

# Muconato-bridged Manganese Coordination Polymer exhibiting rare Distorted-trigonal Prismatic Coordination Arrangement

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**Abstract.** Novel poly[Mn(H<sub>2</sub>O)(dmb)(muco)] (**1**) (H<sub>2</sub>muco = *trans,trans*-muconic acid; dmb = 5,5'-dimethyl-2,2'-bipyridine) was obtained by self-assembly, one-pot, solution reaction. **1** crystallizes in a monoclinic system with *P*2<sub>1</sub> space group and forms an infinite one-dimensional (1D) polymer. Remarkably, the six-coordinate Mn<sup>II</sup> display a rare distorted trigonal prismatic configuration. This unusual co-

ordination arrangement appears to be acquired due to the supramolecular interactions of the polymeric structure of **1**, mainly throughout hydrogen bonding, giving rise to a 2D framework. Magnetic properties measurements reveal that **1** possesses weak antiferromagnetic interactions with  $\theta_{(C-W)} = -1.0$  K and  $J = 458$  cm<sup>-1</sup>.

## Introduction

Coordination polymers continue being a relevant topic due to their almost infinite structural possibilities and their important intrinsic properties and potential applications.<sup>[1]</sup> *Trans,trans*-muconic acid employed as a bridging ligand has been reported in just a handful Ni, Co, Cu, and Zn coordination polymers,<sup>[2–5]</sup> Mo dinuclear complexes,<sup>[6]</sup> and a Pt macrocycle,<sup>[7]</sup> among the most relevant literature. To the best of our knowledge, there are not reports on coordination polymers with Mn<sup>II</sup> using this dicarboxylate compound; neither magnetic studies of Mn<sup>II</sup> complexes bearing muconato have been described previously. The use of 2,2'-bipyridine as ancillary ligand had become relevant in our earlier studies on coordination polymers.<sup>[8]</sup>

Therefore, we have been using one of the most studied nitrogen donor ligand,<sup>[9]</sup> and just varying the alkyl-substituents on it, in order to verify the possible influence of the steric hindrance on the transition metal coordination spheres, dimensionality, and crystalline structures of coordination polymers. As it is well known, transition metal six-coordination continues to be ruled by octahedral arrangements. Nonetheless, in the last two decades, a series of transition-metal complexes

with trigonal-prismatic environment were obtained due to the use of non-innocent multi-chelating ligands and by ligand design.<sup>[10]</sup> Furthermore, in fewer cases, this arrangement has been revealed in complexes using innocent bidentate ligands, such as bipyridine and acac, and even in complexes with monodentate ligands.<sup>[11]</sup>

Herein, we describe the synthesis, crystal structure details and magnetic properties of polymer [Mn(H<sub>2</sub>O)(dmb)(muco)] (**1**) (H<sub>2</sub>muco = *trans,trans*-muconic acid; dmb = 5,5'-dimethyl-2,2'-bipyridine), which shows an unusual distorted trigonal prismatic coordination sphere, that include innocent ligands and an aqua ligand, as well as a 2D supramolecular array through hydrogen bonding. Self-assembly of small molecules, compounds or complexes, has demonstrated to be an appreciated process for synthesizing large structures with a minimum effort.<sup>[12]</sup>

## Results and Discussion

The synthesis of **1** was performed at ambient conditions by mixing MnCl<sub>2</sub>·4H<sub>2</sub>O with the muco and dmb ligands in a water-methanol solution, giving rise to yellow crystals of **1**, which structure was determined by elemental analysis, IR, and single-crystal X-ray diffraction analysis (see Scheme 1).

