Discrete metal complexes of two multiply-armed ligands.

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Abstract

The syntheses and metal complexes of 1,2,4,5-tetrakis(8-quinolyloxy)methyl)benzene (1) and hexakis(8-quinolyloxy)methyl)benzene (2) are described. X-Ray crystal structures are reported of the free ligand 1, a binuclear silver(I) and a tetranuclear copper(I) complex of 1, as well as a binuclear cobalt(II) and trinuclear palladium(II) and silver(I) complexes of 2. Within these discrete metal complexes the ligands are found to adopt a range of coordination modes, with considerable variation in the relative orientations of the ligand arms as a result of the flexibility imparted by the CH$_2$O linker units.
Introduction

In a recent paper\textsuperscript{[1]} we described synthetic and structural studies of complexes of two ligands that contain two 8-hydroxyquinoline (oxine) subunits joined through ether linkages by xylylene spacer groups. These versatile ligands formed a diverse range of complexes of varying nuclearity in response to the coordination requirements of the metal concerned. We have now extended this design principle to more highly substituted examples.

Ligands based around a central aromatic core with several radiating groups capable of metal coordination have been employed in the construction of an intriguing array of fascinating two- and three-dimensional metallosupramolecular species, such as molecular cages,\textsuperscript{[2]} helicates\textsuperscript{[3]} and metalloendrimers.\textsuperscript{[4]} For example, we, and others, have described the use of ligands consisting of a central benzene core to which are appended four or six nitrogen heterocyclic donor groups, such as pyrazoles\textsuperscript{[5]} or pyridines.\textsuperscript{[6]} Recently, much use has been made of the ability to facially segregate substituents in ligands containing six flexible substituents in a hexasubstituted benzene because of their pre-organisation on alternating faces of the ring.\textsuperscript{[7]}

We now describe preparations of the two new ligands 1 and 2 (Scheme 1), each of which might be expected to display a variety of binding modes with the ligands acting as multidentate bridges between metal centres in either discrete, dendrimeric or other polymeric architectures. Such metal-organic frameworks and coordination polymers are finding useful applications as functional materials.\textsuperscript{[8]} Furthermore, ligands incorporating 8-quinolinyloxy subunits have long been known to form complexes with alkali and alkaline earth metals.\textsuperscript{[9]} In this report we describe the X-ray crystal structures of discrete transition metal complexes in which these new ligands act as bridges between up to four metal centres in complexes with novel molecular topologies.

\[\text{Scheme 1 here}\]
Results and Discussion

The ligands, 1,2,4,5-tetrakis(8-quinolyloxymethyl)benzene (1) and hexakis(8-quinolyloxymethyl)benzene (2), were prepared in moderate yields by reaction of 8-hydroxyquinoline with the appropriate oligo(bromomethyl)benzene in DMF solution in the presence of sodium hydroxide. The ligands were characterized by mass spectrometry and $^1$H NMR spectroscopy, which indicated a symmetrical environment for all the attached quinoline substituents. Whereas benzene derivatives with six appended flexible substituents are known\cite{7,10} to prefer an arrangement in which the substituents alternate on opposite sides of the plane of the aromatic ring, the same cannot be said for tetrasubstituted benzenes. Thus, in order to determine the relative orientation of the four substituents in 1 a single crystal X-ray crystal structure determination of the free ligand was carried out.

