

# Poly[ $(\mu_3\text{-}4\text{-carboxypyridine}\text{-}3\text{-carboxylato}\text{-}\kappa^3\text{N}\text{:O}^3\text{:O}^4)$ (triphenylphosphine-\kappa P)-silver(I)]

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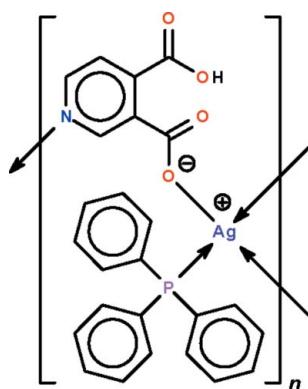
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C-C}) = 0.003$  Å;  $R$  factor = 0.020;  $wR$  factor = 0.055; data-to-parameter ratio = 16.9.

In the title 1:1 silver(I) 4-carboxypyridine-3-carboxylate adduct with triphenylphosphine,  $[\text{Ag}(\text{C}_7\text{H}_4\text{NO}_4)(\text{C}_{18}\text{H}_{15}\text{P})]_n$ , the carboxylate anion bridges the phosphine-coordinated Ag atoms through its N and O atoms, generating a coordination polymer forming layers in the  $bc$  plane. The Ag atom exists in a distorted tetrahedral geometry. The H atom of the carboxylate is midway between two O atoms of the two carboxyl groups, thus forming a strong intramolecular hydrogen bond.

## Related literature

For the synthesis of the silver reactant used in the synthesis, see: Hanna & Ng (1999); Ng & Othman (1997). For a related structure, see: Drew *et al.* (1971).



## Experimental

### Crystal data

$[\text{Ag}(\text{C}_7\text{H}_4\text{NO}_4)(\text{C}_{18}\text{H}_{15}\text{P})]$   
 $M_r = 536.25$

Monoclinic,  $P2_1/c$   
 $a = 14.2472$  (7) Å  
 $b = 10.2431$  (5) Å  
 $c = 16.3146$  (8) Å  
 $\beta = 115.206$  (1)°

$V = 2154.18$  (18) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 1.04$  mm<sup>-1</sup>  
 $T = 100$  K  
0.35 × 0.30 × 0.15 mm

### Data collection

Bruker SMART APEX  
diffractometer  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.712$ ,  $T_{\max} = 0.859$

13432 measured reflections  
4942 independent reflections  
4587 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.055$   
 $S = 1.05$   
4942 reflections  
293 parameters

H atoms treated by a mixture of  
independent and constrained  
refinement  
 $\Delta\rho_{\text{max}} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.48$  e Å<sup>-3</sup>

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

We thank Shahid Beheshti University and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5322).

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# supporting information

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## Poly[ $(\mu_3\text{-}4\text{-carboxypyridine}\text{-}3\text{-carboxylato}\text{-}\kappa^3\text{N}\text{:O}^3\text{:O}^4)$ (triphenylphosphine- $\kappa P$ )silver(I)]

**Omid Sadeghi, Mostafa M. Amini and Seik Weng Ng**

### S1. Comment

We have used bis(silver acetate-2triphenylphosphine) monohydrate sesquiethanol (Hanna & Ng, 1999; Ng & Othman, 1997) as a template in the synthesis of triphenylphosphine adducts of other silver carboxylates; the silver carboxylates themselves cannot be synthesized directly by the reaction of a silver salt with the carboxylate anion as the reaction invariably leads to the formation of some insoluble gray material.

The crystal structure of the silver(II) derivative of the monobasic 3-carboxypyridyl-4-carboxylate anion was reported a long time ago (Drew *et al.*, 1971); the silver atom is *N,O*-chelated by two anions in an approximate square-planar environment.

The silver(I) 3-carboxypyridyl-4-carboxylate-triphenylphosphine adduct (Scheme I) exists as a polymeric compound (Fig. 1) in which the anion bridges adjacent silver atoms through one carboxyl group and the pyridyl N atom (Fig. 2). The diffraction measurements are of a sufficiently high quality for the acid H atom to be refined; the refinement places this atom mid-way between the O atoms of the two carboxyl O atoms, at a distance of 1.20 (4) Å. The O···H···O interaction is an intramolecular hydrogen bond. The pyridyl ring and the carboxyl –CO<sub>2</sub> unit that is engaged in Ag coordination enclose a dihedral angle of 14.3 (2) ° whereas the free carboxyl group encloses a dihedral angle of 15.2 (3) ° with the pyridyl ring; such minimal twist probably locks the acid H atom in its place.

