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Crystal structure of *cyclo*-bis(μ_4-2,2-diallyl-malonato-$\kappa^6O^1,O^3:O^3:O^{1'},O^3:O^{1'}$)tetrakis(triphenylphosphane-κP)tetrasilver(I)

Peter Frenzel, Alexander Jakob, Dieter Schaarschmidt, Tobias Rüffer and Heinrich Lang*

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, 09107 Chemnitz, Germany. *Correspondence e-mail: heinrich.lang@chemie.tu-chemnitz.de

In the tetranuclear molecule of the title compound, $[Ag_4(C_9H_{10}O_4)_2(C_{18}H_{15}P)_4]$, the Ag^I ion is coordinated by one P and three O atoms in a considerably distorted tetrahedral environment. The two 2,2-diallylmalonate anions bridge four Ag^I ions in a μ_4-($\kappa^6O^1,O^3:O^3:O^{1'},O^3:O^{1'}$) mode, setting up an $Ag_4O_8P_4$ core (point group symmetry $\bar{4}$..) of corner-sharing tetrahedra. The shortest intramolecular $Ag\cdots Ag$ distance of 3.9510 (3) Å reveals that no direct $d^{10}\cdots d^{10}$ interactions are present. Four weak intramolecular C—H$\cdots$O hydrogen bonds are observed in the crystal structure of the title compound, which most likely stabilize the tetranuclear silver core.

1. Chemical context

Silver(I) carboxylates of general type $[AgO_2CR]_n$ (n is the degree of aggregation) are of interest due to their versatile structures in the solid state and in solution, their synthetic methodologies and their manifold reaction behavior (see, for example: Schliebe *et al.*, 2013; Jahn *et al.*, 2010; Wang *et al.*, 2008; Fernández *et al.*, 2007; Olson *et al.*, 2006; Szymańska *et al.*, 2007). These metal-organic complexes are of importance not only in the field of basic research but also in multipurpose applications including, for example, metallization processes for micro- and nano-structured new materials in electronic systems and devices (*e.g.* using chemical vapour deposition, CVD), since silver possesses the highest electrical conductivity of any element (Jakob *et al.*, 2010; Lang & Dietrich, 2013), catalytic processes (Steffan *et al.*, 2009) and their use in biological studies (Djokić, 2008; Zhu *et al.*, 2003).
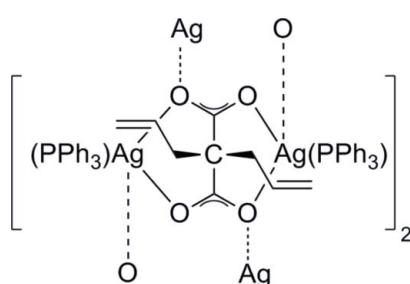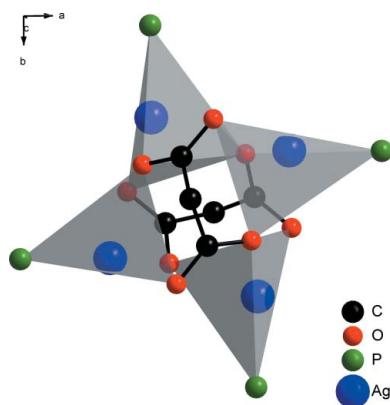
The CVD process requires metal precursors possessing high vapour pressures. On a molecular level this is typically achieved by designing low aggregated metal compounds. In the case of silver, this can be realized by the use of phosphanes as a Lewis base; however, the concomitant increase of the molecular weight of the transition metal complex may decrease its vapour pressure. Circumventing this difficulty, we

