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Aggregation of metallo-supramolecular architectures by metallo-assembled hydrogen bonding sites†

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Metal–ligand interactions are used not only to design metallo-supramolecular architectures but also to assemble multiple hydrogen bond sites at the periphery of these architectures. The hydrogen bond sites aggregate the architectures into polymeric arrays with the selection of anion determining whether this is self H-bond aggregation or anion-mediated H-bond aggregation.

Biological systems make extensive use of non-covalent self-assembly events to generate large and functional arrays. Chemists too have made considerable progress in using supramolecular interactions to design large molecules of defined shape.[1] Yet underpinning the supramolecular approach is the use of covalent synthesis to design the building blocks. Covalent synthesis introduces limitations to the size of building blocks and thus of the subsequent supramolecular array. One approach to circumvent this is to use multiple recognition events in sequence, *i.e.* to use an initial supramolecular event to construct small supramolecular units which are then used as building blocks in a second supramolecular event to give a higher order (and larger) aggregate. In this context we have recently illustrated how metal–ligand and π–π interactions can be used in concert, π-interactions aggregating metallo-supramolecular units into larger nanoscale arrays.[2] We have similarly demonstrated sequential assembly using two different types of metal–ligand interaction.[3] Very recently Bermejo, Gatteschi *et al.* have applied the approach to design magnetic materials assembled from cupric helicates.[4] Still more sophisticated assemblies might be envisaged in which many different supramolecular events are designed into the assembly pathway. For this reason we are exploring routes to employ alternate supramolecular interactions too. We describe herein the use of hydrogen bonds to aggregate metallo-assembled boxes and helicates into larger arrays.

Although a number of mononuclear metal complexes containing H-bonding sites have been described, examples with metallo-supramolecular architectures are rare.[5] To achieve directional control, two or more hydrogen bonds must be formed between each component, yet building blocks containing multiple hydrogen bonding acceptors and donors are often associated with challenging covalent synthesis (and potential solubility problems). Our design employs ligands function-alised with discrete sites that can form just a single hydrogen bond. However, these sites are positioned such that in the metallo-supramolecular architecture they are brought together to create a multiple hydrogen bond unit. Thus the metal–ligand interactions will not only form the desired architecture but also create the aggregation sites. This approach has considerable potential benefits in terms of simplifying the covalent synthesis.
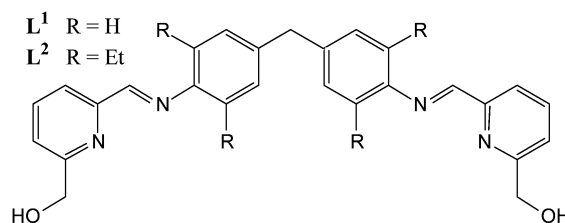
The functionalised ligands (L^1 and L^2) are readily-prepared from the condensation of the appropriate diamine with 6-hydroxymethylpyridine-2-carboxaldehyde which we have prepared in a single step from commercial 2,6-pyridinedimethanol. Hydroxy groups were selected as they are simple units which can act as either H-bond donors or acceptors. We have previously demonstrated that the unsubstituted analogues of these ligands react with tetrahedral monocations to form two dinuclear species: a dimeric box (*meso*-isomer) and a dimeric helicate (*rac*-isomer).[6] The introduction of ethyl groups onto the spacer leads to the exclusive formation of the *rac*-isomer.

Reaction of L^1 with [Cu(MeCN)$_4$][PF$_6$] in methanol led to the formation of a red-brown complex of dinuclear [Cu$_2$(L^1)$_2$]$^{2+}$ formulation. The room temperature ^{1}H NMR spectrum in CD$_3$CN showed a single set of resonances, some of which were broadened, and low temperature studies confirmed the presence of two species (the *meso*- and *rac*- isomers; readily identified from the central CH$_2$ resonance which is a singlet for the *rac*-isomer and two doublets for the *meso*-isomer) in solution. The *meso*-isomer is the enthalpic product, while the *rac*-isomer is favoured entropically.[6] Recrystallisation from acetonitrile by the slow diffusion of diethyl ether afforded crystals of the *meso*-isomer suitable for X-ray crystallography. The structure (Fig. 1) reveals the expected metallo-supramolecular box units. The metal coordination does indeed create di- hydrogen bond sites and the boxes are linked together through pairs of hydrogen bonds to give infinite chains of boxes (O–H···O 1.98 Å; O···O 2.68 Å; ∠OHO 140°). The cavities of the boxes are filled with acetonitrile solvent molecules (see supplementary information†).

