

catena-Poly[[trifluoromethylphosphane- κP]-silver(I)- μ -4,4'-bipyridine- $\kappa^2 N:N'$ -[trifluoromethylphosphane- κP]silver(I)]-di- μ -chlorido]

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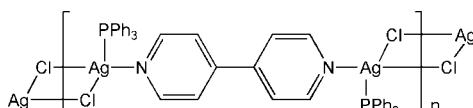
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.039; wR factor = 0.092; data-to-parameter ratio = 19.7.

In the title coordination polymer, $[Ag_2Cl_2(C_{10}H_8N_2)-(C_{18}H_{15}P)_2]_n$, the Ag^I cation is coordinated by a 4,4'-bipyridine N atom, a trifluoromethylphosphane P atom and two Cl^- anions in a distorted tetrahedral geometry. The 4,4'-bipyridine and Cl^- anions bridge the Ag^I cations, forming polymeric chains running along [21̄]. In the crystal, weak C–H···Cl interactions link the polymeric chains into a three-dimensional supramolecular architecture.

Related literature

For background to silver coordination polymers, see: Hung-Low & Klausmeyer (2008); Mishra *et al.* (2007); Pyykkö (2004); Yam & Lo (1999); Zaworotko (1994). For related structures, see: Lu *et al.* (1997); Sampanthar & Vittal (2000); Sun *et al.* (2009).



Experimental

Crystal data

$[Ag_2Cl_2(C_{10}H_8N_2)(C_{18}H_{15}P)_2]$

$M_r = 967.36$

Triclinic, $P\bar{1}$

$a = 9.1042 (16)$ Å

$b = 13.887 (2)$ Å

$c = 17.826 (3)$ Å

$\alpha = 70.753 (3)^\circ$

$\beta = 79.332 (4)^\circ$

$\gamma = 75.190 (3)^\circ$

$V = 2044.5 (6)$ Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 1.20$ mm^{−1}
 $T = 296$ K

0.23 × 0.17 × 0.14 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{min} = 0.770$, $T_{max} = 0.850$

14039 measured reflections
9594 independent reflections
6338 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.092$
 $S = 1.01$
9594 reflections

487 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.59$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.44$ e Å^{−3}

Table 1
Selected bond lengths (Å).

| | | | |
|----------------------|-------------|-----------------------|-------------|
| Ag1—P1 | 2.4069 (9) | Ag2—P2 | 2.4162 (9) |
| Ag1—N1 | 2.430 (3) | Ag2—N2 | 2.386 (3) |
| Ag1—Cl1 | 2.5709 (10) | Ag2—Cl2 | 2.6111 (9) |
| Ag1—Cl1 ⁱ | 2.6639 (10) | Ag2—Cl2 ⁱⁱ | 2.6809 (10) |

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

Table 2
Hydrogen-bond geometry (Å, °).

| $D\cdots H\cdots A$ | $D\cdots H$ | $H\cdots A$ | $D\cdots A$ | $D\cdots H\cdots A$ |
|----------------------------|-------------|-------------|-------------|---------------------|
| C9—H9···Cl2 ⁱⁱⁱ | 0.93 | 2.82 | 3.669 (4) | 153 |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5704).

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supplementary materials

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catena-Poly[[(triphenylphosphane- κP)silver(I)]- μ -4,4'-bipyridine- $\kappa^2 N:N'$ -[(triphenylphosphane- κP)silver(I)]-di- μ -chlorido]

Xiao-Ming Song, Feng Hu, Hua-Tian Shi, Qun Chen and Qian-Feng Zhang

Comment

There has been an extensive interest in d^{10} metal complexes with phosphane ligands due to their potential application in luminescence (Yam & Lo, 1999), for this important reason, the study of d^{10} "closed-shell" interactions that exist between the monovalent elements of group 11 has been active for many years (Pyykko, 2004). Actually, these metal-metal interactions are typically associated with the ligand-bridged, hydrogen-bonded and pi-pi stacked effects, which may result in formation of supramolecular assemblies (Mishra *et al.*, 2007; Zaworotko, 1994). Metal coordination polymers with linear spacer ligands have been exploited by many research workers to construct a variety of network structures. Specifically silver(I) ion has been extensively used in inorganic crystal engineering using self-assembly of tailored building-blocks (Hung-Low & Klausmeyer, 2008). In recent decade, self-assembly of silver(I) salts with different aliphatic dinitrile ligands such as 4,4'-bipyridyl (4,4'-bpy) have also been successfully made resulting into novel coordination polymers (Sampanthar & Vittal, 2000). With this in mind, we have chosen a simple AgCl salt and a linear spacer 4,4'-bpy and allowed them to react separately with PPh_3 as an ancillary ligand. The results of this work are reported in this paper.

