

Synthesis and X-ray characterization of helical polymer complexes $[\text{Ag}(1,2,3\text{-L})(\text{PPh}_3)_2]_n$ and $[\text{Ag}(1,2,4\text{-L})(\text{PPh}_3)_2]_n$ (HL = triazole) and their antimicrobial activities

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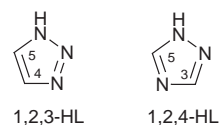
Two novel polymeric silver(I)–triphenylphosphine complexes with nitrogen-containing heterocycles, $[\text{Ag}(1,2,3\text{-L})(\text{PPh}_3)_2]_n$ **3** and $[\text{Ag}(1,2,4\text{-L})(\text{PPh}_3)_2]_n$ **4** (HL = triazole) were synthesized from reactions of polymeric precursors $[\text{Ag}(1,2,3\text{-L})]_n$ **1** and $[\text{Ag}(1,2,4\text{-L})]_n$ **2** with 3 equivalents of PPh_3 in CH_2Cl_2 , respectively. The polymeric precursors **1** and **2** have been obtained as non-crystalline, colorless powder-solids: **2** showed a wide spectrum of excellent antibacterial activities, but **1** did not. The antimicrobial activities of the complexes **1–4**, evaluated by minimum inhibitory concentration, were compared and key factors affecting them discussed. The crystal structures of the complexes **3** and **4** were determined by single-crystal X-ray diffraction. The complexes **3** and **4** in the solid state were helical polymers consisting of AgN_2P_2 cores formed by bridging triazololate anions and two PPh_3 ligands. The complexes **3** and **4** were also fully characterized by elemental analyses, TG/DTA and FT-IR in the solid state and by various solution NMR (^{31}P , ^{109}Ag , ^1H and ^{13}C) spectroscopies and molecular weight measurements in solution.

In the medicinally or pharmaceutically active compounds of silver(I) and gold(I), most of the complexes formed with thiol and nitrogen-containing heterocyclic ligands are difficult to crystallize and are believed to be polymeric,^{1–10} unless tertiary phosphine ligands are also employed.^{11,12} Recently, we found that a non-crystalline, colorless powder-solid of polymeric silver(I) imidazololate $[\text{Ag}(\text{im})]_n$ (Him = imidazole), formed by a bridging imidazololate anion, showed a wide spectrum of excellent antibacterial and antifungal activities.¹³ Ligand-replacement abilities of related silver(I) complexes with organic ligands have suggested that a primary target for the inhibition of bacteria and yeast by the complex $[\text{Ag}(\text{im})]_n$ is protein (acting as a sulfur-donor ligand), but not nucleic acids (as N/O donors). The structure of the $[\text{Ag}(\text{im})]_n$ has been recently determined by Rietveld analysis using powder X-ray diffraction data.¹⁴ Our interest in this bioinorganic compound results as the ease of ligand replacement in $\text{Ag}^{\text{I}}\text{-N}$ compounds appears to be one of the key factors leading to a wide spectrum of antimicrobial activities,¹³ despite the water-insolubility of this compound.

Of bioinorganic, Group 11 metal complexes with both nitrogen-containing heterocycle and tertiary phosphine ligands, several examples of structurally characterized compounds with an $\text{N-Au}^{\text{I}}\text{-P}$ unit are known, e.g., [5-fluoro-1-(tetrahydro-2-furanyl)-2,4(1*H*,3*H*)-pyrimidinedionato-*N*³](triphenylphosphine)gold(I),¹⁵ $[\text{Au}(\text{Him})(\text{PPh}_3)]^+(\text{Z})^-$ (HZ = picric acid),¹⁶ $[\text{Au}(\text{im}-2\text{-R})(\text{PPh}_3)]$ (R = H, Me, Prⁱ or Ph)¹⁷ and $[\text{Au}(\text{pz})(\text{PPh}_3)]$ (Hpz = pyrazole).¹⁸ On the contrary, examples of the corresponding compounds with an $\text{N-Ag}^{\text{I}}\text{-P}$ unit are scarce, except the very recently reported $[\text{Ag}_2(\text{pz})_2(\text{PPh}_3)_2]$ and $[\text{Ag}_2(\text{pz})_2(\text{PPh}_3)_3]$.¹⁹ On the other hand, in the complexes with both thiol and tertiary phosphine ligands, a number of monomeric compounds comprising an $\text{S-Au}^{\text{I}}\text{-P}$ unit have been reported^{12,20} and a few of the corresponding silver(I) compounds are found.²¹

Very recently, we found that a novel monomeric complex $[\text{Ag}(\text{im})(\text{PPh}_3)_3]$ composed of an AgNP_3 core was successfully isolated as colorless, plate crystals from a reaction of the polymeric precursor $[\text{Ag}(\text{im})]_n$ dispersed in CH_2Cl_2 with 3 equivalents of PPh_3 , although its crystal structure was not

determined. This complex has hitherto not been derived from any reaction of precursors such as $[\text{AgCl}(\text{PPh}_3)_3]$ and/or $[\text{AgCl}(\text{PPh}_3)_2]$ with free Him in solutions.²¹ Also, we found that related nitrogen-containing heterocycles, 1,2,3-triazole and 1,2,4-triazole, gave a polymeric non-crystalline powder-solid of silver(I) triazolates $[\text{Ag}(1,2,3\text{-L})]_n$ **1** and $[\text{Ag}(1,2,4\text{-L})]_n$ **2** (HL = triazole). In this work, we have isolated their PPh_3 derivatives $[\text{Ag}(1,2,3\text{-L})(\text{PPh}_3)_2]_n$ **3** and $[\text{Ag}(1,2,4\text{-L})(\text{PPh}_3)_2]_n$ **4** as crystals from the reactions of **1** and **2** dispersed in CH_2Cl_2 with free PPh_3 , respectively, and structurally characterized **3** and **4** to be helical polymers in the solid state.



Herein we report the full details of the synthesis and isolation of **1** and **2**, and the two novel polymeric silver(I) complexes, **3** and **4** as colorless needle crystals and **4** as pale tan plate crystals. The compositional characterization of **3** and **4** in the solid state has been achieved by elemental analysis, FT-IR spectroscopy, thermogravimetric and differential thermal analysis (TG/DTA) and structural characterization using single-crystal X-ray crystallography. Also reported is the characterization of **3** and **4** by various solution NMR (^{31}P , ^{109}Ag , ^1H and ^{13}C) spectroscopies and molecular weight measurements in solution. Mention is also made of key factors affecting the antimicrobial activities of complexes **1–4** evaluated by MIC (minimum inhibitory concentration).

