DALTON
FULL PAPER

Synthesis and crystal structures of silver(I) and palladium(II) complexes of new bis(2-pyridyloxy)benzenes and methylene extended analogues

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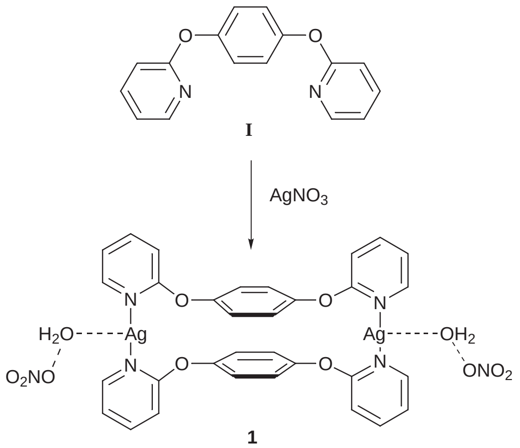
Four new ligands, 1,3-bis(2-pyridyloxy)benzene **II**, 1,2-bis(2-pyridyloxy)benzene **III**, 1,4-bis(2-pyridyloxymethyl)-benzene **IV** and 1,4-bis(2-pyridylmethoxy)benzene **V**, have been prepared, and their complexes with silver(I) nitrate and palladium(II) chloride synthesized. The silver complex of ligand **II** is shown, by a crystal structure determination, to be a M_2L_2 20-membered macrocycle with close π–π stacking of the benzene rings of the ligands, similar to the analogous complex of the *para* substituted isomer of this ligand. The structure of the mononuclear palladium complex of ligand **III** shows the ligand co-ordinated to the metal in a nine-membered chelate ring, with evidence for a weak interaction between the metal and the central benzene ring. Structures of the silver complexes of ligands **IV** and **V** reveal that these are polymeric species, with the molecular packing controlled by π–π stacking interactions between aromatic rings. The crystal structure of the palladium complex of ligand **V** shows that it self-assembles into a M_2L_2 26-membered macrocycle, but without intramolecular π–π stacking.

Introduction

The term metallosupramolecular chemistry was introduced by Constable[1] to describe the self-assembly of larger molecular aggregates from combinations of transition metal ions and polydentate ligands. Often this involves the use of metal ions that have defined co-ordination numbers and stereochemical preferences, to encode the rational assembly of specific molecular architectures by recognition of the inherent properties of logically designed ligands. In this way, many recent reports[2] have described the formation of numerous metallosupramolecular species with novel topological structures, such as squares, cages, ladders, bricks, helicates and polycatenates, some of which contain interlocking rings and interpenetrating 3-D networks, much of which has provided useful information for the rapidly expanding area of crystal engineering.[3] However, this approach imposes natural restrictions on the architectures available, due to the limited range of angular motifs available from stereorigid metals. Thus, we are presently studying the chemistry of metal ions that have less well defined co-ordination numbers and geometries. For example, the d^{10} metal silver(I) forms complexes with various co-ordination numbers, and, within a given co-ordination number, has very flexible geometrical requirements.

Previously, we reported the synthesis of the new ligand **I** and its reaction with silver nitrate to produce the novel M_2L_2 dimetalloparacyclophane **1** containing a π–π stacked subunit (Scheme 1).[4] We were curious to know whether this was simply a serendipitous event or a more general reaction that would apply to other structurally related ligands. Specifically, we were interested to determine the extent to which the π–π stacking was responsible for the self-assembly of this dimeric structure and whether the oxygen atoms of the ligand played a role in the dimer formation. Accordingly, we have now synthesized four new ligands and studied their reactions with silver(I) nitrate and, for comparative purposes, palladium(II) chloride. Since our previous report of the reaction of **I**, a number of structurally related M_2L_2 dimers of various ligands with silver[5] and other metals[6] have been reported; however none of these displays such intimate π–π stacking of aromatic rings.



Scheme 1

Results and discussion

Two approaches were adopted for structural modification of the ligand **I**, in order to assess the generality of the dimer formation. First, the *para* substitution in the benzene ring was replaced by the *meta* and *ortho* isomers and, secondly, methylene spacer groups were introduced on either side of the oxygen atoms. Thus, the four new ligands **II**–**V** were synthesized, all by nucleophilic substitution reactions. By analogy with the method used to prepare the *para* isomer **I**,[4] 2-bromopyridine was treated with 1,3-dihydroxybenzene (resorcinol) and 1,2-dihydroxybenzene (catechol), in the presence of potassium carbonate, to give the *meta* and *ortho* isomers **II** and **III**, respectively. The methylene extended homologue **IV** was prepared by reaction of 2-bromopyridine with 1,4-benzenedimethanol, in an adaptation of a reported method for the synthesis of benzyl 2-pyridyl ether.[7] The isomer **V** was prepared by reaction of 1,4-dihydroxybenzene (hydroquinone) with 2-chloromethylpyridine under phase-transfer catalysed conditions. The ^1H and ^{13}C NMR spectra of all four ligands were fully assigned, by a combination of 1- and

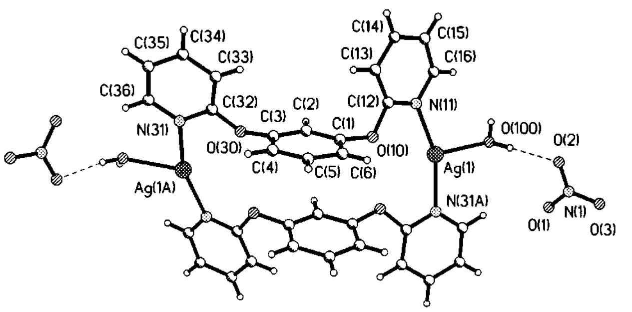
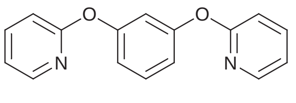
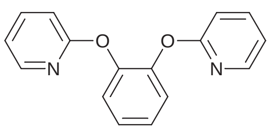


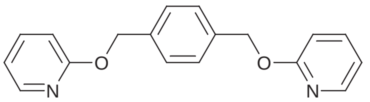
Fig. 1 Perspective view and atom labelling of the crystal structure of complex **2**. Selected interatomic distances (Å) and angles (°): Ag(1)–N(11) 2.196(2), Ag(1)–N(31A) 2.218(2), Ag(1)–O(100) 2.486(2), Ag(1)···O(10) 3.063(2), Ag(1)···O(30A) 2.899(2); N(11)–Ag(1)–N(31A) 158.06(6), N(11)–Ag(1)–O(100) 109.17(6), N(31A)–Ag(1)–O(100) 92.75(6).



