P, *O*-Ligands. Complexes of tetraphenylmethylenediphosphine oxide with silver nitrate

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The 1 : 1 and 1 : 2 complexes of $AgNO_3$ with $Ph_2PCH_2P(O)Ph_2$ were prepared and their structures were established by IR and ^{31}P NMR spectroscopy and X-ray diffraction analysis. The crystal of the 1 : 1 complex consists of centrosymmetric dimers based on the ten-membered macrocycle $\overline{AgOPCH_2PAgOPCH_2P}$. Each neutral ligand serves as a bridge between two silver ions, the latter being coordinated by the NO_3 group in the monodentate fashion. In the 1 : 2 complex, the dimeric structure is retained, but both NO_3 groups are replaced by the ligand molecules.

Key words: silver complexes, methylenediphosphine oxide, X-ray diffraction analysis, ^{31}P NMR spectroscopy, IR spectroscopy.

Silver nitrate forms complexes with various trivalent phosphorus compounds. In these complexes, the ratio of the components (Ag : L) can be 1 : 1, 1 : 2, 1 : 3, or 1 : 4. Complexes of 1 : 1 composition exist as tetramers, *e.g.*, $[AgI \cdot PEt_3]_4$,[1] $[AgI \cdot PPh_3]_4$,[2] or $[AgCl \cdot PPh_3]_4$,[2] or polymers, *e.g.*, $[AgNO_3 \cdot PPh_3]_n$,[3] whereas complexes of 1 : 4 composition have the ionic structure $[Ag(PPh_3)_4]^+X^-$ ($X = ClO_4^-$, BrO_3^-, or NO_3^-) and correspond in conductivity to monovalent electrolytes.[4—6] The reaction of tetraphenylmethylenediphosphine ($Ph_2PCH_2PPh_2$) with $AgNO_3$ afforded the eight-membered cyclic dimer $\overline{AgPCH_2PAgPCH_2P}$.[7]

The replacement of one PPh_2 group in the diphosphine $Ph_2P(CH_2)_nPPh_2$ ligand by NR_2, SR, or $R_2P(O)$ offers alternative possibilities. Thus, the ligand can be coordinated through the P^{III} atom, the heteroatom, or both centers simultaneously. Recently, such "unsymmetrical" ligands have attracted considerable attention, especially because their complexes with "soft" transition metals (Rh^I, Pt^{II}, or Ru^{II}) find use as catalysts.[8—10] Neutral silver complexes containing the Ag—O=P bond are unavailable in the literature.

Previously,[11] we have studied silver complexes with tetraphenylalkylenediphosphines $Ag[Ph_2P(CH_2)_nP(S)Ph_2]_m \cdot NO_3$ ($n = 2—4$, $m = 1$ or 2). In the present investigation, of concern to us was the question of whether the mode of coordination of the Ag atom is changed on going from sulfides to the corresponding oxides.

In the present study, we synthesized complexes of $Ph_2PCH_2P(O)Ph_2$ (L) with $AgNO_3$ of compositions metal : ligand = 1 : 1 (**1**) and 1 : 2 (**2**) and investigated their structures in crystals and solutions by IR and ^{31}P NMR spectroscopy and X-ray diffraction analysis.

Results and Discussion

The structure of the $Ag(L)NO_3$ complex of composition 1 : 1 (1). The structure of complex **1** (Figs. 1 and 2; Tables 1 and 2) consists of the centrosymmetric binuclear $[Ag_2(L)_2(NO_3)_2]$ molecules with the Ag(1)...Ag(1A) distance of 3.301(1) Å. The coordination environment about the Ag atom is formed by the O(1) and P(1) atoms of the ligand L and the O(2) atom of the monodentate NO_3^- anion. The triangular polyhedron adopts a distorted T-shaped form in which one of the bond angles is substantially larger than the other two angles:

Angle	ω/deg
O(2)—Ag(1)—P(1)	158.50(7)
O(2)—Ag(1)—O(1)	79.07(9)
P(1)—Ag(1)—O(1)	121.09(7)