Results and Discussion

Compositional characterization of complexes **1–4**

Compounds **1** and **2**, both of which are obtained as a colorless powder insoluble in most solvents, are polymers just as the recently reported $[\text{Ag}(\text{im})]_n$ ¹³ and $[\text{Ag}(\text{pz})]_n$.¹⁴ Elemental analyses of **1** and **2** (C, H and N) showed their compositions with molar ratios of $\text{Ag}^{\text{I}}:\text{L}^- = 1:1$ and did not contain any solvent molecules and were not contaminated with NO_3^- ion. The

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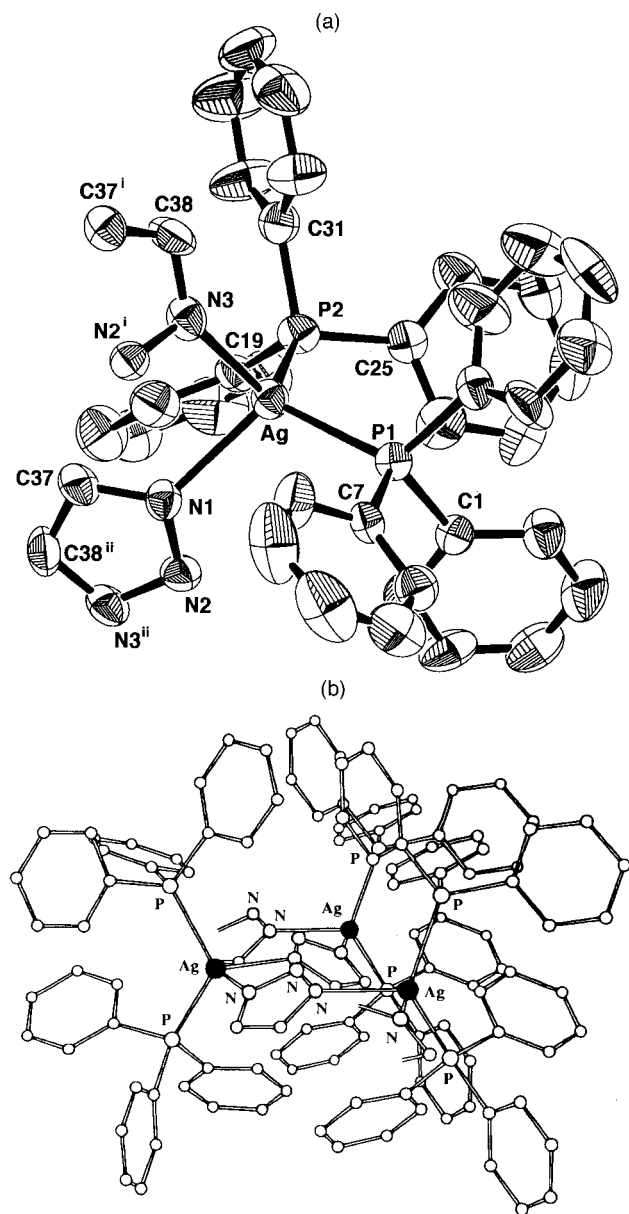


Fig. 1 (a) Molecular structure of the local co-ordination around each silver(I) center of $[\text{Ag}(1,2,3\text{-L})(\text{PPh}_3)_2]_n$ **3** with 50% probability ellipsoids (symmetry operations; i $x, -y, z - 0.5$; ii $x, -y, z + 0.5$) and (b) the helical and polymeric structure of **3**

synthetic conditions presented here using $\text{AgNO}_3 : \text{HL} : \text{NaOH} = 1 : 2 : 1$ were crucial factors in determining yields and purities. When other molar ratios, *e.g.*, $\text{AgNO}_3 : \text{HL} : \text{NaOH} = 1 : 1 : 1$ were used, it was found by IR spectroscopy that the products were usually contaminated by the NO_3^- ion. Furthermore, the purities of **1** and **2** significantly influenced those of the PPh_3 derivatives **3** and **4**.

The PPh_3 derivatives **3** and **4** were prepared using the molar ratio of $[\text{Ag}(\text{L})]_n$ (**1** or **2**): $\text{PPh}_3 = 1 : 3$ in dichloromethane and their crystallization was performed in a 1 : 1 mixed solvent of dichloromethane and ethanol. Elemental analysis of the silver(I) complex **3** (C, H and N) and complete elemental analysis of **4** (C, H, N, P and Ag) showed that their compositions had molar ratios of $\text{Ag}^+ : \text{L}^- : \text{PPh}_3 = 1 : 1 : 2$. Their TG/DTA measurements confirmed the absence of any solvated molecules because no weight loss was observed below 150°C . Decomposition of **3** began around 147°C , while that of **4** began around 166°C .

Infrared measurements confirm the presence of co-ordinated PPh_3 molecules in **3** as typical vibrational bands at $1478, 1434, 742, 693$ and 512 cm^{-1} , and also in **4**. In both complexes, the IR

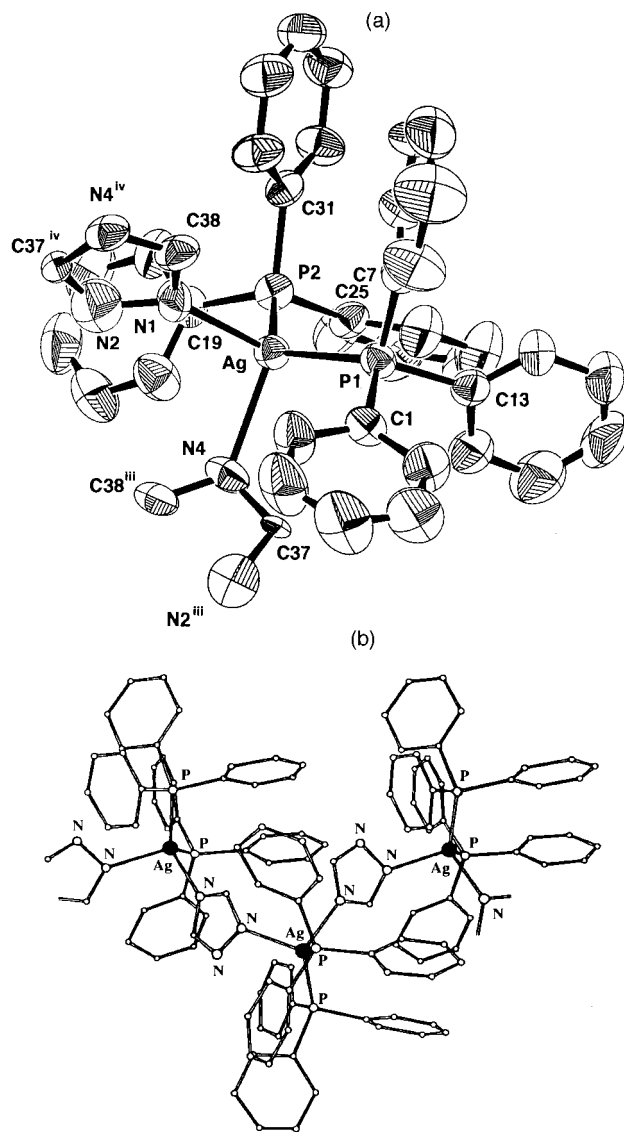


Fig. 2 (a) Molecular structure of the local co-ordination around each silver(I) center of $[\text{Ag}(1,2,4\text{-L})(\text{PPh}_3)_2]_n$ **4** with 50% probability ellipsoids (symmetry operations; iii $1.5 - x, y - 0.5, 0.5 - z$; iv $1.5 - x, y + 0.5, 0.5 - z$) and (b) the helical and polymeric structure of **4**

measurements also show that L co-ordinates to the silver(I) atom as a triazolate anion, but not as a neutral triazole, because multiple vibrational bands due to N–H stretching observed in free HL in the region $3100\text{--}2600\text{ cm}^{-1}$ disappear. Thus, molecular formulae of **3** and **4** in the solid state can then be represented by the general formula of $[\text{Ag}(\text{L})(\text{PPh}_3)_2]_n$.

