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Self-assembly of trigonal prismatic $M_6(\mu\text{–}L)_9$ coordination cages

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ABSTRACT

The new ligand bis-bidentate ligand L, containing two pyrazolyl-pyridine chelating units connected to a 1,8-anthracene-diyl core *via* methylene spacers, reacts with Zn(II), Cd(II) and Cu(II) salts to form trigonal prismatic coordination cages $[M_6(\mu\text{–}L)_9]^{12+}$ in which a metal ion occupies each vertex and a bridging ligand spans each edge; the structure is stabilised by anions which occupy the central cavity and the gaps in the centres of the triangular faces, and also by extensive inter-ligand aromatic stacking between anthracenyl and pyrazolyl-pyridine groups.

The study by many groups of polyhedral coordination cages is a fascinating aspect of supramolecular chemistry [1]. These cage complexes generally contain an array of metal ions in a regular polyhedral shape, connected by bridging ligands that span edges (connecting two metal ions), faces (connecting three or more metal ions), or both. Correct understanding and control of the geometric principles underlying the assembly can result in the ability to assembly very large cages with a high degree of confidence, as exemplified by rational syntheses of cages varying from M_4L_6 tetrahedra [2] to $M_{24}L_{48}$ cages which contain seventy-two components in a single assembly [3]. Apart from the fascination with their regular structures, cages of all sizes are characterised by hollow cavities in their centres which can form the basis of host–guest chemistry and the occurrence of unusual forms of chemical reactivity in confined environments [1-3].

Our contribution to this field has consisted of the preparation and characterisation of a family of cages based on deceptively simple ligands which contain two or three pyrazolyl-pyridine chelating termini connected to a central aromatic spacer by flexible methylene 'hinges' [1]. Two features of the ligands have turned out to be essential: (i) the flexibility of the ligands imparted by the methylene groups, whilst it precludes rational design of cages, facilitates their formation by allowing the ligand to adopt whatever conformation is most conducive to cage formation; and (ii) the central electron-rich aromatic units become involved in inter-ligand aromatic π-stacking interactions with the electron-deficient pyrazolyl-pyridine units around the periphery of the cages, which seems to play an important role in ensuring the stability of the cages in solution. The resulting family of cages is extensive and ranges in size from M_4L_6 tetrahedra [4] up to $M_{16}L_{24}$ tetra-capped truncated tetrahedra [5], including both Platonic and Archimidean solids. Some noteworthy examples include a mixed-ligand cuboctahedral cage based on a combination of edge-bridging and face-capping ligands which self-select from a mixture [6]; and a M_8L_{12} 'cuneane' which is an unusual topological isomer of a cube [7].

A tempting avenue of exploration at the moment is to incorporate fluorescent aromatic groups into bridging ligands such that the central cavity is surrounded by an array of fluorophores. This opens up the possibility of the host cage also acting as an antenna group and participating in photoinduced electron- or energy-transfer to the guest. Two series of recently-described cages have incorporated naphthyl groups in the superstructure and show fluorescence from the ligands which is modified when the cage assembles [8]; we have also prepared tetrahedral M_4L_6 and cubic M_8L_{12} cages based on anthracene-containing ligands [4,8]. Here, we describe a new ligand based on a 1,8-disubstituted anthracenyl core with two pendant pyrazolyl-pyridine units, which forms unusual trigonal prismatic M_6L_9 cages on assembly with a range of transition metal dications.

The new ligand L was prepared by reaction of 3-(2-pyridyl)pyrazole with 1,8-bis(bromomethyl)anthracene [9-11] (Scheme 1). This in turn was prepared in a multi-step procedure starting from commercial 1,8-dichloro-9,10-anthraquinone using literature methods [10]. The crystal structure of L is shown in Fig. 1[12-14]; individual bond distances and angles are unremarkable. The fluorescence spectrum of L in CH_2Cl_2 shows the usual anthracene-based emission profile (Fig. 2).

Reaction of L with $Zn(BF_4)_2$, $Cd(BF_4)_2$ or $Cu(ClO_4)_2$ in a 2:3 metal: ligand ratio, either under solvothermal conditions [15] or simply by stirring in MeOH at reflux and cooling [16], afforded solid products from which X-ray quality crystals could be grown by diffusion of diethyl ether vapour into nitromethane or MeCN solutions of the

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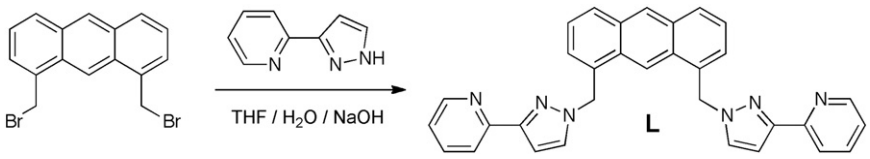

Scheme 1. Synthesis of the new ligand L.

crude materials. In all cases the crystals scattered weakly due to a combination of disorder of anions / solvent molecules, and rapid solvent loss which compromised the crystal quality. Consequently refinements are relatively poor although the gross structures and connectivities of the complex cations are clear. We use as an illustration the structure of $[Zn_6L_9](BF_4)_8(SiF_6)_2$•6MeCN for which the R_1 value is 13.3% [17].

