# metal-organic papers

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
R factor = 0.066
wR factor = 0.131
Data-to-parameter ratio = 14.7

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

Bis[μ-methylenebis(diphenylphosphine)-κ²P:P′]disilver(I) diperchlorate acetonitrile disolvate

The dication in the title compound, $[Ag_2(\mu_2\text{-dppm})_2]$-$(ClO_4)_2 \cdot 2CH_3CN$, where dppm is bis(diphenylphosphino)-methane ($C_{25}H_{22}P_2$), is situated across an inversion centre. Each Ag atom is two-coordinate and exists in an approximately linear geometry. An Ag···N contact of 2.874 (10) Å is observed in the structure.

Comment

Binuclear complexes of silver with certain bidentate ligands are of great interest due to their rich luminescence and bonding properties. Several compounds of binuclear $[Ag_2(\mu_2\text{-dppm})_2]^{2+}$ dications, counterbalanced by various anionic species, have been reported previously (Ahrens & Jones, 1998; Lusser & Peringer, 1985; Ho & Bau, 1983). Here we report the crystal structure of the title compound, $[Ag_2(\mu_2\text{-dppm})_2]$-$(ClO_4)_2 \cdot 2CH_3CN$, (I).

(I)
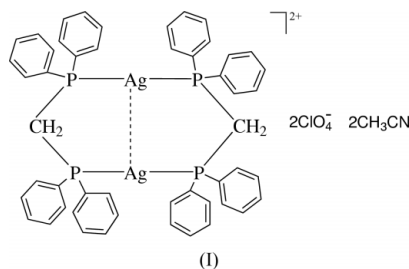
The asymmetric unit of (I) consists of one-half of an $[Ag_2(\mu_2\text{-dppm})_2]^{2+}$ dication, situated across a crystallographic inversion centre, one independent ClO_4^- anion and an acetonitrile solvent molecule. The structure of the dication with atomic numbering scheme is shown in Fig. 1. In the dication, the Ag atoms are doubly bridged by two dppm ligands, forming an eight-membered $Ag_2P_4C_2$ ring. The formation of an $M_2P_4C_2$ ring (M = Cu, Ag, Au, Pt and Pd) has been reported previously (Ho & Bau, 1983; Neo et al., 1995; Van der Ploeg et al., 1979; Yam et al., 1997). The eight-membered ring displays a pseudo-chair conformation, as observed in $[Ag_2(\mu_2\text{-dppm})_2](ClO_4)_2 \cdot 2CH_2Cl_2$ (Ahrens & Jones, 1998). In the ring, the Ag centers are two-coordinate, exhibiting an approximately linear coordination geometry, with a P1—Ag1—P2^{i} [symmetry code: (i) $-x, 1 - y, -z$] angle of 174.95 (7)°. The intramolecular Ag···Ag contact is 3.0581 (12) Å, which is longer than that observed in other silver systems; 2.9532 (7) Å in $[Ag_2(\mu_2\text{-dppm})_2](ClO_4)_2$·-$2CH_2Cl_2$ (Ahrens & Jones, 1998) and 2.987 (2) Å in $[Ag_2(\mu_2\text{-dppm})_3](NO_3)_2 \cdot 2H_2O$ (Hong et al., 1997). The Ag—P distances of 2.408 (2) and 2.410 (2) Å are comparable to those observed in the above two complexes.
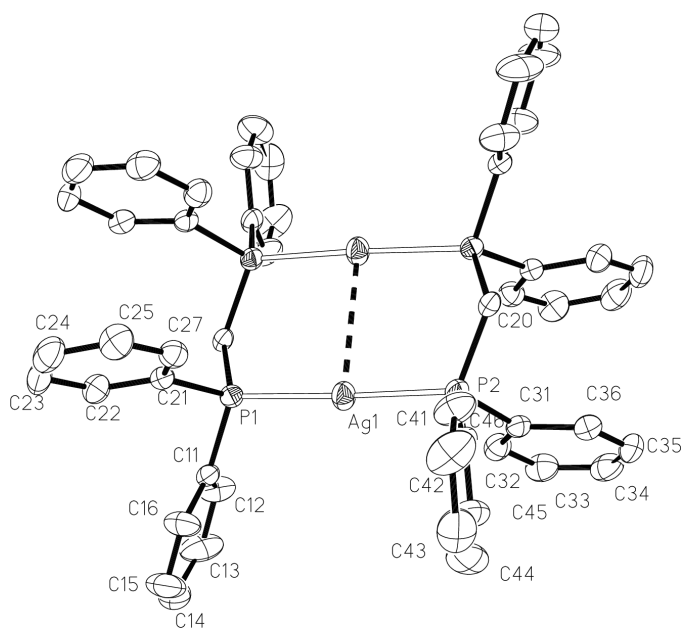
Figure 1
The structure of the dication of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

