Formation of Interwoven or Partially Interwoven Metallomacrocyclic Networks in Copper(II) or Zinc(II) Complexes with N,N'-p-phenylenedimethylenebis(pyridin-4-one)

David M. L. Goodgame, Stephan Menzer, Amanda M. Smith and David J. Williams

Chemistry Department, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY

X-Ray structural studies show that in the compounds [Cu₂(p-XBP4)₃(NO₃)₂](NO₃)₂·2H₂O and [Zn₂(p-XBP4)₄](BF₄)₄·4H₂O [p-XBP4 = N,N'-p-phenylenedimethylenebis(pyridin-4-one)] pyridone oxygen atoms bridge pairs of metal ions to form M_2O_2 units which, in turn, are linked by p-XBP4 bridges to produce complex arrays of, for Zn, 34- and 38-membered rings or, for Cu, 68-membered rings 'threaded' by interwoven p-XBP4 strands.

The creation of molecular networks, either those purely organic in nature or those incorporating metal ions in pre-determined spatial arrays, is currently receiving considerable attention.[1] We have found that a particularly fruitful strategy for the generation of such materials is the use of extended reach ligands, such as I–III, bonded to transition metal or lanthanide ions.[2]

Alteration of the ligand design to IV, N,N'-p-phenylene-dimethylenebis(pyridin-4-one) p-XBP4, led to the formation of [Mn(p-XBP4)₃](ClO₄)₂, 1, with a remarkable interwoven, polycatenane structure.[3] Structures of this type are particularly rare and, although it is possible retrospectively to analyse some of the intermolecular forces associated with these solid-state structures, the available examples are too few to permit reliable predictions of the final structural forms. Because of this and because the full extent of the contributing intermolecular interactions have not been identified, we have extended our studies of the network-forming abilities of IV to other metals and counter ions. Here we report the structures of two new polymeric compounds, [Zn₂(p-XBP4)₄](BF₄)₄·4H₂O 2 and [Cu₂(p-XBP4)₃(NO₃)₂](NO₃)₂·2H₂O 3, obtained by the reac-

tion of p-XBP4 with zinc(II) tetrafluoroborate or copper(II) nitrate, respectively, in a mixture of methanol and acetonitrile.† Single crystal X-ray studies‡ show that these compounds incorporate a new aspect of the coordinating ability of IV—namely the formation of pyridone O-atom bridges between pairs of metal centres. The long-range bridging mode of IV is also maintained, with formation of arrays of large rings and, in the copper complex, this is accompanied by ligand threading similar to that observed in 1.

The X-ray analysis of 2 shows that, as in 1, there are two p-XBP4 ligand geometries both of which are of the desired 'extended reach' type but whose roles differ. In one case (type A) one pyridyl ring is in a near orthogonal orientation with respect to the central $p\text{-}CH_2C_6H_4CH_2$ unit, whilst the other is
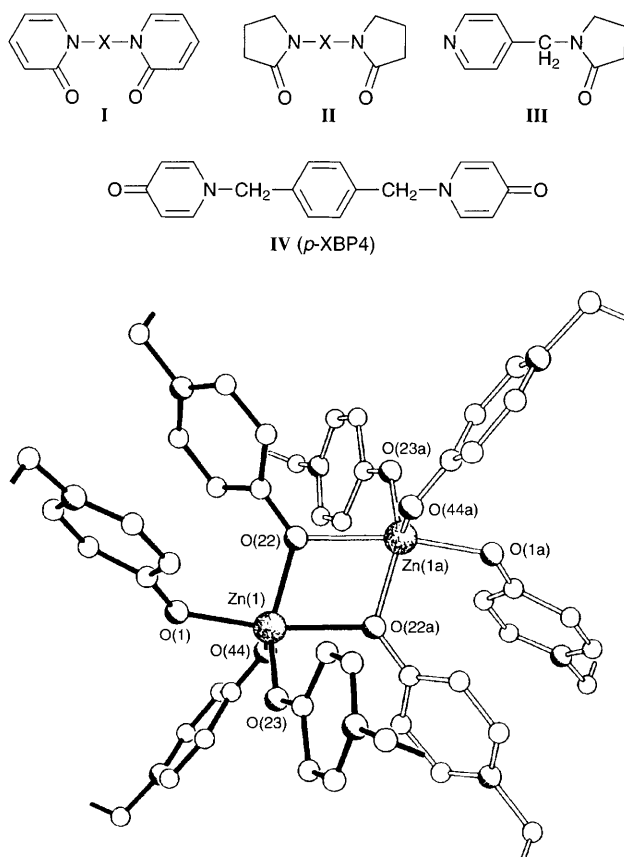

