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Synthesis and structural characterization of adducts of silver(I) oxyanion salts, AgX (X = ClO_4, NO_3), with $Ph_2E(CH_2)_xEPh_2$ (‘dpex’; E = P, As; x = 1–4) and oligodentate aromatic N-bases derivative of 2,2′-bipyridyl, ‘L’, AgX:dpex:L (2:1:2)

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Abstract

The syntheses and the spectroscopic characterization (IR, ^1H, ^{13}C and ^{31}P NMR, ESI-MS and conductivity studies) of a number of adducts of silver(I) perchlorate and nitrate, AgX, with *N*,*N*′(,*N*″)-oligodentate ligands L, derivative of 2,2′-bipyridyl, together with $Ph_2E(CH_2)_xEPh_2$ (≡‘dpex’, x predominantly 1,2 (‘dpem’, ‘dpee’) but also 3,4 (‘dppp’, ‘dppb’), E = P, As) are reported, of stoichiometry AgX:dpex:L (2:1:2), L = 2,2′-bipyridyl (‘bpy’); 1,10-phenanthroline (‘phen’); 2,9-dimethyl, 1,10-phenanthroline (‘dmp’); bis(2-pyridyl)amine (‘dpa’); 2,2′-biquinolyl (‘bq’); 2,2′:6′,2″-terpyridyl (‘tpy’). For $AgClO_4$:dppm:bpy, phen, dmp, tpy; $AgClO_4$:dpem:phen, dmp, tpy; $AgNO_3$:dppm:bpy, bq (2:1:2), the compounds are of the form [LAg(*E*-dpem-*E*′)AgL]X_2, the pair of Ag–E bonds lying *cis*/parallel about the ECH_2E core, of quasi-C_{2v} symmetry; for $AgClO_4$:dppm:dpa; $AgNO_3$:dppm:bpy (2:1:2), the Ag–E bonds lie *trans*, with a cation symmetry (quasi-)2. In $AgNO_3$:dppm, dpam:dmp (2:1:2), loosely coordinated nitrate ions approach one of the silver atoms as unidentate ligands, Ag–E being ‘*cis*’: [(O_2N*O*)(dmp)Ag(*E*-dpem-*E*′)Ag(dpm)](NO_3). The majority of [LAg(*E*-dpex-*E*′)AgL] (dpex = dpee, dpeb) arrays ($AgClO_4$:dppe:bpy, bq, dpa, tmp, tpy; $AgClO_4$:dpae:bpy, bq; $AgClO_4$:dpdae:dmp (*E* = P, *E*′ = As); $AgClO_4$:dppb:dpa, bq, tpy; $AgNO_3$:dppb:tpy (2:1:2)) are centrosymmetric and *trans*-oid with close approaches to the silver atoms by oxyanions or solvent (MeCN) molecules; $AgClO_4$:dpae:dmp (2:1:2) is *cis*-oid, as also are the dppp adducts, $AgClO_4$:dppp:dmp, bq (2:1:2). A novel bridging tpy coordination mode is found, whereby pairs of silver atoms are linked η^2 (σ,π) into a single stranded polymer in $AgClO_4$:dppp:tpy (2:1:2), thus [. . .Ag(*P*-dppp-*P*′)Ag((μ-N″)tpy)$_2$. . .]$_{(\infty|\infty)}$.

Keywords: Silver salts; Oxyanion; 2:1:2 Adducts; N-donor ligands; Complexes; Structures; Diphosphine; Aromatic N-bases; Single crystal X-ray studies; NMR

1. Introduction

Recent series of publications have approached comprehensive and systematic definition by structural methods of the possible arrays of complexes formed with simple coinage metal(I) salts with simple or important group 15 donor bases. Reports thus far have been primarily focussed on adducts of copper(I) and silver(I) (pseudo-)halide and oxyanion salts, firstly with uni- and (oligo-/)bi-dentate (aromatic (pyridine)) nitrogen bases with varying degrees of steric hindrance [1,2] with parallel studies of systems

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with unidentate ER_3 (E = P, As, Sb) and bidentate $Ph_2E(CH_2)_xPPh_2$ (E = P, As) dpex ligands, of diverse stoichiometries. Recent studies of the latter arrays have been concerned with systems primarily of the form AgX:dpex of $(1:1)_{(n)}$ and $(2:3)_{(n)}$ stoichiometries [3–7]. Studies of mixed ligand systems have been more limited; the present report describes the synthesis and structural definition, of a quasi-systematic and comprehensive nature, of adducts of the form AgX (X = oxyanion (NO_3, ClO_4)):dpex (= 'dppm', $Ph_2PCH_2PPh_2$; 'dpam', $Ph_2AsCH_2AsPh_2$; 'dppe', $Ph_2P(CH_2)_2PPh_2$; 'dpae', $Ph_2As(CH_2)_2AsPh_2$; 'dpdae', $Ph_2P(CH_2)_2AsPh_2$; 'dppp', $Ph_2P(CH_2)_3PPh_2$; 'dppb', $Ph_2P(CH_2)_4PPh_2$):L (= 2,2′-bipyridyl, 'bpy'; 1,10-phenanthroline, 'phen'; 2,9-dimethyl, 1,10-phenanthroline, 'dmp'; 2,2′-biquinolyl, 'bq'; bis(2-pyridyl)amine, 'dpa'; and 2,2′:6′,2″-terpyridyl, 'tpy'), defining arrays of 2:1:2 stoichiometry, with different novel forms described. Complementary studies, including unidentate ER_3 ligands and different stoichiometries, are offered in accompanying papers [8–11].

2. Experimental

All syntheses and handlings 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, and 162.1 MHz for ^{31}P). H and C chemical shifts are reported in ppm versus $SiMe_4$, P chemical shifts in ppm versus 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. Positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, masses and intensities were compared to those calculated by using the IsoPro Isotopic Abundance Simulator, version 2.1 [12]; peaks containing silver(I) ions are identified as the centres of isotopic clusters. Unless stated otherwise, crystals for the X-ray work were obtained from a few mL of acetonitrile solutions of the reagents on a millimolar scale by slow cooling and/or evaporation in ambience, these crystals frequently being solvated forms of the adducts.

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. AgX (=ClO_4):dpex:L (2:1:2) (·nS) complexes

*2.1.1.1. Synthesis of $AgClO_4$:dppm:bpy (2:1:2) (**1**).* A solution containing $AgClO_4$ (0.414 g, 2.0 mmol), dppm (0.384 g, 1.0 mmol) and bpy (0.312 g, 2.0 mmol) in 10 mL of CH_3CN 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** (1.089 g, yield: 98%); m.p. 229–232 °C (dec), 272–273 °C. *Anal.* Calc. for $C_{45}H_{38}Ag_2Cl_2N_4O_8P_2$: C, 48.63; H, 3.45; N, 5.04. Found: C, 48.80; H, 3.51; N, 5.13%. IR (nujol, cm^{-1}): 1589s, 1567m, 1537sh ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1100sh, 1088sbr, 625s, 620s, $\nu(ClO_4)$, 530w, 505w, 478w, 403w. ^1H NMR (CD_3CN, 293 K): δ, 3.96 (t, 2H, $CH_{2\text{dppm}}$), 7.45 (m, 12H, $C_6H_{5\text{dppm}}$ + 4H, CH_{bpy}), 7.70 (m, 8H, $C_6H_{5\text{dppm}}$), 7.98 (m, 8H, CH_{bpy}), 8.43 (m, 4H, CH_{bpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.06 (m, $CH_{2\text{dppm}}$), 123.63 (t, $C5_{\text{bpy}}$), 127.14 (s, $C3_{\text{bpy}}$), 130.44 (m, C_{dppm}), 131.62 (m, C_{dppm}), 132.65 (s, C_{dppm}), 134.15 (t, C_{dppm}), 140.90 (m, $C4_{\text{bpy}} + C_{\text{dppm}}$), 151.85 (s, $C6_{\text{bpy}}$), 152.00 (s, $C2_{\text{bpy}}$). ^{31}P NMR (CD_3CN, 293 K): δ, 12.5 (d, $^1J(^{31}P\text{–}Ag)$: 670.9 Hz). ESI MS (+): 189 (35) $[Ag(MeCN)_2]^+$, 304 (45) $[Ag(bpy)(MeCN)]^+$, 492 (100) $[Ag_2(dppm)_2]^{2+}$, 1018 (15) $[Ag_2(dppm)_2Cl]^+$, 1082 (25) $[Ag_2(dppm)_2ClO_4]^+$.

*2.1.1.2. Synthesis of $AgClO_4$:dppm:phen (2:1:2) (**2**).* $AgClO_4$ (0.414 g, 2.0 mmol) and dppm (0.384 g, 1 mmol) were added to an acetonitrile solution (10 mL) containing 0.360 g (2.0 mmol) of phen. A colorless precipitate immediately formed. The suspension was stirred overnight, then was filtered off and the colorless residue washed with diethyl ether and shown to be compound **2** (0.629 g, yield: 54%). Re-crystallization from MeCN gives the MeCN solvate, **2** · MeCN; m.p. 293–294 °C. *Anal.* Calc. for $C_{49}H_{38}Ag_2Cl_2N_4O_8P_2$: C, 50.76; H, 3.30; N, 4.83. Found: C, 50.93; H, 3.21; N, 4.80%. IR (nujol, cm^{-1}): 1620s, 1589s, 1572s, 1512s ν(C$\overset{\cdots}{-}$C, C$\overset{\cdots}{-}$N), 1110sh, 1073sbr, 625s, 620s $\nu(ClO_4)$, 520m, 503m, 483m, 470m, 448m, 420m, 338w, 273m, 246m. ^1H NMR (CD_3CN, 293 K): δ, 4.07 (t, 2H, $CH_{2\text{dppm}}$), 7.48–7.53 (m, 12H, $C_6H_{5\text{dppm}}$), 7.73–7.84 (m, 8H, $C_6H_{5\text{dppm}}$), 7.59–7.55 (m, 4H, CH_{phen}), 7.69 (s, 4H, CH_{phen}), 8.23 (dd, 4H, CH_{phen}), 8.71 (m, 4H, CH_{phen}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.53 (m, $CH_{2\text{dppm}}$), 125.80 (s, C_{phen}), 128.04 (s, C_{phen}), 129.72 (s, C_{phen}), 130.49 (m, C_{dppm}), 132.68 (s, C_{dppm}), 132 (m br, C_{dppm}), 134.31 (m, C_{dppm}), 139.93 (s, C_{phen}), 141.89 (s, C_{phen}), 152.23 (s, C_{phen}). ^{31}P NMR (CD_3CN, 293 K): δ, 14.9 (m, $^1J(^{31}P\text{–}Ag)$: 670.9 Hz). For the material re-crystallized from CH_3CN as **2** · MeCN: ESI MS (+): 189 (35) $[Ag(MeCN)_2]^+$, 328 (45) $[Ag(phen)(MeCN)]^+$, 467 (85) $[Ag(phen)_2]^+$, 672 (100) $[Ag(dppm)(phen)]^+$, 872 (25) $[Ag_2(dppm)(phen)ClO_4]^+$, 1018 (25) $[Ag_2(dppm)_2Cl]^+$, 1058 (25) $[Ag_2(dppm)(phen)_2ClO_4]^+$, 1082 (25) $[Ag_2(dppm)_2ClO_4]^+$.

*2.1.1.3. Synthesis of $AgClO_4$:dppm:dmp (2:1:2) (**3**).* Compound **3** has been prepared in 34% yield (0.456 g) following a procedure similar to that reported for **2** by using $AgClO_4$ (0.414 g, 2.0 mmol), dppm (0.384 g, 1.0 mmol) and dmp (0.416 g, 2.0 mmol). Re-crystallization from MeCN gives **3**. MeCN; m.p. 318–319 °C. *Anal.* Calc. for $C_{53}H_{46}Ag_2Cl_2N_4O_8P_2$: C, 52.37; H, 3.81; N, 4.61. Found: C, 52.53; H, 3.78; N, 4.48%. IR (nujol, cm^{-1}): 1619s, 1589s, 1573sh, 1555s, 1503s ν(C$\cdots$C, C$\cdots$N), 1100sh, 1076sbr, 621s $\nu(ClO_4)$, 550m, 522m, 506m, 478m, 443m, 426m, 403w, 360w, 341w. ^1H NMR (CD_3CN, 293 K): δ, 2.69 (s, 12H, CH_{3dmp}), 4.03 (t, 2H, CH_{2dppm}), 7.38–7.45 (m, 4H, $C_6H_{5dppm} + CH_{dmp}$), 7.67–7.80 (m, 4H, $C_6H_{5dppm} + CH_{dmp}$), 8.13 (m, 4H, CH_{dmp}). ^{13}C NMR (CD_3CN, 293 K): δ, 25.04 (m, CH_{2dppm}), 29.47 (s, CH_{3dmp}), 125.80 (s, C_{dmp}), 127.07 (s, C_{dmp}), 128.07 (s, C_{dmp}), 130.32 (m, C_{dppm}), 132.30 (s, C_{dmp}), 132.62 (s, C_{dppm}), 133.87 (m, C_{dppm}), 140.16 (s, C_{dmp}), 159.61 (s, C_{dmp}). ^{31}P NMR (CD_3CN, 293 K): δ, 8.3 (m, $^1J(^{31}P–Ag)$: 642.5 Hz). For the material re-crystallized from MeCN as **3**.MeCN: ESI MS (+): 356 (20) $[Ag(dmp)(MeCN)]^+$, 525 (100) $[Ag(dmp)_2]^+$, 701 (38) $[Ag(dppm)(dmp)]^+$, 1018 (5) $[Ag_2(dppm)_2Cl]^+$, 1082 (5) $[Ag_2(dppm)_2ClO_4]^+$.

*2.1.1.4. Synthesis of $AgClO_4$:dppm:bq (2:1:2) (**4**).* Compound **4** (0.243 g, yield: 74%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppm (0.096 g, 0.25 mmol), and bq (0.128 g, 0.5 mmol); m.p. 300–301 °C. *Anal.* Calc. for $C_{61}H_{46}Ag_2Cl_2N_4O_8P_2$: C, 55.86; H, 3.53; N, 4.27. Found: C, 55.03; H, 3.59; N, 4.23%. IR (nujol, cm^{-1}): 1618m, 1589s, 1556w, 1534w, 1503w ν(C$\cdots$C, C$\cdots$N), 1083sbr $\nu(ClO_4)$, 522w, 477m, 267w. ^1H NMR (CD_3CN, 293 K): δ, 4.29 (m, 2H, CH_{2dppm}), 7.26–7.87 (m, 20H, $C_6H_{5dppm} + CH_{bq}$), 8.15 (d, 4H, CH_{bq}), 8.40 (d, 4H, CH_{bq}). ^{13}C NMR (CD_3CN, 293 K): δ, 30.94 (s, CH_{2dppm}), 120.63 (s, $C3_{bq}$), 129.27, 129.55, 129.69, 130.41, 132.87 (s, $C_{bq} + C_{dppm}$), 130.50 (m, C_{dppm}), 132.61 (s, C_{dppm}), 134.10 (m, C_{dppm}), 141.35 (s, $C4_{bq}$), 145.94 (s, $C10_{bq}$), 152.37 (s, $C2_{bq}$). ^{31}P NMR (CD_3CN, 293 K): δ, 11.6 (d, $^1J(^{31}P–Ag)$: 653.6 Hz).

*2.1.1.5. Synthesis of $AgClO_4$:dppm:dpa (2:1:2) (**5**).* Compound **5** (0.276 g, yield: 97%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppm (0.096 g, 0.25 mmol), and dpa (0.085 g, 0.5 mmol). Re-crystallization from MeCN in ambience yielded the material modelled in the X-ray study as **5** · 1/3 H_2O; m.p. 146–147 °C (dec), >239 °C. *Anal.* Calc. for $C_{45}H_{40}Ag_2Cl_2N_6O_8P_2$: C, 47.35; H, 3.53; N, 7.37. Found: C, 47.10; H, 3.57; N, 7.32%. IR (nujol, cm^{-1}): 3331w ν(N–H), 1643s, 1632s, 1573s, 1530s ν(C$\cdots$C, C$\cdots$N), 1082sbr $\nu(ClO_4)$, 519m, 505m, 472m, 407m, 333w. ^1H NMR (CD_3CN, 293 K): δ, 3.80 (s, 2H, CH_{2dppm}), 6.84 (t, 4H, CH_{dpa}), 7.19 (d, 4H, CH_{dpa}), 7.40 (m, 12H, C_6H_{5dppm}), 7.61–7.75 (m, 12H, C_6H_{5dppm} + 4H, CH_{dpa}), 7.95 (m, 4H, CH_{dpa}), 8.21 (sbr, 1H, NH_{dpa}). ^{13}C NMR (CD_3CN, 293 K): δ, 25.7 (m, CH_{2dppm}), 114.2, 117.1 (s, C_{dpa}), 129.3 (br, C_{dppm}), 131.0 (br, C_{dppm}), 131.6 (m, C_{dppm}), 133.0 (br, C_{dppm}), 139.5 (s, C_{dpa}), 148.2 (s, C_{dpa}), 154.1 (s, C_{dpa}). ^{31}P NMR (CD_3CN, 293 K): δ, 7.4 (d, $^1J(^{31}P–Ag)$: 668.4 Hz). For the material re-crystallized from MeCN as **5** · 1/3 H_2O: ESI MS (+): 189 (35) $[Ag(MeCN)_2]^+$, 663 (50) $[Ag(dpa)(dppm)]^+$, 868 (25) $[Ag_2(dppm)(dpa)ClO_4]^+$.

*2.1.1.6. Synthesis of $AgClO_4$:dppm:tpy (2:1:2) (**6**).* Compound **6** (0.266 g, yield: 80%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppm (0.096 g, 0.25 mmol) and tpy (0.116 g, 0.5 mmol); m.p. 295–296 °C. *Anal.* Calc. for $C_{55}H_{44}Ag_2Cl_2N_6O_8P_2$: C, 52.20; H, 3.50; N, 6.64. Found: C, 52.10; H, 3.60; N, 6.77%. IR (nujol, cm^{-1}): 2318m, 2000w, 1600m, 1573m, 1555m ν(C$\cdots$C, C$\cdots$N), 1079sbr, 622s $\nu(ClO_4)$, 473w, 346w, 290w. ^1H NMR (CD_3CN, 293 K): δ, 3.76 (t, 2H, CH_{2dppm}), 7.27–7.54 (m, 20H, C_6H_{5dppm} + 6H, CH_{tpy}), 7.90 (m, 4H, CH_{tpy}), 8.06–8.20 (m, 12H, CH_{tpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 25.0 (m, CH_{2dppm}), 123.88, 124.15 (s, C_{tpy}), 126.3 (s, C_{tpy}), 130.23 (br, C_{dppm}), 132.4 (br, C_{dppm}), 133.9 (m, C_{dppm}), 139.8 (s, C_{tpy}), 141.3 (s, C_{tpy}), 151.4 (s, C_{tpy}), 153.3 (s, C_{tpy}), 153.8(s, C_{tpy}). ^{31}P NMR (CD_3CN, 293 K): δ, 6.4 (d, $^1J(^{31}P–Ag)$: 569.6 Hz).

*2.1.1.7. Synthesis of $AgClO_4$:dpam:phen (2:1:2) (**7**), $AgClO_4$:dpam:dmp (2:1:2) (**8**), and $AgClO_4$:dpam:tpy (2:1:2) (**9**).* Complexes **7**–**9** were obtained by crystallization of millimolar stoichiometries of silver perchlorate with dpam and the appropriate aromatic oligodentate ligand L from acetonitrile solution, by standing and evaporation in ambience. Satisfactory bulk sample analyses were obtained from the following:

7*(·¼MeCN):* $AgClO_4$:dpam:phen (2:1:2) · ¼MeCN. *Anal.* Calc. for $C_{49.5}H_{38.75}Ag_2As_2Cl_2N_{4.25}O_8$: C, 47.28; H, 3.11; N, 4.73. Found: C, 47.50; H, 3.11; N, 4.64%; m.p. slow decomposition at room temperature.

8*(·MeCN):* $AgClO_4$:dpam:dmp (2:1:2) · MeCN. *Anal.* Calc. for $C_{55}H_{49}Ag_2As_2Cl_2N_5O_8$: C, 49.13; H, 3.67; N, 5.21. Found: C, 49.22; H, 3.72; N, 5.05%.

9*:* $AgClO_4$:dpam:tpy (2:1:2). *Anal.* Calc. for $C_{55}H_{44}Ag_2As_2Cl_2N_6O_8$: C, 48.81; H, 3.28; N, 6.21. Found: C, 48.75; H, 3.27; N, 6.21%; m.p. 262–265 °C.

*2.1.1.8. Synthesis of $AgClO_4$:dppe:bpy (2:1:2) (**10**).* Compound **10** (1.114 g, yield: 99%) has been prepared following a procedure similar to that reported for **1**, by using $AgClO_4$ (0.414 g, 2 mmol), dppe (0.398 g, 1 mmol), and bpy (0.312 g, 2 mmol); m.p. 251–252 °C. *Anal.* Calc. for $C_{46}H_{40}Ag_2Cl_2N_4O_8P_2$: C, 49.09; H, 3.58; N, 4.98. Found: C, 48.95; H, 3.44; N, 4.80%. IR (nujol, cm^{-1}): 1590s, 1573m, 1567m, 1556w, 1537w, 1504w ν(C$\cdots$C, C$\cdots$N), 1093sbr, 621s $\nu(ClO_4)$, 506w, 490w, 448w, 412w, 329w, 254w. ^1H NMR (CD_3CN, 293 K): δ, 2.61 (d, 4H, CH_{2dppe}), 7.49–7.63 (m, 20H, C_6H_{5dppe} + 4H, CH_{bpy}), 8.06–8.14 (m, 4H, CH_{bpy}), 8.32 (d, 4H, CH_{bpy}), 8.61 (d, 4H, CH_{bpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.96 (d, $C$$H_{2\text{dppe}}$), 123.76 (s, $C5_{\text{bpy}}$), 126.94 (s, $C3_{\text{bpy}}$), 130.40 (d, C_{dppe}), 132.43 (d, C_{dppe}), 133.89 (d, C_{dppe}), 140.70 (s, $C4_{\text{bpy}}$), 151.99 (s, $C6_{\text{bpy}}$), 152.87 (s, $C2_{\text{bpy}}$). ^{31}P NMR (CD_3CN, 293 K): δ, 11.5br. ^{31}P NMR (CD_3CN, 233 K): δ, 12.6 (d, $^1J(^{31}$P–Ag): 686 Hz).

