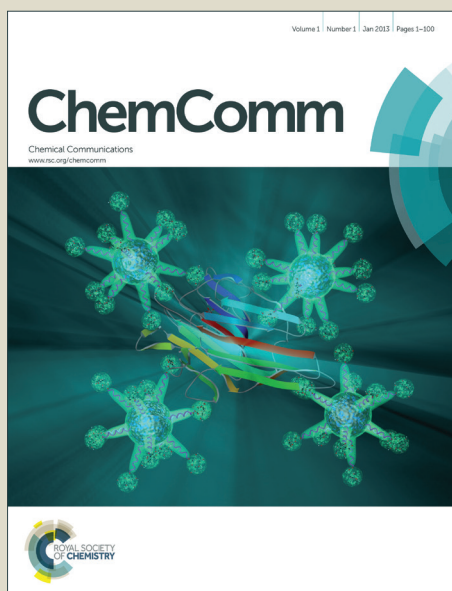


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COMMUNICATION

Molecular Self-recognition: A Chiral [Mn(II)₆] Wheel via Donor-Acceptor $\pi \cdots \pi$ Contacts and H-Bonds

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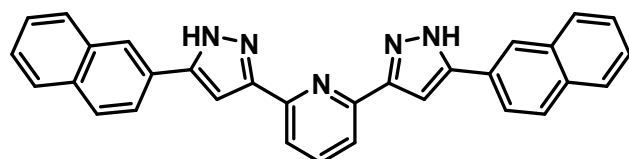
L. A. Barrios,^a J. Salinas-Uber^a O. Roubeau,^b S. J. Teat^c and G. Aromí^{a,*}Received 00th January 2012,
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A multinucleating ligand capable of establishing different types of intermolecular interactions combined with acetate groups leads to the assembly 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, finding one of its maximum expressions in the 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 A particularly relevant area of supramolecular chemistry involves however metal containing molecules.⁷ In this context, helical coordination complexes have proven successful in binding non-covalently to the major groove of DNA⁸ and also at the heart of Y junctions featured occasionally by this macromolecule.⁹ These interactions have proven to influence dramatically 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. We have here employed the new ligand 2,6-bis-(5-(naphth-2-yl)-pyrazol-3-yl)pyridine (H₂L, Scheme I, details will be reported elsewhere),¹¹ exhibiting several coordinating atoms for

Scheme I H₂L.

binding to metals. In addition, H₂L incorporates potential donor and acceptor moieties for the establishment of hydrogen bonds as well as 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 helical nature. The structural details of this assembly resulting from a self-recognition process together with its physico-chemical properties are presented here.

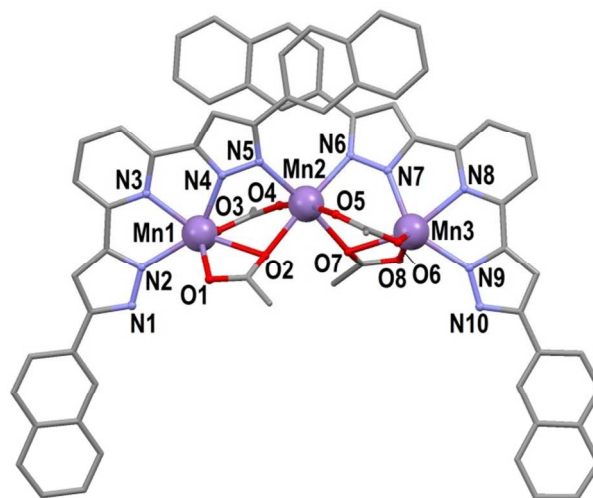


Figure 1 Molecular representation of [Mn₃(AcO)₄(HL)₂] (**1**), with heteroatoms labelled (only one unique molecule shown). Carbon atoms are in grey and hydrogen atoms not shown. Average selected parameters (Å or °): Mn–N_{py}, 2.251; Mn–N_{pyr}, 2.242; Mn–O, 2.212; Mn $\cdots$ Mn_(adj.), 3.649; Mn–O–Mn, 105.68; Mn–Mn–Mn, 148.48.

