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Synthesis and structural characterization of adducts of silver(I) oxyanion salts, AgX (X = ClO₄, NO₃), with Ph₂E(CH₂)_xEPh₂ ('dpex'; E = P, As; x = 1-3) and oligodentate aromatic N-bases derivative of 2,2'-bipyridyl, 'L', AgX:dpex:L (2:1:1) or (1:1:1)

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Abstract

Six new adducts of silver(I) perchlorate and nitrate, AgX, with N,N'(,-N'')-oligodentate ligands L, derivative of 2,2'-bipyridyl, together with Ph₂E(CH₂)_xEPh₂ (='dpex'), are reported and characterized by spectroscopic and structural studies. Two different stoichiometries were found: AgNO₃:dpex:'tpy' (2:1:1), ('tpy' = 2,2':6',2''-terpyridyl; 1: dpex = 'dppm' (Ph₂PCH₂PPh₂); **2**: dpex = 'dpam' (Ph₂AsCH₂AsPh₂); **3**: dpex = 'dppp' (Ph₂P(CH₂)₃PPh₂)) and AgClO₄:dpex:L (1:1:1), (**4**: dpex = 'dpae' (Ph₂As(CH₂)₂AsPh₂), L = tpy); **5**: dpex = dppp; L = 'phen' (1,10-phenanthroline); **6**: dpex = dppp; L = 'dmp' (2,9-dimethyl,1,10-phenanthroline)). In AgNO₃:dpem:tpy (2:1:1) (**1**,**2**), tpy acts as a bridging bis(chelate), the central pyridine donor in 'crevice' coordination mode: [(ONO₂)-Ag(*E*-dpem-*E'*)(*N*,*N'*-tpy-*N'*,*N''*)Ag(*O*₂NO)]. A further bridging tpy is found in tetranuclear AgNO₃:dppp:tpy (2:1:1)₂ (**3**), in which the wrapping of a centrosymmetric Ag(μ -ONO₂)₂Ag kernel by *P*-dppp-*P'* to form [Ag(μ -ONO₂)₂(*P*-dppp-*P'*)₂Ag] is pre-empted by the insertion of (Agtpy) into one of the potential Ag–P bonds of each ligand, the third pyridine of the bidentate tpy bridging to a kernel silver atom. AgClO₄:dpae:tpy (1:1:1)_(∞|∞) (**4**) is a single-stranded polymer (···Ag(tpy)(*As*-dpae-*As'*)Ag(tpy)···)_(∞|∞), while AgClO₄:dppp:L (1:1:1)₂ (**5**,**6**) are dimers of the form [LAg(*P*-dppp-*P'*)₂AgL]. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

In the preceding paper [1] we have described the synthesis, spectroscopic properties and structural features of a quasi-systematic and comprehensive nature of adducts of the form AgX (X = oxyanion (NO₃, ClO₄)):dpex (= (Ph₂E(CH₂)_xEPh₂)),E = P, As:L (L = oligodentate-N_n donors, derivative of 2,2'-bipyridyl), all defining arrays of

2:1:2 stoichiometry, with some novel forms described, most being $[LAg(E-dpex-E')AgL]X_2$ salts, those with x even being centrosymmetric and *trans*-oid, with close approaches to the silver atoms by oxyanions or solvent (MeCN, H₂O) molecules, while those with x = 1 exhibited an AgE ... EAg '*cis*' form. 2,2':6',2"-Terpyridyl, 'tpy', has been also found in its role as a ligand able to bridge pairs of silver atoms, linking them into a single-stranded polymer as in AgClO₄: dppp:tpy (2:1:2). For reasons concerned with solubility or other less tangible considerations, a number of dpex:L combinations did not yield adducts of 2:1:2 stoichiometry, but,

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rather, other stoichiometries, specifically 2:1:1 or 1:1:1 AgX:dpex:L. We record these in the present paper.

2. Experimental

Experimental procedures follow those recorded in the preceding paper [1]; in the majority of cases crystals suitable for the X-ray work were readily obtained from a few mL of MeCN solutions of the reagents on a millimolar scale by slow cooling and/or evaporation in ambience.

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 handed with great caution.

2.1.1. AgX (=NO₃):dpex:L (=tpy) (2:1:1)_(n)(·nS) complexes

2.1.1.1. Synthesis of $AgNO_3$: dppm: tpy (2:1:1) (1). A solution containing AgNO₃ (0.169 g, 1.0 mmol), 'dppm' (Ph₂P(CH₂)PPh₂) (0.199 g, 0.5 mmol), and tpy (0.116 g, 0.5 mmol) in 20 mL of CH₃CN was stirred for 12 h at room temperature. The solution was then evaporated under vacuum and the colorless residue washed with diethyl ether and shown to be compound 1 (0.160 g, 35 %, yield). M.p. 225-226 °C. Anal. Calc. for C₄₀H₃₃Ag₂N₆O₆P₂: C, 49.46; H, 3.42; N, 8.65. Found: C, 49.33; H, 3.40; N, 8.64%. IR (nujol, cm^{-1}): 1950w, 1891w, 1817w, 1743w $v(NO_3)$, 1615br, 1593s, 1574s v(C---C, C---N), 1434s, 1380sh, 1301s, 1008m, 822s v(NO₃), 519s, 504s, 467s, 426w, 409w, 350w. ¹H NMR (CD₃CN, 293 K): δ 3.60 (t, 2H, CH₂ dppm), 3.75 (sbr, 1H, CH_{2dppm}), 2.72 (sbr, 1H, CH_{2dppm}), 7.28–7.51 (m, 20H, C_6H_{5dppm} + 2H, CH_{tpv}), 8.02 (t, 2H, CH_{tpv}), 8.25 (m, 5H, CH_{tpy}), 8.31 (d, 2H, CH_{tpy}). ¹³C NMR (CD₃CN, 293 K): δ 25.0 (br, CH_{2dppm}), 124.6 (d, C_{dppm}), 126.63 (s, *C*_{tpy}), 130.1 (br, *C*_{dppm}), 132.3 (d, *C*_{dppm}), 134.1 (br, *C*_{dppm}), 140.17 (s, C_{tpy}), 141.5 (s, C_{tpy}), 151.83 (s, C_{tpy}), 153.78 (s, C_{tpy}), 154.52 (s, C_{tpy}). ³¹P NMR (CD₃CN, 293 K): δ 7.0 $(d, {}^{1}J({}^{31}P-Ag): 500.7 \text{ Hz}); 6.0 \text{ i}(d \text{ br}, {}^{1}J({}^{31}P-Ag): 580 \text{ Hz}).$ The compound was re-crystallized from MeCN as $1 \cdot 1\frac{1}{2}$ MeCN.

