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Full Paper

Flexibility in the Self-Assembly of Silver Complexes: Coordination Polymers from Multi-Armed Pyridylmethyleneoxy Ligands

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The syntheses of new silver complexes of five isomeric bis(pyridylmethyleneoxy)benzenes, differing in the position of substitution on the benzene and pyridine rings, and three isomeric 1,3,5-tris(pyridylmethyleneoxy)benzenes, differing in the position of substitution on the pyridine ring, are described. The structures of six of these complexes were characterised using X-ray crystallography, showing the formation of coordination polymers for 3-pyridyl- and 4-pyridyl-armed ligands and discrete complexes for 2-pyridyl-armed ligands. The precise nature of the structure was further determined by the relative orientation of the pyridine rings in each case.

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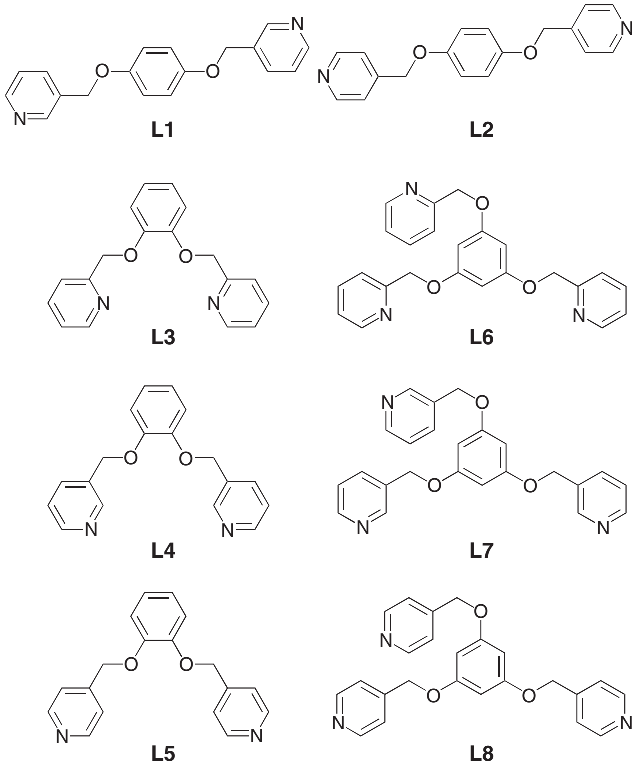
Introduction

The self-assembly of suitably designed organic ligands with metal fragments to construct discrete and polymeric metallosupramolecular assemblies represents a well-developed route to diverse architectures.[1] This approach has been used to form coordination polymers and networks that are magnetically,[2] photochemically[3] or catalytically active,[4] and frameworks that are able to absorb gases and small molecules.[5] Functional sections can be included as part of ligands, from the metal connectors, or arise from the network.[6] However, an understanding of the self-assembly processes is required in order to allow controlled formation of desired architectures. Controlled self-assembly using rigid ligands based on N-heterocyclic and carboxylate ligands with defined geometric bridging potential has proved an excellent method for the formation of polygons, polyhedra, and extended networks.[6a,7] However, for many years we,[8] and others,[9] have investigated ligands that have included a degree of flexibility, and have had success in the formation of architectures that would be unavailable to more rigid ligands.

In particular, we have concentrated on synthesising ligands with pyridine groups appended to an aromatic core by flexible linkers.[8b,10] This allows the conformational flexibility of the ligand to orient the coordinating groups towards metal atoms in ways that are unavailable to more rigid ligands. Thus, multi-armed ligands of this type have given rise to one-, two-, and three-dimensional metallosupramolecular helicates,[8e,11] cages,[12] and networks.[11,13] In combination with weakly coordinating metals, such as acidic silver cations, which can attain varying coordination number and geometry, the formation of a variety of different structures is possible.[14] The fluid nature of interaction between silver and ligand allows weaker interactions, such as weak hydrogen bonds[15] or interaction with non-coordinating anions,[16] to dominate the formation of the product structures.

In this paper, we report our studies of the silver complexes formed from a range of bis- and tris-armed ligands (**L1**–**L8**), as shown in Scheme 1. These differ in the position and number of coordinating arms of the central benzene ring, and the point of attachment on the pyridyl ring. Previously, several ligands with



Scheme 1.

2-pyridylmethyleneoxy arms attached to benzene rings have demonstrated ability to form macrocycles,[17] and one- and two-dimensional networks in the case of 1,4-disubstituted benzene rings.[18] Three-dimensional networks are formed in the reactions of 1,3,5-trisubstituted benzene rings with both 2-pyridylmethyleneoxy and 3-pyridylmethyleneoxy derivatives.[19]

Results and Discussion

The ligand series for this investigation was drawn from several literature compounds, combined with new ligands synthesised by us. Ligands **L1**,[20] **L2**,[21] **L3**,[22] and **L6**–**L8**[23] were synthesised using literature procedures. The remaining ligands were synthesised using modified literature procedures. Catechol or resorcinol was combined with the appropriate chloromethylpyridine hydrochloride and potassium carbonate in DMF. This mixture was then heated to 110°C overnight, and the product purified by column chromatography and recrystallisation, providing the ligands in low yield (**L4**, 24 %, and **L5**, 22 %). The ligands were characterised by ^{1}H NMR, ^{13}C NMR, HR-ESMS and elemental analysis.

Initially, we decided to investigate the effect changing the substitution of the pyridine rings system would have on the structures formed. Thus, **L1** and **L2**, which correspond to a change in substitution position of the pyridine to 3- and 4-substituted, were reacted with silver nitrate. The complexes **1** and **2** were isolated as crystalline powders from their respective solutions. Analysis of the complexes by NMR showed only the presence of ligand, indicating the complexes formed were not stable in typical NMR solvents, as observed by us in previous investigations.[17] The crystalline solids of **1** and **2** both showed a 1 : 1 metal-to-ligand stoichiometry, but only **1** could be induced to form single crystals, despite numerous attempts. The structure of **1** was determined from crystals grown by the slow evaporation of a solution of **1** in acetonitrile.