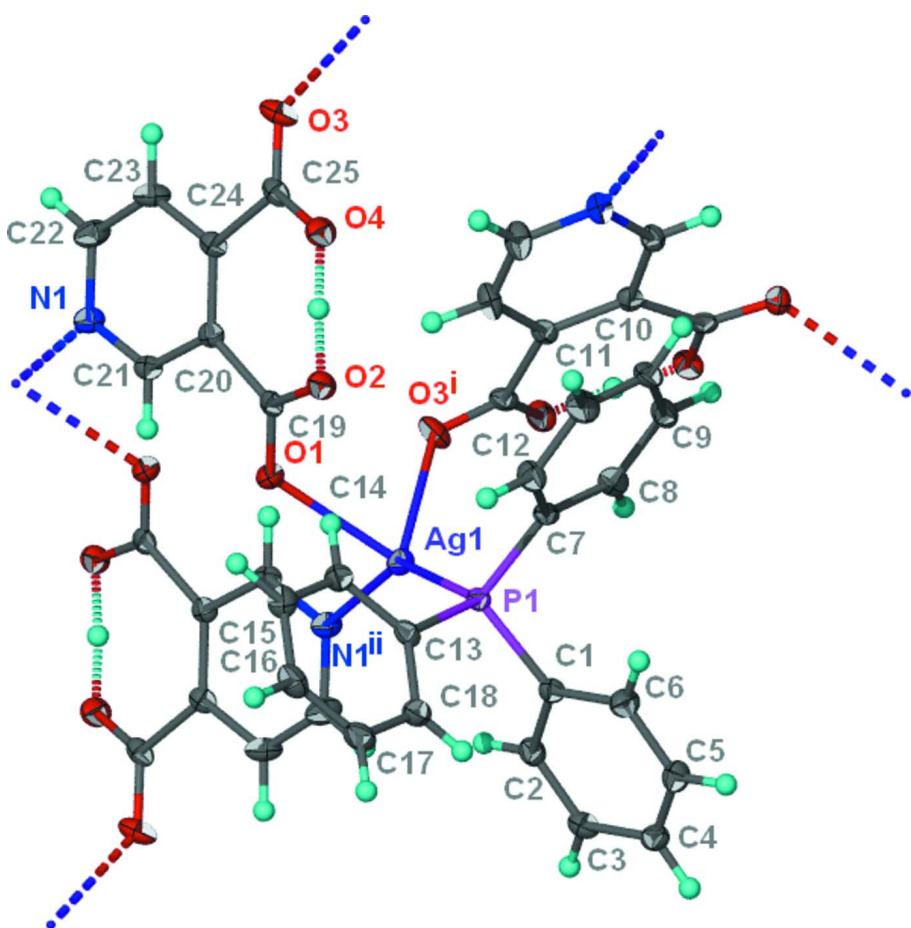
### S2. Experimental

Silver acetate (1 mmol, 0.17 g) and triphenylphosphine (2 mmol, 0.53 g) were heated in ethanol (50 ml) until the reactants dissolved completely. Gray insoluble material was removed by filtration and the solvent removed to yield bis(silver acetate-2triphenylphosphine) monohydrate sesquiethanol (Hanna & Ng, 1999; Ng & Othman, 1997).

The adduct (0.5 mmol, 0.69 g) and 3,4-pyridinedicarboxylic acid (1 mmol, 0.17 g) were placed in a convection tube; the tube was filled with a 1:1 methanol/ethanol mixture and kept at 333 K. Colorless crystals were collected after 3 days (m.p. > 550 K).

### S3. Refinement

Hydrogen atoms bonded to C were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with  $U(\text{H})$  set to 1.2 $U_{\text{eq}}(\text{C})$ . The carboxylic H-atom was freely refined.

**Figure 1**

Anisotropic displacement ellipsoid plot (Barbour, 2001) of a portion of the title polymer; ellipsoids are drawn at the 70% probability level and H atoms are of arbitrary radius. Symmetry transformations are given in Table 1.:  $i = 1 - x, 1 - y, 1 - z$ ;  $ii = 3/2 - x, y - 1/2, 3/2 - z$ .