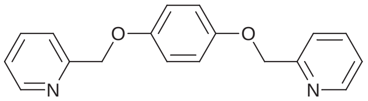
II



III



IV



V

2-D NMR techniques, and are given in the Experimental section.

The ligands **II**–**V** reacted smoothly with silver nitrate, under similar conditions to those used to prepare **1**, to give complexes **2**–**5**, in excellent yields. The crystal structures of three of these are described below. In order to determine whether stereochemically less flexible metals would also form the M_2L_2 dimers, palladium(II) was chosen as a representative square-planar co-ordinating metal, which has been much used in metallosupramolecular self-assemblies.[8] Reactions of **I** and **II**–**V** with palladium chloride afforded complexes **6**–**10** of 1:1 stoichiometry, in excellent yields. Unfortunately, only two of these complexes were sufficiently soluble for NMR studies and for recrystallisation to furnish X-ray quality crystals. The crystal structures of these are also described below.

The silver nitrate complex **2**, of 1,3-bis(2-pyridyloxy)benzene **II**, crystallises in the monoclinic space group *C*2/*c*. Like **1**, it is a M_2L_2 dimeric macrocycle, but in this case has C_2 crystallographic symmetry, rather than a centre of inversion. Fig. 1 shows a perspective view of the structure, with atom labelling of the asymmetric unit. Selected interatomic distances and angles are also listed. To each silver atom are co-ordinated two pyridine nitrogens and a water oxygen atom. The silver–donor bond distances are similar to those of **1**, although the Ag–O(100) distance [2.486(2) Å] is slightly shorter than the analogous bond in **1** [2.528(2) Å]. The geometry at the silver atom is distorted T-shaped with a similar N–Ag–N angle [158.08(6)°] to that in **1**. However, whereas in **1** the water oxygen bisects this angle, in the case of **2** it subtends two very different O–Ag–N angles [109.17(6) and 92.75(6)°]. As with **1**, the co-ordinated water hydrogen atoms are hydrogen-bonded to oxygen atoms of two different nitrate anions, with O···O separations of 2.878(3) and 3.034(3) Å. The intramolecular Ag···Ag separation [9.405(1) Å] in the 20-membered macrocycle **2** of the *meta* isomer is considerably less than that [10.384(1) Å] in the 22-membered macrocyclic complex of the *para* disubstituted ligand.[4]

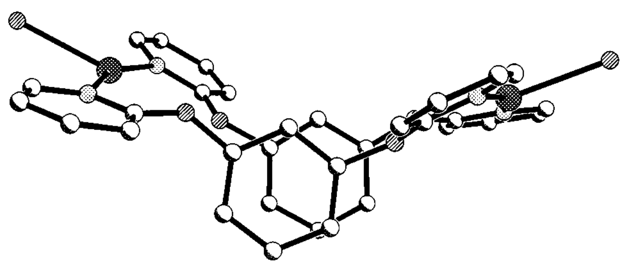


Fig. 2 Top view of complex **2** showing the relationship of the π–π stacked benzene rings.

The benzene and two pyridine rings are each planar, but, as was observed with complex **1**, the oxygen linking atoms, O(10) and O(30), are both significantly out of the plane of the benzene ring [0.088(4) and 0.163(4) Å, respectively]. Again, this distortion is towards the proximate silver atom, which, in combination with the O···Ag distances [2.899(2) and 3.063(2) Å], suggests the existence of weak ether–oxygen–silver interactions. The change in topology of the ligand from 1,4- to 1,3-disubstitution also changes the relative inclinations of the various aromatic rings. The mean planes of the pyridine rings are now inclined at angles of 83.6(1) and 103.9(1)° to that of the linking benzene ring, while the two pyridine ring mean planes at each silver atom are inclined to one another at an angle of 17.5(1)°. Again, the silver atom is significantly out of the extended mean planes of the co-ordinated pyridine rings to the extent of 0.164(2) and 0.121(2) Å.

An important feature of this structure is the preservation of the π–π stacking of the benzene rings. In particular, it is interesting that this complex crystallises in a conformation with the two *meta* disubstituted benzene rings oriented in the same direction (with C_{2v} molecular symmetry), rather than an alternative possible orientation with one of the benzene rings inverted (with C_{2h} symmetry). We believe that the observed orientation occurs in order to maximise the favourable π–π stacking interaction. Nevertheless, unlike the centrosymmetric isomer **1**, in the structure of **2** the benzene rings are not parallel, with mean planes inclined at an angle of 9.1°. However, despite this slight splaying of the benzene rings away from each other, they are still displaced from one another in the same manner as in **1**, with the centroid of one ring lying above an atom of the other ring, as shown in the alternative view of the structure displayed in Fig. 2. We have previously noted that this seems to be the most favourable orientation for parallel stacked aromatic rings, as has been suggested by computational studies.[9] The spacing between the two parallel benzene rings in **1** is 3.33(1) Å; in **2** the slight splaying of the rings has the result that the corresponding values range from 3.343(3) Å, for C(2), to 3.777(3) Å, for C(5).