The structure of **1**, shown in Fig. 1, was found to be a one-dimensional polymer. The structure contains two independent half molecules, which are arranged around a centre of inversion at the centre of the benzene ring. This orients the coordinating pyridine nitrogens away from one another, while the ether oxygen atoms are non-coordinating. The silver atoms have a slightly distorted linear coordination geometry with an N–Ag–N angle of 176.7(1)°, and Ag–N bond lengths of 2.134(3) and 2.137(3) Å, giving the polymer a zig-zag shape. The silver is also weakly interacting with an adjacent nitrate counterion lying above the polymer (Ag–O 3.061(3) Å), which accounts for the slight distortion from linearity. Owing to the enhanced flexibility of the backbone, the independent pyridine rings are free to rotate, and orient themselves at almost identical angles of 70.4(1)° and 70.2(1)° to the central benzene ring. The pyridine rings are almost coplanar, with their respective mean planes having an angle of 2.3(1)° to one another.

The polymeric chains of **1** propagate perpendicularly to the *a*-unit cell edge, and stack with the silver atoms 5.465(2) Å apart. They are staggered, such that each benzene ring is held by edge-to-face π–π interactions from pyridine rings on either side. These interactions are characterised by the close approach between hydrogen atoms of the benzene rings to the plane of the pyridine ring (2.76(8) and 2.81(8) Å). The solvate water molecules and nitrate counterions occupy the spaces between the polymeric chains, and form a hydrogen-bonded polymer perpendicular to the direction of the coordination polymer. The nitrate ion is involved in hydrogen-bonding interactions with water molecules through different oxygen atoms, with distances of O20A···O13 2.849(4) Å and O20B···O12 2.861(5) Å, and donor-hydrogen-acceptor (DHA) angles of 166(4)° and 174(5)°, respectively.

The reaction of the three *ortho*-substituted ligands **L3**, **L4**, and **L5** with silver nitrate gave complexes **3**, **4**, and **5**. Pleasingly, crystals of all three complexes could be formed, by diffusion of diethyl ether into the reaction mixture in the case of **3**, and into an acetonitrile solution of the complex in the case of complexes **4** and **5**. We expected that ligand **L3** would likely form a tetradentate mononuclear complex with silver, a structural motif that had already been observed for this ligand in an iron(II) complex.[22] The structure of the silver nitrate complex **3** was unusual, in that it contained four discrete ligand–metal units, all with very similar structures. Fig. 2 illustrates both the structures of the units and their similarity by overlaying the four independent ligand–metal units. In each of the units, the silver forms strong bonds to the pyridine nitrogen atoms, with lengths ranging between 2.192(2) and 2.265(2) Å, with N–Ag–N bond angles in the range 156.7(2)–163.3(2)°. However, despite our initial assumptions about the potential for the ligand to be tetradentate, the silver formed only relatively weak interactions with the ligand oxygen atoms, with Ag···O distances between 2.611(2) and 2.679(2) Å. The nitrate counterions occupy spaces between the mononuclear units, with each of the counterions interacting with a silver atom through an oxygen. Three of these interactions are in the range 2.883(2)–2.993(2) Å. The fourth is considerably closer, with an Ag···O distance of 2.678(2) Å, which, in part, destroys any higher-symmetry relationships between the mononuclear units. The oxygen atoms of the nitrate counterions are also involved in C–H···O interactions with the

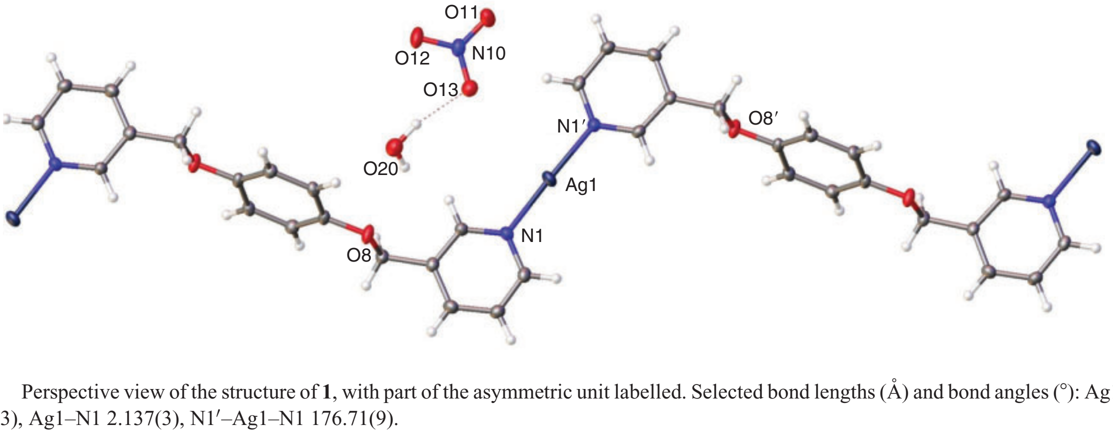


Fig. 1. Perspective view of the structure of **1**, with part of the asymmetric unit labelled. Selected bond lengths (Å) and bond angles (°): Ag1–N1′ 2.134(3), Ag1–N1 2.137(3), N1′–Ag1–N1 176.71(9).

ligand, with H···O distances between 2.405(4) and 2.939(4) Å (see Supplementary Information).

The mononuclear units are planar, with the angle of each pyridine ring mean plane to its attached benzene ring between 4.9(1)° and 17.0(1)°. These units are arranged in layers that stack parallel to the *bc*-face of the unit cell, with the nitrate counterions occupying spaces between molecules in each layer. This arrangement maximises face-to-face π–π interactions involving off-set rings, with distances between planes of 3.4–4.8 Å, and precludes any edge-to-face interactions.