Molecular weight measurements in CH_2Cl_2 solution revealed that both complexes **3** and **4** were present as monomeric species in solution.

Molecular structures of complexes **3** and **4**

The molecular structures of **3** and **4** with the atom numbering scheme are depicted in Figs. 1(a) and 2(a), respectively. Selected bond distances and angles with their estimated standard deviations are listed in Table 1.

The two complexes are polymers consisting of $\text{Ag}^+(\text{PPh}_3)_2$ fragments bridged by triazolate anions as shown in Figs. 1(b) and 2(b). The bond angles around the silver(I) atoms decrease in the order: $\text{P} - \text{Ag} - \text{P} > \text{P} - \text{Ag} - \text{N} > \text{N} - \text{Ag} - \text{N}$. The geometries of the silver(I) atoms in these complexes are both described as having distorted tetrahedral co-ordination. In complex **3**, two PPh_3 and two 1,2,3-triazolates co-ordinate to a silver(I) center *via* P1, P2, N1 and N3 atoms. The N3ⁱⁱ atom, located next to the N2 atom, co-ordinates to the adjacent silver(I) atom

Table 1 Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

3		4	
Ag–P1	2.460(2)	Ag–P1	2.469(2)
Ag–P2	2.512(2)	Ag–P2	2.441(2)
Ag–N1	2.327(7)	Ag–N1	2.321(5)
Ag–N3	2.326(7)	Ag–N4	2.309(5)
P1–C1	1.832(9)	P1–C1	1.816(7)
P1–C7	1.792(9)	P1–C7	1.808(7)
P1–C13	1.826(9)	P1–C13	1.819(7)
P2–C19	1.827(9)	P2–C19	1.811(7)
P2–C25	1.815(10)	P2–C25	1.826(6)
P2–C31	1.814(10)	P2–C31	1.826(7)
N1–N2	1.349(9)	N1–N2	1.377(8)
N1–C37	1.33(1)	N1–C38	1.346(8)
N2–N3 ⁱⁱ	1.325(10)	N2–C37 ^{iv}	1.296(9)
N3–C38	1.35(1)	N4–C37	1.341(8)
C37–C38 ⁱⁱⁱ	1.38(1)	N4–C38 ⁱⁱⁱ	1.334(8)
P1–Ag–P2	116.63(8)	P1–Ag–P2	126.29(7)
P1–Ag–N1	109.5(2)	P1–Ag–N1	104.7(2)
P1–Ag–N3	112.5(2)	P1–Ag–N4	101.9(2)
P2–Ag–N1	108.1(2)	P2–Ag–N1	107.5(2)
P2–Ag–N3	114.3(2)	P2–Ag–N4	114.8(1)
N1–Ag–N3	93.1(3)	N1–Ag–N4	97.7(2)
Ag–P1–C1	113.9(3)	Ag–P1–C1	116.2(2)
Ag–P1–C7	114.6(3)	Ag–P1–C7	113.7(2)
Ag–P1–C13	116.4(3)	Ag–P1–C13	116.6(2)
Ag–P2–C19	116.6(3)	Ag–P2–C19	113.3(2)
Ag–P2–C25	116.9(3)	Ag–P2–C25	116.4(2)
Ag–P2–C31	114.7(3)	Ag–P2–C31	113.7(2)
Ag–N1–N2	120.4(6)	Ag–N1–N2	129.1(5)
Ag–N1–C37	125.2(6)	Ag–N1–C38	129.3(5)
Ag–N3–N2 ⁱ	114.4(6)	Ag–N4–C37	116.2(4)
Ag–N3–C38	137.6(6)	Ag–N4–C38 ⁱⁱⁱ	128.3(5)
N2 ⁱ –N3–C38	107.7(8)	N2–C37 ^{iv} –N4 ^{iv}	105.2(6)
N1–N2–N3 ⁱⁱ	108.1(7)	N1–C38–N4 ^{iv}	110.7(6)
N1–C37–C38 ⁱⁱⁱ	105.3(9)	C37–N4–C38 ⁱⁱⁱ	108.7(5)
N3 ⁱⁱ –C38 ⁱⁱⁱ –C37	108.9(9)	N2–N1–C38	101.5(6)
N2–N1–C37	110.1(7)	N1–N2–C37 ^{iv}	113.8(7)

Symmetry operations: i $x, -y, z - 0.5$; ii $x, -y, z + 0.5$; iii $1.5 - x, y - 0.5, 0.5 - z$; iv $1.5 - x, y + 0.5, 0.5 - z$.

(symmetry operation ii $x, -y, z + 0.5$). Thus, the [Ag(1,2,3-L)-(PPh₃)₂] moiety is arranged helically along the *a* axis. The pitch of the helix, *i.e.*, the distance between the silver(I) atoms of Ag–1,2,3-L–Ag–1,2,3-L–Ag, is 9.12 Å. Among the three nitrogen atoms of 1,2,3-triazolate, the N2 atom does not participate in co-ordination. In complex **4**, two PPh₃ and two 1,2,4-triazolates also co-ordinate to the silver(I) atom *via* P1, P2, N1 and N4 atoms. The N4^{iv} atom next to C38 co-ordinates to a different silver(I) atom (symmetry operation iv $1.5 - x, y - 0.5, 0.5 - z$). The polymer chain of the complex **4** is extended along the *b* axis. The pitch of the helical chain, or the distance between the silver(I) atoms of Ag–1,2,4-L–Ag–1,2,4-L–Ag, is 9.53 Å, which is slightly longer than that of the complex **3**. The N2 atom of 1,2,4-triazolate similarly does not participate in the co-ordination to silver(I).

