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Bis-μ-[methylenebis(diphenylphosphine)]-dinitratodisilver(I) Dichloroform Solvate

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Abstract. $[Ag_2(NO_3)_2(C_{25}H_{22}P_2)_2].2CHCl_3$, $[Ag(NO_3)(Ph_2PCH_2PPh_2)]_2.2CHCl_3$, $M_r = 1347{\cdot}2$, triclinic, $P\bar{1}$, $a = 11{\cdot}232\,(1)$, $b = 12{\cdot}085\,(1)$, $c = 10{\cdot}844\,(1)$ Å, $\alpha = 98{\cdot}81\,(1)$, $\beta = 100{\cdot}06\,(1)$, $\gamma = 88{\cdot}19\,(1)^\circ$, $V = 1432\,(1)$ Å^3, $D_x = 1{\cdot}562$ Mg m^{-3} for $Z = 1$ (dimer), Mo $K\bar{\alpha}$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}065$ mm^{-1}, $F(000) = 676$, $T = 295\,(2)$ K, $R = 0{\cdot}028$ for 5133 observed reflections. The title compound exists as a centrosymmetric dimer in which two diphosphine ligands bridge two Ag atoms thereby forming an eight-membered ring. The ring adopts a staggered conformation with significant bending at the Ag atoms; Ag—P 2·452 (1) and 2·422 (1) Å, P—Ag—P 149·4 (1)°. The two nitrate anions each weakly chelate an Ag atom with Ag—O bond distances of 2·659 (3) and 2·652 (3) Å so that the Ag atoms are tetracoordinated.

Introduction. There are several studies in the literature concerning the interaction of silver(I) salts with the diphosphine bis(diphenylphosphine)methane (hereafter dppm) (Dean, Vittal & Srivastava, 1987; Obendorf, Probst, Peringer, Falk & Müller, 1988). Crystal structures are available for the 1:1 (*i.e.* 1 Ag : 1 dppm) complexes $[Ag_2(dppm)_2(NO_3)_2]$, $[Ag_4(dppm)_4(NO_3)_2][PF_6]_2$ (Ho & Bau, 1983) and $[Ag_3(dppm)_3Br_2]Br$ (Schubert, Neugebauer & Aly, 1980). A recent report of the chloro analogue of the latter compound has also appeared, namely $[Ag_3(dppm)_3Cl_2][Ph_2Sn(NO_3)_2Cl]$ (Franzoni, Pelizzi, Predieri, Tarasconi, Vitali & Pelizzi, 1989). In the dinuclear structure of $[Ag_2(dppm)_2(NO_3)_2]$, the P—Ag—P angles were found to be non-linear [138·3 (1)°] such that the eight-membered ring adopted the unusual conformation in which the two methylene C atoms were eclipsed (Ho & Bau, 1983). In the tetranuclear species $[Ag_4(dppm)_4(NO_3)_2][PF_6]_2$, which arises as a result of bridging nitrate groups, the two $[Ag_2(dppm)_2]$ units were also found to adopt the less usual conformation (Ho & Bau, 1983). A third structural type is found in the trinuclear cations $[Ag_3(dppm)_3Br_2]^+$ and $[Ag_3(dppm)_3Cl_2]^+$ in which each edge of a triangle of Ag atoms is bridged by a dppm ligand; the two coordinated halide atoms each cap a triangular face leading to a coordination polyhedron based on a trigonal bipyramid (Schubert *et al.*, 1980; Franzoni *et al.*, 1989). This communication reports the crystallographic characterization of a second isomer of $[Ag_2(dppm)_2(NO_3)_2]$ isolated as its chloroform solvate in which the $[Ag_2(dppm)_2]$ units are found to adopt the more usual staggered conformation.

