

Phyllo-poly[[silver(I)-di- μ_2 -4-aminomethylpyridine- $\kappa^2N:N'$] hexafluorophosphate]: a two-dimensional coordination polymer formed by the reaction of silver(I) hexafluorophosphate with 4-aminomethylpyridine

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Key indicators

Single-crystal X-ray study
 $T = 110$ K
 Mean $\sigma(C-C) = 0.002$ Å
 R factor = 0.021
 wR factor = 0.051
 Data-to-parameter ratio = 18.9

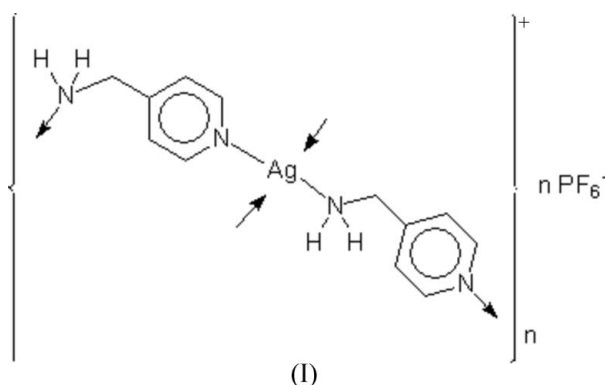
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title two-dimensional coordination polymer, $\{[Ag(C_6H_8N_2)_2]PF_6\}_n$, has been formed by the self-assembly of 4-aminomethylpyridine (amp) ligands with silver(I) hexafluorophosphate in a 2:1 ratio. The polymer consists of dimeric silver–amp rectangles that are linked together to make a larger hexametallc rectangle.

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Comment

Silver(I) coordination polymers are intriguing species that display a wide range of useful properties. They have found applications in ion exchange (Jung *et al.*, 2001), display a wealth of structural motifs, and demonstrate a host of electronic and medicinal uses (Blake *et al.*, 1999; Khlobystov *et al.*, 2001). A number of these complexes have also exhibited luminescent properties and are being explored for possible application in light emitting devices (LEDs) (Tong *et al.*, 2002; Zhang *et al.*, 2002; Zheng *et al.*, 2001). Our interests in silver-based coordination polymers of highly flexible 3- and 4-pyridyl-substituted phosphines have produced a number of compounds that possess useful properties and display a range of supramolecular structures (Feazell *et al.*, 2004, 2005; Klausmeyer *et al.*, 2004; Seward *et al.*, 2003). We have found that similar silver(I) coordination polymer networks can be constructed using bidentate aminomethylpyridine (amp) ligands. An interesting feature of these aminopyridine–silver



complexes is the ability to effect drastic structural changes upon them by simply changing the ratio of ligand to metal in the reaction mixture from which they are made. These facile modifications stem from the ability of the silver(I) cation to readily change its coordination number from 2 to 6 depending on the size, donating ability and concentration of a given

ligand in solution (Caruso *et al.*, 1995). The two-dimensional structure of the title compound, (I), formed by the 2:1 reaction of 4-aminomethylpyridine with silver(I) hexafluorophosphate, is an example of this, differing from the structure obtained from the 1:1 reaction that has been previously reported (Sailaja & Rajasekharan, 2003). As is seen in the scheme, each of the silver centers of the current structure are four-coordinate with N-donors. In the previous study, each metal was linear two-coordinate in a one-dimensional polymer.

It is seen that, when 4-amp is reacted with AgPF_6 in a 2:1 ratio, the two-dimensional sheets shown in Fig. 1 are formed. These sheets are made up of tetrahedral Ag atoms surrounded by two pyridine and two amine donors such that the environment of each metal center is identical. There are two unique 4-amp ligands around each Ag that are used in the construction of two distinct substructures of the network. As shown in Fig. 2, the N1 ligand and its symmetry equivalent are used to construct a small bimetallic head-to-tail-connected ring. The N3 ligand extends outward to bridge four of these smaller rings (two using the entire ring and two using only a single metal vertex) into larger hexametallc diamonds, as shown in Fig. 3. The molecular structure of the unique portion of the polymeric sheet of (I) is shown in Fig. 4. No distinction can be made between the pyridine and amine N atoms on the basis of bond distances, both the shortest and longest Ag–N bonds seen in the polymer being Ag–amine bonds (Ag1–N2^i and Ag1–N4^{ii} ; see Table 1). The Ag–pyridine bond distances are both intermediate between those for the amines (see Table 1). Angles around the Ag atom are only slightly distorted from tetrahedral, ranging from $98.33(5)$ to $124.25(5)^\circ$. The PF_6^- anions are dispersed throughout the voids formed in the plane of the two-dimensional network and are held in place *via* hydrogen bonds to the amine H atoms. Hydrogen-bonding distances are collected in Table 2. All other bond angles and distances fall within expected ranges.