I   II   III

IV (p-XBP4)

Fig. 1 The coordination geometry of the binuclear unit present in 2, with selected bond lengths (Å): Zn(1)–O(1) 2.034(4), Zn(1)–O(22) 1.996(4), Zn(1)–O(22a) 2.255(4), Zn(1)–O(23) 1.957(4), Zn(1)–O(44) 1.943(4)
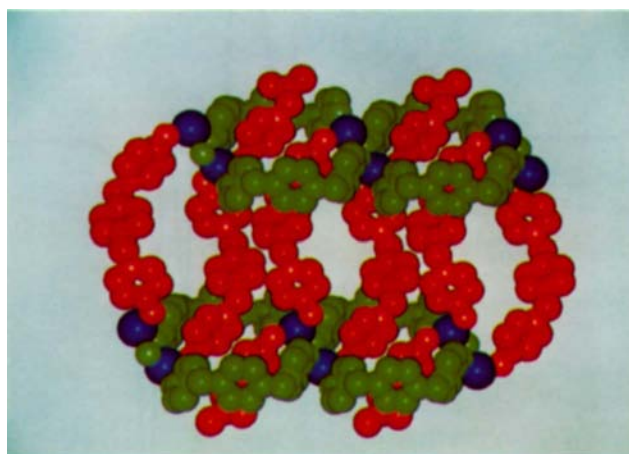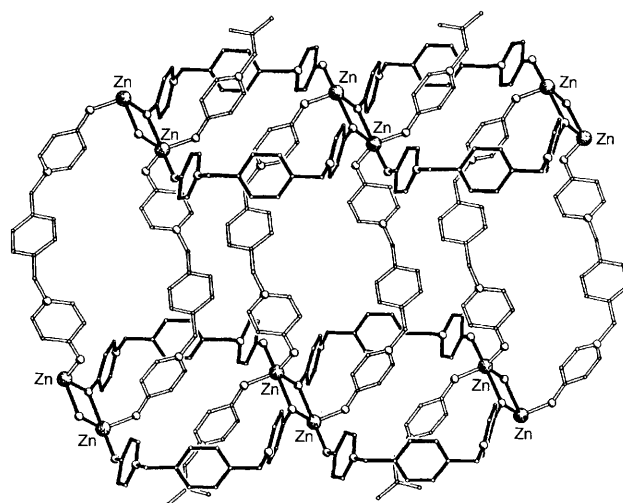

Fig. 2 Part of the extended two-dimensional network of the partially inter-threaded 34- and 38-membered rings present in the structure of 2. The type A ligands are shown with open bonds and the type B ligands with filled bonds (top). A partial space filling representation is shown below with type A ligands in red and type B in green.

oriented in an open-book conformation. In the other, (type B), one pyridyl is in an open-book conformation with respect to the p-$CH_2C_6H_4CH_2$ unit whereas the other is skewed. Ligands of type A serve to bridge lattice-translated zinc centres, analogous to their role in **1**. Ligands of type B display a new role in which one oxygen atom is binucleating whereas the other is mono-nucleating. This binding mode of the type B ligands results in the formation of C_i symmetric dinuclear units, as illustrated in Fig. 1.

Each zinc centre adopts a distorted trigonal-bipyramidal coordination geometry, with Zn–O distances in the range 1.943(4)–1.996(4) Å for the equatorial bonds and 2.034(4) and 2.255(4) Å for the axial oxygen atoms; the longest Zn–O bond is that to the bridging oxygen atom O(22a). The equatorial O–Zn–O angles are in the range 113.5(2)–129.2(2)° and the axial O–Zn–O angle is 167.9(2)°. The Zn–O–Zn bridge is
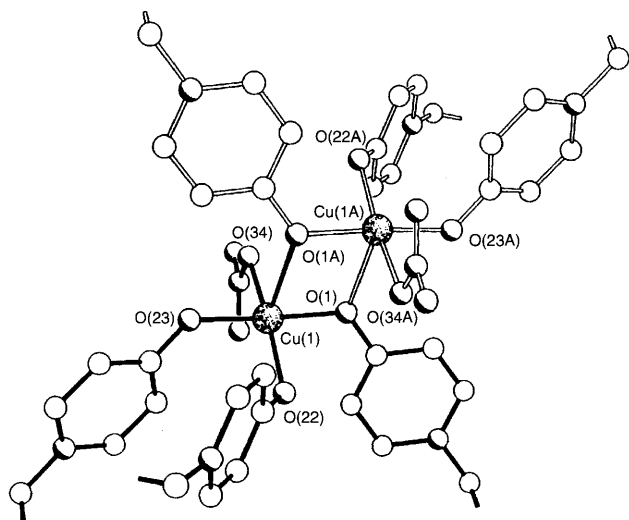
asymmetric, with trans-annular Zn···Zn and O···O distances of 3.41 and 2.55 Å respectively and O–Zn–O angles of 73.6(2)°.