### Poly[ $(\mu_3\text{-}4\text{-carboxypyridine}\text{-}3\text{-carboxylato-}\kappa^3\text{N:O}^3\text{:O}^4)$ (triphenylphosphine- $\kappa P$ )silver(I)]

#### Crystal data



$M_r = 536.25$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 14.2472 (7) \text{ \AA}$

$b = 10.2431 (5) \text{ \AA}$

$c = 16.3146 (8) \text{ \AA}$

$\beta = 115.206 (1)^\circ$

$V = 2154.18 (18) \text{ \AA}^3$

$Z = 4$

$F(000) = 1080$

$D_x = 1.653 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 9293 reflections

$\theta = 2.4\text{--}28.3^\circ$

$\mu = 1.04 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, colorless

$0.35 \times 0.30 \times 0.15 \text{ mm}$

#### Data collection

Bruker SMART APEX  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator  
 $\omega$  scans

Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.712$ ,  $T_{\max} = 0.859$   
 13432 measured reflections  
 4942 independent reflections  
 4587 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$   
 $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 1.6^\circ$   
 $h = -18 \rightarrow 18$   
 $k = -10 \rightarrow 13$   
 $l = -21 \rightarrow 20$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.055$   
 $S = 1.05$   
 4942 reflections  
 293 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 1.0816P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | $x$          | $y$           | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| Ag1 | 0.618798 (9) | 0.207715 (12) | 0.474714 (8) | 0.01345 (5)                      |
| P1  | 0.76750 (3)  | 0.10818 (4)   | 0.47440 (3)  | 0.01115 (8)                      |
| O1  | 0.62846 (9)  | 0.44669 (12)  | 0.47885 (7)  | 0.0165 (2)                       |
| O2  | 0.69543 (9)  | 0.48204 (12)  | 0.38079 (8)  | 0.0166 (2)                       |
| O3  | 0.53857 (9)  | 0.75596 (13)  | 0.16600 (8)  | 0.0193 (2)                       |
| O4  | 0.66107 (9)  | 0.61847 (12)  | 0.25149 (8)  | 0.0178 (2)                       |
| H4  | 0.679 (3)    | 0.554 (4)     | 0.318 (2)    | 0.095 (12)*                      |
| N1  | 0.46880 (10) | 0.77905 (13)  | 0.43864 (10) | 0.0148 (3)                       |
| C1  | 0.78294 (12) | -0.06194 (15) | 0.50936 (10) | 0.0127 (3)                       |
| C2  | 0.73968 (12) | -0.10399 (16) | 0.56721 (11) | 0.0146 (3)                       |
| H2  | 0.6994       | -0.0453       | 0.5842       | 0.018*                           |
| C3  | 0.75513 (13) | -0.23085 (17) | 0.60006 (11) | 0.0160 (3)                       |
| H3  | 0.7260       | -0.2587       | 0.6398       | 0.019*                           |
| C4  | 0.81319 (13) | -0.31702 (16) | 0.57480 (11) | 0.0158 (3)                       |
| H4A | 0.8246       | -0.4036       | 0.5979       | 0.019*                           |
| C5  | 0.85461 (14) | -0.27720 (17) | 0.51589 (12) | 0.0175 (3)                       |
| H5  | 0.8930       | -0.3372       | 0.4977       | 0.021*                           |
| C6  | 0.84020 (13) | -0.14963 (17) | 0.48331 (11) | 0.0166 (3)                       |
| H6  | 0.8693       | -0.1223       | 0.4434       | 0.020*                           |
| C7  | 0.77577 (12) | 0.10772 (15)  | 0.36598 (10) | 0.0122 (3)                       |
| C8  | 0.69787 (12) | 0.04132 (16)  | 0.29445 (11) | 0.0159 (3)                       |
| H8  | 0.6462       | -0.0053       | 0.3047       | 0.019*                           |
| C9  | 0.69546 (13) | 0.04295 (17)  | 0.20850 (11) | 0.0176 (3)                       |
| H9  | 0.6430       | -0.0036       | 0.1604       | 0.021*                           |
| C10 | 0.76977 (13) | 0.11260 (17)  | 0.19307 (11) | 0.0189 (3)                       |
| H10 | 0.7670       | 0.1157        | 0.1339       | 0.023*                           |
| C11 | 0.84788 (14) | 0.17757 (18)  | 0.26345 (12) | 0.0211 (4)                       |