Figure 1 shows a perspective view of the structure of 1. In the solid-state the molecule adopts an unusual conformation in which two adjacent quinolyloxymethyl substituents lie approximately coplanar with the central ring, while the other two adjacent rings are approximately orthogonal to the plane of the central ring and arranged on opposite sides of it. Specifically, the angles between the mean-plane of the central ring and the four quinoline rings are 104.9, 96.9, 29.8 and 10.3°. The origin of this unusual conformation probably lies in the crystal packing which involves a number of $\pi-\pi$ aromatic stacking interactions.\cite{11}

[Figure 1 here]

The conformation observed for this ligand in the solid-state need not persist in its metal complexes. The same applies to the alternating arrangement of the arms in the hexasubstituted free ligand 2, the X-ray structure of which was also determined. This structure is not reported here as we were unable to achieve a satisfactory refinement due to the presence of diffuse poorly resolved solvate molecules, which were found to mingle with the ligand molecules in the crystal lattice. Each of these new ligands was reacted with a selected range of transition metal salts in various stoichiometric ratios. From such reactions, five complexes, 3-7, were isolated that furnished crystals suitable for X-ray crystallography.
Reaction of the quadruply armed ligand 1 with two equivalents of silver(I) triflate gave a discrete M$_2$L complex 3 in 48% yield. It crystallizes about a centre of inversion in the triclinic space group P-1, with one molecule of ligand 1, two silver triflate units, two disordered methanol molecules and half a water molecule in the unit cell. Figure 2 shows a perspective view of the dinuclear cation in the structure of 3, with selected atom labelling and bonding geometry. In this complex the ligand 1 acts as a doubly chelating bridge between two silver atoms. Each silver is coordinated to two quinoline nitrogens in an approximately linear fashion with weaker contacts to the ether oxygen atoms. Chelation involves coordination by adjacent arms of the ligand. The resulting fused 5,7,5-membered chelate ring system is similar to that observed in the mononuclear complexes of the simpler ortho-disubstituted ligand described an earlier paper.[1] This arrangement has the planes of the quinoline rings approximately orthogonal to that of the central aromatic ring, with adjacent arms on opposite sides of the central ring, one up (u) and one down (d). For the quadruply armed ligand this could lead to two diastereoisomers, designated uduu or uddu depending on whether the meta-related substituents are on opposite sides (du) or on the same side (dd, uu). The isolated structure has the uddu arrangement with C$_{2v}$ local symmetry, rather than the chiral uduu isomer with D$_2$ symmetry. We believe that the observed isomer is favoured by its centrosymmetric nature. In this complex, the ligand bridges two silver atoms separated by 11.333(1) Å. There are no unusual intermolecular packing interactions.

[Figure 2 here]

Reaction of ligand 1 with copper(I) iodide produced a complex (4) with a very different topology. It crystallizes in the tetragonal space group I4/m with a quarter of the ligand, half a Cu$_2$I$_2$ unit and two partially occupied acetonitrile solvate molecules in the asymmetric unit. Figure 3 shows a perspective view of the structure, along with selected atom labelling and bonding geometry. The discrete tetranuclear complex consists of two Cu$_2$I$_2$ rhombuses bridged by the ligand 1. However, the bridging mode is notably different from that observed in complex 3. In the copper complex the Cu$_2$I$_2$ units do not chelate to adjacent (ortho) arms of the ligand but to those disposed with a meta relationship. A similar bridging mode was observed in a mononuclear copper(II) complex of the simpler 1,3-disubsituted ligand
reported previously.\textsuperscript{[1]} The difference most probably reflects the greater size of the Cu$_2$I$_2$ unit compared to that of a single silver(I) atom.

The copper atoms are formally three coordinate, being bonded to two iodine atoms (with approximately equal bond lengths) and one nitrogen donor. However, the copper atom is noticeably pyramidalised away from a trigonal planar geometry, as a consequence of a weaker interaction with the adjacent oxygen donors [2.496(3) Å]. The Cu$_2$I$_2$ units themselves are planar with bonding geometry similar to that observed in other complexes of this type.\textsuperscript{[12]} The Cu–Cu interatomic distance is relatively short at 2.507(1) Å. The plane of the Cu$_2$I$_2$ unit is inclined to the plane of the central ring at an angle of 24.3(1) °. The full three-dimensional structure is far from planar with the two Cu$_2$I$_2$ units positioned on opposite faces of the central ring. This, once again, requires a uddu arrangement of the four arms of the ligand, which is accommodated by the internal centre of inversion.