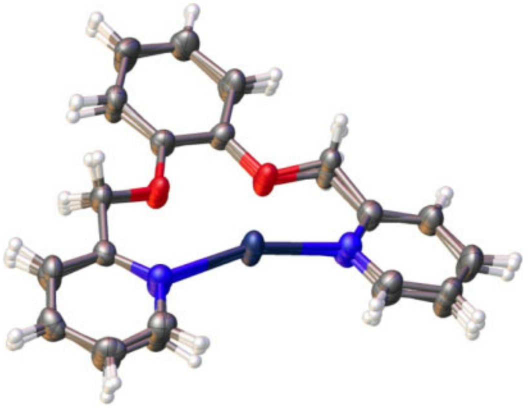


Fig. 2. Perspective view overlaying the four independent ligand–metal units of **3**.

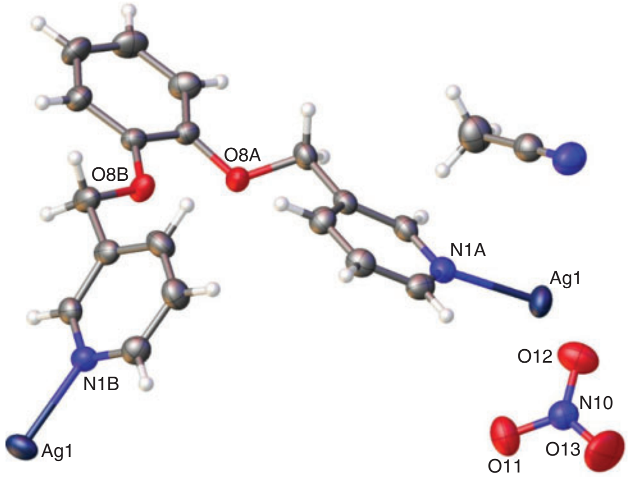


Fig. 3. Perspective view of the structure of **4**, showing the asymmetric unit as part of the polymeric chain. Selected bond lengths (Å) and bond angles (°): Ag1–N1A 2.184(3), Ag1–N1BA 2.188(3), N1A–Ag1–N1BA 171.35(9).

Unlike **L3**, the ligand in **4** was not expected to be planar, as it was less likely to chelate a metal atom, although large chelate rings have been observed for flexible ligands.[24] The silver nitrate complex **4** required recrystallisation from the original sample, which showed an intriguing 2 : 3 ligand-to-metal ratio on analysis, to give crystals suitable for single-crystal structural analysis. The recrystallised complex forms in the monoclinic space group $P2_1/c$, with an asymmetric unit containing one silver nitrate, one molecule of **L4** and one acetonitrile solvate molecule. This 1 : 1 metal–ligand stoichiometry represents a reorganisation of the structure during crystal growth in the donating acetonitrile solvent. The complex has a one-dimensional structure, with the **L4** molecule bridging two silver atoms at a distance of 11.674(2) Å, as shown in Fig. 3. The pyridine rings of the ligand bridge the metal atoms, are significantly twisted away from each other (71.6(2)°), and have quite different angles to the mean plane of the benzene ring (14.6(2)° and 64.0(2)°). The silver atom has a linear geometry, with an angle of 171.35(9)° between the nitrogen atoms, and with Ag–N bond lengths of 2.184(3) and 2.188(3) Å. Combined with the twist of the ligand, which gives an angle between the Ag–N bonds of 108.0(9)°, the polymer has an undulating structure. The silver atom is also weakly interacting with the oxygen atoms of two nitrate counterions, with Ag···O distances of 2.698(3) and 2.709(3) Å. The nitrate counterions bridge two metal atoms, which are 3.263(3) Å apart. Such a close approach implies an interaction between the two metal atoms, being within the van der Waals radius for the atoms. This has the effect of forming a two-dimensional brick-wall structure, with the silver–silver interactions making the silver atoms into T-shaped connectors, with N–Ag···Ag angles of 77.25(7)° and 42.07(7)°, as shown in Fig. 4. The close approach of the interacting silver atoms is also aided by face-to-face π–π interactions between the pairs of coordinated pyridine rings, which are coplanar (9.3(2)°) and slightly offset, so that the closest approach is 3.47(1) Å. The pyridine rings across the centre of the 'bricks', which are related by a centre of inversion, are slightly closer with the mean planes 3.39(1) Å apart. The twisting of the ligand orients the edges of pyridine rings and the central benzene rings towards faces of adjacent aromatic systems, but these are not oriented close

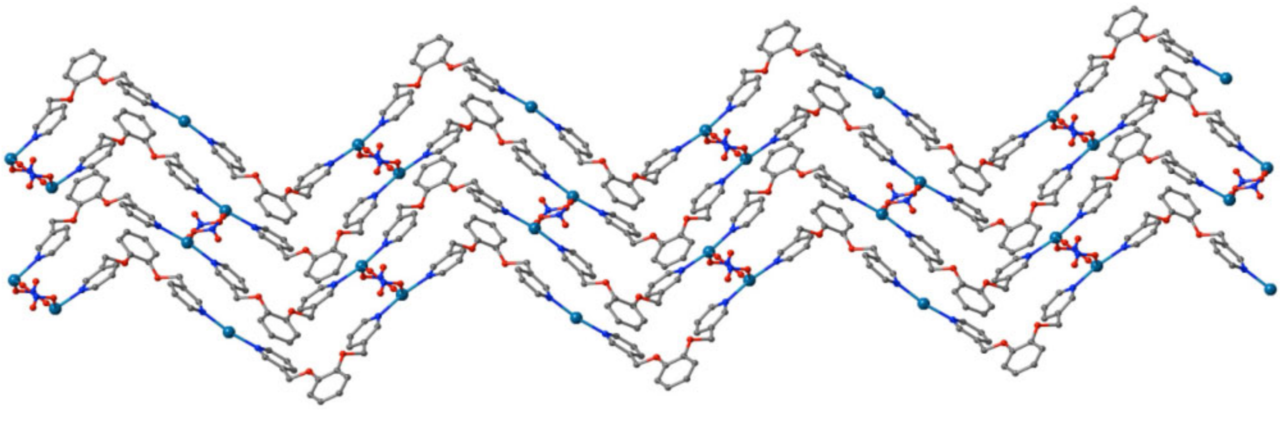


Fig. 4. Perspective view of a section of the two-dimensional brick-wall structure of **4**.

