Available online at www.sciencedirect.com
SCIENCE DIRECT®

Inorganica Chimica Acta 359 (2006) 2170–2177

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Novel solvates in AgX:dpex (*n*:1) systems ($n = 1$ or 2); X = oxyanion; dppx = $Ph_2P(Y)PPh_2$, Y = $(CH_2)_3$, Fc

Augusto Cingolani [a], Effendy [b,c], Claudio Pettinari [a,*], Brian W. Skelton [b], Allan H. White [b]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Via S. Agostino 1, 62032 Camerino MC, Italy*
[b] *Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia*
[c] *Jurusan Kimia, FMIPA Universitas Negeri Malang, Jalan Surabaya 6, Malang 65145, Indonesia*

Received 2 November 2005; accepted 11 December 2005
Available online 8 February 2006

Abstract

Novel solvated forms are spectroscopically (^1H, ^{13}C, ^{31}P, IR and conductivity studies) and structurally described for diverse silver oxyanion salt:bis(diphenylphosphino)-ligand adducts of 2:1:*n* (AgX:dppx:S) stoichiometry. $AgClO_4$:dppf:MeCN (2:1:4) ('dppf' = bis(diphenylphosphino)ferrocene) is a binuclear centrosymmetric species: $[(O_3ClO)(MeCN)_2Ag(P\text{-dppf-}P')Ag(NCMe)_2(OClO_3)]$, Ag–P short at 2.368(1) Å. Two MeOH/H_2O solvates are described, of AgX:dppp (2:1) stoichiometry, both single stranded polymers (X = carboxylate: 'ac' = acetate, 'tfa' = trifluoroacetate; 'dppp' = $Ph_2P(CH_2)_xPPh_2$; $x = 3$), with silver atoms spanned alternately by: (i) a *P*-dppp-*P′* bridge, supported by tenuously bridging water or methanol, and (ii) *O*-ac, tfa-*O′* bridge(s), being assigned stoichiometries Agtfa:dppp:H_2O (2:1:1) · MeOH and Agac:dppp:MeOH(2:1:0.5) · $3\frac{1}{2}H_2O$. The structure of $AgClO_4$:dppe:MeCN (1:1:1) ('dppe', $x = 2$), also a one-dimensional polymer, but with all Ag…Ag sequences bridged by the *P*,*P′* ligand, and with unidentate MeCN and $OClO_3$ coordinated to the silver, is also recorded.

Keywords: Silver; Diphosphine; Solvate silver complexes; X-ray; NMR spectroscopy; Polynuclear complexes

1. Introduction

As noted in the preceding paper [1], the formation of adducts of MX:dpex (2:1) stoichiometry (M = Cu(I), Ag(I); X = simple anion; dpex = $Ph_2E(CH_2)_xEPh_2$, E = P, As(, Sb)) results in the possibility of situations where coordinative unsaturation may arise in consequence of the dearth of ligand donor atoms, particularly so where the anion is a weak donor, leading to the possibility of coordination by solvent molecules. With Cu(I), acetonitrile is a particularly potent donor solvent, and we have described the structural characterisation of a number of diverse solvates of such complexes. With Ag(I) analogues, acetonitrile is a less effective donor; in the present paper we describe a few solvates that we have obtained in such circumstances, only one of 2:1 stoichiometry being with acetonitrile, namely $AgClO_4$:dppf:MeCN (2:1:4) ('dppf' = bis(diphenylphosphino)ferrocene), while with the silver(I) carboxylates Agac, Agtfa ('ac' = $CH_3CO_2^-$; tfa = $CF_3CO_2^-$), a pair of novel one-dimensional polymers obtained from (aqueous) methanol are described. An adduct of 1:1 $AgClO_4$:dppe stoichiometry also forms a solvated polymer: $AgClO_4$:dppe:MeCN (1:1:1).

2. Experimental

All syntheses and handling were carried out in the air. All chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C, H, N) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Mercury Plus Varian 400 NMR spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C,

---

[*] Corresponding author. Tel.: +39 0737 402234; fax: +39 0737 637345.
E-mail address: claudio.pettinari@unicam.it (C. Pettinari).

0020-1693/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.12.015

and 162.1 MHz for ^{31}P). H and C chemical shifts are reported in ppm versus $\mathrm{SiMe_4}$, P chemical shifts in ppm versus $\mathrm{H_3PO_4}$ 85%. The electrical conductances of the acetone, dichloromethane, DMSO and acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

2.1. Syntheses

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.

2.1.1. Agtfa:dppp:H_2O (2:1:1)·MeOH (1)

Agtfa (0.440 g, 2.0 mmol) was added to a methanol solution (10 mL) containing dppp (0.412 g, 1 mmol). A colorless precipitate immediately formed. The suspension was stirred overnight, then was filtered off and the colorless residue washed with a methanol:diethyl ether mixture (1:1) and shown to be compound **1** (0.497 g, yield 55%); a few more substantial crystals were obtained from the mother liquor on standing. M.p. 160 °C dec. *Anal.* Calc. for $\mathrm{C_{32}H_{32}Ag_2F_6O_6P_2}$: C, 42.50; H, 3.57. Found: C, 42.57; H, 3.56%. IR (nujol, $\mathrm{cm^{-1}}$): 3300br ν(OH), 1667s, 1651s, 1436s ν(CO), 1196s, 1137m, 1099s, 516m, 480m, 459w, 423w, 270w. ^{1}H NMR ($\mathrm{CD_3CN}$, 293 K): δ, 1.8 (m, 2H, $\mathrm{C}H_{2\mathrm{dppp}}$), 2.22 (br, 2H, $\mathrm{H_2O}$), 2.47 (q, 4H, $\mathrm{C}H_{2\mathrm{dppp}}$), 3.35 (s, 3H, $\mathrm{C}H_3\mathrm{OH}$), 7.5 (m, 12H, $\mathrm{C_6}H_{5\mathrm{dppp}}$), 7.6 (pt, 8H, $\mathrm{C_6}H_{5\mathrm{dppp}}$). ^{13}C NMR ($\mathrm{CD_3CN}$, 293 K): δ, 23.5 (m, $C\mathrm{H}_{2\mathrm{dppp}}$), 28.20 (s, $C\mathrm{H}_{2\mathrm{dppp}}$), 28.5 (s, $C\mathrm{H}_{2\mathrm{dppp}}$), 130.2 (d, C_{dppp}), 132.0 (s, C_{dppp}), 133.9 (d, C_{dppp}), 207.56 (s, CO). ^{31}P NMR ($\mathrm{CD_3CN}$, 293 K): δ, 8.0br. ^{31}P NMR ($\mathrm{CD_3CN}$, 233 K): δ, 7.8 (d br, $^1J(^{31}\mathrm{P}\text{–}\mathrm{Ag})$: 705 Hz).