The Ag–P distances are 2.460(2) and 2.512(2) Å in complex **3** and 2.469(2) and 2.441(2) Å in complex **4**. These distances are longer than that of [Ag₂(pz)₂(PPh₃)₂] [2.376(1) Å],¹⁹ and similar to those of [AgCl(PPh₃)₂] [2.467(2) and 2.472(2) Å]²² and [Ag₂(pz)₂(PPh₃)₃] [2.461(1), 2.484(1) and 2.370(1) Å],¹⁹ but shorter than those of [AgCl(PPh₃)₃] [2.556(1), 2.520(1) and 2.552(1) Å].²³ The Ag–N distances of complex **3** are 2.327(7) and 2.326(7) Å and those of complex **4** are 2.321(5) and 2.309(5) Å. These Ag–N distances are longer than those of [Ag₂(pz)₂(PPh₃)₂] [2.204(3) and 2.213(3) Å],¹⁹ and those of [Ag(im)]_n [2.05(1) and 2.08(1) Å], the structure of which has been solved by the Rietveld analysis using conventional X-ray powder diffraction data,¹⁴ but similar to those of [Ag₂(pz)₂(PPh₃)₃] [2.295(2), 2.323(2), 2.235(2) and 2.176(2) Å].¹⁹

The related single-strand helical polymer complex, [Ag(NO₃)-

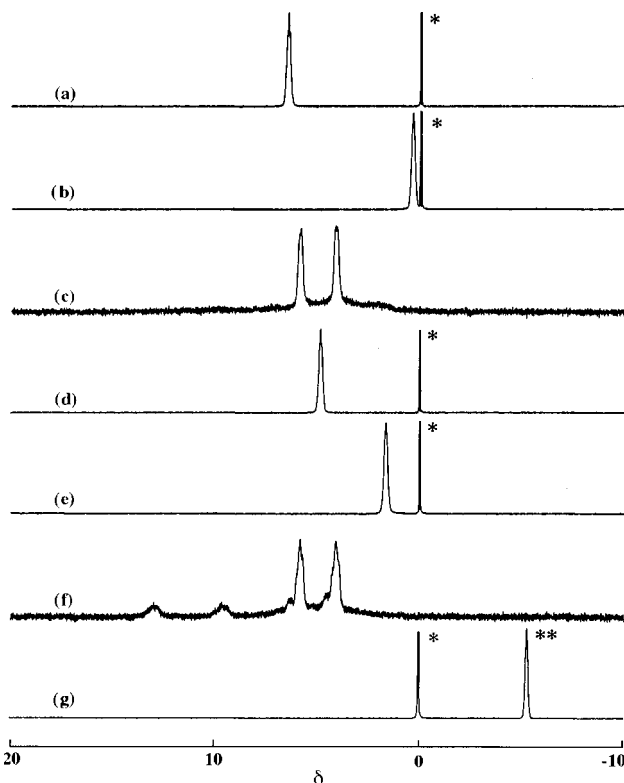


Fig. 3 The ³¹P NMR spectra with reference to external 25% H₃PO₄ of (a) [Ag(1,2,3-L)(PPh₃)₂]_n **3** in CDCl₃ measured at room temperature, (b) the solution of **3** containing an additional 2 equivalents of free PPh₃ ligand at room temperature, (c) **3** in CD₂Cl₂ at –90 °C, (d) [Ag(1,2,4-L)-(PPh₃)₂]_n **4** in CDCl₃ at room temperature, (e) the solution of **4** containing an additional 2 equivalents of free PPh₃ at room temperature, (f) **4** in CD₂Cl₂ at –90 °C, and (g) free PPh₃ in CDCl₃ at room temperature. Phosphorus signals denoted by (*) and (**) are from the external standard of 25% aqueous H₃PO₄ and the free PPh₃ alone, respectively

(H₂biim)]_n (H₂biim = 2,2'-biimidazole), was recently reported, the molecular structure of which was based on linear two-coordinate silver(I) and H₂biim.²⁴

Solution NMR (³¹P, ¹⁰⁹Ag, ¹H and ¹³C) spectroscopy of complexes **3** and **4**

The ³¹P NMR spectra [Fig. 3(a) and 3(d)] measured at room temperature in CDCl₃ of **3** and **4** have shown only one resonance at δ 6.48 and 4.84, respectively, the chemical shifts of which are in the region usually observed for PPh₃ ligands co-ordinated to silver(I) and can be compared with those of related compounds: [AgCl(PPh₃)₃] observed at δ 4.55, [AgCl(PPh₃)₂]₂ at δ 7.01, [Ag(im)(PPh₃)₃] at δ 3.71,²¹ [Ag₂(pz)₂(PPh₃)₂] at δ 9.87 and [Ag₂(pz)₂(PPh₃)₃] at δ 6.13.¹⁹

These resonances are observed at much higher field than those of PPh₃ co-ordinated to gold(I); *e.g.*, [Au(im)(PPh₃)₃] at δ 32.46 and [AuCl(PPh₃)₃] at δ 33.40.²¹ However, the single resonances observed at δ 6.48 in **3** and at δ 4.84 in **4** do not necessarily exhibit the ³¹P signal of the four co-ordinate silver(I) complexes **3** and **4** themselves. Although there is no polymeric species in solution based on their molecular weight measurements (in solution), there should be various degrees of association in addition to dissociation of PPh₃ and perhaps also of L, *i.e.*, an equilibrium based on dynamic exchange, which takes place very rapidly on the NMR time-scale, just as observed in [Ag(im)(PPh₃)₃],²¹ and [Ag₂(pz)₂(PPh₃)₃].¹⁹ As a matter of fact, in the low-temperature ³¹P-¹H NMR spectrum of [Ag₂(pz)₂(PPh₃)₃] in CD₂Cl₂-CDCl₃, several species given by dynamic exchange have been found such as the trigonal planar species (sp²-hybridized silver center) [Ag(pz)(PPh₃)₂] generated from [Ag₂(pz)₂(PPh₃)₃] by dissociation of one PPh₃ ligand, the ionic species [Ag(PPh₃)₄]⁺[pz][–], the mononuclear covalent sp³-

Table 2 Chemical shifts and coupling constants in low-temperature ^{31}P NMR spectra for tetrahedral silver(I) phosphine complexes

Complex	δ/ppm	J/Hz^a		Ref.
		$^{107}\text{Ag}-^{31}\text{P}$	$^{109}\text{Ag}-^{31}\text{P}$	
$[\text{AgCl}(\text{PPh}_3)_3]^b$	3.0	277	318	25
$[\text{Ag}(\text{dppe})_2]\text{NO}_3^c$	4.4	231	266	26
$[\text{Ag}(\text{im})(\text{PPh}_3)_3]^d$	1.97	280	321	21
$[\text{Ag}(\text{pz})(\text{PPh}_3)_3]^e$		253	292	19
$[\text{Ag}(\text{PPh}_3)_4](\text{pz})^e$	4.85		223	19
$[\text{Ag}(1,2,3\text{-L})(\text{PPh}_3)_2]_n \mathbf{3}^d$	ca. 4.3	ca. 280		This work
$[\text{Ag}(1,2,4\text{-L})(\text{PPh}_3)_2]_n \mathbf{4}^d$	ca. 4.3	ca. 280		This work

^a It has been pointed out by the $^{109}\text{Ag}\{-^{31}\text{P}\}$ NMR INEPT experiments for $[\text{Ag}(\text{dppe})_2]\text{NO}_3$ that the coupling constants are negative.²⁵ ^b In CH_2Cl_2 at 193 K. ^c In CDCl_3 at 300 K. ^d In CD_2Cl_2 at 183 K. ^e In $\text{CD}_2\text{Cl}_2\text{-CDCl}_3$ at 158 K.

hybridized silver species $[\text{Ag}(\text{pz})(\text{PPh}_3)_3]$ and $[\text{Ag}(\text{pz})_2(\text{PPh}_3)_2]$.¹⁹ The presence of the rapid equilibrium due to dynamic exchange is further supported by the following fact: (i) the original single peaks in **3** and **4** were shifted to single peaks at δ 0.38 and 1.65, respectively, when 2 equivalents of solid PPh_3 were added to the original CDCl_3 solutions [Fig. 3(b) and 3(e)] and (ii) they were further shifted to single peaks at δ -2.48 and -3.08 by addition of a total of 10 equivalents of PPh_3 to the original solutions.