2.1.1.2. Synthesis of $AgNO_3$: dpam: tpy (2:1:1) (2). A solution of tpy (0.116 g, 0.5 mmol) in 10 mL of CH₃CN was added to a solution containing AgNO₃ (0.169 g, 1.0 mmol) and 'dpam' (Ph₂As(CH₂)AsPh₂) (0.286 g, 0.5 mmol). A precipitate was immediately formed and the suspension was stirred 12 h at room temperature, then filtered off; the precipitate was re-crystallized from MeCN/ethanol and washed with ethanol and shown to be compound **2**. 2EtOH (0.318 g, 56%, yield). M.p. >141 °C. Anal. Calc. for C₄₄H₄₅Ag₂As₂N₅O₈: C, 46.46; H, 3.99; N, 6.16. Found: C, 46.60; H, 4.15; N, 6.32%. IR (nujol, cm⁻¹): 3300br (OH), 3060 (CH) 1955br, 1890w, 1815w, 1740w $v(NO_3)$, 1615br, 1593s, 1574s v(C--C, C, -N), 1434 s, 1380sh,

1301s, 1008m, 822s v(NO₃), 519s, 504s, 467s, 426w, 409w, 350w. ¹H NMR (CD₃CN, 293 K): δ 3.15 (s, 2H, CH₂ dppm), 7.2–7.6 (m, 20H, C₆H_{5dppm} + 2H, CH_{tpy}), 8.00 (t, 2H, CH_{tpy}), 8.20 (m, 5H, CH_{tpy}), 8.30 (d, 2H, CH_{tpy}).

2.1.1.3. Synthesis of $AgNO_3$: dppp: tpy (2:1:1) (3). Compound 3 (0.124 g, 25% yield) has been prepared following a procedure similar to that reported for 1 by using $AgNO_3$ $(0.169 \text{ g}, 1 \text{ mmol}), \text{ 'dppp'} (Ph_2P(CH_2)_3PPh_2) (0.206 \text{ g}, 1000 \text{ g})$ 0.5 mmol), and tpy (0.116 g, 0.5 mmol). M.p. 284-285 °C. Anal. Calc. for C₄₂H₃₇Ag₂N₆O₆P₂: C, 50.47; H, 3.73; N, 8.41. Found: C, 50.38; H, 3.70; N, 8.34%. IR (nujol, cm⁻¹): 3048w (CH), 1970w, 1954w, 1881w, 1812w, 1739w v(NO₃), 1586s, 1556sh v(C---C, C---N), 1435s, 1376s, 1298s, 1036m, 991m, 821m, 520s, 505s, 482s, 474s, 448s, 312w. ¹H NMR (CD₃CN, 293 K): δ 1.8 (br, 4H, CH₂dppp), 2.50 (t, 4H, CH_{2dppp}), 7.2-7.5 (m, 20H, C_6H_{5dppm} + 2H, CH_{tpy}), 8.02 (t, 2H, CH_{tpy}), 8.25 (m, 5H, CH_{tpy}), 8.31 (d, 2H, CH_{tpy}). ³¹P NMR (CD₃CN, 293 K): δ 5.5 br. ³¹P NMR (CD₃CN, 233 K): δ 0.1 (d br, J(P-Ag): 659 Hz). It was re-crystallized from MeCN in ambience as $3 \cdot H_2O$.

2.1.2. $AgX (=ClO_4):dpex:L (1:1:1)_{(2)} (:nS)$ complexes

2.1.2.1. Synthesis of $AgClO_4$: dpae:tpy (1:1:1) (4). Compound 4 has been obtained as $4 \cdot 2MeCN$ by crystallization of millimolar stoichiometries of the silver salt with 'dpae' (Ph₂As(CH₂)₂AsPh₂) and tpy, from acetonitrile solution by standing and evaporation in ambience. *Anal.* Calc. for C₄₅H₄₁AgAs₂ClN₅O₄: C, 53.57; H, 4.10; N, 6.94. Found: C, 53.01; H, 3.91; N, 6.72%. M.p. 213–216 °C (dec).