Thus, in the two crystalline complexes 3 and 4, ligand 1 has been shown to be capable of adopting chelating modes of coordination similar to both the ortho and meta isomers of the doubly armed ligands previously described.\textsuperscript{[1]} On this basis, one might anticipate a diverse range of coordination possibilities for the more heavily substituted ligand 2.

Reaction of the hexasubstituted ligand 2 with six equivalents of cobalt(II) bromide resulted in the isolation of a binuclear complex (5), the structure of which is shown in Figure 4. It crystallizes in the monoclinic space group P2$_1$/n, with half the bridging ligand, a CoBr$_2$ unit, two dichloromethane solvate molecules and an ethanol molecule, disordered over two orientations, in the asymmetric unit. This discrete binuclear complex lies on a crystallographic centre of inversion. Within the complex, ligand 2 is hypodentate, using only four of its six arms for coordination to cobalt. Each coordinated arm acts as an N,O-chelating bidentate group and each metal is bound to two adjacent (ortho) arms. The two non-coordinated arms are para-related. As a result the overall role of the bridging ligand is similar to that of the tetrasubstituted ligand 1 in complex 3, with the two additional arms simply being spectator groups. This analogy also holds for the relative (uddu) orientation of the four coordinated arms. However, intriguingly, the two remaining non-coordinated arms
have the same orientation as their two adjacent coordinated arms. This results in an unusual \textit{uuuuddd} arrangement of the six arms of the ligand, very different from the normal, fully-alternating pattern\textsuperscript{[7,10]} that exists in the free ligand. As a result the full complex has an armchair-like shape.

[Figure 4 here]

The cobalt atoms have octahedral coordination with bond angles deviating from the idealized values due to the five membered chelate rings and the differing bond lengths to the various donor types. Theses lengths are similar to those in other cobalt(II) structures that have an N\textsubscript{2}O\textsubscript{2}Br\textsubscript{2} donor set.\textsuperscript{[13]} The Co1…Co1A interatomic separation is 10.703(2) Å, which is slightly less than the analogous distance between the silver atoms in complex 3.

Reaction of ligand 2 with three equivalents of palladium(II) chloride gave, as expected, a trinuclear complex. However, the structure of this was somewhat different from that anticipated. Figure 5 shows a perspective view, along with selected atom labelling and bonding geometry, for the structure of 6. It crystallizes in the monoclinic space group P2\textsubscript{1}/c and has an asymmetric unit comprised of a full molecule of 2, three PdCl\textsubscript{2} units and five acetonitrile molecules, two of which are coordinated. Instead of a trinuclear complex involving palladium atoms attached to all six nitrogens, a less symmetrical structure is formed in which the bridging ligand is again hypodentate with two of the arms non-coordinated.

[Figure 5 here]

The ligand acts in a tetradentate fashion with one of the palladiums (Pd1) being bonded to two quinoline nitrogens, with the formation of a \textit{trans}-spanning\textsuperscript{[14]} 13-membered chelate ring. The other two palladiums are also \textit{trans}-coordinated, but with only one quinoline donor and a coordinated acetonitrile molecule. These two palladiums occupy unusual positions, being folded backed into the interior of the complex. Two possible explanations for this observation were considered. The first was an additional weak interaction between the palladium atoms and the nearby oxygen atoms; however, these interatomic distances [2.630(5) and 2.673(5) Å] are relatively long and such an interaction is not evidenced by any significant pyramidalization\textsuperscript{[15]} of the square planar palladium atoms. Instead, we believe that
this topology of the complex is supported by $\pi-\pi$ stacking interactions between the central aromatic ring and the two coordinated acetonitrile molecules. The central aromatic ring is sandwiched between these two groups at distances of 3.5 Å. The overall structure has approximate (but non-crystallographic) two-fold rotation symmetry. Interestingly, in this case the six arms adopt the expected $ududud$ orientation.