*2.1.1.9. Synthesis of AgClO$_4$:dppe:dmp (2:1:2) (**11**).* Compound **11** (0.550 g, yield: 79%) has been prepared as **11** · 2MeCN following a procedure similar to that reported for **2** by using $AgClO_4$ (0.207 g, 1 mmol), dppe (0.198 g, 0.5 mmol) and dmp (0.208 g, 1 mmol); m.p. >79 °C, 290–291 °C. *Anal.* Calc. for $C_{62}H_{60}Ag_2Cl_2N_8O_8P_2$: C, 53.43; H, 4.34; N, 8.04. Found: C, 53.28; H, 4.20; N, 7.89%. IR (nujol, cm^{-1}): 1620s, 1590s, 1556s, 1503s ν(C⎓C, C⎓N), 1083sbr, 621s $\nu(ClO_4)$, 548w, 509w, 478w, 343w. ^{1}H NMR (CD_3CN, 293 K): δ, 2.17 (s, 12H, CH_3CN) 2.61 (d, 4H, C$H_{2\text{dppe}}$), 2.68 (s, 12H, C$H_{3\text{dmp}}$), 7.44–7.57 (m, 20H, $C_6H_{5\text{dppe}}$), 7.73 (d, 4H, CH_{dmp}), 8.46 (d, 4H, CH_{dmp}). ^{13}C NMR (CD_3CN, 293 K): δ, 24.01 (m, CH$_{2\text{dppe}}$), 28.40 (s, CH$_{3\text{dmp}}$), 126.14 (s, C_{dmp}), 127.19 (s, C_{dmp}), 128.54 (s, C_{dmp}), 130.45 (m, C_{dppe}), 132.36 (s, C_{dppe}), 133.73 (m, C_{dppe}), 140.00 (s, C_{dmp}), 142.87 (s, C_{dmp}), 160.06 (s, C_{dmp}). ^{31}P NMR (CD_3CN, 293 K): δ, 8.9 (d, $^1J(^{31}$P–Ag): 623.9 Hz).

*2.1.1.10. Synthesis of AgClO$_4$:dppe:bq (2:1:2) (**12**).* Compound **12** (0.295 g, yield: 89%) has been synthesised following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppe (0.099 g, 0.25 mmol), and bq (0.128 g, 0.5 mmol); m.p. 305–306 °C. *Anal.* Calc. for $C_{62}H_{48}Ag_2Cl_2N_4O_8P_2$: C, 56.17; H, 3.65; N, 4.23. Found: C, 56.20; H, 3.61; N, 4.12%. IR (nujol, cm^{-1}): 1620s, 1591m, 1555m, 1537w, 1503w ν(C⎓C, C⎓N), 1091sbr, 620br $\nu(ClO_4)$, 510w, 483w, 449w, 334w. ^{1}H NMR (CD_3CN, 293 K): δ, 2.73 (d, 4H, C$H_{2\text{dppe}}$), 7.44–7.59 (m, 20H, $C_6H_{5\text{dppe}}$ + 8H, CH_{bq}), 7.86 (d, 4H, CH_{bq}), 8.00 (d, 4H, CH_{bq}), 8.44 (d, 4H, CH_{bq}), 8.57 (d, 4H, CH_{bq}). *^{13}C NMR (CD_3CN, 293 K):* δ, 23.26 (m, CH$_{2\text{dppe}}$), 121.15 (s, $C3_{\text{bq}}$), 129.43, 129.64, 130.14, 130.46, 132.15 (s, C_{bq}), 130.67 (m, C_{dppe}), 132.97 (s, C_{dppe}), 133.70 (m, C_{dppe}) 141.11 (s, $C4_{\text{bq}}$), 146.91 (s, $C10_{\text{bq}}$), 153.41 (s, $C2_{\text{bq}}$). ^{31}P NMR (CD_3CN, 293 K): δ, 8.8 (d, $^1J(^{31}$P–Ag): 601.7 Hz). Compound **12** was re-crystallized from MeCN as **12** · 2MeCN.

*2.1.1.11. Synthesis of AgClO$_4$:dppe:dpa (2:1:2) (**13**).* Compound **13** (0.307 g, yield: 98%) has been synthesised as **13** · 2MeCN · H_2O following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppe (0.099 g, 0.25 mmol), and dpa (0.085 g, 0.5 mmol); m.p. 211–212 °C. *Anal.* Calc. for $C_{46}H_{42}Ag_2Cl_2N_6O_8P_2$: C, 47.83; H, 4.01; N, 8.92. Found: C, 47.59; H, 3.86; N, 9.11%. IR (nujol, cm^{-1}): 3338m, 3240w, 3218m, 3180m, ν(N–H) + ν(O–H), 2197 (CN) 1632s, 1578s, 1529s ν(C⎓C, C⎓N), 1094sbr, 639s, 621s $\nu(ClO_4)$, 507m, 478m, 407m, 331m. ^{1}H NMR (CD_3CN, 293 K): δ, 2.16, 2.19 (s, 8H, CH_3CN + H_2O), 2.39 (br, 4H, C$H_{2\text{dppe}}$), 6.94 (t, 4H, CH_{dpa}), 7.36–7.48 (m, 20H, $C_6H_{5\text{dppe}}$ + 4H, CH_{dpa}), 7.74 (m, 4H, CH_{dpa}), 8.19 (m, 4H, CH_{dpa}). ^{13}C NMR (CD_3CN, 293 K): δ, 24.20 (m, CH$_{2\text{dppe}}$), 114.54, 118.40 (s, C_{dpa}), 130.42 (m, C_{dppe}), 132.35 (s, C_{dppe}), 133.70 (m, C_{dppe}) 140.07 (s, C_{dpa}), 149.30 (s, C_{dpa}), 155.64 (s, C_{dpa}). ^{31}P NMR (CD_3CN, 293 K): δ, 10.4 (d, $^1J(^{31}$P–Ag): 443.9 Hz). Re-crystallization from MeCN in ambience yielded a material modelled in the X-ray study as **13** · MeCN · H_2O.

*2.1.1.12. Synthesis of AgClO$_4$:dppe:tpy (2:1:2) (**14**).* Compound **14** (0.313 g, yield: 98%) has been obtained following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppe (0.099 g, 0.25 mmol), and tpy (0.116 g, 0.5 mmol); m.p. 229 °C. *Anal.* Calc. for $C_{56}H_{46}Ag_2Cl_2N_6O_8P_2$: C, 52.56; H, 3.62; N, 6.57. Found: C, 52.40; H, 3.70; N, 6.37%. IR (nujol, cm^{-1}): 1597m, 1573m, 1555, 1503w ν(C⎓C, C⎓N), 1081sbr, 620s $\nu(ClO_4)$, 512w, 349w, 250w. ^{1}H NMR (CD_3CN, 293 K): δ, 2.08 (d, 4H, C$H_{2\text{dppe}}$), 7.16–7.53 (m, 20H, $C_6H_{5\text{dppe}}$ + 6H, CH_{tpy}), 7.94 (m, 4H, CH_{tpy}), 8.22–8.34 (m, 12H, CH_{tpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 23.98 (m, CH$_{2\text{dppe}}$), 123.90, 124.21, 126.40 (s, C_{tpy}), 130.20 (m, C_{dppe}), 132.02 (s, C_{dppe}), 133.37 (m, C_{dppe}) 139.77, 141.36 (s, C_{tpy}), 151.40 (s, C_{tpy}), 153.45, 154.01 (s, C_{tpy}). ^{31}P NMR (CD_3CN, 293 K): δ, 6.32s br. ^{31}P NMR (CD_3CN, 233 K): δ, 5.84 (d, $^1J(^{31}$P–Ag): 631 Hz). Compound **14** was re-crystallized from MeCN as **14** · 2MeCN.

*2.1.1.13. Synthesis of AgClO$_4$:dpae:bpy (2:1:2) (**15**), AgClO$_4$:dpae:dmp (2:1:2) (**16**), AgClO$_4$:dpae:bq (2:1:2) (**17**) and AgClO$_4$:dpdae:bq (2:1:2) (**18**).* Complexes **15**–**18** were obtained by crystallization of millimolar stoichiometries of silver perchlorate with dpam or dpdae and the appropriate aromatic oligodentate ligand L, from acetonitrile solution, by standing and evaporation in ambience. Satisfactory bulk sample analyses were obtained from the following:

***15**:* $AgClO_4$:dpae:bpy (2:1:2). *Anal.* Calc. for $C_{46}H_{40}Ag_2As_2Cl_2N_4O_8$: C, 45.54; H, 3.32; N, 4.62. Found: C, 45.45; H, 3.47; N, 4.72%; m.p. 208–211 °C (dec).

***16**(·H$_2$O):* $AgClO_4$:dpae:dmp (2:1:2) · H_2O. *Anal.* Calc. for $C_{54}H_{50}Ag_2As_2Cl_2N_4O_9$: C, 48.83; H, 3.72; N, 4.26. Found: C, 48.42; H, 3.64; N, 4.31%; m.p. >144 °C (dec).

***17**(·2MeCN):* $AgClO_4$:dpae:bq (2:1:2) · 2MeCN. *Anal.* Calc. for $C_{66}H_{54}Ag_2As_2Cl_2N_6O_8$: C, 53.00; H, 3.64; N, 5.62. Found: C, 52.92; H, 4.08; N, 5.15%; m.p. >78 °C (dec).

***18**(·2MeCN):* $AgClO_4$:dpdae:bq (2:1:2) · 2MeCN. *Anal.* Calc. for $C_{66}H_{54}Ag_2AsCl_2N_6O_8P$: C, 54.61; H, 3.75; N, 5.75. Found: C, 54.49; H, 3.90; N, 5.62%.

*2.1.1.14. Synthesis of AgClO$_4$:dppp:bq (2:1:2) (**19**).* Compound **19** (0.096 g, yield: 29%) has been synthesised following a procedure similar to that reported for **1** by using

$AgClO_4$ (0.104 g, 0.5 mmol), dppp (0.103 g, 0.25 mmol), and bq (0.128 g, 0.5 mmol); m.p. 285–286 °C. *Anal.* Calc. for $C_{63}H_{50}Ag_2Cl_2N_4O_8P_2$: C, 56.48; H, 3.76; N, 4.18. Found: C, 56.20; H, 3.81; N, 4.06%. IR (nujol, cm^{-1}): 1617s, 1591s, 1555m, 1503w, ν(C⎓C, C⎓N), 1088sbr, 621s $\nu(ClO_4)$, 522m, 513m, 480s, 448m, 395w, 318w, 274w. ^{1}H NMR (CD_3CN, 293 K): δ, 2.60 (sbr, 2H, C$H_{2\mathrm{dppp}}$), 2.82 (sbr, 4H, C$H_{2\mathrm{dppp}}$), 7.40–7.59 (m, 20H, $C_6H_{5\mathrm{dppp}}$ + 8H, CH_{bq}), 7.83 (m, 8H, CH_{bq}), 8.37 (d, 4H, CH_{bq}), 8.51 (d, 4H, CH_{bq}). ^{13}C NMR (CD_3CN, 293 K): δ, 23.26, 28.40 (m, CH$_{2\mathrm{dppp}}$), 121.05 (s, C_{bq}), 129.35, 129.45, 129.99, 130.64, 132.25 (s, C_{bq}), 130.40 (d, C_{dppp}), 132.51 (s, C_{dppp}), 133.70 (d, C_{dppp}) 141.07 (s, C_{bq}), 146.64 (s, C_{bq}), 153.13 (s, C_{bq}). ^{31}P NMR (CD_3CN, 293 K): δ, 7.9 (d, $^1J(^{31}$P–Ag): 630.0 Hz). Compound **19** was re-crystallized from MeCN as **19** · 2MeCN.

*2.1.1.15. Synthesis of AgClO$_4$:dppp:dpa (2:1:2) (**20**).* Compound **20** (0.287 g, yield: 98%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppp (0.099 g, 0.25 mmol), and dpa (0.085 g, 0.5 mmol); m.p. 115–116 °C. *Anal.* Calc. for $C_{48}H_{46}Ag_2Cl_2N_6O_8P_2$: C, 48.27; H, 3.79; N, 7.19. Found: C, 48.29; H, 3.66; N, 7.10%. IR (nujol, cm^{-1}): 3339m ν(N–H), 1640sbr, 1573sbr, 1530sbr ν(C⎓C, C⎓N), 1080sbr, 639s, 620s $\nu(ClO_4)$, 514m, 484m, 452w, 407w, 332m. ^{1}H NMR (CD_3CN, 293 K): δ, 1.70 (sbr, 2H, C$H_{2\mathrm{dppp}}$), 2.57 (sbr, 4H, C$H_{2\mathrm{dppp}}$), 6.85 (t, 4H, CH_{dpa}), 7.28 (d, 4H, CH_{dpa}), 7.50 (m, 20H, $C_6H_{5\mathrm{dppp}}$), 7.73 (t, 4H, CH_{dpa}), 8.08 (d, 4H, CH_{dpa}). ^{13}C NMR (CD_3CN, 293 K): δ, 23.77, 28.58 (m, CH$_{2\mathrm{dppp}}$), 114.86, 118.10 (s, C_{dpa}), 130.35 (d, C_{dppp}), 132.14 (s, C_{dppp}), 133.60 (d, C_{dppp}) 140.21 (s, C_{dpa}), 149.53 (s, C_{dpa}), 155.60 (s, C_{dpa}). ^{31}P NMR (CD_3CN, 293 K): δ, 7.2 (d, $^1J(^{31}$P–Ag): 655.9 Hz).

*2.1.1.16. Synthesis of AgClO$_4$:dppp:tpy (2:1:2) (**21**).* Compound **21** (0.316 g, yield: 98%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppp (0.099 g, 0.25 mmol), and tpy (0.116 g, 0.5 mmol); m.p. 217–218 °C. *Anal.* Calc. for $C_{57}H_{48}Ag_2Cl_2N_6O_8P_2$: C, 52.92; H, 3.74; N, 6.50. Found: C, 52.89; H, 3.66; N, 6.48%. IR (nujol, cm^{-1}): 1586sbr, 1514w ν(C⎓C, C⎓N), 1100sh, 1071sbr, 621s $\nu(ClO_4)$, 514w, 474w, 322w, 292w. ^{1}H NMR (CD_3CN, 293 K): δ, 1.43 (sbr, 2H, C$H_{2\mathrm{dppp}}$), 2.16 (sbr, 4H, C$H_{2\mathrm{dppp}}$), 7.35 (m, 20H, $C_6H_{5\mathrm{dppp}}$), 7.42 (m, 4H, CH_{tpy}), 7.88 (m, 4H, CH_{tpy}), 8.17 (m, 8H, CH_{tpy}), 8.28 (m, 4H, CH_{tpy}). ^{31}P NMR (CD_3CN, 293 K): δ, 3.5 (d br, $^1J(^{31}$P–Ag): 506.9 Hz).

*2.1.1.17. Synthesis of AgClO$_4$:dppb:bpy (2:1:2) (**22**).* Compound **22** (0.565 g, yield: 98%) has been synthesised following a procedure similar to that reported for **1** by using $AgClO_4$ (0.207 g, 1 mmol), dppb (0.197 g, 0.5 mmol), and bpy (0.156 g, 1 mmol); m.p. 195–196 °C. *Anal.* Calc. for $C_{48}H_{44}Ag_2Cl_2N_4O_8P_2$: C, 49.98; H, 3.84; N, 4.86. Found: C, 50.11; H, 3.64; N, 4.78%. IR (nujol, cm^{-1}): 1667m, 1630s, 1589s, 1565s ν(C⎓C, C⎓N), 1090sbr, 630s, 618 s $\nu(ClO_4)$, 521m, 485m, 466w, 419m, 398w, 350w, 311m. ^{1}H NMR (CD_3CN, 293 K): δ, 1.77 (m, 4H, C$H_{2\mathrm{dppb}}$), 2.48 (d, 4H, C$H_{2\mathrm{dppb}}$), 7.45–7.71 (m, 20H, $C_6H_{5\mathrm{dppb}}$ + 4H, CH_{bpy}), 8.06–8.15 (m, 4H, CH_{bpy}), 8.35 (m, 4H, CH_{bpy}), 8.68 (m, 4H, CH_{bpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.96 (d, CH$_{2\mathrm{dppb}}$), 28.00 (m, CH$_{2\mathrm{dppb}}$), 123.72 (s, $C5_{\mathrm{bpy}}$), 126.97 (s, $C3_{\mathrm{bpy}}$), 130.23 (d, C_{dppb}), 132.17 (s, C_{dppb}), 133.00 (d, C_{dppb}), 133.85 (d, C_{dppb}), 140.71 (s, $C4_{\mathrm{bpy}}$), 152.05 (s, $C3_{\mathrm{bpy}}$), 152.89 (s, $C2_{\mathrm{bpy}}$). ^{31}P NMR (CD_3CN, 293 K): δ, 10.1 (d, $^1J(^{31}$P–Ag): 681.2 Hz). Compound **22** was re-crystallized from MeCN as **22** · 2MeCN.

*2.1.1.18. Synthesis of AgClO$_4$:dppb:bq (2:1:2) (**23**).* Compound **23** (0.140 g, yield: 41%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppb (0.106 g, 0. 25 mmol), and bq (0.128 g, 0.5 mmol); m.p. 298–299 °C. *Anal.* Calc. for $C_{64}H_{52}Ag_2Cl_2N_4O_8P_2$: C, 56.78; H, 3.87; N, 4.14. Found: C, 56.50; H, 3.77; N, 4.01%. IR (nujol, cm^{-1}): 1614s, 1591s, 1555m, 1503s, ν(C⎓C, C⎓N), 1094sbr, 622s $\nu(ClO_4)$, 514s, 486s, 461w, 398w. ^{1}H NMR (CD_3CN, 293 K): δ, 1.88 (sbr, 4H, C$H_{2\mathrm{dppb}}$), 2.58 (sbr, 4H, C$H_{2\mathrm{dppb}}$), 7.40–7.55 (m, 20H, $C_6H_{5\mathrm{dppb}}$ + 8H, CH_{bq}), 7.87 (m, 8H, CH_{bq}), 8.40 (d, 4H, CH_{bq}), 8.53 (d, 4H, CH_{bq}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.96 (d, CH$_{2\mathrm{dppb}}$), 28.00 (q, CH$_{2\mathrm{dppb}}$), 121.04 (s, C_{bq}), 129.36, 129.55, 130.05, 130.78, 132.14 (s, C_{bq}), 130.35 (d, C_{dppb}), 132.54 (s, C_{dppb}), 133.85 (d, C_{dppb}) 140.98 (s, C_{bq}), 147.02 (s, C_{bq}), 153.59 (s, C_{bq}). ^{31}P NMR (CD_3CN, 293 K): δ, 5.9 (d, $^1J(^{31}$P–Ag): 683.3 Hz). Compound **23** was re-crystallized from MeCN/EtOH as **23** · 2MeCN · EtOH. ESI MS (+): 404 (20) $[Ag(bq)(MeCN)]^+$, 532 (50) $[Ag(dppb)]^+$, 576 (20) $[Ag_2(dppb)(bq)_2]^{2+}$, 620 (100) $[Ag(bq)_2]^+$, 791 (45) $[Ag(dppb)(bq)]^+$.

*2.1.1.19. Synthesis of AgClO$_4$:dppb:tpy (2:1:2) (**24**).* Compound **24** (0.227 g, yield: 69%) has been prepared following a procedure similar to that reported for **1** by using $AgClO_4$ (0.104 g, 0.5 mmol), dppb (0.109 g, 0.25 mmol), and tpy (0.116 g, 0.5 mmol); m.p. 104–105 °C. *Anal.* Calc. for $C_{58}H_{50}Ag_2Cl_2N_6O_8P_2$: C, 53.27; H, 3.85; N, 6.43. Found: C, 53.30; H, 3.70; N, 6.40%. IR (nujol, cm^{-1}): 1570sbr, 1537sbr, 1503sbr ν(C⎓C, C⎓N), 1083sbr, 621s $\nu(ClO_4)$, 515w, 482w, 406w, 306w. ^{1}H NMR (CD_3CN, 293 K): δ, 1.43 (sbr, 4H, C$H_{2\mathrm{dppb}}$), 2.18 (sbr, 4H, C$H_{2\mathrm{dppb}}$), 7.35 (m, 20H, $C_6H_{5\mathrm{dppb}}$), 7.91 (m, 4H, CH_{tpy}), 8.17–8.27 (m, 14H, CH_{tpy}), 8.37 (m, 4H, CH_{tpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.70 (m, CH$_{2\mathrm{dppb}}$), 27.49 (m, CH$_{2\mathrm{dppb}}$), 123.80, 124.12, 126.32 (s, C_{tpy}), 130.12 (m, C_{dppb}), 131.67 (s, C_{dppb}), 133.60 (m, C_{dppb}) 139.64, 141.20 (s, C_{tpy}), 151.43 (s, C_{tpy}), 153.67, 154.11 (s, C_{tpy}). ^{31}P NMR (CD_3CN, 293 K): δ, 4.1 (d, $^1J(^{31}$P–Ag): 548.6 Hz). Compound **24** has been re-crystallized from ethanol as **24** · EtOH · ESI MS (+): 340 (70) $[Ag(tpy)]^+$, 533 (100) $[Ag(dppb)]^+$, 766

(20) $[Ag_2(dppb)(tpy)]^+$, 1102 (45) $[Ag_2(dppb)_2(Cl)]^+$, 1168 (45) $[Ag_2(dppb)_2(ClO_4)]^+$.

2.1.2. AgX (=NO$_3$):dpex:L (2:1:2) (·nS) complexes

*2.1.2.1. Synthesis of AgNO$_3$:dppm:bpy (2:1:2) (**25**).* Compound **25** (0.484 g, yield: 93%) has been prepared following a procedure similar to that reported for **2** by using $AgNO_3$ (0.169 g, 1.0 mmol), dppm (0.192 g, 0.5 mmol) and bpy (0.156 g, 1.0 mmol); m.p. 181–182 °C. *Anal.* Calc. for $C_{45}H_{38}Ag_2N_6O_6P_2$: C, 52.15; H, 3.70; N, 8.11. Found: C, 52.08; H, 3.61; N, 8.13%. IR (nujol, cm^{-1}): 1587s, 1555s, 1537s, 1504s, 1503m, 1464m, ν(C$\cdots$C, C$\cdots$N), 1446m, 1375s, 828s (NO_3), 519w, 481w, 447w, 211s. ^1H NMR (CD_3CN, 293 K): δ, 4.01 (t, 2H, CH_{2dppm}), 7.43 (m, 12H, C_6H_{5dppm} + 4H, CH_{bpy}), 7.71 (m, 8H, C_6H_{5dppm}), 7.96 (m, 4H, CH_{bpy}), 8.08 (m, 4H, CH_{bpy}), 8.47 (m, 4H, CH_{bpy}). *^{13}C NMR (CD_3CN, 293 K):* δ, 26.06 (m, CH_{2dppm}), 123.51 (m, C_{dppm}), 126.96 (s, C_{bpy}), 130.44 (m, C_{dppm}), 131.9 (m, C_{dppm}), 132.65 (s, C_{bpy}), 134.18 (m, C_{dppm}), 140.7 (t, C_{bpy}), 151.9 (s, C_{bpy}), 152.06 (s, C_{bpy}), 152.26 (s, C_{bpy}). ^{31}P NMR (CD_3CN, 293 K): δ, 12.0 (d, $^1J(^{31}P–Ag)$: 668.6 Hz). Compound **25** was re-crystallized from MeCN/EtOH/$CHCl_3$ in ambience as **25** · H_2O. ESI MS (+): 189 (20) $[Ag(MeCN)_2]^+$, 263 (25) $[Ag(bpy)]^+$, 304 (70) $[Ag(bpy)(MeCN)]^+$, 419 (100) $[Ag(bpy)_2]^+$, 647 (10) $[Ag(dppm)(bpy)]^+$, 1018 (25) $[Ag_2(dppm)_2Cl]^+$, 1046 (25) $[Ag_2(dppm)_2NO_3]^+$.

