

Novel three-dimensional coordination polymer of 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatriacyclo)[3.3.1.1^{3,7}]decane with silver(I)-tetrafluoroborate

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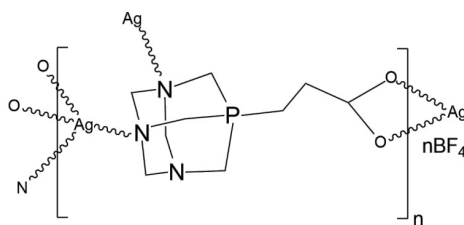
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Abstract

An Ag(I)-based coordination polymer (CP) was synthesized in an aqueous solution of the zwitterionic 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatriacyclo)[3.3.1.1^{3,7}]decane (L) and AgBF₄ with exclusion of light at room temperature. The colourless and light insensitive CP crystallized in the monoclinic space group *Cc*. The asymmetric unit consists of an Ag(I) cation, the zwitterionic L ligand and a BF₄⁻ counter ion. Each Ag(I) ion is coordinated by two carboxylate oxygen atoms in chelate coordination mode, as well as one of the nitrogen atoms of two neighboring L. The crystal structure of CP was classified as a unique 3D arrangement. CP was also characterized in aqueous solutions by multinuclear NMR and HRMS spectroscopies and elemental analysis.



1. Chemical context

The architectures and antimicrobial properties of self-assembly silver-based coordination polymers or MOFs (Metal-Organic Frameworks), bridged by phosphatrotropines, have been widely studied [Guerriero *et al.*, 2018]. According to our previous studies, the aqueous reaction of zwitterionic 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatriacyclo)[3.3.1.1^{3,7}]decane (L) with AgX (X=PF₆, SO₃C₆H₄CH₃, SO₃CF₃) yielded various 1D Ag-based coordination polymers [Udvardy *et al.*, 2021]. The architectures of these Ag(I)-complexes depend on their counter ions and the position of the ligand, which contain both rigid and flexible molecular moieties.

Herein, we report the crystal structure of CP prepared by aqueous reaction of 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatriacyclo)[3.3.1.1^{3,7}]decane and AgBF₄ with exclusion of light at 5°C (**Fig. 1**). The colourless crystals of CP were isolated by filtration, were dissolved in water and characterized by ¹H-, ¹³C-, ³¹P-NMR spectroscopy, ESI mass spectrometry, as well as by elemental analysis.

The chemical shift of the phosphorus atom in CP ($\delta = -37.5$ ppm in D₂O) – was the same as that in the free ligand. Similar to the hexafluorophosphate, tosylate (tos) and triflate (OTf) derivatives [Udvardy *et al.*, 2021], the ¹H-NMR spectrum showed differences between the P⁺-CH₂-N and N-CH₂-N signals, which clearly indicated the coordination of silver ions to the nitrogen donor atoms of the L.

The most intense ESI-MS signals of **CP** (aqueous solution, positive ion mode) were observed at m/z 252.0878 ($[\text{L}+\text{Na}]^+$, $\text{C}_9\text{H}_{16}\text{N}_3\text{NaO}_2\text{P}$, calculated. 252.0872), 336.0026 ($[\text{L}+\text{Ag}]^+$, $\text{C}_9\text{H}_{16}\text{N}_3\text{AgO}_2\text{P}$, calculated 336.0026), and 565.1009 ($[\text{2L}+\text{Ag}]^+$, $\text{C}_{18}\text{H}_{32}\text{N}_6\text{NaO}_4\text{P}_2$, calculated 565.1005). Similar ions were detected for **CP** formed with AgPF_6 , $\text{AgSO}_3\text{C}_6\text{H}_4\text{CH}_3$, AgSO_3CF_3 and PTA in aqueous solutions.

Figure 1

2. Structural commentary

The molecular structure of the title compound is shown in **Fig. 2**. **CP** crystallized in the monoclinic Cc space group. The asymmetric unit consists of a silver(I)-cation, a zwitterionic **L** ligand and a BF_4^- counter ion, in which the N, N', O, O' coordination mode of the silver(I)-ions creates a 3D coordination architecture (**Fig. 2**).