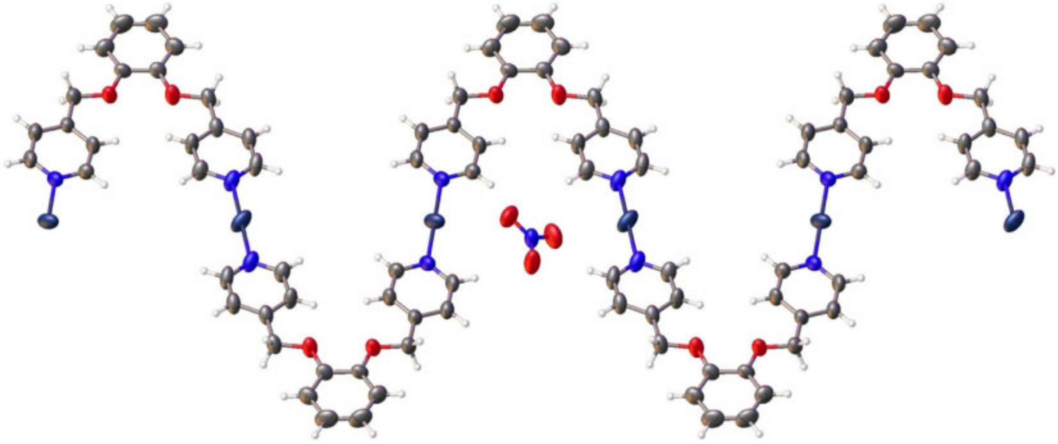


Fig. 5. Perspective view of a section of the polymeric chain of **5**, with the atomic labelling shown. Selected bond length (Å): Ag1–N1 2.151(3).

enough for edge-to-face π–π interactions.[25] The acetonitrile solvate molecules are found between the two-dimensional layers.

The silver nitrate complex **5** also formed a one-dimensional polymeric structure, as shown in Fig. 5. The complex crystallises in the monoclinic space group *C2/c*, with half silver atoms and half-molecules of **L5** occupying a centre of inversion and a two-fold axis (through the centre of the benzene ring), respectively. The ligand is arranged with the pyridine rings oriented in the same direction, bridging strictly linear silver atoms (Ag–N bond length 2.151(3) Å) at an angle of 17.8(2)° (angle subtended by the Ag–N bonds) to give a zig-zag polymer.

The polymer chains of **5** are remarkably planar, with the ligand having a mean deviation of only 0.052(7) Å from the mean plane of all non-hydrogen atoms. The silver atom deviates only slightly from the plane of the pyridine ring (0.011(7) Å). The polymeric chains of **5** are planar, and propagate along the *ac*-diagonal, with the distance between the silver atoms of the chain 7.715(2) Å. The nitrate counterions are found in the plane of the polymer, and are non-coordinating (closest approach O12 3.037(3) Å), occupying the spaces between the silver atoms. The planar chains stack to form a sandwich of layers, with the polymeric chains offset so that the benzene of one chain lies above the silver atom of an adjacent chain. This offset means that the aromatic rings of the chains do not overlap, which is required for any π–π face-to-face interactions.

We next decided to investigate the effect of adding another coordinating arm to the central benzene ring. We choose to maximise symmetry of the ligands by using phloroglucinol as the parent alcohol, giving 1,3,5-trisubstituted benzene cores. The ligands differ in the substitution pattern of the pyridine ring. The reaction of **L6** with silver nitrate gave a crystalline precipitate of complex **6** in quantitative yield (98 %). Crystals of **6** suitable for X-ray single-crystal structure determination were grown by diffusion of pentane into an acetonitrile solution of **6.** The reaction of **L7** and **L8** with silver nitrate gave only products that discoloured quickly on isolation from the solvent, possibly indicating reduction of the silver cation. Alternatively, **L7** and **L8** were reacted with silver tetrafluoroborate in acetonitrile to give **7** and **8**, which were isolated by diffusion of pentane into the reaction mixtures. Complex **7** was isolated as crystals suitable for structure determination, whereas suitable crystals of **8** could not be grown despite numerous attempts.

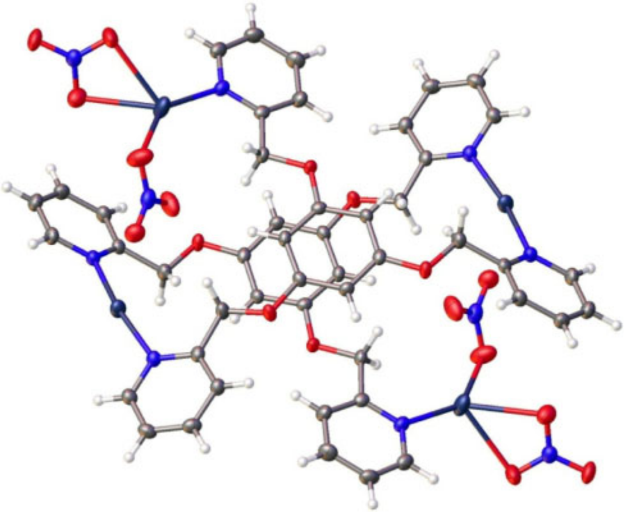


Fig. 6. Perspective view of the macrocyclic structure of **6**, showing the face-to-face overlap of the central benzene rings. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1–N1A 2.218(3), Ag1–O22 2.347(3), Ag1–O13 2.459(3), Ag1–O12 2.573(3), Ag2–N1B 2.188(3), Ag2–N1CA 2.189(3), N1A–Ag1–O22 142.2(1), N1A–Ag1–O13 133.3(1), O22–Ag1–O13 82.9(1), N1A–Ag1–O12 113.60(9), O22–Ag1–O12 97.6(1), N1B–Ag2–N1CA 170.6(1).