2.1.2. Agac:dppp:MeOH(2:1:0.5) · $3\frac{1}{2}H_2O$ (2)

Compound **2** has been prepared in 70% yield (0.576 g) following a procedure similar to that reported for **1** by using Agac (0.334 g, 2.0 mmol) and dppp (0.412 g, 1.0 mmol). M.p. 118–120 °C. *Anal.* Calc. for $\mathrm{C_{31.5}H_{41}Ag_2O_8P_2}$: C, 45.84; H, 5.01. Found: C, 45.67; H, 4.86%. IR (nujol, $\mathrm{cm^{-1}}$): 3300br ν(OH), 1560s, 1375 shsh br ν(CO), 1100m, 516m, 483m, 459w, 414w, 324w, 279w. ^{1}H NMR ($\mathrm{CD_3CN}$, 293 K): δ, 1.85 (m, 2H, $\mathrm{C}H_{2\mathrm{dppp}}$), 1.9 (br, 2H, $\mathrm{H_2O}$), 2.47 (q, 4H, $\mathrm{C}H_{2\mathrm{dppp}}$), 3.35 (s, 3H, $\mathrm{C}H_3\mathrm{OH}$), 4.8 (OH), 7.5 (m, 12H, $\mathrm{C_6}H_{5\mathrm{dppp}}$), 7.6 (pt, 8H, $\mathrm{C_6}H_{5\mathrm{dppp}}$). ^{13}C NMR ($\mathrm{CD_3CN}$, 293 K): δ, 23.5 (m, $C\mathrm{H}_{2\mathrm{dppp}}$), 28.20 (s, $C\mathrm{H}_{2\mathrm{dppp}}$), 28.5 (s, $C\mathrm{H}_{2\mathrm{dppp}}$), 130.2 (d, C_{dppp}), 132.0 (s, C_{dppp}), 133.9 (d, C_{dppp}), 207.56 (s, CO). ^{31}P NMR ($\mathrm{CD_3CN}$, 293 K): δ, 8.5br. ^{31}P NMR ($\mathrm{CD_3CN}$, 233 K): δ, 7.96 (dd, $^1J(^{31}\mathrm{P}\text{–}^{109}\mathrm{Ag})$): 759 Hz, $^1J(^{31}\mathrm{P}\text{–}^{107}\mathrm{Ag})$: 664 Hz.

2.1.3. $AgClO_4$:dppf:MeCN (2:1:4) (3)

$\mathrm{AgClO_4}$ (0.41 g, 2.0 mmol) was added to an acetonitrile solution (10 mL) containing dppf (0.53 g, 1 mmol). The clear pale-yellow solution was stirred overnight, then evaporated under vacuum until a pale-yellow precipitate formed which was filtered off and shown to be compound **3** (0.790 g, yield 70%); a few more substantial crystals were obtained from the mother liquor on standing. M.p. 94–96 °C dec. *Anal.* Calc. for $\mathrm{C_{42}H_{40}Ag_2Cl_2FeN_4O_8P_2}$: C, 44.51; H, 3.56; N, 4.94. Found: C, 44.35; H, 3.76; N, 5.11%. IR (nujol, $\mathrm{cm^{-1}}$): 2310w ν(CN), 1090sbr, 621s $\nu(\mathrm{ClO_4})$, 541m, 520m, 513m, 485m, 487m, 450br sh, 420w, 399w, 303w, 280m. ^{1}H NMR ($\mathrm{CD_3CN}$, 293 K): δ, 2.22 (s, 12H, $\mathrm{C}H_{3\mathrm{MeCN}}$), 4.15 (s, 4H, $\mathrm{C_5}H_{4\mathrm{Fc}}$), 4.56 (s, 4H, $\mathrm{C_5}H_{4\mathrm{Fc}}$), 7.5br (s, 20H, $\mathrm{C_6}H_{5\mathrm{Fc}}$). ^{13}C NMR ($\mathrm{CD_3CN}$, 293 K): δ, 74.96, 75.32, 75.40, 130.0 (m, $C_6\mathrm{H}_{5\mathrm{dppf}}$), 131.88 (s, $C_6\mathrm{H}_{5\mathrm{dppf}}$), 134.13 (m, $C_6\mathrm{H}_{5\mathrm{dppf}}$). ^{31}P NMR ($\mathrm{CD_3CN}$, 293 K): δ, 0.1br. ^{31}P NMR ($\mathrm{CD_3CN}$, 233 K): δ, 1.0 (dd, $^1J(^{31}\mathrm{P}\text{–}^{109}\mathrm{Ag})$: 730 Hz, $^1J(^{31}\mathrm{P}\text{–}^{107}\mathrm{Ag})$: 633 Hz).