The ligand 2 was reacted with a variety of silver(I) substrates, since silver has played an important role in the formation of many intriguing metallosupramolecular species in recent reports.\cite{16} Reaction with silver triflate led to a trinuclear complex (7) in good yield. It crystallizes in the triclinic space group P-1 and has a full molecule of 2, three silver atoms, three triflate anions (one disordered) and four acetonitrile molecules (two coordinated) in the asymmetric unit. Figure 6 shows the structure of 7, along with atom labelling and bonding geometry. Pleasingly, in this complex the bridging ligand utilises all of its six nitrogen donors for coordination to silver. To a first approximation each silver atom has trigonal coordination with an N$_3$ donor set, consisting of two quinoline nitrogens and one acetonitrile nitrogen. One of the acetonitrile molecules acts as a bifurcated bridge between two silver atoms. Remarkably, this appears to be the first example of the structural characterisation of a complex in which acetonitrile bridges two silver atoms. Similar bridging of two and three mercury(II) centres has recently been reported.\cite{17} The geometries of the silver atoms are not trigonal planar (Figure 6), with each being significantly pyramidalized due to additional weaker interactions with nearby ether oxygen donors.

[Figure 6 here]

In this complex the shapes of the 13-membered chelate rings, resulting from chelation by adjacent arms of the ligand, are very different to those in the earlier structures, where the chelating arms were on opposite sides of the plane of the central aromatic ring and the metal approximately coplanar with central ring. In complex 7 the chelating arms are on the same sides of the substituted benzene core with the silver atoms lying well above the central ring. The arms of the ligand describe an $uuudddd$ arrangement. This is necessitated by the role of the bridging acetonitrile which helps to organise two silver atoms and four arms of the ligand on one side of the central ring. On the other side of the ring the acetonitrile molecule (coordinated to Ag2) again appears to be involved in a $\pi-\pi$ stacking interaction with the
benzene ring, lying ca 3.5 Å above it. Another π-π stacking interaction exists between two of the quinoline ring systems (those including N31 and N41) which are separated by ca 3.5 Å. The overall structure of this complex represents a topologically novel metallosupramolecular architecture.

**Conclusion**

The two new ligands described in this paper consist of four or six quinolyloxyethyl substituents attached to a central benzene core. These ligands have been shown to adopt a variety of coordination modes, with considerable variation in the relative orientations of the ligand arms as a result of the flexibility imparted by the CH₂O linker units. We believe that these ligands represent useful additions to the library of multiply armed molecules available for use in coordination and metallosupramolecular chemistry.
Experimental

General Procedures

NMR spectra were recorded on a Varian Unity 300 spectrometer with a 3 mm probe and operating at 300 MHz and 75 MHz for $^1$H and $^{13}$C, respectively. Mass spectra were recorded using a Micromass LCT TOF spectrometer. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago. 1,2,4,5-Tetrakis(bromomethyl)benzene$^{[18]}$ and hexakis(bromomethyl)benzene$^{[19]}$ were prepared by literature procedures. Solvents were purified according to literature procedures. Other reagents were obtained from commercial sources and used as supplied.

Preparation of Ligand 1.

1,2,4,5-Tetrakis(bromomethyl)benzene (0.500 g, 1.11 mmol) dissolved in 10 mL DMF was added dropwise to a stirred solution of 8-hydroxyquinoline (0.645 g, 4.44 mmol) and KOH (0.249 g, 4.44 mmol) in 10 mL DMF at 90 °C. The mixture was kept at 90 °C for 3 hours, cooled, filtered and the solvent removed. The residue was dissolved in dichloromethane, washed twice with dilute NaOH, then with water and then dried with Na$_2$SO$_4$. Chromatography on silica gel with 4:1 EtOAc/MeOH gave 1 (0.42 g, 53%) as a white solid, m.p. 243-244 °C. (Found: C 76.31, H 4.83, N 7.80%. C$_{46}$H$_{34}$N$_4$O$_4$.H$_2$O requires C 76.23, H 5.01, N 7.73%). $\delta$H (CDCl$_3$) 8.87 (4H, dd, H2'), 8.06 (4H, dd, H4'), 7.79 (2H, s, H3, H6), 7.37 (4H, dd, H3'), 7.25 (8H, m, H5', H7'), 7.01(4H, t, H6'), 5.62 (8H, s, CH2). ESMS: C$_{46}$H$_{35}$N$_4$O$_4$ requires MH$^+$ 707.2658; found 707.2662.