The title coordination polymer crystallizes in the triclinic centrosymmetric *P*-1 space group with $Z = 2$ as it contains one half molecule in an asymmetric unit. A view of the structure of building block in the title polymeric complex is depicted in Fig. 1. The structure consists of $\{(\mu\text{-Cl})(\text{AgPPh}_3)\}_2$ units bridged by 4,4'-bipy ligands to form a zig-zig infinite chain, as shown in Fig. 2. This structure is isostructural to $[(\mu\text{-4,4'-bipy})(\mu\text{-I})_2(\text{AgPPh}_3)_2]_n$ (Sampanthar & Vittal, 2000) and $[(\mu\text{-4,4'-bipy})(\mu\text{-Cl})_2(\text{CuPPh}_3)_2]_n$ (Lu *et al.*, 1997). The coordination polymer possesses to the crystallographic inversion center through the middle of Ag_2Cl_2 squares. Two pyridine rings in the 4,4'-bipy are non-planar with dihedral angle of 22.4 (3) $^\circ$. The average $\text{Ag}\cdots\text{Ag}$ distance in the Ag_2Cl_2 ring is 3.392 (1) Å, which is slightly longer than that of 3.139 (1) Å in $[(\mu\text{-4,4'-bipy})(\mu\text{-I})_2(\text{AgPPh}_3)_2]_n$ (Sampanthar & Vittal, 2000). Each silver(I) ion in the title coordination polymer is coordinated by one nitrogen atom of 4,4'-bipy ligand, one phosphorous atom of PPh_3 ligand and two chloride atoms, leading to the distorted tetrahedron with the angles around silver varying from 94.24 (7) $^\circ$ to 130.08 (3) $^\circ$. Two silver(I) ions are separated by 4,4'-bipy groups at a distances of 10.957 (1) Å along with axial direction. The average $\text{Ag}-\text{N}$ and $\text{Ag}-\text{P}$ bond lengths are 2.408 (3) Å and 2.4116 (9) Å, respectively, which almost similar to the values reported in the related other complexes (Sampanthar & Vittal, 2000, Sun *et al.*, 2009). The $\text{Ag}-\text{Cl}-\text{Ag}$ angles of 97.37 (3) $^\circ$ and 102.05 (2) $^\circ$ in the title coordination polymer are obviously larger than the $\text{Ag}-\text{I}-\text{Ag}$ angle of 66.27 (1) $^\circ$ in $[(\mu\text{-4,4'-bipy})(\mu\text{-I})_2(\text{AgPPh}_3)_2]_n$ (Sampanthar & Vittal, 2000).

Experimental

AgCl (0.080 g, 0.56 mmol) and PPh_3 (0.162 g, 0.62 mmol) were mixed together and stirred in a mixture of CH_2Cl_2 (15 mL) and MeCN (5 mL) for 45 min to get a clear solution. An MeCN solution (5 mL) of 4,4'-bipyridyl (0.043 g, 0.28 mmol) was added slowly to the above solution with stirring. The clear solution was filtered and left for slow evaporation. Colorless crystals were collected by decanting the solvent and washed with MeOH (5 mL) and Et_2O (5 x 2 mL) then air-dried. Yield: 157 mg, 58 %. Analysis for $\text{C}_{46}\text{H}_{38}\text{N}_2\text{Cl}_2\text{P}_2\text{Ag}_2$: calcd C 57.11, H 3.96, N 2.90 %; found C 57.07, H 4.03, N 2.88 %.

Refinement

H atoms were placed in geometrically idealized positions and refined in riding model with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

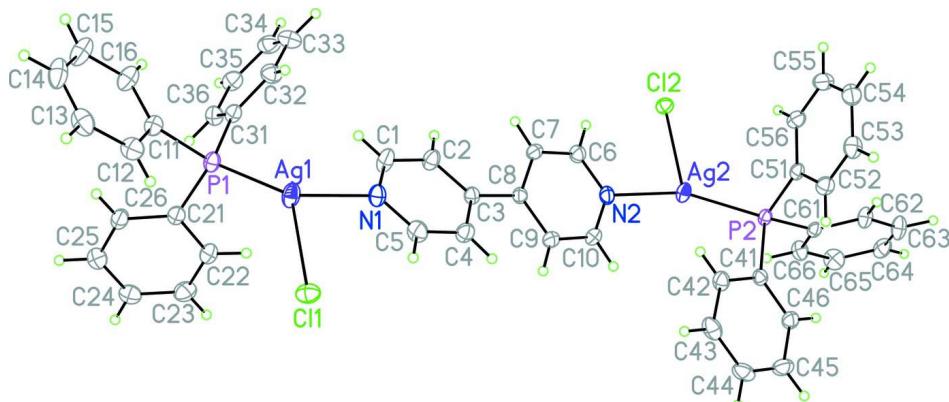


Figure 1

The structure of the title coordination polymer, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

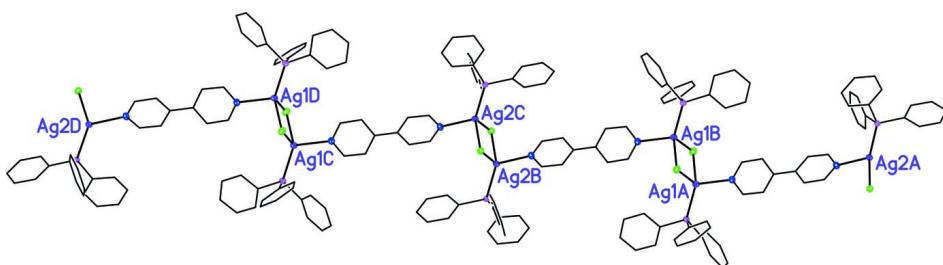


Figure 2

A view the $[(\mu\text{-}4,4'\text{-bipy})(\mu\text{-Cl})_2(\text{AgPPh}_3)_2]_n$ chain, four unit cells along as drawn by ORTEP with 50% probability level.

catena-Poly[[triphosphane- κP)silver(I)]- μ -4,4'-bipyridine- $\kappa^2 N:N'$ -[(triphosphane- κP)silver(I)]-di- μ -chlorido]*Crystal data*

| | |
|---|---|
| $[Ag_2Cl_2(C_{10}H_8N_2)(C_{18}H_{15}P)_2]$ | $Z = 2$ |
| $M_r = 967.36$ | $F(000) = 972$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.571 \text{ Mg m}^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 9.1042 (16) \text{ \AA}$ | Cell parameters from 4454 reflections |
| $b = 13.887 (2) \text{ \AA}$ | $\theta = 2.3\text{--}28.9^\circ$ |
| $c = 17.826 (3) \text{ \AA}$ | $\mu = 1.20 \text{ mm}^{-1}$ |
| $\alpha = 70.753 (3)^\circ$ | $T = 296 \text{ K}$ |
| $\beta = 79.332 (4)^\circ$ | Block, light yellow |
| $\gamma = 75.190 (3)^\circ$ | $0.23 \times 0.17 \times 0.14 \text{ mm}$ |
| $V = 2044.5 (6) \text{ \AA}^3$ | |