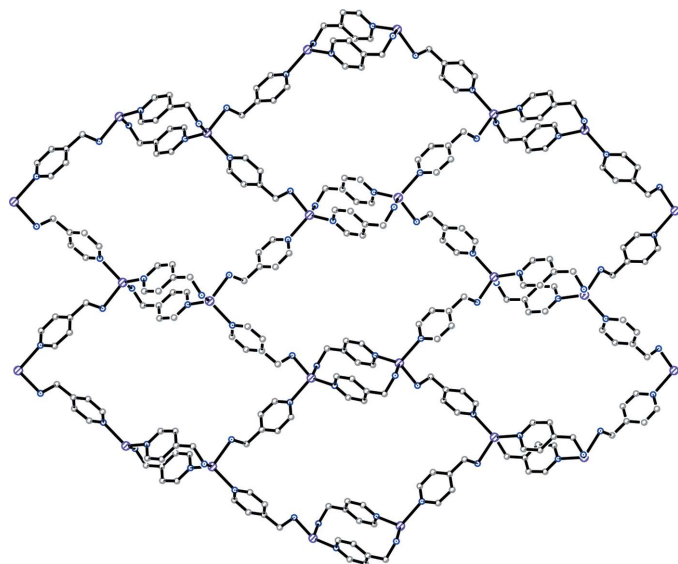


Figure 1
Extended view of the two-dimensional polymer formed by (I). H atoms have been omitted.

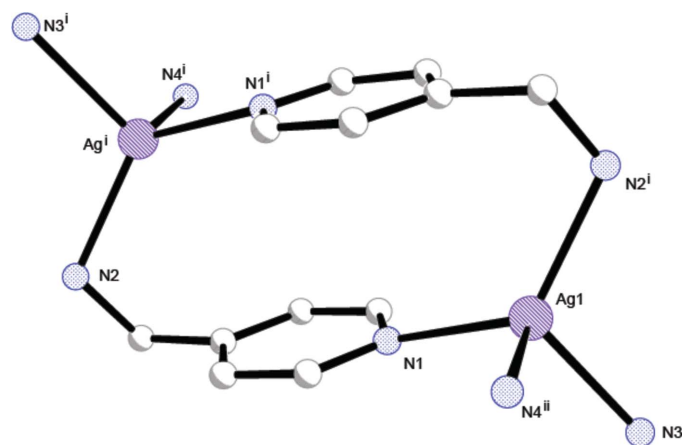


Figure 2
A view of the bimetallic ring formed by the head-to-tail action of two equivalent 4-amp ligands. [Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

Experimental

Standard Schlenk techniques were employed in the synthesis of compound (I). Reaction vessels were covered with aluminium foil to protect against photodecomposition of the silver salt. Solvents were distilled over the appropriate drying agent. Compound (I) was obtained by the reaction of 4-aminomethylpyridine (0.200 g, 1.85 mmol) in CH_3CN (5 ml) with silver hexafluorophosphate (0.234 g, 0.926 mmol) in CH_3CN (5 ml). The clear colorless solution that resulted was stirred for 10 min and then dried *in vacuo* to leave (I) as a white powder. Colorless blocks of (I) were obtained by slow diffusion of diethyl ether into an acetonitrile solution at 278 K.

Crystal data

$[\text{Ag}(\text{C}_6\text{H}_8\text{N}_2)_2]\text{PF}_6$
 $M_r = 469.13$
 Monoclinic, $P2_1/c$
 $a = 11.2159(12) \text{ \AA}$
 $b = 11.7722(12) \text{ \AA}$
 $c = 13.2758(13) \text{ \AA}$
 $\beta = 93.454(4)^\circ$
 $V = 1749.7(3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.781 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 6955 reflections
 $\theta = 2.3\text{--}28.2^\circ$
 $\mu = 1.30 \text{ mm}^{-1}$
 $T = 110(2) \text{ K}$
 Block, colorless
 $0.18 \times 0.13 \times 0.11 \text{ mm}$