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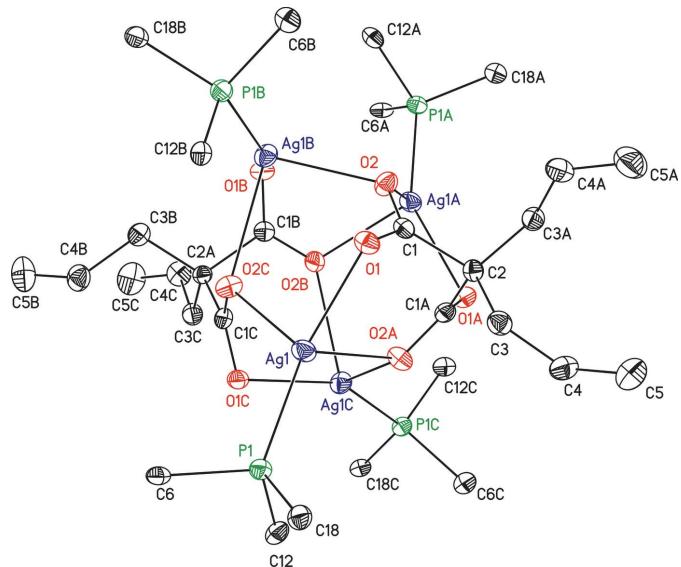
Figure 1
The Ag$_4$O$_8$P$_4$ core of the title compound with surrounding atoms. Displacement ellipsoids are displayed at the 50% probability level. The carbon atoms of the phenyl substituents except the *ipso*-carbon atoms and all hydrogen atoms have been omitted for clarity. [Symmetry codes: (A) –x + 1, –y + 1, z; (B) y, –x + 1, –z + 2; (C) –y + 1, x, –z + 2.]

have investigated the use of olefines as ligands for silver(I) carboxylates, in which the olefin is covalently bonded to the carboxylate. In the context of this approach, the title compound [{(Ph$_3$P)Ag}$_4${(O$_2$C)$_2$C(CH$_2$CH═CH$_2$)$_2$}$_2$], (I), was obtained by the reaction of the silver salt of 2,2-diallylmalonic acid with triphenylphosphane.

2. Structural commentary

The asymmetric unit of (I) contains one quarter of the molecule which is completed by application of a fourfold screw axis as the symmetry element. The resulting tetranuclear silver core is decorated by four triphenylphosphane ligands, whereby the metal ions are bridged by two 2,2-diallylmalonate anions in a μ_4-($\kappa^6 O^1,O^3{:}O^3{:}O^{1'},O^{3'}{:}O^{1'}$) mode (Fig. 1). There is no example in the literature of a transition metal malonate displaying this type of coordination. The environment around silver, set up by one phosphorus and three oxygen atoms, is best described as distorted tetrahedral. Ag1 is oriented slightly above the plane of O1, P1 and O2^{ii} [distance 0.2911 (10) Å], which is supported by the respective bond angles around Ag1 (Table 1) summing up to 354.3°. The O—Ag1—P1 angles are substantially larger than the O—Ag1—O angles, which may be

Table 1
Selected bond lengths (Å) and bond angles (°).

Ag1—O1	2.323 (2)	O1—Ag1—O2^i	82.45 (7)
Ag1—P1	2.3483 (8)	O1—Ag1—O2^{ii}	90.28 (8)
Ag1—O2^i	2.592 (2)	P1—Ag1—O2^i	112.26 (5)
Ag1—O2^{ii}	2.344 (2)	P1—Ag1—O2^{ii}	115.95 (6)
O1—Ag1—P1	148.09 (6)	O2^i—Ag1—O2^{ii}	92.63 (10)

Symmetry codes: (i) −x + 1, −y + 1, z; (ii) −y + 1, x, −z + 2.
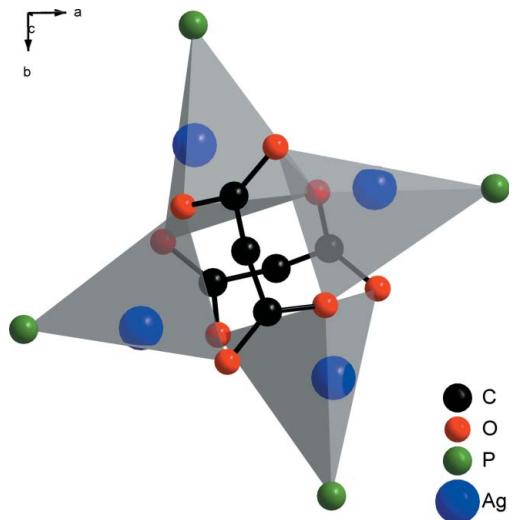
Figure 2
Structure fragment showing the cyclic corner-sharing arrangement of the AgO$_3$P polyhedra giving the tetranuclear silver core of composition Ag$_4$O$_8$P$_4$.

attributed to the chelating coordination of the malonate ligands and the bulkiness of the triphenylphosphane ligand. The Ag—O bond lengths are more than 0.2 Å shorter for the two oxygen atoms of the aforementioned plane than for the third apical oxygen atom (Table 1). However, the values are in the expected range for Ag—O bonds in silver carboxylates.