*2.1.2.2. Synthesis of AgNO$_3$:dppm:dmp (2:1:2) (**26**).* Compound **26** (0.295 g, yield: 52%) has been prepared following a procedure similar to that reported for **2** by using $AgNO_3$ (0.169 g, 1 mmol), dppm (0.192 g, 0.5 mmol) and dmp (0.208 g, 1 mmol); m.p. 258–259 °C. *Anal.* Calc. for $C_{53}H_{46}Ag_2N_6O_6P_2$: C, 55.81; H, 4.06; N, 7.37. Found: C, 55.68; H, 4.04; N, 7.29%. IR (nujol, cm^{-1}): 1621s, 1590s, 1573m, 1556s, 1503m ν(C$\cdots$C, C$\cdots$N), 1410m, 1370s, 1250sh, 1095m, 860s, 838m, 827m, 741m, 728m, (NO_3), 549m, 523m, 510m, 475m, 447w, 431w, 355w. ^1H NMR (CD_3CN, 293 K): δ, 2.69 (s, 12H, CH_{3dmp}), 4.04 (t, 2H, CH_{2dppm}), 7.28–7.48 (m, 4H, CH_{dmp} + 12H, C_6H_{5dppm}), 7.72–7.83 (m, 4H, CH_{dmp} + 8H, C_6H_{5dppm}), 8.15 (mbr, 4H, CH_{dmp}). ^{13}C NMR (CD_3CN, 293 K): δ, 24.79 (t, CH_{2dppm}), 29.28 (s, CH_{3dmp}), 125.87 (s, C_{dmp}), 127.07 (s, C_{dmp}), 128.11 (s, C_{dmp}), 130.31 (m, C_{dppm}), 132.13 (s, C_{dmp}), 132.57 (s, C_{dppm}), 133.92 (m, C_{dppm}), 140.16 (s, C_{dmp}), 159.71 (s, C_{dmp}). ^{31}P NMR (CD_3CN, 293 K): δ, 8.2 (d, $^1J(^{31}P–Ag)$: 643.8 Hz). Compound **26** was re-crystallized from MeCN in ambience as **26** · 3/2 MeCN · ½ H_2O. ESI MS (+): 356 (10) $[Ag(dmp)(MeCN)]^+$, 523 (100) $[Ag(dmp)_2]^+$, 701 (20) $[Ag(dppm)(dmp)]^+$.

*2.1.2.3. Synthesis of AgNO$_3$:dppm:bq (2:1:2) (**27**).* Compound **27** (0.187 g, 60%) has been prepared following a procedure similar to that reported for **1** by using $AgNO_3$ (0.084 g, 0.5 mmol), dppm (0.096 g, 0.25 mmol), and bq (0.128 g, 0.5 mmol); m.p. 238–239 °C. *Anal.* Calc. for $C_{61}H_{46}Ag_2N_6O_6P_2$: C, 59.24; H, 3.75; N, 6.80. Found: C, 59.13; H, 3.69; N, 6.78%. IR (nujol, cm^{-1}): 1615m, 1590s, 1556w, 1534w, 1503s ν(C$\cdots$C, C$\cdots$N), 1434m, 1375s, 824s (NO_3), 521m, 507w, 477m, 269m. ^1H NMR (CD_3CN, 293 K): δ, 4.30 (t, 2H, CH_{2dppm}), 7.34 (m, 4H, CH_{bq}), 7.46 (m, 12H, C_6H_{5dppm}), 7.55 (m, 4H, CH_{bq}), 7.82 (m, 8H, C_6H_{5dppm} + 8H, CH_{bq}), 8.22 (m, 4H, CH_{bq}), 8.37 (m, 4H, CH_{bq}). ^{13}C NMR (CD_3CN, 293 K): δ, 26.0 (br, CH_{2dppm}), 120.68 (s, C_{bq}), 129.25, 129.49, 129.74, 129.96, 130.50 (m, C_{dppm}), 130.6 (s, C_{bq}), 132.0 (br, C_{dppm}), 132.5, 132.8 (s, C_{dppm} + C_{bq}) 134.12 (m, C_{dppm}) 141.13 (s, C_{bq}), 146.24 (s, C_{bq}), 152.8 (br, C_{bq}). ^{31}P NMR (CD_3CN, 293 K): δ, 11.3 (dbr, $^1J(^{31}P–Ag)$: 616.6 Hz). Compound **27** was re-crystallized from MeCN in ambience as **27** · 2MeCN · ½ H_2O. ESI MS (+): 621 (100) $[Ag(bq)_2]^+$, 1018 (10) $[Ag_2(dppm)_2Cl]^+$, 1046 (5) $[Ag_2(dppm)_2NO_3]^+$.

*2.1.2.4. Synthesis of AgNO$_3$:dpam:dmp (2:1:2) (**28**).* Complex **28** (·1½MeCN · H_2O) was obtained by crystallization of millimolar stoichiometries of the silver nitrate with dpam and dmp from acetonitrile solution by standing and evaporation in ambience. *Anal.* Calc. for $C_{56}H_{54.5}Ag_2As_2N_{7.5}O_8$: C, 50.72; H, 4.19; N, 7.92. Found: C, 51.12; H, 4.18; N, 7.89%; m.p. >137 °C (dec).

*2.1.2.5. Synthesis of AgNO$_3$:dppp:dmp (2:1:2) (**29**).* Compound **29** (0.393 g, yield: 67%) has been prepared following a procedure similar to that reported for **2** by using $AgNO_3$ (0.169 g, 1 mmol), dppp (0.206 g, 0.5 mmol) and dmp (0.208 g, 1 mmol); m.p. 266–267 °C. *Anal.* Calc. for $C_{55}H_{50}Ag_2N_6O_6P_2$: C, 56.62; H, 4.15; N, 7.20. Found: C, 56.50; H, 4.09; N, 7.16%. IR (nujol, cm^{-1}): 1619s, 1594s, 1557s, 1503m ν(C$\cdots$C, C$\cdots$N), 1435m, 1420sh, 1376s, 1300sh, 1030m, 855s, 827m, 737m, 727m (NO_3), 549s, 522s, 480s, 461w, 442w, 433w, 401w, 318w. ^1H NMR (CD_3CN, 293 K): δ, 2.62 (s, 12H, CH_{3dmp}), 2.78 (br, 6H, CH_{2dppp}), 7.39–7.46 (m, 4H, CH_{dmp} + 12H, C_6H_{5dppm}), 7.59 (mbr, 8H, C_6H_{5dppp}), 7.90 (s, 4H, CH_{dmp}), 8.37 (d, 4H, CH_{dmp}). ^{13}C NMR (CD_3CN, 293 K): δ, 24.70 (m, CH_{2dppp}), 29.31 (s, CH_{3dmp}), 126.02 (s, C_{dmp}), 127.12 (s, C_{dmp}), 128.44 (s, C_{dmp}), 130.20 (m, C_{dppp}), 132.07 (s, C_{dmp}), 132.74 (s, C_{dppp}), 133.60 (m, C_{dppp}), 139.87 (s, C_{dmp}), 159.99 (s, C_{dmp}). ^{31}P NMR (CD_3CN, 293 K): δ, 6.7 (d, $^1J(^{31}P–Ag)$: 658.5 Hz). Compound **29** was re-crystallized from MeCN as **29** · ½ MeCN.

*2.1.2.6. Synthesis of AgNO$_3$:dppb:tpy (2:1:2) (**30**).* Compound **30** (0.209 g, yield: 67%) has been obtained following a procedure similar to that reported for **1** by using $AgNO_3$ (0.085 g, 0.5 mmol), dppb (0.109 g, 0.25 mmol), and tpy (0.116 g, 0.5 mmol); m.p. 229–230 °C. *Anal.* Calc. for $C_{58}H_{50}Ag_2N_8O_6P_2$: C, 56.51; H, 4.09; N, 9.09. Found: C, 56.44; H, 4.06; N, 9.00%. IR (nujol, cm^{-1}): 1587s, 1576s, 1567s ν(C$\cdots$C, C$\cdots$N), 1450s, 1420s, 1380br, 1290sh, 1096s, 1000m, 848m, 824m, 737s, 719s (NO_3) 516s, 479s, 457w, 423s, 304w. ^1H NMR (CD_3CN, 293 K): δ, 1.48 (sbr, 4H, CH_{2dppb}), 2.72 (sbr, 4H, CH_{2dppb}), 7.38 (m, 20H, $C_6H_{5\mathrm{dppb}}$ + 4H, CH_{tpy}), 7.93 (m, 4H, CH_{tpy}), 8.15 (t, 2H, CH_{tpy}), 8.30 (m, 8H, CH_{tpy}), 8.52 (d, 4H, CH_{tpy}). ^{13}C NMR (CD_3CN, 293 K): δ, 23.6 (m, $CH_{2\mathrm{dppb}}$), 28.3 (m, $CH_{2\mathrm{dppb}}$), 123.87, 124.22, 126.34 (s, C_{tpy}), 130.30 (d, C_{dppb}), 131.89 (s, C_{dppb}), 133.50 (d, C_{dppb}) 139.72, 141.32 (s, C_{tpy}), 151.36 (s, C_{tpy}), 153.67, 154.14 (s, C_{tpy}). ^{31}P NMR (CD_3CN, 293 K): δ, 1.75 br. ^{31}P NMR (CD_3CN, 223 K): δ, 2.24 (dd, $^1J(^{31}\mathrm{P}–^{109}\mathrm{Ag})$: 689 Hz; $^1J(^{31}\mathrm{P}–^{107}\mathrm{Ag})$: 599 Hz).

2.2. Structure determinations

Full spheres of 'low'-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K), yielding $N_{\mathrm{t(otal)}}$ reflections, these merging to N unique after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the large block/full matrix least square refinements, refining anisotropic displacement parameters forms for the non-hydrogen atoms, $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ being included, constrained at estimates where possible. Conventional residuals R, R_w on $|F|$ at convergence are cited (reflection weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$). Neutral atom complex scattering factors were employed within the XTAL 3.7 program system [13]. Pertinent results are given below and in the tables and figures, the latter showing 50% probability displacement amplitudes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å; carbon atoms, if labelled, may be denoted by number only, for economy of space. Individual divergences/variations in procedure are cited as 'variata'.

2.2.1. Crystal/refinement data

2.2.1.1. AgX (=ClO$_4$):dpex:L (2:1:2) (·nS) complexes.

*2.2.1.1.1. AgClO$_4$:dppm:bpy (2:1:2) (**1**).* $C_{45}H_{38}Ag_2Cl_2N_4O_8P_2$, $M = 1111.4$. Orthorhombic, space group $Pna2_1$ (C_{2v}^9, No. 33), $a = 25.472(4)$ Å, $b = 13.630(4)$ Å, $c = 25.248(2)$ Å, $V = 8770$ Å^3. D_{calc} $(Z = 8) = 1.68_3$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.15$ mm^{-1}; specimen: $0.42 \times 0.37 \times 0.36$ mm; '$T_{\mathrm{min/max}}$' = 0.72. $2\theta_{\max} = 58°$; $N_t = 80239$, $N = 11181$ ($R_{\mathrm{int}} = 0.052$), $N_o = 9317$; $R = 0.045$, $R_w = 0.062$; $x_{\mathrm{abs}} = 0.14(3)$.

*2.2.1.1.2. AgClO$_4$:dppm:phen (2:1:2) · MeCN (**2** · MeCN).* $C_{51}H_{41}Ag_2Cl_2N_5O_8P_2$, $M = 1200.5$. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14 (variant)), $a = 13.689(1)$ Å, $b = 12.563(1)$ Å, $c = 27.945(3)$ Å, $\beta = 92.057(2)°$, $V = 4803$ Å^3. D_{calc} $(Z = 4) = 1.66_0$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.05$ mm^{-1}; specimen: $0.35 \times 0.29 \times 0.18$ mm; '$T_{\mathrm{min/max}}$' = 0.87. $2\theta_{\max} = 65°$; $N_t = 85367$, $N = 17362$ ($R_{\mathrm{int}} = 0.044$), $N_o = 13219$; $R = 0.043$, $R_w = 0.060$.

Variata. Phenyl ring 12× was modelled as disordered over two sets of sites, site occupancies set at 0.5 after trial refinement, with rigid body constraints. Acetonitrile atom assignments, here and below, were confirmed by refinement behaviour and location of the hydrogen atoms. It is isomorphous with its dpam analogue (see **7** below) and was refined in the same cell and coordinate setting.

*2.2.1.1.3. AgClO$_4$:dppm:dmp (2:1:2) · MeCN (**3** · MeCN).* $C_{55}H_{49}Ag_2Cl_2N_5O_8P_2$, $M = 1256.7$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 13.158(1)$ Å, $b = 13.814(1)$ Å, $c = 14.447(1)$ Å, $\alpha = 98.506(2)°$, $\beta = 100.208(2)°$, $\gamma = 94.028(2)°$, $V = 2543$ Å^3. D_{calc} $(Z = 2) = 1.64_1$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.00$ mm^{-1}; specimen: $0.26 \times 0.18 \times 0.13$ mm; '$T_{\mathrm{min/max}}$' = 0.75. $2\theta_{\max} = 70°$; $N_t = 50806$, $N = 22084$ ($R_{\mathrm{int}} = 0.051$), $N_o = 13969$; $R = 0.050$, $R_w = 0.057$.

Variata. This complex is isomorphous with its dpam analogue (see below, **8**) and was refined in the same cell and coordinate setting.

*2.2.1.1.4. AgClO$_4$:dppm:dpa (2:1:2) · 1/3 H$_2$O (**5** · 1/3 H$_2$O).* $C_{45}H_{40.67}Ag_2Cl_2N_6O_{8.33}P_2$, $M = 1147.5$. Orthorhombic, space group $Pbca$ (D_{2h}^{15}, No. 61), $a = 22.886(3)$ Å, $b = 41.453(4)$ Å, $c = 14.168(2)$ Å, $V = 13441$ Å^3. D_{calc} $(Z = 12) = 1.70_1$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.13$ mm^{-1}; specimen: $0.26 \times 0.20 \times 0.10$ mm; '$T_{\mathrm{min/max}}$' = 0.80. $2\theta_{\max} = 50°$; $N_t = 124713$, $N = 12169$ ($R_{\mathrm{int}} = 0.10$), $N_o = 8557$; $R = 0.074$, $R_w = 0.12$.

*2.2.1.1.5. AgClO$_4$:dppm:tpy (2:1:2) (**6**).* $C_{55}H_{44}Ag_2Cl_2N_6O_8P_2$, $M = 1265.6$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 14.338(2)$ Å, $b = 13.137(2)$ Å, $c = 27.856(3)$ Å, $\beta = 96.657(2)°$, $V = 5212$ Å^3. D_{calc} $(Z = 4) = 1.61_3$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.98$ mm^{-1}; specimen: $0.28 \times 0.26 \times 0.22$ mm; '$T_{\mathrm{min/max}}$' = 0.90. $2\theta_{\max} = 58°$; $N_t = 49784$, $N = 12904$ ($R_{\mathrm{int}} = 0.025$), $N_o = 9432$; $R = 0.043$, $R_w = 0.058$.

Variata. This complex is isomorphous with its dpam analogue (see below, **9**) and was refined in the same cell and coordinate setting. T was 298 K for this study.

*2.2.1.1.6. AgClO$_4$:dpam:phen (2:1:2) · ¼ MeCN (**7** · ¼ MeCN).* $C_{49.5}H_{38.75}Ag_2As_2Cl_2N_{4.25}O_8$, $M = 1257.7$. Monoclinic, space group $P2_1/n$, $a = 13.468(2)$ Å, $b = 12.612(2)$ Å, $c = 28.014(5)$ Å, $\beta = 91.987(3)°$, $V = 4756$ Å^3. D_{calc} $(Z = 4) = 1.75_6$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 2.38$ mm^{-1}; specimen: $0.11 \times 0.10 \times 0.03$ mm; '$T_{\mathrm{min/max}}$' = 0.81. $2\theta_{\max} = 50°$; $N_t = 38272$, $N = 8331$ ($R_{\mathrm{int}} = 0.080$), $N_o = 5816$; $R = 0.061$, $R_w = 0.080$.

Variata. This complex is isomorphous with its dppm analogue (see above, **2**), albeit only obtained as much smaller crystals. The acetonitrile site occupancy was constrained at 0.25 after trial refinement.

*2.2.1.1.7. AgClO$_4$:dpam:dmp (2:1:2) · MeCN (**8** · MeCN).* $C_{55}H_{49}Ag_2As_2Cl_2N_5O_8$, $M = 1344.6$. Triclinic, space group $P\bar{1}$, $a = 13.198(1)$ Å, $b = 14.256(1)$ Å, $c = 14.440(1)$ Å, $\alpha = 97.050(2)°$, $\beta = 99.389(2)°$, $\gamma = 95.210(2)°$, $V = 2643$ Å^3. D_{calc} $(Z = 2) = 1.69_8$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 2.1$ mm^{-1}; specimen: $0.17 \times 0.14 \times 0.09$ mm; '$T_{\mathrm{min/max}}$' = 0.82. $2\theta_{\max} = 58°$; $N_t = 32321$, $N = 14138$ ($R_{\mathrm{int}} = 0.026$), $N_o = 9556$; $R = 0.041$, $R_w = 0.054$.

Variata. The compound is isomorphous with its dppm analogue (see above, **3**). T was 298 K for this study.

*2.2.1.1.8. AgClO$_4$:dpam:tpy (2:1:2) (**9**).* $C_{55}H_{44}Ag_2As_2Cl_2N_6O_8$, $M = 1353.5$. Monoclinic, space group $P2_1/c$, $a = 14.058(1)$ Å, $b = 13.249(1)$ Å, $c = 27.604(2)$ Å, $\beta = 98.058(2)°$, $V = 5091$ Å^3. D_{calc} $(Z = 4) = 1.76_6$ g cm^{-3}.

$\mu_{\mathrm{Mo}} = 2.2\ \mathrm{mm}^{-1}$; specimen: $0.25 \times 0.22 \times 0.16$ mm; '$T_{\mathrm{min/max}}$' = 0.81. $2\theta_{\mathrm{max}} = 70°$; $N_{\mathrm{t}} = 100806$, $N = 22433$ ($R_{\mathrm{int}} = 0.051$), $N_{\mathrm{o}} = 15229$; $R = 0.041$, $R_{\mathrm{w}} = 0.050$.

Variata. The compound is isomorphous with its dppm analogue (see above, **6**).

*2.2.1.1.9. AgClO$_4$:dppe:bpy (2:1:2) (**10**).* $C_{46}H_{40}Ag_2Cl_2N_4O_8P_2$, $M = 1125.4$. Triclinic, space group $P\bar{1}$, $a = 9.5497(7)$ Å, $b = 10.5432(8)$ Å, $c = 12.816(1)$ Å, $\alpha = 68.672(2)°$, $\beta = 70.046(2)°$, $\gamma = 73.058(2)°$, $V = 1109$ Å^3. D_{calc} ($Z = 1$) $= 1.68_5$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.1\ \mathrm{mm}^{-1}$; specimen: $0.25 \times 0.17 \times 0.12$ mm; '$T_{\mathrm{min/max}}$' = 0.78. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 21288$, $N = 10819$ ($R_{\mathrm{int}} = 0.016$), $N_{\mathrm{o}} = 9392$; $R = 0.027$, $R_{\mathrm{w}} = 0.034$.

*2.2.1.1.10. AgClO$_4$:dppe:dmp:MeCN (2:1:2:2) · 2MeCN (**11** · 2MeCN).* $C_{62}H_{60}Ag_2Cl_2N_8O_8P_2$, $M = 1393.8$. Triclinic, space group $P\bar{1}$, $a = 11.0425(5)$ Å, $b = 12.0947(6)$ Å, $c = 12.7527(6)$ Å, $\alpha = 94.988(1)°$, $\beta = 100.749(1)°$, $\gamma = 111.323(1)°$, $V = 1536$ Å^3. D_{calc} ($Z = 1$) $= 1.50_6$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.84\ \mathrm{mm}^{-1}$; specimen: $0.30 \times 0.20 \times 0.15$ mm; '$T_{\mathrm{min/max}}$' = 0.86. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 28987$, $N = 14863$ ($R_{\mathrm{int}} = 0.021$), $N_{\mathrm{o}} = 12181$; $R = 0.032$, $R_{\mathrm{w}} = 0.038$.

*2.2.1.1.11. AgClO$_4$:dppe:bq (2:1:2) · 2MeCN (**12** · 2MeCN).* $C_{66}H_{54}Ag_2Cl_2N_6O_8P_2$, $M = 1407.8$. Triclinic, space group $P\bar{1}$, $a = 10.7328(8)$ Å, $b = 10.8086(8)$ Å, $c = 14.470(1)$ Å, $\alpha = 107.208(2)°$, $\beta = 103.093(2)°$, $\gamma = 104.661(2)°$, $V = 1466$ Å^3. D_{calc} ($Z = 1$) $= 1.59_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.88\ \mathrm{mm}^{-1}$; specimen: $0.25 \times 0.20 \times 0.10$ mm; '$T_{\mathrm{min/max}}$' = 0.80. $2\theta_{\mathrm{max}} = 65°$; $N_{\mathrm{t}} = 22433$, $N = 10538$ ($R_{\mathrm{int}} = 0.033$), $N_{\mathrm{o}} = 8017$; $R = 0.044$, $R_{\mathrm{w}} = 0.048$.

Variata. The compound is isomorphous with its P/As and As$_2$ counterparts (see below, **17**, **18**) and was refined in the same cell and coordinate setting.