Experimental. The title compound was prepared by mixing equimolar quantities of $AgNO_3$ (Johnson Matthey) and dppm (Strem) in aqueous ethanol. The resultant precipitate was recrystallized from a chloroform/373–393 K petroleum spirit solution at room temperature. Crystals were obtained as a $CHCl_3$ solvate and were found to be stable to light but decomposed on exposure to air presumably as a result of solvent loss. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation; $\omega{:}2\theta$ scan technique. Cell parameters on crystal 0·34 ×

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0·41 × 0·58 mm by least squares on 25 reflections (14 $\leq \theta \leq$ 17°) (de Boer & Duisenberg, 1984). Analytical absorption correction applied; max. and min. transmission factors 0·702 and 0·646 (Sheldrick, 1976). Total of 7422 reflections (1·5 $\leq \theta \leq$ 27·5°) measured in the range $-14 \leq h \leq 14$, $-13 \leq k \leq 13$, $-14 \leq l \leq 1$. No significant variation in the net intensities of three reference reflections ($\bar{3}\bar{8}2$, $\bar{2}\bar{7}5$, $\bar{6}\bar{1}7$) measured every 7200 s. 6544 unique reflections ($R_{\text{int}} = 0{\cdot}011$) and 5133 satisfied $I \geq 2{\cdot}5\sigma(I)$. Structure solved by Patterson method, full-matrix least-squares refinement of 327 parameters based on F (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms included at their calculated positions. At convergence $R = 0{\cdot}028$, $wR = 0{\cdot}034$, $w = 0{\cdot}72/[\sigma^2(F) + 0{\cdot}0001F^2]$, $S = 1{\cdot}15$, $(\Delta/\sigma)_{\max} \leq 0{\cdot}001$, $\Delta\rho_{\max} = 0{\cdot}59$, $\Delta\rho_{\min} = -0{\cdot}64$ e Å^{-3}; no extinction correction. Scattering factors for H, C, Cl, N, O and P given in *SHELX*76 (Sheldrick, 1976) and those for neutral Ag corrected for f' and f'' from *International Tables for X-ray Crystallography* (1974). All calculations on SUN4/280 computer system. Atomic parameters are given in Table 1, selected parameters in Table 2* and the numbering scheme used in shown in Fig. 1 [drawn with *ORTEP* (Johnson, 1971) at 15% probability ellipsoids].

Discussion. The molecular structure of $[Ag_2(dppm)_2(NO_3)_2]$ is shown in Fig. 1(a) from which it can be seen that the centrosymmetric molecule comprises two Ag atoms bridged by two dppm ligands; the eight-membered ring thus formed adopts the more common staggered conformation as emphasized in Fig. 1(b). This conformation contrasts the eclipsed conformation found in the unsolvated $[Ag_2(dppm)_2(NO_3)_2]$ structure which has crystallographic twofold symmetry (Ho & Bau, 1983). The coordination geometry about each Ag atom in the solvate is completed by a weakly associated, bidentate nitrate group; the Ag atoms are therefore tetracoordinated. In CD_3CN solution the ^1H NMR spectrum shows the same features as reported in the earlier study (most notably a multiplet at $\delta = 3{\cdot}77$) which was interpreted as being consistent with a non-folded structure (Ho & Bau, 1983). The implication of this observation is that there is a small difference in energy between the isomers and that the two conformations found in the solid state arise as a result of different crystallization procedures.

The Ag—P bond distances are comparable in the two isomers at 2·452 (1), 2·422 (1) Å and 2·436 (2), 2·417 (2) Å in the solvated and unsolvated (Ho & Bau, 1983) structures respectively. The P—Ag—P angles differ markedly [149·4 (1) and 138·3 (1)° respectively] but the degree of flexibility in the eight-membered rings is emphasized when one compares these values to the P—Ag—P angles of 152·0 (1) and 141·5 (1)° found in the closely related structure of $[Ag_4(dppm)_4(NO_3)_2][PF_6]_2$ (Ho & Bau, 1983). The Ag···Ag separation found in solvated $[Ag_2(dppm)_2(NO_3)_2]$ of 3·109 (1) Å agrees with the comparable separations of 3·085 (1) and 3·099 (1) Å found in $[Ag_2(dppm)_2(NO_3)_2]$ and $[Ag_4(dppm)_4(NO_3)_2][PF_6]$ respectively (Ho & Bau, 1983). These distances are not indicative of significant bonding between the Ag atoms.