The Ag atom deviates from the O(1)—O(2)—P(1) plane by 0.126(2) Å, *i.e.*, the coordination polyhedron is a highly flattened trigonal pyramid. The Ag(1)—P(1) bond length (2.355(2) Å) is substantially smaller than the average length of the bonds between the Ag atom and various phosphine ligands (the average Ag—PPh_3, Ag—PPh_2Me, and Ag—$Ph_2PCH_2PPh_2$ bond lengths are 2.419, 2.438, and 2.427 Å, respectively).[12] The Ag(1)—O(2) bond with the monodentate NO_3^- anion is also substantially shortened (2.220(3) Å). Of the struc-

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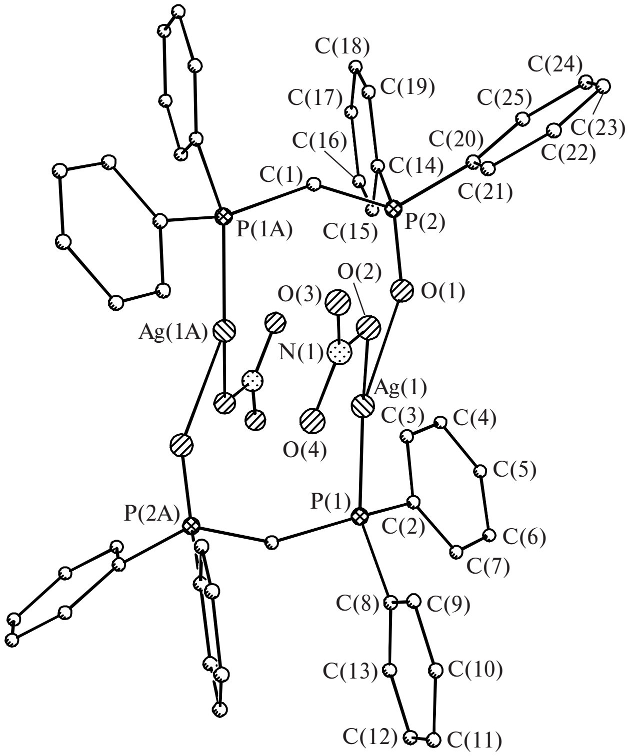


Fig. 1. Structure of the complex Ag[Ph$_2$PCH$_2$P(O)Ph$_2$]NO$_3$ (**1**) (H atoms are omitted).

Table 1. Selected bond lengths (*d*) in complex **1**

Bond	*d*/Å	Bond	*d*/Å
Ag(1)—O(2)	2.220(3)	P(2)—C(20)	1.801(3)
Ag(1)—P(1)	2.355(2)	P(2)—C(14)	1.804(3)
Ag(1)—O(1)	2.416(2)	P(2)—C(1)	1.805(4)
P(1)—C(8)	1.815(4)	N(1)—O(4)	1.220(4)
P(1)—C(2)	1.826(3)	N(1)—O(3)	1.229(4)
P(1)—C(1)*	1.839(3)	N(1)—O(2)	1.265(4)
P(2)—O(1)	1.485(3)		

* The atom is generated from the basis atom by the symmetry operation $-x$, $-y + 1$, $-z$.

Table 2. Selected bond angles (ω) in complex **1**

Angle	ω/deg	Angle	ω/deg
O(2)—Ag(1)—P(1)	158.50(7)	C(20)—P(2)—C(14)	107.65(15)
O(2)—Ag(1)—O(1)	79.07(9)	O(1)—P(2)—C(1)	112.22(19)
P(1)—Ag(1)—O(1)	121.09(7)	C(20)—P(2)—C(1)	103.63(18)
C(8)—P(1)—C(2)	109.04(17)	C(14)—P(2)—C(1)	106.87(16)
C(8)—P(1)—C(1)*	103.06(19)	O(4)—N(1)—O(3)	122.9(3)
C(2)—P(1)—C(1)*	101.37(15)	O(4)—N(1)—O(2)	119.5(4)
C(8)—P(1)—Ag(1)	115.54(15)	O(3)—N(1)—O(2)	117.6(3)
C(2)—P(1)—Ag(1)	109.48(13)	P(2)—O(1)—Ag(1)	137.36(13)
C(1)*—P(1)—Ag(1)	117.19(17)	N(1)—O(2)—Ag(1)	118.2(2)
O(1)—P(2)—C(20)	114.41(15)	P(2)—C(1)—P(1)*	113.9(2)
O(1)—P(2)—C(14)	111.49(16)		