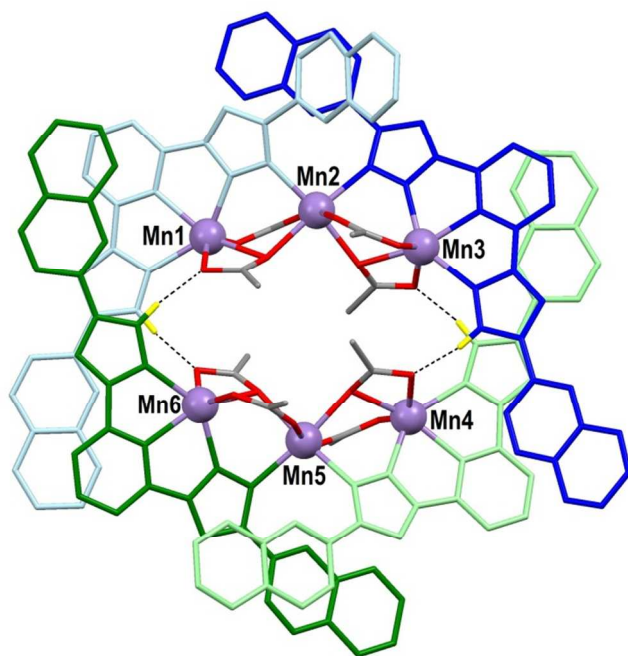


Figure 2 Representation of two molecules of $[\text{Mn}_3(\text{AcO})_4(\text{HL})_2]$ (**1**), linked by a network of intermolecular interactions consisting of eight donor-acceptor $\pi \cdots \pi$ interactions of varying strength and four hydrogen bonds. Only metal atoms labelled. HL^- ligands from both molecules are light or dark blue and green colours, respectively. Oxygen is in red, carbon from acetate is grey. Only hydrogen atoms riding on heteroatoms shown (in yellow).

Ligand H_2L is analogous to other derivatives of 2,6-bis-(pyrazol-3-yl)pyridine ligands exhibiting aromatic extensions at both ends of the central core, which have proven successful to foster intermolecular interactions in the context of spin crossover molecular materials.^{12–14} It could be easily formed in high yield by reaction with hydrazine of the bis- β -diketone precursor,¹⁵ which we have made through a modified form of the Claisen condensation usually employed.¹⁶ It reacts with $\text{Mn}(\text{II})$ from a mixture of $\text{Mn}(\text{AcO})_2$ and NBu_4MnO_4 originally intended to contain also $\text{Mn}(\text{III})$, as a way to emulate the rich chemistry demonstrated^{17, 18} by the 2-hydroxyphenyl counterpart of the naphthyl ligand H_2L . The resulting coordination product, $[\text{Mn}_3(\text{AcO})_4(\text{HL})_2]$ (**1**), only contains $\text{Mn}(\text{II})$. However, it was not possible to generate this compound in the absence of the permanganate salt. While the crucial role of NBu_4MnO_4 in this process is not clear, it could be related to the necessity of a good base to partially deprotonate H_2L . 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 $[\text{H}_2\text{L} \cdot (\text{Bu}_4\text{N})(\text{AcO}) \cdot \text{H}_2\text{O}]$ (Fig S1 and Tables S1 and S2). Compound **1**, in turn, crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit consists of two crystallographically distinct $[\text{Mn}_3(\text{AcO})_4(\text{HL})_2]$ 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 $[\text{Mn}_3]_2$ dimers of helical nature. The crystal possesses by virtue of inversion symmetry an equal amount of analogous species of opposite chirality, thus constituting perfect racemic mixtures. Crystallographic data and metric parameters are listed in the S1 (Tables S1 and S3–S5), while selected numbers can be found at

the legend of Fig. 1. Each neutral $[\text{Mn}_3(\text{AcO})_4(\text{HL})_2]$ complex (Figs. 1 and S2) comprises three $\text{Mn}(\text{II})$ atoms in pseudo-octahedral N_2O_4 (central ion) or N_3O_3 (end ions) coordination environments disposed 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 of each bpp group bridges its own external Mn ion to the central one. The bridging is completed by two AcO^- groups per side. Thus, the heteroleptic assembly comprises two $\mu\text{-HL}^-$ ligands and four $\mu\text{-AcO}^-$ groups, leading to a chiral helical structure. Each molecule is perfectly configured to interact face-to-face 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). In addition, each electron-rich naphthyl moiety is establishing a donor/acceptor interaction with one electron-deficient (and metal coordinated) pyrazolylpyridine moiety, the ensemble of interactions (of varying strength) summing up a total of eight (Fig. S2 and Table S5). 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_2L , in that case the electron rich group was acting as a spacer of two electron deficient fragments and the interactions were *intramolecular*, conferring added stability to the resulting molecular cluster. Here, the donor/acceptor $\pi \cdots \pi$ bonds are between different species and the result is a supramolecular dimer of cyclic, helical nature. The cycles interact at both ends with four symmetry-related equal entities (Fig. S3). On one side the $[\text{Mn}_3]_2$ assemblies feature one type of chirality while on the other side they exhibit the opposite parity. These contacts occur in form of $\pi \cdots \pi$ stacking interactions that are more efficient

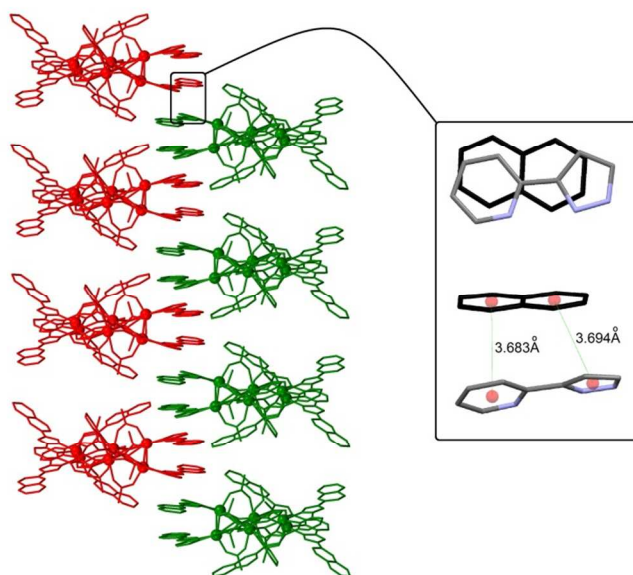


Figure 3 Representation of the interactions between iso-chiral $[\text{Mn}_3]_2$ dimers of **1**, forming adjacent rods parallel to the b axis. Two views of the four donor/acceptor interactions established between each pair of $[\text{Mn}_3]_2$ dimers are shown in the right side, with inter-centroid distances indicated.

