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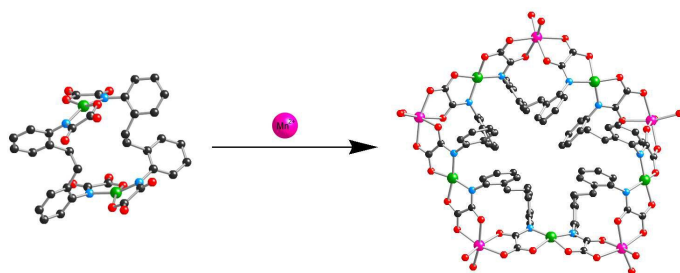
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A Heterobimetallic $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ Nanowheel Modulated by a Flexible Bis-Oxamate Type Ligand[†]

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The reaction of the dicopper(II) metallacyclophane $[\text{Cu}_2(\text{edpba})_2]^{2-}$ with fully solvated Manganese(II) ions yields the nanowheel $[\text{Mn}_5\text{Cu}_5(\text{edpba})_5]$ with a $S = 10$ low-lying spin state.



COMMUNICATION

A Heterobimetallic $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ Nanowheel Modulated by a Flexible Bis-Oxamate Type Ligand†

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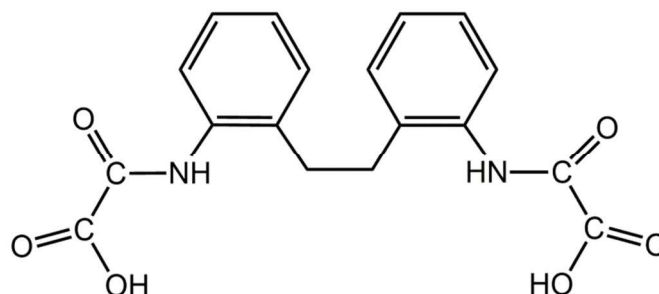
The synthesis, crystal structure and preliminary magnetic characterization of a new heterobimetallic $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ wheel containing a flexible bis-oxamate type ligand are described. This decanuclear compound exhibits a relatively strong intra-wheel antiferromagnetic interaction leading to a ground spin state $S = 10$.

The search for high nuclearity Magnetic Metal Organic Materials (MMOMs) is a very active research domain, one of the main reasons for this interest being based on the possibility to build molecule-based devices. One of the examples of these MMOMs, the so-called metallacycles, can present different size, symmetry and shape such as cages, squares, grids, double-decker wheels, “ring of rings”, metal-organic frameworks (MOFs), etc.¹ Since these chemical systems can behave as nanoparticles due to their limited size, several applications can be envisaged, such as gas storage systems, catalysts, single molecule magnets (SMMs) or magnetic coolers.² Although a good variety of magnetic homometallic macrocycles have been described in the literature,³ the number of examples of heterometallic wheels are by far less abundant.^{3b,4}

In this work, we present a new example of heterometallic wheel-shaped motif, $[\text{Mn}_5\text{Cu}_5(\text{edpba})_5(\text{dmsO})_7(\text{H}_2\text{O})_7] \cdot 4\text{dmsO} \cdot 2\text{H}_2\text{O}$ (**1**) hereafter noted $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ [$\text{H}_4\text{edpba} = N,N'-2,2'$ -ethylenediphenylenebis(oxamic acid); see Scheme 1].⁵ Due to the presence of the $-\text{CH}_2-\text{CH}_2-$ fragment between the two phenylene rings in the edpba^{4-} tetra-anion, this bis-oxamate type ligand can adopts the *anti* or *gauche* conformations depending on the conditions of the synthesis.^{5,6} It deserves to be noted that a few examples of oxamate derivatives resulting in metallacycles have been reported, most of them being based on metallacyclophane moieties.⁷

Single crystals of **1** were obtained from the diffusion reaction between $(\text{Bu}_4\text{N})_4[\text{Cu}_2(\text{edpba})_2] \cdot 4\text{H}_2\text{O}$ (Bu_4N^+ = tetra-*n*-butylammonium cation) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a dmsO/water (1:1 v/v) solvent mixture. Crystal structure was refined using PLATON/SQUEEZE routine,⁸ since dmsO and/or water molecules in the voids of $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ ($\sim 3070 \text{ \AA}^3$) could not be properly modelled. **1** crystallizes in the monoclinic $P2_1/c$ space group and its

crystal structure shows the occurrence of neutral decanuclear $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ rings containing five fully deprotonated edpba^{4-} ligands (see Figure 1). The oxamate groups of each edpba^{4-} ligand in **1** adopt bis-bidentate bridging modes. Two solvent molecules in *cis* positions [dmsO/water] complete the somewhat distorted octahedral environments around the five crystallographically independent Mn^{II} ions [Mn1, Mn2, Mn3, Mn4 and Mn5]. The set of the five Mn^{II} ions within each decanuclear ring in **1** exhibits an envelope conformation (Figure S1 in the ESI†). One of the five crystallographically independent Cu^{II} ions in **1** [Cu1] is four-coordinate in a distorted square planar environment built by two amidate-nitrogen and two carboxylate-oxygen atoms from two oxamate groups. This donor set also occurs in the other four copper(II) ions, but all of them are five-coordinate in a distorted square pyramidal surrounding with a water (Cu4) or a dmsO molecule (Cu2, Cu3 and Cu5) in the apical position.