2.1.4. $AgClO_4$:dppe:MeCN (1:1:1) (4)

$\mathrm{AgClO_4}$ (0.41 g, 2.0 mmol) was added to an acetonitrile solution (10 mL) containing dppe (0.80 g, 2.0 mmol). The clear pale-yellow solution was stirred overnight, then evaporated under vacuum until a pale-yellow precipitate formed which was filtered off and shown to be compound **4** (0.64 g, yield 50%); a few more substantial crystals were obtained from the mother liquor on standing. M.p. 163–165 °C. *Anal.* Calc. for $\mathrm{C_{28}H_{27}AgClNO_4P_2}$: C, 52.00; H, 4.21; N, 2.17. Found: C, 51.95; H, 4.36; N, 2.11%. IR (nujol, $\mathrm{cm^{-1}}$): 2310w ν(CN), 1099sbr, 620s $\nu(\mathrm{ClO_4})$, 507m, 480m, 421w, 400w, 30w, 345w, 320w, 280w, 255w. ^{1}H NMR ($\mathrm{CD_3CN}$, 293 K): δ, 2.19 (s, 3H, $\mathrm{C}H_{3\mathrm{MeCN}}$), 2.45 (s, 4H, $\mathrm{C}H_{2\mathrm{dppe}}$), 7.5 (br, 20H, $\mathrm{C_6}H_{5\mathrm{dpp}}$). ^{13}C NMR ($\mathrm{CD_3CN}$, 293 K): δ, 24.82 (s, $C\mathrm{H}_{2\mathrm{dppe}}$), 130.71, 132.46, 134.04 (br, $C_6\mathrm{H}_{5\mathrm{dppe}}$). ^{31}P NMR ($\mathrm{CD_3CN}$, 293 K): δ, 6.1br. ^{31}P NMR ($\mathrm{CD_3CN}$, 233 K): δ, 6.88 (d, $^1J(^{31}\mathrm{P}\text{–}\mathrm{Ag})$: 460 Hz), 5.6 (d, $^1J(^{31}\mathrm{P}\text{–}\mathrm{Ag})$: 502 Hz).

2.2. Structure determinations

General procedures are described in the preceding paper [1]; specific details are as follows. CCDC 286292–286295.

2.2.1. Agtfa:dppp:H_2O (2:1:1)·MeOH, **1** ≡ $C_{32}H_{32}Ag_2F_6O_6P_2$, $M = 904.3$

Monoclinic, space group Pn (C_2^5, No. 7 (variant)), $a = 12.845(2)$, $b = 7.978(1)$, $c = 17.002(2)$ Å, $\beta = 101.547(2)°$, $V = 1708$ Å^3. D_c ($Z = 2$) $= 1.75_8$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 13.2$ cm^{-1}; specimen: $0.73 \times 0.15 \times 0.12$ mm; 'T'$_{\mathrm{min/max}} = 0.65$. $2\theta_{\mathrm{max}} = 58°$; $N_t = 15276$, $N = 3931$ ($R_{\mathrm{int}} = 0.047$), $N_o = 3636$; $R = 0.056$, $R_w = 0.074$. CCD instrument, T ca. 153 K.

Variata: Methanol hydrogen atoms were not located.

2.2.2. Agac:dppp:MeOH(2:1:0.5) · $3\frac{1}{2}H_2O$, **2** ≡ $C_{31.5}H_{41}Ag_2O_8P_2$

Monoclinic, space group $P2_1/n$ (C_{2h}^5, No.14), $a = 8.042(2)$, $b = 19.245(4)$, $c = 22.136(4)$ Å, $\beta = 91.660(5)°$, $V = 3425$ Å^3. D_c ($Z = 4$) $= 1.60_1$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 12.8$ cm^{-1}; specimen: $0.15 \times 0.10 \times 0.08$ mm; 'T'$_{\mathrm{min/max}} = 0.54$. $2\theta_{\mathrm{max}} = 58°$; $N_t = 48607$, $N = 9076$ ($R_{\mathrm{int}} = 0.097$), $N_o = 5794$; $R = 0.063$, $R_w = 0.073$. CCD instrument, T ca. 153 K.

Variata: One of the two independent acetate groups in the structure is modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement; it bridges a pair of silver atoms, one of which is coordinated by the methanol group, whose occupancy refines also to ca. 0.5, (at which value it was constrained), occupancy perhaps in concert with one of the acetate orientations; the associated OH hydrogen atom was not located. Other difference map residues were modelled as water molecule oxygen atoms (hydrogens not located), with large displacement parameters but seemingly of total occupancy in refinement.

2.2.3. $AgClO_4$:dppf:MeCN (2:1:4), **3** ≡ $C_{42}H_{40}Ag_2Cl_2Fe\text{-}N_4O_8P_2$, $M = 1133.3$

Monoclinic, space group $P2_1/c$ (C^5_{2h}, No.14), $a = 10.528(3)$, $b = 25.979(6)$, $c = 8.565(3)$ Å, $\beta = 91.39(2)°$, $V = 2342$ Å^3. D_c ($Z = 2$) $= 1.60_7$ g cm^{-3}. $\mu_{Mo} = 13.7$ cm^{-1}; specimen: $0.42 \times 0.30 \times 0.62$ mm; $T_{min,max} = 0.58$, 0.71. $2\theta_{max} = 50°$; $N = 4112$, $N_o = 2555$; $R = 0.040$, $R_w = 0.041$. Single counter instrument, T ca. 295 K.

Variata: Disorder was resolvable in two of the perchlorate oxygen atoms, one of them coordinated, and in one of the acetonitrile groups coordinated to the same silver atom, presumably concerted; site occupancies of the disordered components were set at 0.5 after trial refinement.