Crystals suitable for X-ray analysis were obtained by diffusion of diethyl ether into a solution of the ligand in CH$_2$Cl$_2$/MeOH solution.

Preparation of Ligand 2.

Hexakis(bromomethyl)benzene (1.00 g, 1.57 mmol) was added in small amounts at a time to a stirred solution of 8-hydroxyquinoline (1.370 g, 9.44 mmol) and KOH (0.530 g, 9.44 mmol) in 20 mL DMF at 80 °C. The mixture was kept at 80 °C for 3 hours, cooled and the solvent removed. The residue was dissolved in dichloromethane, washed twice with dilute NaOH, then with water and then dried with Na$_2$SO$_4$. The solution was concentrated to 5 ml to
give a white solid, which was filtered and washed with EtOH, to give pure 2 (0.90 g, 56%), m.p. 246 °C. (Found C 77.92, H 4.74, N 8.39%. C₆₆H₄₈N₆O₆ requires C 77.63, H 4.74, N 8.23%). δH (CDCl₃) 8.68 (6H, d, H₂'), 7.99 (6H, d, H₄'), 7.37 (4H, dd, H₃'), 7.25 (12H, m, H₅', H₇'), 7.18 (6H, d, H₆'), 5.83 (12H, s, CH₂). ESMS: C₆₆H₄₉N₆O₆ requires MH⁺ 1021.3714; found 1021.3694.

Preparation of Complex 3.

To ligand 1 (20.0 mg, 0.028 mmol) in CH₂Cl₂ (2 mL) was added MeOH dropwise until it dissolved. Then Ag(CF₃SO₃) (14.0 mg, 0.054 mmol) in MeOH (1 mL) was added and a precipitate formed. MeCN was added dropwise until the precipitate dissolved and then diethyl ether was diffused into the solution to give colourless crystals of [Ag₂(1)](CF₃SO₃)₂, suitable for X-ray analysis (16 mg, 49%), m.p. 256 °C. (Found C 47.48, H 2.62, N 4.54%. C₄₈H₃₄N₄O₁₀F₆S₂Ag₂ requires C 47.23, H 2.81, N 4.56%).

Preparation of Complex 4.

CuI (11 mg, 0.058 mmol) dissolved in MeCN (1 mL) was layered onto a solution of ligand 1 (20.0 mg, 0.028 mmol) in CH₂Cl₂ (2 mL) to give orange crystals of [(Cu₂I₂)₂(1)], suitable for X-ray analysis (11 mg, 52%) m.p. 182 °C. (Found C 37.37, H 2.29, N 4.22%. C₄₆H₃₄N₄O₄Cu₄I₄ requires C 37.62, H 2.33, N 3.82%).

Preparation of Complex 5.

CoBr₂ (26 mg, 0.12 mmol) dissolved in EtOH (1 mL) was added to a solution of ligand 2 (20 mg, 0.020 mmol) in CH₂Cl₂ (1 mL) to give a purple precipitate of [(CoBr₂)₂(2)](CH₂Cl₂)₃/2.EtOH (22 mg, 67%) m.p. > 300 °C. (Found C 51.09, H 3.06, N 5.16%. C₆₉.₅H₅₇N₆O₇Co₂Br₄Cl₃ requires C 51.15, H 3.52, N, 5.15%).

