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Ring, polymer and network structures in silver(I) complexes with dipyridyl and diphosphine ligands

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Interesting molecular architectures are obtained by self-assembly from silver(I) trifluoroacetate with a combination of the diphosphine ligands [$Ph_2P(CH_2)_nPPh_2$, $n = 1$–6] and *trans*-1,2-bis(4-pyridyl)ethylene (bipyen); in complexes with stoichiometry $Ag_2(O_2CCF_3)_2\{Ph_2P(CH_2)_nPPh_2\}$(bipyen), the complexes crystallize in the form of macrocyclic rings [$Ag_4(O_2CCF_3)_4\{\mu$-$Ph_2P(CH_2)_nPPh_2\}_2(\mu$-bipyen$)_2$] when n = 1 or 5, but as a one-dimensional polymer [$\{Ag_2(O_2CCF_3)_2\{\mu$-$Ph_2P(CH_2)_nPPh_2\}(\mu$-bipyen$)\}_x$] when n = 6. The complex [$\{Ag\{\mu$-$Ph_2P(CH_2)_3PPh_2\}(\mu$-bipyen$)\}_x](CF_3CO_2)_x$ has a novel network structure.

There is intense current interest in polymeric coordination networks,[1] but there are surprisingly few examples containing silver(I) or phosphine ligands, and very few architectures with mixed bridging ligands.[2,3] Given the interesting electronic,[4] medicinal,[5] and structural[4–6] properties of silver(I) phosphine complexes, the synthesis of polymeric diphosphine bridged silver(I) complexes was attempted. The strategy was to form mixed ligand complexes, using the rigid linear dipyridyl ligand *trans*-1,2-bis(4-pyridyl)ethylene (bipyen) in conjunction with the more flexible diphosphine ligands $Ph_2P(CH_2)_nPPh_2$, since the diphosphines alone tend to give chelate complexes or other ring structures with silver(I).[4–6] This article shows that linear and network polymers, as well as ring complexes, can be formed by this strategy and that the variable coordination number of silver(I) is a key feature in allowing formation of a particularly interesting series of compounds.[7]

The new silver(I) complexes were prepared by reaction of silver(I) trifluoroacetate with the appropriate ligand $Ph_2P(CH_2)_nPPh_2$ (n = 1–6) followed by reaction with *trans*-1,2-bis(4-pyridyl)ethylene (bipyen).† Studies of the reaction solutions by ^1H or ^{31}P NMR spectroscopy indicated that mixtures of products were formed but, in favourable cases, it was possible to crystallize pure products for structure determination and these are representative of major components of the equilibrium system.‡

Three complexes were crystallized having the formula $Ag_2(O_2CCF_3)_2\{Ph_2P(CH_2)_nPPh_2\}$(bipyen) of which two formed macrocyclic ring structures (**1**, n = 1; **2**, n = 5) and one formed a one-dimensional polymer (**3**, n = 6). The structures are shown in Figs. 1 and 2. In the 30-membered ring complex **1** two of the trifluoroacetate ions bridge silver atoms in the ring while two are not coordinated, so the complex is formulated as $[Ag_4(\mu$-$O_2CCF_3)_2(\mu$-$Ph_2PCH_2PPh_2)_2(\mu$-bipyen$)_2]^{2+}$, with each silver(I) ion having distorted trigonal planar stereochemistry. There is a short intramolecular silver–silver distance Ag(1)–Ag(2) 3.0479(8) Å, which is about equal to the distance P(1)–P(2) 3.051(2) Å but significantly shorter than N(11)–N(21) 3.507(4) Å, so indicating the presence of a secondary Ag···Ag bond.[4,8] In the related 38-membered ring structure **2**, all trifluoroacetate ions are close enough to silver(I) to influence the stereochemistry so **2** is formulated as $[Ag_4(\mu$-$O_2CCF_3)_4\{\mu$-$Ph_2P(CH_2)_5PPh_2\}_2(\mu$-bipyen$)_2]$. The longer Ag···O bonds are shown in Fig. 1 as broken lines; if all are considered bonds, then each silver(I) ion is four-coordinate. The transannular distance Ag(1)–Ag(4) 3.936(1) Å is too long for a bonding interaction