The Ag1$\cdots$N1 contact distance of 2.874 (10) Å is shorter than that observed [3.160 (6) Å] in [Ag$_3$\{HC(PPh$_2$)$_3$\}$_2$]-(ClO$_4$)$_3\cdot$2CH$_3$CN (Che *et al.*, 1992) but longer than that observed [2.552 (2) Å] in [Ag$_3$(dppm)$_2$(CH$_3$CN)$_2$]-(ClO$_4$)$_2\cdot$(CH$_3$CH$_2$)$_2$O (Che *et al.*, 1991). The Ag$\cdots$O contact distances in (I) [Ag1$\cdots$O12 = 3.071 (7) Å and Ag1$\cdots$O12^i = 3.367 (6) Å] lie in the range 2.959 (3)–3.514 (2) Å reported for [Ag$_2$(μ_2-dppm)$_2$](ClO$_4$)$_2\cdot$2CH$_2$Cl$_2$ (Ahrens & Jones, 1998) but lie outside the range 2.418 (5)–2.689 (6) Å reported for [Ag$_2$(dppm)$_2$(NO$_3$)$_2$] (Ho & Bau, 1983).

Experimental

The title compound was synthesized by a modification of a literature procedure (Lusser & Peringer, 1985). The complex was obtained by the reaction between [Cu$_2$(μ_2-dppm)$_2$](ClO$_4$)$_2$ and AgCCC(CH$_3$)$_3$ in a 1:2 ratio in acetonitrile solution under anaerobic conditions for 24 h. Well formed colorless crystals suitable for X-ray diffraction measurements were grown by the slow diffusion of diethyl ether into an acetonitrile solution at room temperature.

Crystal data

[Ag$_2$(C$_{25}$H$_{22}$P$_4$)$_2$](ClO$_2$)$_2\cdot$2C$_2$H$_3$N	D_x = 1.538 Mg m^{-3}
M_r = 1265.48	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2900
a = 11.4553 (3) Å	reflections
b = 15.1766 (1) Å	θ = 2.3–25.0°
c = 16.0597 (5) Å	μ = 0.99 mm^{-1}
β = 101.826 (2)°	T = 293 (2) K
V = 2732.76 (11) Å^3	Prism, colorless
Z = 2	0.32 × 0.30 × 0.28 mm

Data collection

Siemens SMART CCD diffractometer	4806 independent reflections
ω scans	2920 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	R_{int} = 0.060
(*SADABS*; Sheldrick, 1996)	θ_{max} = 25.0°
T_{min} = 0.723, T_{max} = 0.759	h = −13 → 9
9485 measured reflections	k = −18 → 15
	l = −14 → 19

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.066	$+ 7.4956P]$
$wR(F^2)$ = 0.131	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.14	$(\Delta/\sigma)_{max}$ = 0.001
4806 reflections	$\Delta\rho_{max}$ = 0.63 e Å^{-3}
326 parameters	$\Delta\rho_{min}$ = −0.53 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ag1—P1	2.4081 (18)	P1—C21	1.806 (7)
Ag1—P2^i	2.4097 (18)	P1—C11	1.820 (7)
Ag1$\cdots$Ag1^i	3.0581 (12)	P1—C20	1.836 (6)
P1—Ag1—P2^i	174.95 (7)	C11—P1—C20	105.4 (3)
P1—Ag1$\cdots$Ag1^i	90.22 (5)	C21—P1—Ag1	117.1 (2)
P2^i—Ag1$\cdots$Ag1^i	89.07 (5)	C11—P1—Ag1	112.8 (2)
C21—P1—C11	102.0 (3)	C20—P1—Ag1	112.3 (2)
C21—P1—C20	106.1 (3)		

Symmetry code: (i) −x, 1 − y, −z.

The H atoms were positioned geometrically (C—H bond lengths were fixed in the range 0.93–0.97 Å), assigned isotropic displacement parameters and allowed to ride on their respective parent C atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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