



A neutral 2D oxalate-based soluble magnet assembled by hydrogen bonding interactions

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Dedicated to Professor Dante Gatteschi in occasion of his 60th birthday.

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ABSTRACT

Herein we describe the synthesis, structure and magnetic properties of a novel oxalate-based layered magnetic system: $\{[\text{Mn}(\text{OH}_2)_2(\text{S})_2][\text{Mn}(\text{S})(\text{OH}_2)]_2[\text{Cr}(\text{ox})_3]_2(18\text{-crown-6})\}_\infty$ ($\text{S} = \text{CH}_3\text{OH}$; $\text{ox} = \text{C}_2\text{O}_4^{2-}$; 18-crown-6 = $\text{C}_{12}\text{H}_{24}\text{O}_6$) (**1**). In this case, no cationic templating agent is required to promote the assembling of low-dimensional oxalate-bridged metallic complexes in solution. Instead, strong enough hydrogen bonding interactions are responsible for their packing in the solid state. This magnet is soluble and presents two different types of oxalate bridges: the common bis(bidentate) and the unusual bidentate-monodentate. This structural feature has drastic consequences on the magnetism of this compound, as it shows ferrimagnetic ordering below 5.5 K.

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1. Introduction

For more than 20 years, coordination chemists have shown high control on the design and synthesis of molecular frameworks whose physical properties and dimensionality are strongly dependent on the nature of both: their constituting metallic complexes and molecular linkers used to interconnect them in the solid state. Molecular magnetism has taken advantage of this expertise in order to provide a wide number of metallic polynuclear complexes exhibiting interesting magnetic properties. Probably, one of the most important aspects in the design of the magnetically active systems is the suitable choice of the linker that will support magnetic interactions. In this direction, those ligands presenting small size (constituted by a few number of atoms) while simultaneously offering a π and a σ electronic pathway for the magnetic superexchange, such as oxalate $\text{C}_2\text{O}_4^{2-}$ [1], oxamate (pbaOH) [2], cyanide (CN^-) [3] or dicyanamide ($[\text{N}(\text{CN})_2]^-$) [4] have yielded the greater part of molecule-based magnets reported up to now.

In particular, employment of homoleptic $[\text{M}^{\text{III}}(\text{ox})_3]^{3-}$ ($\text{M}^{\text{III}} = \text{Cr}$, Fe, Ru, Rh, Mn and V; $\text{C}_2\text{O}_4^{2-}$ tris-oxalate metalate octahedral complexes as ligands towards first-row transition metal ions has been widely described. In a first step, interaction between $[\text{M}^{\text{III}}(\text{ox})_3]^{3-}$ complexes and M (II) ions leads to the formation of low-dimensional oxalate-bridged oligomeric species, which remain in

solution thanks to their charged nature. Next, the presence of a cationic templating agent is required in order to drive their assembling thus generating neutral coordination polymers, which can be subsequently isolated from solution. As widely described in the literature, nature of the cationic complex is a key element to determine the resulting structure of the oxalate-based heterometallic framework. The great part of extended structures obtained through this method can be classified in two main categories:

- 2D compounds presenting a layered bidimensional honeycomb structure [5] described by the general formula $[\text{A}][\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})]$ ($\text{A}^+ = \text{NR}_4, \text{PR}_4$; $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$; $\text{M}^{\text{III}} = \text{Cr}, \text{Fe}, \text{Ru}, \text{Rh}, \text{V}, \text{Mn}$) exhibiting ferro, ferri or weak ferromagnetic ordering with critical temperatures up to 45 K [6].
- 3D families $[\text{Z}^{\text{II}}(\text{bpy})_3]$ [7] $[\text{MM}'(\text{ox})_3]$ [8] and $[\text{Z}'(\text{ppy})(\text{bpy})_2][\text{MM}'(\text{ox})_3]$ [9] ($\text{Z}^{\text{II}} = \text{Fe}, \text{Co}, \text{Ni}, \text{Ru}$; $\text{Z}' = \text{Ru}, \text{Ir}$; $\text{X} = \text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-$; $\text{M}, \text{M}' = \text{Li}^+, \text{Na}^+, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Rh}^{\text{III}}, \text{Co}^{\text{III}}, \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}$; $\text{bpy} = 2,2'$ -dipyridyl, $\text{ppy} = \text{phenylpyridine}$) for whom tris-bipyridyl chiral complexes, presenting the appropriate D_3 symmetry, induce the $[\text{M}^{\text{III}}(\text{ox})_3]^{3-}$ building blocks to adopt an homochiral configuration ($\Delta\Delta$ or $\Lambda\Lambda$). These higher dimensional systems present ferro- and ferromagnetic behaviour but with lower critical temperatures than their 2D analogs.