*2.2.1.1.12. AgClO$_4$:dppe:dpa:MeCN:H$_2$O (2:1:2:2:1) (**13** · 2MeCN · H$_2$O).* $C_{50}H_{50}Ag_2Cl_2N_8O_9P_2$, $M = 1255.6$. Triclinic, space group $P\bar{1}$, $a = 10.824(1)$ Å, $b = 11.220(1)$ Å, $c = 12.175(1)$ Å, $\alpha = 107.778(2)°$, $\beta = 97.072(2)°$, $\gamma = 105.826(2)°$, $V = 1320$ Å^3. D_{calc} ($Z = 1$) $= 1.58_0$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.97\ \mathrm{mm}^{-1}$; specimen: $0.22 \times 0.17 \times 0.12$ mm; '$T_{\mathrm{min/max}}$' = 0.81. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 25315$, $N = 12878$ ($R_{\mathrm{int}} = 0.027$), $N_{\mathrm{o}} = 9620$; $R = 0.046$, $R_{\mathrm{w}} = 0.053$.

Variata. The perchlorate was modelled as rotationally disordered over two sets of sites about one of the Cl–O bonds, site occupancies of the relevant atoms set at 0.5 after trial refinement. 'Water molecule oxygen' hydrogen atoms were not located.

*2.2.1.1.13. AgClO$_4$:dppe:tpy (2:1:2) · 2MeCN (**14** · 2MeCN).* $C_{60}H_{52}Ag_2Cl_2N_8O_8P_2$, $M = 1361.7$. Triclinic, space group $P\bar{1}$, $a = 10.5276(5)$ Å, $b = 11.1687(5)$ Å, $c = 13.1763(7)$ Å, $\alpha = 73.337(1)°$, $\beta = 81.449(1)°$, $\gamma = 75.880(1)°$, $V = 1434$ Å^3. D_{calc} ($Z = 1$) $= 1.57_6$ cm^{-3}. $\mu_{\mathrm{Mo}} = 0.90\ \mathrm{mm}^{-1}$; specimen: $0.17 \times 0.14 \times 0.10$ mm; '$T_{\mathrm{min/max}}$' = 0.92. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 28793$, $N = 13461$ ($R_{\mathrm{int}} = 0.017$), $N_{\mathrm{o}} = 10583$; $R = 0.033$, $R_{\mathrm{w}} = 0.039$.

Variata. The CN component of the acetonitrile was modelled as disordered over two sets of sites, occupancies refining to 0.726(5) and complement.

*2.2.1.1.14. AgClO$_4$:dpae:bpy (2:1:2) (**15**).* $C_{46}H_{40}Ag_2As_2Cl_2N_4O_8$, $M = 1213.3$. Triclinic, space group $P\bar{1}$, $a = 8.6503(5)$ Å, $b = 11.2273(7)$ Å, $c = 12.4476(8)$ Å, $\alpha = 70.019(1)°$, $\beta = 83.360(1)°$, $\gamma = 84.229(1)°$, $V = 1126$ Å^3. D_{calc} ($Z = 1$) $= 1.78_9$ cm^{-3}. $\mu_{\mathrm{Mo}} = 2.50\ \mathrm{mm}^{-1}$; specimen: $0.24 \times 0.14 \times 0.12$ mm; '$T_{\mathrm{min/max}}$' = 0.76. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 23397$, $N = 11604$ ($R_{\mathrm{int}} = 0.026$), $N_{\mathrm{o}} = 8084$; $R = 0.034$, $R_{\mathrm{w}} = 0.037$.

*2.2.1.1.15. AgClO$_4$:dpae:dmp (2:1:2) · H$_2$O (**16** · H$_2$O).* $C_{54}H_{50}Ag_2As_2Cl_2N_4O_9$, $M = 1335.6$. Triclinic, space group $P\bar{1}$, $a = 13.734(1)$ Å, $b = 14.487(1)$ Å, $c = 16.455(1)$ Å, $\alpha = 100.305(2)°$, $\beta = 105.108(2)°$, $\gamma = 114.202(2)°$, $V = 2727$ Å^3. D_{calc} ($Z = 2$) $= 1.62_6$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 2.08\ \mathrm{mm}^{-1}$; specimen: $0.11 \times 0.08 \times 0.07$ mm; '$T_{\mathrm{min/max}}$' = 0.82. $2\theta_{\mathrm{max}} = 60°$; $N_{\mathrm{t}} = 53870$, $N = 15817$ ($R_{\mathrm{int}} = 0.035$), $N_{\mathrm{o}} = 11533$; $R = 0.054$, $R_{\mathrm{w}} = 0.080$.

Variata. Perchlorates 1 and 3 were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement; the oxygen atoms of perchlorate 2 were modelled as disordered about Cl(2), set at an inversion centre.

*2.2.1.1.16. AgClO$_4$:dpae:bq (2:1:2) · 2MeCN (**17**).* $C_{66}H_{54}Ag_2As_2Cl_2N_6O_8$, $M = 1495.7$. Triclinic, space group $P\bar{1}$, $a = 10.8068(7)$ Å, $b = 10.8429(7)$ Å, $c = 14.3374(9)$ Å, $\alpha = 105.823(1)°$, $\beta = 102.818(1)°$, $\gamma = 104.812(1)°$, $V = 1484$ Å^3. D_{calc} ($Z = 1$) $= 1.67_3$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.92\ \mathrm{mm}^{-1}$; specimen: $0.38 \times 0.32 \times 0.23$ mm; '$T_{\mathrm{min/max}}$' = 0.72. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 30166$, $N = 15134$ ($R_{\mathrm{int}} = 0.023$), $N_{\mathrm{o}} = 11502$; $R = 0.032$, $R_{\mathrm{w}} = 0.038$.

Variata. The compound is isomorphous with its dppe (see above, **12**) and dpdae (see next, **18**) analogues.

*2.2.1.1.17. AgClO$_4$:dpdae:bq (2:1:2) · 2MeCN (**18** · 2MeCN).* $C_{66}H_{54}Ag_2AsCl_2N_6O_8P$, $M = 1451.7$. Triclinic, space group $P\bar{1}$, $a = 10.7696(6)$ Å, $b = 10.8373(7)$ Å, $c = 14.4036(9)$ Å, $\alpha = 106.731(1)°$, $\beta = 102.924(1)°$, $\gamma = 104.717(1)°$, $V = 1475$ Å^3. D_{calc} ($Z = 1$) $= 1.63_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.40\ \mathrm{mm}^{-1}$; specimen: $0.38 \times 0.24 \times 0.12$ mm; '$T_{\mathrm{min/max}}$' = 0.74. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 30032$, $N = 15059$ ($R_{\mathrm{int}} = 0.022$), $N_{\mathrm{o}} = 11623$; $R = 0.030$, $R_{\mathrm{w}} = 0.037$.

Variata. This compound is isomorphous with the analogue preceding (**18**); P, As were modelled as composites.

*2.2.1.1.18. AgClO$_4$:dppp:bq (2:1:2) · 2MeCN (**19** · 2MeCN).* $C_{67}H_{56}Ag_2Cl_2N_6O_8P_2$, $M = 1421.8$. Monoclinic, space group $P2_1/n$, $a = 13.8061(8)$ Å, $b = 30.128(2)$ Å, $c = 14.5565(9)$ Å, $\beta = 97.959(1)°$, $V = 5997$ Å^3. D_{calc} ($Z = 4$) $= 1.57_5$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.86\ \mathrm{mm}^{-1}$; specimen: $0.56 \times 0.24 \times 0.13$ mm; '$T_{\mathrm{min/max}}$' = 0.69. $2\theta_{\mathrm{max}} = 67°$; $N_{\mathrm{t}} = 85786$, $N = 22008$ ($R_{\mathrm{int}} = 0.037$), $N_{\mathrm{o}} = 17059$; $R = 0.036$, $R_{\mathrm{w}} = 0.042$.

*2.2.1.1.19. AgClO$_4$:dppp:dpa (2:1:2) (**20**).* $C_{48}H_{46}Ag_2Cl_2N_6O_8P_2$, $M = 1183.5$. Triclinic, space group $P\bar{1}$, $a = 10.424(1)$ Å, $b = 11.628(2)$ Å, $c = 12.236(1)$ Å, $\alpha = 64.999(2)°$, $\beta = 71.941(2)°$, $\gamma = 86.992(2)°$, $V = 1273$ Å^3. D_{calc} ($Z = 1$) $= 1.54_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.99\ \mathrm{mm}^{-1}$; specimen: $0.47 \times 0.42 \times 0.32$ mm; '$T_{\mathrm{min/max}}$' = 0.72. $2\theta_{\mathrm{max}} = 58°$; $N_{\mathrm{t}} = 26126$, $N = 6765$ ($R_{\mathrm{int}} = 0.028$), $N_{\mathrm{o}} = 5248$; $R = 0.044$, $R_{\mathrm{w}} = 0.051$.

Variata. The material underwent a phase transformation at low temperature, and data were acquired at ca. 298 K.

*2.2.1.1.20. AgClO$_4$:dppp:tpy (2:1:2) (**21**).* $C_{57}H_{48}Ag_2Cl_2N_6O_8P_2$, $M = 1293.6$. Monoclinic, space group $P2_1/c$, $a = 10.8782(6)$ Å, $b = 22.379(1)$ Å, $c = 22.258(1)$ Å, $\beta = 102.804(1)°$, $V = 5284$ Å^3. $D_{\mathrm{calc}} = 1.62_6$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.97$ mm^{-1}; specimen: $0.60 \times 0.18 \times 0.14$ mm; '$T_{\mathrm{min/max}}$' = 0.84. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 108356$, $N = 27658$ ($R_{\mathrm{int}} = 0.048$), $N_{\mathrm{o}} = 16802$; $R = 0.039$, $R_{\mathrm{w}} = 0.040$.

*2.2.1.1.21. AgClO$_4$:dppb:bpy (2:1:2) · 2MeCN (**22** · 2MeCN).* $C_{52}H_{50}Ag_2Cl_2N_6O_8P_2$, $M = 1235.6$. Monoclinic, space group $P2_1/c$, $a = 20.819(2)$ Å, $b = 17.471(1)$ Å, $c = 14.853(1)$ Å, $\beta = 106.156(2)°$, $V = 5189$ Å^3. D_{calc} ($Z =$! 4) $= 1.58_1$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.98$ mm^{-1}; specimen: $0.32 \times 0.25 \times 0.30$ mm; '$T_{\mathrm{min/max}}$' = 0.80. $2\theta_{\mathrm{max}} = 65°$; $N_{\mathrm{t}} = 92967$, $N = 18334$ ($R_{\mathrm{int}} = 0.047$), $N_{\mathrm{o}} = 12404$; $R = 0.035$, $R_{\mathrm{w}} = 0.038$.

Variata. Perchlorate group 1 was modelled with a ClO_2 component disordered over two sets of sites, in concert with perchlorate 2, rotationally disordered about a Cl–O bond, site occupancies of the two components of each refining to 0.791(4) and complement.

*2.2.1.1.22. AgClO$_4$:dppb:bq (2:1:2) · 2MeCN · EtOH (**23** · 2MeCN · EtOH).* $C_{70}H_{64}Ag_2Cl_2N_6O_9P_2$, $M = 1481.9$. Triclinic, space group $P\bar{1}$, $a = 11.3309(8)$ Å, $b = 12.0313(9)$ Å, $c = 13.854(1)$ Å, $\alpha = 96.510(2)°$, $\beta = 99.706(2)°$, $\gamma = 117.470(2)°$, $V = 1612$ Å^3. D_{calc} ($Z = 1$) $= 1.52_7$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.80$ mm^{-1}; specimen: $0.18 \times 0.16 \times 0.09$ mm; '$T_{\mathrm{min/max}}$' = 0.86. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 33028$, $N = 16475$ ($R_{\mathrm{int}} = 0.026$), $N_{\mathrm{o}} = 11896$; $R = 0.040$, $R_{\mathrm{w}} = 0.044$.

Variata. Difference map residues were modelled as EtOH disordered about a centre of symmetry, the oxygen further disordered over two sites whose occupancies were set at 0.25.

*2.2.1.1.23. AgClO$_4$:dppb:tpy (2:1:2) · EtOH (**24** · EtOH).* $C_{60}H_{56}Ag_2Cl_2N_6O_9P_2$, $M = 1353.7$. Triclinic, space group $P\bar{1}$, $a = 9.950(1)$ Å, $b = 11.414(1)$ Å, $c = 14.582(2)$ Å, $\alpha = 102.349(3)°$, $\beta = 104.173(3)°$, $\gamma = 109.482(3)°$, $V = 1433$ Å^3. D_{calc} ($Z = 1$) $= 1.56_9$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.90$ mm^{-1}; specimen: $0.28 \times 0.22 \times 0.16$ mm; '$T_{\mathrm{min/max}}$' = 0.80. $2\theta_{\mathrm{max}} = 75°$; $N_{\mathrm{t}} = 28999$, $N = 14594$ ($R_{\mathrm{int}} = 0.023$), $N_{\mathrm{o}} = 12558$; $R = 0.032$, $R_{\mathrm{w}} = 0.041$.

Variata. As in the previous case the oxygen atom of the ethanol, disposed about an inversion centre, was modelled as disordered over two sites, occupancies set at 0.25.

2.2.1.2. AgX (=NO$_3$):dpex:L (2:1:2) (·nS) complexes.

*2.2.1.2.1. AgNO$_3$:dppm:bpy (2:1:2) · H$_2$O (**25** · H$_2$O).* $C_{45}H_{40}Ag_2N_6O_7P_2$, $M = 1054.5$. Monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), $a = 31.733(3)$ Å, $b = 17.302(2)$ Å, $c = 16.953(2)$ Å, $\beta = 114.243(2)°$, $V = 8487$ Å^3. D_{calc} ($Z = 8$) $= 1.65_0$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 1.06$ mm^{-1}; specimen: $0.15 \times 0.13 \times 0.10$ mm; '$T_{\mathrm{min/max}}$' = 0.78. $2\theta_{\mathrm{max}} = 58°$; $N_{\mathrm{t}} = 88831$, $N = 11270$ ($R_{\mathrm{int}} = 0.062$), $N_{\mathrm{o}} = 8175$; $R = 0.040$, $R_{\mathrm{w}} = 0.046$.

Variata. Phenyl ring 21 and anion and solvent components were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement. Water molecule hydrogen atoms were not located.

*2.2.1.2.2. AgNO$_3$:dppm:dmp (2:1:2) · MeCN · ½H$_2$O (**26** · MeCN · ½H$_2$O).* $C_{55}H_{50}Ag_2N_7O_{6.5}P_2$, $M = 1190.7$. Triclinic, space group $P\bar{1}$, $a = 13.453(1)$ Å, $b = 14.047(1)$ Å, $c = 14.553(2)$ Å, $\alpha = 67.164(3)°$, $\beta = 86.515(3)°$, $\gamma = 79.838(3)°$, $V = 2495$ Å^3. D_{calc} ($Z = 2$) $= 1.58_5$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.91$ mm^{-1}; specimen: $0.35 \times 0.20 \times 0.03$ mm; '$T_{\mathrm{min/max}}$' = 0.75. $2\theta_{\mathrm{max}} = 58°$; $N_{\mathrm{t}} = 42804$, $N = 20249$ ($R_{\mathrm{int}} = 0.055$), $N_{\mathrm{o}} = 12371$; $R = 0.047$, $R_{\mathrm{w}} = 0.048$.

Variata. The 'water molecule oxygen' residue (no associated hydrogen atoms were located) was assigned a site occupancy of 0.5 after trial refinement.

*2.2.1.2.3. AgNO$_3$:dppm:bq (2:1:2) · 2MeCN · ½H$_2$O (**27** · 2MeCN · ½H$_2$O).* $C_{65}H_{53}Ag_2N_8O_{6.5}P_2$, $M = 1327.9$. Monoclinic, space group $P2_1/c$, $a = 14.951(2)$ Å, $b = 12.750(2)$ Å, $c = 30.237(4)$ Å, $\beta = 98.105(4)°$, $V = 5706$ Å^3. D_{calc} ($Z = 4$) $= 1.54_5$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.81$ mm^{-1}; specimen: $0.16 \times 0.10 \times 0.05$ mm; '$T_{\mathrm{min/max}}$' = 0.74. $2\theta_{\mathrm{max}} = 58°$; $N_{\mathrm{t}} = 118513$, $N = 15175$ ($R_{\mathrm{int}} = 0.11$), $N_{\mathrm{o}} = 11177$; $R = 0.042$, $R_{\mathrm{w}} = 0.047$.

Variata. The 'water molecule oxygen' was modelled similarly to the previous compound.

*2.2.1.2.4. AgNO$_3$: dpam : dmp (2 : 1 : 2) · 1½MeCN · H$_2$O (**28** · 1½MeCN · H$_2$O).* $C_{56}H_{54.5}Ag_2As_2N_{7.5}O_8$, $M = 1326.2$. Monoclinic, space group $P2_1/c$, $a = 18.6310(11)$ Å, $b = 11.0495(7)$ Å, $c = 25.7580(15)$ Å, $\beta = 95.872(1)°$, $V = 5275$ Å^3. D_{calc} ($Z = 4$) $= 1.67_0$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 2.05$ mm^{-1}; specimen: $0.26 \times 0.25 \times 0.23$ mm; '$T_{\mathrm{min/max}}$' = 0.82. $2\theta_{\mathrm{max}} = 70°$; $N_{\mathrm{t}} = 96917$, $N = 23180$ ($R_{\mathrm{int}} = 0.047$), $N_{\mathrm{o}} = 16849$; $R = 0.041$, $R_{\mathrm{w}} = 0.055$.

Variata. Difference map residues were modelled in terms of a second acetonitrile and a water molecule oxygen, both disordered, with site occupancies set at 0.5 after trial refinement.

*2.2.1.2.5. AgNO$_3$:dppp:dmp (2:1:2) · ½MeCN (**29** · ½MeCN).* $C_{56}H_{51.5}Ag_2N_{6.5}O_6P_2$, $M = 1182.2$. Monoclinic, space group $P2_1/c$, $a = 10.726(1)$ Å, $b = 20.375(3)$ Å, $c = 23.891(3)$ Å, $\beta = 102.790(2)°$, $V = 5092$ Å^3. D_{calc} ($Z = 4$) $= 1.55_1$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.89$ mm^{-1}; specimen: $0.16 \times 0.13 \times 0.11$ mm; '$T_{\mathrm{min/max}}$' = 0.91. $2\theta_{\mathrm{max}} = 58°$; $N_{\mathrm{t}} = 47074$, $N = 12805$ ($R_{\mathrm{int}} = 0.046$), $N_{\mathrm{o}} = 9203$; $R = 0.049$, $R_{\mathrm{w}} = 0.061$.

Variata. Nitrate 1 was modelled as disordered over two sets of sites, occupancies set at 0.5 with constrained geometries, and isotropic displacement parameter forms. Acetonitrile (non-disordered) was refined similarly.

*2.2.1.2.6. AgNO$_3$:dppb:tpy (2:1:2) (**30**).* $C_{58}H_{50}Ag_2N_8O_6P_2$, $M = 1232.8$. Triclinic, space group $P\bar{1}$, $a = 9.8410(6)$ Å, $b = 10.7735(7)$ Å, $c = 12.9754(8)$ Å, $\alpha = 102.995(1)°$, $\beta = 104.253(1)°$, $\gamma = 94.987(1)°$, $V = 1284$ Å^3. D_{calc} ($Z = 1$) $= 1.59_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 0.89$ mm^{-1}; specimen: $0.43 \times 0.22 \times 0.21$ mm; '$T_{\mathrm{min/max}}$' = 0.85. $2\theta_{\mathrm{max}} = 70°$; $N_{\mathrm{t}} = 25532$, $N = 11209$ ($R_{\mathrm{int}} = 0.021$), $N_{\mathrm{o}} = 9769$; $R = 0.032$, $R_{\mathrm{w}} = 0.043$.

3. Results and discussion

3.1. Syntheses

A number of adducts of general formula AgX:dpex:L (2:1:2) (Charts 1–8) have been synthesised by the reaction of two equivalents of *N*,*N*′-bidentate (bpy, phen, dmp, bq, dpa) or *N*,*N*′,*N*″-tridentate (tpy) aromatic ligands, L, derivative of 2,2′-bipyridyl, with two equivalents of silver(I) perchlorate or nitrate and one equivalent of an *E*,*E*′-bidentate dpex ligand according to

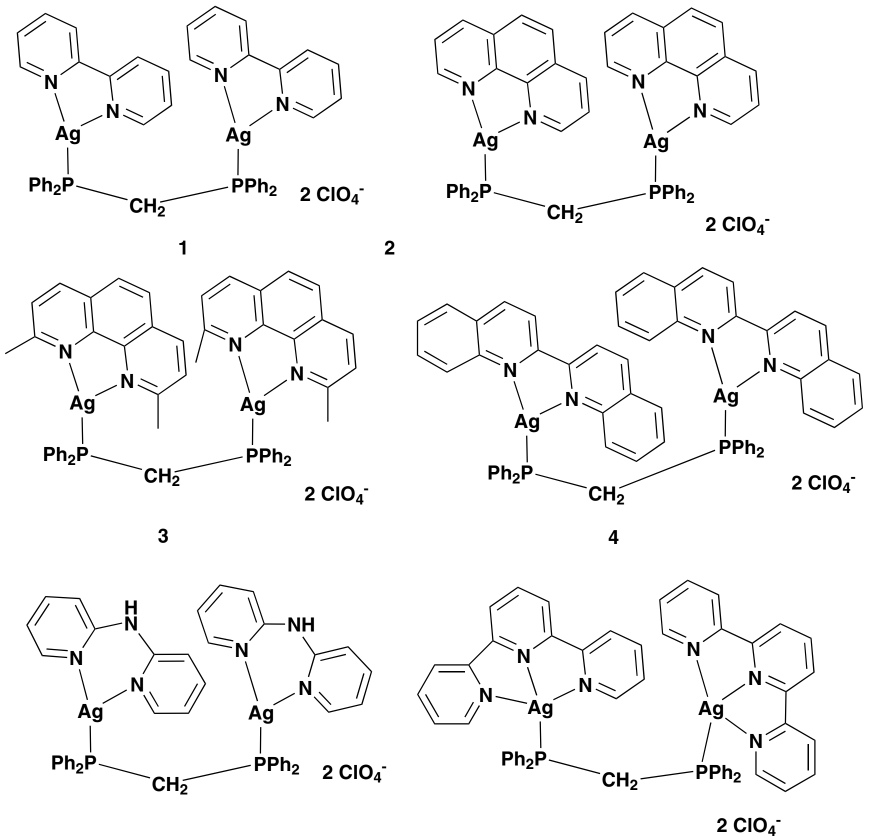
$$2\mathrm{AgX} + 1\mathrm{dpex} + 2\mathrm{L} + y\mathrm{H_2O} \xrightarrow{S} \mathrm{AgX} : \mathrm{dpex} : \mathrm{L}(: x\mathrm{S} : y\mathrm{H_2O})(2 : 1 : 2(x : y)) \quad (1)$$

When less than two equivalents of the ligand L were used, some unreacted starting material was often recovered from the reaction. On the other hand, when more than one equivalent of *E*,*E*′-bidentate dpex was employed, the dpex: AgX (2:1) adducts were the predominant species obtained, no adducts containing *N*,*N*′-donor ligands being isolated. All the compounds, air-stable, colorless materials, are insoluble in diethyl ether and ethanol and soluble in acetone, acetonitrile, and DMSO. The nitrato derivatives **25**–**30** are moderately soluble also in chlorinated solvents. The conductivity measurements are in accordance with the ionic formulations found in the solid state for most of the derivatives. In addition, compounds containing weakly coordinated $\mathrm{ClO_4}$ or $\mathrm{NO_3}$ undergo complete ionic dissociation, not only in acetonitrile but also in non-ionizing solvents such as dichloromethane, values in the former solvent being in the range 40–50 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

3.2. Spectroscopy

The infrared spectra (Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the organic *N*,*N*′-donor, and the bidentate phosphine or arsine ligands [14]. In the far-IR spectra of all phosphino derivatives we assigned, on the basis of previous reports, the broad absorptions near 500 $\mathrm{cm^{-1}}$ and those at 480–400 $\mathrm{cm^{-1}}$ to Whiffen's *y* and *t* vibrations [15].

