

## Self-assembly of a mixed-ligand silver-based coordination polymer

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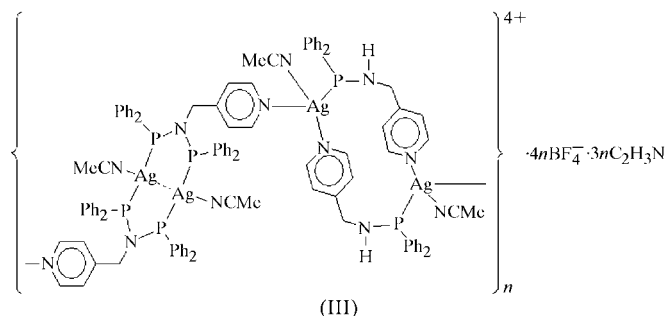
The novel title silver(I) coordination polymer, *catenapoly*[[acetonitrilesilver(I)]-di- $\mu$ -4-[*N*-(diphenylphosphino)aminomethyl]pyridine- $\kappa^2 N^1:P$ ;  $\kappa^2 P:P^1$ -[acetonitrilesilver(I)]- $\mu_3$ -4-[*N,N*-bis(diphenylphosphino)aminomethyl]pyridine- $\kappa^3 N^1:P:P'$ -bis[acetonitrilesilver(I)(Ag—Ag)]- $\mu_3$ -4-[*N,N*-bis(diphenylphosphino)aminomethyl]pyridine- $\kappa^3 P:P'$ : $N^1$ ] tetrakis(tetrafluoroborate) acetonitrile trisolvate],  $\{[Ag_4(C_2H_3N)_4(C_{18}H_{17}N_2P)_2(C_{30}H_{26}N_2P_2)_2](BF_4)_4 \cdot 3C_2H_3N\}_n$ , is formed by the self-assembly of the  $Ph_2P(4-NHCH_2C_5H_4N)$  and  $(Ph_2P)_2(4-NCH_2C_5H_4N)$  ligands with silver tetrafluoroborate. The polymer consists of alternating rings (which lie about inversion centers) bridged by the pyridyl rings of the bisphosphine-substituted ligands, with anions hydrogen bonded the length of the chain. Two distinctly different metal coordination environments exist in the polymer, *viz.* distorted tetrahedral and trigonal geometries.

### Comment

Silver-based coordination polymers have received a great deal of attention in recent years, owing particularly to the abundant chemistry that these compounds possess (Batten *et al.*, 1999; Muthu *et al.*, 2002; Reger *et al.*, 2003). Silver(I) phosphine and pyridine complexes that demonstrate a wealth of novel electronic, medicinal and structural properties have been constructed (Blake *et al.*, 1999; Khlobystov *et al.*, 2001). A large number of these polymers, constructed of pyridyl donors and other conjugated systems, have exhibited luminescent properties (Tong *et al.*, 2002; Zhang *et al.*, 2002; Zheng *et al.*, 2001), and these compounds are of interest for possible use in light emitting devices (LEDs). Other studies of pyridyl-substituted phosphine–silver complexes have demonstrated the variability of the silver coordination environment (Klausmeyer *et al.*, 2004, and references therein; Seward *et al.*, 2003).

Pyridyl-substituted phosphines are an interesting species in that they contain relatively harder and softer donors in the form of the pyridyl N atom and the tertiary phosphine group,

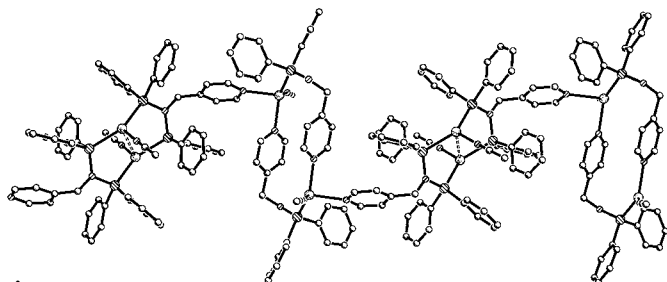
respectively, in a single molecule. By adding an amine linkage between these two moieties, it is possible to expand further the chemistry of an already intriguing ligand by imparting such features as pH dependence on the coordination chemistry and luminescence (Dollberg & Turro, 2001), and added coordination ability of the ligand is achieved by the presence of the extra donor.