All the discussed examples present one common aspect; coordination polymers are assembled in solution by the interaction

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of anionic low-dimensional oligomeric species with a templating cationic complex. The construction of new, even more complex molecular restructures implies the control of how the molecular building blocks get ordered in the solid state. By means of this control, synthesis of new materials with predictable structure and properties will be accessible. In this direction, important attention must be paid not only to covalent bonding or cation–anion electrostatic interactions but also to weaker supramolecular interactions.

The low directionality and weakness of hydrogen bonding interactions makes it difficult to predict how molecular components will get assembled in the crystalline packing [10]. However, they have been widely employed as effective supramolecular bonding forces in the design of purely organic magnets [11]. Inspired by this work, we have studied how these weak interactions might play an important role in the design and isolation of novel hybrid metal–organic extended structures. We recently reported the synthesis and magnetic characterization of the 2D bimetallic oxalate-bridged system: $[\text{Co}(\text{H}_2\text{O})_2]_3[\text{Cr}(\text{ox})_3]_2(18\text{-crown-6})_2$ [12]. As no cation was required for its isolation, it constitutes the first example of a neutral oxalate-based magnet. In that particular case, it was the presence of hydrogen bonding interaction between the neutral bimetallic coordination polymer host and a guest molecule, the 18-crown-6 ether molecule, the driving force allowing for its assembling and further isolation. We have now successfully extended this synthetic strategy to other first-row divalent metallic ions, Mn (II) for instance. Herein, we describe the structure and magnetic properties of the resulting $\{[\text{Mn}(\text{OH}_2)_2(\text{CH}_3\text{OH})_2][\text{Mn}(\text{CH}_3\text{OH})(\text{OH}_2)]_2[\text{Cr}(\text{ox})_3]_2(18\text{-crown-6})\}_\infty \cdot \text{CH}_3\text{OH}$ compound. The influence of divalent metallic ion substitution on the resulting magnetic properties and hydrogen bonding intermolecular interactions effect on the oxalate ligand coordination modes and the consequential crystalline packing will be also discussed in this paper.

2. Experimental

2.1. Synthesis

All reagents and solvents were of commercially available grade and were used without any previous purification. $\text{K}_3[\text{Cr}(\text{ox})_3]$ salt was prepared following a previously described method. [13] The $\text{Ag}_3[\text{Cr}(\text{ox})_3]$ derivative was obtained by metathesis of the potassium salt and protected from light to avoid decomposition. Compound $\{[\text{Mn}(\text{OH}_2)(\text{CH}_3\text{OH})][\text{Mn}(\text{OH}_2)_2]_2[\text{Cr}(\text{ox})_3]_2(18\text{-crown-6})\} \cdot \text{CH}_3\text{OH}$ (**1**) was prepared as single crystals suitable for X-ray diffraction by slow diffusion of its components in a H-tube. $\text{Ag}_3[\text{Cr}(\text{ox})_3]$ (698 mg; 1 mmol) and $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ (396 mg; 2 mmol) were suspended in 15 mL of methanol and mechanically stirred for 20 min. The solution gets coloured as the Cr (III) oxalate complex dissolves. The resulting mixture was left to stand at room temperature and the $\text{AgCl}(\text{s})$ white precipitate was filtered off. The resulting purple solution was poured into one H-tube leg while solid 18-crown-6 (264 mg; 1 mmol) was added to the other. Subsequently, methanol was carefully dropped to both legs until the tube was completely filled. The system was protected from light and left to stand at room temperature. Formation of purple crystals of **1** was observed after 15 days. They were separated from their mother-liquor, washed thoroughly with methanol and dried in air. Yield: 57%. Anal. Calc. for $\text{H}_{74}\text{C}_{42}\text{Cr}_2\text{Mn}_3\text{O}_{46}$ (1583.83): C, 31.85; H, 4.71. Found: C, 32.0; H, 4.88%.