|     |              |              |              |            |
|-----|--------------|--------------|--------------|------------|
| H11 | 0.8992       | 0.2241       | 0.2527       | 0.025*     |
| C12 | 0.85148 (13) | 0.17507 (17) | 0.35027 (11) | 0.0173 (3) |
| H12 | 0.9055       | 0.2193       | 0.3986       | 0.021*     |
| C13 | 0.88689 (12) | 0.18607 (16) | 0.55374 (11) | 0.0132 (3) |
| C14 | 0.89652 (13) | 0.32173 (17) | 0.54761 (11) | 0.0155 (3) |
| H14 | 0.8419       | 0.3704       | 0.5029       | 0.019*     |
| C15 | 0.98636 (13) | 0.38491 (17) | 0.60728 (11) | 0.0185 (3) |
| H15 | 0.9934       | 0.4765       | 0.6024       | 0.022*     |
| C16 | 1.06569 (13) | 0.31447 (18) | 0.67385 (12) | 0.0191 (3) |
| H16 | 1.1267       | 0.3578       | 0.7145       | 0.023*     |
| C17 | 1.05556 (13) | 0.18084 (18) | 0.68081 (11) | 0.0186 (3) |
| H17 | 1.1096       | 0.1328       | 0.7266       | 0.022*     |
| C18 | 0.96635 (12) | 0.11650 (17) | 0.62095 (11) | 0.0158 (3) |
| H18 | 0.9598       | 0.0249       | 0.6261       | 0.019*     |
| C19 | 0.63603 (11) | 0.51340 (15) | 0.41887 (10) | 0.0127 (3) |
| C20 | 0.57237 (11) | 0.63798 (15) | 0.39057 (10) | 0.0119 (3) |
| C21 | 0.52976 (12) | 0.67522 (16) | 0.44994 (11) | 0.0130 (3) |
| H21 | 0.5453       | 0.6228       | 0.5022       | 0.016*     |
| C22 | 0.44636 (13) | 0.85140 (18) | 0.36360 (12) | 0.0191 (3) |
| H22 | 0.4028       | 0.9256       | 0.3536       | 0.023*     |
| C23 | 0.48410 (13) | 0.82197 (17) | 0.30104 (12) | 0.0177 (3) |
| H23 | 0.4657       | 0.8755       | 0.2489       | 0.021*     |
| C24 | 0.54897 (12) | 0.71481 (15) | 0.31276 (11) | 0.0124 (3) |
| C25 | 0.58450 (12) | 0.69438 (16) | 0.23706 (11) | 0.0140 (3) |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Ag1 | 0.01300 (7)  | 0.01372 (7)  | 0.01545 (7)  | 0.00322 (4)  | 0.00782 (5)  | 0.00133 (4)  |
| P1  | 0.01137 (17) | 0.01234 (19) | 0.01010 (18) | 0.00181 (14) | 0.00492 (15) | 0.00062 (14) |
| O1  | 0.0218 (6)   | 0.0127 (6)   | 0.0151 (6)   | 0.0016 (4)   | 0.0081 (5)   | 0.0017 (4)   |
| O2  | 0.0175 (5)   | 0.0186 (6)   | 0.0147 (5)   | 0.0052 (5)   | 0.0077 (5)   | 0.0007 (5)   |
| O3  | 0.0168 (6)   | 0.0290 (7)   | 0.0106 (5)   | -0.0030 (5)  | 0.0043 (5)   | 0.0032 (5)   |
| O4  | 0.0212 (6)   | 0.0192 (6)   | 0.0168 (6)   | 0.0025 (5)   | 0.0118 (5)   | 0.0012 (5)   |
| N1  | 0.0136 (6)   | 0.0163 (7)   | 0.0156 (7)   | 0.0025 (5)   | 0.0074 (5)   | 0.0031 (5)   |
| C1  | 0.0123 (7)   | 0.0135 (7)   | 0.0110 (7)   | 0.0007 (6)   | 0.0037 (6)   | 0.0004 (6)   |
| C2  | 0.0143 (7)   | 0.0170 (8)   | 0.0134 (7)   | 0.0018 (6)   | 0.0067 (6)   | -0.0013 (6)  |
| C3  | 0.0154 (7)   | 0.0197 (8)   | 0.0124 (7)   | -0.0016 (6)  | 0.0056 (6)   | 0.0011 (6)   |
| C4  | 0.0160 (7)   | 0.0136 (8)   | 0.0139 (7)   | -0.0004 (6)  | 0.0026 (6)   | 0.0007 (6)   |
| C5  | 0.0184 (8)   | 0.0162 (8)   | 0.0188 (8)   | 0.0035 (6)   | 0.0088 (7)   | -0.0010 (6)  |
| C6  | 0.0182 (8)   | 0.0166 (8)   | 0.0175 (8)   | 0.0024 (6)   | 0.0101 (7)   | 0.0019 (6)   |
| C7  | 0.0133 (7)   | 0.0138 (8)   | 0.0103 (7)   | 0.0041 (6)   | 0.0057 (6)   | 0.0021 (6)   |
| C8  | 0.0131 (7)   | 0.0181 (8)   | 0.0155 (8)   | 0.0009 (6)   | 0.0053 (6)   | 0.0005 (6)   |
| C9  | 0.0172 (7)   | 0.0191 (8)   | 0.0123 (7)   | 0.0038 (6)   | 0.0023 (6)   | -0.0025 (6)  |
| C10 | 0.0262 (8)   | 0.0205 (9)   | 0.0119 (7)   | 0.0066 (7)   | 0.0097 (7)   | 0.0016 (6)   |
| C11 | 0.0255 (9)   | 0.0229 (9)   | 0.0202 (9)   | -0.0037 (7)  | 0.0148 (7)   | -0.0001 (7)  |
| C12 | 0.0178 (8)   | 0.0188 (8)   | 0.0153 (8)   | -0.0036 (6)  | 0.0070 (6)   | -0.0026 (6)  |
| C13 | 0.0127 (7)   | 0.0176 (8)   | 0.0101 (7)   | 0.0018 (6)   | 0.0056 (6)   | -0.0011 (6)  |

