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Supramolecular Click Assembly of a Fused Double-Stranded [Mn^{II}_3] Dihelicate

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A trinuclear Mn^{II} complex was obtained by reaction of manganese(II) perchlorate with the ligand 2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenol in methanol. The X-ray crystal structure of $[Mn_3L_4](ClO_4)_2(H_2O)_2$ (**1**) reveals that the "bent" chain of the Mn^{II} ions is assembled by a unique click-assembly of two double-stranded helicates. Magnetic susceptibility measurements show weak ferromagnetic interactions between the metal ions.

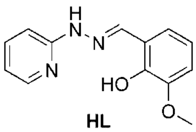
Introduction

The self-assembly between metal centres and selected ligands into predetermined molecular architectures is now ubiquitous in chemistry.[1] This is especially relevant in the field of magnetic materials,[2–4] as remarkable metal–metal interactions may be achieved through the formation of such supramolecular architectures.[5] In this context, helicates are amazing metallosupramolecular assemblies that have been comprehensively investigated during the past two decades, both for their aesthetic nature and for their potential physical properties.[6–9] Most multistranded helicates reported feature two metal centres.[10] Examples containing a trinuclear (or higher) array of metal ions are less common, but they are increasingly described.[11]

In the course of our investigations on the design and preparation of polynuclear metal complexes with attractive magnetic properties, the potentially tetradentate, rigid N,O-ligand 2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenol[12] (HL) was used to generate metal clusters. We report here a new structural type in metallosupramolecular chemistry, namely, a double-stranded trinuclear dihelicate.

Results and Discussion

The reaction of two equivalents of hydrated manganese(II) perchlorate with one equivalent of HL in methanol produces orange block-shaped crystals of $[Mn_3L_4](ClO_4)_2(H_2O)_2$ (**1**), whose X-ray structure is depicted in Figures 1 and S1. The structure of **1** shows a dicationic trinuclear "bent" chain of Mn^{II} ions [angle Mn1–Mn2–Mn3 147.6(1)°] assembled by four deprotonated L^- ligands. Each L^- ligand acts as a tetradentate and tris-chelating donor, and the pyridyl and imine N atoms and both the methoxy and phenoxide O atoms are used for coordination.



HL

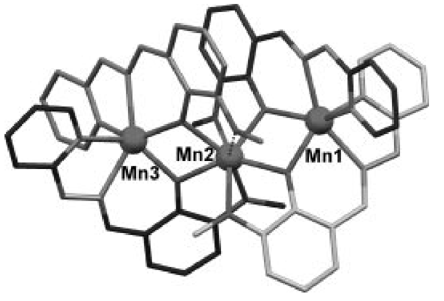


Figure 1. Representation of the trinuclear complex cation of **1**, which shows the three manganese(II) ions coordinated by four different deprotonated **L** ligands.

The bending of the metal array is most likely due to steric constraints around the central Mn2 ion. The charge of the complex is compensated by two ClO_4^- anions. The oxidation state of +2 for the three manganese ions is corroborated by valence bond sum analysis[13] and the magnetic behaviour of the compound (see below). The external six-coordinate metal centres, Mn1 and Mn3, exhibit rare distorted trigonal-prismatic geometries with N_4O_2 donor sets.[14,15] This unusual coordination geometry is most likely

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due to: (1) the small NN bite angles of the ligands [the N–Mn–N angles range from 70.8(2) to 71.6(2)°], (2) the rigidity of the dinucleating ligand HL and (3) steric constraints resulting from the coordination of four ligands to the central Mn2 ion (for instance, two ligands coordinated to Mn2 are stacked; Figures 1 and 2). The Mn–N and Mn–O bond lengths (Table S1) are within the usual ranges found for this type of coordination environment.[16] The coordination angles (Table S1) reflect the distortion of the trigonal prisms. Thus, the trigonal twist angles[17] (Figure S2) vary from 4.65 to 23.60° for Mn1 and from 4.07 to 26.47° for Mn3. These values suggest that the distortion of the trigonal prismatic geometry is more pronounced in Mn3. The central Mn2 ion is in fact heptacoordinated (Figure S3), and it has one additional Mn–O contact at a rather long distance of 2.616(5) Å [see bond lengths in Table S1; a longer bond at 3.022(7) Å neither is nor considered as coordination]. The unusual geometry around the Mn2 ion is best described as highly distorted capped trigonal-prismatic; the capping atom is O27 (Figure S4). The trigonal twist angles vary from 5.10 to 32.70°. The Mn–O bond lengths are comparable to those of seven-coordinate Mn^{II} centres reported earlier.[18,19]