We have synthesized two new pyridyl-substituted amino-phosphine ligands that, when coordinated to silver tetrafluoroborate, self-assemble into a polymeric structure of strictly repeating units.  $Ph_2P(4-NHCH_2C_5H_4N)$ , (I), and  $(Ph_2P)_2(4-NCH_2C_5H_4N)$ , (II), have been obtained by the reaction of 4-methylaminopyridine with one and two equivalents of chlorodiphenylphosphine, respectively. Compound (I) was obtained in a relatively pure form by the slow addition of chlorodiphenylphosphine to a chilled solution of 4-amino-methylpyridine and triethylamine. Rapid addition of an excess of phosphine resulted in a mixture of (I) and (II), while addition of a full second equivalent caused only the disubstituted ligand, (II), to be formed.

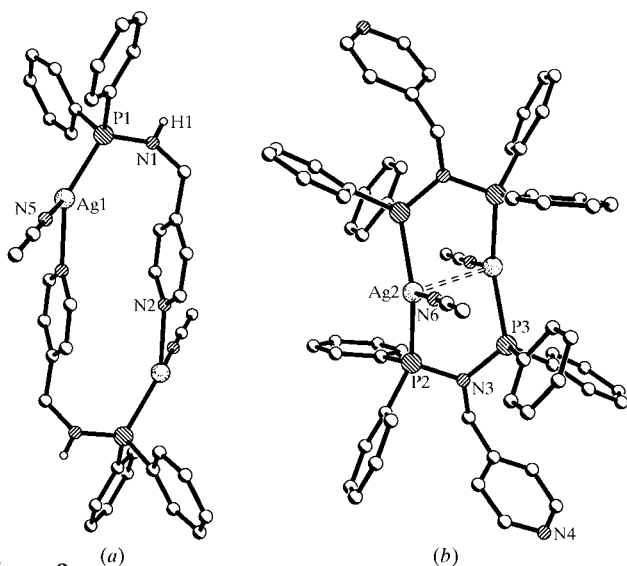
Reaction of the (I)–(II) mixture that results from the rapid combination of ligand components with silver(I) tetrafluoroborate yields the coordination polymer (III), shown in Fig. 1. The polymeric backbone of (III) is perpetuated by the repetition of the two distinct rings shown in Fig. 2; one consists of a head-to-tail-type coordination of (I) around the distorted tetrahedron of atom Ag1, and the other, smaller, ring is constructed by the head-to-head  $\eta^2, \mu_2$ -action of the disubstituted ligand (II) coordinated to the trigonal atom Ag2. The rings alternate in position in the polymer and are joined by the outstretched pyridyl group of ligand (II), which completes the coordination sphere of atom Ag1.

The molecular structure of the unique portion of (III) is shown in Fig. 3. Steric distortions around the metal centers are

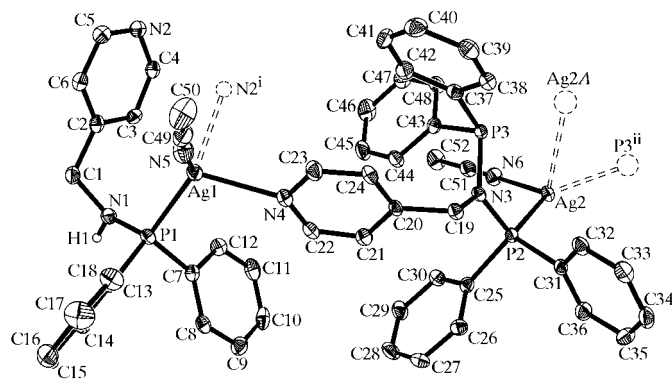


**Figure 1**

A view of the extended structure of the cationic polymer of (III), with H atoms omitted for clarity. Atomic radii are arbitrary.



**Figure 2** Ball-and-stick representations of repeating rings formed by (a) *N*-(diphenylphosphino)-4-aminomethylpyridine and (b) *N,N*-bis(diphenylphosphino)-4-aminomethylpyridine.