Crystals suitable for X-ray analysis were obtained by layering a solution of CoBr₂ in EtOH onto a solution of the ligand in CH₂Cl₂.

Preparation of Complex 6.

Ligand 2 (10 mg, 0.010 mmol) in CH₂Cl₂ (1 mL) was added to PdCl₂ (5.2 mg, 0.029 mmol) dissolved in a hot 1:1 MeCN/MeOH mixture (20 mL). The mixture was stirred briefly, filtered, then left for slow evaporation of the solvent which furnished orange crystals of [(PdCl₂)₃(2)](MeCN)₂(MeCN)₃, suitable for X-ray analysis (10 mg, 60%) m.p. 237 °C
(decomp). (Found C 49.59, H 3.48, N 6.18%. [C₆₆H₄₈N₆O₆(PdCl₂)₃(MeCN)₂]CH₂Cl₂ requires C 49.58, H 3.28, N 6.51%).

**Preparation of Complex 7.**

To ligand 2 (20 mg, 0.019 mmol) suspended and stirred in MeCN (2 mL) was added Ag(CF₃SO₃) (30 mg, 0.117 mmol) in MeCN (1 mL). Diethyl ether was diffused into the resulting solution to give colourless crystals of [Ag₃(2)](CF₃SO₃)₃(MeCN)₂, suitable for X-ray analysis (26 mg, 76%) m.p. 255 °C. (Found C 46.17, H 2.67, N 4.96%. C₆₉H₄₈N₆O₁₅F₉S₃Ag₃ requires C 46.25, H 2.70, N 4.69%).

**X-Ray Crystallography**

The crystal data and details of the data collections and refinements for the six structures are listed in Table 1. Measurements were made with a SMART CCD area detector using graphite-monochromatized Mo Kα (λ = 0.71073Å) radiation. The structures were solved by direct methods using SHELXS[20] and refined on F² using all data by full-matrix least-squares procedures with SHELXL-97.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The functions minimised were Σw (Fo² - Fc²), with w = [σ²(Fo²) + aP² + bP]⁻¹, where P = [max(Fo)² + 2Fc²]/3. Full tables of atom coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. CCDC 213696-213701 contains the supplementary crystallographic data for this paper. Copies can be obtained free of charge the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).

[Table 1 here]

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References


Scheme 1.
Figure Captions:

**Fig. 1.** Perspective view of the X-ray crystal structure of 1.

**Fig. 2.** Perspective view of the X-ray crystal structure of 3. The counterions and solvate molecules are not shown for clarity. Selected interatomic distances (Å) and angles (°): Ag1-N21 2.213(4), Ag1-N11 2.219(4), Ag1-O1 2.546(3), Ag1-O2 2.549(3), N21-Ag1-N11 172.63(16), N21-Ag1-O1 104.61(13), N11-Ag1-O1 68.06(14), N21-Ag1-O2 67.62(13), N11-Ag1-O2 108.58(13), O1-Ag1-O2 64.86(11).

**Fig. 3.** Perspective view of the X-ray crystal structure of 4. The acetonitrile solvate molecules are not shown. Selected interatomic distances (Å) and angles (°): Cu1-N11 2.009(4), Cu1-I2 2.565(1), Cu1-I1 2.608(1), N11-Cu1-Cu1A 160.77(11), N11-Cu1-I2 118.97(11), Cu1A-Cu1-I2 60.744(15), N11-Cu1-I1 115.37(11), Cu1A-Cu1-I1 61.273(15), I2-Cu1-I1 122.02(3), Cu1A-I1-Cu1 57.45(3), Cu1-I2-Cu1A 58.51(3).