2.2. X-ray data collection and analysis

A purple crystal of compound **1** was collected by hand, fixed on a 200 μm MicroMount [14] and mounted on a Nonius-Kappa CCD single crystal diffractometer equipped with graphite-monochro-

mated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ nm) at 293(2) K. Data collection was performed by using the program COLLECT [15]. Data reduction and cell refinement were performed with programs DENZO and SCALEPACK [16]. Crystal structure was solved by direct methods using the program SIR97 [17], followed by Fourier synthesis and refined on F^2 with SHELXL-97 [18]. Hydrogen atoms positions from the water molecules bonded to Mn ions were located through Fourier differences, the rest of them were calculated and their thermal parameters were fixed to be 50% larger than those of the atoms they are connected to. All crystallographic plots were obtained by using the CRYSTMALMAKER program [19]. Anisotropic least-squares refinement of all non-H atoms was performed. Table 2 summarizes the crystal, data collection and refinement parameters of **1**.

2.3. Physical measurements

Carbon, nitrogen and hydrogen contents were determined by micro analytical procedures using an EA 1110 CHNS-O Elemental Analyzer from CE Instruments. Metallic composition of bulk samples was determined by electron probe microanalysis (EPMA) performed in a Philips SEM XL30 equipped with an EDAX DX-4 microsonde. Infrared spectra were recorded in a FT-IR Nicolet 5700 spectrometer in the 4000–400 cm^{-1} range using powdered hand collected crystal samples in KBr pellets. Magnetic susceptibil-

Table 1
Relevant hydrogen bonding parameters for compound **1**

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O(13)–H(131)...O(4C)	0.83	2.02	2.8395	173
O(13)–H(132)...O(6C)	0.88	2.24	3.0930	163
O(15)–H(151)...O(1C)	0.91	1.84	2.7479	177
O(15)–H(151)...O(2C)	0.91	2.60	2.9566	104
O(15)–H(152)...O(3C)	0.83	2.01	2.8300	168
C(10C)–H(10B)...O(4)	0.97	2.43	3.3397	156
C(12C)–H(12B)...O(9)	0.97	2.46	3.3707	157
C(6C)–H(61)...O(8)	0.97	2.50	3.3837	152
C(8C)–H(81)...O(5)	0.97	2.58	3.3415	136

Table 2
Crystallographic data for $\{[\text{Mn}(\text{OH}_2)(\text{CH}_3\text{OH})][\text{Mn}(\text{CH}_3\text{OH})_2(\text{OH}_2)_2]_2[\text{Cr}(\text{ox})_3]_2(18\text{-crown-6})\} \cdot \text{CH}_3\text{OH}$ (**1**)

Formula	$\text{H}_{74}\text{C}_{42}\text{Cr}_2\text{Mn}_3\text{O}_{46}$
Size (mm)	0.1 × 0.2 × 0.2
Molecular weight	1583.83
T (K)	293(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.0220(2)
b (Å)	15.3770(3)
c (Å)	19.9230(4)
α (°)	90
γ (°)	97.7470(8)
β (°)	90
V (Å ³)	3345.84(11)
Z	2
ρ_{calc} (g cm^{-3})	1.572
μ (Mo $\text{K}\alpha$) (cm^{-1})	0.971
F(000)	1634
2 θ Limit	2.96–27.49
Goodness-of-fit	0.964
Reflections/parameters	7569/437
R_1^a	0.0588
R_2^b	0.1632
Maximum difference in peak and hole	0.500 and –0.595

$$^a R_1 = \sum(F_o - F_c) / \sum(F_o)$$

$$^b R_2 = [\sum(\omega(F_o^2 - F_c^2)^2) / \sum(\omega(F_o^2)^2)]^{1/2}; \omega = 1 / [\sigma^2(F_o^2) + (0.0343P)^2 + 2.4502P]; P = (F_o^2 + 2F_c^2) / 3.$$

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