The IR spectra of the perchlorato silver complexes **1**–**9**, **11**, **13**–**19**, and **21**–**23** always showed two absorptions characteristic of ionic perchlorate groups: a strong broad band in the range 1110–1080 $\mathrm{cm^{-1}}$ (ν_3) and a sharp medium or strong band at ca. 625 $\mathrm{cm^{-1}}$ (ν_4) [16]. They are indicative of uncomplexed ionic or weakly interacting $\mathrm{ClO_4}^-$ groups in accordance with the structures found in the solid state, and with the behaviour shown by these complexes in solution. The absorptions are very similar to those found for the ionic $[(\mathrm{PPh_3})_4\mathrm{Cu}]\mathrm{ClO_4}$ and different from those found in the strongly distorted trigonal planar $[(\mathrm{cy_3P})_2\mathrm{CuOClO_3}]$



1 2 3 4 5 6

Chart 1.

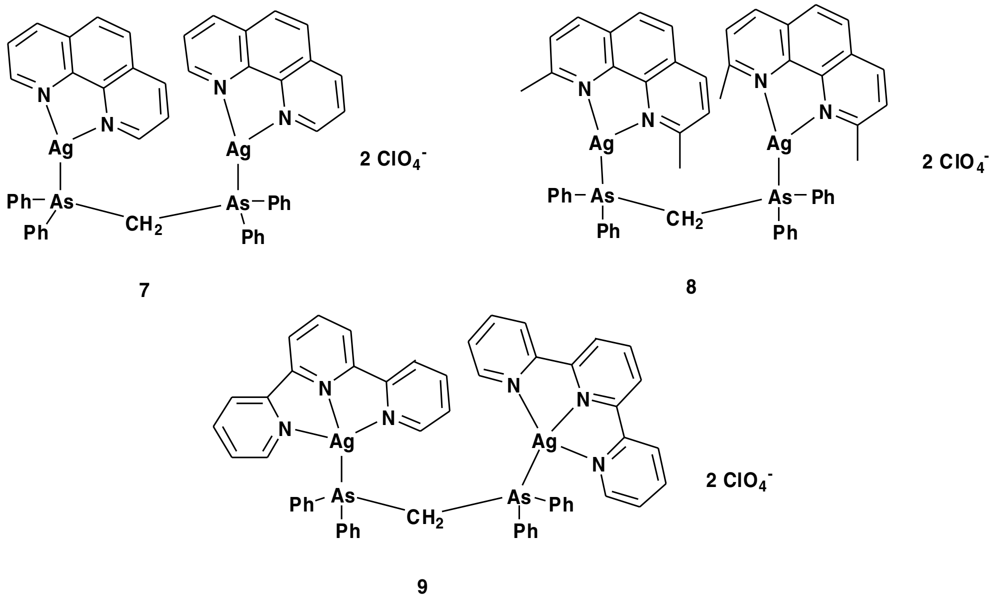


Chart 2.

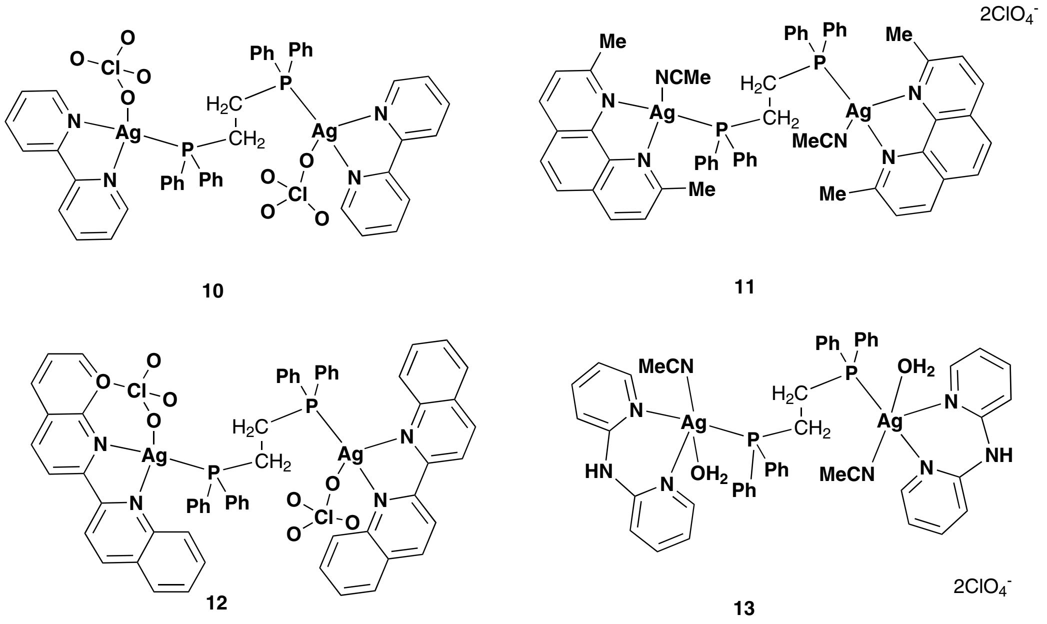
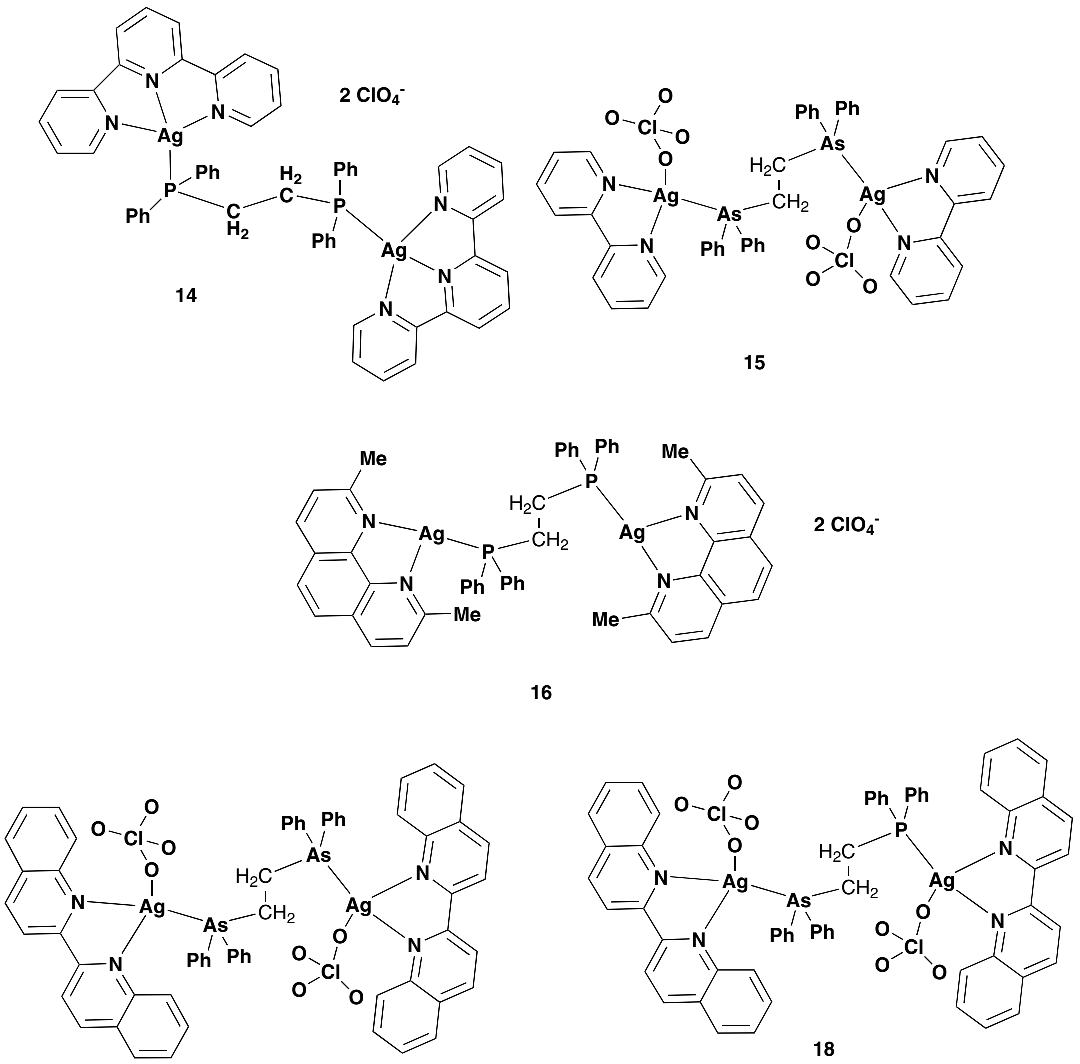


Chart 3.

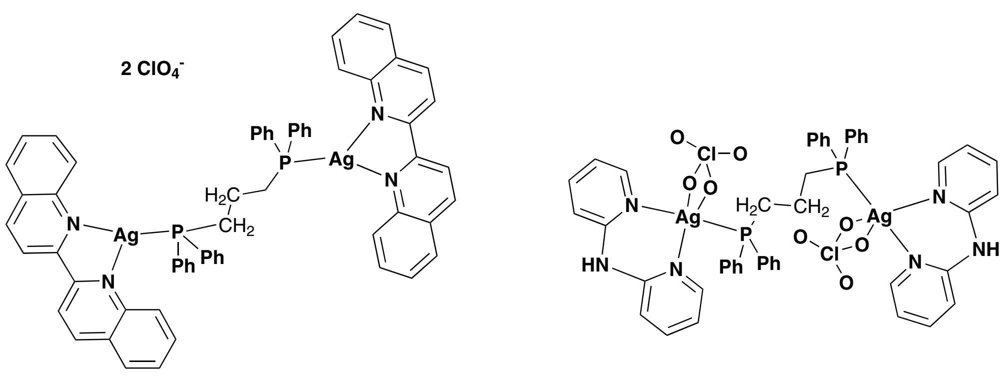
containing a unidentate perchlorate group [17,18]. The IR spectrum of **20** exhibits three strong absorptions at ca. 1160, 1120 and 1080 cm^{-1}, respectively, typical of ν_8, ν_6 and ν_1, and two absorptions at ca. 639 and 620 cm^{-1} presumably due to ν_3 and ν_7, all indicative of a bidentate perchlorate group as found in the solid state. The IR spectra of **10**, **12** and **24** (for which the single crystal X-ray studies indicated unidentate ClO_4^- groups) exhibit in the regions 1100–1000 and 640–600 cm^{-1} analogous bands to those found for the ionic complexes **1**–**9**, **11**, **13**–**19**, and **21**–**23**, suggesting very weak interactions between the ClO_4^- ions and the silver centres.

In the spectra of derivatives **25** and **26**, the ν_2, ν_3 and ν_4 modes of vibration of ionic NO_3^- groups (D_{3h} symmetry) and a unique weak $\nu_1 + \nu_4$ combination band in the overtone region 1700–1800 cm^{-1} have been detected throughout in accordance with their ionic structures [19]. In the spectra of complexes **29** and **30**, the separation between ν_1 and ν_4 is ca. 40 cm^{-1}, consistent with a unidentate nitrato ligand $\nu_1 + \nu_4$ [20]. The weak interactions between the silver(I) cations and the nitrate groups in **29** and **30** are reflected in the small magnitudes of the splittings of the asymmetric N–O stretching modes [21]. The presence of two different absorptions due to ν_{asym} at 1420 and 1370 cm^{-1} and to out-of



14 **15** **16** **17** **18**

Chart 4.



19 **20**

Chart 5.

plane deformation at ca. 840 and 820 cm^{-1} in the spectrum of derivative **28** is consistent with the presence of both ionic and unidentate NO_3 groups (see below). The decrease in energy of the out-of-plane deformation mode, ν_2, in passing from derivative **26**–**30** is consistent with increasing coordination of the nitrate oxygens [21].

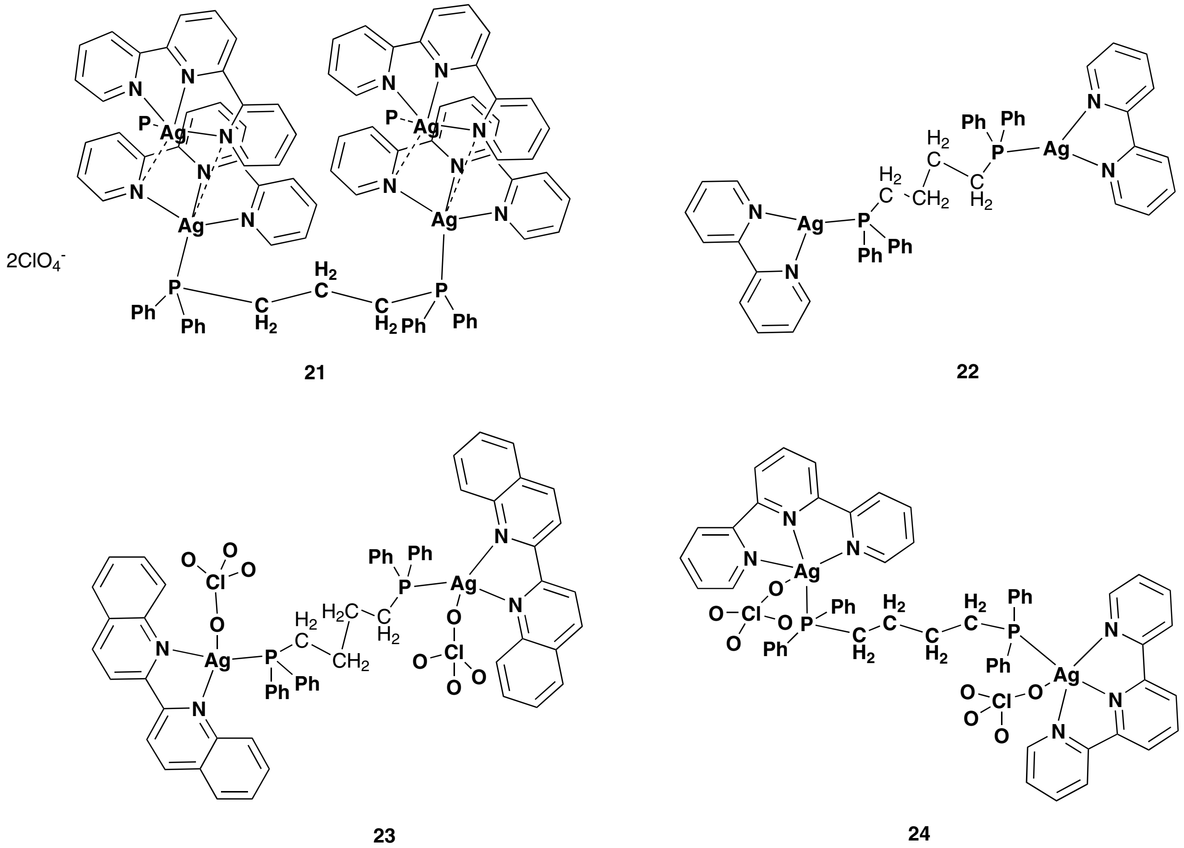


Chart 6.

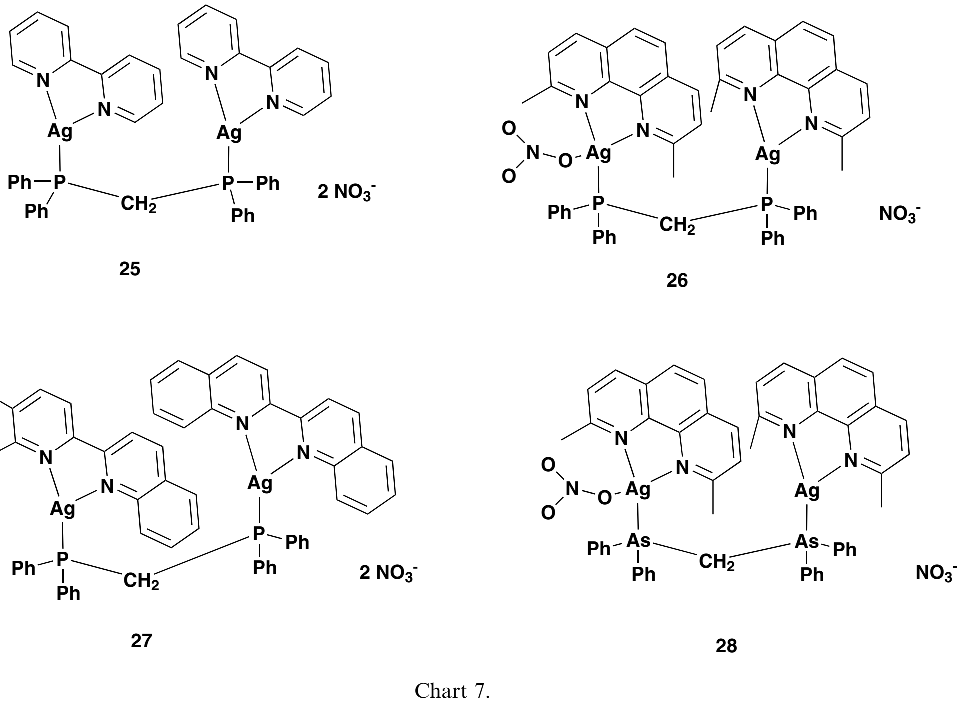
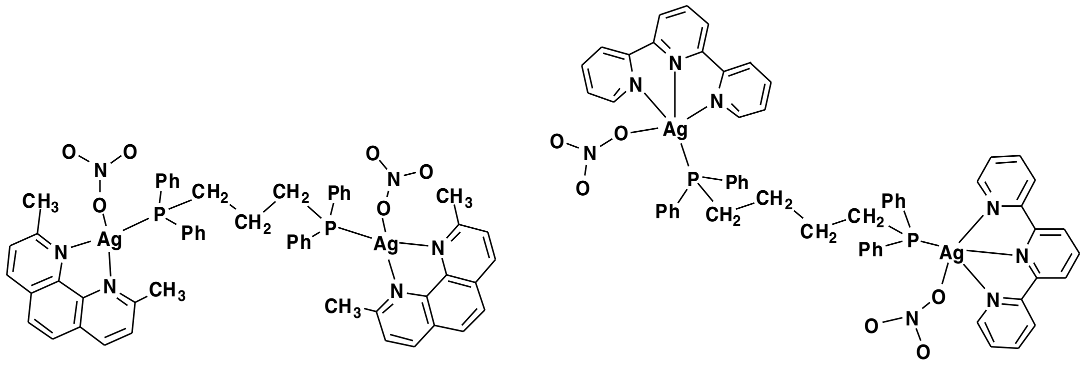


Chart 7.

In the ^{1}H and ^{13}C NMR spectra (see Section 2), the signals due to the diphosphine and *N*,*N*′-donor ligands show different patterns with respect to those found for the free donors, confirming the existence of the complexes in solution. For example, in the ^{1}H NMR spectra the bridging methylene resonances appear as broad singlets or multiplets between 1.40 and 4.33 ppm downfield shifted with respect to those found in the free donors. The chemical



29 **30**

Chart 8.

shifts depend on the ancillary *N*,*N*′-donor ligands, the greater δ being found in the case of the bq derivatives, the lower in the case of the tpy complexes.

The ^{31}P NMR data (chemical shifts, Ag–^{31}P coupling constants) in CD_3CN solution of all complexes confirm their stability in this solvent. The room temperature ^{31}P NMR spectra of complexes **10**, **14**, and **30** consist of broad singlets, presumably in consequence of exchange equilibria that are reasonably fast in relation to the NMR time scale. Exchange is quenched at low temperature (233 K), and one and/or two unresolved doublets or resolved pairs of doublets, arising from coupling between the phosphorus and silver atoms, are observed in the accessible temperature range. In particular, in the spectrum of derivative **30**, typical pairs of doublets, due to $^1J(^{31}P–^{107}Ag)$ and $^1J(^{31}P–^{109}Ag)$ coupling, are resolved at 233 K and the observed $^1J(^{31}P–^{107}Ag)/^1J(^{31}P–^{109}Ag)$ ratio is in good agreement with that calculated from the gyromagnetic ratio of the Ag nuclei $\gamma(^{107}Ag)/\gamma(^{109}Ag)$ [22]. For all the other derivatives broad doublets were also observed at room temperature, suggesting that rapid exchange equilibria are not operative in these compounds.

The ^{31}P NMR spectra of compounds **2** (Fig. 1) and **3** exhibit at room temperature an AA′XXA′A pattern [23] because of the non-equivalence of the phosphorus atoms (consistent with the X-ray data) resulting from the large ^2J(P–P), for the three possible combinations of the two silver isotopes. It is interesting to note that the pattern is similar to that found by us also for $[Ag_2(dppm)_2(X)_2]$ [24] species. Muetterties and Alegranti [25] and Goel and Pilon [26] indicated that the spin–spin constant (*J*) between phosphorus and silver is dependant on the number of coordinated phosphorus atoms in the silver complex, and that it is possible to determine the number of the latter from measurement of the *J* values in the ^{31}P NMR spectra. On the basis of the detected values, $AgPN_3$ coordination environments are probable in solution for compounds **6**, **21** and **24**, cf. $AgPN_2$ coordination environments for compounds **1**–**5**, **22**, **23**, **25**, **27**, **29** and **30**, consistent with the structures found in the solid state.