Figure 2

In the **CP**, the central Ag^+ ion is coordinated by an **L** ligand via two carboxylate oxygen atoms ($\text{Ag1}^2-\text{O11}=2.594$ (9) Å and $\text{Ag1}^2-\text{O12}=2.298$ (8) Å) and two nitrogen atoms from two adjacent PTA moieties of **L** ($\text{Ag1}-\text{N1}=2.225$ (7) Å and $\text{Ag1}^1-\text{N3}=2.505$ (7) Å). The $\text{N1}-\text{Ag}-\text{N3}^3$ and $\text{O11}^4-\text{Ag}-\text{O12}^4$ bond angles are 119.6 (3)° and 52.9 (2)°, respectively. The selected bond lengths and bond angles are presented in the Geometric parameters part in SI. The coordination geometry shows a distorted tetrahedral shape ($\tau_4=0.65$ and $\tau_4^1=0.66$ [Yang *et al.*, 2007], [Okuniewski *et al.*, 2015]), in which the Ag(I) is located at the center. Among the 3D polymer backbones, the voids are occupied by BF_4^- counter ions (**Fig. 3**). The chemical composition was also determined by elemental analysis, which shows a good agreement with the SC-XRD results (see in the Synthesis and crystallization chapter).

3. Supramolecular features

Because of the lack of primary H-donor groups no classic hydrogen bonds were found in the crystal lattice in the title coordination polymer. The main intermolecular interactions among the molecules in the crystal are only weak $\text{C}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{O}$ type hydrogen bonds. The BF_4^- anion is generally classified as a non-coordinating anion, owing to its weak Lewis base properties [Grabowski, 2020]. These secondary interactions play a major role in stabilizing the crystal lattice by connecting the molecular units to each other, which result in a 3D coordination polymer. All the fluorine atoms of a BF_4^- counter ion are connected to at least one of a $\text{C}-\text{H}$ hydrogen atom by a weak $\text{C}-\text{H}\cdots\text{F}$ type hydrogen bond. The shortest $\text{C}-\text{H}\cdots\text{F}$ distance is the $\text{C2}-\text{H2B}\cdots\text{F3}$ interaction ($\text{C2}-\text{F3} = 3.183$ (13) Å), where the F3 atom of the BF_4^- counter ion is also able to coordinate to the central Ag^+ ion with a distance of 3.010 (11) Å (**Fig. 3**). This ionic attraction between the Ag^+ and BF_4^- is strong enough to arrange even a part of the whole complex molecule and form a bent 3D structure. In comparison, the value of the longest $\text{C}-\text{H}\cdots\text{F}$ distance is 3.417 (14) Å ($\text{C4}-\text{H4B}\cdots\text{F2}$, **Fig. 3**) owing to the rigid PTA cage which is unable to change its conformation. There are numerous examples in the literature, where the $\text{C}-\text{H}\cdots\text{F}$ distances were investigated in the presence of BF_4^- counter ions [i.e. BIXBIT03 and SUXHID01]. In case of the *bis*(μ_2 -1,1'-naphthalene-1,8-diyl-bis(1H-pyrazole))-tris(acetonitrile)-di-silver(I)-bis(BF_4) acetonitrile solvate structure (Ref Code: OGINOI) [Liddle *et al.*, 2009] it was found that the typical $\text{C}\cdots\text{F}$ distances are between 3.179 (2) - 3.406 (3) Å, which shows a good agreement with our results. The carboxylate oxygen atoms are also able to form weak $\text{C}-\text{H}\cdots\text{O}$ type interactions with the $\text{C}-\text{H}$ atoms of the complex molecule. Their atomic distances can also be compared to the $\text{C}-\text{H}\cdots\text{F}$ secondary interactions. An intramolecular hydrogen bond also helps to form a bent 3D structure in crystal **CP** ($\text{C2}-\text{O12} = 2.812$ (12)Å). For the selected hydrogen bond distances and angles see **Fig. 3b**, and **Table 1**. The considerably high calculated density ($2.102 \text{ Mg}\cdot\text{m}^{-3}$) and KPI (Kitaigorodskii packing index=74.2%) [Spek, 2020] indicate the tight packing arrangement of the molecules, resulting in no residual solvent-accessible voids in the crystal lattice.

Figure 3

Table 1

4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.42, Sept. 2021 update; [Groom *et al.*, 2016]) disclosed the zwitterionic 7-(2-carboxyethyl)-1,3,5-triaza-7-phosphoniatricyclo[3.3.1.1^{3,7}]decane dihydrate (**L**) (SIJPOR, [Tang *et al.*, 2007]) and three 1D Ag-based coordination polymers containing **L**. These are the [Ag(μ_3 -**L**- κ^3 N:O:O')]_n(PF₆)_n (UPUCAM, [Udvardy *et al.*, 2021]), [Ag(OTf)(μ_3 -**L**- κ^3 N:O:O')]_n (UPUCIU, [Udvardy *et al.*, 2021]) and the [Ag(tos)(μ_3 -**L**- κ^3 N:O:O')]_n·nH₂O (UPUCEQ, [Udvardy *et al.*, 2021]). While in the cases of UPUCAM, UPUCIU and UPUCEQ only 1D polymers were obtained, the Ag(I) complex – in case of the present **CP** – was able to form a 3D coordination polymer owing to the relatively small size of the BF₄⁻ counter ion which is able to occupy a smaller space compared to the PF₆⁻, triflate or tosylate anions. These results show how a counter ion can influence the packing arrangement and the coordination mode of an [(Ag-L)-X] type polymer compound.