Table 1. *Fractional atomic coordinates and* B_{eq} *values* (Å^2)

$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$

	x	y	z	B_{eq}
Ag	0·12494 (2)	0·44528 (2)	0·04069 (2)	3·02
P(1)	0·17480 (5)	0·55115 (5)	−0·11900 (6)	2·71
P(2)	0·08490 (5)	0·44236 (5)	0·25255 (5)	2·72
N(1)	0·1797 (2)	0·2263 (2)	−0·1270 (2)	3·93
O(1)	0·0917 (2)	0·2851 (2)	−0·1593 (3)	6·05
O(2)	0·2418 (3)	0·2565 (3)	−0·0220 (3)	7·03
O(3)	0·2062 (3)	0·1441 (2)	−0·1981 (3)	7·75
C(1)	0·0709 (2)	0·5130 (2)	−0·2692 (2)	2·96
C(111)	0·1644 (2)	0·7026 (2)	−0·0905 (3)	3·22
C(112)	0·1283 (3)	0·7534 (3)	0·0195 (3)	4·52
C(113)	0·1139 (4)	0·8691 (3)	0·0408 (5)	6·30
C(114)	0·1362 (4)	0·9325 (3)	−0·0466 (5)	6·66
C(115)	0·1716 (3)	0·8821 (3)	−0·1584 (5)	5·80
C(116)	0·1862 (3)	0·7679 (3)	−0·1794 (3)	4·42
C(121)	0·3225 (2)	0·5179 (2)	−0·1620 (2)	3·24
C(122)	0·3414 (3)	0·4147 (3)	−0·2322 (3)	4·12
C(123)	0·4565 (3)	0·3841 (3)	−0·2577 (4)	5·52
C(124)	0·5530 (3)	0·4578 (4)	−0·2093 (4)	5·71
C(125)	0·5345 (3)	0·5589 (4)	−0·1402 (3)	5·32
C(126)	0·4200 (2)	0·5907 (3)	−0·1156 (3)	4·03
C(211)	0·1083 (2)	0·3119 (2)	0·3175 (2)	3·21
C(212)	0·1678 (3)	0·2244 (3)	0·2556 (3)	4·99
C(213)	0·1906 (5)	0·1268 (3)	0·3092 (5)	7·26
C(214)	0·1531 (4)	0·1162 (3)	0·4207 (5)	6·87
C(215)	0·0944 (4)	0·2026 (3)	0·4826 (3)	5·97
C(216)	0·0706 (3)	0·2999 (3)	0·4311 (3)	4·49
C(221)	0·1792 (2)	0·5445 (2)	0·3674 (2)	3·18
C(222)	0·2741 (3)	0·5117 (3)	0·4536 (3)	4·26
C(223)	0·3537 (3)	0·5903 (4)	0·5296 (3)	5·08
C(224)	0·3376 (3)	0·7017 (4)	0·5193 (4)	5·56
C(225)	0·2424 (4)	0·7353 (3)	0·4327 (4)	5·45
C(226)	0·1627 (3)	0·6571 (3)	0·3577 (3)	4·20
C(3)	0·4688 (4)	0·0293 (4)	−0·2035 (5)	6·93
Cl(31)	0·5853 (2)	0·1274 (1)	−0·1529 (2)	9·63
Cl(32)	0·5166 (2)	−0·0981 (1)	−0·1578 (2)	11·21
Cl(33)	0·4243 (2)	0·0180 (2)	−0·3640 (2)	12·37

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Primed atoms are related by a centre of inversion.

Ag—P(1)	2·452 (1)	Ag—P(2)	2·422 (1)
Ag—O(1)	2·659 (3)	Ag—O(2)	2·652 (3)
P(1)—C(1)	1·835 (3)	P(2′)—C(1)	1·846 (3)
N(1)—O(1)	1·231 (3)	N(1)—O(2)	1·236 (4)
N(1)—O(3)	1·223 (3)	Ag···Ag′	3·109 (1)
P(1)—Ag—P(2)	149·4 (1)	P(1)—Ag—O(1)	80·9 (1)
P(1)—Ag—O(2)	98·9 (1)	P(2)—Ag—O(1)	129·2 (1)
P(2)—Ag—O(2)	106·5 (1)	O(1)—Ag—O(2)	46·7 (1)
Ag—P(1)—C(1)	109·8 (2)	Ag—P(2)—C(1′)	112·4 (2)
P(1)—C(1)—P(2′)	110·5 (2)	O(1)—N(1)—O(2)	117·0 (3)
O(1)—N(1)—O(3)	121·0 (3)	O(2)—N(1)—O(3)	122·0 (3)
Ag—O(1)—N(1)	98·1 (2)	Ag—O(2)—N(1)	98·2 (2)