The coupling constant values found for **11**, **12**, **19** and **26** are in accordance with $AgPN_2$ coordination environments perturbed by the presence of weakly bonded counter-ions or solvent molecules. The coupling constant value determined for compound **13** (443 Hz) is representative of an AgP_2N_2 coordination environment and indicates a dissociation of the complex in solution in accordance with the following equilibrium:

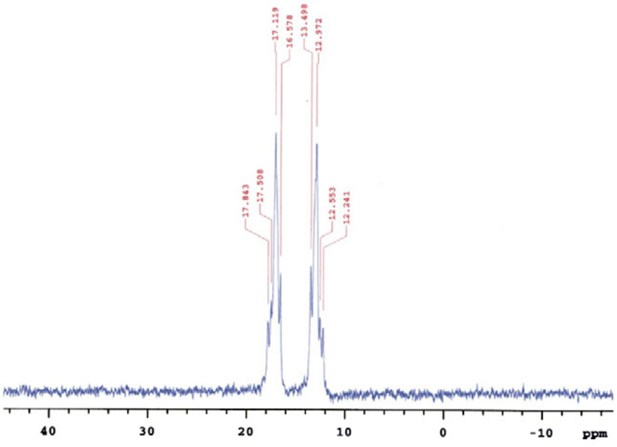


Fig. 1. ^{31}P NMR spectrum of compound **2**.

$$[(dpa)Ag(H_2O)(P\text{-}dppe\text{-}P)(MeCN)Ag(dpa)](ClO_4)_2 \\ \rightarrow [(dppe)Ag(dpa)](ClO_4) + [Ag(dpa)(ClO_4)] \qquad (2)$$

It should be noted that the signals for every free diphosphine appear upfield of those of the corresponding silver(I) complexes. $\Delta\delta(^{31}P) = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$; the differences in shift between each free diphosphine and the corresponding silver(I) derivatives are of the order of 28–34 ppm for dppm, 18–23.5 ppm for dppe, 20.3–24.7 for dppp and finally 17.2–25.6 for dppb. The shifts are a function of the chain length in the P-donor and the nature of the ancillary *N*,*N*′-donor ligands, but do not depend on the nature of the counter-ions, the perchlorate complex δ values being close to those found for the analogous nitrate species and suggesting the absence of any interaction between silver and the counter-ions also in solution. The shift is greater in the case of the bidentate *N*,*N*′-donors bpy and phen and decreases with increasing basicity of the *N*,*N*′-donor. As expected δ strongly diminishes with increasing number

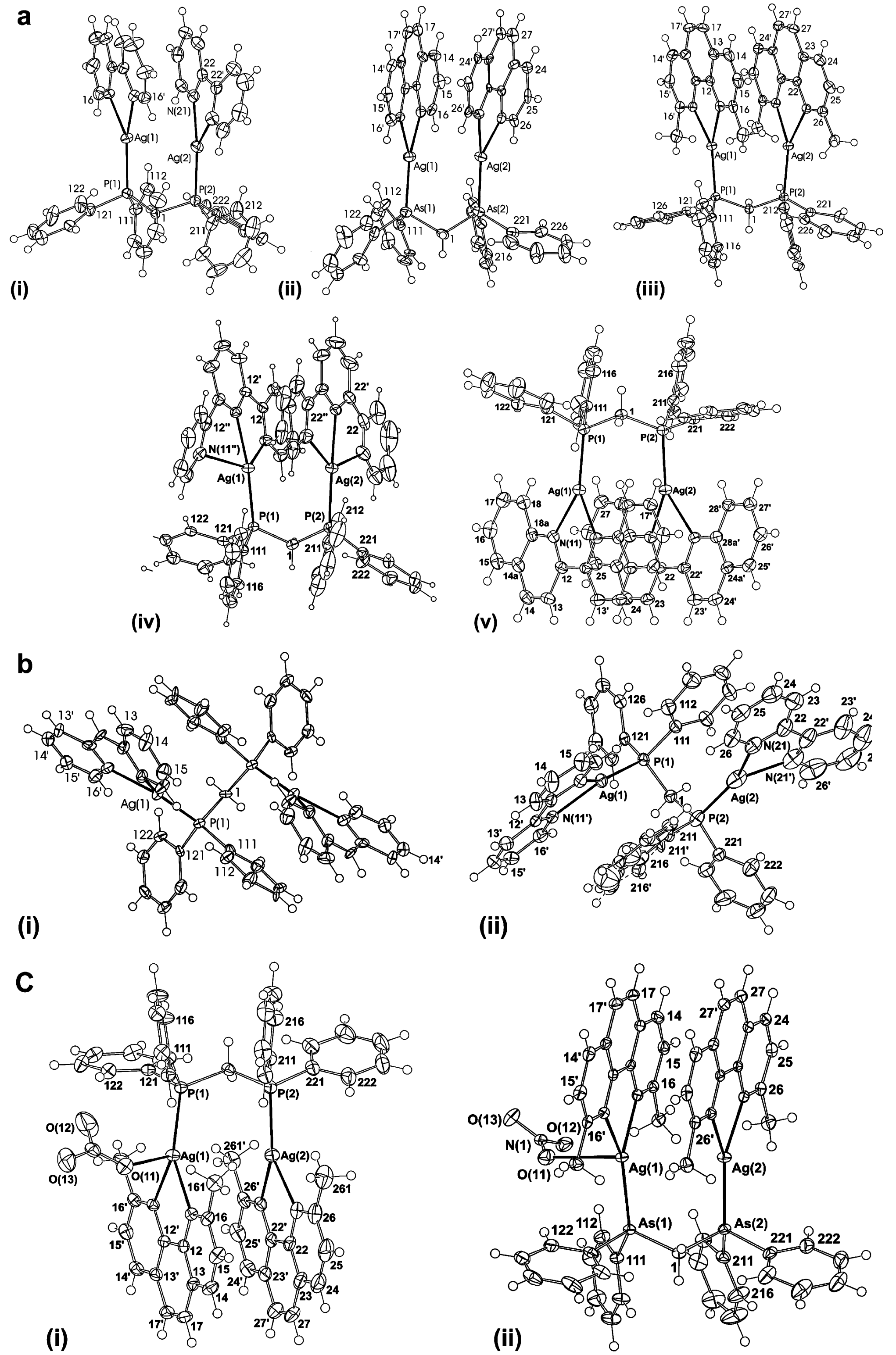


Fig. 2. Projection of the $[LAg(E\text{-dpem-}E)AgL]^{2+}$ aggregates of the 2:1:2 AgX:dpem:L complexes. Internal crystallographic symmetry is noted. (a) Species with '*cis*'-dispositions of the pair of L ligands: (i) $[(bpy)Ag(dppm)Ag(bpy)]^{2+}$, in **1** (cation 1; cation 2 is similar) (perchlorate salt); (ii) $[(phen)Ag(dpam)Ag(phen)]^{2+}$, in **7** · ¼MeCN (the E = P analogue (**2**) is isomorphous) (perchlorate salt); (iii) $[(dmp)Ag(dppm)Ag(dmp)]^{2+}$, in **3** · MeCN (the E = As analogue (**8**) is isomorphous) (perchlorate salt); (iv) $[(tpy)Ag(dppm)Ag(tpy)]^{2+}$, in **6** (the E = As analogue (**9**) is isomorphous) (perchlorate salt); (v) $[(bq)Ag(dppm)Ag(bq)]^{2+}$, in **27** · 2MeCN · ½$H_2O$ (nitrate salt). (b) Species with '*trans*'-dispositions of the pair of L ligands: (i) $[(dpa)Ag(dppm)Ag(dpa)]^{2+}$, in **5** · ⅓$H_2O$ (cation 1; cations 2, 3 are similar, all cations being disposed on crystallographic 2-axes); (ii) $[(bpy)Ag(dppm)Ag(bpy)]^{2+}$, in **25** · H_2O. (c) Species with additional coordinative interactions from anion (or solvent (none)). (i) $[(O_2NO)(dmp)Ag(dppm)Ag(dmp)]^{+}$, in **26** · MeCN · ½$H_2O$; (ii) $[(O_2NO)(dmp)Ag(dpam)Ag(dmp)]^{+}$, in **28** · 1½MeCN · H_2O.

of N donor atoms, the lower δ always being found in the tpy derivatives.

The positive electrospray mass spectra of selected derivatives (the most relevant data are reported in Section 2) suggest, under our experimental conditions, not only the existence in acetonitrile solution of $[Ag_2(dpex)(L)_2]^{2+}$ species in acetonitrile solution, but also large dissociation towards mononuclear fragments such as $[Ag(dpex)(L)]^+$, $[Ag(L)_2]^+$ $[Ag(dpex)_2]^+$ and $[Ag(dpex)(solvent)]^+$. It is noteworthy that the major peak in the positive spectra of all species is always due to the cationic species $[Ag(L)]^+$ and $[Ag(dpex)(L)]^+$, consequent upon the breaking of bridging bonds due to the diphosphine ligand. In some cases, peaks due to dinuclear species $[Ag_2(dpex)X]^+$ have been detected. The negative electrospray spectra are always dominated by the presence of molecular peaks due to X and AgX_2^-.

3.3. Single crystal X-ray studies

The twenty-nine compounds described here are of $(x{:}y{:}z)$ = AgX:dpex:L (2:1:2) stoichiometry, incorporating

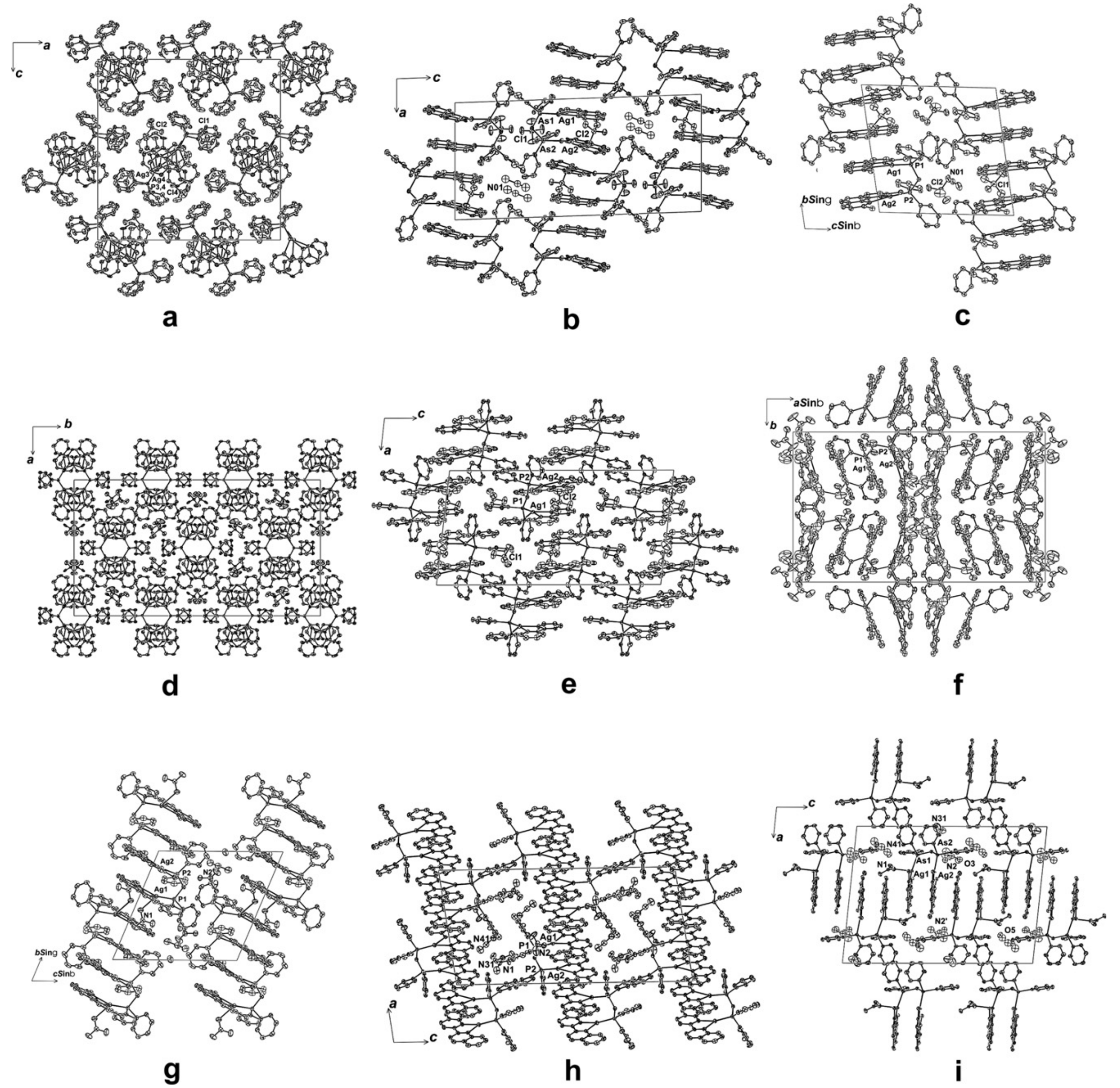


Fig. 3. Unit cell contents of: (a) $[(bpy)Ag(dppm)Ag(bpy)](ClO_4)_2$, **1**, projected down *b*; (b) $[(phen)Ag(dpam)Ag(phen)](ClO_4)_2 \cdot \frac{1}{4}MeCN$, **7** · ¼ MeCN, projected down *b*; (c) $[(dmp)Ag(dppm)Ag(dmp)](ClO_4)_2 \cdot MeCN$, **3** · MeCN, projected down *a*; (d) $[(dpa)Ag(dppm)Ag(dpa)](ClO_4)_2 \cdot \frac{1}{3}H_2O$, **5** · $\frac{1}{3}H_2O$, projected down *c*; (e) $[(tpy)Ag(dppm)Ag(tpy)](ClO_4)_2$, **6**, projected down *b*; (f) $[(bpy)Ag(dppm)Ag(bpy)](NO_3)_2 \cdot H_2O$, **25** · H_2O, projected down *c*; (g) $[(dmp)(O_2NO)Ag(dppm)Ag(dmp)](NO_3) \cdot MeCN \cdot \frac{1}{2}H_2O$, **26** · MeCN · $\frac{1}{2}H_2O$, projected down *a*; (h) $[(bq)Ag(dppm)Ag(bq)](NO_3)_2 \cdot 2MeCN \cdot \frac{1}{2}H_2O$, **27** · 2MeCN · $\frac{1}{2}H_2O$, projected down *b*. (i) $[(dmp)(O_2NO)Ag(dpam)Ag(dmp)](NO_3) \cdot 1\frac{1}{2}MeCN \cdot \frac{1}{2}H_2O$, **28** · $1\frac{1}{2}$MeCN · $\frac{1}{2}H_2O$, projected down *b*.

all forms of dpex ligands employed. All but one of these ($AgClO_4$:dppp:tpy (2:1:2), **21**) contain binuclear species, predominantly of the form $[LAg(E\text{-dpex-}E')AgL]^{2+}(X^-)_2$, containing three-coordinate (four in the L = tpy complexes) $(N,N'(,N'')\text{-L})AgE$ environments, simply that in the case of most of the dpem adducts, but in the cases of the dpee, dppp, dppb adducts, subject to augmentation by interactions of diverse strengths with unidentate solvent (usually MeC*N*) or uni- or (semi-)bidentate *O*(,*O*′)-anions, the latter phenomenon presumably consequent on the more spacious disposition of the binuclear arrays permitted by expansion of the polymethylene dpex string, and in some cases the more spacious and less powerful donor characteristics of E = As dpex ligands; e.g. with dpam and the more basic nitrate, such interactions may also be found. Insofar as the *N*,*N*′-bidentate ligands are concerned, all these behave as chelates (bpy, bq, dpa always in their '*cis*'-forms) with similar 'bite' angles and Ag–N distances, dpa excepted where the chelate ring is six-membered rather than five; bpy, bq and dpa ligands are essentially planar although the interplanar dihedral angle between the pair of aromatic components may be as great as 22° (Table 2). With these

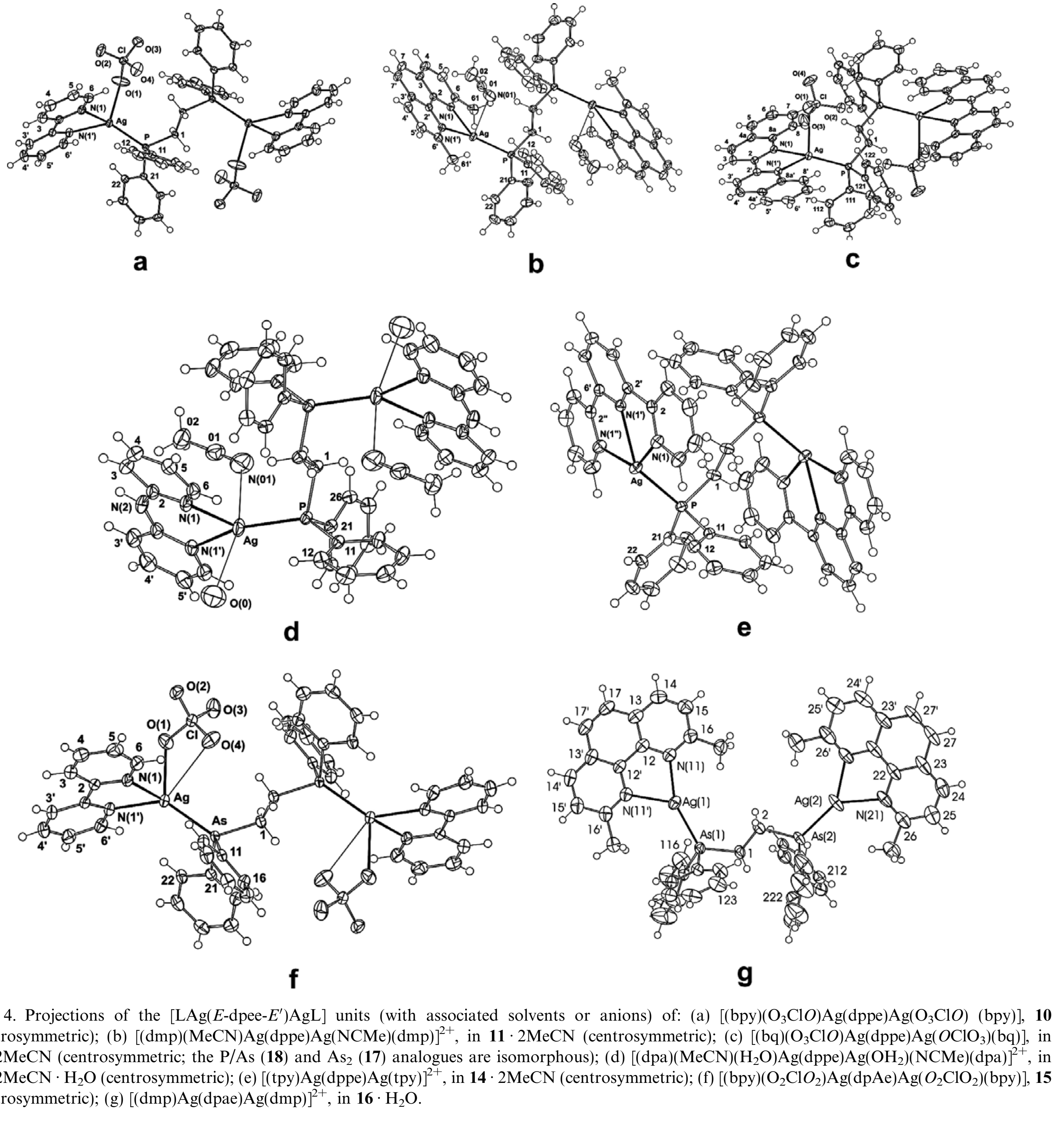


Fig. 4. Projections of the $[LAg(E\text{-dpee-}E')AgL]$ units (with associated solvents or anions) of: (a) $[(bpy)(O_3ClO)Ag(dppe)Ag(O_3ClO)(bpy)]$, **10** (centrosymmetric); (b) $[(dmp)(MeCN)Ag(dppe)Ag(NCMe)(dmp)]^{2+}$, in **11** · 2MeCN (centrosymmetric); (c) $[(bq)(O_3ClO)Ag(dppe)Ag(OClO_3)(bq)]$, in **12** · 2MeCN (centrosymmetric; the P/As (**18**) and As_2 (**17**) analogues are isomorphous); (d) $[(dpa)(MeCN)(H_2O)Ag(dppe)Ag(OH_2)(NCMe)(dpa)]^{2+}$, in **13** · 2MeCN · H_2O (centrosymmetric); (e) $[(tpy)Ag(dppe)Ag(tpy)]^{2+}$, in **14** · 2MeCN (centrosymmetric); (f) $[(bpy)(O_2ClO_2)Ag(dpAe)Ag(O_2ClO_2)(bpy)]$, **15** (centrosymmetric); (g) $[(dmp)Ag(dpae)Ag(dmp)]^{2+}$, in **16** · H_2O.

rather general comments in mind, we discuss the individual arrays, representative depictions being given in Figs. 1–7, with geometries and conformational descriptors being summarised in Tables 1–4. In a number of cases, the planar arrays of the *N*,*N*′-base ligands, in particular, lead to interesting stackings, also portrayed in the figures.