5. Synthesis and crystallization

Water-soluble PTA [Daigle, 1998] and 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)-[3.3.1.1^{3,7}]decane(**L**) [Tang *et al.*, 2007], [Udvardy *et al.*, 2021] were prepared according to literature methods.

CP: With the exclusion of light, 4 mL aqueous solution containing 194.7 mg (1 mmol) AgBF₄ was added to an aqueous solution (4 mL) of **L** (100 mg, 0.44 mmol). The reaction mixture was stored at 5 °C. After two days, **CP** was formed as colourless crystals, which were separated by filtration and dried. Yield (based on **L**) 112 mg, 60 %. ¹H NMR (360 MHz, D₂O, 25 °C) δ 4.73–4.37 (*m*, 12H, ⁺P-CH₂-N, N-CH₂-N), 2.58 (*dt*, *J*=24, 7 Hz, 2H, P⁺-CH₂-CH₂-COO), 2.44–2.22 (*m*, 2H, P⁺-CH₂-CH₂-COO) ppm. ¹³C{¹H} NMR (90 MHz, D₂O, 25 °C) δ 179.5 (*s*, COO⁻), 71.5 (*d*, ³J_{PC} = 8 Hz, N-CH₂-N), 49.1 (*d*, ¹J_{PC} = 37 Hz, ⁺P-CH₂-N), 29.0 (*d*, ²J_{PC} = 7 Hz, P⁺-CH₂-CH₂-COO⁻), 18.5 (*d*, ¹J_{PC} = 35 Hz, P⁺-CH₂-CH₂-COO⁻) ppm. ³¹P{¹H} NMR (145 MHz, D₂O, 25 °C) δ -37.5 (*s*) ppm. Elemental analysis: C₉H₁₆AgBF₄N₃O₂P (423.89): calculated C 25.05, H 3.80, N 9.91; found C 25.64, H 4.10, N 9.95.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in **Table 2**. All hydrogen atoms of the **CP** complex were positioned geometrically and refined using a riding model, with C—H = 0.97 Å.

Table 1

Table 1. Selected hydrogen bond distances (Å) and angles (°) in crystal CP

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···F2	0.97	2.40	3.201 (13)	140
C1—H1B···O11 ⁽ⁱ⁾	0.97	2.49	3.213 (12)	131
C2—H2A···O11 ⁽ⁱ⁾	0.97	2.56	3.254 (12)	129
C2—H2B···F3 ⁽ⁱⁱ⁾	0.97	2.35	3.183 (13)	143
C2—H2B···O12	0.97	2.22	2.812 (12)	118
C3—H3A···F4 ⁽ⁱⁱⁱ⁾	0.97	2.45	3.290 (15)	145
C3—H3B···F2	0.97	2.51	3.283 (12)	136
C4—H4A···F4 ^(iv)	0.97	2.43	3.298 (12)	148
C4—H4B···F2 ^(v)	0.97	2.51	3.417 (14)	155
C5—H5A···F1	0.97	2.49	3.370 (13)	151
C5—H5B···F4 ^(iv)	0.97	2.54	3.373 (14)	144

C6—H6B···F2 ^(iv)	0.97	2.34	3.314 (13)	177
C7—H7A···O11 ⁽ⁱⁱ⁾	0.97	2.48	3.165 (13)	128
C7—H7A···F1 ^(vi)	0.97	2.37	3.137 (12)	135

Symmetry codes: ⁽ⁱ⁾ x, -1-y, -1/2+z; ⁽ⁱⁱ⁾ -1+x, y, z; ⁽ⁱⁱⁱ⁾ -1/2+x, -1/2-y, 1/2+z; ^(iv) -1/2+x, 1/2+y, z; ^(v) -1/2+x, -1/2-y, -1/2+z; ^(vi) -1/2+x, -1/2+y, z

Table 2

Experimental details

Crystal data	
Chemical formula	C ₉ H ₁₆ AgN ₃ O ₂ P·BF ₄
<i>M_r</i>	423.90
Crystal system, space group	Monoclinic, <i>Cc</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.116 (5), 12.186 (5), 10.979 (5)
β (°)	98.260 (5)
<i>V</i> (Å ³)	1339.4 (11)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.68
Crystal size (mm)	0.35 × 0.2 × 0.15
Data collection	
Diffractometer	Enraf Nonius CAD4
Absorption correction	ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) <i>Acta. Cryst.</i> A24, 351-359 Number of ψ scan sets used was 3 Theta correction was applied. Averaged transmission function was used. Fourier smoothing - Window value 5
<i>T_{min}</i> , <i>T_{max}</i>	0.558, 0.755
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	1358, 1313, 1299
<i>R_{int}</i>	0.009
(sin θ/λ) _{max} (Å ⁻¹)	0.605
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.048, 0.123, 1.13
No. of reflections	1313
No. of parameters	190
No. of restraints	2
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.20, -1.54
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower.
Absolute structure parameter	0.13 (6)