The cyclic corner-sharing arrangement of the described O$_3$P tetrahedra gives the tetranuclear structure of (I) (Fig. 2). The four silver ions are oriented in a butterfly-like arrangement, which delimits the title compound from Ag$_4$O$_4$ heterocubanes (Jakob *et al.*, 2011; Zhang *et al.*, 2008, Kühnert *et al.*, 2007) in which the four silver ions form a tetrahedron. In contrast, there are some similarities with [bis(1,8-naphthalenedicarboxylato)][tetrakis(triphenylphosphane)silver(I)] (van der Ploeg *et al.*, 1979); however, in the structure of this compound one silver ion is pentacoordinated.

3. Supramolecular features

Four weak intramolecular C—H···O hydrogen bonds (Steiner, 2002) are observed in the crystal structure of (I) (Table 2), which most likely stabilize the silver core.

In contrast to iridium and platinum complexes of 2,2-diallylmalonic acid and derivatives thereof, the C═C double bond does not coordinate the transition metal in (I). Furthermore, no obvious π–π stacking interactions are observed between the allyl and the phenyl substituents. Therefore, the packing seems to be dominated by dispersion forces (Fig. 3).

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

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O2^i	0.93	2.51	3.351 (4)	150

Symmetry code: (i) −x + 1, −y + 1, z.
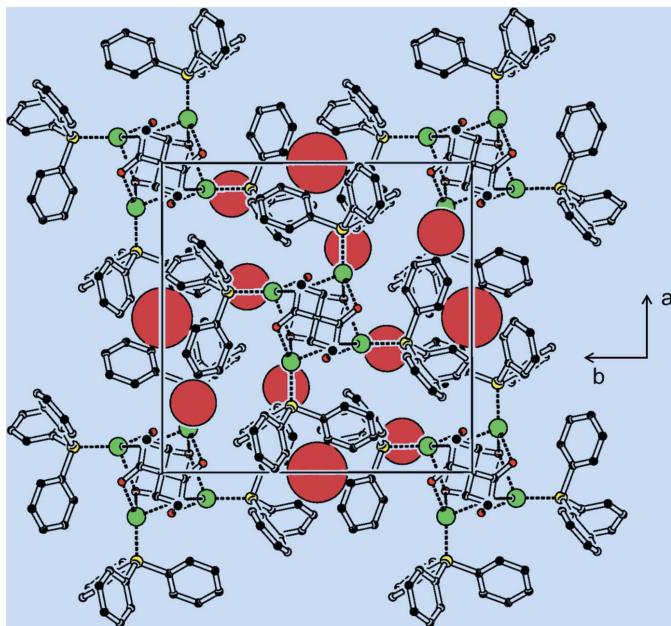
Figure 3
Packing diagram of the title compound along the *c* axis; voids in the structure are represented by red spheres [drawn using the CAVITY-PLOT routine in *PLATON* (Spek, 2009)]. The hydrogen atoms have been omitted for clarity. Colour code: black (C), red (O), yellow (P), green (Ag).

4. Database survey

2,2-Diallylmalonic acid and derivatives thereof have only been used as ligands in four mononuclear platinum and one iridium complex, in which coordination of the transition metal occurs either through (O,O′)-, (O,alkene)- or (alkene,alkene′)-chelation (Berthon-Gelloz *et al.*, 2007; Makino *et al.*, 2004; Jung *et al.*, 1999; Lee *et al.*, 1999). To the best of our knowledge, no diallylmalonate silver(I) compounds have been described in the literature so far.

5. Synthesis and crystallization

Complex $[\{(Ph_3P)Ag\}_4\{(O_2C)_2C(CH_2CH=CH_2)_2\}_2]$ was prepared by the addition of PPh_3 (132 mg, 0.503 mmol) to a suspension of $[(AgO_2C)_2C(CH_2CH=CH_2)_2]$ (100 mg, 0.251 mmol) in dichloromethane (30 ml) at 273 K. After stirring for 2 h at this temperature, the reaction mixture was filtered through a pad of celite. Afterwards, all volatiles were removed in oil-pump vacuum, and (I) was obtained as a pale-grey solid. Colourless crystals of (I) were obtained by solvent diffusion of a chloroform solution of (I) against pentane at ambient temperature. Yield: 230 mg (0.125 mmol, 99% based on $[(AgO_2C)_2C(CH_2CH=CH_2)_2]$).