The silver nitrate complex **6** forms a macrocyclic structure consisting of two molecules of **6** bridged by two silver atoms, giving a 24-membered dimetallomacrocycle, as shown in Fig. 6. As for the structure of **3** above, the potentially chelating ability of the arms of **L6** is not observed in this structure. The silver atoms are only coordinated to the ligand through the pyridine nitrogens, which are twisted away from the ether oxygens. The silver atoms that are part of the 24-membered macrocycle have a slightly distorted linear coordination geometry, with Ag–N bond lengths of 2.188(3) and 2.189(3) Å. The remaining silver atom is coordinated by one pyridine, with an Ag–N bond length of 2.218(3) Å, and three oxygen atoms of two nitrate anions. One of the nitrate anions chelates the silver through two oxygen atoms with bond lengths 2.459(3) and 2.573(3) Å, whereas the other is monodentate with an Ag–O bond length of 2.347(3) Å, giving the silver atom a distorted tetrahedral geometry.

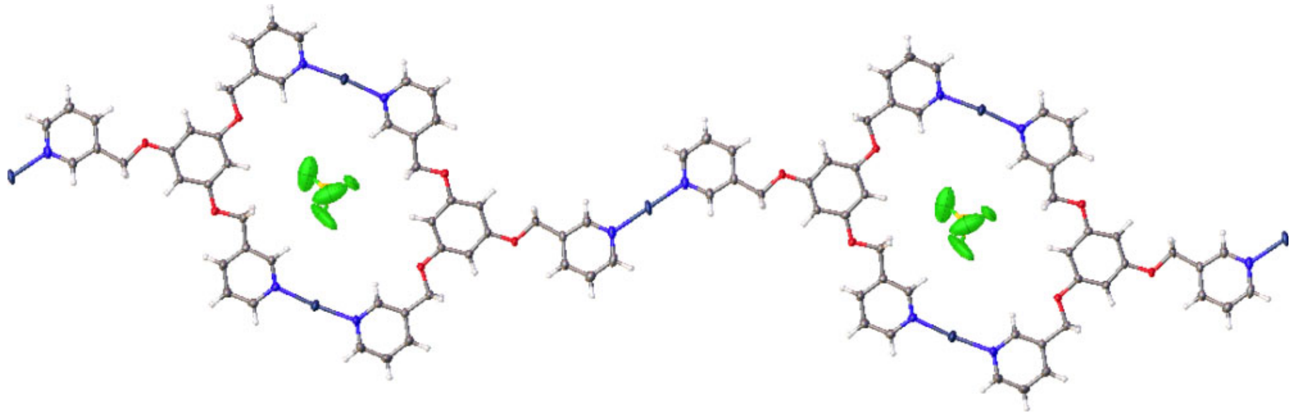


Fig. 7. Perspective view of a section of polymeric chain of the structure of **7**. Selected bond lengths (Å) and bond angles (°): Ag1–N1B 2.183(2), Ag2–N1A 2.146(2), Ag2–N1CA 2.152(2), N1A–Ag2–N1CA 174.27(9).

The pyridine rings of the ligand molecules are slightly tilted relative to the central benzene ring at angles of 23.9(7)°, 18.4(7)°, and 40.7(7)°. This, combined with the flexibility of the spacer groups, allows the ligands to form a macrocyclic structure with the remaining pyridine rings pointed in opposite directions, or *anti* to one another. The structure forms in the triclinic space group *P-1*, with a centre of inversion in the middle of the macrocycle making the opposite benzene rings necessarily coplanar. These rings overlap, with the centre of the C1–C2 bond 3.49(1) Å above the adjacent ring, indicating π–π face-to-face stacking.

The macrocyclic units pack with numerous interactions between adjacent units. The benzene cores arrange with the edges overlapped and 3.385(5) Å apart, indicating a π–π interaction. The non-coordinated oxygen atom of the chelating nitrate anion interacts with the bridging silver atom (Ag···O 2.727(3) Å), and this interaction distorts the silver atom from a linear geometry. The non-coordinated oxygen atoms of the nitrate anions also interact with numerous hydrogen atoms, the closest of which has an O···H distance of 2.30(5) Å.

The silver tetrafluoroborate structure **7** was also found to form a macrocyclic structure, with the remaining pyridine ring bridging two ligands to from a one-dimensional polymer of rings, as shown in Fig. 7. The structure forms in the triclinic space group *P-1* with an asymmetric unit comprising one molecule of **L7** and one-and-a-half silver tetrafluoroborates with two acetonitrile solvate molecules. This corresponds to the M_3L_2 stoichiometry found in the elemental analysis, assuming that the acetonitrile molecules were lost during sample preparation. As with the structure of **6**, the complex forms a macrocycle surrounding a centre of inversion, which relates the two halves of the macrocycle. The silver atoms of the 28-membered macrocycle are coordinated by two pyridine nitrogen atoms, with Ag–N bond lengths of 2.146(2) and 2.152(2) Å, and have a slightly distorted linear coordination geometry (N–Ag–N 174.27(9)°). The silver atoms that link the macrocyclic units to form the polymeric chain reside on centres of inversion, with an Ag–N bond length of 2.183(2) Å and a strictly linear coordination geometry.