Computer programs: MACH3/PC (Enraf Nonius, 1992), PROFIT (Streltsov & Zavodnik, 1989), *SIR97* (Burla *et al.*, 2007), *SHELXL* (Sheldrick, 2015), Olex2 1.3 (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010).

Acknowledgements

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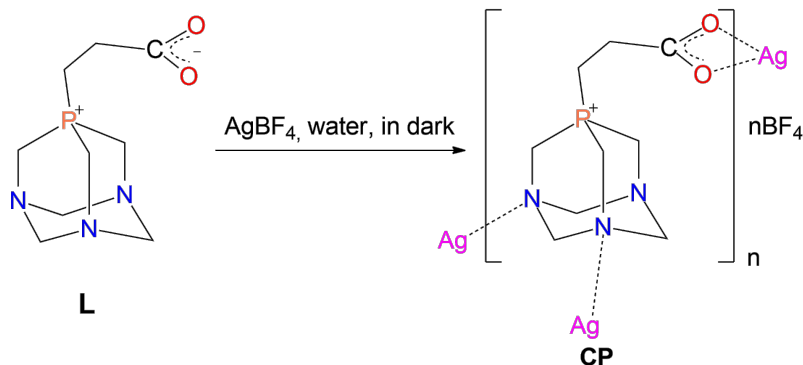
The financial support of the Hungarian National Research, Development and Innovation Office (FK-128333) is greatly acknowledged. Project no. TKP2020-NKA-04 has been implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the 2020-4.1.1-TKP2020 funding scheme. The research was supported by the EU and co-financed by the European Regional Development Fund under the projects GINOP-2.3.3-15-2016-00004 and GINOP 2.3.2-15-2016-00008.

Funding information

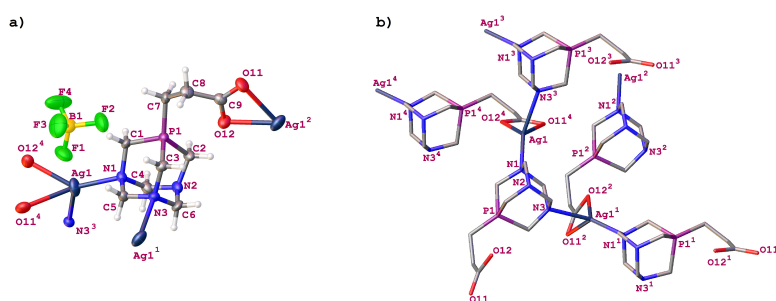
Funding for this research was provided by: Hungarian National Research, Development and Innovation Office (contract No. FK-128333); Development and Innovation Fund of Hungary (contract No. 2020-4.1.1-TKP2020, Project no. TKP2020-NKA-04); European Regional Development Fund (contract No. GINOP-2.3.3-15-2016-00004; contract No. GINOP 2.3.2-15-2016-00008).

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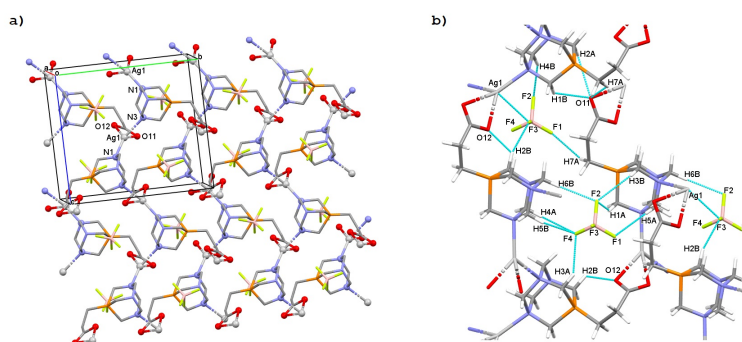
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Figure 1

[Schematic diagram of formation of the title compound.]


Figure 2

[(a) A view of the CP with the atomic labels. The atomic displacement ellipsoids are drawn at 50% probability level. (b) The coordination architecture of the CP with the atomic labels of the coordination sphere. Hydrogen atoms and BF_4^- -ions are omitted for clarity. (Symmetry codes: $^1+x, -y, 1/2+z$; $^2-1/2+x, -1/2-y, 1/2+z$; $^3+x, -y, -1/2+z$; $^41/2+x, -1/2-y, -1/2+z$.)]