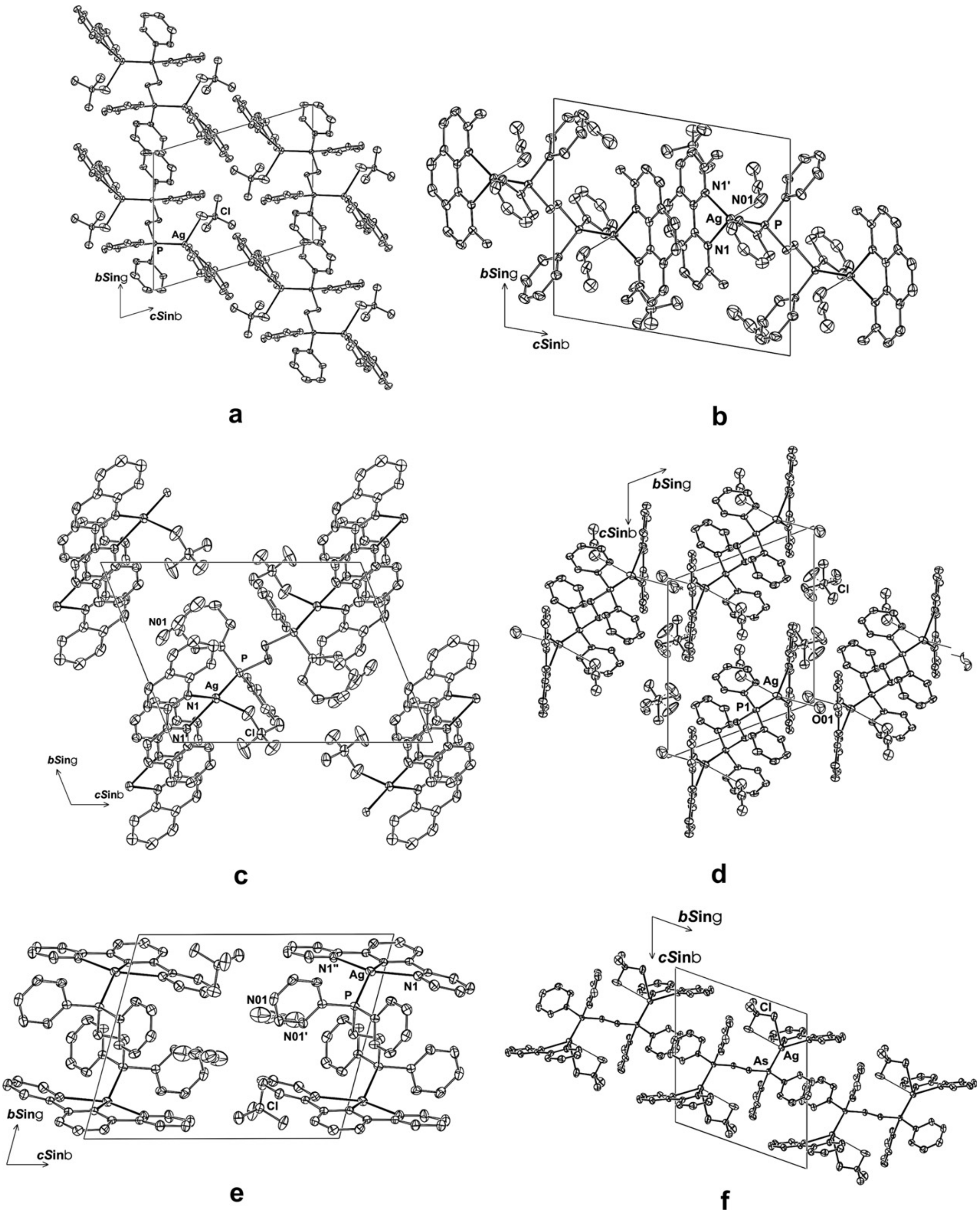


Fig. 5. Unit cell contents of: (a) [(bpy)($O_3Cl\mathit{O}$)Ag(dppe)Ag($\mathit{O}ClO_3$)(bpy)], **10**, projected down *a*; (b) [(dmp)(MeCN)Ag(dppe)Ag(NCMe)(dmp)]-$(ClO_4)_2 \cdot 2MeCN$, **11** · 2MeCN, projected down *a*; (c) [(bq)($O_3Cl\mathit{O}$)Ag(dppe)Ag($\mathit{O}ClO_3$)(bq)] · 2MeCN, **12** · 2MeCN, projected down *a*; (d) [(dpa)-(MeCN)(H_2O)Ag(dppe)Ag(OH_2)(NCMe)(dpa)]$(ClO_4)_2$ · MeCN · H_2O, **13** · MeCN · H_2O, projected down *a*; (e) [(tpy)Ag(dppe)Ag(tpy)](ClO_4) · 2MeCN, **14** · 2MeCN, projected down *a*; (f) [(bpy)($O_2Cl\mathit{O}_2$)Ag(dpae)Ag(O_2ClO_2)(bpy)], **15**, projected down *a*.

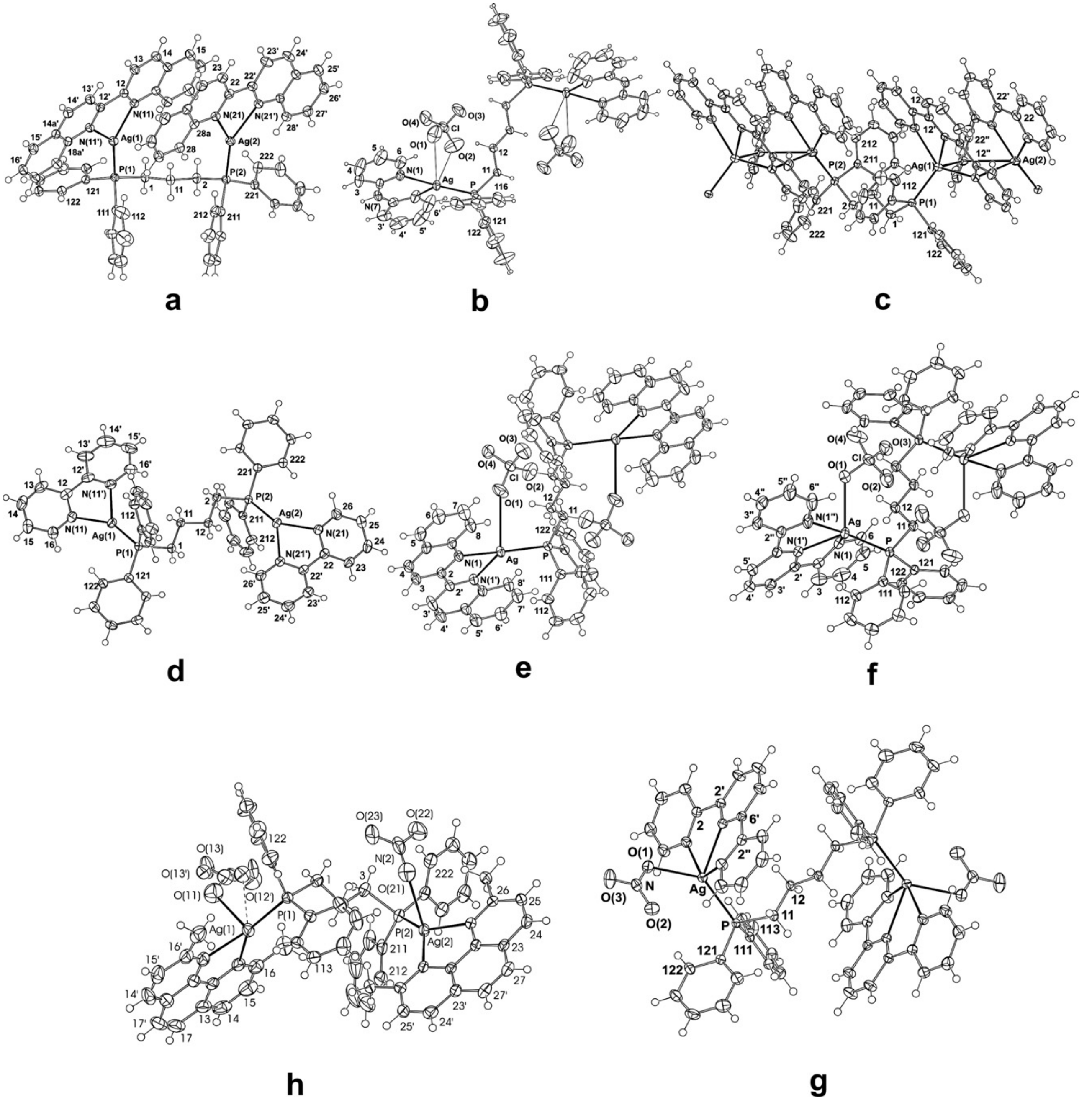


Fig. 6. Projections of the binuclear [LAg(*P*-dppx-*P*′)AgL] units of: (a) $[(bq)Ag(dppp)Ag(bq)]^{2+}$, in **19** · 2MeCN; (b) $[(dpa)(O_2ClO_2)Ag(dppp)Ag(O_2ClO_2)(dpa)]$, **20**; (c) $[\ldots Ag(tpy)_2Ag(dppp)\ldots]_{(\infty|\infty)}{}^{2+}$, in **21**; (d) $[(bpy)Ag(dppb)Ag(bpy)]^{2+}$, in **22** · 2MeCN; (e) $[(bq)(O_3ClO)Ag(dppb)Ag(O_3ClO)(bq)]$ in **23** · 2MeCN · EtOH (centrosymmetric); (f) $[(tpy)(O_3ClO)Ag(dppb)Ag(OClO_3)(tpy)]$, in **24** · EtOH (centrosymmetric); (g) $[(dmp)(O_2NO)Ag(dppp)Ag(ONO_2)(dmp)]$, **29**; (h) $[(tpy)(O_2NO)Ag(dppb)Ag(ONO_2)(tpy)]$, in **30** (centrosymmetric).

*3.3.1. The AgX:dpem:L (2:1:2) complexes (**1–3**; **5–9**) (X = ClO₄); **25–28** (X = NO₃) (·nS)*

The ‘simple’ $[LAg(dppm)AgL]X_2$ salts, found for both $X = ClO_4$, NO_3, are the most numerous and fall into two forms. The disposition of the substituents of the E atom are ‘staggered’ with respect to the hydrogens of the central methylene group, such that one pair of substituents, X, form a quasi-planar array XPCPX, the other two substituents pendant to either side of that plane. In the majority of cases, the coplanar ‘X’ substituents are Ag; in a situation which we call ‘*cis*’, the torsion Ag–P…P–Ag is close to zero (Fig. 2; Table 2), compounds of this *cis*-type being exemplified by the (2:1:2) adducts: $AgClO_4$:dppm:bpy, phen, dmp, tpy (**1–3**, **6**); $AgClO_4$:dpam:phen, dmp, tpy (**7–9**) (the three latter compounds being isomorphous with their dppm counterparts); $AgNO_3$:dppm:bpy, bq (**25**, **27**). The putative symmetry of the core of this array is $mm2/C_{2v}$, but this is diminished (a), by the deviation of the methylene group from the Ag_2E_2 plane, (b), by differences in torsions of the phenyl rings, which may be accommodating (c) torsions

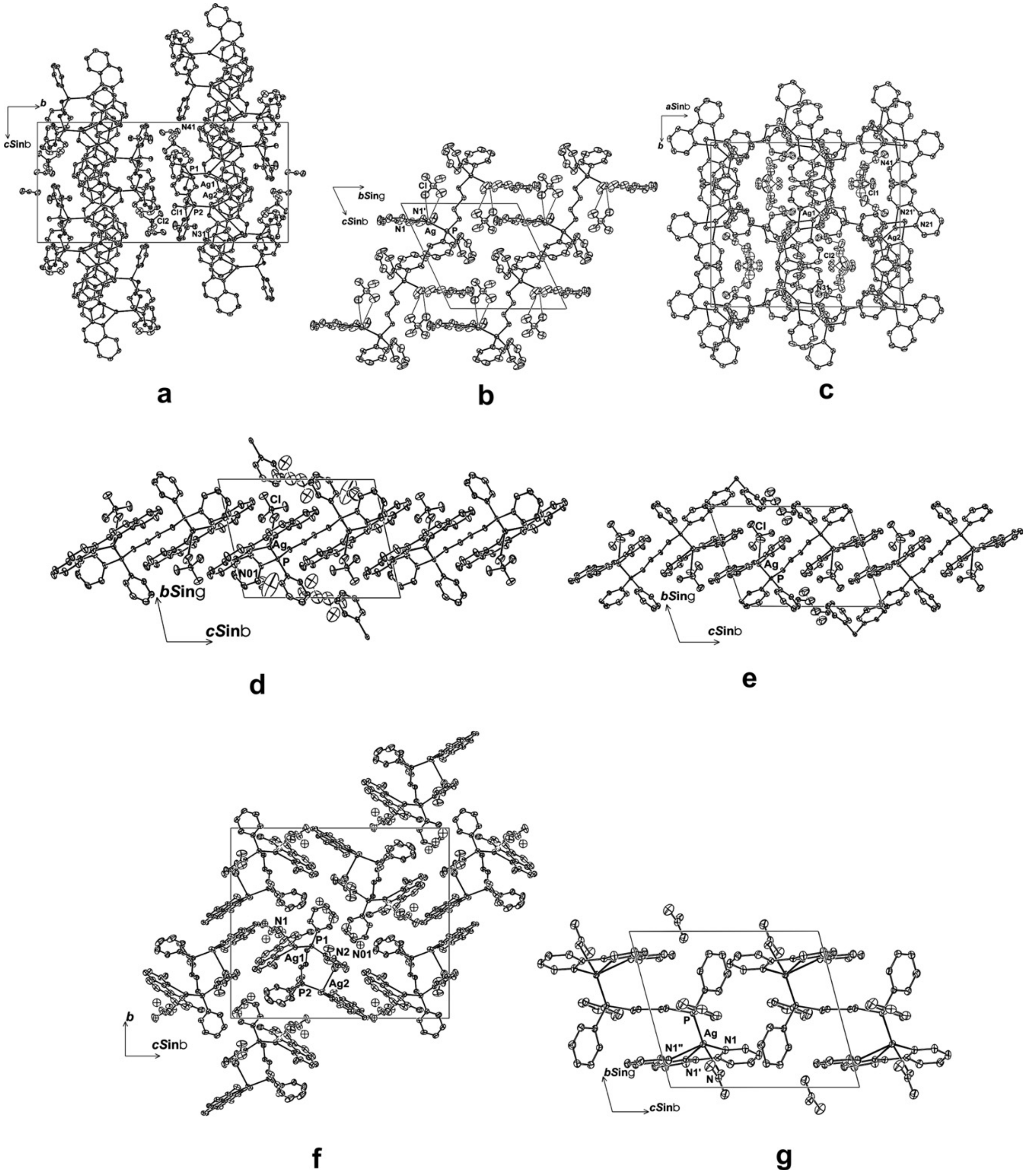


Fig. 7. Unit cell contents of: (a) [(bq)Ag(dppp)Ag(bq)](ClO$_4$)$_2$ · 2MeCN, **19** · 2MeCN, projected down *a*; (b) [(dpa)($\mathrm{O_2Cl}O_2$)Ag(dppp)Ag($O_2\mathrm{ClO_2}$)(dpa)], **20**, projected down *a*; (c) [(bpy)Ag(dppb)Ag(bpy)](ClO$_4$)$_2$ · 2MeCN, **22** · 2MeCN, projected down *c*; (d) [(bq)($\mathrm{O_3Cl}O$)Ag(dppb)Ag(OClO$_2$)(bq)] · 2MeCN · EtOH, **23** · 2MeCN · EtOH, projected down *a*; (e) [(tpy)($\mathrm{O_3Cl}O$)Ag(dppb)Ag($O\mathrm{ClO_3}$)(tpy)] · EtOH, **24** · EtOH, projected down *a*; (f) [(dmp)-($\mathrm{O_2N}O$)Ag(dppp)Ag($O\mathrm{NO_2}$)(dmp)], **29** · EtOH, projected down *a*; (g) [(tpy)($\mathrm{O_2N}O$)Ag(dppb)Ag($O\mathrm{NO_2}$)(tpy)], **30**, projected down *a*.

of the AgN$_2$ ligand planes. The driver of the latter may be 'packing' forces (a) within the lattices (see Fig. 3) or (b) within the cation, arising from interligand overlaps. There are substantial deviations in some cases from equivalence of the pair of E-Ag-*N*,*N*′ angles, with, sometimes, counterpart differences in Ag-*N*,*N*′. Deviations of the silver atoms from the ligand planes may be considerable, most notably so in bpy, bq, and dpa adducts where the pyridyl rings containing the donor atoms are not fused, as in phen, dmp. In all of these cases, one formula unit, devoid of

Table 1

Geometrical descriptors of dpem complexes: **1**–**3**, **5**–**9** (X = ClO_4); **25**–**28** (X = NO_3)

X/dpem/L	Ag	Ag–E (Å)	Ag–N (Å)	Ag. . .Ag (Å)	E–Ag–N (°)	N–Ag–N (°)	Ag–E–C (°)	E–C–E (°)
Adducts of 2:1:2 stoichiometry: binuclear [LAg(dpem)AgL]$^{2+}$ *arrays*								
(ClO_4/)dppm/bpy (**1**)	Ag(1)	2.363(3)	2.277(8), 2.360(8)	3.073(1)	145.5(2), 141.2(2)	71.6(3)	119.1(3)	112.7(5)
	Ag(2)	2.337(3)	2.311(9), 2.251(8)		130.6(2), 155.2(2)	74.1(2)	110.1(3)	
	Ag(3)	2.366(3)	2.279(9), 2.352(8)	3.113(1)	147.0(2), 140.5(2)	72.2(3)	115.4(3)	113.0(5)
	Ag(4)	2.344(3)	2.244(9), 2.366(3)		151.0(2), 134.3(2)	73.7(3)	112.6(3)	
phen (**2**)	Ag(1)	2.3347(7)	2.250(2), 2.318(2)	3.0946(4)	154.43(6), 130.14(6)	73.89(8)	117.51(7)	112.6(1)
	Ag(2)	2.3489(7)	2.282(2), 2.314(2)		145.92(6), 140.88(6)	73.06(8)	111.35(9)	
dmp (**3**)	Ag(1)	2.3483(7)	2.258(3), 2.319(2)	3.5057(4)	147.06(7), 139.11(7)	73.8(1)	113.99(9)	116.8(2)
	Ag(2)	2.3669(7)	2.318(3), 2.296(2)		145.68(7), 141.34(7)	72.99(9)	114.7(1)	
dpa (**5**)	Ag(1)	2.340(3)	2.249(9), 2.284(8)		145.6(2), 131.6(2)	82.8(3)	112.4(2)	112.6(2)
	Ag(2)	2.335(3)	2.237(9), 2.292(8)		146.6(2), 129.2(2)	84.1(3)	113.5(2)	114.4(7)
	Ag(3)	2.355(3)	2.260(9), 2.292(8)		140.3(2), 135.1(2)	84.5(8)	110.1(2)	114.2(8)
tpy (**6**)	Ag(1)	2.3825(9)	2.389(3), 2.324(3), 2.674(4)	3.4057(6)	115.98(8), 172.36(8), 106.32(8)	131.1(1), 69.6(1), 66.5(1)	118.0(1)	114.2(2)
	Ag(2)	2.414(1)	2.460(4), 2.388(4), 2.492(4)		110.0(1), 177.37(9), 115.4(1)	134.5(1), 67.4(1), 67.2(1)	111.6(1)	
(NO_3/)dppm/bpy (**25**)	Ag(1)	2.3308(9)	2.272(3), 2.287(3)		147.91(8), 139.49(7)	72.6(1)	110.7(1)	112.7(1)
	Ag(2)	2.336(1)	2.263(3), 2.285(5)		151.2(1), 135.2(1)	73.1(1)	112.3(1)	
dmp[a] (**26**)	Ag(1)	2.377(1)	2.300(2), 2.383(3)	3.4180(5)	153.00(8), 129.35(7)	72.08(9)	119.31(9)	115.0(2)
	Ag(2)	2.3457(9)	2.278(3), 2.298(3)		147.55(9), 136.53(7)	74.0(1)	110.9(1)	
bq (**27**)	Ag(1)	2.361(1)	2.289(3), 2.307(3)	3.3507(6)	145.40(8), 142.01(7)	72.5(1)	111.7(1)	113.2(1)
	Ag(2)	2.384(1)	2.294(3), 2.337(3)		153.89(8), 134.43(7)	71.7(1)	116.7(1)	
(ClO_4/)dpam/phen (**7**)	Ag(1)	2.449(1)	2.317(8), 2.290(8)	3.125(1)	141.7(2), 144.9(2)	73.1(3)	113.1(3)	109.5(4)
	Ag(2)	2.431(1)	2.324(8), 2.246(8)		130.3(2), 154.3(2)	74.2(3)	118.4(3)	
dmp (**8**)	Ag(1)	2.440(5)	2.259(4), 2.314(3)	3.7380(6)	148.1(1), 138.03(9)	73.9(1)	116.6(1)	114.9(2)
	Ag(2)	2.4486(5)	2.290(4), 2.278(3)		144.7(1), 141.29(9)	73.9(1)	115.8(1)	
tpy (**9**)	Ag(1)	2.4829(3)	2.395(2), 2.333(2), 2.532(3)	3.5799(5)	133.33(6), 177.63(6), 109.83(6)	133.10(8), 69.04(8), 67.94(8)	121.85(8)	112.1(1)
	Ag(2)	2.5059(4)	2.433(3), 2.381(3), 2.447(3)		110.01(7), 175.92(6), 112.49(7)	136.4(1), 68.2(1), 68.3(1)	113.33(8)	
(NO_3/)dpam/dmp[a] (**28**)	Ag(1)	2.4586(3)	2.272(2), 2.369(2)	3.4624(3)	153.61(6), 130.21(6)	72.82(8)	119.91(8)	110.9(1)
	Ag(2)	2.4457(3)	2.269(2), 2.298(2)		149.59(6), 135.35(6)	73.87(8)	111.25(8)	

[a] In these two adducts, significant interactions between anion and Ag(1) are found, Ag–O 2.630(3), 2.593(2) Å.