2.1.2.2. Synthesis of AgClO₄: dppp:phen (1:1:1) (5). Compound 5 (0.312 g, yield 39%) has been prepared following a procedure similar to that reported for 1 by using $AgClO_4$ (0.104 g, 0.5 mmol), dppp (0.206 g, 0.5 mmol), and 'phen' (1,10-phenanthroline) (0.091 g, 0.5 mmol). M.p. 134-135 °C. Anal. Calc. for C39H34AgCINO4P: C, 58.56; H, 4.28; N, 3.50. Found: C, 58.46; H, 4.22; N, 3.39%. IR (nujol, cm⁻¹): 3046w, 2000br, 1890br, 1817br, 1620m, 1587m, 1567m, 1537m v(C---C, C---N), 1076 sbr, 621br v(ClO₄), 508w, 477w, 414w, 320w, 241w. ¹H NMR (CD₃CN, 293 K): δ 2.02 (sbr, 2H, CH_{2dppp}), 2.54 (sbr, 4H, CH_{2dppp}), 7.16–7.32 (m, 20H, C_6H_{5dppp}), 7.65 (m, 2H, CH_{phen}), 7.90 (s, 2H, CH_{phen}), 8.43 (m, 2H, CH_{phen}), 8.68 (sbr, 2H, CH_{phen}). ¹³C NMR (CD₃CN, 293 K): δ 25.0br, 29.0br (CH_{2dppp}), 125.22 (s, C_{phen}), 128.11 (s, C_{phen}), 129.98 (br, C_{dppp}), 130.52 (s, C_{phen}), 131.51 (br, C_{dppp}), 133.23 (br, C_{dppp}), 138.61 (s, C_{phen}), 144.97 (s, C_{phen}), 151.34 (s, C_{phen}). ³¹*P* NMR (CD₃CN, 293 K): δ 3.8 (d, $J(^{31}\text{P}-\text{Ag})$: 410.6 Hz). It was re-crystallized from MeCN/CHCl₃ in ambience as $5 \cdot CHCl_3 \cdot \frac{1}{2}H_2O.$

2.1.2.3. Synthesis of $AgClO_4$: dppp: dmp (1:1:1) (6). Compound 6 (0.360 g,% yield) has been prepared following a procedure similar to that reported for 1 by using AgClO₄

(0.208 g, 1.0 mmol), dppp (0.412 g, 1.0 mmol), and 'dmp' (2,9-dimethyl,1,10-phenanthroline) (0.208 g, 1.0 mmol). M.p. 241–242 °C. Anal. Calc. for C₄₁H₃₈AgClN₂O₄P₂: C, 59.47; H, 4.63; N, 3.38. Found: C, 59.30; H, 4.58; N, 3.34%. IR (nujol, cm⁻¹): 3048 (CH), 2007w, 1955w, 1895w, 1805w v(ClO₄), 1618s, 1590s, 1556m, 1502s v(C---C, C---N), 1083 sbr, 622s v(ClO₄), 548m, 512s, 481s, 468m, 445m, 429w, 395m, 327w, 311w. ¹H NMR (CD₃CN, 293 K): δ 1.91 (s, 2H, CH_{2dppp}), 2.53 (br, 12H, CH_{3dmp}), 2.70 (br, 4H, CH_{2dppp}), 7.28 (m br, 20H, C₆H_{5dppp}), 7.67 (d, 2H, CH_{dmp}), 7.99 (s, 2H, CH_{dmp}), 8.47 (d, 2H, CH_{dmp}). ¹³C NMR (CD₃CN, 293 K): δ 27.11 (s, CH_{3dmp}), 27.9 (br, CH_{2dppp}), 124.72 (s, C_{dmp}), 126.08 (s, C_{dmp}), 127.71 (s, C_{dmp}), 128.95 (s, C_{dppp}), 130.39 (s, C_{dppp}), 131.98 (br, C_{dppp}), 139.87 (s, C_{dmp}), 142.53 (s, C_{dmp}), 159.99 (s, C_{dmp}). ³¹P NMR (CD₃CN, 293 K): δ 2.5br, -0.1br, -2.9 s br; -5.6 (d, ${}^{1}J({}^{31}P-Ag)$: 231.8 Hz). It was re-crystallized from MeCN as $6 \cdot 2$ MeCN.

2.2. Structure determinations

General procedures are described in an accompanying paper [1]; specific details are given below. CCDC 295270–295275.

2.2.1. Crystallrefinement data

2.2.1.1. AgX (= NO_3):dpex:L (=tpy) (2:1:1)_(n)($\cdot nS$) complexes.

2.2.1.1.1. $AgNO_3:dppm:tpy (2:1:1) \cdot 1\frac{1}{2}MeCN (1 \cdot 1\frac{1}{2}MeCN. C_{43}H_{37.5}Ag_2N_{6.5}O_6P_2, M = 1019.0.$ Monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14), a = 10.400(3), b = 15.902(4), c = 26.033(6) Å, $\beta = 100.705(3)^\circ, V = 4230$ Å³. D_c (Z = 4) = 1.60₀ g cm⁻³. $\mu_{Mo} = 1.06$ mm⁻¹; specimen: 0.42 × 0.05 × 0.05 mm; ' $T_{min/max} = 0.80.$ $2\theta_{max} = 58^\circ$; $N_t = 43029, N = 11196$ ($R_{int} = 0.099$), $N_o = 5522$; $R = 0.053, R_w = 0.050$.

Variata. Acetonitriles 3, 4 were modelled as disordered, the former over a pair of sites (occupancies set at 0.5), the latter about a centre of symmetry, with geometrical constraints. Displacement parameters throughout the structure were generally rather high.

2.2.1.1.2. $AgNO_3:dpam:tpy~(2:1:1) \cdot 2EtOH~(2 \cdot 2EtOH)$. $C_{44}H_{45}Ag_2As_2N_5O_8, M = 1137.5.$ Triclinic, space group $P\overline{1}$ $(C_i^1, \text{ No. } 2), a = 10.5899(7), b = 13.5459(9), c = 15.6398$ $(10) \text{ Å}, \alpha = 94.108(2), \beta = 90.491(2), \gamma = 101.240(2)^\circ, V = 2194 \text{ Å}^3.$ $D_c~(Z = 2) = 1.72_1 \text{ g cm}^{-3}.$ $\mu_{Mo} = 2.45 \text{ mm}^{-1}$; specimen: $0.29 \times 0.22 \times 0.11 \text{ mm}$; $T_{\min/max}^* = 0.70.$ $2\theta_{max} = 65^\circ$; $N_t = 43.890, N = 15.783$ $(R_{int} = 0.037), N_o = 11774$; $R = 0.045, R_w = 0.059.$

Variata. Phenyl ring 12x was modelled as disordered over two sites of equal occupancy after trial refinement (rigid body constraints). The hydroxylic hydrogen atom of EtOH (2) was not located.