Analysis calculated for $C_{90}H_{80}Ag_4O_8P_4$ (1844.96): C 58.59, H 4.37. Found: C 58.53, H 4.34. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K, ppm): δ = 2.79 (*d*, 8H, $^{3}J_{HH}$ = 6.5 Hz, CH_2CH=CH$_2$), 4.97 (*d*, 4H, $^{3}J_{HH}$ = 10.2 Hz, CH$_2$CH=CH_2), 5.03 (*d*, 4H, $^{3}J_{HH}$ = 17.1 Hz, CH$_2$CH=CH_2), 5.90 (*m*, 4H, CH$_2$CH=CH$_2$), 7.30–7.51 (*m*, 60H, C$_6$H$_5$). $^{31}P\{^{1}H\}$ NMR (203 MHz, CDCl$_3$, 298 K, ppm): δ = 15.7 (*d*, $^{1}J_{AgP}$ = 680 Hz). IR (KBr, cm^{-1}): ν = 1637

(*w*, C=C), 1559 (*vs*, C=O), 1440 (*vs*, P−Ph), 692 (*vs*), 521 (*vs*).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ag_4(C_9H_{10}O_4)_2(C_{18}H_{15}P)_4]$
M_r	1844.90
Crystal system, space group	Tetragonal, $I\bar{4}$
Temperature (K)	105
a, c (Å)	16.0462 (1), 15.3337 (2)
V (Å^3)	3948.13 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.12
Crystal size (mm)	$0.2 \times 0.1 \times 0.1$
Data collection	
Diffractometer	Oxford Gemini S
Absorption correction	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min}, T_{max}	0.903, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21141, 4571, 4425
R_{int}	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.671
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.048, 1.04
No. of reflections	4571
No. of parameters	240
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.40, −0.52
Absolute structure	Flack x determined using 1620 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004)
Absolute structure parameter	−0.051 (9)

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2006), *SHELXS2013*, *SHELXL2013* and *SHELXTL* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *DIAMOND* (Brandenburg, 1996), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bonded H atoms were placed in calculated positions and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ and a C−H distance of 0.93 Å for aromatic and vinylic as well as 0.97 Å for methylene protons. The unit cell contains two voids of 34(1.4) Å^3. Void volume calculation using the SQUEEZE routine in *PLATON* (Spek, 2009) gives a total electron count in the voids per cell of 3 e^{-} Å^{-3} suggesting that no solvent molecules occupy these voids. The Flack parameter is −0.051 (9); however, this ambiguity is resolved as the Flack parameter of the inverted structure is calculated to 1.052 (9). This indicates that the original absolute structure has been assigned correctly.

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supporting information

Crystal structure of *cyclo*-bis(*µ*₄-2,2-diallylmalonato-*κ*⁶*O*¹,*O*³:*O*³:*O*¹',*O*³':*O*¹')tetrakis(triphenylphosphane-*κP*)tetrasilver(I)

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Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

cyclo-Bis(*µ*₄-2,2-diallylmalonato- *κ*⁶*O*¹,*O*³:*O*³:*O*¹',*O*³':*O*¹')tetrakis(triphenylphosphane-*κP*)tetrasilver(I)

Crystal data
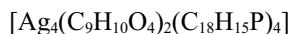
[Ag₄(C₉H₁₀O₄)₂(C₁₈H₁₅P)₄]	$D_x = 1.552$ Mg m⁻³
$M_r = 1844.90$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $I\bar{4}$	Cell parameters from 14970 reflections
$a = 16.0462\ (1)$ Å	$\theta = 3.2$–28.4°
$c = 15.3337\ (2)$ Å	$\mu = 1.12$ mm⁻¹
$V = 3948.13\ (7)$ Å³	$T = 105$ K
$Z = 2$	Block, colourless
$F(000) = 1864$	0.2 × 0.1 × 0.1 mm