The ligand molecules are remarkably planar, with the pyridine rings of the macrocycle tilted by 7.1(2)° and 5.7(2)° to the benzene ring, and the linking pyridine tilted at an angle of 11.1(2)° to the benzene ring. The macrocycle is also quite planar, with a mean deviation of only 0.112(5) Å from planarity for its 28 atoms. The planarity of the polymer allows the adjacent chains to be involved in π–π face-to-face interactions. The closest of these interactions occurs between one of the pyridine rings and a benzene ring of an adjacent chain. These rings are almost coplanar (7.1(2)°) and slightly offset, with C2A 3.34(4) Å above the centre of the benzene ring.

The planarity and proximity of the chains also allow an Ag···π interaction to occur between Ag1 and the C2–C3 bond of an adjacent benzene ring. This interaction is not symmetrical, with distances of 3.339(3) and 3.378(3) Å between the silver atom and C2 and C3 respectively. The interaction is quite weak compared with other silver–arene complexes, which typically have bonding distances of ~2.6 Å. The distance from the silver atom to the midpoint of the double bond is 3.286(4) Å, which is shorter than the proposed silver to double-bond van der Waals interaction distance of 3.42 Å.[26]

The one-dimensional polymeric chain of 'loops and rods' topology of **7**, although rare, has been described on various occasions. These polymers usually involve flexible bidentate ligands and metals atoms that bridge three ligand molecules. The silver nitrate and zinc nitrate complexes of 1,4-bis(1-imidazolylmethyl)benzene have similar structures, which are slightly more complex owing to interpenetration of the polymeric strands to form a two-dimensional polyrotaxane network[27] and a polyrotaxane column,[28] respectively. There are also examples of structures with this topology using rigid bidentate ligands such as the silver hexafluorophosphate complex of 1,4-bis(3-pyridyl)1,2,4,5-tetrazine.[29] However, the structure of **7** represents the first example of this topology type where the roles of the components have been reversed; here the flexible ligand **L7** is tridentate and the silver atoms each bridge two ligand molecules, giving an M_3L_2, rather than an M_2L_3, stoichiometry for the polymer.

The polymers of **7** are arranged with coplanar chains stacked offset by half a ligand unit. This offset gives the structure a 'honeycomb' appearance, with columnar channels, as shown in Fig. 8. These channels contain the tetrafluoroborate counterions and acetonitrile solvate molecules. One of the tetrafluoroborate counterions resides on a centre of inversion, and is therefore disordered over two orientations. Both of the tetrafluoroborate counterions are involved in numerous CH···F interactions with H···F distances between 2.30 and 3.00 Å. The majority of their interactions occur between the tetrafluoroborate counterions and the acetonitrile solvate molecules, which in turn weakly interact with the silver atoms of the polymeric chains, with Ag···N distances in the range 2.78–2.96 Å.

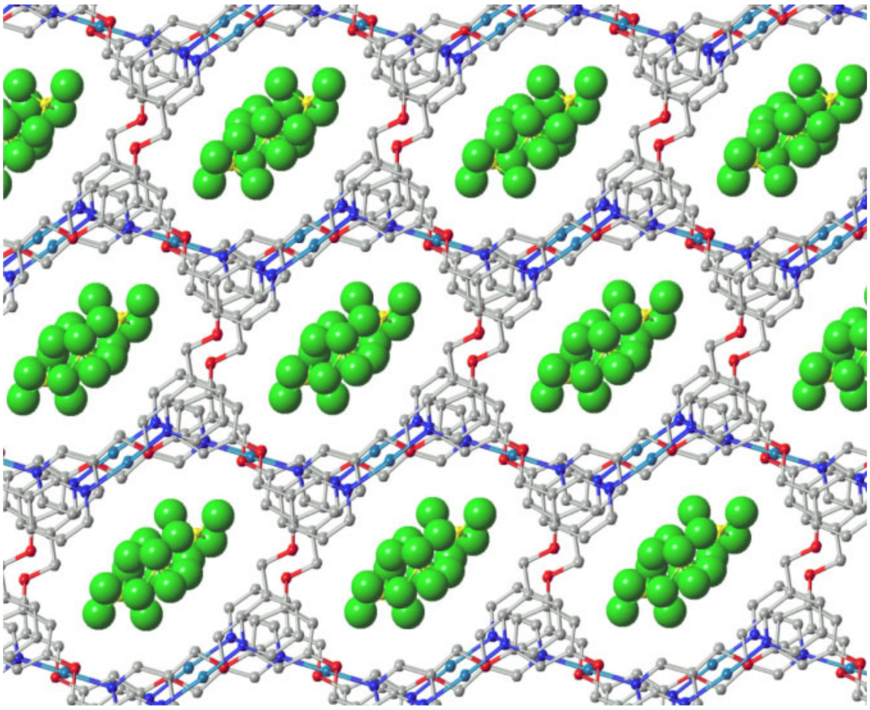


Fig. 8. Perspective view of the offset co-planar chains of **7** down the *bc*-diagonal, showing the channels filled with tetrafluoroborate counterions (fluorine atoms as spheres). The solvate molecules and hydrogen atoms have been removed for clarity.

Conclusions

The six crystal structures presented here show that two- and three-armed flexible ligands based on pyridylmethyleneoxy substituents are able to form both discrete and polymeric complexes with silver. The formation of coordination polymers was shown to be more likely with 3- and 4-substituted pyridine-based ligands, but the precise complex formation was driven by the relative conformation of the pyridine rings. We believe that these ligands represent useful additions to the library of multiply armed molecules available for use in the formation of coordination polymers.