Scheme 1. Representation of the molecular structure of H_4edpba .

The intraring distances between neighbouring metal ions in **1** are in the range 8.264(2)–8.884(2) Å ($\text{Cu} \cdots \text{Cu}$), 5.395(2)–5.489(2) Å ($\text{Cu} \cdots \text{Mn}$) and 10.556(2)–10.786(2) Å ($\text{Mn} \cdots \text{Mn}$). The neutral rings are well separated from each other. The shortest inter-ring metal-metal separations being 6.913(2) (Mn4 \cdots Mn5ⁱ), 6.173(2) (Cu1 \cdots Cu1ⁱⁱ) and 7.708(2) Å (Cu5 \cdots Mn4ⁱ) [symmetry code: (i) = 1–x, 1–y, –z and (ii) = –x, 1–y, –z].

The π -stacking interactions of the aromatic rings involving the edpba^{4-} ligands creates lipophilic cavities in each ring of **1**, this structural feature being most likely the driven force accounting for

the formation of wheels instead of linear chains.⁹ No solvent molecules are found within these cavities and the empty space results in a sort of star-like shape owing to the flexibility of the –CH₂–CH₂– bonds. The elemental analysis and thermal study (TGA and DTA measurements) of **1** allowed us to fix the number of crystallization molecules and the chemical formula (see Figs. S2 and S3, ESI).

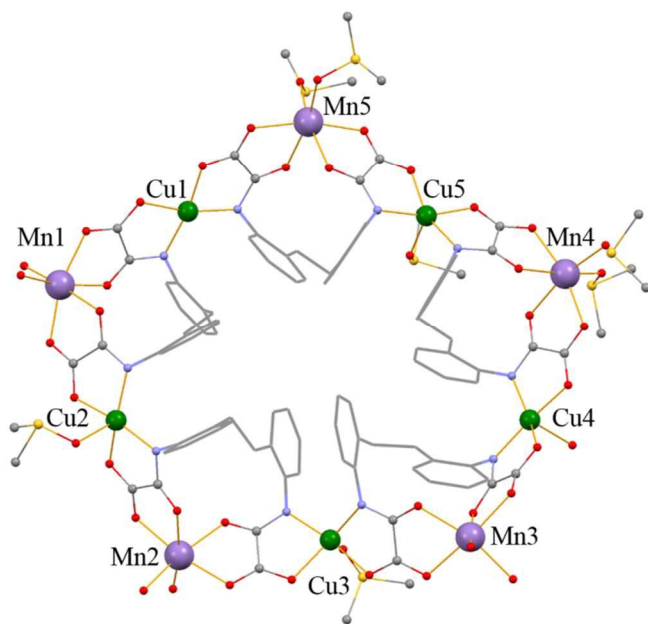


Fig. 1 Perspective drawing of the crystal structure of the [Mn^{II}₅Cu^{II}₅] decanuclear ring with the atomic numbering scheme related to the metal ions. Hydrogen atoms and the non-coordinated solvent molecules were omitted for the sake of clarity. Carbon, oxygen and nitrogen atoms are represented in grey, red and sky blue colours, respectively.

The magnetic properties of crushed single crystals of **1** were investigated in the 2.0–300 K temperature range. They are shown in Figure 2 in the form of $\chi_M T$ vs. T plot [χ_M being the magnetic susceptibility per Mn^{II}₅Cu^{II}₅ unit]. At room temperature, $\chi_M T$ is equal to 21.5 cm³ mol^{−1} K, a value which is smaller than that expected for a set of five manganese(II) ($S_{Mn} = 5/2$) and five copper(II) ($S_{Cu} = 1/2$) ions magnetically non-interacting [$\chi_M T = 23.5$ cm³ mol^{−1} K with $g_{Mn} = 1.98$ and $g_{Cu} = 2.08$]. Upon cooling, $\chi_M T$ decreases continuously to reach a minimum at ca. 108 K, and it further increases sharply to attain a quasi-plateau below 10 K with $\chi_M T$ ca. 51.5 cm³ mol^{−1} K. These features are typical of a ferrimagnetic behaviour arising from the intraring antiferromagnetic interaction between the Cu^{II} and Mn^{II} through the oxamate bridge that would lead to a ground spin state $S = 10$. The fact that the value of $\chi_M T$ at very low temperatures is somewhat below that calculated for $S = 10$ (ca. 55 cm³ mol^{−1} K) reveals the occurrence of dipolar or inter-ring antiferromagnetic interactions. The M versus H plot at 2.0 K for **1** (see Fig. 3) provides additional support to the occurrence of a ground spin state $S = 10$, the quasi saturation value of M at 5 T being very close to the expected one (ca. 19.5 instead of 20.0 BM).