2.2.1.1.3. $AgNO_3:dppp:tpy$ (4:2:2) · H_2O (3 · H_2O). C₈₄-H₇₆Ag₄N₁₀O₁₃P₄, M = 1989.0. Triclinic, space group $P\bar{1}$, a = 10.556(4), b = 18.557(7), c = 20.700(7) Å, $\alpha =$ 83.766(5), $\beta = 89.204(6)$, $\gamma = 74.579(7)^{\circ}$, $V = 3885 \text{ Å}^3$. D_c $(Z = 2) = 1.70_0 \text{ g cm}^{-3}$. $\mu_{Mo} = 1.15 \text{ mm}^{-1}$; specimen: 0.23 $\times 0.15 \times 0.14 \text{ mm}$; $T_{\text{min/max}}^{\circ} = 0.87$. $2\theta_{\text{max}} = 55^{\circ}$; $N_t = 36970$, N = 17573 ($R_{\text{int}} = 0.037$), $N_o = 13682$; R = 0.061, $R_w = 0.092$.

Variata. Water molecule hydrogen atoms were not located.

2.2.1.2. $AgX (=ClO_4):dpex:L (1:1:1)_{(2)} (\cdot nS)$ complexes. 2.2.1.2.1. $AgClO_4:dpae:tpy (1:1:1)_{(\infty|\infty)} \cdot 2MeCN$ $(4 \cdot 2MeCN)$. $C_{45}H_{41}AgAs_2ClN_5O_4$, M = 1009.0. Monoclinic, space group C2/c (C_{2h}^6 , No. 15), a = 26.943(3), b = 12.647(1), c = 27.331(3) Å, $\beta = 112.303(2)^\circ$, V = 8616Å³. $D_c (Z = 8) = 1.55_5$ g cm⁻³. $\mu_{Mo} = 2.10$ mm⁻¹; specimen: $0.24 \times 0.17 \times 0.04$ mm; ' $T_{min/max} = 0.73.2\theta_{max} = 60^\circ$; $N_t = 62491$, N = 12556 ($R_{int} = 0.060$), $N_o = 9089$; R = 0.043, $R_w = 0.056$.

2.2.1.2.2. $AgClO_4:dpp:phen (1:1:1)_2 \cdot CHCl_3 \cdot \frac{1}{2}H_2O$ (5 · $CHCl_3 \cdot \frac{1}{2}H_2O$). $C_{79}H_{70}Ag_2Cl_5N_4O_{8.5}P_4$, M = 1728.3. Orthorhombic, space group $Pnma (D_{2h_2}^{16}$ No. 62), a = 25.110(2), b = 24.185(1), c = 12.6723(7) Å, V = 7695 Å³. $D_c (Z = 4) = 1.49_2$ g cm⁻³. $\mu_{Mo} = 0.82$ mm⁻¹; specimen: $0.30 \times 0.20 \times 0.17$ mm; ' $T_{min/max} = 0.90$. $2\theta_{max} = 68^\circ$; $N_t = 159800$, N = 15947 ($R_{int} = 0.092$), $N_o = 8894$; R = 0.044, $R_w = 0.047$.

Variata. Perchlorate, chloroform and water molecules were modelled as disordered.

2.2.1.2.3. $AgClO_4:dpp:dmp (1:1:1)_2 \cdot 2MeCN (6 \cdot 2Me-CN)$. $C_{86}H_{82}Ag_2Cl_2N_6O_8P_4$, M = 1738.2. Triclinic, space group $P\overline{1}$, a = 11.1399(6), b = 13.5758(7), c = 13.7822(7) Å, $\alpha = 105.572(1)$, $\beta = 99.532(1)$, $\gamma = 91.127(1)^\circ$, V = 1976 Å³. $D_c (Z = 1) = 1.46_1$ g cm⁻³. $\mu_{Mo} = 0.71$ mm⁻¹; specimen: $0.25 \times 0.13 \times 0.11$ mm; ' $T_{min/max} = 0.90.2\theta_{max} = 75^\circ$; $N_t = 40210$, N = 20148 ($R_{int} = 0.021$), $N_o = 15213$; R = 0.034, $R_w = 0.038$. (x, y, z, $U_{iso})_H$ refined.

3. Discussion

3.1. Syntheses

The reaction of two equivalents of $AgNO_3$ with 1 equivalent of 2,2':6',2"-terpyridyl (tpy) and 1 equivalent of bis(diphenyl)phosphinomethane (dppm) or bis(diphenyl)arsinomethane (dpam) in acetonitrile at room temperature gave rise to compounds $AgNO_3$:dppm:tpy (2:1:1), (1), and $AgNO_3$:dpam:tpy (2:1:1), (2), respectively (Chart 1), variously solvated, in which tpy and dppm bridge together two silver metal centers. Both compounds formed only when this reactant stoichiometry was rigorously used.

When dppp (=1,3-bis(diphenylphosphino)propane) was employed as ligand, AgNO₃:dppp:tpy (2:1:1)₂ (**3**) (Chart 2), characterized as having the same stoichiometry but different nuclearity, has been obtained, formed, presumably, as a consequence of the longer methylene chain in dppp.

The reaction between 1 equivalent of dpae, $AgClO_4$ and tpy produces the polymeric species $AgClO_4$:dpae:tpy (1:1:1). 2MeCN (4) (Chart 3).







Chart 2.