|     |            |            |            |             |            |             |
|-----|------------|------------|------------|-------------|------------|-------------|
| C14 | 0.0152 (7) | 0.0158 (8) | 0.0141 (7) | 0.0027 (6)  | 0.0047 (6) | 0.0004 (6)  |
| C15 | 0.0186 (8) | 0.0180 (8) | 0.0188 (8) | -0.0004 (6) | 0.0078 (7) | -0.0018 (7) |
| C16 | 0.0158 (8) | 0.0246 (9) | 0.0146 (8) | -0.0008 (7) | 0.0041 (6) | -0.0043 (7) |
| C17 | 0.0161 (8) | 0.0245 (9) | 0.0128 (8) | 0.0057 (7)  | 0.0037 (6) | 0.0006 (6)  |
| C18 | 0.0161 (7) | 0.0177 (8) | 0.0139 (7) | 0.0044 (6)  | 0.0066 (6) | 0.0011 (6)  |
| C19 | 0.0109 (7) | 0.0133 (8) | 0.0098 (7) | -0.0009 (6) | 0.0007 (6) | -0.0026 (6) |
| C20 | 0.0092 (6) | 0.0132 (7) | 0.0114 (7) | -0.0010 (6) | 0.0027 (6) | -0.0005 (6) |
| C21 | 0.0117 (7) | 0.0143 (7) | 0.0119 (7) | -0.0008 (6) | 0.0041 (6) | 0.0016 (6)  |
| C22 | 0.0178 (8) | 0.0194 (9) | 0.0227 (8) | 0.0071 (7)  | 0.0113 (7) | 0.0076 (7)  |
| C23 | 0.0161 (8) | 0.0213 (9) | 0.0165 (8) | 0.0038 (6)  | 0.0078 (6) | 0.0083 (7)  |
| C24 | 0.0098 (7) | 0.0156 (8) | 0.0108 (7) | -0.0023 (6) | 0.0035 (6) | -0.0005 (6) |
| C25 | 0.0133 (7) | 0.0179 (8) | 0.0110 (7) | -0.0063 (6) | 0.0054 (6) | -0.0031 (6) |