The structure is that of a hexanuclear trigonal prismatic cage, with a bridging ligand at each vertex and a bridging ligand spanning every edge (Figs. 3, 4). Zn–N distances are unremarkable. The 2:3 metal:ligand ratio arises from the fact that each metal ion is a tris-chelate which requires six donor atoms, and each ligand can provide only four donors, so coordinative saturation requires 1.5 ligands per metal cation. As in other polyhedral cages of this family this stoichiometric condition can be met by cages which have a 2:3 ratio of vertices (metal ions) to bridging ligands (edges) and this limitation defines the range of polyhedral structures that can form [1]. Thus an octahedron—a sterically lower energy array of six metal ions than a trigonal prism – is not possible here as it would require twelve bridging ligands acting as edges, with each metal ion required to be 8-coordinate.

The arrangement of ligands is such that the two triangular faces of the prism have circular helical M_3L_3 structures with threefold symmetry due to the C_3 axis running through the centres of the triangular faces. These two cyclic helical subunits are enantiomeric, although they are not crystallographically related by an inversion centre such that the structure as a whole is still chiral. The two M_3L_3 faces are then linked by three vertical 'pillar' ligands, each of which connects a Zn(1) and a Zn(2) centre and which are all therefore crystallographically equivalent. We have noted before how many of the polyhedral cages in this family can be considered to be based on highly conserved M_3L_3 cyclic helicates that form triangular faces and are connected in a range of different ways [5]. Connecting two such faces in an approximately eclipsed manner with three bridging ligands is the simplest way in which this can be achieved. The separation between the Zn(1) centres in one face is 10.50 Å; and the separation between Zn(2) ions in the other face is 10.14 Å. The Zn(1)•••Zn(2) separation along the edges of the trigonal prism between the triangular faces is 10.48 Å.

The structure is characterised by regions of aromatic π-stacking between ligands around the periphery (Fig. 5). These stacks are invariably based on alternating sequences of relatively electron-deficient aromatic units (pyrazolyl-pyridine ligands coordinated to M^{2+} cations) and electron-rich units (anthracenyl fragments) [1]. Within each triangular helical face, for example, every anthracenyl group is sandwiched between two coordinated pyrazolyl-pyridine

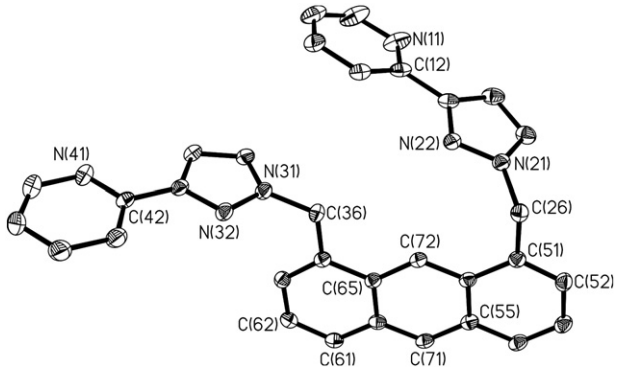

Fig. 1. Molecular structure of L taken from crystallographic data (thermal ellipsoids shown at the 40% probability level).

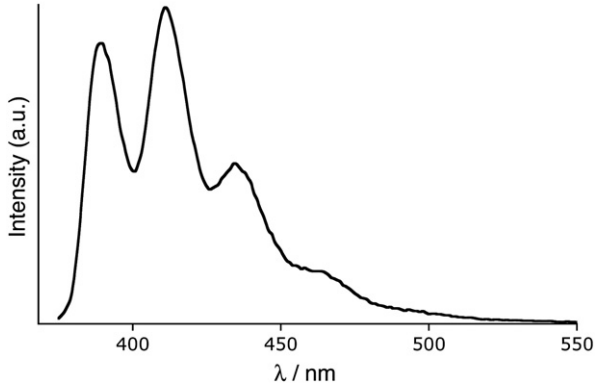

Fig. 2. Fluorescence spectrum of L in CH_2Cl_2 (room temperature).

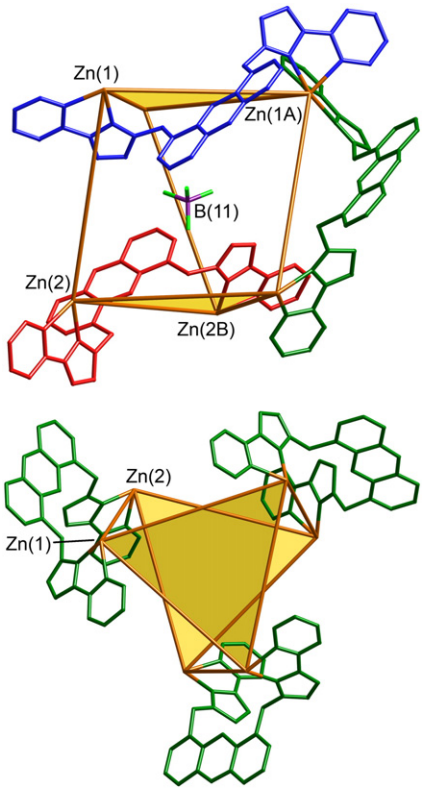

Fig. 3. Two partial views of the complex cation of $[Zn_6L_9](BF_4)_8(SiF_6)_2$•6MeCN. (a) The trigonal prismatic core of Zn(II) ions with three of the bridging ligands shown; the triangular faces which form M_3L_3 cyclic helicates are coloured in yellow, and the central tetrafluoroborate anion is also shown. (b) An alternative view looking down the crystallographic C_3 axis showing the three 'pillar' ligands which connect the two triangular faces. The offset between the two triangular units is also clear.