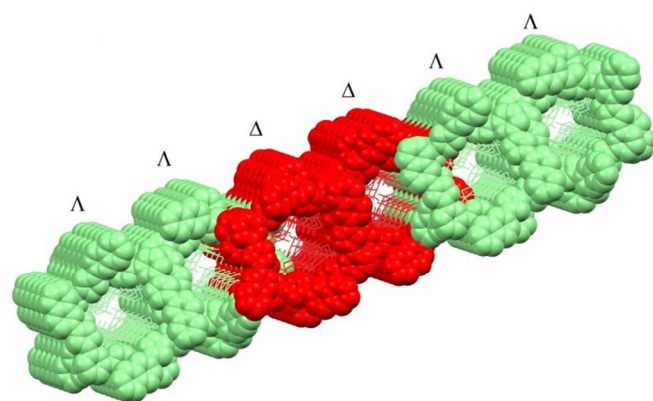


Figure 4 Representation of six adjacent rods of $[\text{Mn}_3]_2$ dimers of **1**, running parallel to the crystallographic b axis. Pairs of adjacent rods of one chirality alternate with pairs of the opposite chirality.

between species of the same chirality that in the opposite case. In the first situation, adjacent dimers establish four well-defined complementary donor/acceptor interactions as these 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) $\pi \cdots \pi$ 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, thus significantly redshifted with respect to the emission of naphthalene based moieties²⁰ and in fact, from that exhibited by the free ligand in the same conditions. The redshift is similar to that attributed to the formation of exciplexes (association of non-equal aromatic moieties in solution by $\pi \cdots \pi$ interactions)²¹ and is caused by the stabilization 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 does neither confirm nor rule out the persistence of the $[\text{Mn}_3]_2$ dimers in solution.

The magnetic properties of the $[\text{Mn}_3]_2$ wheels were examined through variable temperature bulk magnetization measurements under a constant magnetic field (of 3 kG). A plot of χT vs T (χ is the molar paramagnetic susceptibility) indicates that the Mn(II) ions within **1** exhibit primarily antiferromagnetic interactions (Fig. S4). These data were fit to the Van Vleck equation²² that results from considering the spin Hamiltonian of Eq. 1.

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

In Eq. 1, all the spin operators are $\hat{S}_i = 5/2$, and the subscripts coincide with the labels of the metals in Fig. 1. The best fit was obtained for the following parameters; $J_1 = -0.38 \text{ cm}^{-1}$, $J_2 = -0.03 \text{ cm}^{-1}$ with $g_{\text{Mn}} = 2.0$ as a fixed parameter. The weak magnetic coupling is consistent with what is usually observed

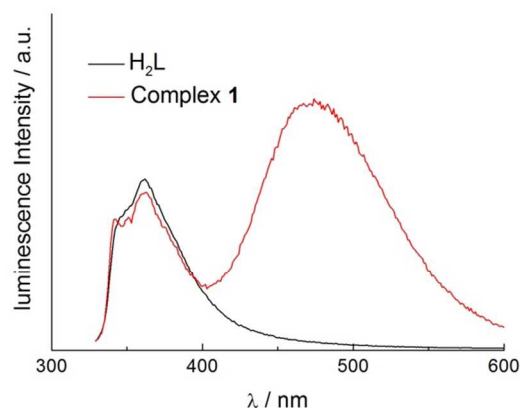


Figure 5 Fluorescence spectra in DMSO ($\lambda_{\text{exc}} = 309 \text{ nm}$) of the $[\text{Mn}_3]_2$ dimers of **1** (red line) and of the ligand H_2L .

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 $[\text{Mn}_3]$ 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 $\mu\text{-AcO}^-$ group and a bridging OH^- ligand between Mn ions. In this case however, the external metal ions are Mn(III).²⁴

Conclusions

The combination of a naphthyl substituted bis-pyrazolylpyridine and carboxylates with Mn(II) favour the formation of a chiral $[\text{Mn}_3]$ cluster that dimerizes as helical wheels by a process of molecular recognition through an array of intermolecular interactions of various types. Fluorescence spectra suggests 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 specific sites of macrobiomolecules.

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^a Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain. Tel: +34 934039760; E-mail: guillem.aromi.qi.ub.es

^b Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC and Universidad de Zaragoza, Plaza San Francisco s/n, 50009, Zaragoza, Spain.

^c Advanced Light Source, Berkeley Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA.

[†] Electronic Supplementary Information (ESI) available: Experimental, crystallographic details, tables and figures, magnetic plots. See DOI: 10.1039/c000000x/

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