Thus, the formation of a second M_2L_2 dimer has demonstrated that the structure **1** was not a fortuitous singularity and may represent a general self-assembly process, controlled by the π–π stacking interaction. Attention, therefore, was turned to the *ortho* isomer **III**. Unfortunately, the silver nitrate complex of this ligand failed to provide crystals suitable for X-ray analysis. Elemental analysis suggested an intriguing M_5L_4 stoichiometry; however, this complex was not able to be characterised further. Reaction of palladium chloride with **III** provided a 1:1 complex **8** which was more amenable to study, being soluble in dichloromethane, suggestive of a monomeric structure. The ^{1}H NMR spectrum in CD_2Cl_2 shows only six signals, which indicates the complex has two-fold symmetry. Significant co-ordination-induced changes in chemical shift are observed in comparing the spectra of **III** and **8** in CD_2Cl_2. In particular, the two pairs of benzene hydrogens have the same chemical shift (δ 7.27) for free **III**, while different chemical shifts downfield of

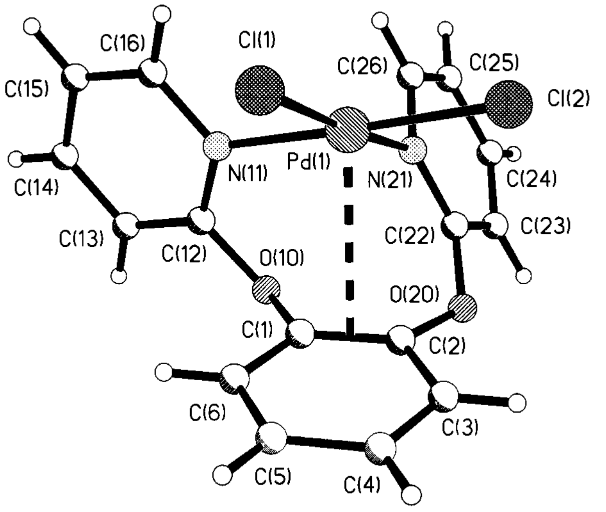
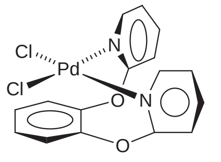


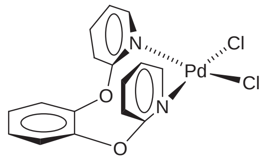
Fig. 3 Perspective view and atom labelling of the crystal structure of complex **8**. Selected interatomic distances (Å) and angles (°): Pd(1)–N(11) 2.059(2), Pd(1)–N(21) 2.040(2), Pd(1)–Cl(1) 2.2831(7), Pd(1)–Cl(2) 2.2871(7); N(11)–Pd(1)–N(21) 88.33(8), N(11)–Pd(1)–Cl(1) 90.77(6), N(21)–Pd(1)–Cl(2) 89.07(6), Cl(1)–Pd(1)–Cl(2) 91.67(3), N(11)–Pd(1)–Cl(2) 176.63, N(21)–Pd(1)–Cl(1) 175.78(6).

this are observed for complex **8** (δ 7.32 and 7.59). Such changes in chemical shift can result from a number of factors such as a change in the conformation of the ligand upon co-ordination and through-space ring-current anisotropy effects.[10]

Assuming *cis* co-ordination by the two pyridine nitrogens, this complex would possess a nine-membered chelate ring. Furthermore, two distinct structures are possible, depending upon whether the benzene ring is proximate (**8a**) or distal (**8b**) to the palladium atom. Inspection of molecular models suggested that interconversion between these two isomers would not be a facile process. Significantly, no NOE enhancement of any pyridine hydrogen signal was observed upon irradiation of either benzene hydrogen signal. Inspection of molecular models showed that this would be so only for isomer **8a**, which in turn raises the interesting possibility that there may also be an interaction between the palladium atom and the benzene ring. Thus a crystal structure determination of **8** was carried out.



8a



8b

The palladium complex **8** crystallises in the monoclinic space group $P2_1/c$. Fig. 3 shows a perspective view and atom labelling of the structure, along with selected bonding geometry. The ligand, **III**, is indeed *cis*-chelated to the palladium, producing a nine-membered chelate ring. A search of the Cambridge Structural Database revealed that this is the first structure involving palladium in a nine-membered chelate ring with N,N-donors, although analogous structures with P,P-donors are known.[11] The Pd–N and Pd–Cl distances are within the range of values previously reported for related structures.[12] In the solid state, the twofold symmetry observed in solution is not crystallographically present, with the mean planes of the two pyridine rings inclined at angles of 90.6(1) and 119.8(1)° to the benzene ring, and at 79.7(1)° to each other.

As suggested by the NMR experiments, the complex exists as isomer **8a**. We believe that this is due to a weak interaction between the palladium atom and the benzene ring, as indicated by certain features of the structure. The palladium atom lies at a distance of 2.879(3) Å from the centre of the C(1)–C(2) bond. This interaction is sufficient slightly to pyramidalise the square-planar palladium, by pulling it out of the co-ordination plane and towards the benzene ring. In turn, the oxygen atoms are displaced, by 0.134(4) and 0.142(4) Å [O(10) and O(20), respectively], on the opposite side of the plane of the benzene ring, indicating pyramidalisation of the attached carbons. This intramolecular interaction between the benzene π orbitals and the palladium d_{z^2} orbital is analogous to those proposed to account for the intermolecular packing of palladium complexes containing aromatic ligands. Thus **III** represents an interesting new chelating ligand.