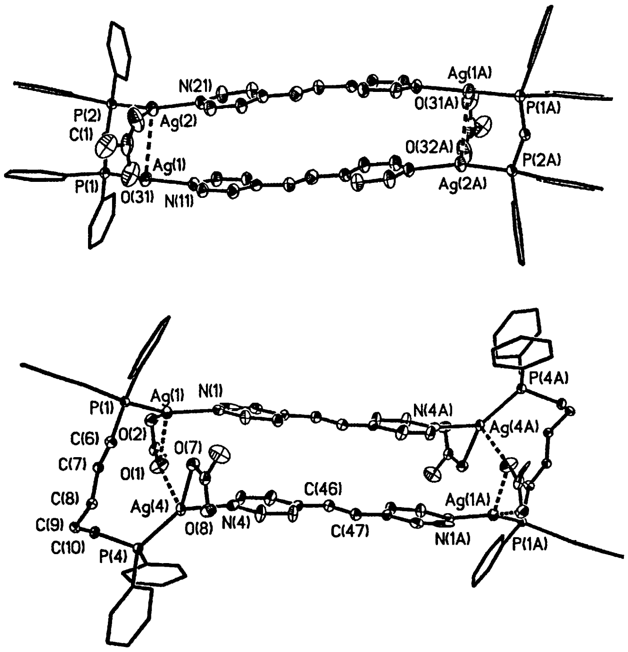

Fig. 1 Views of the structures of the macrocyclic ring complexes **1** (above) and **2** (below). Thermal ellipsoids for phenyl carbon atoms, and fluorine atoms of the trifluoroacetate groups, are not shown for clarity. Selected geometrical parameters (Å, °) for **1**: Ag(1)–P(1) 2.360(1), Ag(2)–P(2) 2.366(1), Ag(1)–N(11) 2.199(4), Ag(2)–N(21) 2.217(5), Ag(1)–O(31) 2.506(7), Ag(2)–O(32) 2.496(7); N(11)–Ag(1)–P(1) 157.5(1), N(21)–Ag(2)–P(2) 155.3(1). For **2**: Ag(1)–P(1) 2.348(3), Ag(4)–P(4) 2.363(3), Ag(1)–N(1) 2.20(1), Ag(4)–N(4) 2.23(1), Ag(1)–O(1) 2.63(1), Ag(1)–O(2) 2.63(1), Ag(4)–O(7) 2.379(9), Ag(4)–O(1) 2.63(1); N(1)–Ag(1)–P(1) 149.5(3), N(4)–Ag(4)–P(4) 130.1(3).

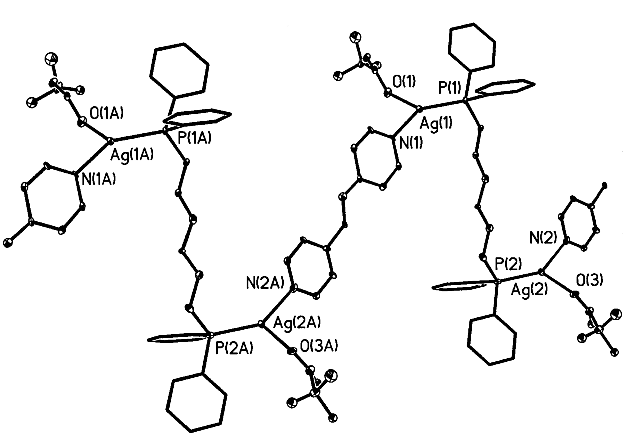

Fig. 2 A view of the structure of the polymeric complex **3**. Thermal ellipsoids for phenyl carbon atoms are not shown for clarity. Selected geometrical parameters (Å, °): Ag(1)–P(1) 2.377(6), Ag(2)–P(2) 2.367(7), Ag(1)–N(1) 2.18(2), Ag(2)–N(2) 2.31(3), Ag(1)–O(1) 2.38(2), Ag(2)–O(3) 2.46(2); N(1)–Ag(1)–P(1) 143.5(6), N(2)–Ag(2)–P(2) 143.4(6).

and the conformation may be controlled by the weakly bridging trifluoroacetate ligand and by π-stacking of the bipyen groups (the transannular distance between centroids of pyridyl rings in **2** is 3.86 Å).

Part of the polymeric chain structure of complex **3** is shown in Fig. 2. All trifluoroacetate ions are coordinated so the complex is formulated as $[Ag_2(O_2CCF_3)_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(\mu\text{-bipyen})]_x$. The change in structure is attributed to the preference for the *syn* or *anti* conformation of the phosphorus donors when there is an odd or even number of methylene bridges in $Ph_2P(CH_2)_nPPh_2$,[7] leading naturally to ring structures **1** and **2**, when n = 1 and 5, but a polymer **3** when n = 6. This conformational change is clear from a comparison of Fig. 1 and 2. The polymer could be considered to be formed by ring-opening polymerization of the corresponding ring complex.

With higher ligand:silver ratios, more complex product mixtures were formed and only in one case (n = 3) was a pure complex crystallized. The complex **4** is formulated as $[\{Ag\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(\mu\text{-bipyen})\}_x]^{x+}$, isolated as the trifluoroacetate salt, and its network structure is shown in Fig. 3, illustrating the presence of channels that are occupied by the anions and by solvent molecules. Each silver(I) ion is roughly tetrahedral with AgP_2N_2 coordination, and all silver centres are identical, but the overall structure is more complex. One view would be to consider the structure as spiral chains $[\{Ag(\mu\text{-dppp})\}_x]^{x+}$ [dppp = $Ph_2P(CH_2)_3PPh_2$], running roughly perpendicular to the plane in Fig. 3 crosslinked by μ-bipyen ligands. The smallest rings incorporated into these units are 46-membered $\{\text{–}Ag(\mu\text{-dppp})Ag(\mu\text{-dppp})Ag(\mu\text{-bipyen})\}_2$. Another view is to consider the structure to be formed from crossing zigzag polymers $[\{Ag(\mu\text{-bipyen})\}_x]^{x+}$ crosslinked by μ-dppp ligands. The conformation of the diphosphine is neither *syn* nor *anti* but intermediate such that the diphosphine links chains that are roughly orthogonal. The smallest ring structure is 56-membered $\{\text{–}Ag(\mu\text{-bipyen})Ag(\mu\text{-bipyen})Ag(\mu\text{-dppp})\}_2$ and they lie roughly in the plane of Fig. 3.

