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# Molecular self-recognition: a chiral [Mn(II)6] wheel *via* donor–acceptor π···π contacts and H-bonds†

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A multinucleating ligand capable of establishing different types of intermolecular interactions, when combined with acetate groups leads to the assembly of a chiral [Mn(II)3] cluster poised for a process of self-recognition through a combination of perfectly complementary weak forces.

Molecular recognition phenomena are of paramount importance in biochemistry, with one of the most useful expressions found in their double helix of DNA. Synthetic chemists have been able to recreate these processes by exploiting the intermolecular interactions expected between judiciously designed molecules, especially in the arena of organic chemistry.[1–6] However, a particularly relevant area of supramolecular chemistry involves metal-containing molecules.[7] In this context, helical coordination complexes have proven to bind non-covalently to the major groove of DNA[8] and also to the heart of the Y junctions featured occasionally by this macro-molecule.[9] These interactions have been proven to dramatically influence the normal development of crucial DNA transactions.[10] Such precedents suggest that the design and development of coordination assemblies incorporating specific functions for molecular recognition represent a promising avenue to influence or perturb biological processes through selective interaction with macro biomolecules.

Here, we have employed the new ligand 2,6-bis-(5-(naphth-2-yl)-pyrazol-3-yl)pyridine (H2L, Scheme 1, details have been reported elsewhere),[11] exhibiting several coordinating atoms for binding to metals. In addition, H2L incorporates potential donor and acceptor moieties for the establishment of hydrogen bonds, as well as
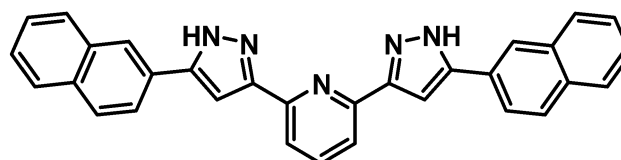
Scheme 1 The structure of H2L.

electron rich and electron poor aromatic fragments. Upon reacting with Mn(AcO)2, this ligand facilitates the formation of the chiral trinuclear cluster [Mn3(AcO)4(HL)2] (**1**), which possesses all the ingredients for molecular recognition. In fact, pairs of molecules with the same parity interact with each other by means of a series of complementary intermolecular contacts leading to metallo-supramolecular dimers of a helical nature. The structural details of this assembly, resulting from a self-recognition process, together with its physico-chemical properties, are presented here.

The H2L ligand is analogous to other 2,6-bis-(pyrazol-3-yl)pyridine ligand derivatives, exhibiting aromatic extensions at both ends of the central core, which have proven successful in fostering intermolecular interactions in the context of spin crossover molecular materials.[12–14] The ligand could be easily formed in a high yield by reacting the bis-β-diketone precursor,[15] which we have made using a modified form of the Claisen con-densation, with hydrazine.[16] It reacts with Mn(II) from a mixture of Mn(AcO)2 and NBu4MnO4, originally intended to contain also Mn(III), as a way to emulate the rich chemistry demonstrated[17,18] by the 2-hydroxyphenyl counterpart of the naphthyl ligand H2L. The resulting coordination product, [Mn3(AcO)4(HL)2] (**1**), only contains Mn(II). However, it was not possible to generate this compound in the absence of the permanganate salt. While the crucial role of NBu4MnO4 in this process is not clear, it could be related to the necessity of a good base to partially deprotonate H2L. However, attempts to form **1** from its constituents in basic conditions were unsuccessful and in fact, they only led to the crystallization of the composite ensemble [H2L·(Bu4N)(AcO)·H2O] (Fig. S1 and Tables S1 and S2, ESI†). Compound **1**, in turn, crystallizes in the monoclinic

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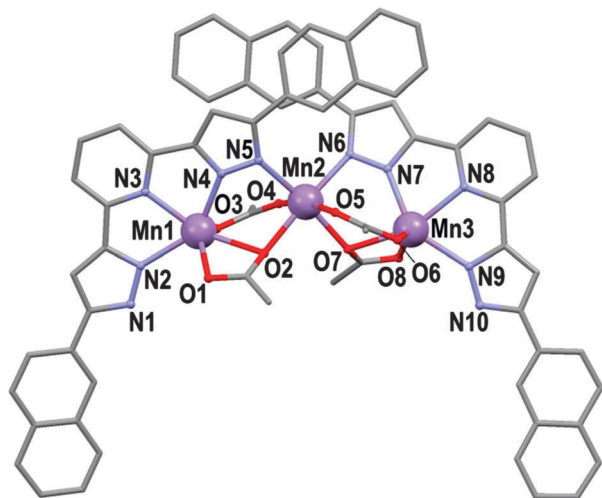*[c] Advanced Light Source, Berkeley Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA*