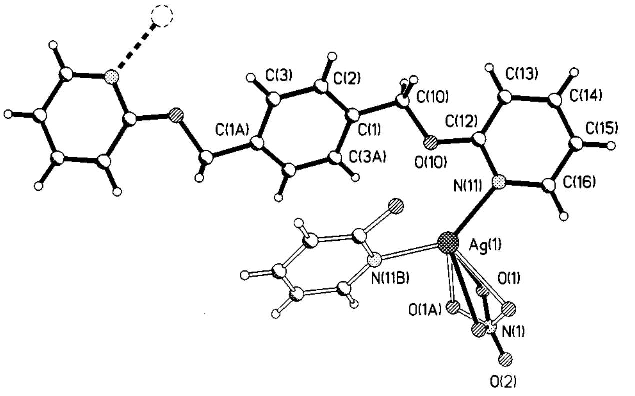


Fig. 4 Perspective view and atom labelling of the crystal structure of complex **4**. Selected interatomic distances (Å) and angles (°): Ag(1)–N(11) 2.216(5), Ag(1)–O(1) 2.545(3), Ag(1)–O(1A) 2.503(4), Ag(1) · · · O(10) 2.874(4); N(11)–Ag(1)–N(11B) 139.6(2), N(11)–Ag(1)–O(1) 97.0(2), N(11)–Ag(1)–O(1A) 120.0(2).

As described above, the two methylene extended ligands **IV** and **V** were prepared to determine whether they would self-assemble into larger dimeric macrocycles, and to examine the possible role of the oxygen atoms in this process. Each of these ligands was treated with silver nitrate to produce, in excellent yields, crystalline complexes (**4** and **5**), suitable for structure determination.

The complex **4** crystallises in the monoclinic space group $C2/c$, and is a metallopolymer, rather than a dimetallocycle. The asymmetric unit contains half of the ligand **IV**, positioned about a centre of inversion, that is co-ordinated to a silver atom, which, in turn, lies on a twofold rotation axis. The chelated nitrate ion, which is disordered over two orientations, also lies with two atoms on this axis. Fig. 4 shows the labelled contents of the asymmetric unit, together with adjacent groups and selected interatomic distances and angles. The silver atom is co-ordinated to two pyridine nitrogens with non-linear geometry [N(11)–Ag(1)–N(11B) 139.6(2)°]. The silver–donor bond distances are similar to those in related literature compounds.[13] The mean plane of the pyridine ring is inclined to that of the benzene at an angle of 46.5(6)°, while the two pyridine ring mean planes at each silver atom are inclined to one another at an angle of 62.8(6)°.

Although this ligand does not produce a dimeric structure, it is interesting that both of the types of interaction discussed above are still found in the extended structure of complex **4**. Specifically, the ether oxygen shows a similar weak interaction with the silver atom [Ag(1) · · · O(10) 2.874(4) Å], being pulled towards the silver as seen in the distortion from ideal geometry around C(12) [O(10)–C(12)–N(11) 111.4(7), O(10)–C(12)–C(13) 125.1(8)°]. Also, the packing of the metallopolymeric structure still appears to be controlled in part by π–π interactions, but, in this case, between pyridine and benzene rings of adjacent units, rather than the benzene–benzene stacks of **1** and **2**. As shown in Fig. 5, the zigzag shaped chain of the polymer is

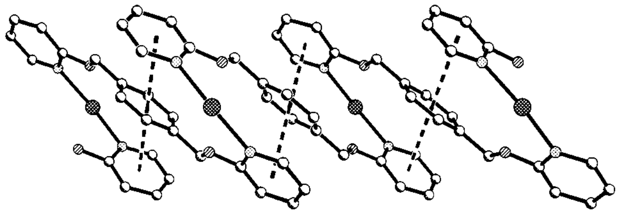


Fig. 5 View down the *b* axis of the polymeric chain structure of complex **4**, with hydrogen and nitrate atoms omitted, showing the inter-ligand π–π stacking of aromatic rings.

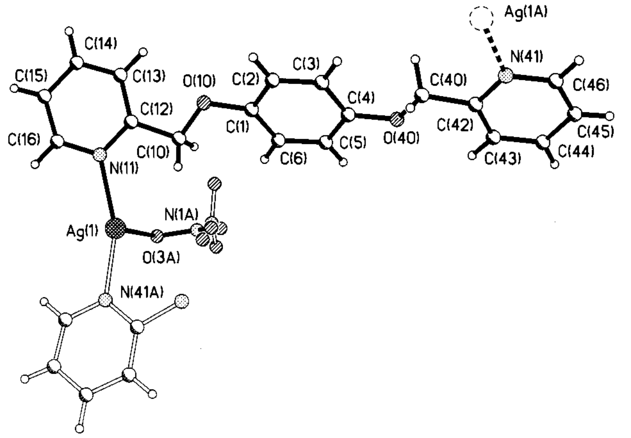


Fig. 6 Perspective view and atom labelling of the crystal structure of complex **5**. Selected interatomic distances (Å) and angles (°): Ag(1)–N(11) 2.203(3), Ag(1)–N(41A) 2.195(3), Ag(1)–O(3A) 2.557(5); N(11)–Ag(1)–N(41A) 150.3(1), N(11)–Ag(1)–O(3A) 104.9(1), N(41A)–Ag(1)–O(3A) 104.2(1).

such that each benzene ring exhibits π–π stacking with two pyridine rings that are inclined at an angle of 17.9(8)°.

The structure of the silver complex **5** of the isomeric ligand **V** is somewhat similar. It crystallises in the monoclinic space group $P2_1/c$ and is also a one dimensional metallopolymer. Fig. 6 shows the labelled contents of the asymmetric unit, along with selected adjacent groups. The silver atom is co-ordinated to two pyridine nitrogens and in half of the units to an oxygen of the nitrate counter ion, which is again disordered over two equally occupied sites. The silver–donor bond distances are again in agreement with the distances of related literature compounds.[13] The pyridine–silver–pyridine co-ordination geometry is non-linear, with the half occupancy co-ordinated oxygen bisecting the larger N–Ag–N angle. The mean planes of the pyridine rings are inclined at angles of 48.4(3) and 2.4(3)° to that of the linking benzene ring.

