7(7)	C(49)—C(50)—C(51)	118.6(11)
C(40)—P(3)—C(34)	106.4(3)	C(20)—C(21)—C(16)	121.7(7)	C(46)—C(51)—C(50)	121.5(8)
C(40)—P(3)—C(4)	106.5(3)	C(27)—C(22)—C(23)	118.7(7)	C(57)—C(52)—C(53)	118.8(7)
C(34)—P(3)—C(4)	104.8(3)	C(27)—C(22)—P(2)	125.6(6)	C(57)—C(52)—P(4)	121.2(5)
C(40)—P(3)—S(1)	113.6(3)	C(23)—C(22)—P(2)	115.7(6)	C(53)—C(52)—P(4)	120.0(6)
C(34)—P(3)—S(1)	112.9(2)	C(24)—C(23)—C(22)	119.9(10)	C(52)—C(53)—C(54)	120.8(9)
C(4)—P(3)—S(1)	112.0(2)	C(23)—C(24)—C(25)	121.5(11)	C(55)—C(54)—C(53)	120.7(9)
C(52)—P(4)—C(2)	104.4(3)	C(24)—C(25)—C(26)	119.9(10)	C(54)—C(55)—C(56)	120.0(8)
C(52)—P(4)—C(46)	106.4(3)	C(25)—C(26)—C(27)	119.0(11)	C(55)—C(56)—C(57)	119.7(9)
C(2)—P(4)—C(46)	103.8(3)	C(22)—C(27)—C(26)	121.0(10)	C(52)—C(57)—C(56)	119.9(8)
C(52)—P(4)—S(2)	113.0(2)	C(29)—C(28)—C(33)	118.6(7)	C(59)—C(58)—C(63)	116(2)
C(2)—P(4)—S(2)	113.3(3)	C(29)—C(28)—P(2)	123.2(6)	C(60)—C(59)—C(58)	128(2)
C(46)—P(4)—S(2)	115.1(3)	C(33)—C(28)—P(2)	118.2(6)	C(59)—C(60)—C(61)	113(2)
C(2)—C(1)—P(1)	110.0(4)	C(28)—C(29)—C(30)	121.4(10)	C(62)—C(61)—C(60)	124(2)
C(1)—C(2)—P(4)	112.1(4)	C(29)—C(30)—C(31)	119.1(10)	C(61)—C(62)—C(63)	116(2)
C(4)—C(3)—P(2)	109.7(4)	C(32)—C(31)—C(30)	119.9(8)	C(58)—C(63)—C(62)	121(2)
C(3)—C(4)—P(3)	111.7(4)	C(31)—C(32)—C(33)	121.7(10)	O(2)—Ag(1)—N(2)	112.5(6)
N(2)—C(5)—C(6)	123.7(8)	C(28)—C(33)—C(32)	119.2(9)	O(2)—Ag(1)—P(1)	111.4(5)
C(5)—C(6)—C(7)	118.4(10)	C(39)—C(34)—C(35)	115.1(7)	O(2)—Ag(1)—P(2)	83.7(5)
C(8)—C(7)—C(6)	118.3(9)	C(39)—C(34)—P(3)	121.1(6)		

The data of elemental analysis correspond to the metal : ligand composition of 1 : 2 with two pyridine molecules.

X-ray diffraction analysis of complex 3. Transparent colorless crystals of $\{Ag[Ph_2P(S)(CH_2)_2PPh_2]_2NO_3Py\}Py$ (3), $C_{62}H_{58}AgN_3O_3P_4S_2$ (M = 1188.98) are monoclinic, at 20 °C a = 9.423(2) Å, b = 28.682(6) Å, c = 11.178(2) Å, β = 102.30(3)°, V = 2952(1) Å^3, d_{calc} = 1.338 g cm^{-3}, Z = 2, space group $P2_1$.

The unit cell parameters and intensities of 7813 reflections were measured on an automated four-circle CAD-4 Enraf-Nonius diffractometer (Mo-Kα radiation, $\theta/(5/3)\theta$-scanning technique, graphite monochromator, $\theta < 30°$, μ = 5.67 cm^{-1}; no absorption corrections were made). The structure was solved by the direct method and refined by the full-matrix least-squares method. The difference electron density syntheses calculated in the course of the solution of the structure revealed electron density peaks corresponding to the pyridine molecule of solvation, which is, apparently, disordered. We did not attempt to locate the position of the N atom in the pyridine molecule. All nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located from difference electron density syntheses (except for the atoms of the Py molecule of solvation) and refined isotropically. The final R factors were as follows: R_1 = 0.0392 (based on F for 5201 reflections with $I > 2\sigma(6)$) and wR_2 = 0.2191 (based on F^2 for all 6931 independent reflections used in the refinement). The absolute structure was determined using the refinement of Flack's parameter (x parameter).[10] According to recommendations,[11] two special refinements with different starting values of the x parameter were carried out (options BASF 0.01 and TWIN and options BASF 0.99 and TWIN, respectively). The final values of the x parameter obtained in two cases were virtually identical and were close to zero (0.034(6) and 0.040(5), respectively), which indicates that the absolute structure was unambiguously determined. All calculations were carried out using the SHELXTL PLUS 5 program package (the gamma version).

The atomic coordinates and the temperature factors are given in Table 5. The bond lengths and the bond angles are listed in Table 6.

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