Data collection

| | |
|--|---|
| Bruker SMART APEXII CCD area-detector | 14039 measured reflections |
| diffractometer | 9594 independent reflections |
| Radiation source: fine-focus sealed tube | 6338 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{\text{int}} = 0.018$ |
| φ and ω scans | $\theta_{\text{max}} = 29.2^\circ, \theta_{\text{min}} = 1.6^\circ$ |
| Absorption correction: multi-scan | $h = -10 \rightarrow 12$ |
| (<i>SADABS</i> ; Bruker, 2001) | $k = -12 \rightarrow 19$ |
| $T_{\text{min}} = 0.770, T_{\text{max}} = 0.850$ | $l = -15 \rightarrow 23$ |

Refinement

| | |
|---|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier |
| Least-squares matrix: full | map |
| $R[F^2 > 2\sigma(F^2)] = 0.039$ | Hydrogen site location: inferred from |
| $wR(F^2) = 0.092$ | neighbouring sites |
| $S = 1.01$ | H-atom parameters constrained |
| 9594 reflections | $w = 1/[c^2(F_o^2) + (0.0251P)^2 + 1.3705P]$ |
| 487 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| Primary atom site location: structure-invariant | $\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$ |
| direct methods | $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$ |

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^* / U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|------------------------------------|
| Ag1 | 0.34094 (3) | 1.07363 (2) | 0.539814 (18) | 0.05839 (9) |
| Ag2 | -0.34478 (3) | 0.431910 (18) | 0.960631 (16) | 0.05064 (8) |

| | | | | |
|-----|--------------|-------------|--------------|--------------|
| C11 | 0.59763 (10) | 0.97839 (8) | 0.59551 (5) | 0.0607 (2) |
| Cl2 | -0.60355 (9) | 0.52295 (6) | 0.90046 (5) | 0.04829 (19) |
| P1 | 0.20766 (10) | 1.25225 (6) | 0.52007 (5) | 0.0454 (2) |
| P2 | -0.21810 (8) | 0.25279 (6) | 0.97259 (5) | 0.03729 (17) |
| N1 | 0.1967 (3) | 0.9471 (2) | 0.62893 (17) | 0.0524 (7) |
| N2 | -0.2206 (3) | 0.5717 (2) | 0.88543 (16) | 0.0469 (6) |
| C1 | 0.0440 (4) | 0.9661 (3) | 0.6366 (2) | 0.0638 (10) |
| H1 | -0.0076 | 1.0305 | 0.6071 | 0.077* |
| C2 | -0.0412 (4) | 0.8954 (3) | 0.6859 (2) | 0.0558 (9) |
| H2 | -0.1473 | 0.9127 | 0.6886 | 0.067* |
| C3 | 0.0305 (3) | 0.7994 (2) | 0.73101 (18) | 0.0416 (7) |
| C4 | 0.1897 (4) | 0.7796 (3) | 0.7233 (2) | 0.0559 (9) |
| H4 | 0.2444 | 0.7161 | 0.7524 | 0.067* |
| C5 | 0.2660 (4) | 0.8549 (3) | 0.6722 (2) | 0.0608 (10) |
| H5 | 0.3723 | 0.8397 | 0.6680 | 0.073* |
| C6 | -0.2807 (4) | 0.6486 (3) | 0.8242 (2) | 0.0490 (8) |
| H6 | -0.3798 | 0.6521 | 0.8155 | 0.059* |
| C7 | -0.2039 (4) | 0.7233 (2) | 0.77318 (19) | 0.0468 (8) |
| H7 | -0.2510 | 0.7751 | 0.7313 | 0.056* |
| C8 | -0.0565 (3) | 0.7208 (2) | 0.78454 (18) | 0.0391 (7) |
| C9 | 0.0055 (4) | 0.6417 (3) | 0.8484 (2) | 0.0530 (9) |
| H9 | 0.1040 | 0.6365 | 0.8589 | 0.064* |
| C10 | -0.0804 (4) | 0.5706 (3) | 0.8963 (2) | 0.0555 (9) |
| H10 | -0.0366 | 0.5184 | 0.9390 | 0.067* |
| C11 | 0.2506 (4) | 1.3467 (3) | 0.42354 (19) | 0.0480 (8) |
| C12 | 0.4036 (4) | 1.3413 (3) | 0.3919 (2) | 0.0631 (10) |
| H12 | 0.4798 | 1.2891 | 0.4181 | 0.076* |
| C13 | 0.4405 (5) | 1.4153 (4) | 0.3205 (2) | 0.0745 (12) |
| H13 | 0.5423 | 1.4133 | 0.2995 | 0.089* |
| C14 | 0.3284 (7) | 1.4907 (3) | 0.2812 (3) | 0.0820 (14) |
| H14 | 0.3544 | 1.5396 | 0.2336 | 0.098* |
| C15 | 0.1790 (6) | 1.4946 (3) | 0.3112 (2) | 0.0799 (13) |
| H15 | 0.1029 | 1.5451 | 0.2835 | 0.096* |
| C16 | 0.1408 (5) | 1.4234 (3) | 0.3828 (2) | 0.0637 (10) |
| H16 | 0.0387 | 1.4275 | 0.4037 | 0.076* |
| C21 | 0.2366 (3) | 1.3116 (3) | 0.5928 (2) | 0.0460 (7) |
| C22 | 0.2340 (5) | 1.2515 (3) | 0.6731 (2) | 0.0629 (10) |
| H22 | 0.2216 | 1.1830 | 0.6877 | 0.075* |
| C23 | 0.2498 (5) | 1.2930 (4) | 0.7306 (2) | 0.0761 (12) |
| H23 | 0.2447 | 1.2530 | 0.7840 | 0.091* |
| C24 | 0.2731 (5) | 1.3926 (4) | 0.7100 (3) | 0.0721 (11) |
| H24 | 0.2849 | 1.4200 | 0.7491 | 0.087* |
| C25 | 0.2789 (5) | 1.4516 (3) | 0.6310 (3) | 0.0729 (11) |
| H25 | 0.2951 | 1.5191 | 0.6165 | 0.087* |
| C26 | 0.2608 (4) | 1.4113 (3) | 0.5732 (2) | 0.0577 (9) |
| H26 | 0.2649 | 1.4520 | 0.5200 | 0.069* |
| C31 | 0.0001 (4) | 1.2669 (2) | 0.52947 (19) | 0.0445 (7) |
| C32 | -0.0577 (4) | 1.2105 (3) | 0.4944 (2) | 0.0605 (9) |
| H32 | 0.0088 | 1.1696 | 0.4651 | 0.073* |