Fig. 1 Structure of the chains of cations observed in the structure of [Cu$_2$(L^1)$_2$][PF$_6$]$_2$; hydrogens are omitted except those in the H-bonds
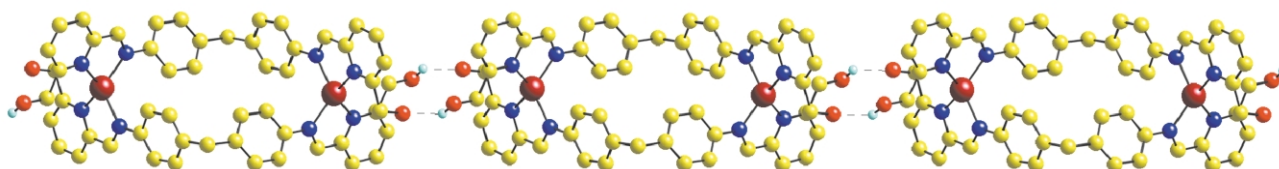
Fig. 2 Structure of the chains of cations observed in the structure of $[Cu_2(L^2)_2][PF_6]_2$; hydrogens are omitted except those in the H-bonds.
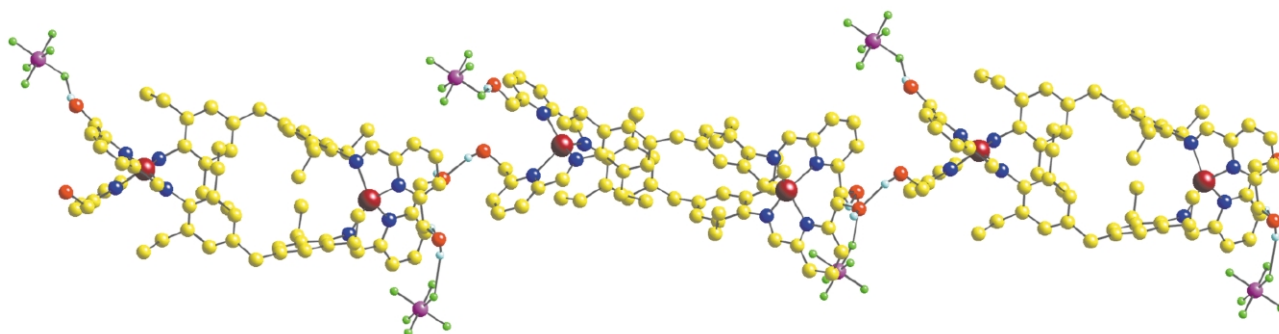

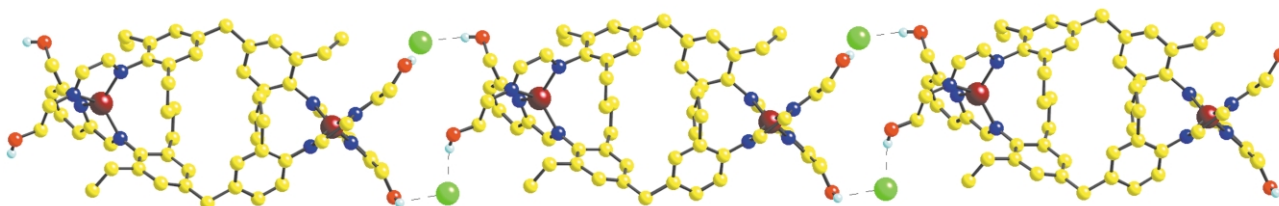**Fig. 3** Structure of the chains of cations observed in the structure of $[Cu_2(L^2)_2]Cl_2$; hydrogens are omitted except those in the H-bonds.