* The atom is generated from the basis atom by the symmetry operation $-x$, $-y + 1$, $-z$.

tures available in the Cambridge Structural Database (CSD),[13] the shortest Ag—O bonds (2.259, 2.302, and 2.370 Å) for the monodentate NO$_3^-$ anions were found in complexes containing chelate five-membered rings formed by the py or bipy ligands. In most of the silver complexes, these bond lengths are larger than 2.4 Å (among the shortest bonds are 2.422,[13] 2.411,[13] and 2.417 Å [14]). In the Ag$_2$[Ph$_2$P(CH$_2$)$_4$PPh$_2$]$_2$(NO$_3$)$_2$ complex, which is structurally similar to complex **1**, the lengths of the Ag—O bonds with the monodentate NO$_3^-$ anions are 2.419 and 2.423 Å. The Ag(1)—O(2) bond length in complex **1** is virtually equal to the sum of the ionic radii of Ag$^+$ and O^{2-} (0.83 and 1.35 Å, respectively[15]).

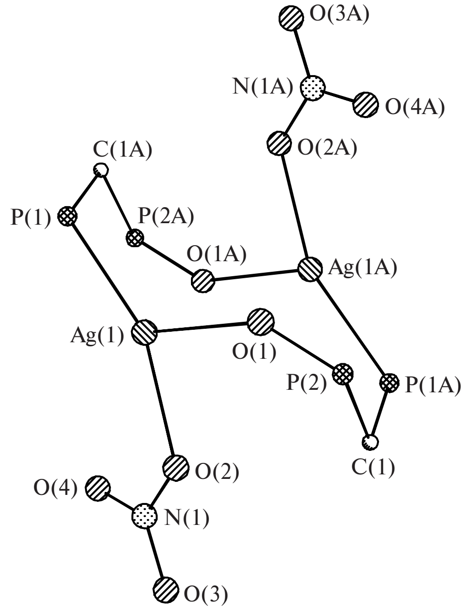


Fig. 2. Conformation of the ten-membered cyclic core of the complex Ag[Ph$_2$PCH$_2$P(O)Ph$_2$]NO$_3$ (**1**).

On the contrary, the Ag(1)—O(1) bond with the O=PPh$_2$ fragment is noticeably longer (2.416(2) Å) than those observed in the silver bis(diphenylphosphynyl)amide complex [Ph$_2$P(O)NP(O)Ph$_2$Ag] (2.196 and 2.269 Å). The structures of Ag complexes with Ph$_2$P(=O)-containing ligands are unavailable in the CSD. The P=O bond length in complex **1** (1.485(3) Å) is equal to those in the noncoordinated CH$_2$P(O)Ph$_2$ fragments (1.485—1.489 Å).[13] However, there is evidence that the P=O bond is slightly elongated upon coordination (1.503—1.497 Å).[13]

Hence, an increase of the O(2)—Ag(1)—P(1) bond angle to 158.07° and shortening of the O(2)—Ag(1) and Ag(1)—P(1) bonds in the coordination triangle of the Ag atom are indicative of strengthening of the ionic character of the third Ag(1)—O(1) bond present in the complex. An analogous dependence has been found for the P—Ag(X)—P angle and for the Ag—P and Ag—X bond lengths in a number of diphenylphosphine complexes.[16] The same regularity was observed in complexes containing the S—Ag(NO_3)—P fragment.[11] In the case of the triangular coordination about the monovalent silver atom, this phenomenon has, apparently, a more general character.