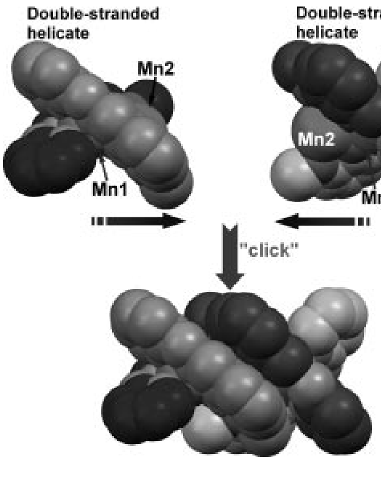

Figure 2. Fused double-stranded trinuclear dihelicate generated by supramolecular click self-assembly.

This compound exhibits fascinating features from a supramolecular point of view. It results from the fusion of two double-stranded helicates to form a unique trinuclear double-stranded dihelicate (Figure 2). Actually, the manganese(II) ions Mn1 and Mn2 are bridged by two L^- ligands (Figure 2, top left), which constitutes a double-stranded bimetallic helicate with a Δ configuration[20] (Figure 3). Similarly, Mn2 and Mn3 can be regarded as a Δ-configured helicate together with two other L^- ligands (Figure 2, top right). Because Mn2 belongs to both double-stranded helicates, it acts as a link between them, and it is thus coordinated by four different L^- ligands (Figure 2 bottom and Figure 3). This "click self-assembly" leads to an unprecedented trinuclear helical structure (Figures 2 and 3). Indeed, to the best of our knowledge, all linear trimetallic helicates so far described in the literature exhibit metal arrays whose formation is achieved by trinucleating ligands.[8] In the present example, the trimetallic chain is assembled with only dinucleating ligands.

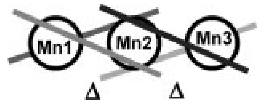

Figure 3. Schematic representation of the double-stranded dihelicate, which shows the stereochemistry of each helical subunit.

The X-band EPR spectrum of compound **1** (Figure S5), recorded at 77 K on a powdered sample, shows an intense and broad signal centred at $g = 2.14$ ($\Delta H_{pp} = 990$ G). A weaker line is also detected at 95 mT (Figure S5), which suggests that there are weak interactions between the Mn centres within complex **1**. Variable-temperature magnetic susceptibility measurements were performed on powdered **1** in the 3–300 K range under a constant magnetic field of 0.5 T. The results are shown in Figure 4 in form of a $\chi_M T$ vs. T curve (χ_M is the molar paramagnetic susceptibility). The $\chi_M T$ value increases from 16.15 $cm^3 K mol^{-1}$ at 300 K (the expected value for three uncoupled Mn^{II} ions with $S = 5/2$ and $g = 2.2$) and reaches a maximum value of 16.6 $cm^3 K mol^{-1}$ at 10 K, followed by a sudden drop at lower temperatures down to 13.95 $cm^3 K mol^{-1}$ at 3 K. To interpret this behaviour, the experimental data were simulated through a least-squares fitting procedure by using the isotropic Heisenberg Hamiltonian in Equation (1).

$$H = -2J_1(S_1S_2 + S_2S_3) - 2J_2(S_1S_3) \quad (1)$$

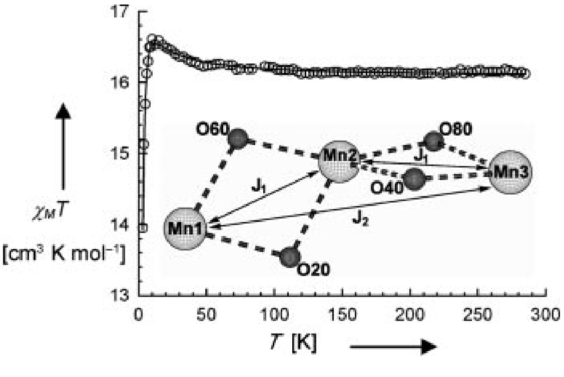

Figure 4. Plot of $\chi_M T$ vs. T per mol of complex **1**. The solid line is a fit to the experimental data. The inset shows the core of the complex, together with the spin coupling scheme.

