Ferrimagnetic behavior in a naphthalene templated manganese(II) 1,1-cyclohexanediacetate compound

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\textbf{ABSTRACT}

A new manganese(II) 1,1-cyclohexanediacetate compound of formula \([\text{Mn}_{13}\text{chda}_{12}\text{H}_2\text{O}_4\text{OH}_2]_n\text{nap}\) has been synthesized by a hydrothermal reaction and characterized through single crystal X-ray synchrotron diffraction, exhibiting a 3D architecture, where the nap molecules are weakly anchored in the cavities of the \([\text{Mn}_{13}\text{chda}_{12}\text{H}_2\text{O}_4\text{OH}_2]_n\) coordination polymer through steric interactions. Magnetic analysis reveals a long-range ferrimagnetic order below 2.4 K, most likely due to non-compensation of the magnetic moments. The non-compensation in spin moments arises, for topological reasons, from the network of exchange couplings associated to the binding modes (carboxylate and \(\mu\)-oxo). This compound is one of the few examples of homometallic topological ferrimagnets built up from carboxylate ligands.

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1. Introduction

Multidimensional molecular-based magnets have been the subject of considerable research over the past decades, both from a fundamental and device point of view [1–6]. Specifically, 3D coordination polymers with large cavity structures are of interest in the field of molecular magnetism and material-chemistry due to their fascinating structural diversities and their potential application as functional materials [7]. A commonly used strategy in the construction of such extended architectures is to employ appropriate bridging ligands that act as connectors between different metal centers. The role of the bridging ligand is twofold, stabilizing the 3D crystal structure and transmitting the magnetic interaction between the magnetic metal centers. In order to build materials with larger cavities, the bridging ligands must connect the metal centers further apart. For this reason, although a large number of these new materials, commonly known as MOFs (metal organic frameworks), with large cavities have been reported in recent years, the number of magnetic MOFs remains small [8–10].

Together with this strategy, the addition of a template, involving a self-assembly process through weak interactions, promotes the synthesis and crystallization of new coordination polymers [11]. The investigation of templated polymerizations is essential to develop a deeper understanding of the binding interaction between the host coordination polymer and guest template molecules [12,13].

In this work, we study manganese(II) coordination compounds of 1,1-cyclohexanedicarboxylate (dianion of the 1,1-cyclohexanedicarboxylic acid, H₂chda; see scheme 1). There is only one previous report of a Mn(II)-chda compound, but in combination with the 1,10-phenanthroline chelating ligand [14]. The 1,1-cyclohexanedicarboxylate is a flexible and versatile ligand, but poorly explored [14–23]. The occurrence of two acetate groups in the same position of the cyclohexane ring allow this ligand to adopt simultaneously chelating bidentate and different carboxylate bridging modes (syn-syn or anti-syn involving one or both carboxylate groups). Together with the ability of the carboxylate bridge to mediate ferro- or antiferromagnetically between paramagnetic metal ions, this ligand is of interest for the design of high-dimensional magnetic systems that promote long-range magnetic order. None of the complexes synthesized with 1,1-cyclohexanedicarboxylate as ligand are three-dimensional coordination compounds. The bulky, hydrophobic cyclohexane group aggregates and builds layered systems like the one constructed with Co(II) [16].

Several routes were attempted to synthesize a highly-connected Mn(II) containing 1,1-cyclohexanedicarboxylate, but classical hydrothermal and solvothermal strategies failed
to yield a compound. Therefore, we opted for a template approach, but the selection of the guest molecule acting as template must take into account the possible guest-guest and guest-host interactions, and thus it cannot be arbitrary. When the host-guest interaction is strong and the guest-guest interaction weak, the guest molecules are uniformly dispersed over the cavities anchored to the host binding sites and therefore it is not necessary that the guests entirely fill the available void space, except of course when the host binding sites coverage is very high. In the other extreme, a strong guest-guest interaction could lead to a competition between templated and non-templated self-assembly and to polydisperse aggregates that are potentially larger on average than the template size. We introduce a non-coordinating neutral aromatic polycycle (naphthalene) as template in the hydrothermal synthetic route to create hydrophobic pockets attracting the cyclohexane groups of the ligand. To the best of our knowledge, this work represents the first three-dimensional coordination complex obtained with naphthalene as template that cannot be obtained without the templating strategy.