The low-temperature ^{31}P NMR measurements showed that (i) the single peaks in **3** and **4** in CDCl_3 observed at δ 6.48 and 4.84, respectively, at room temperature were changed in CDCl_3 at -50°C to very broad peaks at δ 4.90 and 4.83, respectively, and (ii) these spectra were, furthermore, changed to those of intense sharp peaks and several broad minor peaks at -90°C in CD_2Cl_2 : the single-line spectrum of **3** at δ 6.48 in CDCl_3 at room temperature changed to one of two intense sharp peaks at δ 5.14 and 3.42 and very broad minor peaks around δ 1 [Fig. 3(c)] and, the single-line spectrum of **4** at δ 4.84 at room temperature changed to that of two intense sharp peaks at δ 5.13 and 3.38 and very broad minor peaks at δ 12.3, 9.0, 5.5 and 3.7 [Fig. 3(f)]. The two intense sharp peaks with unresolved splittings both in **3** and **4** are probably attributable to a coupling of ^{31}P with ^{109}Ag ($I = \frac{1}{2}$) or ^{107}Ag ($I = \frac{1}{2}$) as previously observed in $[\text{Ag}(\text{im})(\text{PPh}_3)_3]$,²¹ $[\text{AgCl}(\text{PPh}_3)_3]$ ²⁵ and $[\text{Ag}(\text{dppe})_2]\text{NO}_3$ [dppe = 1,2-bis(diphenylphosphino)ethane].²⁶ The coupling constants $^1J(^{109}\text{Ag}-^{31}\text{P})$ and $^1J(^{107}\text{Ag}-^{31}\text{P})$ of **3** and **4** were not precisely determined because of their unresolved splittings, but they were roughly estimated as about 280 Hz for both **3** and **4**, and their chemical shifts were as $\delta(^{31}\text{P}) = \text{ca. } 4.3$ for both. Nevertheless, these data are consistent with those reported for the four-coordinate tetrahedral complexes in solution summarized in Table 2.

The very broad minor peaks observed around δ 1 in **3** and those observed at δ 12.3, 9.0, 5.5 and 3.7 in **4** are due to several species in solution produced by dynamic exchange. Several such broad minor peaks at -90°C were also found in the related silver(I) complexes such as $[\text{Ag}(\text{im})(\text{PPh}_3)_3]$, $[\text{AgCl}(\text{PPh}_3)_3]$ and $[\text{AgCl}(\text{PPh}_3)_2]_2$ at -90°C in CD_2Cl_2 .[‡] As an example of the related compounds, $[\text{Ag}(\text{Htsa})(\text{PPh}_3)_3]$ (H_2tsa = thiosalicylic acid) which did not show dynamic exchange in solution, the distorted tetrahedral geometry of the Ag^+SP_3 core has been determined in the solid state by X-ray crystallography and that the four co-ordinate geometry is maintained in solution has been confirmed by solution ^{31}P NMR spectroscopy: the ^{31}P NMR spectrum, observed as only one signal at δ 4.79 in CDCl_3

[‡] The ^{31}P NMR spectra in CD_2Cl_2 measured at -90°C with reference to an external 25% H_3PO_4 by a substitution method: major peaks at δ 2.90 and 1.04 and minor peaks at δ 7.76 and 5.00 for $[\text{Ag}(\text{im})(\text{PPh}_3)_3]$, major peaks at δ 2.85 and 1.02 and minor peaks at δ 8.23, 5.48 and -1.93 for $[\text{AgCl}(\text{PPh}_3)_3]$, and major peaks at δ 2.78 and 1.01 and minor peaks at δ 7.79, 5.31, 3.70, 0.43 and -2.03 for $[\text{AgCl}(\text{PPh}_3)_2]_2$.

at room temperature, became two peaks with equal intensity at δ 4.90 and 3.26 in CD_2Cl_2 at -90°C without any other minor peaks, each peak of which was split due to the coupling of ^{31}P with ^{109}Ag or ^{107}Ag ($J \approx 265$ Hz).²⁷

The ^{109}Ag NMR spectra of **3** and **4** measured at room temperature in CDCl_3 that demonstrate only single peaks at δ 994 and 925, respectively, should be considered as averaged signals resulting from rapid dynamic exchange among several unequivalent ^{109}Ag species. These signals can be compared with that of the averaged single peak at δ 1186 observed in $[\text{Ag}(\text{im})(\text{PPh}_3)_3]$.²¹ The ^1H and ^{13}C NMR spectra of **3** and **4** measured at room temperature in CDCl_3 that exhibit only one resonance for the co-ordinating triazolate anion, respectively, also result from dynamic exchange.

Antimicrobial activities

Antimicrobial activities of the polymeric silver(I)-N bonded compounds **1** and **2**, and of their PPh_3 derivatives **3** and **4**, together with those of the free 1,2,3- and 1,2,4-HL, are listed in Table 3, as estimated by the minimum inhibitory concentration (MIC; $\mu\text{g mL}^{-1}$).

Antimicrobial activities of 1,2,3- and 1,2,4-HL were estimated as $>1000 \mu\text{g mL}^{-1}$ for bacteria (*E. coli*, *B. subtilis*, *S. aureus* and *P. aeruginosa*), yeast (*C. albicans* and *S. cerevisiae*) and mold (*A. niger* and *P. citrinum*), except $125 \mu\text{g mL}^{-1}$ for *P. aeruginosa* by 1,2,3-HL, suggesting that they do not show any activity. The polymer $[\text{Ag}(1,2,4\text{-L})]_n \mathbf{2}$, on the contrary, showed a wide spectrum of remarkable and superior activity against bacteria and yeast, but no activity against mold, whereas the other polymer $[\text{Ag}(1,2,3\text{-L})]_n \mathbf{1}$ showed only limited activities for three organisms of bacteria. Similar wide spectra to those observed in complex **2** have been found in the recently reported complex $[\text{Ag}(\text{im})]_n$, formed only by $\text{Ag}^+\text{-N}$ bonding.¹³ On the other hand, other polymeric PPh_3 derivatives $[\text{Ag}(1,2,3\text{-L})]_n \mathbf{3}$ and $[\text{Ag}(1,2,4\text{-L})(\text{PPh}_3)_2]_n \mathbf{4}$ showed no activity ($>1000 \mu\text{g mL}^{-1}$, except $500 \mu\text{g mL}^{-1}$ for *S. aureus* by **4**). In general, the mixed-ligand complexes containing phosphorus-donor ligands have never shown any antimicrobial activity.¹³ This fact could be attributed to whether or not the complexes possess the ability of further ligand-replacement with the biological ligands such as proteins and DNA, but not to their low-solubility in water.