2.2.4. $AgClO_4$:dppe:MeCN (1:1:1), **4** ≡ $C_{28}H_{27}AgClNO_4P_2$, $M = 646.8$

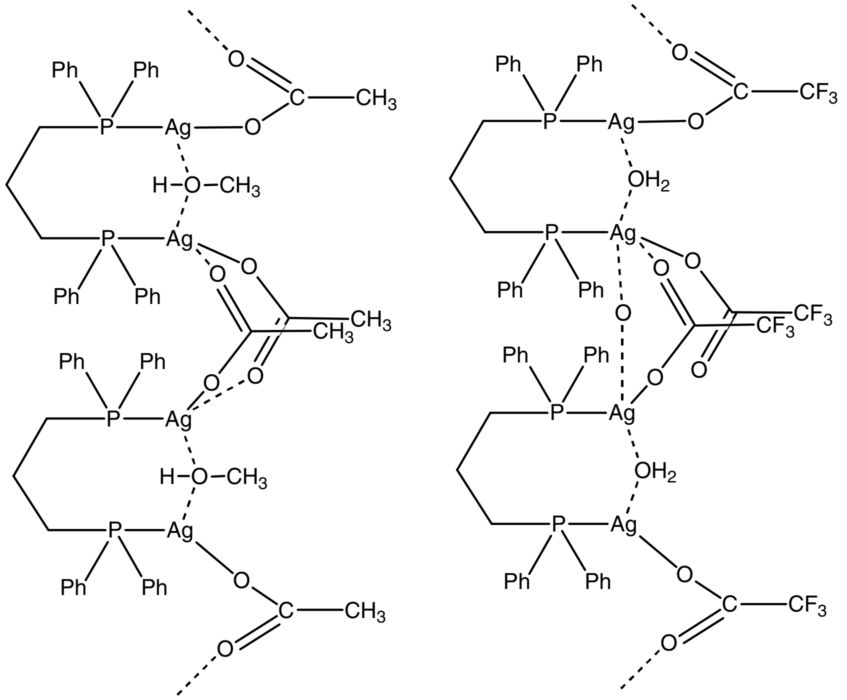
Triclinic, space group $P\bar{1}$ (C^1_i, No. 2), $a = 13.450(2)$, $b = 11.278(6)$, $c = 10.118(2)$ Å, $\alpha = 100.52(4)$, $\beta = 96.12(2)$, $\gamma = 105.99(3)°$, $V = 1431$ Å^3. D_c ($Z = 2$) $= 1.50_1$ g cm^{-3}. $\mu_{Mo} = 9.4$ cm^{-1}; specimen: $0.38 \times 0.20 \times 0.18$ mm; $T_{min,max} = 0.72$, 0.84. $2\theta_{max} = 50°$; $N = 5010$, $N_o = 3436$; $R = 0.048$, $R_w = 0.050$. Single counter instrument, T ca. 295 K.

3. Results and discussion

3.1. Syntheses

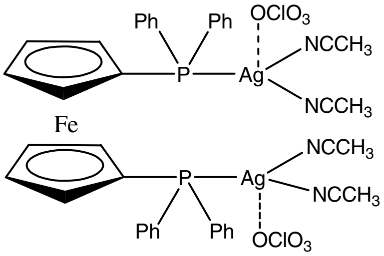
The reaction of two equivalents of AgX (X = ac or tfa) with one equivalent of 1,3-bis(diphenylphosphino)propane (dppp) at room temperature in methanol gave rise to the compounds *Agtfa:dppp:H_2O (2:1:1) · MeOH (**1**)* and *Agac:dppp:MeOH (2:1:0.5) · $3\frac{1}{2}H_2O$ (**2**)*, respectively (Chart 1). The choice of solvent and the ligand to metal ratio are both determinants in the formation of the compounds. For example, when both reactants were mixed and stirred in a 1:1 ligand to metal molar ratio, the well-known 1:1 adducts have been obtained. A strict 1:2 ligand to metal ratio is required in order to prevent formation of 1:1 [2] or 2:1 adducts. The adduct *$AgClO_4$:dppf:MeCN (2:1:4) (**3**)* (Chart 2) has been obtained with limited crystalline components from the slow evaporation of the mother liquor of an MeCN solution containing the metal salt and dppf in 2:1 molar ratio.

The compound *$AgClO_4$:dppe:MeCN (1:1:1) (**4**)* (Chart 3) has been obtained only when a 1:1 ligand to metal ratio has been employed. When a ligand excess was employed, the previously reported 2:1 species formed [3], whereas when a metal excess was used, only intractable material



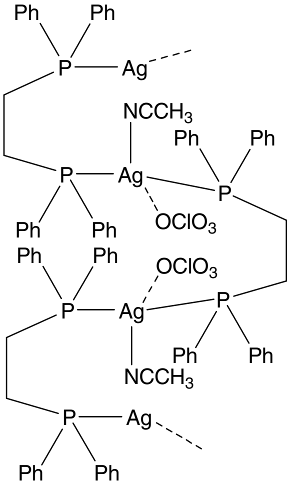
1 **2**

Chart 1.



3

Chart 2.



4

Chart 3.

has been recovered. Compounds **1**–**4** are soluble in acetonitrile and DMSO, insoluble in alcohols and diethyl ether. **1** and **2** are moderately soluble also in chlorinated solvents. Conductivity measurements, as expected, indicated that the perchlorate complexes **3** and **4** are electrolytes, not only in MeCN but also in dichloromethane solution, the values of Λ_M being for these compounds greater than 40 Ω^{-1} cm^2 mol^{-1}. The carboxylate species **1** and **2** exhibit values typical of partly ionized species in CH_2Cl_2.

3.2. Spectroscopy

The infrared spectra of **1**–**4** (see Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the counter-ion and of the diphosphine donors [4]. The bands due to the phosphine ligands are only slightly shifted with respect to those of the free donors. In the far-IR spectra of derivatives **1**–**4** we assigned, on the basis of a previous report on phosphino silver(I) derivatives [5,6], the broad absorptions near 500 cm^{-1} and those at 450–400 cm^{-1} to Whiffen's *y* and *t* vibrations, respectively.