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

|                         |             |             |             |
|-------------------------|-------------|-------------|-------------|
| Ag1—P1                  | 2.3531 (4)  | C8—C9       | 1.388 (2)   |
| Ag1—O1                  | 2.451 (1)   | C8—H8       | 0.9500      |
| Ag1—O3 <sup>i</sup>     | 2.481 (1)   | C9—C10      | 1.386 (2)   |
| Ag1—N1 <sup>ii</sup>    | 2.253 (1)   | C9—H9       | 0.9500      |
| P1—C1                   | 1.8175 (16) | C10—C11     | 1.383 (3)   |
| P1—C7                   | 1.8222 (15) | C10—H10     | 0.9500      |
| P1—C13                  | 1.8248 (17) | C11—C12     | 1.396 (2)   |
| O1—C19                  | 1.2353 (19) | C11—H11     | 0.9500      |
| O2—C19                  | 1.2858 (18) | C12—H12     | 0.9500      |
| O3—C25                  | 1.235 (2)   | C13—C18     | 1.391 (2)   |
| O3—Ag1 <sup>iii</sup>   | 2.4814 (12) | C13—C14     | 1.404 (2)   |
| O4—C25                  | 1.277 (2)   | C14—C15     | 1.394 (2)   |
| O4—H4                   | 1.20 (4)    | C14—H14     | 0.9500      |
| N1—C21                  | 1.335 (2)   | C15—C16     | 1.390 (2)   |
| N1—C22                  | 1.348 (2)   | C15—H15     | 0.9500      |
| N1—Ag1 <sup>ii</sup>    | 2.2531 (13) | C16—C17     | 1.386 (2)   |
| C1—C6                   | 1.396 (2)   | C16—H16     | 0.9500      |
| C1—C2                   | 1.397 (2)   | C17—C18     | 1.395 (2)   |
| C2—C3                   | 1.387 (2)   | C17—H17     | 0.9500      |
| C2—H2                   | 0.9500      | C18—H18     | 0.9500      |
| C3—C4                   | 1.387 (2)   | C19—C20     | 1.519 (2)   |
| C3—H3                   | 0.9500      | C20—C21     | 1.397 (2)   |
| C4—C5                   | 1.386 (2)   | C20—C24     | 1.408 (2)   |
| C4—H4A                  | 0.9500      | C21—H21     | 0.9500      |
| C5—C6                   | 1.392 (2)   | C22—C23     | 1.374 (2)   |
| C5—H5                   | 0.9500      | C22—H22     | 0.9500      |
| C6—H6                   | 0.9500      | C23—C24     | 1.395 (2)   |
| C7—C12                  | 1.393 (2)   | C23—H23     | 0.9500      |
| C7—C8                   | 1.398 (2)   | C24—C25     | 1.536 (2)   |
| P1—Ag1—O1               | 113.12 (3)  | C9—C10—H10  | 119.9       |
| P1—Ag1—O3 <sup>i</sup>  | 122.95 (3)  | C10—C11—C12 | 120.18 (16) |
| P1—Ag1—N1 <sup>ii</sup> | 140.10 (4)  | C10—C11—H11 | 119.9       |