Previous data also showed that an oligomeric, thiomalato-silver(I) complex $\{\text{Na}[\text{Ag}(\text{Htma})\cdot 0.5\text{H}_2\text{O}]\}_n$ (H_3tma = thiomalic acid; $n = 24\text{--}34$)⁶ and a thiosalicylatosilver(I) complex $\{\text{Na}[\text{Ag}(\text{tsa})\cdot \text{H}_2\text{O}]\}_n$ ($n = 21\text{--}27$),⁸ both of which have been formed only by silver(I)-bridged S-bonding, have antimicrobial activities in different modes of action. The spectra observed in the silver(I)-S bonded compounds were more limited than those observed in the above silver(I)-N bound compounds **2** and $[\text{Ag}(\text{im})]_n$. Also observed was the lack of activity with their PPh_3 derivatives.

Recently, we have proposed that at least one of the key factors determining antimicrobial effects and their spectra is the type of atom co-ordinated to silver(I) and their bonding properties, rather than the polymerization degree of the silver(I) complexes, its solubility in water and whether or not the ligand is neutral.^{13,21} Since the silver(I)-N bound ligand can easily exchange with stronger donors such as S and P atoms, it should play an important role in showing the wide spectra of antimicrobial activities.

Ionic species such as $[\text{Ag}(\text{PPh}_3)_4]^+\text{L}^-$ and $[\text{Ag}(\text{PPh}_3)_2]^+\text{L}^-$, if they are present in solution as dominant species generated from **3** and **4** by dynamic exchange, will not show any activity, because the non-co-ordinating L^- does not show any activity. Even if the species predominantly present in solution is the mononuclear covalent complex $[\text{Ag}(\text{L})(\text{PPh}_3)_3]$, such species will restrict further ligand-replacement with biological ligands as observed in $[\text{Ag}(\text{im})(\text{PPh}_3)_3]$ without any activity.¹³

Table 3 Antimicrobial activities of some silver(I) compounds evaluated by MIC*

	1,2,3-HL	1,2,4-HL	[Ag(1,2,3-L)] _n 1	[Ag(1,2,4-L)] _n 2	[Ag(1,2,3-L)(PPh ₃) ₂] _n 3	[Ag(1,2,4-L)(PPh ₃) ₂] _n 4
<i>Escherichia coli</i>	>1000	>1000	250	4.0	>1000	>1000
<i>Bacillus subtilis</i>	>1000	>1000	500	7.9	>1000	>1000
<i>Staphylococcus aureus</i>	>1000	>1000	>1000	125	>1000	500
<i>Pseudomonas aeruginosa</i>	125	>1000	500	7.9	>1000	>1000
<i>Candida albicans</i>	>1000	>1000	1000	15.7	>1000	>1000
<i>Saccharomyces cerevisiae</i>	>1000	>1000	>1000	7.9	>1000	>1000
<i>Aspergillus niger</i>	>1000	>1000	>1000	1000	>1000	>1000
<i>Penicillium citrinum</i>	>1000	>1000	>1000	>1000	>1000	>1000

* Minimum inhibitory concentration ($\mu\text{g mL}^{-1}$).

Despite the common silver(I)-N bonding in compounds **1** and **2**, and almost the same insolubility in water, the fact that they showed quite different antimicrobial action may reflect the difference of their structure.

Conclusion

Nitrogen-containing heterocycles, 1,2,3-triazole and 1,2,4-triazole, act as bridging ligands to form the polymeric silver(I) complexes [Ag(1,2,3-L)]_n **1** and [Ag(1,2,4-L)]_n **2**: the latter shows excellent antibacterial activity, but the former does not.

Using **1** and **2** as precursors, two novel triphenylphosphine complexes [Ag(1,2,3-L)(PPh₃)₂]_n **3** and [Ag(1,2,4-L)(PPh₃)₂]_n **4** were derived in good yields and their crystal structures determined by single-crystal X-ray diffraction. These complexes in the solid state were also polymers consisting of Ag^I(PPh₃)₂ fragments bridged by triazolate anions and the co-ordination geometry around each silver(I) center was a distorted tetrahedron. In **3** and **4**, both [Ag(L)(PPh₃)₂] moieties were arranged helically with different pitches; 9.12 Å for **3** and 9.53 Å for **4**. On the other hand, **3** and **4** in solution were present as monomeric species. Their (³¹P, ¹⁰⁹Ag, ¹H and ¹³C) NMR spectra measured at room temperature were interpreted based on the presence of an equilibrium due to rapid dynamic exchange on the NMR time-scale, the presence of which was evidenced from low-temperature ³¹P NMR measurements.

The antimicrobial activities of complexes **1–4** and, in particular, the effects by which several ionic and neutral species may be generated from **3** and **4** by dynamic exchange were discussed primarily with regard to their ligand-replacement properties and, secondly, based on their structural factors.

Experimental

Materials

The following were used as received: 1,2,4-triazole, AgNO₃, NaOH, triphenylphosphine, dichloromethane, ethanol, diethyl ether, CD₂Cl₂ (all from Wako); 1,2,3-triazole, CDCl₃ (Aldrich).

Instrumentation/analytical procedures

Elemental analyses after overnight drying under 10⁻³–10⁻⁴ Torr were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Rigaku TG 8101D and TAS 300 data processing system. The TG/DTA measurements were run under air with a temperature ramp of 1 °C min⁻¹ between 20 and 500 °C. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer as KBr discs at room temperature.

Molecular weight measurements in CH₂Cl₂ solutions based

on the cryoscopic method were done by Mikroanalytisches Labor Pascher (Remagen, Germany) and evaluated as molmass values for 12.93 mg of complex **3** dissolved in 1.4457 g of CH₂Cl₂ and for 17.16 mg of complex **4** dissolved in 1.289 g of CH₂Cl₂.

Proton (399.65 MHz), ¹³C-¹H (100.40 MHz) and ³¹P-¹H NMR (161.70 MHz) spectra in solution were recorded at 22 °C in 5 mm external diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. Proton and ¹³C-¹H NMR spectra of the complexes were measured in CDCl₃ solution with reference to internal SiMe₄. Chemical shifts are reported on the δ scale and resonances downfield of SiMe₄ (δ 0) are recorded as positive. Phosphorus-31 (161.70 Hz) spectra were measured in CDCl₃ solution with reference to an external standard of 25% H₃PO₄ in H₂O in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H₃PO₄ (δ 0).