This work shows that combination of flexible diphosphine and linear dipyridyl ligands with silver(I) can give interesting new molecular architectures that are significantly different from those obtained with only nitrogen-donor ligands,[1,2] and that factors such as the preferred conformation of the diphosphine ligand[7] and the variable coordination number of silver(I)[1–6] can determine the preferred structure. There is clear potential for design of still more complex molecular topologies by application of these principles.

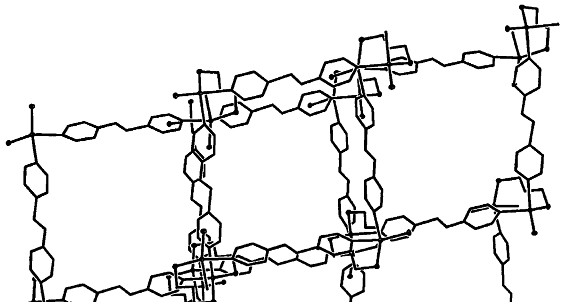

Fig. 3 A view of the structure of the network polymeric complex **4**. Phenyl carbon atoms are not shown for clarity. Selected geometrical parameters (Å, °): Ag–P(1) 2.444(3), Ag–P(2) 2.448(3), Ag–N(1) 2.425(8), Ag–N(2) 2.370(7); N(1)–Ag–N(2) 90.4(2), P(1)–Ag–P(2) 123.36(5), N(1)–Ag–P(1) 121.6(2), N(1)–Ag–P(2) 98.4(2), N(2)–Ag–P(1) 98.0(2), N(2)–Ag–P(2) 121.9(2).

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Notes and references

† *Typical synthetic procedure*: $[Ag_4(\mu\text{-}O_2CCF_3)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)_2](CF_3CO_2)_2$, **1**: bis(diphenylphosphino)methane (0.107 g, 0.278 mmol) was added to a solution of CF_3CO_2Ag (0.123 g, 0.556 mmol) in THF (15 mL) and after 1 h *trans*-1,2-bis(4-pyridyl)ethylene (0.051 g, 0.279 mmol) was added. After 1.5 h, the volume was reduced until the product formed as a white precipitate, which was collected by filtration, washed with diethyl ether and pentane and dried *in vacuo*. Yield: 0.17 g (60%). Anal. Calc. for $C_{41}H_{32}N_2O_4F_6P_2Ag_2$: C, 48.84; H, 3.20, N, 2.78. Found: C, 49.26; H, 3.03, N, 2.82%.

‡ *Crystal data*: for **1**·2THF: $C_{87}H_{69}Ag_4F_{12}N_4O_9P_4$, M = 2097.82, 296 K, triclinic, space group $P\bar{1}$, a = 10.4879(2), b = 15.2385(5), c = 19.7575(5) Å, α = 99.008(1), β = 95.106(2), γ = 96.283(2)°, V = 3081.8(1) Å^3, Z = 1, μ = 0.737 mm^{-1}, 21543 reflections, $R1$ = 0.0836, $wR2$ = 0.2891.

For **2**: $C_{90}H_{80}Ag_4F_{12}N_4O_8P_4$, M = 2128.94, 200 K, triclinic, space group $P\bar{1}$, a = 15.079(3), b = 17.850(4), c = 20.232(4) Å, α = 80.72(3), β = 86.72(3), γ = 75.02(3)°, V = 5191(2) Å^3, Z = 2, μ = 0.875 mm^{-1}, 29338 reflections, $R1$ = 0.1168, $wR2$ = 0.3223.

For **3**: $C_{48}H_{50}Ag_2F_6N_2O_6P_2$, M = 1142.58, 150 K, triclinic, space group, $P\bar{1}$, a = 9.747(2), b = 9.588(2), c = 15.104(3) Å, α = 83.85(3), β = 73.80(3), γ = 62.91(3)°, V = 1206.5(4) Å^3, Z = 1, μ = 0.950 mm^{-1}, 4358 reflections, $R1$ = 0.0604, $wR2$ = 0.1410.

For **4**: (CH_2Cl_2, MeOH solvate), $C_{43}H_{43}AgCl_2F_3N_2O_3P_2$, M = 933.50, 150 K, orthorhombic, space group $Fdd2$, a = 31.5201(7), b = 39.636(1), c = 13.9957(4) Å, V = 17485.5(8) Å^3, Z = 16, μ = 0.709 mm^{-1}, 9871 reflections, $R1$ = 0.0699, $wR2$ = 0.1961.

CCDC reference numbers 165406–165409. See http://www.rsc.org/suppdata/cc/b1/b104857k/ for crystallographic data in CIF or other electronic format.

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