Similarly the reaction between equimolar quantities of AgClO₄, dppp, and phenanthroline (phen) or 2,9-dimethylphenanthroline (dmp) in MeCN at room temperature always yielded the derivatives AgClO₄:dppp:phen (1:1:1) (**5**) and AgClO₄:dppp:dmp (1:1:1) (**6**) respectively (Chart 4). Compound 5 formed also when an excess of $AgClO_4$ and dppp was employed.

Complexes 1-3, 5 and 6 are air-stable colorless materials, soluble in polar solvents such as acetonitrile, dimethylformamide and dimethylsulfoxide. They are, however, insoluble in water, ether and tetrahydrofuran, and exhibit moderate solubility in chlorinated hydrocarbons.

Solid samples of these compounds generally show no sensitivity to light, although their solutions are sometimes unstable, darkening after 1 day. Conductivity data are in accordance with an ionic nature in acetonitrile solution.

3.2. Spectroscopy

The infrared spectra of **1–6** (see Section 2) are consistent with the formulations proposed, showing all the bands required by the presence of the nitrato or perchlorato counter-ions, phosphino or arsino donors, and N-donor ligands. The IR spectra of the nitrate derivatives **1** and **2** are very similar, showing broad bands at ca. 1300 cm⁻¹ due to v_4 , and sharp bands at ca. 1000, 800 and 750 cm⁻¹ due to v_2 , v_3 and v_5 , consistent with the bidentate O₂NO coordination mode found in the crystal structures [2]. The IR spectrum of **3** is very complex in the same region, as expected for the presence of bridging bidentate and ionic nitrate group. The IR spectra of the perchlorato silver complexes **4–6**



Chart 3.





show two absorptions characteristic of ionic perchlorate groups: in each case, a strong band at ca. 1080 cm⁻¹ (v_3) and a sharp medium or strong band at ca. 625 cm⁻¹ (v_4) [3].

In the ^{f}H NMR spectra of **1–6** the signals due to the diphosphine or diarsine show a different pattern cf. those found for the free donors, confirming the existence, at least partial, of complexes in solution.

 31 P chemical shifts (CD₃CN) solution and 31 P–Ag coupling constants for derivatives **1**, **3**, **5** and **6** are reported in Section 2. They have been found to be slightly dependent on the dilution of the solution. Our experiments have been carried out in the range of concentration 0.003–0.005 mol/L.

The room temperature ³¹P NMR spectrum of 1 consists of a more intense doublet at 7.0 ppm, flanked by a broad doublet at ca. 6.0 ppm, both arising from coupling between the phosphorus and silver atoms. The ¹J(Ag–P) coupling constant values for the first signal lie intermediate between those expected for the AgP and AgP₂ moieties and are lower than those expected for AgPN₂ and AgPN₃ coordination cores [4–6]. These values are analogous to those found in systems containing AgPO₂N₂ cores, supporting the retention of complex 1 in solution, while the second signal could be assigned to an ionic species originating from nitrate dissociation in solution. The δ and coupling



Fig. 1. Projections of the molecules of (a), (b) $[(ONO_2)Ag(E-dppm,dpam-E')(N,N'-tpy-N',N'')Ag(O_2NO)]$ (= AgNO₃:dpem:tpy (2:1:1)₂), in $1 \cdot 1\frac{1}{2}MeCN$, **2** · EtOH.

Table 1	
Geometrical descriptors of AgNO ₃ :dpem:tpy (2:1:1) (1, 2)	

X/dpem/L	Ag	Ag–E (Å)	Ag–N (Å)	$Ag{\cdots}Ag\;(\mathring{A})$	E-Ag-N (°)	N–Ag–N (°)	Ag–E–C (°)	E-C-E (°)
(NO ₃ /)dppm/tpy (1) ^a	Ag(1)	2.356(2)	2.243(8)(p) 2.737(5)(c/b)	2.9965(8)	147.0(2)(p) 127.4(1)(c/p)	68.4(2)	113.3(2)	111.1(3)
	Ag(2)	2.390(2)	2.311(5)(p) 2.582(5)(c/b)		119.7(1)(p) 137.5(1)(c/p)	68.0(2)	112.6(2)	
$(NO_3/)dpam/tpy (2)^a$	Ag(1)	2.4694(4)	2.324(3)(p) 2.450(3)(c/b)	3.0154(4)	115.35(8)(p) 142.82(7)(c/p)	69.4(1)	109.4(1)	110.1(2)
	Ag(2)	2.4702(5)	2.262(4)(p) 2.804(3)(c/b)		145.27(8)(p) 121.10(7)(c)	66.2(1)	113.4(1)	

Ag–O(11,12;21,22) 2.462(5), 2.718(6); 2.379(5), 2.955(4)(dppm adduct); 2.390(3), 2.857(3); 2.445(3), 2.690(4) Å (dpam adduct). O(11)–Ag(1)–E(1),N(11,11'); O(21)–Ag(2)–E(2), N(1',1'') are: 113.8(1), 98.2(2), 72.9(2); 131.1(1), 80.9(2), 100.6(2)(dppm): 125.72(6), 108.8(1), 81.7(9); 113.2(1), 71.5(1), 101.4(1)°(dpam). 'c' and 'p' denote central and peripheral rings of the tpy ligand.

^a In these two adducts, the silver coordination spheres are augmented by chelating nitrate approaches.