Fig. 1 A molecular representation of [Mn$_3$(AcO)$_4$(HL)$_2$] (**1**), with the hetero-atoms and metal atoms labelled (only one unique molecule shown). The carbon atoms are in grey and the hydrogen atoms are not shown. Average selected parameters (Å or °): Mn–N$_{pz}$, 2.251; Mn–N$_{py}$, 2.242; Mn–O, 2.212; Mn···Mn$_{(adj.)}$, 3.649; Mn–O–Mn, 105.68; Mn–Mn–Mn, 148.48.
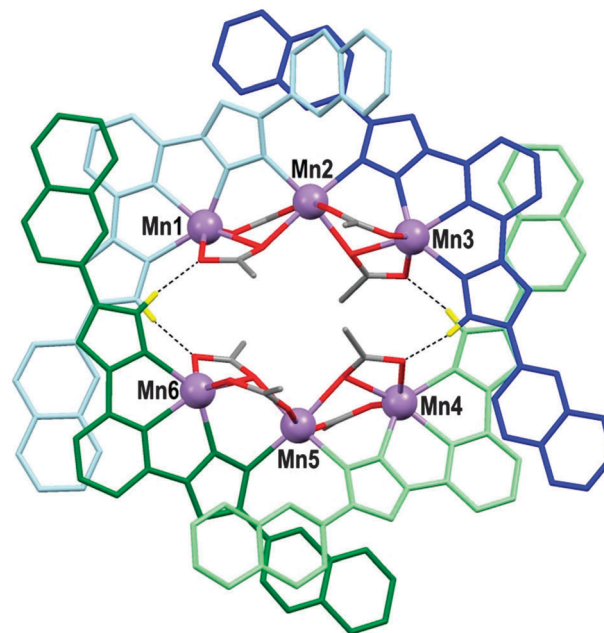

Fig. 2 The representation of two molecules of [Mn$_3$(AcO)$_4$(HL)$_2$] (**1**), linked through a network of intermolecular interactions consisting of eight donor–acceptor π···π interactions of varying strength and four hydrogen bonds (dashed lines). Only the metal atoms are labelled. The HL$^-$ ligands from both molecules are light or dark blue and green colours. The oxygen atoms are in red, and the carbon atoms from the acetates are in grey. Only the hydrogen atoms situated on the heteroatoms are shown (in yellow).

space group $P2_1/c$, and the asymmetric unit consists of two crystal-lographically distinct [Mn$_3$(AcO)$_4$(HL)$_2$] moieties together with two lattice molecules of THF. The molecule (Fig. 1) is chiral and in the crystal, it is intimately associated with another molecule of the same parity forming supramolecular [Mn$_3$]$_2$ dimers of a helical nature. The crystal possesses, by virtue of inversion symmetry, an equal amount of an analogous species of opposite chirality, thus consti-tuting a perfect racemic mixture. Crystallographic data and metric parameters are listed in the ESI† (Tables S1 and S3–S5), while selected numbers can be found listed in the Fig. 1 caption. Each neutral [Mn$_3$(AcO)$_4$(HL)$_2$] complex (Fig. 1 and Fig. S2, ESI†) com-prises three Mn(II) atoms in pseudo-octahedral N$_2$O$_4$ (central ion) or N$_3$O$_3$ (end ions) coordination environments posed in an angular configuration. The distal ions are chelated by the three N-atoms of a bis-pyrazolylpyridine (bpp) moiety and a carboxylate ligand while forming a bond to a second, bridging carboxylate. One pyrazolyl ring from each bpp group bridges its own external Mn ion to the central one. The bridging is completed by two AcO$^-$ groups each side. Thus, the heteroleptic assembly comprises two μ-HL$^-$ ligands and four μ-AcO$^-$ groups, leading to a chiral helical structure. Each molecule is perfectly configured for face-to-face interaction with an (idealized) identical partner, *i.e.* the other molecule in the asymmetric unit, through a series of cooperative, complementary intermolecular interactions (Fig. 2). First of all, the pyrazolyl N–H group of each HL$^-$ ligand acts as the donor end of a hydrogen bond with an O-atom from a chelating AcO$^-$ group in the opposite molecule, thus completing a total of four such interactions (Table S4, ESI†). In addition, each electron-rich naphthyl moiety establishes a donor–acceptor interaction with one electron-deficient (and metal coordi-nated) pyrazolylpyridine moiety, and the ensemble of interactions (of varying strength) sums to a total of eight (Fig. S2 and Table S5, ESI†). These complementary interactions are analogous to those seen within coordination cages made from a ligand also comprising both naphthyl and metal bound pyrazolylpyridine moieties.[19] As opposed