| | | | | |
|-----|-------------|-------------|--------------|-------------|
| C33 | -0.2136 (5) | 1.2147 (4) | 0.5027 (3) | 0.0779 (12) |
| H33 | -0.2515 | 1.1756 | 0.4803 | 0.093* |
| C34 | -0.3120 (5) | 1.2778 (4) | 0.5448 (2) | 0.0697 (11) |
| H34 | -0.4167 | 1.2810 | 0.5507 | 0.084* |
| C35 | -0.2569 (4) | 1.3350 (3) | 0.5774 (2) | 0.0602 (9) |
| H35 | -0.3240 | 1.3783 | 0.6046 | 0.072* |
| C36 | -0.1008 (4) | 1.3293 (3) | 0.5703 (2) | 0.0510 (8) |
| H36 | -0.0640 | 1.3682 | 0.5935 | 0.061* |
| C41 | -0.0208 (3) | 0.2281 (2) | 0.99274 (19) | 0.0405 (7) |
| C42 | 0.0690 (4) | 0.2968 (3) | 0.9441 (2) | 0.0515 (8) |
| H42 | 0.0294 | 0.3501 | 0.9007 | 0.062* |
| C43 | 0.2169 (4) | 0.2874 (3) | 0.9591 (3) | 0.0659 (11) |
| H43 | 0.2756 | 0.3344 | 0.9262 | 0.079* |
| C44 | 0.2764 (4) | 0.2080 (3) | 1.0228 (3) | 0.0658 (11) |
| H44 | 0.3754 | 0.2015 | 1.0334 | 0.079* |
| C45 | 0.1892 (4) | 0.1383 (3) | 1.0709 (2) | 0.0639 (10) |
| H45 | 0.2300 | 0.0839 | 1.1134 | 0.077* |
| C46 | 0.0410 (4) | 0.1492 (3) | 1.0561 (2) | 0.0509 (8) |
| H46 | -0.0177 | 0.1025 | 1.0894 | 0.061* |
| C51 | -0.2043 (3) | 0.2094 (2) | 0.88489 (18) | 0.0390 (7) |
| C52 | -0.0742 (4) | 0.1461 (3) | 0.8581 (2) | 0.0512 (8) |
| H52 | 0.0140 | 0.1270 | 0.8834 | 0.061* |
| C53 | -0.0759 (4) | 0.1116 (3) | 0.7940 (2) | 0.0590 (9) |
| H53 | 0.0108 | 0.0685 | 0.7769 | 0.071* |
| C54 | -0.2042 (5) | 0.1402 (3) | 0.7555 (2) | 0.0654 (10) |
| H54 | -0.2037 | 0.1174 | 0.7119 | 0.078* |
| C55 | -0.3335 (5) | 0.2025 (3) | 0.7812 (2) | 0.0658 (10) |
| H55 | -0.4212 | 0.2207 | 0.7556 | 0.079* |
| C56 | -0.3337 (4) | 0.2382 (3) | 0.8448 (2) | 0.0524 (8) |
| H56 | -0.4209 | 0.2817 | 0.8611 | 0.063* |
| C61 | -0.3002 (3) | 0.1526 (2) | 1.05223 (18) | 0.0392 (7) |
| C62 | -0.3049 (4) | 0.0577 (3) | 1.0440 (2) | 0.0542 (9) |
| H62 | -0.2648 | 0.0424 | 0.9963 | 0.065* |
| C63 | -0.3694 (5) | -0.0147 (3) | 1.1068 (2) | 0.0696 (11) |
| H63 | -0.3700 | -0.0789 | 1.1015 | 0.084* |
| C64 | -0.4319 (4) | 0.0076 (3) | 1.1765 (2) | 0.0632 (10) |
| H64 | -0.4768 | -0.0406 | 1.2180 | 0.076* |
| C65 | -0.4280 (5) | 0.1006 (3) | 1.1847 (2) | 0.0688 (11) |
| H65 | -0.4692 | 0.1153 | 1.2325 | 0.083* |
| C66 | -0.3637 (4) | 0.1737 (3) | 1.1232 (2) | 0.0551 (9) |
| H66 | -0.3631 | 0.2374 | 1.1296 | 0.066* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| Ag1 | 0.04979 (16) | 0.03807 (14) | 0.0748 (2) | -0.00268 (11) | 0.00765 (13) | -0.01311 (13) |
| Ag2 | 0.04678 (15) | 0.03340 (13) | 0.06182 (17) | -0.00289 (10) | 0.00090 (12) | -0.00901 (11) |
| Cl1 | 0.0483 (5) | 0.0784 (6) | 0.0510 (5) | -0.0104 (4) | -0.0062 (4) | -0.0153 (4) |
| Cl2 | 0.0403 (4) | 0.0520 (5) | 0.0485 (5) | -0.0089 (3) | -0.0058 (3) | -0.0095 (4) |
| P1 | 0.0429 (4) | 0.0348 (4) | 0.0514 (5) | -0.0040 (3) | 0.0009 (4) | -0.0100 (4) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| P2 | 0.0322 (4) | 0.0296 (4) | 0.0454 (5) | -0.0046 (3) | -0.0019 (3) | -0.0078 (3) |
| N1 | 0.0519 (17) | 0.0442 (16) | 0.0566 (18) | -0.0153 (13) | 0.0060 (14) | -0.0115 (13) |
| N2 | 0.0563 (17) | 0.0388 (14) | 0.0472 (16) | -0.0181 (12) | -0.0025 (13) | -0.0104 (12) |
| C1 | 0.053 (2) | 0.0410 (19) | 0.077 (3) | -0.0055 (16) | 0.0042 (19) | 0.0007 (17) |
| C2 | 0.0427 (18) | 0.0443 (19) | 0.068 (2) | -0.0069 (15) | -0.0014 (16) | -0.0042 (16) |
| C3 | 0.0412 (16) | 0.0386 (16) | 0.0449 (18) | -0.0114 (13) | -0.0023 (14) | -0.0113 (13) |
| C4 | 0.0414 (18) | 0.049 (2) | 0.068 (2) | -0.0087 (15) | -0.0081 (17) | -0.0046 (17) |
| C5 | 0.0434 (19) | 0.067 (2) | 0.070 (2) | -0.0206 (18) | 0.0038 (17) | -0.016 (2) |