|                                       |             |                |              |
|---------------------------------------|-------------|----------------|--------------|
| O1—Ag1—O3 <sup>i</sup>                | 81.06 (4)   | C12—C11—H11    | 119.9        |
| O1—Ag1—N1 <sup>ii</sup>               | 87.84 (4)   | C7—C12—C11     | 119.94 (16)  |
| O3 <sup>i</sup> —Ag1—N1 <sup>ii</sup> | 92.57 (4)   | C7—C12—H12     | 120.0        |
| C1—P1—C7                              | 104.65 (7)  | C11—C12—H12    | 120.0        |
| C1—P1—C13                             | 104.18 (7)  | C18—C13—C14    | 119.46 (15)  |
| C7—P1—C13                             | 105.28 (7)  | C18—C13—P1     | 122.35 (13)  |
| C1—P1—Ag1                             | 113.79 (5)  | C14—C13—P1     | 118.16 (12)  |
| C7—P1—Ag1                             | 115.70 (5)  | C15—C14—C13    | 119.88 (15)  |
| C13—P1—Ag1                            | 112.16 (5)  | C15—C14—H14    | 120.1        |
| C19—O1—Ag1                            | 123.60 (10) | C13—C14—H14    | 120.1        |
| C25—O3—Ag1 <sup>iii</sup>             | 132.51 (11) | C16—C15—C14    | 120.26 (16)  |
| C25—O4—H4                             | 110.1 (17)  | C16—C15—H15    | 119.9        |
| C21—N1—C22                            | 116.87 (14) | C14—C15—H15    | 119.9        |
| C21—N1—Ag1 <sup>ii</sup>              | 117.57 (10) | C17—C16—C15    | 119.88 (16)  |
| C22—N1—Ag1 <sup>ii</sup>              | 123.80 (11) | C17—C16—H16    | 120.1        |
| C6—C1—C2                              | 119.38 (15) | C15—C16—H16    | 120.1        |
| C6—C1—P1                              | 121.99 (12) | C16—C17—C18    | 120.31 (16)  |
| C2—C1—P1                              | 118.58 (12) | C16—C17—H17    | 119.8        |
| C3—C2—C1                              | 120.45 (14) | C18—C17—H17    | 119.8        |
| C3—C2—H2                              | 119.8       | C13—C18—C17    | 120.19 (16)  |
| C1—C2—H2                              | 119.8       | C13—C18—H18    | 119.9        |
| C2—C3—C4                              | 119.87 (15) | C17—C18—H18    | 119.9        |
| C2—C3—H3                              | 120.1       | O1—C19—O2      | 122.82 (15)  |
| C4—C3—H3                              | 120.1       | O1—C19—C20     | 117.60 (13)  |
| C5—C4—C3                              | 120.17 (16) | O2—C19—C20     | 119.58 (14)  |
| C5—C4—H4A                             | 119.9       | C21—C20—C24    | 117.80 (14)  |
| C3—C4—H4A                             | 119.9       | C21—C20—C19    | 113.46 (13)  |
| C4—C5—C6                              | 120.25 (15) | C24—C20—C19    | 128.70 (14)  |
| C4—C5—H5                              | 119.9       | N1—C21—C20     | 124.81 (14)  |
| C6—C5—H5                              | 119.9       | N1—C21—H21     | 117.6        |
| C5—C6—C1                              | 119.86 (15) | C20—C21—H21    | 117.6        |
| C5—C6—H6                              | 120.1       | N1—C22—C23     | 122.51 (15)  |
| C1—C6—H6                              | 120.1       | N1—C22—H22     | 118.7        |
| C12—C7—C8                             | 119.29 (14) | C23—C22—H22    | 118.7        |
| C12—C7—P1                             | 123.54 (12) | C22—C23—C24    | 121.11 (15)  |
| C8—C7—P1                              | 117.08 (11) | C22—C23—H23    | 119.4        |
| C9—C8—C7                              | 120.46 (15) | C24—C23—H23    | 119.4        |
| C9—C8—H8                              | 119.8       | C23—C24—C20    | 116.89 (14)  |
| C7—C8—H8                              | 119.8       | C23—C24—C25    | 115.03 (14)  |
| C10—C9—C8                             | 119.84 (15) | C20—C24—C25    | 128.06 (14)  |
| C10—C9—H9                             | 120.1       | O3—C25—O4      | 123.62 (15)  |
| C8—C9—H9                              | 120.1       | O3—C25—C24     | 117.47 (14)  |
| C11—C10—C9                            | 120.26 (15) | O4—C25—C24     | 118.88 (14)  |
| C11—C10—H10                           | 119.9       |                |              |
| N1 <sup>ii</sup> —Ag1—P1—C1           | 43.84 (8)   | C1—P1—C13—C18  | 1.57 (15)    |
| O1—Ag1—P1—C1                          | 160.37 (6)  | C7—P1—C13—C18  | -108.28 (14) |
| O3 <sup>i</sup> —Ag1—P1—C1            | -105.31 (7) | Ag1—P1—C13—C18 | 125.08 (12)  |