In the cases of carboxylate derivatives it is generally accepted [7] that it is possible to distinguish between ionic, unidentate, chelating bidentate or bridging bidentate groups on the basis of Δ values (where $\Delta = \nu_a(COO)-\nu_s(COO)$), the trend generally accepted being:

$$\Delta_{\text{unidentate}} > \Delta_{\text{ionic}} > \Delta_{\text{bridging bidentate}} > \Delta_{\text{chelating bidentate}}$$

In compounds **1** and **2** the Δ is ca. 180 cm^{-1}, respectively, in accordance with unsymmetrical bidentate coordination of the carboxylate group, and consistent with the X-ray data.

In the case of ionic ClO_4^- T_d geometry only two vibrations (ν_3 and ν_4) are expected to be IR active [8], as in fact is found in **3** and **4**, at ca. 1100 and 620 cm^{-1}, in good accordance with the results found in the solid state that suggest the existence of a weak perturbation of ClO_4^-.

Solution studies, being unlikely to reflect, in detail or more generally, the complexed polymeric forms present in the solid, should be considered with that caveat in mind. In the ^1H NMR spectra of **1**–**4** in CD_3CN (Section 2), the signals due to the diphosphine exhibit a different pattern relative to those found for the free donors, confirming the occurrence at least of partial complexation in solution. The bridging methylene resonances in **1**, **2** and **4**, appear as broad singlets or resolved multiplets generally between 1.00 and 2.50 ppm downfield shifted with respect to those found in the free donors.

^{31}P chemical shifts ($CDCl_3$ solution) and ^{31}P–Ag coupling-constants for all derivatives are reported in Section 2. Our experiments have been carried out at a concentration of 0.005 mol/L.

The room temperature ^{31}P NMR spectra of compounds **1, 2** and **4** all exhibit a broad signal (in the range 4–8 ppm), ascribed to rapid bond-breaking processes. The absorption is downfield shifted with respect to the corresponding signal in the free ligand. The ^{31}P,Ag coupling constant values and the chemical shifts are typical of species containing AgP environments [9].

3.3. Structural studies

Structurally defined adducts of the form AgX:dppf (*m*:*n*) have recently been surveyed and augmented [10]. The most extensively recorded stoichiometry is of $(1{:}1)_{(n)}$ adducts, for which there are now numerous examples. By contrast, as with other AgX:dppx combinations, adducts of AgX:dppf 2:1 stoichiometry are limited in number, being represented only by an acetate [11], although that report also records the synthesis of a 2:1 benzoate. The acetate is a centrosymmetric tetranuclear array, in which the two independent silver atoms are (quasi-) four-coordinate, the coordination number being achieved by virtue of the chelating and/or bridging coordination modes of the carboxylates; the dppf ligand bridges the two independent silver atoms of the asymmetric unit.

The present array, *$AgClO_4$:dppf:MeCN (2:1:4), (**3**)*, is simpler, being an elegant binuclear centrosymmetric dimer, $[\{(MeCN)_2(O_3ClO)Ag\}_2(P\text{-dppf-}P')]$, the iron atom being disposed at the crystallographic inversion centre with the dppf linking the two-symmetry-related silver atoms through its phosphorus donors (Fig. 1). Ag–P (Table 1) is appreciably shorter than in the array of (1:1)$_2$ adducts recently described, presumably because the complement of other atoms in the silver(I) coordination sphere are here much weaker donors. In the present array, interaction with the perchlorate, which approaches as a unidentate, is feeble; the perchlorate is disordered, the disorder resolvable in two of the oxygen atoms, one of which is the donor, the two components of which lie at disparate distances, long and very long. The remainder of the coordination environment is made up of a pair of acetonitrile molecules, one of which is also disordered (the two components more similar), perhaps in concert with the perchlorate; silver(I) not infrequently displays ambiguous coordination environments, and here, deconvoluted as in Table 1, it might be conjectured that the longer perchlorate approach corresponds to an almost exactly trigonal array of the PAgN$_2$ aggregate, while the shorter is associated with a perturbation of the latter towards tetrahedral.

Table 1
The silver coordination environment(s), AgClO$_4$:dppf:MeCN (2:1:4), **3**

Component 'a'		Component 'b'	
Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ag–P	2.368(1)		
Ag–N(11)	2.318(9)		
Ag–N(21a)	2.20(1)	Ag–N(21b)	2.29(1)
Ag–O(1a)	2.59(1)	Ag–O(1b)	2.94(2)
Angles (°)			
P–Ag–N(11)	119.3(2)		
P–Ag–N(21a)	145.5(3)	P–Ag–N(21b)	134.8(3)
N(11)–Ag–N(21a)	78.6(4)	N(11)–Ag–N(21b)	105.9(4)
$\sum$	343.$_4$	$\sum$	360.$_0$
P–Ag–O(1a)	115.6(3)	P–Ag–O(1b)	117.1(3)
N(11)–Ag–O(1a)	91.6(4)	N(11)–Ag–O(1b)	71.7(4)
N(21a)–Ag–O(1a)	91.2(4)	N(21b)–Ag–O(1b)	76.6(4)

Beyond the above, the only other AgX:dpex (2:1) adducts structurally described are the X = Cl, Br, NCO derivatives with dppm, also the NCO/dpam, all 'step' structures (or close derivatives thereof), and, beyond those, the NO$_3$/dppp adduct, also a tetranuclear species with more tenuous relations to the 'step' form [12]. It is of interest that the array is further extended here with two further dppp adducts, the anions both being carboxylates, 'isoelectronic' with nitrate but stronger donors, so that it is perhaps surprising that, at least thus far, it is the latter forms which are solvated, albeit in one case quite tenuously, although the result is now no longer tetranuclear in either case, both forms being one-dimensional polymers, the asymmetric unit in both cases containing two independent silver atoms. The polymers lie parallel to the short axes of their cells, the generator being the unit translation in each case, otherwise devoid of symmetry, so that the sequences of the silver atoms are both ...1212... Linkage of the silvers is achieved in two ways, one being by way of the dppp ligand, bridging, and the other by bridging carboxylate units, so that the two strings take the form......Ag(*P*-dppp-*P*)Ag(OCO)$_{(1\text{or}2)}$Ag(*P*...; there is a tendency toward two-coordination about (most of) the silver atoms, but ... see below. In detail:

In *Agtfa:dppp:H$_2$O (2:1:1)·(MeOH)* (***1***), (Fig. 2; Table 2) disparate silver atoms are linked by the *P*-dppp-*P*′ linker (torsions, successively, 36.1(9), 175.7(8), 174.0(8), 39.5(8)°), the phosphorus atoms, together with

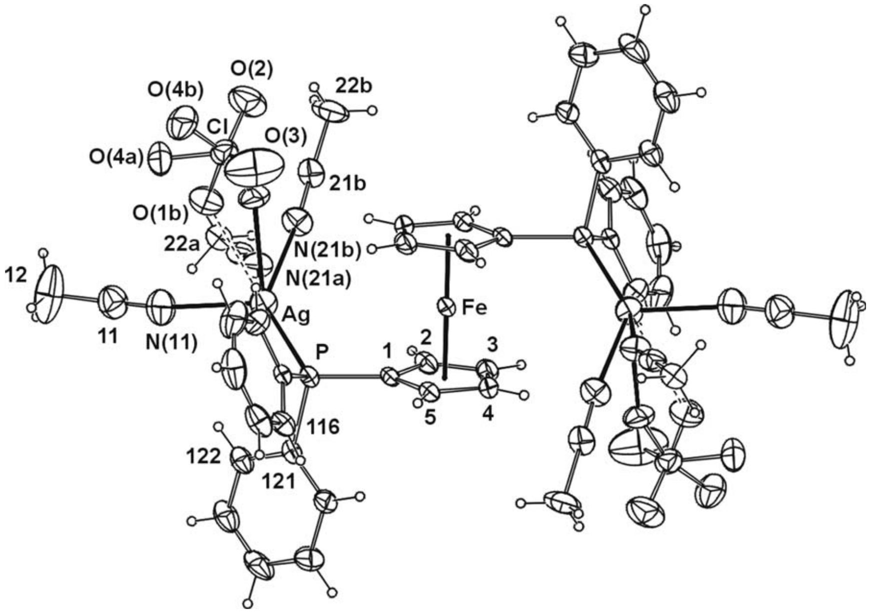


Fig. 1. A single molecule of AgClO$_4$:dppf:MeCN (2:1:4), **3**.

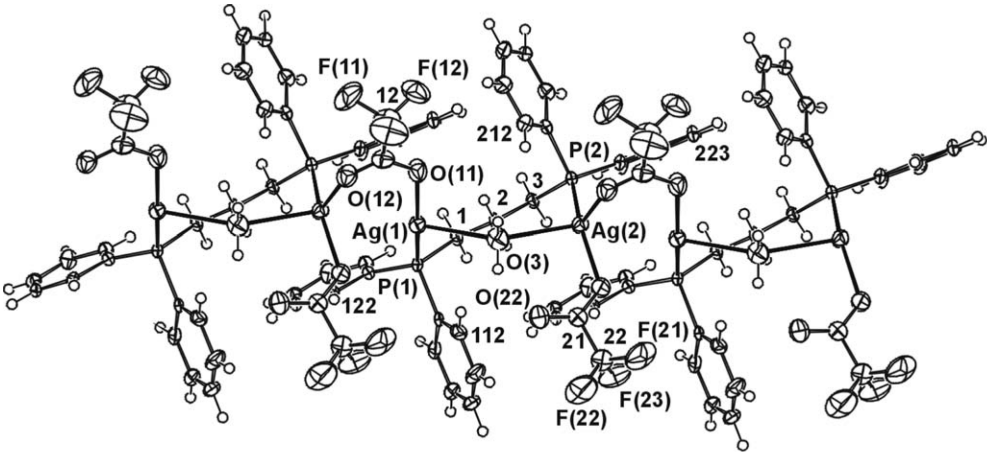


Fig. 2. A strand of the one-dimensional polymer of Agtfa:dppp:H_2O (2:1:1)$_{(\infty|\infty)}$, **1**, projected normal to the polymer axis which lies parallel to *b*.

Table 2
Silver environments, Agtfa:dppp:H_2O (2:1:1)$_{(\infty|\infty)}$ · (MeOH), **1**

Ag(1)		Ag(2)	
Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ag(1)–P(1)	2.382(3)	Ag(2)–P(2)	2.367(3)
Ag(1)–O(11)	2.19(1)	Ag(2)–O(21)	2.25(1)
Ag(1)–O(w)	2.76(1)	Ag(2)–O(12$^{\mathrm{i}}$)	2.45(1)
Ag(1)...O(21$^{\mathrm{ii}}$)	2.92(1)	Ag(2)–O(w)	2.76(1)
Ag(1)...Ag(2)	4.989(2)	Ag(1)...Ag(2$^{\mathrm{ii}}$)	3.00(1)
Angles (°)			
P(1)–Ag(1)–O(11)	161.3(4)	P(2)–Ag(2)–O(21)	152.1(3)
P(1)–Ag(1)–O(w)	105.0(2)	P(2)–Ag(2)–O(w)	108.0(2)
		P(2)–Ag(2)–O(12$^{\mathrm{ii}}$)	115.8(3)
O(11)–Ag(1)–O(w)	82.3(4)	O(21)–Ag(2)–O(w)	87.1(4)
		O(12$^{\mathrm{ii}}$)–Ag(2)–O(w)	92.5(3)
		O(21)–Ag(2)–O(12$^{\mathrm{ii}}$)	85.9(4)
Ag(1)–O(11)–C(11)	121.8(10)	Ag(2)–O(12$^{\mathrm{ii}}$)–C(11$^{\mathrm{ii}}$)	121.1(9)
		Ag(2)–O(21)–C(21)	128.9(10)