Since the ether oxygen atoms are no longer directly attached to the pyridine ring they do not interact with the silver atom. Once again the metallopolymer describes a zigzag shape, which results from π–π stacking interactions. As shown in Fig. 7, there is a weak π–π interaction between alternating pyridine rings in the polymer chain. Stronger interactions exist between different strands of the polymer, with crystallographically equivalent pyridines of adjacent strands, related by a centre of inversion, being coplanar and separated by only 3.33(1) Å. Once again, the rings are displaced such that an atom of one ring lies over the centroid of the other ring, a relationship similar to that existing in complexes **1** and **2**. Hence, π–π interactions appear to contribute to the assembly of the complex, and certainly to its crystal packing.

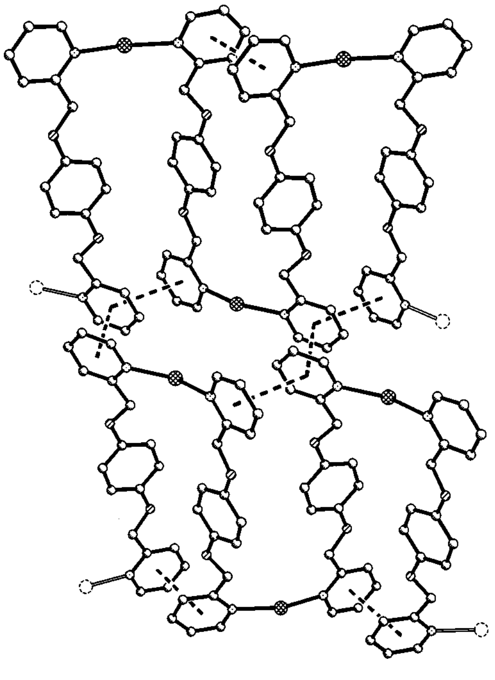


Fig. 7 Perspective view of complex **5**, with hydrogen and nitrate atoms omitted, showing the intra- and inter-polymer π–π stacking of pyridine rings.

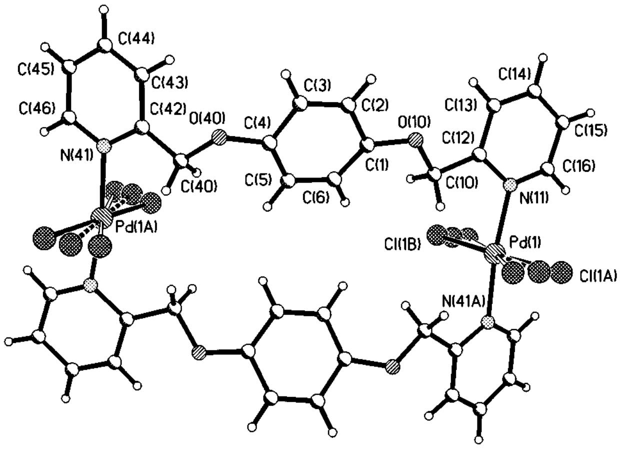


Fig. 8 Perspective view and atom labelling of the crystal structure of complex **10**. Selected interatomic distances (Å) and angles (°): Pd(1)–N(11) 2.03(1), Pd(1)–N(41A) 2.06(1), Pd(1)–Cl range 2.267(6)–2.383(6); N(11)–Pd(1)–N(41A) 172.1(8), N(11)–Pd(1)–Cl range 86.9(4)–92.5(4), N(41A)–Pd(1)–Cl range 87.1(6)–92.1(4), Cl(1A)–Pd(1)–Cl(1B) 178.4(3), Cl(2A)–Pd(1)–Cl(2B) 171.8(7), Cl(3A)–Pd(1)–Cl(3B) 178.6(5).

The palladium chloride complex **10** of this ligand **V** was soluble and stable in DMSO, which allowed for characterisation by ^{1}H NMR spectroscopy. The spectrum, with co-ordination induced shifts ranging between 0.10 and 0.57 ppm downfield from those of the non-co-ordinated ligand, showed that, in solution, the two pyridine rings are equivalent. Although the silver complexes of **IV** and **V** were polymeric, the solubility of **10** suggested that this was not a polymeric species and, hence, a crystal structure determination seemed worthwhile. Suitable crystals were obtained by vapour diffusion of acetone into a DMSO solution of the complex.

The palladium complex **10** crystallises in the monoclinic space group *C*2/*c*, with the asymmetric unit containing one PdLCl$_2$ moiety and half an acetone solvate molecule, the latter lying on a twofold rotation axis. The complex is a dimetallo-paracyclophane incorporating a 26 membered macrocycle. Fig. 8 shows the structure with the asymmetric unit labelled and lists selected interatomic distances and angles. Unfortunately, the structure exhibits considerable disorder. As shown in Fig. 8, each chlorine atom is disordered over three sites. High thermal displacement parameters for some atoms of the ligand suggested that these too are disordered, but this was not included in the refinement model. Consequently, the bonding

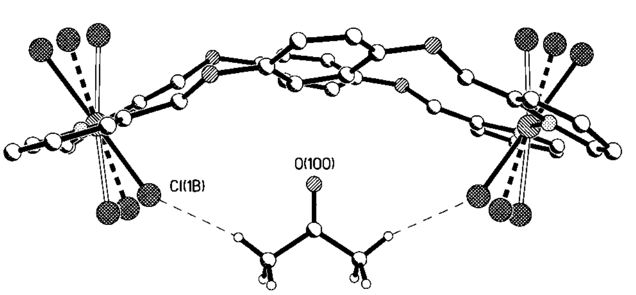


Fig. 9 Side view of complex **10** showing the macrocycle wrapping around the hydrogen-bonded acetone. All hydrogens except those of the acetone are omitted for clarity.

geometry parameters are less well determined than in the other structures.