Data collection

Oxford Gemini S diffractometer	4425 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.034$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)	$\theta_{max} = 28.5°$, $\theta_{min} = 3.1°$
	$h = -19 \rightarrow 20$
$T_{min} = 0.903$, $T_{max} = 1.000$	$k = -21 \rightarrow 21$
21141 measured reflections	$l = -19 \rightarrow 20$
4571 independent reflections	2 standard reflections every 50 reflections
	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 1.5165P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.022$	
$wR(F^2) = 0.048$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.40$ e Å⁻³
4571 reflections	$\Delta\rho_{min} = -0.52$ e Å⁻³
240 parameters	Absolute structure: Flack x determined using 1620 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons & Flack, 2004)
0 restraints	
Hydrogen site location: inferred from neighbouring sites	Absolute structure parameter: −0.051 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.42916 (19)	0.52013 (18)	1.13083 (19)	0.0162 (6)
C2	0.5000	0.5000	1.1958 (3)	0.0156 (8)
C3	0.4814 (2)	0.4235 (2)	1.2530 (2)	0.0205 (7)
H3A	0.4329	0.4350	1.2889	0.025*
H3B	0.4681	0.3765	1.2157	0.025*
C4	0.5527 (2)	0.4007 (2)	1.3107 (2)	0.0258 (7)
H4	0.6037	0.3908	1.2837	0.031*
C5	0.5502 (3)	0.3933 (3)	1.3962 (3)	0.0394 (9)
H5A	0.5005	0.4026	1.4259	0.047*
H5B	0.5980	0.3787	1.4269	0.047*
C6	0.3546 (2)	0.17708 (19)	0.9260 (2)	0.0189 (6)
C7	0.3733 (2)	0.2094 (2)	0.8438 (2)	0.0252 (7)
H7	0.4161	0.2480	0.8373	0.030*
C8	0.3276 (3)	0.1837 (2)	0.7717 (2)	0.0329 (9)
H8	0.3407	0.2047	0.7168	0.039*
C9	0.2631 (3)	0.1274 (2)	0.7803 (3)	0.0389 (10)
H9	0.2332	0.1102	0.7316	0.047*
C10	0.2434 (2)	0.0970 (2)	0.8615 (3)	0.0346 (9)
H10	0.1995	0.0597	0.8675	0.042*
C11	0.2883 (2)	0.1214 (2)	0.9348 (2)	0.0245 (7)
H11	0.2741	0.1007	0.9894	0.029*
C12	0.52112 (19)	0.17391 (19)	0.9931 (2)	0.0191 (6)
C13	0.58867 (19)	0.21305 (19)	1.0339 (2)	0.0230 (6)
H13	0.5799	0.2591	1.0696	0.028*
C14	0.6692 (2)	0.1829 (2)	1.0208 (2)	0.0295 (8)
H14	0.7140	0.2080	1.0489	0.035*
C15	0.6825 (2)	0.1156 (2)	0.9662 (3)	0.0292 (7)
H15	0.7361	0.0952	0.9580	0.035*
C16	0.6160 (2)	0.0786 (2)	0.9240 (2)	0.0267 (7)
H16	0.6252	0.0339	0.8866	0.032*
C17	0.5356 (2)	0.1078 (2)	0.9370 (2)	0.0223 (7)
H17	0.4913	0.0829	0.9079	0.027*
C18	0.38021 (19)	0.14737 (19)	1.1075 (2)	0.0184 (6)
C19	0.3973 (2)	0.0620 (2)	1.1117 (2)	0.0233 (7)
H19	0.4319	0.0376	1.0703	0.028*