The difference in the linking roles of the A and B p-XBP4 ligands results in the formation of two distinct types of macrocycle (Fig. 2). That derived from A-type ligands is 38-membered, whilst that with type B is 34-membered. These two macrocycle types combine to produce an extended two-dimensional array. The centroid–centroid separation between the p-$CH_2C_6H_4CH_2$ units in the macrocycles constructed from type B ligands is 13.4 Å. This is large enough to accommodate the insertion of two pyridyl rings from type A ligands in a π–π stacking arrangement, with an inter-planar separation of 3.4 Å and a ring centroid–ring centroid separation of 3.9 Å.

The p-$CH_2C_6H_4CH_2$–p-$CH_2C_6H_4CH_2$ separation in the macrocycles formed by the type A ligands is much less (9.6 Å), though there are, however, channels through their centres that extend in the crystallographic a direction (the horizontal direction in Fig. 2). These channels are occupied by included solvent molecules. The formation of channels perpendicular to this direction (into the plane of the paper in Fig. 2) is blocked by the BF_4^- anions.

The X-ray analysis of **3** again reveals the presence of dinuclear M_2O_2 units (Fig. 3). Each copper centre adopts, in this case, a distorted square-pyramidal geometry with bridging p-XBP4 oxygen atoms occupying both axial and basal positions and with the remaining coordination positions being occupied

Fig. 3 The coordination geometry of the binuclear unit present in **3**, with selected bond lengths (Å): Cu(1)–O(1) 1.951(5), Cu(1)–O(1A) 2.388(5), Cu(1)–O(22) 1.938(5), Cu(1)–O(23) 1.924(5), Cu(1)–O(34) 2.011(6)
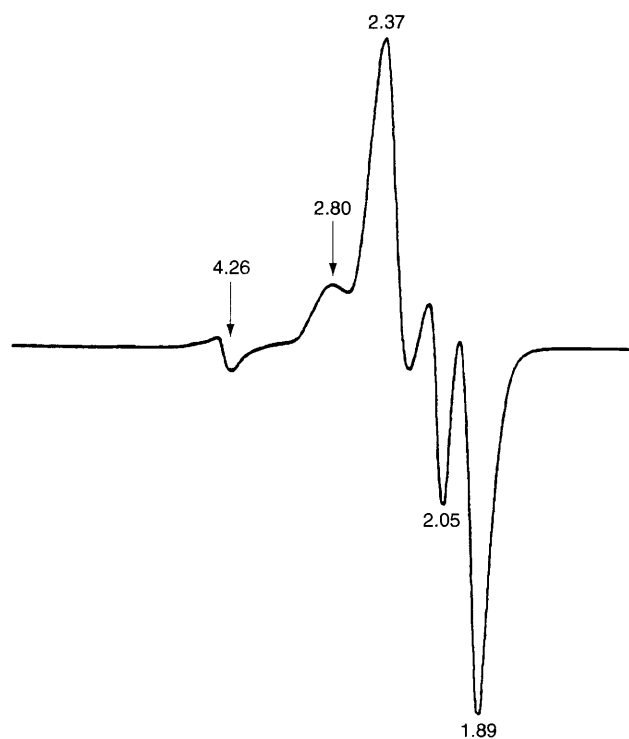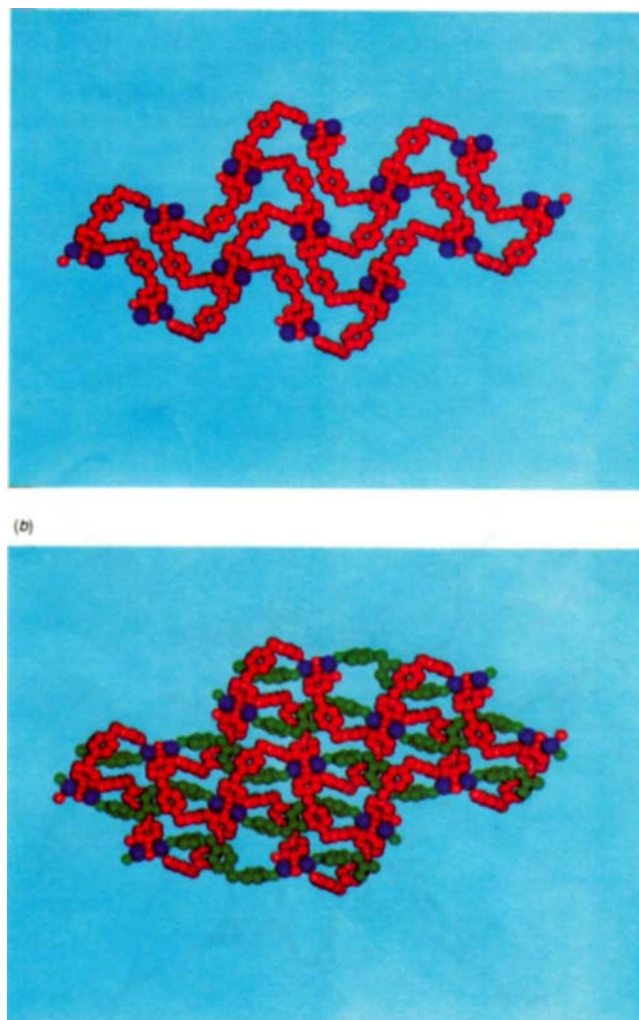