Among the long-range magnetic ordered systems, weak-ferromagnetic behaviors arising from non-compensation of magnetic moments are well represented in the form of ferrimagnetic systems in which two nearest-neighbor ions with different magnetic moments are antiferromagnetically coupled through, for example, cyanide or oxalate groups [24]. For such bridged compounds, long-range ferrimagnetic order arises from non-compensation of the different magnetic sublattices or individual spin moments. This condition is more difficult to obtain when the system is constituted by a single type of magnetic ion, thus giving a homospin and homometallic system. There are only a few examples where homospin and homometallic systems coexist with long-range ferrimagnetic order [25–32]. In particular, the number of high-dimensionality homometallic complexes with ferrimagnetic behaviors is scarce due to the requirement for non-compensation of the individual spin moments, which is difficult to achieve in practice because only one kind of spin is involved [28, 33–36].

In this work, we report the synthesis, crystal structure, and magnetic behavior of a new 3D homometallic and homospin system that presents long-range magnetic order below 2.4 K as a result of the non-compensation of magnetic moments due to the intricate network of exchange coupling interactions present in the system.

2. Experimental

2.1. Materials and methods

The synthetic methods used to obtain suitable crystals for X-ray diffraction of [Mn13(chda)12(H2O)4(OH)2]n·n(nap) are described here. Reagents and solvents used in the syntheses were purchased from commercial sources and used without purification. Elemental analyses (C, H, N) were performed with an EA 1108 CHNS/O automatic analyzer.

Synthesis of [Mn13(chda)12(H2O)4(OH)2]n·n(nap) (1). An aqueous solution (10 mL) of H2chda (0.100 g, 0.5 mmol) was pH adjusted until a value of 5.0 by dropwise addition of an aqueous solution of 0.1 M NaOH. Manganese(II) acetate (0.086 g, 0.5 mmol) dissolved in a minimum amount of water was added to the previous solution and to
this solution was added a small quantity of naphthalene (0.013 g, 0.1 mmol) dissolved in 5 mL of methanol. The resulting mixture was sealed in a 23 mL stainless-steel reactor with a Teflon liner and heated at 120 °C for 96 h. After cooling, colorless needle-shaped crystals suitable for X-ray analysis were collected, washed with water and air dried. Yield: 70%. Anal. Calcd for C_{130}H_{178}Mn_{13}O_{54} (1): C, 47.04; H, 5.41%. Found: C, 47.12; H, 5.32%.

2.2. Physical measurements

Variable temperature magnetic susceptibility measurements on polycrystalline samples of 1 were carried out in the temperature range 1.9–300 K with a Quantum Design SQUID magnetometer under an applied magnetic field from 100 to 10000 G. Magnetization (0 to 5 T) and ac in-phase and out-of-phase measurements (10–1000 Hz) were also carried out. Corrections for the diamagnetic contribution of the constituent atoms and for the magnetization of the sample holder were performed.

2.3. Crystal structure determination and refinement

The X-ray diffraction data collection on single crystal of 1 was performed on the CRISTAL beamline at SOLEIL synchrotron (Saclay, France) with λ = 0.67270 Å at 45 K. Colorless needle-shaped crystals of [Mn_{13}(chda)_{12}(H_{2}O)_{4}(OH)_{2}]_{n}·n(nap) suitable for single crystal diffraction were selected and mounted on a Kapton® loop installed in a metallic pin mounted on a heated goniometric head to avoid the formation of ice during the measurement. A grease drop was used to fix the crystal to the Kapton® loop and it was immediately frozen. Data were measured combining ϕ- and ω-scans to increase the completeness using synchrotron radiation. The final completeness is 99.00% out to 24.873° in θ, corresponding with the maximum resolution achieved. The data were indexed, integrated and scaled with the CrysAlisPro software program [37]. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 using ShelXL-2019/2 program [38].