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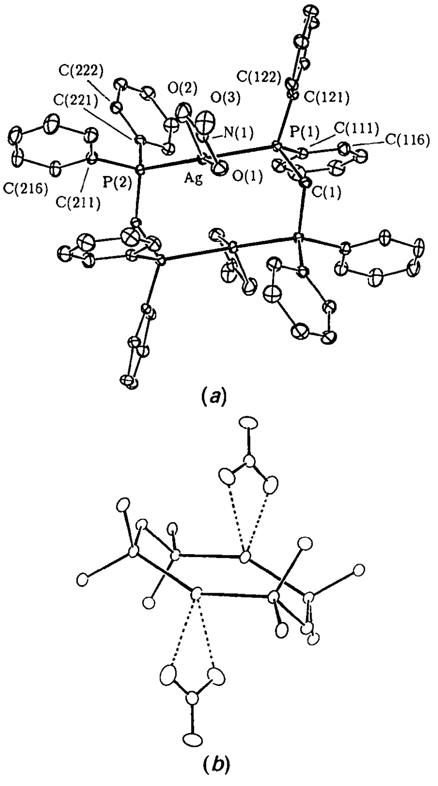
* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52269 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The nitrate groups associate differently in the two isomers. In the $CHCl_3$ solvate the unique nitrate group functions as a weakly bidentate ligand forming Ag—O bond distances of 2·659 (3) and 2·652 (3) Å. These values can be compared to the sum of the van der Waals radii for these atoms of 3·20 Å (Bondi, 1964). In the unsolvated structure the nitrate group also functions as a bidentate ligand but forms disparate Ag—O bond lengths of 2·416 (5) and 2·689 (6) Å. The different modes of association of the nitrate groups can be rationalized in terms of the different steric requirements of the eight-membered rings. The two nitrate groups lie on either side of the eight-membered ring in the staggered conformation and associate with equidistant Ag—O bonds. In the eclipsed conformation, however, both nitrate groups lie on the same side of the molecule and pivot about the Ag—O(1) bond in order to minimize the O···O interactions above the ring.



(a)

(b)

Fig. 1. (a) Molecular structure and numbering scheme for $[Ag_2(dppm)_2(NO_3)_2]$ (Johnson, 1971). (b) Core structure showing the conformation of the eight-membered ring.

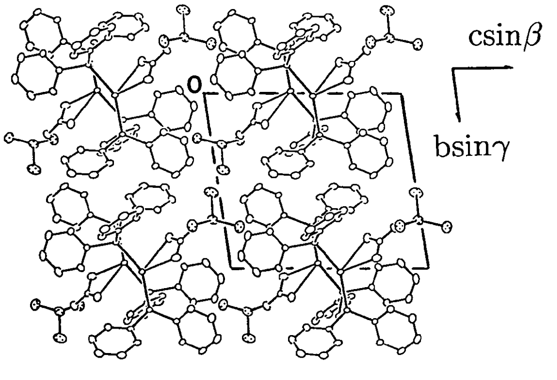


Fig. 2. Unit-cell contents for $[Ag_2(dppm)_2(NO_3)_2].2CHCl_3$ with the chloroform molecules shaded.

The structure found here for solvated $[Ag_2(dppm)_2(NO_3)_2]$ can be related to that found for the bis(dimethylphosphino)methane analogue $[Ag_2(dmpm)_2(NO_3)_2]$ (Karsch & Schubert, 1982). In $[Ag_2(dmpm)_2(NO_3)_2]$ the centrosymmetric eight-membered ring adopts an extended chair conformation owing to the absence of additional Ag···anion interactions with the result that the P—Ag—P angles are almost linear at 174·3 (3)°. A similar structure was found in the gold analogue, $[Au_2(dmpm)_2]Cl_2$, with P—Au—P angles of 176·61 (5)° (Kozelka, Oswald & Dubler, 1986). In the gold/dppm complex, $[Au_2(dppm)_2Cl_2]$, the staggered conformation was found (Schmidbaur, Wohlleben, Schubert, Frank & Huttner, 1977) as for the solvated $[Ag_2(dppm)_2(NO_3)_2]$ species.