The ¹⁰⁹Ag NMR (18.45 MHz) were recorded in 10 mm external diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe. The ¹⁰⁹Ag NMR spectra of the complexes were measured in CDCl₃ with reference to an external standard of saturated AgNO₃-D₂O solution by a substitution method. Chemical shifts are reported as positive for resonances downfield of AgNO₃ (δ 0). Spectral parameters for ¹⁰⁹Ag NMR include: pulse width 13.2 ms; acquisition time 0.39 s; recycle time 1.39 s; sweep width 21008 Hz.

Antimicrobial activity

Antimicrobial activities of the silver(I) compounds prepared here were estimated by a minimum inhibitory concentration (MIC; $\mu\text{g mL}^{-1}$) as usual.^{6,8,13}

Bacteria were inoculated into 5 mL of liquid medium [SCD (soybean, casein and digest) medium] and cultured for 24 h at 35 °C. Yeast were inoculated into 5 mL of liquid medium [GP (glucose and polypeptone) medium] and cultured for 48 h at 30 °C. The cultured fluids were diluted, adjusted to a concentration of 10⁶–10⁷ microorganisms per mL and used for inoculation in the MIC test. As for the mold culture, the agar slant [PD (potato and dextrose) agar medium] for one week cultivation at 27 °C was gently washed with saline containing 0.05% Tween 80. The spore suspension obtained was adjusted to the concentration of 10⁶ microorganisms per mL and used for inoculation in the MIC test.

The test materials, [Ag(1,2,3-L)]_n **1**, [Ag(1,2,4-L)]_n **2**, [Ag(1,2,3-L)(PPh₃)₂]_n **3**, and [Ag(1,2,4-L)(PPh₃)₂]_n **4** were suspended in water, and 1,2,3-HL and 1,2,4-HL were dissolved in water. Such solutions were then diluted with SCD medium for bacteria and with GP medium for yeast and mold. Using them the two-fold diluted solutions with concentrations of 1000 $\mu\text{g mL}^{-1}$ to 2 $\mu\text{g mL}^{-1}$ were prepared. Each 1 mL of culture

medium containing various concentrations of test materials was inoculated with 0.1 mL of the microorganism suspension prepared above.

Bacteria were cultured for 24 h at 35 °C, yeast for 48 h at 30 °C, and mold for one week at 25 °C, then the growth of the microorganisms was observed. When no growth of microorganism was observed in the medium containing the lowest concentration of test materials, the MIC of the test material was defined at this point of dilution.

The SCD, GP and PD media were purchased from Nissui.

Preparations

[Ag(1,2,3-L)]_n 1 and [Ag(1,2,4-L)]_n 2. To a solution of 2.072 g (30.00 mmol) of 1,2,3-triazole in 60 mL water was slowly added a solution of 2.548 g (15.00 mmol) of AgNO₃ in 15 mL water, followed by addition of 15 mL (15.00 mmol) of 1 M NaOH aqueous solution. White precipitates immediately formed. After 3 h stirring, they were collected on a membrane filter (JG 0.2 μm), washed twice with 100 mL water, 100 mL EtOH, and 100 mL diethyl ether, and dried *in vacuo* (2.59 g; yield 98%). The colorless powder obtained as compound **1** was sparingly soluble in all solvents, and light- and thermally-stable {Found: C, 13.71; H, 1.04; N, 23.98. Calc. for C₂H₂AgN₃ as a monomeric unit or [Ag(1,2,3-L)]: C, 13.65; H, 1.15; N, 23.89%}. TG/DTA data: no weight loss observed under 200 °C; decomposition began around 255 °C with exothermic peaks at 282 and 355 °C. Some prominent IR bands at 1700–400 cm⁻¹ region (KBr disc): 1442m, 1411m, 1192w, 1167s, 1092vs, 984w, 967m, 807s, 794vs cm⁻¹.

Compound **2** was also isolated by a similar work-up using 1,2,4-HL, instead of 1,2,3-HL above. The light- and thermally-stable colorless powder obtained (2.31 g; yield 88%) was sparingly soluble in all solvents {Found: C, 13.55; H, 0.92; N, 23.93. Calc. for C₂H₂AgN₃ as a monomeric unit or [Ag(1,2,4-L)]: C, 13.65; H, 1.15; N, 23.89%}. TG/DTA data: no weight loss observed under 200 °C; decomposition began around 245 °C with an exothermic peak at 402 °C. Some prominent IR bands at 1700–400 cm⁻¹ region (KBr disc): 1490vs, 1271s, 1200m, 1152s, 1055m, 981m, 858m, 849m, 666s cm⁻¹.

[Ag(1,2,3-L)(PPh₃)₂]_n 3 and [Ag(1,2,4-L)(PPh₃)₂]_n 4. To a suspension of 0.880 g (5.00 mmol) of [Ag(1,2,3-L)]_n **1** in 10 mL CH₂Cl₂ was added dropwise a solution of 3.931 g (15.00 mmol) of PPh₃ in 20 mL CH₂Cl₂. During 2 h stirring the system changed to a pale yellow, clear solution. The solution was filtered once through a folded filter paper (Whatman no. 2). The clear filtrate was slowly added to 300 mL of diethyl ether. A white precipitate formed which was collected on a membrane filter (JG 0.2 μm), washed twice with 50 mL ether, and dried *in vacuo* for 2 h. The yield at this stage was 1.65 g (47%). To a colorless, clear solution of the white precipitate dissolved in 20 mL CH₂Cl₂ was added 20 mL ethanol, followed by passing through a folded filter paper (Whatman no. 2). The colorless filtrate was slowly evaporated at room temperature to form colorless needle crystals after a few days. They were collected on a membrane filter (JG 0.2 μm), washed twice with 100 mL ethanol and 100 mL ether, and dried *in vacuo* for 2 h. Yield 0.406 g (11.6%). Relatively light- and thermally-stable, colorless needle crystals obtained as compound **3** were soluble in dichloromethane, chloroform and DMSO, sparingly soluble in ethanol and acetone, but insoluble in diethyl ether and water {Found: C, 64.91; H, 4.42; N, 6.00. Calc. for C₃₈H₃₂AgN₃P₂ or [Ag(1,2,3-L)(PPh₃)₂] as a monomeric unit: C, 65.16; H, 4.60; N, 6.00%}. TG/DTA data: no weight loss observed below 150 °C; decomposition began around 147 °C with endothermic peaks at 187 and 227 °C and exothermic peaks at 288 and 328 °C. Molecular weight measurement: 650 in CH₂Cl₂ (experimental error ±5%); calc. 700.5 for [Ag(1,2,3-L)(PPh₃)₂]. Some prominent IR bands in the 1700–400 cm⁻¹ region (KBr disc):