Each palladium atom is approximately square planar and is *trans* co-ordinated to two pyridine nitrogens and two disordered chlorine atoms. The Pd–N and Pd–Cl distances are within the range of reported values for related structures.[14] Within the ligand, the mean planes of the pyridine rings are inclined at angles of 25(1) and 47(1)° to that of the benzene ring, while two pyridines co-ordinated to the same palladium atom are inclined at an angle of 15(1)°. The intramolecular Pd···Pd separation in the macrocycle is 11.269(2) Å. This is significantly larger than those of the silver structures described above, as a result of the additional methylene groups incorporated in the ligand. The two non-stacked benzene rings are inclined at an angle of 44(1)° to each other, with their centroids separated by 6.45(3) Å, which indicates that this dimension of the macrocycle is also enlarged from the earlier structures. The overall shape of the macrocycle is curved (Fig. 9). This is as a result of hydrogen bonding interactions between a co-ordinated chlorine and the acetone solvate molecule [closest Cl···H distance 2.59(2) Å]. This has the effect of wrapping the macrocycle around the solvate to give the concave curvature. Although there are no intramolecular π–π interactions, the molecular packing involves weak intermolecular π–π stacking interactions between the rings of adjacent molecules.

Conclusion

The four new ligands, 1,3-bis(2-pyridyloxy)benzene **II**, 1,2-bis(2-pyridyloxy)benzene **III**, 1,4-bis(2-pyridyloxymethyl)benzene **IV** and 1,4-bis(2-pyridylmethoxy)benzene **V**, have been shown to form complexes with silver nitrate and palladium chloride, in excellent yields. Crystal structure determinations have shown a variety of modes of co-ordination by these ligands, including the formation of a mononuclear chelated complex, bridged binuclear cyclic dimers and bridged polymeric structures. Further experiments designed to rationalise the behaviour of these ligands will be reported subsequently. For example, the accompanying paper describes the silver complexes of structurally related ligands incorporating sulfur atoms rather than oxygen linking groups.

Experimental

General

The ^1H NMR spectra were recorded on a Varian 300 Unity spectrometer with a 3 mm probe operating at 300 MHz, ^{13}C NMR spectra on a Varian 300 Unity or XL-300 spectrometer with a 3 or 5 mm probe, respectively, operating at 75 MHz. Spectra were referenced relative to internal Me_4Si. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Chemistry Department, University of Otago, Dunedin. Solvents were purified according to literature procedures. Unless otherwise stated, reagents were obtained from commercial sources.

Ligand preparations

1,3-Bis(2-pyridyloxy)benzene II. A mixture of 1,3-dihydroxybenzene (1.15 g, 10.4 mmol), 2-bromopyridine (3.31 g, 21.0 mmol) and potassium carbonate (2.90 g, 21.0 mmol) was heated, with stirring, at 210–220 °C for 5 h. The resulting tar was extracted several times with diethyl ether; the extracts were combined and washed with aqueous sodium hydroxide (40%), then water. The solvent was then removed to give a brown oil. Crystallisation of this oil from light petroleum–ethyl acetate (2:1) afforded pure compound **II** (1.06 g, 39%) as colourless crystals, mp 50–51 °C (Found: C, 72.90; H, 4.76; N, 10.56. C_8H_6NO requires C, 72.72; H, 4.58; N, 10.60%). ^1H NMR ($CDCl_3$): δ 6.93 (2 H, d, H3′), 6.96 (1 H, s, H2), 6.99 (2 H, dd, H4,6), 7.00 (2 H, t, H5′), 7.40 (1 H, t, H5), 7.68 (2 H, t, H4′), 8.21 (2 H, d, H6′). ^{13}C NMR ($CDCl_3$): δ 111.48 (C3′), 113.88 (C2), 116.81 (C4,6), 118.56 (C5′), 129.92 (C4), 139.26 (C4′), 147.53 (C6′), 154.98 (C1,3), 163.07 (C2′).

1,2-Bis(2-pyridyloxy)benzene III. 1,2-Dihydroxybenzene was treated as above and gave crude compound **III** as a white solid. Recrystallisation from light petroleum (bp 40–60 °C)–ethyl acetate (2:1) afforded pure **III** (0.87 g, 32%) as colourless crystals, mp 97–98 °C (Found: C, 72.55; H, 4.69; N, 10.70). ^1H NMR ($CDCl_3$): δ 6.70 (2 H, d, H3′), 6.90 (2 H, t, H5′), 7.28 (4 H, s, H3–6), 7.56 (2 H, t, H4′), 8.10 (2 H, d, H6′). ^{13}C NMR ($CDCl_3$): δ 110.73 (C3′), 118.17 (C5′), 123.60 (C3,6), 125.73 (C4,5), 138.96 (C4′), 145.66 (C1,2), 147.31 (C6′), 163.06 (C2′).

1,4-Bis(2-pyridyloxymethyl)benzene IV. A mixture of 1,4-benzenedimethanol (0.57 g, 4.1 mmol), 2-bromopyridine (1.31 g, 8.3 mmol) and potassium hydroxide (1.86 g, 33.2 mmol) was refluxed in toluene (20 ml) for 42 h. The solvent was then removed and the residue divided between chloroform (15 ml) and aqueous (30 ml) layers. The organic layer was then separated, dried (Na_2SO_4) and concentrated to give crude compound **IV**. Unchanged 2-bromopyridine was removed under vacuum at room temperature for 30 min. Trituration of the remaining residue with ice-cold methanol gave a white precipitate which was filtered off to give **IV** (0.41 g, 34%), mp 67–68 °C (Found: C, 72.03; H, 5.55; N, 9.17. $C_{18}H_{16}N_2O_2\cdot 0.5H_2O$ requires C, 71.75; H, 5.69; N, 9.30%). ^1H NMR ($CDCl_3$): δ 5.38 (4 H, s, CH_2), 6.80 (2 H, d, H3′), 6.87 (2 H, t, H5′), 7.47 (4 H, s, H2,3,5,6), 7.57 (2 H, t, H4′), 8.17 (2 H, d, H6′). ^{13}C NMR ($CDCl_3$): δ 67.11 (CH_2), 111.19 (C3′), 116.79 (C5′), 127.96 (C2,3,5,6), 136.87 (C1,4), 138.48 (C4′), 146.70 (C6′), 163.45 (C2′).