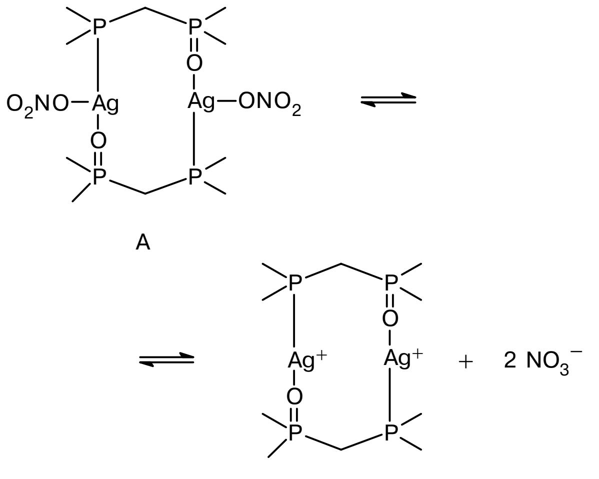
In the $Ph_2PCH_2P(O)Ph_2$ ligand of complex **1**, the P—C bond lengths in the $Ph_2P(1)C$ fragment differ from those in the $CP(2)OPh_2$ fragment. Thus, all three P—C distances involving the P(2) atom are equal (1.801—1.805 Å), whereas the P—C bonds involving the P(1) atom, first, are longer and, second, have somewhat different lengths (1.815(4), 1.839(3), and 1.826(3) Å). This fact also indicates that the coordination interaction between the $CP(O)Ph_2$ fragment and the Ag atom in complex **1** is rather weak. The elongation of the P—C bonds in the $Ph_2P(1)C$ fragment seems to be a reasonable consequence of the electron density redistribution in the coordination polyhedron about the P atom involved in the donor-acceptor bond with the Ag atom. The average P—C(sp^2) and P—C(sp^3) bond lengths in complexes of various metals with the $MePPh_2$ group[12] are 1.823 and 1.827 Å, respectively.

The ten-membered cyclic core of molecule **1** is strongly corrugated (see Fig. 2). The dihedral angles between the Ag(1)—P(1)—P(2A)—O(1A) plane and the Ag(1)—O(1)—Ag(1A)—O(1A) and P(1)—C(1A)—P(2A) planes are 58.3° and 38.9°, respectively. The nitro group is inclined to the Ag(1)—O(1)—Ag(1A)—O(1A) plane at an angle of 65.7°.

Analysis of the X-ray diffraction data demonstrated that complex **1** is structurally very similar to the complex $[Ag_2(Ph_2P(CH_2)_2P(S)Ph_2)_2(NO_3)_2]$ (**3**)[11] with the only difference that the NO_3^- anion in complex **3** is bidentate, unlike the monodentate anion in complex **1**. In complex **3**, the Ag—P bond length is 2.391, the Ag—O bond lengths are 2.587 and 2.671 Å, and the P—Ag—S angle is 167.32°.

IR and ^{31}P NMR spectra of complexes 1 and 2. In the IR spectrum of the free ligand, the absorption band of the P=O group is observed at 1185 cm^{-1}, whereas this band in the spectrum of solid complex **1** is shifted to the low-frequency region (1170 cm^{-1}) and characterizes the coordinated P=O...Ag group. The spectrum of the complex also has intense absorption bands at 1300 and 1400 cm^{-1} corresponding to coordinated NO_3 groups.[17] On the whole, the IR spectral data are consistent with the structure A of complex **1** established by X-ray diffraction analysis.

In the spectrum of a solution of complex **1** in $CHCl_3$, the absorption band of the P=O group is also observed at 1170 cm^{-1}. In the region of vibrations of NO_3 groups, a band at 1355 cm^{-1} assigned to free NO_3 groups appears along with bands of coordinated groups (at 1300 and 1400 cm^{-1}).[18] These data indicate that the ten-membered $Ag_2P_4C_2O_2$ metallocycle is, apparently, retained in solutions. The intensities of the absorption bands of the coordinated NO_3 groups decrease as the solution is diluted, while the intensity of the band at 1355 cm^{-1} assigned to free NO_3 groups increases, which can be related to dissociation in solutions of complex **1**.