**Figure 3** A view of the asymmetric unit of the cationic polymer (III), with displacement ellipsoids drawn at the 50% probability level. All H atoms, except that on the N atom, have been omitted for clarity. The coordination spheres of the Ag atoms are shown completed with symmetry-equivalent atoms of arbitrary radii. See Table 1 for symmetry codes.

immediately apparent. Angles around the distorted tetrahedral Ag1 atom range from the acute  $87.89(9)^\circ$  angle that involves the coordinated acetonitrile group and the pyridyl extension of the disubstituted ligand, to the  $137.72(7)^\circ$  separation of atom P1 and its symmetry-equivalent N-atom donor, N2<sup>i</sup> (see Table 1 for symmetry code). Also of interest are the lengths of the bonds to atom Ag1. The Ag1–N2<sup>i</sup> distance is already slightly elongated at  $2.297(3) \text{ \AA}$ , while the bonds to atoms N4 and N5 are exceptionally long at  $2.405(3)$  and  $2.403(3) \text{ \AA}$ , respectively (Muthu *et al.*, 2001). The Ag1–P1 bond is typical at  $2.3540(8) \text{ \AA}$  (Carnalli *et al.*, 1988). Atom Ag2 is in a trigonal environment with respect to the two phosphorus and acetonitrile N-atom donors. Atom Ag2 deviates from the N6/P2/P3<sup>iii</sup> plane (see Table 1 for symmetry code) by only  $0.0156(9) \text{ \AA}$ . The N6–Ag2–P2 and N6–Ag2–P3<sup>iii</sup> angles are  $114.45(7)$  and  $109.33(7)^\circ$ , respectively,

and the P2–Ag2–P3<sup>iii</sup> angle is  $136.21(3)^\circ$ . It is also seen that atom P3 holds a symmetry-equivalent Ag atom in place, close enough to form a substantial silver–silver interaction with atom Ag2, with the separation at a close  $3.0363(5) \text{ \AA}$  (Chen *et al.*, 2002). This interaction extends nearly perpendicular to the plane formed by the three ligands surrounding atom Ag2. The Ag2–N6 bond is again lengthy at  $2.309(3) \text{ \AA}$ , while the Ag2–P2 and Ag2–P3<sup>iii</sup> bonds are slightly extended at  $2.4387(8)$  and  $2.4496(8) \text{ \AA}$ . The BF<sub>4</sub><sup>−</sup> anions are dispersed between the polymer strands, half being held in place by hydrogen bonding with atom N1. The N1–H1 vector appears to bisect the F7–B2–F8 angle equally, with  $D\cdots H\cdots A$  distances of  $3.136(3)$  and  $3.183(6) \text{ \AA}$  for N1–H1 $\cdots$ F7<sup>iii</sup> and N1–H1 $\cdots$ F8<sup>iii</sup>, respectively (see Table 2 for further details and symmetry code).

## Experimental

Compound (I) was prepared by the addition of dilute chlorodiphenylphosphine to a 1:1 solution of 4-aminomethylpyridine and triethylamine. Triethylamine (0.13 ml, 0.92 mmol) was added to a stirred solution of 4-aminomethylpyridine (0.100 g, 0.92 mmol) in toluene (50 ml). This solution was stirred for 10 min and then cooled to 273 K. A solution of chlorodiphenylphosphine (0.204 g, 0.92 mmol) in toluene (50 ml) was then added dropwise over a period of 1 h. The resulting solution was stirred for an additional hour and then filtered cold through celite. This solution was dried *in vacuo* to leave (I) as a colorless oil. Compound (II) was prepared by the addition of two equivalents of chlorodiphenylphosphine to a 1:2 solution of 4-aminomethylpyridine and triethylamine. Triethylamine (1.3 ml, 9.2 mmol) was added to a stirred solution of 4-aminomethylpyridine (0.500 g, 4.6 mmol) in toluene (15 ml). This solution was stirred for 10 min and then cooled to 273 K. A solution of chlorodiphenylphosphine (2.04 g, 9.2 mmol) in toluene (10 ml) was added dropwise over a period of 10 min. The solution was stirred for 30 min and then allowed to warm to room temperature. This cloudy suspension was filtered through celite and dried *in vacuo* to leave (II) as a clear yellow oil. The ligand mixture was prepared by adding a solution of chlorodiphenylphosphine (2.04 g, 9.24 mmol) dropwise over a period of 10 min to a stirred solution of aminomethylpyridine (1.00 g, 9.25 mmol) and triethylamine (1.3 ml, 9.33 mmol) in toluene (20 ml) at 273 K. This solution was allowed to warm to room temperature and was filtered through celite. The solvent was removed *in vacuo* to leave the Ph<sub>2</sub>P(4-NHCH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N)/(Ph<sub>2</sub>P)<sub>2</sub>(4-NCH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N) mixture as a yellow oil. This mixture (0.10 g) was added to a solution of AgBF<sub>4</sub> (0.67 g, 3.44 mmol) in CH<sub>3</sub>CN (5 ml), stirred for 5 min, and precipitated with ether to leave the coordination polymer (III) as a white solid. Diffraction-quality crystals were obtained by redissolving (III) in acetonitrile and slowly diffusing ether into this solution at 278 K.