Experimental

Materials and Methods

NMR spectra were recorded on Varian Unity 300 or Varian INOVA 500 spectrometers at 300 or 500 MHz for ^{1}H respectively, and 75 MHz for ^{13}C. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and referenced relative to TMS. Electrospray mass spectra were recorded using a Micromass LCT time-of-flight mass spectrometer, with a probe operating at 3200 V and cone voltage of 30 V. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. The Campbell microanalytical laboratory, University of Otago, Dunedin, performed elemental analyses.

1,2-Bis(3-pyridylmethoxy)benzene, ***L4***

Catechol (0.56 g, 5.1 mmol), 3-chloromethylpyridine hydrochloride (1.72 g, 10.4 mmol), and K_2CO_3 (3.61 g, 26 mmol) were stirred at 100°C in dry DMF (10 mL) under nitrogen for 27 h. The resulting suspension was poured onto H_2O (50 mL) and extracted with CH_2Cl_2 (2×75 mL). The organic extracts were combined, washed (2×50 mL H_2O, 50 mL brine), dried (Na_2SO_4) and evaporated under vacuum to a brown solid. Flash chromatography (20 g silica, 90 : 10 EtOAc/MeOH) and recrystallisation from 1 : 1 light petroleum/EtOAc gave **L7** as a white crystalline solid. Yield 0.36 g (24 %), mp 76–77°C. Anal. calc. for $C_{18}H_{16}N_2O_2$: C 73.95, H 5.52, N 9.58. Found: C 73.77, H 5.58, N 9.72 %. δ_H (500 MHz, $CDCl_3$) 8.67 (2H, s, H2′), 8.57 (2H, d, H6′), 7.78 (2H, d, H4′), 7.29 (2H, m, H5′), 6.96 (4H, m, H2,H3,H4,H5), 5.14 (4H, s, CH_2). δ_C (75 MHz, $CDCl_3$) 149.33 (C2′), 148.84 (C6′), 148.56 (C1,C6), 135.17 (C4′), 132.58 (C3′), 123.44 (C5′), 122.14 (C3,C4), 115.85 (C2,C5), 68.89 (CH_2). *m/z* (EI-MS) 292.1219, $C_{18}H_{16}N_2O_2$ requires [M^+] 292.1212.

1,2-Bis(4-pyridylmethoxy)benzene, ***L5***

Catechol (0.60 g, 5.5 mmol), 4-chloromethylpyridine hydrochloride (1.81 g, 11.0 mmol), and K_2CO_3 (3.41 g, 25 mmol) were stirred at 100°C in dry DMF (10 mL) under nitrogen for 21 h. The resulting suspension was poured onto H_2O (50 mL) and extracted with CH_2Cl_2 (2×75 mL). The organic extracts were washed (2×50 mL H_2O, 50 mL brine), dried (Na_2SO_4) and reduced under vacuum to a brown solid. Flash chromatography (20 g silica, 90 : 10 EtOAc/MeOH) and recrystallisation from 1 : 1 light petroleum/EtOAc gave **L8** as a white crystalline solid. Yield 0.35 g (22 %), mp 101–102°C. Anal. calc. for $C_{18}H_{16}N_2O_2$: C 73.95, H 5.52, N 9.58. Found: C 74.12, H 5.59, N 9.69 %. δ_H (500 MHz, $CDCl_3$) 8.61 (4H, s, H2′,H6′), 7.37 (4H, d, H3′,H5′), 6.92 (4H, m, H2,H3,H4,H5), 5.18 (4H, s, CH_2). δ_C (75MHz, $CDCl_3$) 149.86 (C2′,C6′), 148.18 (C1,C6), 146.22 (C4′), 122.03 (C3′,C5′), 121.29 (C3,C4), 114.66 (C2,C5), 69.25 (CH_2). *m/z* (EI-MS) 292.1219, $C_{18}H_{16}N_2O_2$ requires [M^+] 292.1212.

Complex ***1***

Reaction of **L1** (14.6 mg, 0.05 mmol) dissolved in hot acetone with silver nitrate (17.0 mg, 0.10 mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared

Table 1. Crystal data and X-ray experimental details for 1 and 3–7

Compound	1	3	4	5	6	7
Empirical formula	$C_{18}H_{18}N_3O_6Ag$	$C_{18}H_{16}N_3O_5Ag$	$C_{20}H_{19}N_4O_5Ag$	$C_{18}H_{16}N_3O_5Ag$	$C_{48}H_{42}N_{10}O_{18}Ag_4$	$C_{56}H_{54}B_3N_{10}O_6F_{12}Ag_3$
Formula weight	480.22	462.21	503.26	462.21	1478.40	1547.13
Temperature [K]	168.15	168.15	168.15	168.15	168.15	168.15
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	$P2_1/c$	*C2/c*	*P-1*	*P-1*
Unit cell dimensions:						
a [Å]	5.465(5)	14.141(5)	11.827(5)	11.560(4)	8.297(6)	11.151(3)
b [Å]	6.931(6)	15.131(5)	22.938(9)	17.727(6)	10.520(8)	11.553(3)
c [Å]	23.47(2)	16.909(6)	8.104(3)	8.641(3)	14.946(11)	12.764(3)
α [°]	84.090(10)	90.117(4)	90.00	90.00	78.690(10)	75.628(4)
β [°]	85.770(11)	110.099(5)	108.133(5)	98.569(5)	75.663(9)	82.693(3)
γ [°]	89.558(13)	94.830(5)	90.00	90.00	84.997(10)	68.782(3)
Volume [Å^3]	882.0(13)	3384(2)	2089.5(14)	1751.0(11)	1238.3(16)	1483.5(7)
Z	2	8	4	4	1	1
Density (calculated) [Mg m^{-3}]	1.808	1.815	1.600	1.753	1.982	1.732
Absorption coefficient [mm^{-1}]	1.186	1.229	1.004	1.187	1.647	1.078
F(000)	484.0	1856.0	1016.0	928.0	732.0	772.0
Crystal size [mm]	0.55 × 0.46 × 0.16	0.31 × 0.25 × 0.05	0.59 × 0.57 × 0.07	0.34 × 0.24 × 0.17	0.29 × 0.25 × 0.19	0.61 × 0.52 × 0.24
Theta range for data collection [°]	5.24 to 51°	3.78 to 51°	4.04 to 52°	4.6 to 52.72°	3.96 to 50.24°	4.46 to 50.5°
Reflections collected	10066	39367	25399	6083	9267	17683
Independent reflections [R(int)]	3262 [0.0413]	12411 [0.0382]	4078 [0.0432]	1778 [0.0317]	4350 [0.0220]	5334 [0.0198]
Observed reflections [$I > 2\sigma(I)$]	3103	8419	3419	1422	3942	5032
Data/restraints/parameters	3262/0/259	12411/0/973	4078/0/272	1778/0/125	4350/0/361	5334/0/427
Goodness-of-fit on F^2	1.252	1.011	1.100	1.026	1.153	1.071
R_1 [$I > 2\sigma(I)$]	0.0323	0.0305	0.0366	0.0413	0.0278	0.0322
wR_2 (all data)	0.0829	0.0744	0.0871	0.0905	0.0733	0.0804