1478m, 1434s, 1181w, 1156w, 1141w, 1093m, 1060m, 1027m, 997w, 961w, 919w, 847w, 782w, 742s, 693vs, 512m, 499s cm⁻¹. ¹H NMR measured in CDCl₃ with reference to internal SiMe₄ at 25 °C: δ 7.22 (30 H, m, aryl protons), 7.44 (2 H, s, H⁴ + H⁵ of L). ¹³C NMR measured in CDCl₃ with reference to internal SiMe₄ at 25 °C: δ 131.84 (C⁴ + C⁵ of L), 128.64 (Ph), 128.73 (Ph), 129.68 (Ph), 133.63 (Ph), 133.81 (Ph), 133.91 (Ph), 134.07 (Ph). ³¹P NMR measured in CDCl₃ at 25 °C with reference to an external 25% aqueous H₃PO₄ in a sealed capillary: δ 6.48. ³¹P NMR measured in CD₂Cl₂ at -90 °C by a substitution method: δ 3.42, 5.14; δ [minor peak] 1.1–1.4 (br). ¹⁰⁹Ag NMR measured in CDCl₃ at 25 °C with reference to an external saturated AgNO₃ in D₂O by the substitution method: δ 994.

Compound **4** was also isolated by a similar work-up using **2**. Yield was 2.18 g (62.2%). The relatively light- and thermally-stable, pale tan plate crystals were soluble in dichloromethane, chloroform and DMSO, sparingly soluble in ethanol and acetone, but insoluble in diethyl ether and water {Found: C, 64.70; H, 4.72; Ag, 15.4; N, 6.13; P, 8.90; total 99.85%. Calc. for C₃₈H₃₂AgN₃P₂ or [Ag(1,2,4-L)(PPh₃)₂] as a monomeric unit: C, 65.16; H, 4.60; Ag, 15.4; N, 6.00; P, 8.84%}. TG/DTA data: no weight loss observed below 150 °C; decomposition began around 166 °C with an endothermic peak at 233 °C and an exothermic peak at 384 °C. Molecular weight measurement: 650 in CH₂Cl₂ (experimental error ±5%); calc. 700.5 for [Ag(1,2,4-L)(PPh₃)₂]. Some prominent IR bands in the 1700–400 cm⁻¹ region (KBr disc): 1480s, 1434s, 1258w, 1184w, 1146m, 1093m, 1069w, 1027w, 997w, 977w, 923w, 857w, 845w, 742s, 694vs, 676m, 502s cm⁻¹. ¹H NMR measured in CDCl₃ with reference to internal SiMe₄ at 25 °C: δ 7.25 (30 H, m, aryl protons), 7.74 (2 H, s, H³ + H⁵ of L). ¹³C NMR measured in CDCl₃ with reference to internal SiMe₄ at 25 °C: δ 152.12 (C³ + C⁵ of L), 128.67 (Ph), 128.75 (Ph), 129.64 (Ph), 133.70 (Ph), 133.87 (Ph), 134.07 (Ph), 134.22 (Ph). ³¹P NMR measured in CDCl₃ at 25 °C with reference to an external 25% aqueous H₃PO₄ in a sealed capillary: δ 4.84. ³¹P NMR measured in CD₂Cl₂ at -90 °C by the substitution method: δ 5.13, 3.38; δ [minor peak] 12.27 (br), 8.95 (br), 5.53 (br, sh), 3.73 (br, sh). ¹⁰⁹Ag NMR measured in CDCl₃ at 25 °C with reference to external saturated AgNO₃ in D₂O by a substitution method: δ 925.

X-Ray crystallography

Two compounds [Ag(1,2,3-L)(PPh₃)₂]_n **3** and [Ag(1,2,4-L)(PPh₃)₂]_n **4** formed colorless, needle crystals and pale tan plate crystals, respectively, in the solvent mixture dichloromethane–ethanol. During a few days standing of the solutions at room temperature crystals of sufficient quality for single-crystal X-ray diffraction studies were grown.

Each single crystal of compound **3** or **4** was mounted on a glass fiber and transferred to a Rigaku AFC5S diffractometer. Cell contents and orientation matrix of **3** and **4** were obtained from the least-squares refinement of 20 and 25 reflections, respectively. The reflection data were collected using ω–2θ scan with graphite-monochromated Mo-Kα radiation at room temperature. The intensities of three standard reflections which were measured after every 150 reflections remained constant throughout data collection. The data were corrected for Lorentz and polarization effects and empirical absorption corrections based on ψ scans were applied to the data. For the overall averaged transmission curve, the transmission factors of **3** and **4** were in the ranges 0.93–1.00 and 0.94–1.00, respectively. The structures were solved by direct methods followed by subsequent Fourier-difference calculation and refined by a full-matrix least-squares procedure using the TEXSAN package.²⁸ All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically.

A summary of crystal data, data collection, and refinement for **3** and **4** is given in Table 4.

Table 4 Summary of crystal data for complexes **3** and **4**

	[Ag(1,2,3-L)- (PPh ₃) ₂] _n	[Ag(1,2,4-L)- (PPh ₃) ₂] _n
Formula	C ₃₈ H ₃₂ AgN ₃ P ₂	C ₃₈ H ₃₂ AgN ₃ P ₂
<i>M</i>	700.51	700.51
Crystal system	Monoclinic	Monoclinic
Space group	<i>Cc</i> (no. 9)	<i>P2₁/n</i> (no. 14)
<i>a</i> /Å	23.792(4)	14.59(1)
<i>b</i> /Å	15.651(6)	9.525(6)
<i>c</i> /Å	9.119(5)	24.617(3)
β/°	100.06(3)	93.01(2)
<i>U</i> /Å ³	3343(2)	3417(2)
<i>F</i> (000)	1432	1432
<i>Z</i>	4	4
<i>D_c</i> /g cm ⁻³	1.39	1.36
Crystal size/mm	0.1 × 0.2 × 0.2	0.2 × 0.1 × 0.3
No. of reflections used for unit cell dimension (2θ range°)	20 (20.3–24.6)	25 (20.1–26.1)
Radiation (λ/Å)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)
Scan mode	2θ-ω	2θ-ω
Scan width/°	1.47 + 0.30 tan θ	1.22 + 0.3 tan θ
Scan speed/min ⁻¹	32	32
2θ Range/°	6–55	6–55
μ/cm ⁻¹	7.20	7.04
Total reflections	4083	8641
Unique reflections	3989	8326
Observed reflections	2770 [<i>I</i> > 1.5σ(<i>I</i>)]	4063 [<i>I</i> > 2σ(<i>I</i>)]
<i>R</i> , <i>R'</i>	0.052, 0.034	0.055, 0.056
Goodness of fit	1.33	1.51

$R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $R' = \Sigma[w(|F_o| - |F_c|)^2] / (\Sigma w|F_o|^2)^{1/2}$, with $w = 4F_o^2 / [\sigma^2(F_o^2)]$.

CCDC reference number 186/957.

See <http://www.rsc.org/suppdata/dt/1998/1653/> for crystallographic files in .cif format.

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