| C6 | 0.0452 (18) | 0.0458 (18) | 0.056 (2) | -0.0146 (15) | -0.0048 (16) | -0.0110 (16) |
| C7 | 0.0448 (18) | 0.0420 (17) | 0.0492 (19) | -0.0092 (14) | -0.0151 (15) | -0.0024 (14) |
| C8 | 0.0414 (16) | 0.0339 (15) | 0.0425 (17) | -0.0083 (12) | -0.0048 (13) | -0.0115 (13) |
| C9 | 0.0489 (19) | 0.0449 (19) | 0.062 (2) | -0.0109 (15) | -0.0210 (17) | -0.0037 (16) |
| C10 | 0.068 (2) | 0.0412 (18) | 0.053 (2) | -0.0122 (17) | -0.0211 (18) | 0.0005 (15) |
| C11 | 0.0536 (19) | 0.0456 (18) | 0.0419 (18) | -0.0091 (15) | 0.0022 (15) | -0.0141 (14) |
| C12 | 0.058 (2) | 0.078 (3) | 0.055 (2) | -0.020 (2) | 0.0035 (18) | -0.022 (2) |
| C13 | 0.079 (3) | 0.093 (3) | 0.063 (3) | -0.045 (3) | 0.022 (2) | -0.034 (2) |
| C14 | 0.132 (4) | 0.056 (3) | 0.056 (3) | -0.036 (3) | 0.020 (3) | -0.018 (2) |
| C15 | 0.111 (4) | 0.051 (2) | 0.053 (2) | 0.002 (2) | 0.008 (2) | -0.0067 (18) |
| C16 | 0.071 (2) | 0.049 (2) | 0.053 (2) | 0.0042 (18) | 0.0074 (18) | -0.0124 (17) |
| C21 | 0.0366 (16) | 0.0446 (18) | 0.052 (2) | -0.0065 (13) | -0.0017 (14) | -0.0108 (15) |
| C22 | 0.076 (3) | 0.054 (2) | 0.053 (2) | -0.0228 (19) | -0.0103 (19) | 0.0001 (18) |
| C23 | 0.091 (3) | 0.086 (3) | 0.048 (2) | -0.024 (3) | -0.014 (2) | -0.007 (2) |
| C24 | 0.080 (3) | 0.080 (3) | 0.066 (3) | -0.019 (2) | -0.020 (2) | -0.026 (2) |
| C25 | 0.086 (3) | 0.060 (2) | 0.081 (3) | -0.020 (2) | -0.022 (2) | -0.020 (2) |
| C26 | 0.068 (2) | 0.0422 (19) | 0.057 (2) | -0.0104 (17) | -0.0109 (18) | -0.0065 (16) |
| C31 | 0.0426 (17) | 0.0395 (17) | 0.0458 (18) | -0.0078 (13) | -0.0025 (14) | -0.0072 (14) |
| C32 | 0.064 (2) | 0.065 (2) | 0.057 (2) | -0.0107 (19) | -0.0088 (19) | -0.0252 (19) |
| C33 | 0.075 (3) | 0.089 (3) | 0.081 (3) | -0.021 (3) | -0.033 (2) | -0.024 (3) |
| C34 | 0.049 (2) | 0.088 (3) | 0.065 (3) | -0.017 (2) | -0.0140 (19) | -0.007 (2) |
| C35 | 0.0456 (19) | 0.065 (2) | 0.059 (2) | -0.0056 (17) | -0.0021 (17) | -0.0114 (18) |
| C36 | 0.0433 (18) | 0.0493 (19) | 0.059 (2) | -0.0103 (15) | 0.0003 (15) | -0.0168 (16) |
| C41 | 0.0366 (15) | 0.0364 (15) | 0.0501 (19) | -0.0047 (12) | -0.0034 (13) | -0.0181 (14) |
| C42 | 0.0432 (18) | 0.0450 (18) | 0.064 (2) | -0.0134 (14) | 0.0007 (16) | -0.0131 (16) |
| C43 | 0.048 (2) | 0.071 (3) | 0.089 (3) | -0.0266 (19) | 0.009 (2) | -0.035 (2) |
| C44 | 0.0371 (18) | 0.085 (3) | 0.089 (3) | -0.0070 (19) | -0.0128 (19) | -0.046 (3) |
| C45 | 0.050 (2) | 0.068 (3) | 0.070 (3) | 0.0022 (18) | -0.0215 (19) | -0.019 (2) |
| C46 | 0.0411 (17) | 0.0444 (18) | 0.065 (2) | -0.0060 (14) | -0.0097 (16) | -0.0128 (16) |
| C51 | 0.0378 (15) | 0.0311 (14) | 0.0425 (17) | -0.0092 (12) | -0.0017 (13) | -0.0035 (12) |
| C52 | 0.0418 (17) | 0.051 (2) | 0.057 (2) | -0.0059 (15) | -0.0044 (15) | -0.0155 (16) |
| C53 | 0.067 (2) | 0.052 (2) | 0.056 (2) | -0.0120 (18) | 0.0065 (19) | -0.0201 (17) |
| C54 | 0.092 (3) | 0.060 (2) | 0.047 (2) | -0.024 (2) | -0.004 (2) | -0.0149 (18) |
| C55 | 0.069 (3) | 0.068 (3) | 0.061 (2) | -0.018 (2) | -0.024 (2) | -0.008 (2) |
| C56 | 0.0443 (18) | 0.052 (2) | 0.053 (2) | -0.0082 (15) | -0.0091 (16) | -0.0051 (16) |
| C61 | 0.0295 (14) | 0.0334 (15) | 0.0488 (18) | -0.0060 (11) | -0.0051 (13) | -0.0046 (13) |
| C62 | 0.063 (2) | 0.0381 (17) | 0.055 (2) | -0.0130 (15) | 0.0066 (17) | -0.0100 (15) |
| C63 | 0.081 (3) | 0.0387 (19) | 0.079 (3) | -0.0216 (19) | 0.008 (2) | -0.0071 (18) |
| C64 | 0.058 (2) | 0.054 (2) | 0.061 (2) | -0.0197 (18) | -0.0008 (18) | 0.0072 (18) |
| C65 | 0.072 (3) | 0.083 (3) | 0.049 (2) | -0.030 (2) | 0.0130 (19) | -0.017 (2) |
| C66 | 0.061 (2) | 0.054 (2) | 0.052 (2) | -0.0216 (17) | 0.0071 (17) | -0.0181 (16) |