Conformational descri	ptors of Ag	NO3:dpem:tpy (2:1:1), (1	1, 2)					
X/dpem/L	Ag	(py/py,bq/bq) (°) ^a	$\delta Ag (\mathring{A})$	C-E-Ag-N (°)	E-C-E-Ag (°)	E-C-P-C(11,21) (°)	Ag-E-C(1n1)-C-(1nx) (°)	Ag-E···E-Ag (°)
(NO ₃ /)dppm/tpy (1)	Ag(1)	38.6(3), 20.2(3) 53.5(7)(p/p")	0.04(2) 1.98(1)(c)	38.4(4) -70.6(3)(c)	-2.7(4)	-126.0(3), 123.4(4)	11.7(5), -19.5(8)	40.98(5)
	Ag(2)		0.27(1)	31.4(3)	48.2(3)	170.6(3), -81.4(3)	8.1(6), -41.9(5)	
$(NO_3/)dpam/tpy (2)$	Ag(1)	15.5(1), 37.1(2)	0.79(c) 0.023(6)	-57.7(3)(c) -32.0(2)	-46.0(2)	-168.7(2), 86.7(5)/83.3(4)	-17.6(4), -59(1)/ - 79(1)	-42.31(1)
	Ag(2)	47.4(2)(p/p)	0.773(6) 0.245(5)	56.8(2)(c) -20.6(2)	0.7(2)	-129.2(2), 125.3(2)	26.8(3), -27.0(3)	
			2.047(5)(c)	71.9(1)(c)				
^a Interplanar dihedra	1 angles; the	e first pair of entries are	between the per	ripheral ('p') and cen	itral ('c') ring planes	, the third between the peripher	al pair.	

Table 1

constant values found for compound **3** are close to those found for 2:1:2 species as reported in the preceding paper [1], and support the existence of an AgPN₂ coordination environment in solution, all nitrates being ionic, in accordance with conductivity data. As previously found, the $\Delta\delta(^{31}P) = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$, the differences in shift between each free diphosphine and corresponding silver(I) derivatives, are greater in the derivatives **1** and **3**, in which only a P-donor atom is coordinated to silver, than those in **5** and **6** in which two P-donor atoms are coordinated to the metal.

The ³¹P NMR spectrum of **5** is in accordance with a tetrahedral silver center, four-coordinated by two P atoms from two bridging dppm and a chelating N₂-donor, the ${}^{1}J(Ag-P)$ coupling constant being in the range typical of AgP₂N₂ cores.

The ³¹P NMR spectrum of **6** is more complex than in the previous, four different signals being found, suggesting considerable dissociation and the formation of new compounds in solution. The ¹J(Ag–P coupling constant) value determined for the unique sharp doublet found at room temperature is in the range typical of an AgP₄ coordination core [7], suggesting formation of the [Ag(dppp)₂]⁺ cation. The different behaviour with respect to compound **5** is presumably a consequence of the greater steric hindrance of dmp with respect to phen.

3.3. Single crystal X-ray studies

3.3.1. $AgNO_3$: dpem: tpy (2:1:1)(·nS) (1 · 1½MeCN (E = P), 2 · 2EtOH (E = As))

This pair of complexes, diversely solvated, crystallise each with one formula unit, devoid of crystallographic symmetry, as the asymmetric unit of the structure; they



Fig. 2. Projection of the centrosymmetric $[Ag_4(NO_3)_2(tpy)_2(dppp)_2]^{2+1}$ cation, in $3 \cdot H_2O$ (cation 1; cation 2 is similar).



(i)



(ii)



(iii)

Fig. 3. (a) Projections of the cations of: (i) $[\{(tpy)Ag\}dpae]^+_{(\infty)}$, in $4 \cdot 2MeCN$; (ii) $[(phen)Ag(dppp)_2Ag(phen)]^{2+}$, in $5 \cdot CHCl_3 \cdot \frac{1}{2}H_2O$; (iii) $[(dmp)Ag(dppp)_2Ag(dmp)]^{2+}$, in $6 \cdot 2MeCN$. (b) Unit cell contents of: (i) $[\{(tpy)Ag\}dpae]_{(\infty)}(CIO_4)$ (4) $\cdot 2MeCN$, projected down *b*; (ii) $[(phen)Ag(dppp)_2Ag(phen)](CIO_4)_2$ (5) $\cdot CHCl \cdot \frac{1}{2}H_2O$, projected down *c*; (iii) $[(dmp)Ag(dppp)_2Ag(dmp)](CIO_4)_2$ (6) $\cdot 2MeCN$ projected down *a*.

are not isomorphous. In aspect they may be considered as similar to the *cis*-(2:1:2) adducts described in the previous paper [1], with the pair of Ag–E bonds quasi-parallel. The role of the tpy, however, is unusual in that the central

pyridine performs the uncommon role previously described as 'crevice' coordination [8–10]. In lying between the two metal atoms and coordinating to both (via the nitrogen) to either side of the plane, with each peripheral pyridine



Fig. 3 (continued)

ring associated exclusively with one of the metal atoms, the role of the tpy is as a bridging bis(chelate), fulfilling the role of the pair of N,N'-chelates found in the (2:1:2) complexes. (Although rare, such a mode of coordination has been pre-

viously described in AgClO₄:tpy:MeCN (3:5:1) [11]). In consequence, the N₂AgE coordination environment is compact, amply accommodating a chelating O,O'-nitrate approach (Fig. 1, Tables 1,2). The two complexes may be considered as having quasi-2 symmetry and as binuclear neutral molecules [(ONO₂)Ag(*E*-dpem-*E*)(*N*,*N'*-tpy-*N'*,*N''*)Ag(O₂NO)], the totality comprising the asymmetric unit of the structure in each case.