Data collection

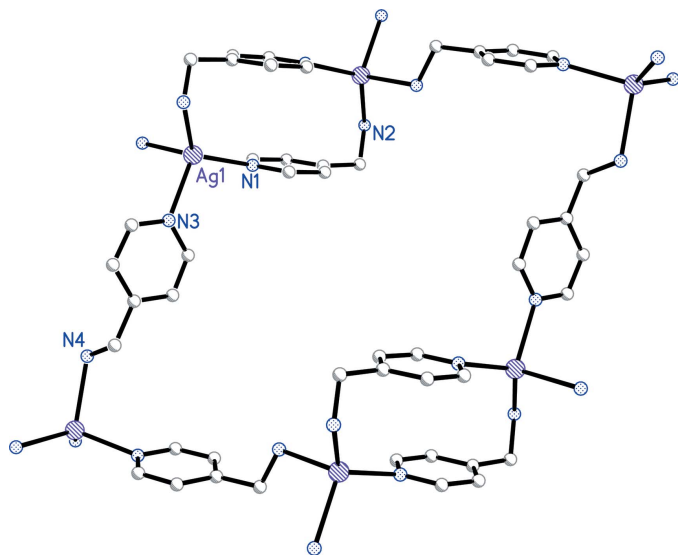
Bruker–Nonius X8 APEX diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.844, T_{\max} = 0.867$
 23273 measured reflections

4333 independent reflections
 3950 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 28.3^\circ$
 $h = -14 \rightarrow 12$
 $k = -15 \rightarrow 14$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.051$
 $S = 1.07$
 4333 reflections
 229 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 1.0267P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.65 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$


Figure 3

The hexametallic diamond, showing the linking of the smaller rings by bridging 4-amp ligands.

Table 1

Selected geometric parameters (Å, °).

Ag1–N1	2.3139 (13)	Ag1–N3	2.3461 (13)
Ag1–N2 ⁱ	2.3126 (14)	Ag1–N4 ⁱⁱ	2.4066 (14)
N1–Ag1–N2 ⁱ	124.25 (5)	N2 ⁱ –Ag1–N3	111.30 (5)
N1–Ag1–N3	108.55 (5)	N2 ⁱ –Ag1–N4 ⁱⁱ	106.64 (5)
N1–Ag1–N4 ⁱⁱ	104.35 (5)	N3–Ag1–N4 ⁱⁱ	98.33 (5)

Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 2

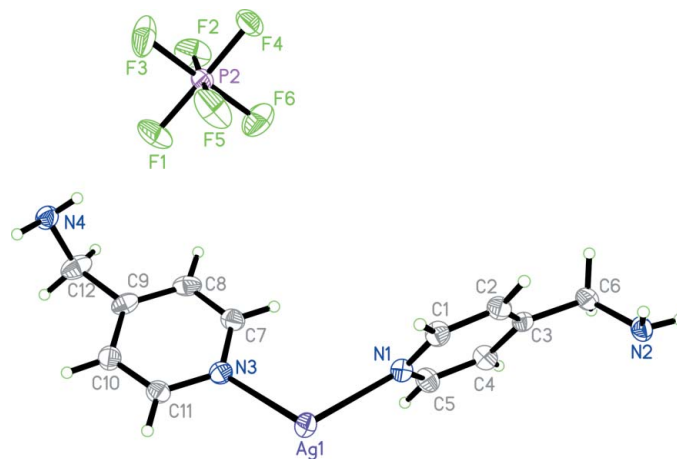
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H3A \cdots F3 ⁱⁱⁱ	0.86 (2)	2.32 (2)	3.0852 (19)	149 (2)
N4–H4B \cdots F1 ^{iv}	0.83 (2)	2.20 (2)	2.9308 (19)	147 (2)
N4–H4A \cdots F5 ^v	0.86 (2)	2.32 (2)	3.1374 (19)	160 (2)

Symmetry codes: (iii) $x, -y + \frac{3}{2}, z - \frac{3}{2}$; (iv) $x - 1, y, z - 1$; (v) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$.

Amine H atoms were located in a difference map and the coordinates were allowed to refine while the isotropic displacement parameters were fixed [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{N})$]. All other H atoms were included in calculated positions ($C-H = 0.95$ and 0.99 Å); isotropic displacement parameters were fixed [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$].

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; 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.


Figure 4

The structure of the asymmetric unit of (I), with displacement ellipsoids shown at the 50% probability level.

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