Geometric parameters (\AA , $\text{^{\circ}}$)

| | | | |
|-----------------------|-------------|---------|-----------|
| Ag1—P1 | 2.4069 (9) | C22—H22 | 0.9300 |
| Ag1—N1 | 2.430 (3) | C23—C24 | 1.371 (6) |
| Ag1—Cl1 | 2.5709 (10) | C23—H23 | 0.9300 |
| Ag1—Cl1 ⁱ | 2.6639 (10) | C24—C25 | 1.376 (6) |
| Ag2—P2 | 2.4162 (9) | C24—H24 | 0.9300 |
| Ag2—N2 | 2.386 (3) | C25—C26 | 1.376 (5) |
| Ag2—Cl2 | 2.6111 (9) | C25—H25 | 0.9300 |
| Ag2—Cl2 ⁱⁱ | 2.6809 (10) | C26—H26 | 0.9300 |
| Ag2—Ag2 ⁱⁱ | 3.3292 (6) | C31—C36 | 1.373 (4) |
| Cl1—Ag1 ⁱ | 2.6639 (11) | C31—C32 | 1.392 (5) |
| Cl2—Ag2 ⁱⁱ | 2.6809 (10) | C32—C33 | 1.387 (5) |
| P1—C31 | 1.830 (3) | C32—H32 | 0.9300 |
| P1—C11 | 1.833 (3) | C33—C34 | 1.384 (6) |
| P1—C21 | 1.836 (4) | C33—H33 | 0.9300 |
| P2—C41 | 1.821 (3) | C34—C35 | 1.355 (6) |
| P2—C51 | 1.825 (3) | C34—H34 | 0.9300 |
| P2—C61 | 1.829 (3) | C35—C36 | 1.388 (5) |
| N1—C5 | 1.322 (5) | C35—H35 | 0.9300 |
| N1—C1 | 1.336 (4) | C36—H36 | 0.9300 |
| N2—C10 | 1.321 (4) | C41—C46 | 1.378 (4) |
| N2—C6 | 1.336 (4) | C41—C42 | 1.387 (4) |
| C1—C2 | 1.381 (5) | C42—C43 | 1.386 (5) |
| C1—H1 | 0.9300 | C42—H42 | 0.9300 |
| C2—C3 | 1.375 (4) | C43—C44 | 1.378 (6) |
| C2—H2 | 0.9300 | C43—H43 | 0.9300 |
| C3—C4 | 1.394 (4) | C44—C45 | 1.376 (5) |
| C3—C8 | 1.485 (4) | C44—H44 | 0.9300 |
| C4—C5 | 1.384 (5) | C45—C46 | 1.384 (5) |
| C4—H4 | 0.9300 | C45—H45 | 0.9300 |
| C5—H5 | 0.9300 | C46—H46 | 0.9300 |
| C6—C7 | 1.381 (4) | C51—C56 | 1.393 (4) |
| C6—H6 | 0.9300 | C51—C52 | 1.394 (4) |
| C7—C8 | 1.383 (4) | C52—C53 | 1.380 (5) |
| C7—H7 | 0.9300 | C52—H52 | 0.9300 |
| C8—C9 | 1.385 (4) | C53—C54 | 1.368 (5) |
| C9—C10 | 1.380 (5) | C53—H53 | 0.9300 |
| C9—H9 | 0.9300 | C54—C55 | 1.374 (6) |
| C10—H10 | 0.9300 | C54—H54 | 0.9300 |
| C11—C16 | 1.370 (5) | C55—C56 | 1.379 (5) |
| C11—C12 | 1.395 (5) | C55—H55 | 0.9300 |
| C12—C13 | 1.396 (5) | C56—H56 | 0.9300 |
| C12—H12 | 0.9300 | C61—C66 | 1.382 (4) |
| C13—C14 | 1.364 (6) | C61—C62 | 1.385 (4) |
| C13—H13 | 0.9300 | C62—C63 | 1.388 (5) |
| C14—C15 | 1.361 (6) | C62—H62 | 0.9300 |
| C14—H14 | 0.9300 | C63—C64 | 1.364 (5) |
| C15—C16 | 1.382 (5) | C63—H63 | 0.9300 |
| C15—H15 | 0.9300 | C64—C65 | 1.357 (6) |