The hydrogen atoms of 1 (except those of the hydroxo-groups) were positioned geometrically and refined with a riding model. The hydrogens of the hydroxo-groups were located from Fourier difference maps and refined with isotropic temperature factors. A summary of the cell parameters and refinement conditions for 1 is listed in Table 1, whereas main bond lengths and bond angles are given in Tables S1 and S2 (see Supplementary material). The final geometrical calculations and the graphical manipulations were carried out with PLATON [39] and DIAMOND [40] programs. Crystallographic data of 1 have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference number 2174643.

3. Results and discussion

3.1. Description of the structure

[Mn_{13}(chda)_{12}(H_{2}O)_{4}(OH)_{2}]_{n}·n(nap) (1) crystallizes in the monoclinic non-standard P2_1/n space group (the standard is P2_1/c). The solution and refinement using a non-standard
group is to preserve the monoclinic angle as close to 90 degrees as possible. The asymmetric unit contains seven independent Mn(II) ions. Six of these manganese ions [from Mn(1) to Mn(6)] are located in general positions, while Mn(7) lays on an inversion center. The metal centers are connected through six independent (chda)²⁻ ligands. The asymmetric unit is completed with one hydroxide group that acts as connector between three independent manganese ions [Mn(2), Mn(4) and Mn(6)], two water molecules that complete the environment of Mn(5) and Mn(6), and half a naphthalene (nap) molecule; the other half of the molecule is generated by the application of an inversion center. 1 forms a neutral 3D coordination polymer with cavities where the naphthalene molecules are weakly anchored.

Considering the inorganic network formed by the six octahedral and one square pyramidal [Mn(3)] manganese ions, the structure could be seen as regular loop chains of edge-shared octahedra running along the a-direction, each loop formed by twelve Mn(II) ions with six of them shared with the two adjacent loops (see Figure 1 and scheme 2). Two manganese ions [Mn(5) and Mn(6)] share only a vertex with the main loop acting as pendant octahedra. Each one of these loop chains are linked to four other adjacent ones through a carboxylate bridge involving the pendant Mn(6) and Mn(5) metal centers, giving the final 3D structure (Figure 1a). This assembly produces

Table 1. Crystal data and details of the structure determination for 1.

| Property                     | Value                        |
|------------------------------|------------------------------|
| Formula                      | C₁₃₀H₁₇₈Mn₁₃O₅₄             |
| Dcalc/g cm⁻³                 | 1.560                        |
| μ/μm⁻¹                       | 1.206                        |
| Formula weight               | 3318.95                      |
| Color                        | Colorless                    |
| Shape                        | Needle-shaped                |
| Size/mm³                     | 0.04 × 0.04 × 0.15           |
| T/K                          | 45(2)                        |
| Crystal system               | Monoclinic                   |
| Space group                  | P2₁/n                        |
| a/Å                          | 10.8720(5)                   |
| b/Å                          | 21.5041(9)                   |
| c/Å                          | 30.4101(16)                  |
| α/°                          | 90                           |
| β/°                          | 96.359(6)                    |
| γ/°                          | 90                           |
| V/Å³                         | 7065.9(6)                    |
| Z                            | 4                            |
| σ                            | 1                            |
| Wavelength/Å                 | 0.6727                       |
| Radiation type               | Synchrotron                  |
| Θmax/°                      | 1.960                        |
| Θmax/°                      | 24.873                       |
| Measured reflections        | 58995                        |
| Independent reflections     | 14249                        |
| Reflections I ≥ 2σ(I)        | 8670                         |
| Rint                         | 0.1476                       |
| Parameters                   | 893                          |
| Restraints                   | 0                            |
| Largest peak                 | 1.247                        |
| Deepest hole                 | −0.940                       |
| GooF                         | 0.996                        |
| wR² (all data)              | 0.1251                       |
| wR²                          | 0.1016                       |
| R₁ (all data)               | 0.1150                       |
| R₁                           | 0.0557                       |
Figure 1. (a) A view along the crystallographic $a$ axis of the MnO$_6$ and MnO$_5$ polyhedra of the structure of 1. (b) A detail of each one of the loop-chains running along the $a$ axis comprising the Mn$_{12}$ wheels. (c) A view of the crystal structure of 1 along the $a$ axis with the cyclohexane groups (ball and sticks) and the naphthalene guests (spacefill style) occupying the pores.