Transformations of the asymmetric unit: i, ii x, $1 + y$, z. The two associated silver atoms lie 0.09(3), 1.11(3) Å out of the plane of carboxylate **1**, Ag(2) 0.55(3) Å out of the plane of carboxylate **2**.

quasi-trans carboxylate oxygens, dominating the coordination environments quasi-linearly. The two silver atoms, separated by 4.989(2) Å, are loosely linked by the water molecule oxygen, completing an eight-membered ring. The other Ag(1)...Ag(2) distance (3.009(2) Å) is shorter, being bridged by carboxylate 1; the second carboxylate is swivelled so that one of its oxygen atoms has no close interaction with a silver atom; rather the first oxygen, O(21) interacts at a long distance with the other silver semi-bridging. Difference map residues model persuasively as lattice methanol (C–O 1.39(3), O...O(w) (≡O(3)) 2.73(2) Å) although no associated hydrogen atoms were located.

In *Agac:dppp:MeOH (2:1:0.5)* · *(3$\frac{1}{2}$$H_2O$)* (**2**) (Fig. 3, Table 3), the Ag...Ag distance spanned by the *P*-dppp-*P′* ligand is greater (5.251(2) Å; ligand torsions: −38.4(4), −175.0(4), −173.2(4), −38.7(4)°); the incipiently spanning solvent oxygen, now methanolic, 'contacts' the two silver atoms at 3.91(1), 2.80(1) Å. The diminution in this tie is compensated by a strengthening in the other Ag...Ag linkage, now 2.887(1) rather than 2.92(1) Å in consequence of both carboxylates now bridging. One of the latter is

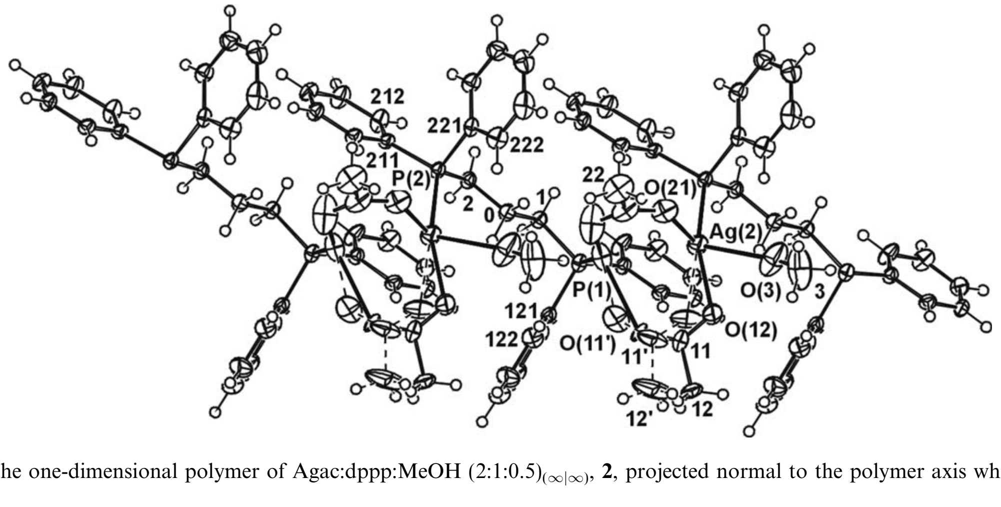


Fig. 3. A strand of the one-dimensional polymer of Agac:dppp:MeOH (2:1:0.5)$_{(\infty|\infty)}$, **2**, projected normal to the polymer axis which lies parallel to *a*.

Table 3
Silver environments, Agac : dppp : MeOH$(2 : 1 : 1/2)_{(\infty|\infty)} \cdot (3\frac{1}{2}H_2O)$, **2**

Ag(1)		Ag(2)	
Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ag(1)–P(1)	2.354(2)	Ag(2)–P(2^i)	2.379(2)
Ag(1)–O(11′)	2.19(1)	Ag(2)–O(21)	2.535(5)
Ag(1)–O(11)	2.57(3)	Ag(2)–O(12)	2.14(1)
Ag(1)...O(22)	2.194(7)	Ag(2)–O(12′)	2.26(2)
Ag(1)...Ag(2)	2.887(1)	Ag(2)–O(3)	2.80(1)
Angles (°)			
P(1)–Ag(1)–O(11′)	117.2(4)	P(2^i)–Ag(2)–O(21)	100.9(1)
P(1)–Ag(1)–O(22)	148.0(2)	P(2^i)–Ag(2)–O(12)	150.1(4)
O(11′)–Ag(1)–O(22)	88.1(4)	P(2^i)–Ag(2)–O(12′)	153.8(4)
$\sum$	$353._3$		
O(11)–Ag(1)–P(1)	103.9(6)	O(21)–Ag(2)–O(12)	108.4(4)
O(11)–Ag(1)–O(22)	105.7(6)	O(21)–Ag(2)–O(12′)	101.6(5)
O(11)–Ag(1)–O(11′)	21.8(7)	O(12)–Ag(2)–O(12′)	20.4(6)

Transformation of the asymmetric unit: i, $x - 1$, y, z.