In the crystal lattice, illustrated in Fig. 2, there are no significant intermolecular contacts between the complex molecules. The crystal packing can be thought of as being comprised of alternate layers of complex and solvent molecules. The closest contact between the chloroform molecule and the complex is 2·39 Å and occurs between C(3)—H(3) and O(3); the C(3)···O(3) separation is 3·22 Å. These values indicate a weak interaction between these atoms.

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Structure of Cytosinium Dihydrogenmonophosphate

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Abstract. $C_4H_6N_3O^+.H_2PO_4^-$, $M_r = 209{\cdot}10$, monoclinic, $P2_1/a$, $a = 6{\cdot}931\ (7)$, $b = 17{\cdot}992\ (8)$, $c = 6{\cdot}520\ (3)$ Å, $\gamma = 97{\cdot}97\ (7)°$, $V = 805\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}725$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}347$ mm^{-1}, $F(000) = 432$, $T = 293$ K, final $R = 0{\cdot}027$ for 2108 independent observed reflections. Layers of $H_2PO_4^-$ anions perpendicular to the b axis alternate with layers of $C_4H_6N_3O^+$ cations. The phosphate groups are linked by hydrogen bonds to form a two-dimensional network. The cytosine groups are interconnected with the phosphoric planes through three hydrogen bonds along **b** and are joined themselves by another hydrogen bond along the mirror a. The plane of the cytosine ring is approximately perpendicular to the layers. A parallel stacking of the base rings appears with an interplanar distance of 3·3 Å in each cytosine layer.

Introduction. It seems that interactions between various kinds of phosphoric acids and nucleic acids have not yet been well investigated. The only compound known in this domain is the adeninium phosphate $C_5H_6N_5^+.H_2PO_4^-$ (Langer & Huml, 1979) prepared from a purine base, adenine. In the present work, we describe another compound resulting from the interaction between monophosphoric acid and a pyrimidine base, cytosine.

Experimental. Crystals of cytosinium dihydrogenmonophosphate are easily prepared by slow evaporation at room temperature of an aqueous solution of H_3PO_4 and cytosine in stoichiometric ratio. Large colorless prisms up to 1 cm long are obtained. Density not measured. Prism fragment: 0·24 × 0·24 × 0·35 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $0k0$, $k = 2n$; $h0l$, $h = 2n$. 22 reflections ($10 < \theta < 14°$) for refining unit-cell dimensions; ω scan. Scan width: 1·20°, scan speed variable between 0·02 and 0·04° s^{-1}, total background measuring time: between 14 and 28 s. 2258 non-zero reflections measured ($3 < \theta < 35°$), $\pm h$, k, l, $h_{\max} = 10$, $k_{\max} = 28$, $l_{\max} = 10$. Two intensity ($3\bar{4}2$ and 0,10,1) and two orientation ($\bar{3}42$ and $34\bar{2}$) reference reflections: no significant variation. Lorentz and polarization corrections, no absorption correction. Crystal structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Unit weights. Final refinement with the complete set of unique reflections (2108). Final $R = 0{\cdot}027$, $wR = 0{\cdot}031$, $S = 0{\cdot}398$, max. $\Delta/\sigma = 0{\cdot}08$. Max. peak height in the final difference Fourier map: 0·308 e Å^{-3}. Extinction not refined. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX. The crystal-structure representations were drawn using *STRUPLO84* (Fischer, 1985).

Discussion. Table 1 reports the final atomic coordinates.* Fig. 1 is a projection of the whole atomic arrangement down the c axis, while Fig. 2 is the projection of a structural detail down the b axis. The main interatomic distances and bond angles are listed in Table 2.

The structure can be described as layers of $H_2PO_4^-$ groups spreading in planes $y \sim 0$ and 0·5 alternating with layers of $C_4H_6N_3O^+$ groups at $y \sim 0{\cdot}25$ and 0·75 (Fig. 1).

Each $H_2PO_4^-$ group is connected by hydrogen bonds with three neighbours across centres of symmetry, to build a two-dimensional network illus-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52252 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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