Figure 3

[(a) Packing arrangement of the three-dimensional structure of the CP crystal viewed from the crystallographic "a" axes. The coordination sphere is labelled and highlighted by a ball and stick model. Hydrogen atoms are omitted for clarity. (b) Selected hydrogen bond geometry in CP showing the weak $C-H \cdots F$ and $C-H \cdots O$ secondary interactions, as well as the $Ag1-F3$ interaction. For symmetry codes see Table 1.]

supporting information

**Novel three-dimensional coordination polymer of 7-(2-carboxy-ethyl)-1,3,5-tri-
aza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane with silver(I)-tetrafluoroborate**

Antal Udvardy, Agnes Katho, Gabor Papp, Ferenc Joo and Gyula Tamas Gal*

Computing details

Data collection: MACH3/PC (Enraf Nonius, 1992); cell refinement: MACH3/PC (Enraf Nonius, 1992); data reduction: PROFIT (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SIR97* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 1.3 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 1.3 (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010).

(CP)*Crystal data*

C₉H₁₆AgN₃O₂P·BF₄
M_r = 423.90
 Monoclinic, *Cc*
a = 10.116 (5) Å
b = 12.186 (5) Å
c = 10.979 (5) Å
 β = 98.260 (5)°
V = 1339.4 (11) Å³
Z = 4

F(000) = 840
D_x = 2.102 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 9.1–17.2°
 μ = 1.68 mm⁻¹
T = 293 K
 Prism, colourless
 0.35 × 0.2 × 0.15 mm

Data collection

Enraf Nonius CAD4
 diffractometer
 profiled $\omega/2\theta$ scans
 Absorption correction: ψ scan
 North A.C.T., Phillips D.C. & Mathews F.S. (1968)
 Acta. Cryst. A24, 351-359 Number of ψ scan sets
 used was 3 Theta correction was applied. Averaged
 transmission function was used. Fourier smoothing -
 Window value 5
T_{min} = 0.558, *T_{max}* = 0.755

1358 measured reflections
 1313 independent reflections
 1299 reflections with *I* > 2 σ (*I*)
R_{int} = 0.009
 θ_{\max} = 25.5°, θ_{\min} = 3.1°
h = 0→12
k = 0→14
l = -13→13
 3 standard reflections every 184 reflections
 intensity decay: 2%

Refinement

Refinement on *F*²
 Least-squares matrix: full
R [*F*² > 2 σ (*F*²)] = 0.048
wR(*F*²) = 0.123
S = 1.13
 1313 reflections
 190 parameters
 2 restraints
 Primary atom site location: structure-invariant direct
 methods

Hydrogen site location: inferred from neighbouring
 sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 4.2725P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.20 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.54 \text{ e } \text{Å}^{-3}$
 Absolute structure: Classical Flack method preferred
 over Parsons because s.u. lower.
 Absolute structure parameter: 0.13 (6)

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.0444 (9)	-0.2414 (7)	-0.2977 (8)	0.0266 (16)
H1A	0.0509	-0.2557	-0.2849	0.032*
H1B	-0.0820	-0.2737	-0.3758	0.032*
C2	-0.2914 (9)	-0.2548 (7)	-0.2148 (9)	0.0302 (19)
H2A	-0.3323	-0.2870	-0.2918	0.036*
H2B	-0.3444	-0.2743	-0.1511	0.036*
C3	-0.0546 (9)	-0.2182 (7)	-0.0445 (8)	0.0284 (17)
H3A	-0.0975	-0.2365	0.0265	0.034*
H3B	0.0408	-0.2298	-0.0232	0.034*
C4	-0.2157 (10)	-0.1011 (7)	-0.3251 (9)	0.0317 (19)
H4A	-0.2311	-0.0233	-0.3392	0.038*
H4B	-0.2532	-0.1397	-0.3994	0.038*
C5	-0.0139 (9)	-0.0704 (7)	-0.1840 (8)	0.0269 (16)
H5A	0.0798	-0.0897	-0.1646	0.032*
H5B	-0.0192	0.0087	-0.1934	0.032*
C6	-0.2256 (10)	-0.0841 (8)	-0.1135 (10)	0.035 (2)
H6A	-0.2706	-0.1113	-0.0472	0.042*
H6B	-0.2418	-0.0057	-0.1203	0.042*
C7	-0.0690 (9)	-0.4434 (7)	-0.1593 (9)	0.0311 (19)
H7A	-0.1281	-0.4868	-0.2178	0.037*
H7B	0.0201	-0.4492	-0.1815	0.037*
C8	-0.0676 (11)	-0.4934 (8)	-0.0308 (9)	0.0340 (19)
H8A	-0.0322	-0.5674	-0.0306	0.041*
H8B	-0.0084	-0.4506	0.0285	0.041*
C9	-0.2032 (10)	-0.4967 (8)	0.0078 (8)	0.0298 (18)
N1	-0.0681 (7)	-0.1216 (6)	-0.3016 (6)	0.0253 (14)
N2	-0.2837 (7)	-0.1355 (6)	-0.2263 (8)	0.0323 (17)
N3	-0.0822 (8)	-0.1022 (6)	-0.0806 (7)	0.0278 (15)
O11	-0.2377 (9)	-0.5691 (6)	0.0750 (8)	0.0444 (17)
O12	-0.2793 (8)	-0.4175 (6)	-0.0319 (7)	0.0408 (16)
P1	-0.1202 (2)	-0.30412 (17)	-0.1746 (2)	0.0234 (4)
B1	0.3222 (13)	-0.2721 (10)	-0.1875 (11)	0.039 (2)
Ag1	0.03866 (7)	-0.03737 (7)	-0.43859 (7)	0.0488 (3)
F1	0.2885 (9)	-0.1691 (6)	-0.2226 (8)	0.062 (2)
F2	0.2229 (8)	-0.3155 (7)	-0.1250 (9)	0.066 (2)
F3	0.4361 (8)	-0.2745 (9)	-0.1032 (10)	0.082 (3)
F4	0.3319 (16)	-0.3351 (7)	-0.2846 (9)	0.104 (4)