Scheme 2.
pores running along the a-axis, where the cyclohexane groups of the (chda)2⁻ ligands are located, leaving enough space in the center to host the naphthalene molecules. Or, most likely, as in reverse micelle formation, the nap guests have attracted the cyclohexane groups of the ligand and the inorganic structure occupies the space among the pores (Figure 1c). The potential solvent accessible void in I is 2.6%, but upon removal of the non-coordinated naphthalene molecules the host framework shows a 28.9% of void space to the total volume [39].

All six coordinated Mn(II) ions show considerable distortion from the perfect octahedron as reflected in their geometric values \( \phi \) and \( s/h \) of 58.50° and 1.22 for Mn(1), 59.18° and 1.23 for Mn(2), 59.68° and 1.23 for Mn(4), 52.89° and 1.21 for Mn(5), 61.14° and 1.17 for Mn(6) and 58.53° and 1.23 for Mn(7) (ideal values \( \phi = 60° \) and \( s/h = 1.22 \)) [41]. The five-coordinate manganese ion Mn(3) exhibits a slightly distorted square-pyramidal environment with a \( \tau \) value of 0.10 [the structural parameter \( \tau \) is equal to 0 for a square-pyramidal geometry and to 1 for an ideal trigonal-bipyramidal environment] [42]. The Mn-O carboxylate, Mn-O water and Mn-O hydroxo bond distances range from 2.088(2)–2.362(2) Å, 2.200(2)–2.305(2) Å and 2.094(1)–2.137(1) Å, respectively (see Table S1). The unique manganese-manganese separations within the edge sharing Mn12 loop (see scheme 2) are Mn(2)…Mn(1): 3.2329(10) Å, Mn(1)…Mn(3): 3.2742(8) Å, Mn(3)…Mn(4): 3.1920(9) Å, Mn(4)…Mn(2): 3.1269(9) Å, Mn(2)…Mn(7): 3.3148(6) Å. The pendant Mn(5) octahedron shares a vertex only with Mn(3) with a 3.6385(11) Å separation. Mn(6), however, shares a vertex [the hydroxo group O(25)] with Mn(2) and Mn(4) with separations of 3.7352(9) and 3.6219(10) Å for Mn(6)…Mn(2) and Mn(6)…Mn(4), respectively. The Mn…Mn separation through the carboxylate bridge is longer, as expected, Mn(5)…Mn(6) being 4.6522(11) Å.

Six crystallographically independent (chda)2⁻ ligands occur in I. One chda ligand simultaneously adopts bis-monodentate and bidentate coordination modes and a second chda group acts simultaneously as tris-monodentate and bidentate. The third chda ligand acts simultaneously as bis-bidentate and bis-monodentate coordination, previously observed in the 2D cobalt(II)-1,1-cyclohexanediacetate coordination compound [16]. The remaining three chda molecules present tetrakis-monodentate/bidentate coordination modes. The eight-member chelate ring, present in all the ligands and built up through the bidentate coordination mode involving two oxygen atoms from two different carboxylate groups, has been previously observed in mononuclear [Mn(phen)(H2O)2(chda)]·3H2O [43] and dinuclear [Mn2(phen)3(H2O)4(ClO4)2(phen)·4H2O] [14] manganese(II) complexes (phen = 1,10-phenanthroline), the sheet-like cobalt(II) complexes [Co(chda)]n [16] and [Co3(Hchda)2(chda)2(bpp)2(H2O)2]n [20] and the nickel(II) complex [Ni3(Hchda)2(chda)2(bpp)2(H2O)2]n [22] which is isomorphous to the last cobalt(II) compound.