Table 2
Conformational descriptors of dpem complexes: **1**–**3**, **5**–**9** (X = ClO_4); **25**–**28** (X = NO_3)

X/dpem/L	Ag	L^1/L^2 (°)	(py/py; bq/bq) (°)	δAg (Å)	C–E–Ag–N (°)	E–C–E–Ag (°)	E–C–P–C(11,21) (°)	Ag–E–C(1n1)–C–(1nx) (°)	Ag–E...E–Ag (°)
Adducts of 2:1:2 stoichiometry: binuclear $[LAg(dpem)AgL]^{2+}$ arrays									
(ClO_4/)dppm/bpy (**1**)	Ag(1)	12.2(4)[a]	11.3(4)	0.34(1), 0.27(1)	83.3(5), −119.9(5)	53.4(6)	−70.7(6), 178.0(5)	−13.4(9), 66.3(8)	8.13(9)
	Ag(2)		17.8(4)	0.21(1), 0.64(1)	115.8(4), −71.3(6)	−39.4(6)	84.9(6), −164.4(5)	−33.44(1), −67.8(9)	
	Ag(3)	2.8(4)	3.8(4)	0.06(2), 0.24(2)	−73.5(5), 115.1(5)	−53.7(5)	69.1(6), −179.2(5)	17.4(10), −77.6(8)	−7.08(9)
	Ag(4)		18.2(4)	0.27(2), 0.66(2)	76.2(5), −121.3(4)	43.8(5)	−82.0(1), 167.5(5)	29.9(10), 57.5(8)	
phen (**2**)	Ag(1)	9.39(5)		0.116(2)	−54.5(2), 148.4(1)	−50.9(2)	77.5(2), −169.7(3)/ −175.1(3)	22.1(3), 81.5(5)	−1.15(3)
	Ag(2)			0.017(2)	90.9(1), −95.5(1)	46.4(2)	−77.7(2), 170.7(2)	27.4(3), 32.4(3)	
dmp (**3**)	Ag(1)	2.69(4)		0.019(3)	−92.4(2), 92.3(2)	56.1(2)	−73.9(2), 176.1(2)	10.4(3), 86.6(3)	1.32(3)
	Ag(2)			0.322(3)	144.9(2), −34.7(2)	−54.8(2)	76.2(2), −176.9(2)	21.5(3), 79.0(2)	
dpa (**5**)	Ag(1)		17.1(4)	0.77(2), 0.05(2)	−106.8(4), 73.2(5)	65.2(2)	−66.6(4), −175.1(3)	6.8(10), 63.3(8)	117.68(9)
	Ag(2)		16.6(4)	0.80(1), 0.07(2)	−107.5(5), 76.3(5)	65.2(2)	−66.1(4), −177.3(4)	4.4(1), 64.3(9)	114.2(1)
	Ag(3)		22.2(4)	0.68(2), 0.35(2)	107.1(5), −79.4(5)	−63.1(2)	172.9(4), 63.9(4)	3.0(9), −21.2(9)	−114.06(9)
tpy (**6**)	Ag(1)	4.3(2)[a]	26.3(2)(p/p″), 4.1(2), 30.4(2)(p/c)	0.140(7), 1.599(7), 0.023(7)(c)	45.7(2), −178.4(5), −159.6(1)	52.5(2)	−84.0(2), 167.9(2)	−16.8(4), −56.4(3)	−5.75(3)
	Ag(2)		6.8(3), 3.6(3), 7.9(3)	0.35(1), 0.22(1), 0.20(1)	−91.7(2), −94(2), 91.9(2)	−56.1(2)	69.4(1), 175.4(2)	−19.4(4), −82.9(4)	
(NO_3/)dppm/bpy (**25**)	Ag(1)	20.04(8)[a]	2.8(1)	0.053(5), 0.072(5)	117.0(2), −64.3(2)	−63.6(2)	64.66(2), 173.1(2)	−18.3(3), −80.0(3)	−110.41(3)
	Ag(2)		12.6(2)	0.382(6), 0.212(7)	106.2(2), −85.9(2)	−59.9(2)	59.2(5)/73.1(5), 177.4(2)	0.5(11)/2.5(8), 33.7(3)	
dmp (**26**)	Ag(1)	1.03(4)		0.084(3)	48.0(2), −89.1(1)	−48.3(2)	79.2(2), −172.3(2)	17.8(3), 65.0(3)	10.31(3)
	Ag(2)			0.165(3)	−164.6(2), 39.7(2)	56.3(2)	−78.2(2), 175.3(2)	−9.4, −62.4(3)	
bq (**27**)	Ag(1)	3.80(9)[a]	4.42(9)	0.099(5), 0.244(5)	−165.4(2), 20.5(2)	61.5(2)	−70.3(2), −177.0(2)	10.6(4), −83.9(3)	15.18(3)
	Ag(2)		1.08(7)	0.382(5), 0.467(4)	66.5(2), −112.0(2)	−45.7(2)	82.9(2), −168.8(2)	15.6(3), 77.8(3)	
(ClO_4/)dpam/phen (**7**)	Ag(1)	8.3(2)		0.014(7)	97.0(4), −91.6(4)	−43.1(5)	82.7(5), −169.3(5)	−29.0(9), −33.1(9)	0.85(4)
	Ag(2)			0.061(7)	−144.3(4), 54.8(6)	46.8(5)	−78.9(5), 172.4(5)	−20.7(9), 87.7(9)	
dmp (**8**)	Ag(1)	3.06(6)		0.020(4)	−90.9(2), 92.3(2)	55.8(2)	−76.1(2), 176.9(2)	5.7(4), 82.7(4)	1.54(2)
	Ag(2)			0.269(4)	144.2(2), −29.8(2)	−53.4(2)	77.8(2), −176.4(2)	22.2(4), 77.9(4)	
tpy (**9**)	Ag(1)	6.8(1)[a]	20.5(1)(p/p), 6.0(1), 26.4(1)(p/c)	0.162(4), 1.318(4), 0.073(4)	41.7(1), −137(1), −157.1(1)	47.8(2)	−90.8(1), 164.4(1)	−12.6(3), −55.7(2)	−7.34(1)
	Ag(2)		6.8(2)(p/p), 5.4(2), 6.0(2)(p/c)	0.309(7), 0.199(7), 0.111(6)	−93.1(1), −171(1), 89.6(1)	−52.4(1)	69.6(2), 174.1(1)	−22.9(3), −73.5(3)	
(NO_3/)dpam/dmp (**28**)	Ag(1)	0.28(4)		0.089(3)	63.8(2), 82.6(1)	−51.1(2)	83.6(2), −172.4(1)	−3.4(3), 59.8(2)	6.80(1)
	Ag(2)			0.042(3)	−157.7(1), 41.6(1)	54.7(1)	−79.3(2), 175.7(1)	−31.8(3), −68.7(2)	

[a] The angle between the planes of the ‘inner’/overlapping py rings of the bpy or bq or the central rings of the tpy is given.

Table 3
Geometrical descriptors of dpex (≠dpem) complexes: **10**–**24**, **29**, **30**

X,S/dpex/L	Ag	Ag/X,S (Å)	Ag–E (Å)	Ag–N (Å)	X,S–Ag–E (°)	X,S–Ag–N (°)	E–Ag–N (°)	N–Ag–N (°)	Σ (°)
Adducts of 2:1:2 stoichiometry: binuclear [(X/S)LAg(dpex)AgL(X/S)]$^{n+}$ arrays									
O$_3$Cl*O*/dppe/bpy (**10**)	Ag(1)	2.539(2)	2.3675(3)	2.317(1), 2.340(1)	108.78(4)	98.64(5), 108.38(5)	129.93(3), 132.39(4)	71.20(4)	333.4$_2$
MeCN/dppe/dmp(ClO$_4$) (**11**)	Ag(1)	3.164(2)	2.3432(4)	2.301(1), 2.270(1)	99.00(4)	86.12(5), 70.02(5)	134.14(3), 150.61(3)	70.02(5)	354.7$_7$
O$_3$Cl*O*/dppe/bq (**12**)	Ag(1)	2.758(4)	2.3594(5)	2.304(3), 2.305(2)	105.30(6)	85.1(1), 108.62(9)	139.67(6), 135.72(7)	71.59(9)	346.9$_8$
MeC*N*/dppe/dpa(ClO$_4$) (**13**)	Ag(1)	3.020(4)	2.3337(6)	2.279(2), 2.265(2)	82.46(8)	95.81(9), 79.4(1)	136.22(7), 138.65(5)	82.67(8)	357.5$_4$
/dppe/tpy(ClO$_4$) (**14**)	Ag(1)		2.4055(5)	2.464(1), 2.443(1)(p), 2.405(1)(c)			109.74(4), 106.89(4)(p), 141.56(3)(c)	67.48(5), 68.00(5), 135.35(5)	352.1$_1$
O$_3$Cl*O*/dpae/bpy (**15**)	Ag(1)	2.683(2)	2.4676(2)	2.316(2), 2.340(1)	119.33(4)	92.16(6), 89.30(6)	135.50(4), 133.28(4)	71.70(6)	340.4$_8$
/dpae/dmp(ClO$_4$) (**16**)	Ag(1)		2.4348(6)	2.254(4), 2.337(6)			156.8(1), 128.5(1)	73.9(2)	359.$_2$
	Ag(2)		2.4386(8)	2.306(7), 2.251(5)			140.7(1), 145.4(2)	73.7(2)	359.$_8$
O$_3$Cl*O*/dpae/bq (**17**)	Ag(1)	2.818(2), 2.980(3)	2.4487(2)	2.294(2), 2.290(1)	99.16(3), 109.29(4)	86.31(6), 113.09(5), 104.69(6), 77.91(6)	138.13(4), 138.35(5)	72.08(6)	348.5$_6$
O$_3$Cl*O*/dpdae/bq (**18**)	Ag(1)	2.787(2)	2.4006(2)	2.298(1), 2.301(1)	102.26(3)	86.01(5), 111.03(4)	139.12(3), 136.69(3)	71.75(5)	347.5$_6$
O$_2$N*O*/dppp/dmp (**29**)	Ag(1)	2.605(9)	2.346(1)	2.292(4), 2.308(4)	106.8(2)	80.2(2), 90.0(2)	143.9(1), 140.2(1)	73.3(1)	357.$_4$
	Ag(2)	2.878(4)	2.354(1)	2.294(3), 2.310(4)	94.91(9)	81.8(1), 100.9(1)	142.0(1), 143.53(8)	73.3(1)	358.$_8$
/dppp/bq(ClO$_4$) (**19**)	Ag(1)		2.3442(6)	2.277(2), 2.288(2)			147.48(4), 138.90(4)	72.99(6)	359.3$_7$
	Ag(2)		2.3638(6)	2.287(2), 2.320(1)			149.09(4), 138.90(4)	71.99(5)	359.9$_8$
/dppp/tpy (ClO$_4$) (**21**) (Note: ‘S’ is the π-tpy N approach)	Ag(1)	2.391(2)	2.3840(5)	2.466(2), 2.505(2), 2.401(2)(c)	124.47(5)	92.09(6), 94.84(6), 115.63(6)(c)	113.32(4), 100.71(4), 119.57(4)(c)	67.76(6), 67.05(6), 132.63(6)(p/p″)	373.8$_8$
	Ag(2)	2.989(2)	2.3531(5)	2.333(2), 3.168(2), 2.295(2)(c)	122.05(4)	80.98(6), 71.64(5), 81.01(5)(c)	131.11(5), 99.55(3), 146.34(4)(c)	72.10(6), 62.24(5), 129.31(5)(p/p″)	365.0$_0$
/dppb/bpy(ClO$_4$) (**22**)	Ag(1)		2.3372(6)	2.262(2), 2.306(2)			146.45(5), 139.18(5)	72.68(7)	358.3$_1$
	Ag(2)		2.3441(6)	2.276(2), 2.313(2)			144.38(5), 140.35(4)	72.51(6)	357.2$_4$
O$_3$Cl*O*/dppb/bq (**23**)	Ag(1)	3.043(2)	2.3687(6)	2.278(2), 2.344(2)	83.01(6)	95.31(7), 126.15(7)	150.10(5), 132.51(5)	71.67(6)	354.2$_8$
O$_3$Cl*O*/dppb/dpa (**20**)	Ag(1)	2.930(7)	2.346(1)	2.263(4), 2.297(3)	106.5(1)	74.6(2), 99.9(2)	141.10(8), 134.5(2)	81.3(2)	356.$_9$
O$_3$Cl*O*/dppb/tpy (**24**)	Ag(1)	2.587(1)	2.3875(4)	2.469(1), 2.488(2), 2.369(1)(c)	111.43(4)	100.49(6), 77.36(6), 110.88(5)	111.64(4), 115.11(5), 136.97(3)	67.49(5), 67.51(5), 130.37(6)	361.6$_6$
O$_2$N*O*/dppb/tpy (**30**)	Ag(1)	2.416(1)	2.3736(5)	2.401(1), 2.598(1), 2.438(1)	136.58(3)	78.44(5), 91.05(4), 96.55(5)	129.67(3), 91.05(4), 123.11(4)	67.97(4), 64.51(4), 129.61(5)	353.$_2$

Table 4
Conformational descriptors of dpex (≠dpem) adducts: **10**–**24**, **29**, **30**

X,S/dpex/L	Ag	(py/py; bq/bq)[†] (°)	δAg (Å)	C–E–Ag–N (°)	C–C–E–Ag (°)	C–C–E–C(11,21) (°)	E,C–C–C–E (°)
Adducts of 2:1:2 stoichiometry: binuclear [(X/S)LAg(dpex)AgL(X/S)]$^{n+}$ arrays							
O_3ClO/dppe/bpy (**10**)	Ag(1)	2.25(6)	0.531(3), 0.657(2)	−122.85(7), 136.00(6)	64.45(8)	−59.77(9), −170.74(7)	180(−)
MeC*N*/dppe/dmp (ClO_4) (**11**)	Ag(1)		0.301(2), 0.376(2)	31.42(5), −126.87(7)	50.1(1)	−74.3(1), 176.6(1)	180(−)
O_3ClO/dppe/bq (**12**)	Ag(1)	4.85(1)	0.359(4), 0.118(4)	81.3(2), −158.3(2)	−52.4(2)	71.7(2), −178.9(2)	180(−)
MeCN/dppe/dpa (ClO_4) (**13**)	Ag(1)	5.18(9)	0.654(4), 0.596(4)	−34.3(1), 120.7(1)	61.5(2)	−67.4(2), −175.2(2)	180(−)
/dppe/tpy (ClO_4) (**14**)	Ag(1)	14.94(6), 12.51(6), 11.61(6)(p/p″)	0.366(9), 0.294(3), 0.420(3)	−77.91(6), 76.10(6), 0.42(8)	56.6(1)	−68.9(1), −177.3(1)	180(−)
O_3ClO/dpae/bpy (**15**)	Ag(1)	9.46(6) (3.1(1))	0.062(4), 0.471(3)	−111.8(1), 138.2(1)	65.6(2)	−58.9(2), −167.4(1)	180(−)
/dpae/dmp (ClO_4) (**16**)	Ag(1)		0.043(4)	−7.4(4), 154.8(3)	35.0(4)	154.9(3), −97.6(4)	167.1(2)
	Ag(2)		0.051(6)	166.2(3), −20.1(3)	173.7(3)	48.1(4), −58.8(4)	
O_3ClO/dpae/bq (**17**)	Ag(1)	5.88(5)	0.315(3), 0.064(3)	76.9(1), −159.0(1)	−49.3(2)	76.5(2), −176.7(1)	180(−)
O_3ClO/dpdae/bq (**18**)	Ag(1)	5.39(4)	0.329(2), 0.088(2)	79.80(9), −158.35(8)	−50.4(1)	74.8(1), −177.1(1)	180(−)
O_2NO/dppp/dmp (**29**)	Ag(1)	(67.67(7))	0.004(4)	29.8(2), −177.9(2)	−77.1(3)	51.7(3), 159.7(3)	175.5(3)
	Ag(2)		0.195(3)	−112.8(2), 86.0(2)	−51.0(3)	76.5(3), −174.7(3)	170.4(3)
/dppp/bq (ClO_4) (**19**)	Ag(1)	5.90(5) (1.57(4))	0.028(2), 0.258(2)	−1.5(1), −167.5(1)	62.0(2)	−61.7(2), −171.2(1)	−176.4(1)
	Ag(2)	5.58(5)	0.158(2), 0.069(3)	72.1(1), −110.0(1)	−67.5(1)	57.9(2), 168.1(1)	176.4(2)
/dppb/bpy/(ClO_4) (**22**)	Ag(1)	16.2(1) (13.4(1))	0.566(4), 0.285(5)	152.3(1), −50.5(1)	43.5(2)	−74.4(2), 176.0(2)	178.3(2)[a]
	Ag(2)	16.9(1)	0.764(4), 0.114(4)	−157.9(1), 51.0(1)	−44.0(2)	75.6(2), −175.5(2)	−173.1(2)
/dppp/tpy (ClO_4) (**21**)	Ag(1)	3.82(7), 2.16(8), 2.79(8)(p/p″)	0.422(3), 0.589(4), 0.610(3)(c)	64.42(8), −149.26(8), 141.17(8)(c)	−58.7(2)	71.6(2), 179.4(1)	−174.6(1)
	Ag(2)	7.25(9), 46.80(8), 51.26(9)(p/p″)	0.66(4), 1.353(3), 0.325(3)(c)	46.5(1), 171.6(1), −135.2(1)	−55.7(2)	65.4(2), 174.9(1)	−167.2(1)
O_3ClO/dppb/bq (**23**)	Ag(1)	1.56(1)	0.173(3), 0.147(3)	−63.6(1), 158.9(1)	51.1(2)	−72.8(2), 177.6(2)	177.1(1)[a]
O_3ClO/dppb/dpa (**20**)	Ag(1)	3.6(3)	0.41(1), 0.65(1)	−112.8(2), 95.8(2)	64.3(2)	−64.5(3), −175.2(2)	−168.7(2)[a]
O_3ClO/dppb/tpy (**24**)	Ag(1)	6.33(7), 20.29(7), 23.50(7)(p/p″)	0.940(3), 0.384(3), 0.613(3)	126.06(8), −71.06(7), −154.34(7)(c)	45.3(1)	−77.0(1), 176.0(1)	−177.8(1)[a]
O_2NO/dppb/tpy (**30**)	Ag(1)	19.41(6), 4.25(6), 19.08(6)(p/p″)	0.319(3), 0.896(3), 0.652(3)(c)	111.54(7), −36.00(6), 23.88(6)(c)	−54.0(1)	72.6(1), 180.0(1)	169.7(1)[a]

[a] C–C–C–C is 178.2(2)° for **22** and (obligate) 180° for **20**, **23**, **24**, **30**.

[†] intraligand values; interligand values in parentheses.

crystallographic symmetry, sometimes inclusive of solvent, comprises the asymmetric unit of the structure (exception: $AgClO_4$:dppm:bpy (2:1:2) (**1**) where two formula units are required).

The alternative form found (among the other possibilities) is '*trans*', where the two silver atoms lie in the opposite sides of the (now) CECEC plane, a situation of potentially 2-symmetry, realized in the $AgClO_4$:dppm:dpa (2:1:2) adduct (**5**), where each of the three independent cations lies with the central carbon disposed on a crystallographic 2-axis. The $AgNO_3$:dppm:bpy (2:1:2) analogue (**25**), although of this disposition, has one independent formula unit in the asymmetric unit of the cell. In both forms, exchange of P for As in the dpem ligand has little effect on associated Ag–N distances, despite the substantial increases in Ag–E. Ag–N(tpy) are rather more irregular than in the other complexes, with no necessary equivalence between the outer (peripheral = 'p') distances for any one ligand, although Ag–N (central = 'c') is always the shortest of the three, sometimes only by a very small margin.

Although they are not isomorphous, the two dmp/NO_3 adducts $AgNO_3$:dppm, dpam:dmp (2:1:2) (**26**, **28**) are intriguing in that a significant, albeit long interaction, with one of the silver atoms with an anion, in each case a unidentate nitrate, is found, so that the binuclear component may be considered an ion pair: $[(O_2NO)(dpm)Ag(dpem)Ag(dpm)]^+$.

3.3.2. The $AgClO_4$:dpee:L (2:1:2) complexes (**10–18**) (·nS)

Expansion of the polymethylene chain from one to two units between the pair of E atoms of the now dpee ligands is accompanied by transformation of the [LAg(dpex)AgL] array from the tightly constrained *cis* array predominant in the dpem complexes, to a form with a more flexible $E(CH_2)_2E$ string and a less favourable arrangement for the close intermolecular approach of parallel aromatic L planes. The predominant form of [LAg(dpee)AgL] observed is one in which one half of a centrosymmetric entity comprises the asymmetric unit of the structure, the centre of symmetry lying at the mid point of the dpee ligand, the central C–C bond of which exhibits a torsion necessarily 180°; the pair of L ligands are well-removed from each other, their planes stacking parallel to those of other inversion related molecules. Such is the situation with $AgClO_4$:dppe:bpy, bq, dpa, dmp, tpy (**10–14**); $AgClO_4$:dpae:bpy, bq, (**15**, **17**), and the adduct of the mixed P/As dpdae ligand $Ph_2P(CH_2)_2AsPh_2$ in which, as usual, the E sites are modelled as scrambled in $AgClO_4$:dpdae:dmp (2:1:2), (**18**). In all of these except the tpy adduct, in which the coordination number of the silver is elevated by the tridentate ligand, the Ag coordination environment is augmented by approaches of perchlorate anions, uni- or semi-bidentate (Figs. 4 and 5; Table 3) or acetonitrile (the latter accompanied in one case by a very distant water molecule oxygen (dppe/dpa) ($\mathbf{13} \cdot 2MeCN \cdot H_2O$)), these approaches concomitant with perturbations of the $EAgN_2(L)$ array from planarity broadly consistent with the closeness of the interaction (Table 3). The only representative in which the full cation is devoid of symmetry, comprising with the anion the asymmetric unit, is $AgClO_4$:dpae:dmp $(2:1:2) \cdot H_2O$, (**16**), in which, despite a *trans* conformation of the central bond of the ligand, one of the C–C–As–Ag strings is also, unusually, *trans*, so that the disposition of the two dmp ligands is *cis*-oid. The dmp ligand planes are essentially parallel (interplanar dihedral angle 3.1(1)°), with their methyl substituents confronting, but beyond the van der Waals' distance; despite the As (rather than P) E donors, there are no close anion approaches to the silver atoms.

The trends described for $AgClO_4$:dppe:L (2:1:2) are carried over into the more limited range of *3.3.3*.

3.3.3. The AgX:dppb:L (2:1:2) complexes (**22–24**) (·nS)

Here again centrosymmetric forms predominate, being found in $AgClO_4$:dppb:bq, tpy (·S) (**23**, **24**) and $AgNO_3$:dppb:tpy (2:1:2) (**30**). In all of these '*trans*' binuclear arrays, inclusive of the tpy adducts, the silver atoms are approached by anion oxygen atoms; a *trans*-oid array, devoid of crystallographic symmetry and any close anion or solvent approach, is also found in $AgClO_4$:dppb:bpy $(2:1:2) \cdot 2MeCN$ (**22**). More subtle are the forms found in

3.3.4. The AgX:dppp:L (2:1:2) complexes (**19–21**) (·nS)

Here with the inability of the ligand to adopt any (quasi-) centrosymmetric conformation (as is also the case with dpem), a diversity of forms is found (Fig. 6; Table 3). Both $AgClO_4$:dppp:dpa, bq (2:1:2) (**19**, **20**) are *cis*-oid with one formula unit in the asymmetric unit of each structure, whereas in the bq adduct the two silver atoms lie on the one side of the CPCCCPC ligand spine 'plane', in such a way that the extended quinolyls oriented oblique to the spine can overlap intramolecularly, the dpa adduct has the silver atoms disposed to either side and no intramolecular ligand overlap is found. Close anion-silver approaches are only found in the latter, presumably precluded by overlaps, both intra- and inter-molecular, in the former.

The bridging role of tpy noted above is manifest in the final (2:1:2) example, unique of its type, in $(AgClO_4$:dppp:tpy$)\ (2:1:2)_{(\infty|\infty)}$, **21**, in which, unlike the pair of (2:1:2) NO_3/dpem adducts described above, in which the tpy bridge a pair of silver atoms in intradimer mode, successive Ag(*P*-dppp-*P*)Ag units are linked by pairs of bridging tpy (Fig. 3; Table 3). Of further interest is the fact that, rather than the central pyridyl of the tpy bridging in 'crevice' $\eta^2(\pi)$-mode, one of the peripheral pyridyl nitrogens bridges in $\eta^2(\sigma,\pi)$ mode, pairs of silver atoms being linked by pairs of such interactions: $[\ldots Ag(P\text{-dppp-}P)Ag((\mu\text{-}N'')\text{-tpy})_2\ldots]_{(\infty|\infty)}$ to form a single stranded polymer (the propagator of which is the *a* translation), the silver atoms lying *cis*-oid about the dppp string. In the AgN_2Ag ring Ag…Ag are 4.1199(2), N…N 3.606(3), Ag–N (bridging) 2.505(2), 3.168(2) (σ); 2.391(2), 2.989(2) Å.

4. Supplementary data

Full .cif depositions, excluding structure factor amplitudes, reside with the Cambridge Crystallographic Data Centre, CCDC 295744–295772.

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