Table 4
Selected geometries, AgClO$_4$:dppe:MeCN $(1:1:1)_{(\infty|\infty)}$, **4**

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ag–P(1)	2.414(2)	Ag–O(1)	2.676(5)
Ag–P(2)	2.416(2)	Ag–N(11)	2.715(9)
Angles (°)			
P(1)–Ag–P(2)	153.43(6)	P(2)–Ag–O(1)	107.9(1)
P(1)–Ag–O(1)	97.3(1)	P(2)–Ag–N(11)	84.3(2)
P(1)–Ag–N(11)	108.4(2)	O(1)–Ag–N(11)	81.1(2)
Ag–O(1)–Cl	109.8(3)	Ag–N(11)–C(11)	150.5(10)

disordered over two sets of sites, presumedly in concert with the occupancy of the methanol solvated, the latter refining to 0.5. Which carboxylate is a concomitant of the solvent's presence is more problematic; O(3) lies closest to Ag(2), but the geometries associated with O(12,12′) are of little assistance in defining the association; the difference in Ag(1)–O(11,11′) is more significant, but Ag(1) lies much further from O(3). It may be noteworthy that O(3)...O(12,12′) are 2.73(2), 3.39(2) Å, the former distance typical of a hydrogen-bonding contact. The relativity in coordination between ac and tfa and between H_2O versus MeOH is interesting; the weaker solvent donor is a concomitant of the stronger anion donor.

By contrast with the present relatively limited number of 2:1 AgX:dppx solvated adducts, a considerable number of solvates have been recorded for adducts of 1:1 stoichiometry, the majority of these being with dpem (= Ph_2E-CH_2EPh_2, E = P, As) ligands [13] in a binuclear form in which two predominantly two-coordinate silver atoms are linked into a binuclear Ag(E-dpem-E′)$_2$Ag eight-membered ring, with the silver coordination number augmented by interactions with anion oxygens and solvent nitrogen (MeCN, py) or oxygen (EtOH). We take the opportunity to record here the structural characterization of an acetonitrile solvated AgX:dppe adduct of 1:1 stoichiometry, being *AgX:dppe:MeCN (1:1:1),* ***4*** (Fig. 4, Table 4). Like the dppp adducts above, this is a one-dimensional polymer (Fig. 4), one formula unit comprising the asymmetric unit of the structure which is propagated along *a* by inversion and translation. All Ag...Ag linkages here are provided by dppe, the mid-points of the C(H$_2$)–C(H$_2$) bonds from two independent linkages lying at successive inversion centres with necessarily trans torsions. The silver atom is quasi-linearly coordinated by a pair of phosphorus atoms from successive ligands, the coordination number being increased to four by rather distant approaches from the solvent molecule and unidentate *O*ClO$_3$ anion (Table 4).

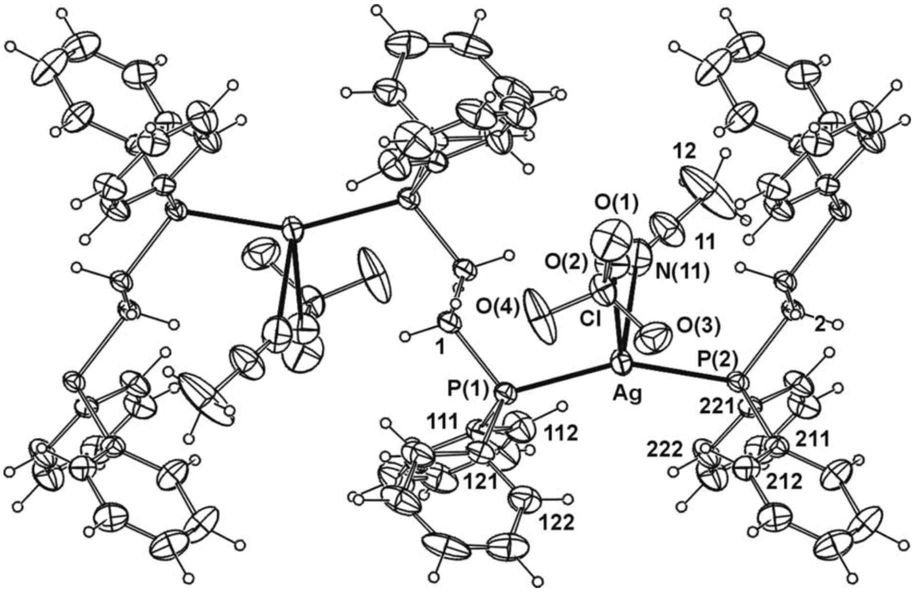


Fig. 4. View of the polymer of AgClO$_4$:dppe:MeCN $(1:1:1)_{(\infty|\infty)}$, **4**, propagated along *a*.

References

[1] C. Di Nicola, G.A. Koutsantonis, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 359 (2006) 2159.

[2] Effendy, C. Di Nicola, M. Fianchini, C. Pettinari, B.W. Skelton, A.H. White, Inorg. Chim. Acta 358 (2005) 763.

[3] C. Di Nicola, C. Pettinari, M. Ricciutelli, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 4003.

[4] K. Shobatake, C. Postmus, J.F. Ferraro, K. Nakamoto, Appl. Spectrosc. 23 (1969) 12.

[5] A. Cingolani, Effendy, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, Inorg. Chem. 41 (2002) 6633.

[6] A. Cingolani, Effendy, J.V. Hanna, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, Inorg. Chem. 42 (2003) 4938.

[7] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.

[8] M.R. Rosenthal, J. Chem. Edu. 50 (1973) 331.

[9] E.L. Muetterties, C.W. Alegranti, J. Am. Chem. Soc. 94 (1972) 6386.

[10] C. di Nicola, Effendy, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 695.

[11] T.S.A. Hor, S.P. Neo, C.S. Tan, T.C.W. Mak, K.W.P. Leung, R.-J. Wang, Inorg. Chem. 31 (1992) 4510.

[12] C. di Nicola, Effendy, C. Pettinari, B.W. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 359 (2006) 53.

[13] Effendy, C. di Nicola, M. Nitiatmodjo, C. Pettinari, B.W. Skelton, A.H. White, Inorg. Chim. Acta 358 (2005) 735.