### 3.2. Magnetic properties

The magnetic behavior of [Mn13(chda)12(H2O)4(OH)2]n·n(nap) is shown in Figure 2 in the form of \( \chi_M T \) versus \( T \) plot (\( \chi_M \) is the magnetic susceptibility per formula unit). This curve shows that at room temperature the \( \chi_M T \) value (48.70 cm³ mol⁻¹ K) corresponds to an effective magnetic moment \( \mu_{\text{eff}} \) \( \approx 5.47 \mu_B/\text{Mn(II)} \), which is consistent with the value of 5.92 \( \mu_B/\text{Mn(II)} \) expected for a magnetically isolated high-spin...
Mn(II) \((S=5/2)\) ion with \(g=2.00\). When the temperature decreases the \(\chi_M T\) values decrease; a minimum \((14.97 \text{ cm}^3 \text{ mol}^{-1} \text{ K})\) is observed at 7.4 K. Below this minimum, \(\chi_M T\) rapidly increases and reaches a very high value of \(320.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}\) at 2.2 K, and, finally, \(\chi_M T\) values again decrease to \(229.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}\) at 2 K. The sudden increase of \(\chi_M T\) value at 7.3 K indicates a ferrimagnetic type behavior due to the complete non-cancellation of homometallic spins. The temperature dependence of reciprocal susceptibility \((\chi_M^{-1})\) above 15 K follows the Curie-Weiss law, with a negative Weiss constant \(\theta = -24.0 \text{ K}\), indicating an overall antiferromagnetic interaction between Mn(II) ions.

This spontaneous ferrimagnetic behavior is confirmed by an \(ac\)-susceptibility measurement (Figure 3). The temperature dependent in-phase and out-of-phase \(ac\)-susceptibility measurements corroborate the existence of long-range ferromagnetic order below 2.4 K; however, a shoulder visible at 3.2 K in both curves indicates an emerging long range magnetic order. This is compatible with a long range magnetic order due to the non-compensating Mn(II) magnetic moments. This signal is frequency-independent, indicating that there are no dynamic effects among the magnetic moments, as seen in spin-glass or single-chain and single-molecule magnets.

The first magnetization shows a sigmoidal-shaped curve at 2 K, typical of metamagnetic systems (Figure 4). This sigmoidal shape indicates the field-induced transition, with a critical field of the 30 Oe, estimated from the maximum in the \(\partial M(H)\). This sigmoidal shape together with the very low value of the critical field indicates that the system is almost isotropic, and therefore, the application of a small external magnetic
field is sufficient to produce imbalance in the population of magnetic domains, resulting in an increase of magnetization in the direction of the applied magnetic field. This behavior is characteristic of a soft-magnet. Even at 5 T, the magnetization value is much lower than that expected for 13 high-spin Mn(II) ions, indicating that the antiferromagnetic interactions are not fully overcome (Figure 5). Moreover, the magnetization curve as a function of the external field is reversible, so the occurrence of a hysteresis loop is not detectable, confirming that the magnetic anisotropy in this system is negligible. These curves are characteristic of a soft-magnet built from a weak ferromagnetism as a consequence of the non-compensation of the antiferromagnetic system.

Complex 1 is an unusual example of a homospin ferrimagnet. The main superexchange pathways present in this complex are the $\mu^\text{COO}$ and the hydroxyl bridges within the loop chains running in the $\alpha$ direction (scheme 2). The angle between manganese ions and the bridging oxygen atoms is expected to play an important role because it is involved in the degree of magnetic orbital overlap of among manganese ions.

Figure 3. In-phase (continuous line) and out-of-phase (dashed line) variable temperature ac magnetic susceptibility for 1.