Fig. 4 X-Band EPR spectrum (at 295 K) of a powdered sample of **3**, showing the g_{eff} values of the bands

Fig. 5 (*a*) The contiguous network of 68-membered rings in the structure of **3**; (*b*) the threading of the second ligand type (shown in green) through the centre of each of the 68-membered rings (depicted in red) of the array shown in (*a*)

by two pyridone oxygen atoms and the oxygen atom of a unidentate nitrate group. The other nitrate is non-coordinated. The Cu–O(basal) distances are in the range 1.924(5)–2.011(6) Å and the Cu–O(axial) distance is 2.388(5) Å. The *trans*-annular Cu⋯Cu and O⋯O distances are 3.34 and 2.87 Å respectively. This close approach of the Cu centres results in Cu⋯Cu spin coupling and an $S = 1$ type EPR spectrum (Fig. 4).

As in **2**, there are two *p*-XBP4 ligand conformations and network-defining roles. One ligand geometry has the type B conformation and has a binucleating/mononucleating role analogous to that observed in **2**. However **2** and **3** differ in the torsional relationship between the binucleating pyridone ring and its associated M_2O_2 unit (48° in **2**, *cf.* 3° in **3**), which, for **3**, results in a doubling of the ring size to 68-membered and the formation of the network shown in [Fig. 5(*a*)]. The other *p*-XBP4 ligand has the pyridone rings centrosymmetrically disposed but skewed to a position intermediate between an orthogonal and an open book conformation with respect to the *p*-CH$_2$C$_6$H$_4$CH$_2$ spacer. These ligands [depicted in green in Fig. 5(*b*)] adopt a threading role very similar to that observed[3] in **1**. They link diametrically opposite copper atoms within the 68-membered ring, with the *p*-CH$_2$C$_6$H$_4$CH$_2$ spacer of the threading linkage sandwiched between those of two type B ligands. This arrangement is stabilised by T-type aromatic–aromatic edge-to-face interactions.§

This result reinforces our previous observation that the *p*-XBP4 ligand has a predilection for forming interwoven networks but also shows that the precise form of the polycatenated or pseudo-polycatenated array that is formed is both metal- and counter ion-dependent. This further emphasizes the importance of the use of ligand conformational preferences and their associated mutual π–π interactions as part of the design strategy for creating new interwoven, polycyclic arrays.

Footnotes

References

1 Lead-in references to some of the approaches adopted include: B. F. Abrahams, B. F. Hoskins, D. M. Michall and R. Robson, *Nature*, 1994, **369**, 727; L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325; M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; H. O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat and O. Kahn, *J. Am. Chem. Soc.*, 1994, **116**, 3866; S. R. Batten, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 820; T. Soma and T. Iwamoto, *Chem. Lett.*, 1995, 271; C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1079; B. F. Hoskins, R. Robson and N. V. Y. Scarlett, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1203.

2 G. A. Doyle, D. M. L. Goodgame, S. P. W. Hill, S. Menzer, A. Sinden and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 2850 and references cited therein.

3 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 574.

4 G. M. Sheldrick, University of Göttingen, 1995.