3.3.2. $AgNO_3$: $dppp: tpy (4:2:2) \cdot H_2O (3 \cdot H_2O)$

Binuclear 'parcel' compounds, of the form AgX:dppx $(1:1)_2 \equiv Ag(\mu-X)_2(P-dppx-P)_2Ag$, have been described previously [12], the central $Ag(\mu - X)_2 Ag$ four-membered kernel being 'wrapped' by a pair of bridging dppx ligands: examples are recorded therein for O-nitrate, dppx = dppb, dpph. Such may be regarded as a take-off point for the present array (Fig. 2, Table 3) in which two independent centrosymmetric tetramers are found, one half of each pertaining to the asymmetric unit; in the pair of centrosymmetric kernels, Ag–O are 2.418(4), 2.591(5); 2.436(4), 2.567(4) Å, with Ag···Ag 4.245(1), 4.184(2) and O···O 2.665(6), 2.748(6) Å, similar to the previously recorded binuclear adducts; Ag-P is 2.354(2) Å, the other Ag–P interaction preempted by the insertion of an independent silver as (AgL, L = tpy), the latter linking to the second phosphorus of the ligand, and one of the peripheral oxygens of the nitrate. The tpy behaves only as a bidentate, the third (peripheral) pyridine completing the coordination sphere of the kernel silver. The pair of silver atoms are *cis*-oid about the dppp ligand, and not coplanar with the PCCCP spine. The nitrate is rather unsymmetrically bound in the kernel (despite similar Ag-O), Ag-O-N being 115.7(4), 126.0(4), 115.1(3), 128.9(4)°; O-N-O range between 119.0(5)° and 120.9(5)°, with N–O 1.226(7)–1.249(6) Å, the longer being to the kernel oxygen. Kernel; peripheral Ag lie 0.49(1), 0.67(1); 0.23(1), 0.12(1); 1.52(1), 1.38(1) Å out of the NO₃ planes, with the latter making dihedral angles of 15.9(2), $18.0(2)^{\circ}$ with the central (obligate) Ag₂O₂ planes. The kernel Ag-N(tpy) distances $(2.233(6) \text{ Å} (2\times))$ are shorter than the outer Ag-N(c,p) distances (2.346(5), 2.326(5); 2.253(7), 2.280(6) Å). The peripheral O-Ag approaches (2.609(5), 2.567(4) Å) may be considered as a perturbing approach to a typical PAgN₂ environment, the angle sums being 354.4°, 354.0°.

The final group of compounds is of 1:1:1 AgX:dpex:L stoichiometry.

3.3.3. Complexes of AgX:dpex:L (1:1:1) stoichiometry

3.3.3.1. $AgClO_4:dpae:tpy \ (1:1:1)_{(\infty|\infty)} \cdot 2MeCN \ (4 \cdot 2Me-CN)$. This complex is essentially simple, one formula unit (plus solvent) comprising the asymmetric unit of the structure, with successive silver atoms linked into a single-stranded polymer chain by As-dpae-As' ligands, the tpy ligands coordinating to the silver as simple tridentates, thus $(\cdots Ag(tpy)(As-dpae-As')Ag(tpy)\cdots)_{(\infty|\infty)}$, the roles of anions and solvents simply those of spectators filling lattice voids (Fig. 3, Tables 4 and 5), with the central axis of the

Table 3 Selected geometries: [Ag₄(NO₃)(tpy)₂(dppp)₂](NO₃)₂ (3)

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Ag(1)–O(11)	2.591(5)	Ag(3)–O(21)	2.567(4)
Ag(1) - O(11)	2.418(4)	Ag(3) - O(21)	2.436(4)
Ag(1) - P(1)	2.354(2)	Ag(3) - P(3)	2.345(2)
Ag(1) - N(11)	2.233(6)	Ag(3)–N(21)	2.233(6)
$Ag(1) \cdot \cdot \cdot Ag(2)$	3.179(1)	$Ag(3) \cdot \cdot \cdot Ag(4)$	3.302(1)
$Ag(1) \cdots Ag(1)$	4.245(2)	$Ag(3) \cdots Ag(3)$	4.183(2)
Ag(2)–O(12)	2.609(5)	Ag(4)–O(22)	2.660(5)
Ag(2) - P(2)	2.340(2)	Ag(4) - P(4)	2.344(2)
Ag(2) - N(11')	2.346(5)	Ag(4) - N(21')	2.326(5)
Ag(2)–N(11")	2.253(7)	Ag(11)–N(21")	2.280(6)
Angles (°)			
O(11)–Ag(1)–O(11)	64.2(1)	O(21)-Ag(3)-O(21)	66.6(1)
O(11) - Ag(1) - P(1)	104.9(1)	O(21)-Ag(3)-P(3)	104.8(1)
O(11)-Ag(1)-N(11)	88.6(2)	O(21)-Ag(3)-N(21)	88.5(2)
O(11) - Ag(1) - P(1)	105.0(1)	O(21) - Ag(3) - P(3)	104.1(1)
O(11)-Ag(1)-N(11)	111.0(2)	O(21)-Ag(3)-N(21)	111.2(2)
P(1)-Ag(1)-N(11)	142.9(1)	P(3)-Ag(3)-N(21)	144.8(1)
Ag(1) - O(11) - Ag(1)	115.8(2)	Ag(3)–O(21)–Ag(3)	113.4(2)
O(12)-Ag(2)-P(2)	90.2(1)	O(22)-Ag(4)-P(4)	91.3(2)
O(12)–Ag(2)–N(11')	124.5(2)	O(22)–Ag(4)–N(21')	121.9(2)
O(12) - Ag(2) - N(11'')	81.3(2)	O(22)–Ag(4)–N(21")	79.1(2)
P(2)-Ag(2)-N(11')	139.3(2)	P(4)-Ag(4)-N(21')	140.5(2)
O(2)–Ag(2)–N(11")	141.2(1)	P(4)-Ag(4)-N(21'')	142.8(1)
N(11')-Ag(2)- $N(11'')$	71.4(2)	N(21') - Ag(4) - N(21'')	70.6(2)
Ag(2)-O(12)-N(1)	124.0(4)	Ag(4)-O(22)-N(2)	126.1(4)
Torsion angles (°)			
Ag(1)-P(1)-C(1)-C(2)	-66.4(6)	Ag(3)-P(3)-C(4)-C(5)	-66.5(6)
P(1)-C(1)-C(2)-C(3)	165.6(5)	P(3)-C(4)-C(5)-C(6)	168.8(5)
C(1)-C(2)-C(3)-P(2)	-178.5(5)	C(4)-C(5)-C(6)-P(4)	179.7(5)
C(2)-C(3)-P(2)-Ag(2)	63.3(5)	C(5)-C(6)-P(4)-Ag(4)	61.4(6)