The corresponding copper(I) complex of L^2 (which contains ethyl groups on the phenyls of the spacer units) was also prepared. As expected the introduction of the ethyl groups leads to the formation of only the *rac*-isomer (double-helicate); Mass spectrometry confirms a dinuclear $[Cu_2(L^2)_2]^{2+}$ formulation and NMR reveals a single solution species, even at low temperature, in which the central CH_2 resonance is a singlet. Recrystallisation of the hexafluorophosphate complex from acetonitrile by diffusion of diethyl ether yielded suitable crystals. The X-ray crystal structure (Fig. 2) confirms the double-helical structure of the cations. These double-helical cations are again linked into infinite chains through hydrogen-bonding interactions (O–H···O 1.89 Å; O···O 2.71 Å; ∠OHO 169°). However, in contrast to the structure with L^1, in this structure a single hydrogen bond links adjacent cations. The other hydroxy groups engage in hydrogen bonding to fluorine groups from the anions (O–H···F 2.16, 2.26 Å; O···F 2.99, 3.09 Å; ∠OHF 166, 169°). Within the chains the helicity of the cations alternates rendering the chains achiral.

The 'interference' of the anions in the hydrogen bonding motif might at first appear to be a potential problem for integrating hydrogen-bonding with assembly of cationic metallo-supramolecular architectures. While the interference could potentially be circumvented by using anions without electronegative atoms, such as tetraphenylborate, such anions will inevitably introduce alternate competing supramolecular interactions (for example Dance[7] has elegantly demonstrated the use of tetraphenylborate in aryl crystal embraces). However the ability of anions to act as H-bond acceptors can be turned to our advantage by incorporating this feature into the supramolecular design; how this can be achieved is illustrated by using chloride as the anion.

The comparatively small, spherical chloride anion has strong potential to act as a hydrogen bond acceptor and can do so to multiple hydroxy groups. Suitable crystals of the chloride salt were obtained from methanol solution by diffusion of benzene. The crystal structure (Fig. 3) again reveals double-helical cations linked into an infinite chain. However, in contrast to the hexafluorophosphate salt, the hydroxy units are not hydrogen bonded to each other but to chloride anions which bridge between hydroxy groups (O–H···Cl 2.21, 2.28, 2.23, 2.50 Å; O···Cl 3.04, 3.11, 2.99, 3.02 Å; ∠OHCl 171, 167, 151, 122°). Thus, rather than acting alternately as donors and acceptors, in

this structure each hydroxy acts as a hydrogen bond donor. Adjacent cations are connected through two such bridges and all hydroxys are involved in the hydrogen bonding network. The anions are now incorporated within the supramolecular chain rather than lying outside it as in the other structures. Within the chains each cation possesses the same helicity (leading to chiral helical chains), while the helicity alternates between chains rendering the overall structure achiral.

We have demonstrated herein that a metal-directed assembly process may be harnessed to create not only supramolecular architectures but also to create multiple H-bond sites using readily prepared ligands bearing discrete H-bond units. These multiple H-bond sites may be used to aggregate the metallo-supramolecules into larger assemblies. Anions can compete with the hydrogen bonding but this feature can be integrated into the molecular design to yield arrays in which the anion is incorporated rather than remote. We are currently exploring how to integrate further supramolecular interactions to design more sophisticated assembly pathways based on multiple recognition events.

Notes and references

1 J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, 1995; *Comprehensive Supramolecular Chemistry*, Eds. J. L. Atwood, J. E. D. Davies, J.-M. Lehn, D. D. MacNicol and F. Vogtle, Pergamon: Oxford, 1996.
2 L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2001, **40**, 1079–1081; L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2002, **41**, 4244.
3 M. J. Hannon, C. L. Painting and W. Errington, *Chem. Commun.*, 1997, 1805.
4 M. Vázquez, A. Taglietti, D. Gatteschi, L. Sorace, C. Sangregorio, A. M. González, M. Maneiro, R. M. Pedrido and M. R. Bermejo, *Chem. Commun.*, 2003, 1840.
5 E. Breuning, U. Ziener, J.-M. Lehn, E. Wegelius and K. Rissanen, *Eur. J. Inorg. Chem.*, 2001, 1515; Z. Qin, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2001, 2676.
6 M. J. Hannon, C. L. Painting and N. W. Alcock, *Chem. Commun.*, 1999, 2023; M. J. Hannon, C. L. Painting, J. Hamblin, A. Jackson and W. Errington, *Chem. Commun.*, 1997, 1807.
7 See for example: P. A. W. Dean, M. Jennings, U. Rajalingam, D. C. Craig, M. L. Scudder and I. G. Dance, *CrystEngComm*, 2002, U1.