In this Hamiltonian (see inset of Figure 4 for coupling scheme), $S_1 = S_3 = S_2 = 5/2$, whereas the respective interactions within the Mn1–Mn2 and Mn2–Mn3 pairs were considered to be equal. This model does not include any effect arising from zero-field splitting. This approximation is reasonable here, as the Mn^{II} ion (d^5) is quite isotropic, and thus, it does not usually conduce to any significant magnetoanisotropy. The solutions of the above Hamiltonian can be found analytically, and correspond to 27 $|S_A,S_T\rangle$ states ($S_A = S_1 + S_3$, S_T = total spin) with a total degeneracy of 216. With these eigenvalues and their corresponding energies, a $\chi_M = f(T)$ expression can then be constructed by using the van Vleck equation.[21] Initially, a term considering the effect of intermolecular magnetic interactions, $-2zJ'$, was added to the Hamiltonian and treated according to the molecular-field approximation approach.[22] The fit resulting from this model (Figure 4) produced the following parameters: $J_1 = +0.23\ \text{cm}^{-1}$, $J_2 = -0.03\ \text{cm}^{-1}$, $-zJ' = -0.07\ \text{cm}^{-1}$ and $g = 2.2$, which leads to a spin ground state of $S_T = 15/2$. These results reveal that all magnetic exchange interactions in this system are very weak (involving energies of less than $1\ \text{cm}^{-1}$) and also suggest that the coupling between Mn1 and Mn3 is negligible. A less satisfactory fit is obtained by fixing zJ' to zero, which led to $J_1 = +0.31\ \text{cm}^{-1}$, $J_2 = -0.44\ \text{cm}^{-1}$ and $g = 2.2$, which conduces to a ground state $S_T = 7/2$. This solution was considered unlikely, because it attributes more weight to the interaction between the external Mn ions than to the coupling of adjacent metals, and therefore, the first solution was preferred. In both cases, the value of g is slightly higher than normal. The g values as obtained from bulk magnetization studies are affected by small experimental errors associated with the sample weight and the molecular mass. In this sense, the value obtained from EPR is more reliable. The above results add to a small collection of data relative to the nature and magnitude of the magnetic exchange between Mn^{II} ions bridged only by two phenolate moieties. In all reported cases the coupling revealed itself to be very weak and examples have been found of both types of interactions, ferro-[23–27] and antiferromagnetic.[28–32]

This investigation is currently being extended to other metals to ascertain whether the concept of interconnected double-stranded trinuclear dihelicates can be generalized.

Experimental Section

Compound 1: Prepared from $Mn(ClO_4)_2\cdot 6H_2O$ (0.50 mmol) and HL (0.25 mmol) in methanol (10 mL). The resulting yellow solution was left unperturbed to allow slow evaporation of the solvent. Orange crystals, suitable for X-ray diffraction analysis, were formed after 1 d. Yield: 35 mg, 41 % (based on the ligand HL). IR (neat): $\tilde{\nu}$ = 3266 (w), 1616 (vs), 1538 (s), 1485 (s), 1464 (s), 1456 (s), 1427 (vs), 1375 (w), 1346 (s), 1286 (s), 1220 (vs), 1074 (vs), 1004 (w), 980 (s), 850 (w), 772 (s), 732 (vs), 622 (vs), 499 (w), 448 (vs), 410 (s) cm^{-1}. $C_{52}H_{52}Cl_2Mn_3N_{12}O_{18}$ (1368.77): calcd. C 45.63, H 3.83, N 12.28; found C 45.60, H 3.49, N 12.11.

X-ray Crystallographic Analysis: Intensity data were recorded with a Nonius Kappa CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) at 173(2) K and were corrected for Lorentz and polarization effects and for absorption. The programs COLLECT,[33] SHELXS-97[34] and SHELXL-97[35] were used for data reduction, structure solution and structure refinement, respectively. All non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The H atoms were not located for the disordered water molecules. Crystal data for **1**: Monoclinic, $C2/c$; a = 37.332(5) Å, b = 15.075(3) Å, c = 24.610(5) Å, V = 12721(4) Å^3, Z = 8, $\rho_{\text{calcd.}}$ = 1.439 g cm^{-3}, μ = 0.747 mm^{-1}, final R_1 = 0.0775 for $I \geq 2\sigma(I)$, wR_2 = 0.1806 for all data. CCDC-648621 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-band EPR studies were carried out with a JEOL electron spin resonance spectrometer equipped with an Esprit 330 data system, with dpph as an internal reference (g = 2.0036).

Magnetic susceptibility measurements on **1** were performed with a Quantum Design MPMS-5 5T SQUID magnetometer at 5000 Oe in the temperature range 3–300 K. Data were corrected for the diamagnetic contributions estimated from Pascal's Tables.[22]

Supporting Information (see footnote on the first page of this article): Schematic representations of the coordination environments of the three Mn^{II} centres of **1**. Selected bond lengths and angles for **1**, as well as X-ray data. Solid-state EPR spectrum of complex **1**.

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