Atomic displacement parameters (\AA^2) for (CP)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.025 (4)	0.023 (4)	0.033 (4)	0.002 (3)	0.013 (3)	-0.004 (3)

C2	0.022 (4)	0.022 (4)	0.047 (5)	0.005 (3)	0.006 (4)	0.005 (4)
C3	0.029 (4)	0.027 (4)	0.029 (4)	0.007 (3)	0.003 (3)	0.001 (3)
C4	0.028 (5)	0.027 (4)	0.040 (5)	-0.001 (3)	0.001 (4)	0.008 (3)
C5	0.029 (4)	0.025 (4)	0.027 (4)	-0.004 (3)	0.008 (3)	-0.003 (3)
C6	0.031 (5)	0.028 (4)	0.049 (5)	0.010 (4)	0.019 (4)	-0.001 (4)
C7	0.026 (4)	0.029 (4)	0.042 (5)	-0.001 (3)	0.016 (4)	0.000 (4)
C8	0.040 (5)	0.031 (4)	0.030 (4)	0.004 (4)	0.001 (4)	0.009 (4)
C9	0.033 (5)	0.026 (4)	0.028 (4)	-0.001 (4)	-0.002 (3)	0.002 (4)
N1	0.023 (3)	0.025 (3)	0.027 (3)	-0.001 (3)	0.003 (3)	0.005 (3)
N2	0.023 (4)	0.027 (4)	0.048 (5)	0.001 (3)	0.008 (3)	0.005 (3)
N3	0.030 (4)	0.021 (3)	0.033 (4)	0.001 (3)	0.009 (3)	-0.002 (3)
O11	0.049 (4)	0.034 (3)	0.052 (4)	-0.002 (3)	0.013 (3)	0.016 (3)
O12	0.042 (4)	0.037 (3)	0.046 (4)	0.011 (3)	0.016 (3)	0.012 (3)
P1	0.0211 (10)	0.0193 (9)	0.0306 (10)	0.0024 (8)	0.0065 (8)	0.0009 (8)
B1	0.043 (7)	0.038 (6)	0.037 (5)	0.009 (5)	0.012 (5)	0.008 (5)
Ag1	0.0465 (4)	0.0623 (5)	0.0407 (4)	-0.0149 (4)	0.0167 (3)	0.0099 (4)
F1	0.059 (4)	0.037 (3)	0.090 (6)	0.000 (3)	0.007 (4)	0.016 (3)
F2	0.040 (4)	0.064 (5)	0.096 (6)	-0.004 (3)	0.016 (4)	0.024 (4)
F3	0.038 (4)	0.114 (8)	0.091 (6)	0.013 (5)	-0.003 (4)	0.020 (6)
F4	0.205 (14)	0.049 (4)	0.065 (5)	0.025 (6)	0.047 (7)	-0.003 (4)

Geometric parameters (\AA , $^\circ$) for (CP)