Figure 4. Magnetization (circles, left axis) and its derivative (bold line, right axis) for 1.
ions. In general, smaller Mn–O–Mn angles (ranging from 80 to 110°) correspond to shorter Mn–Mn separations (ranging from 3.0 to 3.9 Å) (see Figure S1, Supplementary material). Wider angles that correspond to longer metal–metal separations lead to weak magnetic interactions. In our case the bis(μ-COO)-bridged Mn–O–Mn angles within the Mn12 loop chain ranged from 90.44(11) to 98.72(13)° which involve the shortest Mn–Mn separations (see Table 2). The Mn–O–Mn angles of the pendant vertex shared Mn(II) ion being wider [from 106.51(13) to 123.80(15)°]. The magnetism of the triangular [M3(μ3-X)] motifs (X = O, OH, or F) have been extensively investigated and when antiferromagnetic interactions are dominant spin frustration arises [44]. In our case, the [M3(μ3-X)] motif is formed by Mn(2), Mn(4) and Mn(6) (scheme 2) which is highly distorted with the pendant Mn(6) ion exhibiting a longer separation from the other two. Therefore, the strongest exchange couplings among the manganese ions most likely occur within the Mn12 loops of the chain and the topological spin frustration could be at the origin of the ferrimagnetic behavior observed in 1.

Table 2. Mn⋯Mn separations and Mn–O–Mn bond angles for the edge and vertex shared octahedra in 1.

| Angle /°     | Mn⋯Mn separation /Å |
|--------------|----------------------|
| Mn1–O22–Mn2 | 95.29(12) 3.2329(10) |
| Mn1–O19–Mn2 | 94.57(12) 3.2742(8)  |
| Mn1–O18–Mn3 | 98.72(13) 3.2742(8)  |
| Mn1–O23–Mn3 | 97.56(13) 3.2742(8)  |
| Mn2–O5–Mn7  | 96.63(11) 3.3148(6)  |
| Mn2–O7–Mn7  | 98.91(12) 3.3148(6)  |
| Mn3–O11–Mn4 | 95.07(12) 3.1920(9)  |
| Mn3–O15–Mn4 | 94.91(12) 3.1920(9)  |
| Mn4–O13–Mn2 | 90.44(11) 3.1269(9)  |
| Mn4–O25–Mn2 | 95.79(13) 3.1269(9)  |
| Mn3–O9–Mn5  | 106.51(13) 3.6385(11) |
| Mn4–O25–Mn6 | 119.52(16) 3.6219(10) |
| Mn2–O25–Mn6 | 123.80(15) 3.7352(9)  |

Figure 5. Magnetization in the -5.0 to 5.0 T range for 1.
4. Conclusion

This article describes the synthesis and crystal structure of a three-dimensional homometallic and homospin complex containing mixed hydroxide/carboxylate bridged high-spin Mn(II) ions forming an intricate 3D inorganic framework. The structure, built up from flexible (chda)$^2^-$ ligands, gives a 3D coordination polymer with relatively large cavities (2041 Å$^3$/per unit cell) where the naphthalene template molecules are weakly anchored. Complex 1 can only be synthesized in the presence of naphthalene, suggesting that naphthalene molecules play the role of template for the final 3D structure. The inorganic Mn(II)-network forms loop chains with twelve manganese ions per wheel showing the shortest Mn···Mn separations. The magnetic behavior of this compound suggests an overall antiferromagnetic behavior. However, the antiferromagnetic interactions are not completely well-compensated for, thus giving a weak ferromagnetic signal. Therefore, the system can be described from the magnetic point of view as a ferrimagnetic system where the ferromagnetic signal comes from the network topology, which results in a non-compensation of the magnetic moments. Therefore, 1 can be regarded as a new example of a homospin homometallic ferrimagnet. Most likely, topology frustration comes from the different exchange couplings within the high spin Mn(II) wheel; further research will be devoted to understand the influence of each exchange couplings within the Mn$_{12}$ loop.

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Disclosure statement

No conflict of interest has been declared by the authors.

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