| | | | |
|--|-------------|-------------|-----------|
| C16—H16 | 0.9300 | C64—H64 | 0.9300 |
| C21—C26 | 1.377 (5) | C65—C66 | 1.381 (5) |
| C21—C22 | 1.399 (5) | C65—H65 | 0.9300 |
| C22—C23 | 1.374 (6) | C66—H66 | 0.9300 |
| | | | |
| P1—Ag1—N1 | 114.03 (7) | C23—C22—C21 | 120.4 (4) |
| P1—Ag1—Cl1 | 130.08 (3) | C23—C22—H22 | 119.8 |
| N1—Ag1—Cl1 | 95.47 (8) | C21—C22—H22 | 119.8 |
| P1—Ag1—Cl1 ⁱ | 112.23 (3) | C24—C23—C22 | 120.7 (4) |
| N1—Ag1—Cl1 ⁱ | 103.72 (7) | C24—C23—H23 | 119.7 |
| Cl1—Ag1—Cl1 ⁱ | 97.37 (3) | C22—C23—H23 | 119.7 |
| N2—Ag2—P2 | 120.95 (7) | C23—C24—C25 | 119.3 (4) |
| N2—Ag2—Cl2 | 94.24 (7) | C23—C24—H24 | 120.3 |
| P2—Ag2—Cl2 | 124.50 (3) | C25—C24—H24 | 120.3 |
| N2—Ag2—Cl2 ⁱⁱ | 96.68 (7) | C26—C25—C24 | 120.4 (4) |
| P2—Ag2—Cl2 ⁱⁱ | 113.34 (3) | C26—C25—H25 | 119.8 |
| Cl2—Ag2—Cl2 ⁱⁱ | 102.05 (2) | C24—C25—H25 | 119.8 |
| N2—Ag2—Ag2 ⁱⁱ | 98.72 (7) | C25—C26—C21 | 121.1 (4) |
| P2—Ag2—Ag2 ⁱⁱ | 139.76 (2) | C25—C26—H26 | 119.5 |
| Cl2 ⁱⁱ —Ag2—Ag2 ⁱⁱ | 51.96 (2) | C21—C26—H26 | 119.5 |
| Cl2 ⁱⁱ —Ag2—Ag2 ⁱⁱ | 50.090 (19) | C36—C31—C32 | 118.6 (3) |
| Ag1—Cl1—Ag1 ⁱ | 82.63 (3) | C36—C31—P1 | 123.4 (3) |
| Ag2—Cl2—Ag2 ⁱⁱ | 77.95 (2) | C32—C31—P1 | 118.1 (3) |
| C31—P1—C11 | 103.84 (15) | C33—C32—C31 | 120.7 (4) |
| C31—P1—C21 | 103.95 (15) | C33—C32—H32 | 119.7 |
| C11—P1—C21 | 103.26 (15) | C31—C32—H32 | 119.7 |
| C31—P1—Ag1 | 112.39 (11) | C34—C33—C32 | 119.3 (4) |
| C11—P1—Ag1 | 117.37 (11) | C34—C33—H33 | 120.4 |
| C21—P1—Ag1 | 114.55 (11) | C32—C33—H33 | 120.4 |
| C41—P2—C51 | 104.34 (14) | C35—C34—C33 | 120.4 (4) |
| C41—P2—C61 | 104.46 (14) | C35—C34—H34 | 119.8 |
| C51—P2—C61 | 102.45 (14) | C33—C34—H34 | 119.8 |
| C41—P2—Ag2 | 111.14 (10) | C34—C35—C36 | 120.3 (4) |
| C51—P2—Ag2 | 116.42 (10) | C34—C35—H35 | 119.8 |
| C61—P2—Ag2 | 116.60 (10) | C36—C35—H35 | 119.8 |
| C5—N1—C1 | 116.4 (3) | C31—C36—C35 | 120.7 (3) |
| C5—N1—Ag1 | 121.4 (2) | C31—C36—H36 | 119.6 |
| C1—N1—Ag1 | 122.2 (2) | C35—C36—H36 | 119.6 |
| C10—N2—C6 | 116.2 (3) | C46—C41—C42 | 118.4 (3) |
| C10—N2—Ag2 | 121.3 (2) | C46—C41—P2 | 123.8 (2) |
| C6—N2—Ag2 | 122.1 (2) | C42—C41—P2 | 117.7 (2) |
| N1—C1—C2 | 123.6 (3) | C43—C42—C41 | 121.0 (3) |
| N1—C1—H1 | 118.2 | C43—C42—H42 | 119.5 |
| C2—C1—H1 | 118.2 | C41—C42—H42 | 119.5 |
| C3—C2—C1 | 120.1 (3) | C44—C43—C42 | 119.6 (4) |
| C3—C2—H2 | 119.9 | C44—C43—H43 | 120.2 |
| C1—C2—H2 | 119.9 | C42—C43—H43 | 120.2 |
| C2—C3—C4 | 116.3 (3) | C45—C44—C43 | 119.9 (3) |
| C2—C3—C8 | 122.0 (3) | C45—C44—H44 | 120.0 |