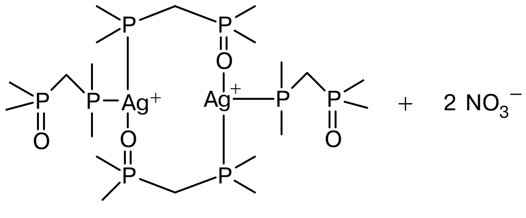


A

B

The region of CH vibrations in the IR spectrum of complex **1** in $CHCl_3$ has a band at 3015 cm^{-1} assigned to the CH groups of the solvent involved in hydrogen bonding with the NO_3^- anions.[19]

The IR spectrum of solid complex **2**, unlike that of **1**, shows two absorption bands with equal intensities, which correspond to the free (1190 cm^{-1}) and coordinated (1170 cm^{-1}) P=O groups, and an intense band at 1360 cm^{-1} assigned to free NO_3^- anions.[18] Comparing the spectra of complexes **1** and **2**, it can be concluded that the formation of complex **2** is accompanied by the replacement of two NO_3^- groups in the structure A by two ligand molecules giving rise to the cationic complex in which the outer-sphere ligands are coordinated to the Ag^+ ions through the P^{III} atoms. In particular, this is evidenced by the appearance of an absorption band of free P=O groups (structure C) in the spectrum of complex **2**.



C

Complex **2** was also prepared by the addition of one mole of the ligand to a solution of complex **1** in CH_2Cl_2. The spectrum of the solution has an absorption band at 1190 cm^{-1} assigned to free P=O groups, while intense bands at 1300 and 1400 cm^{-1} disappear and a band at 1365 cm^{-1} corresponding to free NO_3^- anions appears. On the whole, the IR spectrum of the $Ag(L)NO_3$ + L mixture is analogous to the spectrum of complex **2**.

The ^{31}P NMR spectrum of a solution of the free ligand in CH_2Cl_2 has two doublet signals for P^{III} (δ_P −28.06) and P^V (δ_P 29.17, $J_{P,P}$ = 51.32 Hz). In the spectrum of complex **1**, the signals for P^{III} and P^V are shifted downfield, which indicates that these groups are involved in coordination with the Ag^+ ion (structure A). The shift of the signal for the P^{III} atom directly bound to the silver atom is substantially larger ($\Delta\delta_P$ = 21.01) than that for P^V ($\Delta\delta_P$ = 2.34). In the spectrum of complex **2**, the signal for P^{III} is shifted downfield ($\Delta\delta_P$ = 18.89), whereas the signal for P^V is shifted upfield ($\Delta\delta_P$ = −9.16), which may be associated with the effect of the coordinated P^{III}-containing groups of the outer-sphere ligands (structure C) exerted on the free P=O groups. An analogous upfield shift of the signal of the free P=O groups is observed in the spectra of Rh^I complexes with ω-diphenylphosphinoalkylphosphonic esters.[20] In the spectra of complexes **1** and **2**, splitting of the signals for P^{III} and P^V disappears due, apparently, to rapid ligand exchange. In particular, this is evidenced by broadening of the signals.

To summarize, the reaction of tetraphenylmethylenediphosphine oxide with silver nitrate affords complexes whose structures are based on the centrosymmetric macrocyclic dimer. This dimeric structure is retained in solutions. The replacement of two NO_3 groups in the 1 : 1 complex by two ligand molecules gives rise to the cationic complex of 1 : 2 composition.

From a comparison of the results of the present study with the data obtained previously[11] for silver complexes with tetraphenylalkylenediphosphine sulfides, it can be concluded that binuclear structures containing centrosymmetric macrocycles are typical of both types of complexes, the P=O bond being coordinated to the Ag atom much weaker than the P=S bond. The NO_3 groups in the oxide and sulfide complexes are coordinated in the monodentate and bidentate fashion, respectively.