to H$_2$L, in the coordination cages, the electron rich group acted as a spacer for two electron deficient fragments and the interactions were intramolecular, conferring added stability to the resulting molecular cluster. Here, the donor–acceptor π···π bonds are between different species and the result is a supramolecular dimer of a cyclic, helical nature. The cycles interact at both ends, with four symmetry-related equal entities (Fig. S3, ESI†). On one side, the [Mn$_3$]$_2$ assemblies feature one type of chirality, while on the other side, they exhibit the opposite parity. These contacts occur in form of π···π stacking interactions that are more efficient between species of the same chirality than in the opposite case. In the first situation, adjacent dimers establish four well-defined complementary donor–acceptor interactions, like those described within the dimers (Fig. 3). As a result, the helical cycles are stacked within the crystal, forming supramolecular tubes parallel to the crystallographic b axis. Each tube is thus adjacent to two other tubes of opposite chirality, the ensemble producing planar sheets of well packed rods, where pairs of adjacent tubes of the same chirality (Fig. 4) alternate with pairs of opposite chirality.

Evidence for the persistence of complementary (donor–acceptor) π···π stacking in solution is provided by the fluorescence spectrum of **1** in DMSO (Fig. 5). The spectrum is dominated by a broad signal near 480 nm, which is significantly red-shifted with respect to the emission of naphthalene based moieties[20] and in fact, from that exhibited by the free ligand under the same conditions. The red-shift is similar to that attributed to the formation of exciplexes (the association of non-equal aromatic moieties in solution through π···π interactions)[21] and is caused by the stabilization
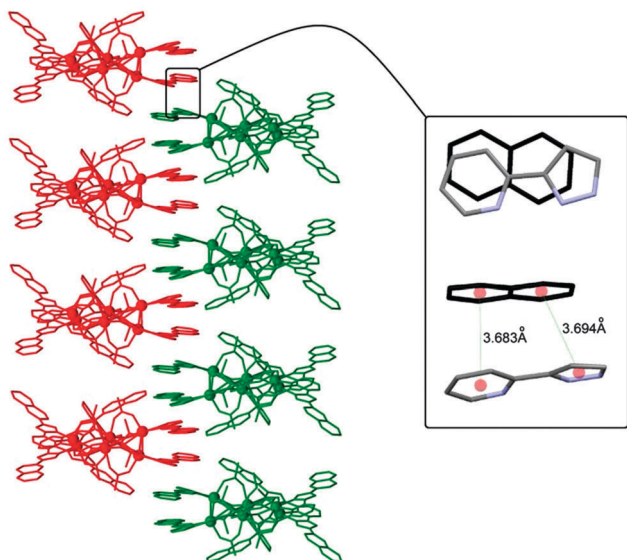
Fig. 3 A representation of the interactions between iso-chiral $[Mn_3]_2$ dimers of **1**, forming adjacent rods parallel to the *b* axis. Two views of the four donor–acceptor interactions established between each pair of $[Mn_3]_2$ dimers are shown on the right side, with inter-centroid distances indicated.