## Crystal data

[Ag <sub>4</sub> (C <sub>2</sub> H <sub>3</sub> N) <sub>4</sub> (C <sub>18</sub> H <sub>17</sub> N <sub>2</sub> P) <sub>2</sub> ·	Z = 1
(C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> P <sub>2</sub> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·3C <sub>2</sub> H <sub>3</sub> N	$D_x = 1.501 \text{ Mg m}^{-3}$
$M_r = 2726.80$	Mo K $\alpha$ radiation
Triclinic, P1	Cell parameters from 5178
$a = 13.2233(8) \text{ \AA}$	reflections
$b = 14.6535(11) \text{ \AA}$	$\theta = 2.4\text{--}25.6^\circ$
$c = 16.7275(12) \text{ \AA}$	$\mu = 0.80 \text{ mm}^{-1}$
$\alpha = 97.085(2)^\circ$	$T = 110(2) \text{ K}$
$\beta = 104.690(2)^\circ$	Parallelepiped, colorless
$\gamma = 101.691(3)^\circ$	$0.14 \times 0.08 \times 0.06 \text{ mm}$
$V = 3017.6(4) \text{ \AA}^3$	

## Data collection

Bruker X8 APEX CCD area-detector diffractometer	12 262 independent reflections
$\varphi$ and $\omega$ scans	8973 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.053$
$T_{\text{min}} = 0.899$ , $T_{\text{max}} = 0.956$	$\theta_{\text{max}} = 26.4^\circ$
32 743 measured reflections	$h = -16 \rightarrow 14$
	$k = -17 \rightarrow 18$
	$l = -18 \rightarrow 20$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0191P)^2 + 1.5905P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.56 \text{ e } \text{\AA}^{-3}$
12 262 reflections	$\Delta\rho_{\text{min}} = -0.57 \text{ e } \text{\AA}^{-3}$
748 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ag1—N2 <sup>i</sup>	2.297 (3)	Ag2—N6	2.309 (3)
Ag1—P1	2.3540 (8)	Ag2—P2	2.4387 (8)
Ag1—N5	2.403 (3)	Ag2—P3 <sup>ii</sup>	2.4496 (8)
Ag1—N4	2.405 (3)	Ag2—Ag2 <sup>ii</sup>	3.0363 (5)
N2 <sup>i</sup> —Ag1—P1	137.72 (7)	N6—Ag2—P2	114.45 (7)
N2 <sup>i</sup> —Ag1—N5	91.09 (9)	N6—Ag2—P3 <sup>ii</sup>	109.33 (7)
P1—Ag1—N5	123.89 (7)	P2—Ag2—P3 <sup>ii</sup>	136.21 (3)
N2 <sup>i</sup> —Ag1—N4	88.78 (9)	N6—Ag2—Ag2 <sup>ii</sup>	110.36 (7)
P1—Ag1—N4	113.03 (6)	P2—Ag2—Ag2 <sup>ii</sup>	87.66 (2)
N5—Ag1—N4	87.89 (9)	P3 <sup>ii</sup> —Ag2—Ag2 <sup>ii</sup>	76.18 (2)

Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $-x, 2-y, 1-z$ .

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 <sup>iii</sup> ...F7 <sup>iii</sup>	0.81 (3)	2.54 (3)	3.136 (3)	131 (3)
N1—H1 <sup>iii</sup> ...F8 <sup>iii</sup>	0.81 (3)	2.38 (3)	3.186 (3)	173 (3)

Symmetry code: (iii)  $1-x, 1-y, -z$ .

H atoms were included in calculated positions ( $C-H = 0.93 \text{ \AA}$ ), except for atom H1, which was located and refined isotropically with an  $N-H$  distance restraint; isotropic displacement parameters for all other H atoms were fixed [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1026). Services for accessing these data are described at the back of the journal.

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