Centrosymmetrically related atoms are *italicized*. tpy C₅N/C₅N interplanar dihedral angles (c/p, c/p"; p/p") (degrees): 31.5(3), 20.1(3), 39.6(3) (ligand 1); 42.4(3), 10.6(3); 44.2(3) (ligand 2). Deviations of silver atoms are: ligand 1 Ag(1)/p, 0.56(1), Ag(2)(c,p") 0.86(1), 0.11(1); ligand 2: Ag(3)/p, 0.35(1), Ag(4)(c,p") 0.73(1), 0.18(1) Å. Nitrates 1,2 make dihedral angles of 15.9(2), 18.0(2)° with the associated Ag₂O₂ planes; silver atom deviations are: nitrate 1: Ag(1), 0.49(1); Ag(1) 0.23(1); Ag(2) 1.52(1); nitrate 2: Ag(3) 0.67(1); Ag(3) 0.12(1); Ag(4) 1.38 (1) Å.

tpy approximately parallel to *b*, and the ligand parallel to the *bc* plane. The five-coordinate geometry about the metal, (tpy- N_3)AgAs₂, provides an As₂ counterpart of that already defined for [(tpy- N_3)Ag(PPh₃)₂](ClO₄), [13], in which Ag–N,N',N" are 2.614(2), 2.457(2), 2.561(2), Ag–P are 2.492(1) and 2.525(1) Å, and P–Ag–P 121.8(1)°.

3.3.3.2. The $AgClO_4$: dppp:L (L = phen, dmp) (1:1:1)₍₂₎-($\cdot nS$) dimers ($5 \cdot CHCl_3 \cdot \frac{1}{2}H_2O$, $6 \cdot 2MeCN$). This pair of complexes, although not isomorphous, and distinctly different, are similar, being of the form [LAg(P-dppp-P)₂AgL] with no close interactions between the dimer and anions or solvent. In each case one half of the dimer comprises the asymmetric unit. However, whereas the dmp complex is centrosymmetric, the phen complex lies on a crystallographic mirror plane (in space group *Pnma*), which passes through the central carbon atoms of the two ligands, the C₃ chains lying normal to that plane and to each other (Fig. 3), whereas in the dmp adduct they are obligate paral-

Table 4								
Geometrical descriptors of the	e dpex (≠dpem) comp	olexes, 4-6						
X,S/dpex/L	Ag/X,S (Å)	Ag-E (Å)	Ag-N (Å)	X,S-Ag-E (°)	X,S–Ag–N (°)	E-Ag-N (°)	N-Ag-N (°)	E-Ag-E (°)
ClO ₄ /dpae/tpy (1:1:1) (4)		2.5224(5)	2.503(3), 2.523(4)			112.03(7), 95.11(9)	67.4(1), 66.8(1)	121.39(2)
		2.5532(5)	2.419(3)(c)			121.76(8)(As(1))	134.1(1)	
						95.98(9), 100.53(8)		
						116.34(8)(As(2))		
ClO ₄ /dppp/phen (1:1:1) (5)	2.4503(8)(P(2))	2.4019(8)	2.393(2), 2.437(2)	(145.49(3))	90.67(6), 97.72(6)	115.13(6), 112.11(6)	(8)(8)(8)	145.49(3)
dmp (1:1:1) (6)	2.4400(4)(P(2))	2.3910(4)	2.384(1), 2.391(1)	(139.24(1))	95.60(3), 98.10(3)	116.18(3), 115.48(3)	70.81(5)	139.24(1)

Conformational descripto.						
X,S/dpex/L	py/py,bq/bd (°)	$\delta Ag ({A})$	C-E-Ag-N (°)	C-C-E-Ag (°)	C-C-E-C(11,21) (°)	E,C-C-CE (°)
ClO ₄ /dpae/tpy (4)	16.7(2), 19.8(2)	0.763(7), 0.722(7)	-80.7(2), 61.4(2)	-55.0(3)	68.9(3), 174.3(3)	180
	11.0(2)(p/p)	0.089(8)	-4.4(2)(As(c))	(As(c))		
			73.6(2), -63.3(2)	-45.8(9)	76.9(4), -177.2(4)	180
			5.9(2)(As(2))	(As(2))		
ClO ₄ /dppp/phen (5)		0.072(3)	81.3(1)	65.1(3)	-62.5(3), -170.5(2)	168.2(2)
			158.7(1)	-73.1(3)	58.9(3), 167.2(3)	-171.0(4)
/dmp (6)		0.453(1)	122.33(1)	-56.5(1)	68.9(1), 178.0(1)	-165.3(1)
			-157.54(7)	73.0(1)	-58.0(1), -166.8(1)	-177.0(1)

lel; for all ligands, the pair of apparent silver atoms are essentially *cis*-oid. The silver environments of the two structures are very similar, perhaps the most striking difference being in the P–Ag–P angle (139.24(1) (dmp), 145.49(3)° (phen)). As might be expected in arrays containing substantial planar components, parallel packing of these, often centrosymmetrically related, is a feature of a number of the lattice arrays; a number of the more spectacular are displayed in the projections of Fig. 3(b).

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