| | | | |
|-------------|-----------|-------------|-----------|
| C4—C3—C8 | 121.7 (3) | C43—C44—H44 | 120.0 |
| C5—C4—C3 | 119.7 (3) | C44—C45—C46 | 120.0 (4) |
| C5—C4—H4 | 120.1 | C44—C45—H45 | 120.0 |
| C3—C4—H4 | 120.1 | C46—C45—H45 | 120.0 |
| N1—C5—C4 | 123.8 (3) | C41—C46—C45 | 121.0 (3) |
| N1—C5—H5 | 118.1 | C41—C46—H46 | 119.5 |
| C4—C5—H5 | 118.1 | C45—C46—H46 | 119.5 |
| N2—C6—C7 | 123.6 (3) | C56—C51—C52 | 118.6 (3) |
| N2—C6—H6 | 118.2 | C56—C51—P2 | 117.7 (2) |
| C7—C6—H6 | 118.2 | C52—C51—P2 | 123.7 (2) |
| C6—C7—C8 | 119.7 (3) | C53—C52—C51 | 120.1 (3) |
| C6—C7—H7 | 120.1 | C53—C52—H52 | 120.0 |
| C8—C7—H7 | 120.1 | C51—C52—H52 | 120.0 |
| C7—C8—C9 | 116.7 (3) | C54—C53—C52 | 120.6 (4) |
| C7—C8—C3 | 121.6 (3) | C54—C53—H53 | 119.7 |
| C9—C8—C3 | 121.7 (3) | C52—C53—H53 | 119.7 |
| C10—C9—C8 | 119.4 (3) | C53—C54—C55 | 120.1 (4) |
| C10—C9—H9 | 120.3 | C53—C54—H54 | 120.0 |
| C8—C9—H9 | 120.3 | C55—C54—H54 | 120.0 |
| N2—C10—C9 | 124.4 (3) | C54—C55—C56 | 120.2 (4) |
| N2—C10—H10 | 117.8 | C54—C55—H55 | 119.9 |
| C9—C10—H10 | 117.8 | C56—C55—H55 | 119.9 |
| C16—C11—C12 | 119.1 (3) | C55—C56—C51 | 120.5 (3) |
| C16—C11—P1 | 123.2 (3) | C55—C56—H56 | 119.8 |
| C12—C11—P1 | 117.7 (3) | C51—C56—H56 | 119.8 |
| C11—C12—C13 | 119.0 (4) | C66—C61—C62 | 118.5 (3) |
| C11—C12—H12 | 120.5 | C66—C61—P2 | 118.3 (2) |
| C13—C12—H12 | 120.5 | C62—C61—P2 | 123.1 (3) |
| C14—C13—C12 | 120.5 (4) | C61—C62—C63 | 120.1 (3) |
| C14—C13—H13 | 119.7 | C61—C62—H62 | 120.0 |
| C12—C13—H13 | 119.7 | C63—C62—H62 | 120.0 |
| C15—C14—C13 | 120.5 (4) | C64—C63—C62 | 120.6 (4) |
| C15—C14—H14 | 119.8 | C64—C63—H63 | 119.7 |
| C13—C14—H14 | 119.8 | C62—C63—H63 | 119.7 |
| C14—C15—C16 | 119.7 (4) | C65—C64—C63 | 119.6 (3) |
| C14—C15—H15 | 120.1 | C65—C64—H64 | 120.2 |
| C16—C15—H15 | 120.1 | C63—C64—H64 | 120.2 |
| C11—C16—C15 | 121.2 (4) | C64—C65—C66 | 121.0 (4) |
| C11—C16—H16 | 119.4 | C64—C65—H65 | 119.5 |
| C15—C16—H16 | 119.4 | C66—C65—H65 | 119.5 |
| C26—C21—C22 | 118.1 (3) | C65—C66—C61 | 120.3 (3) |
| C26—C21—P1 | 124.1 (3) | C65—C66—H66 | 119.9 |
| C22—C21—P1 | 117.8 (3) | C61—C66—H66 | 119.9 |

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

Hydrogen-bond geometry (\AA , $^\circ$)

| $D\text{—H}\cdots A$ | $D\text{—H}$ | $H\cdots A$ | $D\cdots A$ | $D\text{—H}\cdots A$ |
|----------------------|--------------|-------------|-------------|----------------------|
| | | | | |

supplementary materials

| | | | | |
|--------------------------|------|------|-----------|-----|
| C9—H9…Cl2 ⁱⁱⁱ | 0.93 | 2.82 | 3.669 (4) | 153 |
|--------------------------|------|------|-----------|-----|

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