1,4-Bis(2-pyridylmethoxy)benzene V. A mixture of 1,4-dihydroxybenzene (2.05 g, 18.6 mmol), 2-chloromethylpyridine hydrochloride (6.11 g, 37.2 mmol) and 40% aqueous tetrabutylammonium hydroxide (4 drops) was refluxed in benzene (40 ml) and 40% aqueous sodium hydroxide (8 ml) for 24 h. The organic layer was then separated, dried (Na_2SO_4) and concentrated to give crude compound **V**. Recrystallisation from light petroleum–ethyl acetate (10:1) gave pure **V** (2.63 g, 48%), mp 106 °C (Found: C, 73.55; H, 5.51; N, 9.46. C_9H_8NO requires C, 73.96; H, 5.52; N, 9.58%). ^1H NMR ($CDCl_3$): δ 5.16 (4 H, s, CH_2), 6.92 (4 H, s, H2,3,5,6), 7.23 (2 H, t, H5′), 7.53 (2 H, d, H3′), 7.72 (2 H, t, H4′), 8.60 (2 H, d, H6′). ^{13}C NMR ($CDCl_3$): δ 71.14 (CH_2), 115.69 (C2,3,5,6), 121.24 (C3′), 122.54 (C5′), 136.78 (C4′), 149.16 (C6′), 152.81 (C1,4), 157.43 (C2′).

Silver nitrate complexes

$[Ag_2(II)_2(H_2O)_2][NO_3]_2$ 2. Reaction of compound **II** (70 mg, 0.26 mmol), dissolved in methanol (8 ml), with silver nitrate (54 mg, 0.31 mmol), dissolved in water (5 ml), gave, over a period of several days at room temperature, complex **2** as colourless crys-

Table 1 Crystal data and details of data collections and structure refinements for complexes **2**, **4**, **5**, **8** and **10**

	2	**8**	**4**	**5**	**10**
Formula	$C_{32}H_{28}Ag_2N_6O_{12}$	$C_{16}H_{12}Cl_2N_2O_2Pd$	$C_{18}H_{16}AgN_3O_5$	$C_{18}H_{16}AgN_3O_5$	$C_{39}H_{38}Cl_4N_4O_5Pd_2$
Formula weight	904.34	441.58	462.21	462.21	997.34
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	20.751(4)	8.512(1)	15.793(2)	12.235(1)	15.428(4)
b/Å	9.311(1)	17.845(1)	12.699(1)	9.050(1)	7.921(2)
c/Å	18.659(3)	11.172(1)	10.959(1)	15.820(2)	32.63(1)
β/°	113.21(1)	106.41(1)	128.283(8)	97.36(1)	97.86(3)
V/Å^3	3313.4(9)	1627.9(3)	1725.3(4)	1737.3(3)	3950(2)
Space group	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$
Z	4	4	4	4	4
D_c/Mg m^{-3}	1.81	1.80	1.78	1.77	1.68
F(000)	1808	872	928	928	2000
T/K	158(2)	168(2)	188(2)	130(2)	132(2)
Crystal form	Colourless block	Orange block	Colourless block	Colourless block	Yellow plate
Crystal size/mm	0.56 × 0.49 × 0.31	0.60 × 0.19 × 0.16	0.52 × 0.28 × 0.19	0.31 × 0.15 × 0.12	0.68 × 0.41 × 0.03
μ/mm^{-1}	1.26	1.48	1.21	1.20	1.23
2θ range/°	4–55	4–50	4–50	4–50	4–48
Reflections collected	4620	3076	1570	3209	3553
Unique reflections (R_{int})	3797 (0.023)	2874 (0.014)	1513 (0.034)	3057 (0.024)	3083 (0.069)
Parameters	243	208	126	280	254
Difference peaks/e Å^{-3}	0.427	0.428	0.766	0.654	0.964
Goodness of fit	1.074	0.940	1.068	0.766	0.807
R^a [$I > 2\sigma(I)$]	0.0235	0.0213	0.0475	0.0281	0.0622
wR^b (all data)	0.0623	0.0523	0.1182	0.0441	0.1874

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

tals suitable for single crystal structure determination (96 mg, 83%), mp 185–186 °C (Found: C, 42.61; H, 3.29; N, 9.16. $C_{32}H_{24}Ag_2N_6O_{10}\cdot 2H_2O$ requires C, 42.50; H, 3.12; N, 9.29%).

[Ag(NO$_3$)$_5$](III)$_4$(H$_2$O)$_2$ 3. Reaction of compound **III** (70 mg, 0.26 mmol), dissolved in methanol (5 ml), with silver nitrate (54 mg, 0.31 mmol), dissolved in methanol (5 ml), gave a colourless solution. This was concentrated to approximately 5 ml. Subsequent vapour diffusion of diethyl ether into this solution gave microcrystals of complex **3** (101 mg, 80%), mp > 130 °C (Found: C, 39.76; H, 2.50; N, 9.21. $C_{64}H_{48}Ag_5N_{13}O_{23}\cdot 2H_2O$ requires C, 39.57; H, 2.70; N, 9.37%).