C1—H1A	0.9700	C6—N2	1.436 (14)
C1—H1B	0.9700	C6—N3	1.460 (12)
C1—N1	1.479 (11)	C7—H7A	0.9700
C1—P1	1.815 (9)	C7—H7B	0.9700
C2—H2A	0.9700	C7—C8	1.534 (13)
C2—H2B	0.9700	C7—P1	1.775 (9)
C2—N2	1.461 (11)	C8—H8A	0.9700
C2—P1	1.826 (9)	C8—H8B	0.9700
C3—H3A	0.9700	C8—C9	1.494 (15)
C3—H3B	0.9700	C9—O11	1.233 (12)
C3—N3	1.484 (11)	C9—O12	1.272 (12)
C3—P1	1.818 (9)	N1—Ag1	2.225 (7)
C4—H4A	0.9700	N3—Ag1 ⁱ	2.505 (7)
C4—H4B	0.9700	O11—Ag1 ⁱⁱ	2.594 (9)
C4—N1	1.499 (12)	O12—Ag1 ⁱⁱ	2.298 (8)
C4—N2	1.428 (13)	B1—F1	1.343 (14)
C5—H5A	0.9700	B1—F2	1.399 (14)
C5—H5B	0.9700	B1—F3	1.370 (15)
C5—N1	1.467 (10)	B1—F4	1.328 (16)
C5—N3	1.464 (12)	Ag1—N3 ⁱⁱⁱ	2.505 (7)
C6—H6A	0.9700	Ag1—O11 ^{iv}	2.594 (9)
C6—H6B	0.9700	Ag1—O12 ^{iv}	2.298 (8)
H1A—C1—H1B	108.1	C7—C8—H8B	109.1
N1—C1—H1A	109.5	H8A—C8—H8B	107.8
N1—C1—H1B	109.5	C9—C8—C7	112.6 (8)
N1—C1—P1	110.7 (6)	C9—C8—H8A	109.1
P1—C1—H1A	109.5	C9—C8—H8B	109.1

P1—C1—H1B	109.5	O11—C9—C8	122.7 (9)
H2A—C2—H2B	108.6	O11—C9—O12	122.6 (10)
N2—C2—H2A	110.4	O12—C9—C8	114.7 (8)
N2—C2—H2B	110.4	C1—N1—C4	108.8 (7)
N2—C2—P1	106.7 (6)	C1—N1—Ag1	112.5 (5)
P1—C2—H2A	110.4	C4—N1—Ag1	112.0 (5)
P1—C2—H2B	110.4	C5—N1—C1	110.9 (6)
H3A—C3—H3B	108.5	C5—N1—C4	108.6 (7)
N3—C3—H3A	110.2	C5—N1—Ag1	104.0 (5)
N3—C3—H3B	110.2	C4—N2—C2	113.3 (7)
N3—C3—P1	107.8 (6)	C4—N2—C6	110.2 (8)
P1—C3—H3A	110.2	C6—N2—C2	112.3 (8)
P1—C3—H3B	110.2	C3—N3—Ag1 ⁱ	115.1 (5)
H4A—C4—H4B	107.7	C5—N3—C3	111.6 (7)
N1—C4—H4A	108.9	C5—N3—Ag1 ⁱ	93.4 (5)
N1—C4—H4B	108.9	C6—N3—C3	110.6 (7)
N2—C4—H4A	108.9	C6—N3—C5	109.4 (7)
N2—C4—H4B	108.9	C6—N3—Ag1 ⁱ	115.4 (5)
N2—C4—N1	113.4 (7)	C9—O11—Ag1 ⁱⁱ	85.8 (6)
H5A—C5—H5B	107.6	C9—O12—Ag1 ⁱⁱ	98.7 (6)
N1—C5—H5A	108.7	C1—P1—C2	99.7 (4)
N1—C5—H5B	108.7	C1—P1—C3	101.4 (4)
N3—C5—H5A	108.7	C3—P1—C2	103.1 (4)
N3—C5—H5B	108.7	C7—P1—C1	108.9 (4)
N3—C5—N1	114.2 (7)	C7—P1—C2	126.3 (4)
H6A—C6—H6B	107.6	C7—P1—C3	114.0 (4)
N2—C6—H6A	108.6	F1—B1—F2	108.8 (9)
N2—C6—H6B	108.6	F1—B1—F3	111.6 (11)
N2—C6—N3	114.6 (7)	F3—B1—F2	104.7 (9)
N3—C6—H6A	108.6	F4—B1—F1	110.8 (10)
N3—C6—H6B	108.6	F4—B1—F2	108.4 (11)
H7A—C7—H7B	107.5	F4—B1—F3	112.2 (12)
C8—C7—H7A	108.4	N1—Ag1—N3 ⁱⁱⁱ	119.6 (3)
C8—C7—H7B	108.4	N1—Ag1—O11 ^{iv}	134.1 (3)
C8—C7—P1	115.5 (7)	N1—Ag1—O12 ^{iv}	133.5 (3)
P1—C7—H7A	108.4	N3 ⁱⁱⁱ —Ag1—O11 ^{iv}	92.3 (3)
P1—C7—H7B	108.4	O12 ^{iv} —Ag1—N3 ⁱⁱⁱ	103.6 (3)
C7—C8—H8A	109.1	O12 ^{iv} —Ag1—O11 ^{iv}	52.9 (2)
C7—C8—C9—O11	148.3 (10)	N2—C6—N3—C5	53.5 (10)
C7—C8—C9—O12	-33.2 (12)	N2—C6—N3—Ag1 ⁱ	157.2 (6)
C8—C7—P1—C1	153.3 (7)	N3—C3—P1—C1	51.8 (7)
C8—C7—P1—C2	-88.5 (8)	N3—C3—P1—C2	-51.1 (7)
C8—C7—P1—C3	40.9 (8)	N3—C3—P1—C7	168.7 (6)
C8—C9—O11—Ag1 ⁱⁱ	177.7 (9)	N3—C5—N1—C1	-66.7 (9)
C8—C9—O12—Ag1 ⁱⁱ	-177.7 (7)	N3—C5—N1—C4	52.8 (9)
N1—C1—P1—C2	54.5 (7)	N3—C5—N1—Ag1	172.2 (6)
N1—C1—P1—C3	-51.1 (7)	N3—C6—N2—C2	71.6 (10)
N1—C1—P1—C7	-171.6 (6)	N3—C6—N2—C4	-55.7 (10)
N1—C4—N2—C2	-71.1 (10)	O11—C9—O12—Ag1 ⁱⁱ	0.8 (11)
N1—C4—N2—C6	55.6 (10)	O12—C9—O11—Ag1 ⁱⁱ	-0.7 (10)