C20	0.3628 (2)	0.0137 (2)	1.1771 (2)	0.0262 (7)
H20	0.3739	−0.0432	1.1794	0.031*
C21	0.3121 (2)	0.0500 (2)	1.2389 (2)	0.0258 (7)
H21	0.2889	0.0174	1.2828	0.031*
C22	0.2956 (2)	0.1343 (2)	1.2362 (2)	0.0264 (7)
H22	0.2616	0.1584	1.2784	0.032*
C23	0.3297 (2)	0.1832 (2)	1.1707 (2)	0.0207 (7)
H23	0.3187	0.2401	1.1690	0.025*
O1	0.36944 (13)	0.47026 (13)	1.12166 (14)	0.0186 (5)
O2	0.43925 (14)	0.58622 (14)	1.08654 (14)	0.0209 (5)
P1	0.41682 (5)	0.21258 (5)	1.01855 (5)	0.01656 (16)
Ag1	0.41599 (2)	0.35747 (2)	1.04012 (2)	0.01949 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0177 (16)	0.0146 (15)	0.0163 (14)	0.0002 (11)	0.0004 (12)	−0.0030 (11)
C2	0.015 (2)	0.016 (2)	0.0154 (19)	−0.0020 (16)	0.000	0.000
C3	0.0228 (17)	0.0192 (16)	0.0195 (15)	−0.0003 (12)	0.0021 (12)	−0.0004 (12)
C4	0.0282 (19)	0.0209 (17)	0.0284 (18)	0.0034 (13)	−0.0007 (14)	0.0035 (14)
C5	0.050 (3)	0.036 (2)	0.032 (2)	0.0070 (18)	−0.0071 (18)	0.0058 (17)
C6	0.0192 (16)	0.0127 (15)	0.0250 (16)	0.0044 (12)	−0.0039 (12)	−0.0018 (12)
C7	0.0280 (19)	0.0247 (18)	0.0229 (17)	0.0059 (14)	−0.0026 (13)	−0.0032 (13)
C8	0.039 (2)	0.035 (2)	0.0250 (19)	0.0123 (17)	−0.0077 (15)	−0.0018 (16)
C9	0.044 (2)	0.030 (2)	0.042 (2)	0.0116 (17)	−0.0237 (18)	−0.0141 (17)
C10	0.030 (2)	0.0236 (19)	0.050 (2)	0.0006 (15)	−0.0192 (18)	0.0006 (16)
C11	0.0211 (16)	0.0192 (16)	0.0332 (19)	0.0003 (12)	−0.0092 (13)	0.0005 (13)
C12	0.0180 (16)	0.0188 (16)	0.0204 (15)	−0.0011 (12)	−0.0030 (12)	0.0062 (12)
C13	0.0220 (16)	0.0202 (15)	0.0270 (16)	−0.0026 (11)	−0.0015 (14)	0.0025 (14)
C14	0.0206 (17)	0.0303 (19)	0.038 (2)	−0.0044 (14)	−0.0021 (15)	0.0055 (15)
C15	0.0167 (15)	0.0308 (19)	0.040 (2)	0.0026 (12)	0.0062 (16)	0.0078 (17)
C16	0.0252 (18)	0.0231 (18)	0.0318 (18)	0.0028 (14)	0.0071 (14)	0.0032 (14)
C17	0.0214 (16)	0.0205 (16)	0.0250 (18)	−0.0005 (12)	−0.0008 (12)	0.0017 (12)
C18	0.0161 (16)	0.0179 (16)	0.0211 (16)	−0.0015 (11)	−0.0029 (12)	0.0004 (12)
C19	0.0237 (18)	0.0207 (17)	0.0256 (17)	0.0010 (13)	−0.0028 (13)	0.0011 (13)
C20	0.0294 (19)	0.0185 (17)	0.0306 (19)	−0.0010 (13)	−0.0052 (14)	0.0057 (14)
C21	0.0230 (18)	0.0268 (18)	0.0274 (18)	−0.0040 (14)	−0.0028 (14)	0.0097 (14)
C22	0.0217 (19)	0.0320 (19)	0.0255 (18)	0.0024 (14)	0.0021 (14)	0.0041 (14)
C23	0.0191 (17)	0.0198 (17)	0.0234 (17)	0.0030 (12)	−0.0014 (13)	0.0026 (13)
O1	0.0154 (11)	0.0168 (11)	0.0236 (12)	−0.0017 (8)	0.0018 (9)	−0.0032 (9)
O2	0.0212 (12)	0.0188 (11)	0.0225 (12)	−0.0024 (9)	−0.0047 (9)	0.0042 (9)
P1	0.0175 (4)	0.0137 (4)	0.0185 (4)	0.0000 (3)	−0.0015 (3)	0.0002 (3)
Ag1	0.02397 (13)	0.01337 (12)	0.02114 (11)	−0.00192 (9)	0.00038 (10)	0.00018 (9)

Geometric parameters (Å, º)