[Ag(IV)(NO$_3$)]$_n$ 4. Reaction of compound **IV** (50 mg, 0.17 mmol) dissolved in acetone (7 ml) with silver nitrate (29 mg, 0.17 mmol), dissolved in water (3 ml), gave, after slow evaporation at room temperature, colourless crystals of complex **4**, suitable for single crystal structure determination (63 mg, 79%), mp 187–188 °C (Found: C, 46.68; H, 3.39; N, 9.15. $C_{18}H_{16}AgN_3O_5$ requires C, 46.78; H, 3.49; N, 9.09%).

[Ag(V)(NO$_3$)]$_n$ 5. Reaction of compound **V** (50 mg, 0.17 mmol), dissolved in methanol (10 ml), with silver nitrate (29 mg, 0.17 mmol), dissolved in water (10 ml), gave colourless needles of complex **5**, after 15–30 min, which were filtered off and washed with methanol (65 mg, 82%). Slow evaporation of an acetonitrile solution of **5** gave crystals suitable for single crystal structure determination, mp > 190 °C (Found: C, 46.72; H, 3.53; N, 9.23. $C_{18}H_{16}AgN_3O_5$ requires C, 46.78; H, 3.49; N, 9.09%).

Palladium chloride complexes

Pd(I)Cl$_2$ 6. Reaction of compound **I** (46 mg, 0.17 mmol), dissolved in hot methanol (5 ml), with palladium chloride (31 mg, 0.17 mmol), dissolved in hot aqueous hydrochloric acid (5 ml, 2 M), gave complex **6** as an orange precipitate (67 mg, 88%), mp > 300 °C (Found: C, 43.35; H, 2.80; Cl, 15.87; N, 6.26. $C_{16}H_{12}Cl_2N_2O_2Pd$ requires C, 43.52; H, 2.74; Cl, 16.06; N, 6.34%).

Pd(II)Cl$_2$ 7. Reaction of compound **II** (60 mg, 0.23 mmol), dissolved in hot methanol (5 ml), with palladium chloride (40 mg, 0.23 mmol), dissolved in hot aqueous hydrochloric acid (5 ml, 2 M), gave crude complex **7** as an orange precipitate. This was subsequently recrystallised by vapour diffusion of acetone into a DMSO solution of the crude product to give **7** (82 mg, 81%), mp > 235 °C (decomp.) (Found: C, 41.29; H, 3.41; Cl, 14.72; N, 5.98. $C_{16}H_{12}Cl_2N_2O_2Pd\cdot H_2O\cdot 0.25(CH_3)_2SO$ requires C, 41.36; H, 3.26; Cl, 14.80; N, 5.85%).

Pd(III)Cl$_2$ 8. Reaction of compound **III** (61 mg, 0.23 mmol), dissolved in hot methanol (5 ml), with palladium chloride (41 mg, 0.23 mmol), dissolved in hot aqueous hydrochloric acid (5 ml, 2 M), gave complex **8** as orange crystals suitable for single crystal structure determination (79 mg, 78%), mp > 260 °C (decomp.) (Found: C, 43.25; H, 2.65; Cl, 16.00; N, 6.38. $C_{16}H_{12}Cl_2N_2O_2Pd$ requires C, 43.52; H, 2.74; Cl, 16.06; N, 6.34%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.12 (2 H, t, H5′), 7.16 (2 H, d, H3′), 7.32 (2 H, dd, H4,5), 7.59 (2 H, dd, H3,6), 7.84 (2 H, t, H4′), 8.69 (2 H, d, H6′).

Pd(IV)Cl$_2$ 9. Reaction of compound **IV** (60 mg, 0.21 mmol), dissolved in hot methanol (5 ml), with palladium chloride (36 mg, 0.21 mmol), dissolved in hot aqueous hydrochloric acid (5 ml, 2 M), gave complex **9** as an orange precipitate, which was filtered off and washed with hot ethanol (89 mg, 87%), mp > 220 °C (decomp.) (Found: C, 44.26; H, 3.59; Cl, 14.62; N, 5.60. $C_{18}H_{16}Cl_2N_2O_2Pd\cdot H_2O$ requires C, 44.22; H, 3.72; Cl, 14.54; N, 5.74%).

Pd(V)Cl$_2$ 10. Reaction of compound **V** (45 mg, 0.15 mmol), dissolved in hot methanol (5 ml), with palladium chloride (27 mg, 0.15 mmol), dissolved in hot aqueous hydrochloric acid (5 ml, 2 M), gave complex **10** as an orange precipitate (59 mg, 82%), mp > 300 °C. Vapour diffusion of acetone into a dimethyl sulfoxide solution of **10** gave crystals suitable for single crystal structure determination (Found: C, 46.68; H, 3.63; Cl, 14.40; N, 5.70. $C_{36}H_{32}Cl_4N_4O_4Pd_2\cdot CH_3COCH_3$ requires C, 46.97; H, 3.84; Cl, 14.22; N, 5.62%). ^{1}H NMR (DMSO): δ 5.47 (8 H, s, CH$_2$), 7.16 (8 H, s, H2,3,5,6), 7.93 (4 H, t, H5′), 8.06 (4 H, d, H3′), 8.49 (4 H, t, H4′), 8.92 (4 H, d, H6′).

X-Ray crystallography

The crystal data and details of the data collections and refinements for the five structures are listed in Table 1. All measurements were made with a Nicolet P4s diffractometer using graphite monochromatized Mo-Kα ($\lambda = 0.71073$ Å) radiation. Cell parameters were determined by least-squares refinement on diffractometer angles for at least 20 accurately centred reflections. Throughout data collections (ω scan mode, $\pm h + k + l$) the intensities of three standard reflections were monitored at regular intervals and in no case showed variations of >7%. Intensities were corrected for Lorentz-polarisation effects and for minor absorption using a technique based on azimuthal ψ scans.

The structures were solved by direct methods using SHELXS[15] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL 93.[16] 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 atoms. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

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