The dc magnetic susceptibility data were analysed by means of the spin Hamiltonian shown in eq. (1), which includes different g -factors for Cu^{II} (g_{Cu}) and Mn^{II} (g_{Mn}) ions through the Zeeman term and magnetic coupling constant (J) from a isotropic Heisenberg spin model.

$$\hat{H} = -J(\hat{S}_1\hat{S}_{10} + \sum_{i=1}^{N=9} \hat{S}_i\hat{S}_{i+1}) + \beta H \sum_{j=0}^{j=4} (g_{Cu}\hat{S}_{2j+1} + g_{Mn}\hat{S}_{2j+2}) \quad (1)$$

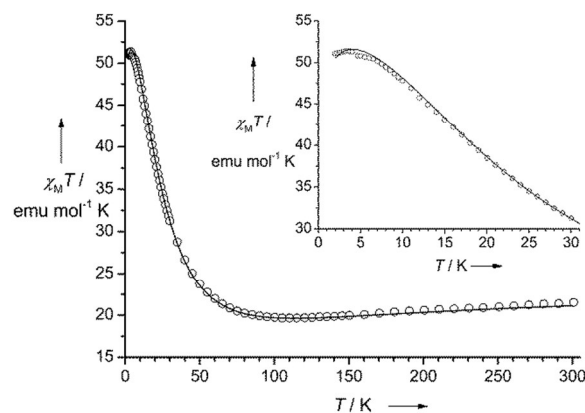


Fig. 2 Temperature dependence of the $\chi_M T$ of **1**: (o) experimental; (—) best-fit curve through eq (1) (see text). The inset shows a detail of the low temperature region.

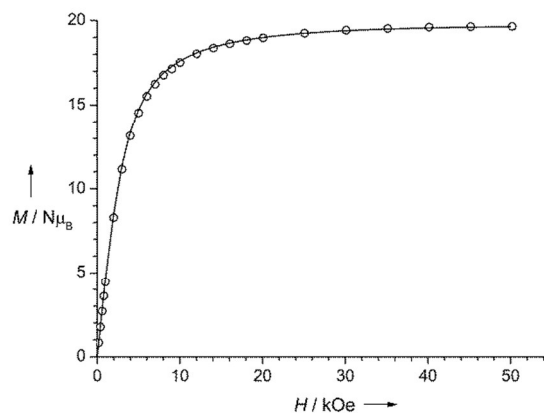


Fig. 3 Magnetic field dependence of the magnetization for **1** at 2.0 K: (o) experimental; (—) theoretical curve simulated from the values of the g_{Cu} , g_{Mn} and J parameters obtained through the fit of the $\chi_M T$ data through eq (1).

Simulations were made by exact diagonalization of the energy matrix built from the use of Irreducible Tensor Operators (ITO). The inclusion of different g values was done through the Wigner-Eckart theorem that reproduces well the exact results for a g_A/g_B ratio smaller than 1.2, being $g_A > g_B$. These techniques were used as they were implemented in the XVPMAG programme.¹⁰ Least-squares best-fit parameters are: $J = -28.1(2)$ cm^{−1}, $g_{Cu} = 2.08(3)$, $g_{Mn} = 1.98(2)$ and $\theta = -0.11(1)$ K with $R = 4.4 \times 10^{-5}$ (R is the agreement factor defined as $\sum[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2 / \sum[(\chi_M T)_{exp}]^2$). The θ term was included to account for the weak inter-ring magnetic interactions, which are detected at very low temperatures (see inset of Fig. 2). The calculated curve reproduces well the magnetic data in the whole temperature range investigated.

The g values of the Cu^{II} and Mn^{II} ions and the nature and magnitude of the magnetic coupling agree with the results observed

in previous magneto-structural studies of oxamate-bridged $\text{Cu}^{\text{II}}\text{-Mn}^{\text{II}}$ systems (values of $-J$ in the range 18.9-32.5 cm^{-1}).¹¹ A good simulation of the experimental magnetization curve at 2.0 K is achieved by using the values of g_{Cu} , g_{Mn} and J from the previous fit (Figure 3), confirming thus their validity. No out-of-phase ac signals were observed in the temperature range 2.0-9.0 K and variable-frequency (0.01-10 kHz) in the presence and absence of a dc magnetic field. No magnetic hysteresis was observed for **1** at 2.0 K (Fig. S4, ESI).

In conclusion, a new example of heterobimetallic oxamate-based $[\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_5]$ molecular wheel with a high-spin low-lying level is described herein. The flexibility of the edpba^{4-} ligands proved by the structure of **1** together with the simplicity of its preparative route allow us to anticipate the achievement of broad family of multifunctional tailor-made metallorings, behaving as single molecule magnets (SMMs) or magnetic coolers for instance.^{2b} Further efforts will be devoted to increase this family and foresee their possible applications.

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† Electronic supplementary information (ESI) available: Experimental preparation, some details of structural refinements, TGA and DTA curves, X-ray diffraction patterns, analytical and spectroscopic characterization data for compound **1**. CCDC number for the structure determined in this work is 1031230. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c000000x/

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