C1—O1	1.256 (3)	C13—C14	1.394 (5)
C1—O2	1.270 (4)	C13—H13	0.9300

C1—C2	1.545 (4)	C14—C15	1.383 (5)
C2—C3	1.539 (4)	C14—H14	0.9300
C2—C3ⁱ	1.539 (4)	C15—C16	1.382 (5)
C2—C1ⁱ	1.545 (4)	C15—H15	0.9300
C3—C4	1.492 (5)	C16—C17	1.386 (5)
C3—H3A	0.9700	C16—H16	0.9300
C3—H3B	0.9700	C17—H17	0.9300
C4—C5	1.318 (5)	C18—C23	1.387 (5)
C4—H4	0.9300	C18—C19	1.399 (4)
C5—H5A	0.9300	C18—P1	1.817 (3)
C5—H5B	0.9300	C19—C20	1.383 (5)
C6—C7	1.397 (5)	C19—H19	0.9300
C6—C11	1.397 (5)	C20—C21	1.378 (5)
C6—P1	1.825 (3)	C20—H20	0.9300
C7—C8	1.389 (5)	C21—C22	1.380 (5)
C7—H7	0.9300	C21—H21	0.9300
C8—C9	1.380 (6)	C22—C23	1.388 (5)
C8—H8	0.9300	C22—H22	0.9300
C9—C10	1.373 (6)	C23—H23	0.9300
C9—H9	0.9300	Ag1—O1	2.323 (2)
C10—C11	1.391 (5)	Ag1—P1	2.3483 (8)
C10—H10	0.9300	Ag1—O2ⁱ	2.592 (2)
C11—H11	0.9300	Ag1—O2ⁱⁱ	2.344 (2)
C12—C17	1.386 (5)	O2—Ag1ⁱⁱⁱ	2.344 (2)
C12—C13	1.400 (4)	O2—Ag1ⁱ	2.592 (2)
C12—P1	1.827 (3)		
O1—C1—O2	124.7 (3)	C15—C14—H14	120.0
O1—C1—C2	120.0 (2)	C13—C14—H14	120.0
O2—C1—C2	115.2 (2)	C16—C15—C14	120.0 (3)
C3—C2—C3ⁱ	110.4 (4)	C16—C15—H15	120.0
C3—C2—C1ⁱ	110.11 (16)	C14—C15—H15	120.0
C3ⁱ—C2—C1ⁱ	113.04 (17)	C15—C16—C17	120.3 (3)
C3—C2—C1	113.04 (17)	C15—C16—H16	119.8
C3ⁱ—C2—C1	110.10 (16)	C17—C16—H16	119.8
C1ⁱ—C2—C1	99.8 (3)	C12—C17—C16	120.3 (3)
C4—C3—C2	112.6 (3)	C12—C17—H17	119.9
C4—C3—H3A	109.1	C16—C17—H17	119.9
C2—C3—H3A	109.1	C23—C18—C19	119.2 (3)
C4—C3—H3B	109.1	C23—C18—P1	118.3 (2)
C2—C3—H3B	109.1	C19—C18—P1	122.4 (2)
H3A—C3—H3B	107.8	C20—C19—C18	120.3 (3)
C5—C4—C3	126.0 (4)	C20—C19—H19	119.9
C5—C4—H4	117.0	C18—C19—H19	119.9
C3—C4—H4	117.0	C21—C20—C19	119.8 (3)
C4—C5—H5A	120.0	C21—C20—H20	120.1
C4—C5—H5B	120.0	C19—C20—H20	120.1
H5A—C5—H5B	120.0	C20—C21—C22	120.5 (3)