on standing for 30 min. Yield 15.0 mg (64 %), mp 224–228°C. Anal. calc. for $C_{18}H_{16}N_3O_5Ag\cdot1/2H_2O$: C 45.88, H 3.64, N 8.92. Found: C 45.87, H 3.67, N 8.85 %. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of **1**.

Complex 2

Reaction of **L2** (14.7 mg, 0.05 mmol) dissolved in hot acetonitrile with silver tetrafluoroborate (20.1 mg, 0.10 mmol) dissolved in hot acetonitrile gave a colourless solution. A crystalline powder formed on diffusion of diethyl ether into the mother liquor. Yield 19.2 mg (70 %), mp 190–191°C. Anal. calc. for $C_{18}H_{16}N_2O_2BF_4Ag\cdot1\frac{1}{2}CH_3CN$: C 45.98, H 3.77, N 8.94. Found: C 45.88, H 3.73, N 8.73 %.

Complex 3

Reaction of **L3** (14.6 mg, 0.05 mmol) in acetone with silver nitrate (17.3 mg, 0.10 mmol) in methanol gave a colourless solution. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into the reaction mixture. Yield 12.1 mg (52 %), mp 134–135°C. Anal. calc. for $C_{18}H_{16}N_3O_5Ag$: C 46.77, H 3.49, N 9.09. Found: C 46.39, H 3.45, N 8.79 %.

Complex 4

Reaction of **L4** (14.6 mg, 0.05 mmol) in acetone with silver nitrate (17.4 mg, 0.10 mmol) in methanol gave a colourless solution. A crystalline product appeared on standing overnight. Yield 22.9 mg (79 %), mp 197–199°C. Anal. calc. for $C_{36}H_{32}N_7O_{13}Ag_3\cdot(CH_3)_2CO$: C 40.65, H 3.32, N 8.51. Found: C 40.70, H 3.39, N 8.78 %. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into an acetonitrile solution of **4**.

Complex 5

Reaction of **L5** (14.4 mg, 0.05 mmol) in acetone with silver nitrate (17.4 mg, 0.10 mmol) in methanol gave a light brown precipitate immediately. Yield 19.2 mg (84 %), mp 164–165°C. Anal. calc. for $C_{18}H_{16}N_3O_5Ag$: C 46.76, H 3.49, N 9.09. Found: C 46.80, H 3.50, N 9.09 %. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into an acetonitrile solution of **5**.

Complex 6

Reaction of **L6** (19.8 mg, 0.05 mmol) in methanol with silver nitrate (26.2 mg, 0.16 mmol) in methanol gave a colourless solution. A crystalline product precipitated in standing for 30 min. Yield 36.0 mg (98 %), mp 199–200°C. Anal. calc. for $C_{24}H_{21}N_5O_9Ag_2$: C 39.00, H 2.86, N 9.47. Found: C 39.07, H 2.76, N 9.35 %. Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into an acetonitrile solution of **6**.

Complex 7

Reaction of **L7** (20.0 mg, 0.05 mmol) in acetonitrile with silver tetrafluoroborate (31.2 mg, 0.16 mmol) in acetonitrile gave a colourless solution. Crystals suitable for X-ray crystallography were obtained from diffusion of pentane into this solution. Yield 25.4 mg (73 %), mp >260°C (dec.). Anal. calc. for $C_{48}H_{42}N_6O_6Ag_3B_3F_{12}$: C 41.72, H 3.06, N 6.08. Found: C 41.51, H 3.41, N 5.88 %.

Complex ***8***

Reaction of **L8** (19.8 mg, 0.05 mmol) in acetonitrile with silver tetrafluoroborate (32.1 mg, 0.16 mmol) in acetonitrile gave a colourless solution. A fawn precipitate appeared on diffusion of pentane into this solution. Yield 28.7 mg (95 %), mp 185–187°C (dec.). Anal. calc. for $C_{24}H_{21}N_3O_3AgBF_4{\cdot}H_2O$: C 47.09, H 3.79, N 6.86. Found: C 46.84, H 3.52, N 6.75 %.

Crystallography

Table 1 lists crystal data and X-ray experimental details for the structures discussed. All measurements were made with a Siemens CCD area detector using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at the temperature indicated in the following table. The data reduction was performed using *SAINT*.[30] Intensities were corrected for Lorentz and polarisation effects and for absorption using *SADABS*.[31] Space groups were determined from systematic absences and checked for higher symmetry. The structures were solved by direct methods using *SHELXS*,[32] and refined on F^2 using all data by full-matrix least-squares procedures with *SHELXL-97*.[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$. In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions. CCDC 903401–903406 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Material

Tables of crystallographic data for all crystal structures are available on the Journal's website.

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