N1—C5—N3—C3	70.1 (9)	P1—C1—N1—C4	-60.8 (8)
N1—C5—N3—C6	-52.7 (9)	P1—C1—N1—C5	58.5 (8)
N1—C5—N3—Ag1 ⁱ	-171.2 (6)	P1—C1—N1—Ag1	174.5 (4)
N2—C2—P1—C1	-53.2 (7)	P1—C2—N2—C4	64.6 (9)
N2—C2—P1—C3	51.0 (7)	P1—C2—N2—C6	-61.0 (8)
N2—C2—P1—C7	-175.5 (6)	P1—C3—N3—C5	-62.5 (8)
N2—C4—N1—C1	66.6 (10)	P1—C3—N3—C6	59.5 (8)
N2—C4—N1—C5	-54.2 (9)	P1—C3—N3—Ag1 ⁱ	-167.4 (3)
N2—C4—N1—Ag1	-168.4 (6)	P1—C7—C8—C9	62.9 (10)
N2—C6—N3—C3	-69.8 (10)		

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

Table 1. Selected hydrogen bond distances (\AA) and angles ($^\circ$) in crystal CP

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
C1—H1A \cdots F2	0.97	2.40	3.201 (13)	140
C1—H1B \cdots O11 ⁽ⁱ⁾	0.97	2.49	3.213 (12)	131
C2—H2A \cdots O11 ⁽ⁱ⁾	0.97	2.56	3.254 (12)	129
C2—H2B \cdots F3 ⁽ⁱⁱ⁾	0.97	2.35	3.183 (13)	143
C2—H2B \cdots O12	0.97	2.22	2.812 (12)	118
C3—H3A \cdots F4 ⁽ⁱⁱⁱ⁾	0.97	2.45	3.290 (15)	145
C3—H3B \cdots F2	0.97	2.51	3.283 (12)	136
C4—H4A \cdots F4 ^(iv)	0.97	2.43	3.298 (12)	148
C4—H4B \cdots F2 ^(v)	0.97	2.51	3.417 (14)	155
C5—H5A \cdots F1	0.97	2.49	3.370 (13)	151
C5—H5B \cdots F4 ^(iv)	0.97	2.54	3.373 (14)	144
C6—H6B \cdots F2 ^(iv)	0.97	2.34	3.314 (13)	177
C7—H7A \cdots O11 ⁽ⁱⁱ⁾	0.97	2.48	3.165 (13)	128
C7—H7A \cdots F1 ^(vi)	0.97	2.37	3.137 (12)	135

Symmetry codes: ⁽ⁱ⁾ $x, -1-y, -1/2+z$; ⁽ⁱⁱ⁾ $-1+x, y, z$; ⁽ⁱⁱⁱ⁾ $-1/2+x, -1/2-y, 1/2+z$; ^(iv) $-1/2+x, 1/2+y, z$; ^(v) $-1/2+x, -1/2-y, -1/2+z$; ^(vi) $-1/2+x, -1/2+y, z$