**Fig. 4.** Perspective view of the X-ray crystal structure of 5. Hydrogen atoms and solvate molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Co1-N31A 2.127(7), Co1-N11 2.148(7), Co1-O3A 2.236(5), Co1-O1 2.249(5), Co1-Br1 2.4789(15), Co1-Br2 2.4800(15), N31A-Co1-N11 167.0(2), N31A-Co1-O3A 73.1(2), N11-Co1-O3A 96.1(2), N31A-Co1-O1 97.1(2), N11-Co1-O1 71.9(2), O3A-Co1-O1 70.36(18), N31A-Co1-Br1 89.93(19), N11-Co1-Br1 98.12(18), O3A-Co1-Br1 93.35(14), O1-Co1-Br1 159.28(14), N31A-Co1-Br2 96.95(18), N11-Co1-Br2 90.86(18), O3A-Co1-Br2 159.14(14), O1-Co1-Br2 93.36(13), Br1-Co1-Br2 105.16(6).

**Fig. 5.** Perspective view of the X-ray crystal structure of 6. Hydrogen atoms and non-coordinated acetonitrile molecules are not shown. Selected interatomic distances (Å) and angles (°): Pd1-N11 2.017(6), Pd1-N21 2.040(5), Pd1-Cl2 2.307(2), Pd1-Cl1 2.313(2), Pd2-N70 1.992(6), Pd2-N41 2.023(5), Pd2-Cl4 2.295(2), Pd2-Cl3 2.317(2), Pd3-N73 1.980(7), Pd3-N51 2.024(6), Pd3-Cl5 2.307(2), Pd3-Cl6 2.320(2), N11-Pd1-N21 172.4(3), N11-Pd1-Cl2 88.8(2), N21-Pd1-Cl2 90.0(2), N11-Pd1-Cl1 91.1(2), N21-Pd1-Cl1 89.9(2), Cl2-Pd1-Cl1 178.23(8), N70-Pd2-N41 177.1(2), N70-Pd2-Cl4 90.5(2), N41-Pd2-Cl4 87.4(2), N70-Pd2-
Cl3 91.1(2), N41-Pd2-Cl3 91.0(2), Cl4-Pd2-Cl3 178.30(7), N73-Pd3-N51 177.8(3), N73-Pd3-Cl5 92.6(2), N51-Pd3-Cl5 87.8(2), N73-Pd3-Cl6 88.5(2), N51-Pd3-Cl6 91.1(2), Cl5-Pd3-Cl6 177.65(7).