C7—C6—C11	119.2 (3)	C20—C21—H21	119.7
C7—C6—P1	118.0 (3)	C22—C21—H21	119.7
C11—C6—P1	122.8 (3)	C21—C22—C23	120.0 (3)
C8—C7—C6	119.7 (3)	C21—C22—H22	120.0
C8—C7—H7	120.2	C23—C22—H22	120.0
C6—C7—H7	120.2	C18—C23—C22	120.1 (3)
C9—C8—C7	120.9 (4)	C18—C23—H23	119.9
C9—C8—H8	119.6	C22—C23—H23	119.9
C7—C8—H8	119.6	C1—O1—Ag1	108.13 (19)
C10—C9—C8	119.5 (3)	C1—O2—Ag1iii	111.05 (19)
C10—C9—H9	120.2	C1—O2—Ag1i	123.53 (19)
C8—C9—H9	120.2	Ag1iii—O2—Ag1i	106.22 (8)
C9—C10—C11	120.9 (4)	C18—P1—C6	103.13 (15)
C9—C10—H10	119.6	C18—P1—C12	105.12 (14)
C11—C10—H10	119.6	C6—P1—C12	103.22 (15)
C10—C11—C6	119.8 (3)	C18—P1—Ag1	117.56 (10)
C10—C11—H11	120.1	C6—P1—Ag1	114.54 (10)
C6—C11—H11	120.1	C12—P1—Ag1	111.81 (10)
C17—C12—C13	119.4 (3)	O1—Ag1—P1	148.09 (6)
C17—C12—P1	123.1 (2)	O1—Ag1—O2i	82.45 (7)
C13—C12—P1	117.5 (2)	O1—Ag1—O2ii	90.28 (8)
C14—C13—C12	119.8 (3)	P1—Ag1—O2i	112.26 (5)
C14—C13—H13	120.1	O2ii—Ag1—P1	115.95 (6)
C12—C13—H13	120.1	O2ii—Ag1—O2i	92.63 (10)
C15—C14—C13	120.1 (3)		
O1—C1—C2—C3	−8.4 (4)	C19—C20—C21—C22	−0.2 (5)
O2—C1—C2—C3	175.2 (3)	C20—C21—C22—C23	0.3 (5)
O1—C1—C2—C3i	−132.4 (3)	C19—C18—C23—C22	−1.0 (5)
O2—C1—C2—C3i	51.2 (4)	P1—C18—C23—C22	175.4 (3)
O1—C1—C2—C1i	108.5 (3)	C21—C22—C23—C18	0.2 (5)
O2—C1—C2—C1i	−67.9 (2)	O2—C1—O1—Ag1	100.7 (3)
C3i—C2—C3—C4	−60.5 (2)	C2—C1—O1—Ag1	−75.4 (3)
C1i—C2—C3—C4	65.0 (4)	O1—C1—O2—Ag1iii	−17.0 (4)
C1—C2—C3—C4	175.6 (2)	C2—C1—O2—Ag1iii	159.23 (19)
C2—C3—C4—C5	124.2 (4)	O1—C1—O2—Ag1i	−144.9 (2)
C11—C6—C7—C8	−2.2 (5)	C2—C1—O2—Ag1i	31.3 (3)
P1—C6—C7—C8	179.7 (3)	C23—C18—P1—C6	−106.6 (3)
C6—C7—C8—C9	1.0 (5)	C19—C18—P1—C6	69.7 (3)
C7—C8—C9—C10	0.5 (6)	C23—C18—P1—C12	145.6 (3)
C8—C9—C10—C11	−0.8 (6)	C19—C18—P1—C12	−38.1 (3)
C9—C10—C11—C6	−0.4 (5)	C23—C18—P1—Ag1	20.5 (3)
C7—C6—C11—C10	1.9 (5)	C19—C18—P1—Ag1	−163.2 (2)
P1—C6—C11—C10	179.9 (3)	C7—C6—P1—C18	−173.8 (2)
C17—C12—C13—C14	−3.0 (5)	C11—C6—P1—C18	8.2 (3)
P1—C12—C13—C14	176.2 (3)	C7—C6—P1—C12	−64.5 (3)
C12—C13—C14—C15	1.4 (5)	C11—C6—P1—C12	117.5 (3)
C13—C14—C15—C16	0.5 (5)	C7—C6—P1—Ag1	57.3 (3)

C14—C15—C16—C17	−1.0 (5)	C11—C6—P1—Ag1	−120.7 (2)
C13—C12—C17—C16	2.5 (5)	C17—C12—P1—C18	85.6 (3)
P1—C12—C17—C16	−176.6 (2)	C13—C12—P1—C18	−93.6 (3)
C15—C16—C17—C12	−0.6 (5)	C17—C12—P1—C6	−22.2 (3)
C23—C18—C19—C20	1.2 (5)	C13—C12—P1—C6	158.7 (2)
P1—C18—C19—C20	−175.1 (3)	C17—C12—P1—Ag1	−145.8 (2)
C18—C19—C20—C21	−0.6 (5)	C13—C12—P1—Ag1	35.1 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O2[i]	0.93	2.51	3.351 (4)	150

Symmetry code: (i) −x+1, −y+1, z.