|                              |              |                                |              |
|------------------------------|--------------|--------------------------------|--------------|
| N1 <sup>ii</sup> —Ag1—P1—C7  | 165.10 (8)   | C1—P1—C13—C14                  | −176.52 (12) |
| O1—Ag1—P1—C7                 | −78.37 (7)   | C7—P1—C13—C14                  | 73.64 (14)   |
| O3 <sup>i</sup> —Ag1—P1—C7   | 15.96 (7)    | Ag1—P1—C13—C14                 | −53.00 (13)  |
| N1 <sup>ii</sup> —Ag1—P1—C13 | −74.11 (8)   | C18—C13—C14—C15                | 1.6 (2)      |
| O1—Ag1—P1—C13                | 42.42 (6)    | P1—C13—C14—C15                 | 179.71 (12)  |
| O3 <sup>i</sup> —Ag1—P1—C13  | 136.75 (7)   | C13—C14—C15—C16                | −1.1 (2)     |
| N1 <sup>ii</sup> —Ag1—O1—C19 | −153.23 (12) | C14—C15—C16—C17                | 0.1 (3)      |
| P1—Ag1—O1—C19                | 61.82 (12)   | C15—C16—C17—C18                | 0.4 (3)      |
| O3 <sup>i</sup> —Ag1—O1—C19  | −60.29 (12)  | C14—C13—C18—C17                | −1.0 (2)     |
| C7—P1—C1—C6                  | 28.81 (15)   | P1—C13—C18—C17                 | −179.09 (12) |
| C13—P1—C1—C6                 | −81.49 (14)  | C16—C17—C18—C13                | 0.1 (2)      |
| Ag1—P1—C1—C6                 | 156.05 (12)  | Ag1—O1—C19—O2                  | −41.8 (2)    |
| C7—P1—C1—C2                  | −153.99 (12) | Ag1—O1—C19—C20                 | 138.75 (11)  |
| C13—P1—C1—C2                 | 95.70 (13)   | O1—C19—C20—C21                 | 12.9 (2)     |
| Ag1—P1—C1—C2                 | −26.75 (14)  | O2—C19—C20—C21                 | −166.63 (14) |
| C6—C1—C2—C3                  | 1.3 (2)      | O1—C19—C20—C24                 | −164.64 (15) |
| P1—C1—C2—C3                  | −175.96 (12) | O2—C19—C20—C24                 | 15.9 (2)     |
| C1—C2—C3—C4                  | −0.5 (2)     | C22—N1—C21—C20                 | 0.8 (2)      |
| C2—C3—C4—C5                  | −0.9 (2)     | Ag1 <sup>ii</sup> —N1—C21—C20  | 166.32 (12)  |
| C3—C4—C5—C6                  | 1.5 (3)      | C24—C20—C21—N1                 | −0.4 (2)     |
| C4—C5—C6—C1                  | −0.7 (3)     | C19—C20—C21—N1                 | −178.22 (14) |
| C2—C1—C6—C5                  | −0.7 (2)     | C21—N1—C22—C23                 | −0.4 (3)     |
| P1—C1—C6—C5                  | 176.45 (13)  | Ag1 <sup>ii</sup> —N1—C22—C23  | −164.87 (13) |
| C1—P1—C7—C12                 | −119.18 (14) | N1—C22—C23—C24                 | −0.5 (3)     |
| C13—P1—C7—C12                | −9.67 (16)   | C22—C23—C24—C20                | 0.9 (2)      |
| Ag1—P1—C7—C12                | 114.76 (13)  | C22—C23—C24—C25                | 179.83 (15)  |
| C1—P1—C7—C8                  | 64.36 (13)   | C21—C20—C24—C23                | −0.4 (2)     |
| C13—P1—C7—C8                 | 173.86 (12)  | C19—C20—C24—C23                | 176.96 (15)  |
| Ag1—P1—C7—C8                 | −61.70 (13)  | C21—C20—C24—C25                | −179.24 (14) |
| C12—C7—C8—C9                 | −0.4 (2)     | C19—C20—C24—C25                | −1.8 (3)     |
| P1—C7—C8—C9                  | 176.25 (12)  | Ag1 <sup>iii</sup> —O3—C25—O4  | 93.68 (18)   |
| C7—C8—C9—C10                 | −1.0 (2)     | Ag1 <sup>iii</sup> —O3—C25—C24 | −88.43 (17)  |
| C8—C9—C10—C11                | 1.7 (3)      | C23—C24—C25—O3                 | −13.6 (2)    |
| C9—C10—C11—C12               | −1.0 (3)     | C20—C24—C25—O3                 | 165.22 (15)  |
| C8—C7—C12—C11                | 1.1 (2)      | C23—C24—C25—O4                 | 164.40 (15)  |
| P1—C7—C12—C11                | −175.27 (13) | C20—C24—C25—O4                 | −16.8 (2)    |
| C10—C11—C12—C7               | −0.5 (3)     |                                |              |

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| $D\cdots H\cdots A$ | $D—H$    | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|---------------------|----------|-------------|-------------|---------------|
| O4—H4 $\cdots$ O2   | 1.20 (4) | 1.20 (4)    | 2.401 (2)   | 176 (4)       |