Experimental

The IR spectra of the complex in KBr pellets and in solutions in $CHCl_3$ and CH_2Cl_2 (l = 0.07—0.10 mm; the concentrations of the solutions were 0.1—0.2 mol L^{-1}) were measured on a UR-20 spectrophotometer (400—3700 cm^{-1}). The $^{31}P-\{^1H\}$ NMR spectra were recorded on Bruker WP-200 SY and Bruker AMX-400 instruments (operating at 81.01 and 162.02 MHz, respectively) with 85% H_3PO_4 as the external standard; the concentrations of the solutions were 0.1—0.2 mol L^{-1}.

Bis[μ-(diphenylphosphinomethyl)diphenylphosphine oxide] $Ph_2PCH_2P(O)Ph_2$ was synthesized according to a procedure reported previously.[21]

Bis[μ-(diphenylphosphinomethyl)diphenylphosphine oxide-*O,P′*]disilver(I) dinitrate $Ag[Ph_2PCH_2P(O)Ph_2]NO_3$ (1). A weighed sample of the ligand (0.1532 g, 0.3826 mmol) was dissolved in $CHCl_3$ and then a solution of $AgNO_3$ (0.065 g, 0.3826 mmol) in MeCN was added. The precipitate that formed upon addition of anhydrous ether was filtered off and dried *in vacuo*. Crystalline complex **1** was obtained in a yield of 0.1632 g (75%), m.p. 174 °C (with decomp.). Found (%): C, 52.5; H, 3.8; N, 2.5. $C_{25}H_{22}AgNO_4P_2$. Calculated (%): C, 52.6; H, 3.9; N, 2.5.

Bis[μ-(diphenylphosphinomethyl)diphenylphosphine oxide-*O,P′*]-bis[(diphenylphosphinomethyl)diphenylphosphine oxide-*P′*]disilver(I) dinitrate $Ag[Ph_2PCH_2P(O)Ph_2]_2NO_3$ (2) was prepared analogously to complex **1** by mixing a solution of the ligand (0.2036 g, 0.5085 mmol) in $CHCl_3$ and a solution of $AgNO_3$ (0.0432 g, 0.2542 mmol) in MeCN. Crystalline complex **2** was obtained in a yield of 0.1751 g (71%), m.p. 185—190 °C (with decomp.). Found (%): C, 61.9; H, 4.6; N, 1.3. $C_{50}H_{44}AgNO_5P_4$. Calculated (%): C, 61.9; H, 4.6; N, 1.4.

X-ray diffraction study of complex 1. Crystals of $Ag_2(L)_2(NO_3)_2$ (L = $Ph_2PCH_2P(O)Ph_2$) (**1**), which were prepared by crystallization from 95% EtOH ($C_{50}H_{44}Ag_2N_2O_8P_4$, M = 1140.49), are monoclinic; at −120 °C, a = 11.870(5), b = 13.477(6), c = 15.519(7) Å, β = 109.70(3)°, V = 2337.2(18) $Å^3$, d_{calc} = 1.621 g cm^{-3}, space group $P2_1/n$, Z = 2. The intensities of 2800 reflections were measured on an automated Syntex $P2_1$ diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, θ = 2.4—23.0°, θ/2θ scanning technique) from a single crystal of dimensions 0.5×0.3×0.2 mm at −120 °C. Averaging of the equivalent reflections gave 2590 independent reflections (R_{int} = 0.0370), which were used in subsequent calculations. Absorption was ignored (μ = 10.32 cm^{-1}).

The structure of **1** was solved by the direct method. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method based on F^2_{hkl} using all independent reflections. The positions of the hydrogen atoms were located from difference electron density syntheses and refined isotropically. The final reliablility factors for the crystal structure of **1** were as follows: R_1 = 0.0271 (calculated based on F_{hkl} for 2477 reflections with $I > 2(I)$) and wR_2 = 0.0729 (calculated based on F^2_{hkl} for all independent reflections); 386 parameters were refined, GOOF = 1.089. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[22]

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