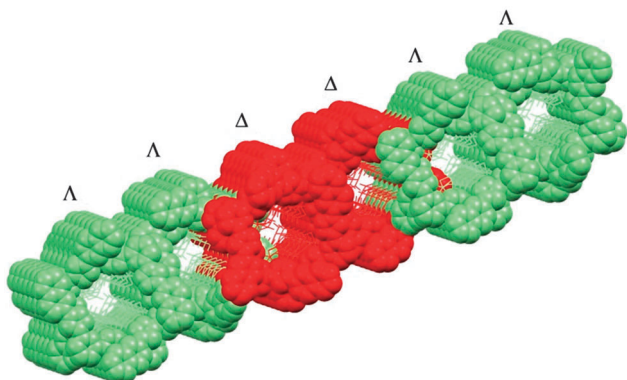**Fig. 4** A representation of six adjacent rods of $[Mn_3]_2$ dimers of **1**, running parallel to the crystallographic *b* axis. Pairs of adjacent rods of one chirality alternate with pairs of the opposite chirality.

of the naphthyl-based excited state involved in the emission as a result of its interaction with electron deficient rings. Here, the interaction would be intramolecular (as seen before with cages involving naphthyl containing ligands)[19,21] and between both members of the supramolecular assembly.

In the spectrum, a significant presence of the non-interacting naphthyl group persists, which can be attributed to a portion of free ligand in equilibrium, to the contribution of the naphthyl moiety non-associated to other rings when the dimers of **1** are dissociated, or both. Thus, the fluorescence spectrum neither confirms nor rules out the persistence of the $[Mn_3]_2$ dimers in solution.

The magnetic properties of the $[Mn_3]_2$ wheels were examined through variable temperature bulk magnetization measurements under a constant magnetic field (of 3 kG). A plot of
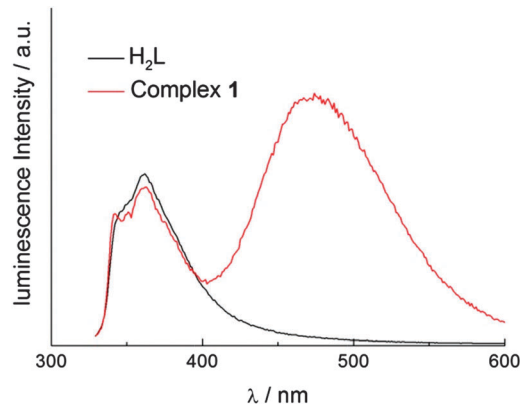

Fig. 5 The fluorescence spectra in DMSO (λ_{exc} = 309 nm) of the $[Mn_3]_2$ dimers in **1** (red line) and of the ligand H_2L.

χT *vs.* T (χ is the molar paramagnetic susceptibility) indicates that the Mn(II) ions within **1** exhibit primarily antiferromagnetic interactions (Fig. S4, ESI†). These data were fitted to the Van Vleck equation[22] that results from considering the spin Hamiltonian of eqn (1).

$$H = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_2) - 2J_2\hat{S}_1\hat{S}_3 \qquad (1)$$

In eqn (1), all of the spin operators are $\hat{S}_i$ = 5/2, and the subscripts coincide with the labels of the metal atoms in Fig. 1. The best fit was obtained for the following parameters; J_1 = −0.38 cm^{-1}, J_2 = −0.03 cm^{-1} with g_{Mn} = 2.0 as a fixed parameter. The weak magnetic coupling is consistent with what is usually observed for Mn(II) ions. There are no precedents in the literature for the exact topology and magnetic pathways observed within the core of **1**. The closest example is a "V" shaped $[Mn_3]$, aggregate, involving a bis-pyrazolyl ligand and carboxylates, however, a comparison is not possible since the central ion in that compound is Mn(III).[23] The second closest example features one NN bridge from a pyrazolyl moiety, a μ-AcO⁻ group and a bridging OH⁻ ligand between the Mn ions. In this case however, the external metal ions are Mn(III).[24]

The combination of a naphthyl substituted bis-pyrazolyl-pyridine and carboxylates with Mn(II) favours the formation of a chiral $[Mn_3]$ cluster that dimerizes as helical wheels by a process of molecular recognition through an array of inter-molecular interactions of various types. The fluorescence spectra suggest the persistence of the assembly in solution. The helicity of the mono and dimeric species, together with their versatile potential for intermolecular interactions could render these species of interest for their interaction with the specific sites of macrobiomolecules.

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