**Fig. 6.** Perspective view of the X-ray crystal structure of 7. Hydrogen atoms, counterions and solvate molecules are not shown. Selected interatomic distances (Å) and angles (°): Ag1-N41 2.317(3), Ag1-N51 2.366(3), Ag1-N73 2.467(4), Ag2-N70 2.209(3), Ag2-N61 2.330(3), Ag2-N11 2.369(3), Ag3-N31 2.265(3), Ag3-N21 2.318(3), Ag3-N73 2.383(4), N41-Ag1-N51 112.82(11), N41-Ag1-N73 138.64(12), N51-Ag1-N73 105.00(12), N70-Ag2-N61 136.53(11), N70-Ag2-N11 120.51(12), N61-Ag2-N11 96.83(10), N31-Ag3-N21 119.19(10), N31-Ag3-N73 117.93(13), N21-Ag3-N73 111.24(13), C74-N73-Ag3 134.1(4), C74-N73-Ag1 116.9(4), Ag3-N73-Ag1 98.27(17).
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Fig. 3. Perspective view of the X-ray crystal structure of 4. The acetonitrile solvate molecules are not shown. Selected interatomic distances (Å) and angles (°): Cu1-N11 2.009(4), Cu1-I2 2.565(1), Cu1-I1 2.608(1), N11-Cu1-Cu1A 160.77(11), N11-Cu1-I2 118.97(11), Cu1A-Cu1-I2 60.744(15), N11-Cu1-I1 115.37(11), Cu1A-Cu1-I1 61.273(15), I2-Cu1-I1 122.02(3), Cu1A-I1-Cu1 57.45(3), Cu1-I2-Cu1A 58.51(3).
Fig. 4. Perspective view of the X-ray crystal structure of 5. Hydrogen atoms and solvate molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Co1-N31A 2.127(7), Co1-N11 2.148(7), Co1-O3A 2.236(5), Co1-O1 2.249(5), Co1-Br1 2.4789(15), Co1-Br2 2.4800(15), N31A-Co1-N11 167.0(2), N31A-Co1-O3A 73.1(2), N11-Co1-O3A 96.1(2), N31A-Co1-O1 97.1(2), N11-Co1-O1 71.9(2), O3A-Co1-O1 70.36(18), N31A-Co1-Br1 89.93(19), N11-Co1-Br1 98.12(18), O3A-Co1-Br1 93.35(14), O1-Co1-Br1 159.28(14), N31A-Co1-Br2 96.95(18), N11-Co1-Br2 90.86(18), O3A-Co1-Br2 159.14(14), O1-Co1-Br2 93.36(13), Br1-Co1-Br2 105.16(6).
Fig. 5. Perspective view of the X-ray crystal structure of 6. Hydrogen atoms and non-coordinated acetonitrile molecules are not shown. Selected interatomic distances (Å) and angles (°): Pd1-N11 2.017(6), Pd1-N21 2.040(5), Pd1-Cl2 2.307(2), Pd1-Cl1 2.313(2), Pd2-N70 1.992(6), Pd2-N41 2.023(5), Pd2-Cl4 2.295(2), Pd2-Cl3 2.317(2), Pd3-N73 1.980(7), Pd3-N51 2.024(6), Pd3-Cl5 2.307(2), Pd3-Cl6 2.320(2), N11-Pd1-N21 172.4(3), N11-Pd1-Cl2 88.8(2), N21-Pd1-Cl2 90.0(2), N11-Pd1-Cl1 91.1(2), N21-Pd1-Cl1 89.9(2), Cl2-Pd1-Cl1 178.23(8), N70-Pd2-N41 177.1(2), N70-Pd2-Cl4 90.5(2), N41-Pd2-Cl4 87.4(2), N70-Pd2-Cl3 91.1(2), N41-Pd2-Cl3 91.0(2), Cl4-Pd2-Cl3 178.30(7), N73-Pd3-N51 177.8(3), N73-Pd3-Cl5 92.6(2), N51-Pd3-Cl5 87.8(2), N73-Pd3-Cl6 88.5(2), N51-Pd3-Cl6 91.1(2), Cl5-Pd3-Cl6 177.65(7).
Fig. 6. Perspective view of the X-ray crystal structure of 7. Hydrogen atoms, counterions and solvate molecules are not shown. Selected interatomic distances (Å) and angles (°): Ag1-N41 2.317(3), Ag1-N51 2.366(3), Ag1-N73 2.467(4), Ag2-N70 2.209(3), Ag2-N61 2.330(3), Ag2-N11 2.369(3), Ag3-N31 2.265(3), Ag3-N21 2.318(3), Ag3-N73 2.383(4), N41-Ag1-N51 112.82(11), N41-Ag1-N73 138.64(12), N51-Ag1-N73 105.00(12), N70-Ag2-N61 136.53(11), N70-Ag2-N11 120.51(12), N61-Ag2-N11 96.83(10), N31-Ag3-N21 119.19(10), N31-Ag3-N73 117.93(13), N21-Ag3-N73 111.24(13), C74-N73-Ag3 134.1(4), C74-N73-Ag1 116.9(4), Ag3-N73-Ag1 98.27(17).
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Graphical Abstract

Discrete metal complexes of two new multiply-armed ligands.

Muna R. A. Al-Mandhary, Christopher M. Fitchett, Peter J. Steel

The synthesis and X-ray crystal structures of five complexes of two new multidentate ligands are described. The ligands are shown to adopt a variety of coordination modes as a consequence of the flexibility imparted by the nature of the connecting groups present in their arms.