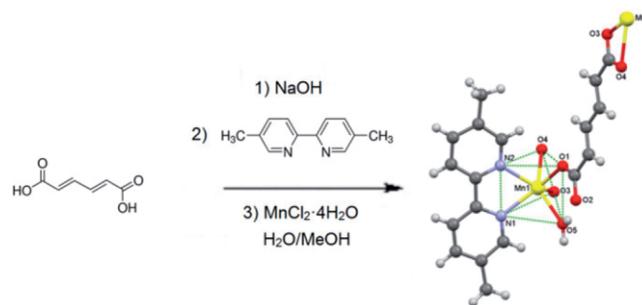
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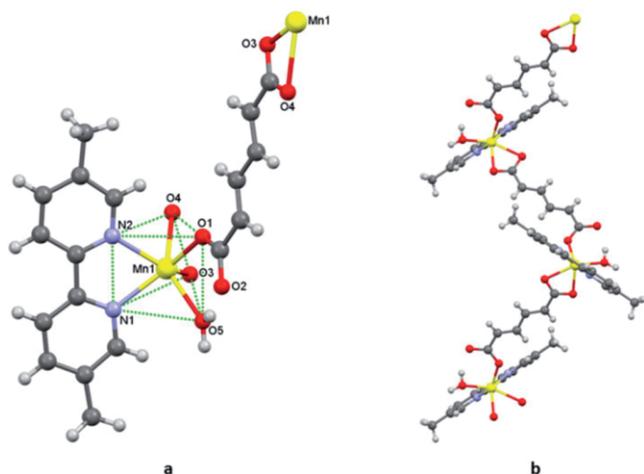
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**Scheme 1.** Self-assembly synthesis of polymer **1**. Molecular crystalline structure is shown.

Polymer **1** crystallizes in a monoclinic system with  $P2_1$  space group and forms an infinite 1D zigzag chain structure (Figure 1). The  $\text{Mn}^{\text{II}}$  atom in **1** is hexacoordinate with a  $\text{N}2\text{O}4$  distorted trigonal-prismatic coordination environment (Figure 1a), coming from two muco ligands, one dmb ligand, and one coordinated water molecule. The metal to nitrogen distances are 2.2412(16) and 2.2482(15) Å. The metal to oxygen distances for the muco ligand are 2.1722(14) and 2.3618(13) Å for the chelate end, and 2.1111(13) Å for the monodentate carboxylate. The Mn–O bond for the coordinated water molecule is 2.1805(13) Å. The bite angle for the chelate end of the muco ligand is  $57.80^\circ$ . The dmb ligand has a bite angle of  $72.37^\circ$ .

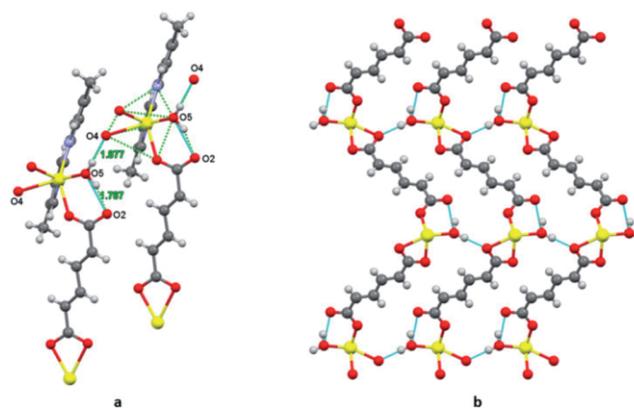


**Figure 1.** Coordination sphere around  $\text{Mn}^{\text{II}}$  ion (a) and 1D polymeric structure for **1**; view perpendicular to  $ab$  plane (b).

The obtuse angles between the least-squares mean planes of the chelate rings (dmb and bidentate chelate muco end), and the plane of the monodentate carboxylate of muco and the water molecule and the metal, lie in the range  $113.99$ – $129.56^\circ$ , in concordance with a distorted trigonal prismatic coordination arrangement. For **1**, the lengths of the triangular sides are in the range  $3.016$ – $3.305$  Å for the triangle  $\text{O}3$ – $\text{N}1$ – $\text{O}5$  and  $3.054(2)$ – $3.131(2)$  Å for the triangle  $\text{O}1$ – $\text{N}2$ – $\text{O}4$ , all angles are in the range  $56.12$ – $65.49^\circ$ . Three muco oxygen atoms ( $\text{O}1$ ,  $\text{O}3$ ,  $\text{O}4$ ) and one oxygen atom ( $\text{O}5$ ) from the aqua ligand make up a trapezoid, which should be a perfect square for ideal trigonal-prismatic arrangement. The sides of which are in the range of  $2.198(3)$ – $3.131(2)$  Å. The remaining two faces of the prism are also trapezoids consisting of three oxygen atoms of the muco ligand and one oxygen atom of the aqua ligand, which are joined by the two nitrogen atoms of the dmb ligand, respectively. Both faces have an O–O distance of  $2.198(3)$  and  $2.912(2)$  Å, an N–O distance in the range  $3.054(2)$ – $3.305(2)$  Å, and a distance of  $2.651(2)$  Å for the  $\text{N}1$ – $\text{N}2$  side. Due to these marked differences in distances of the trapezoid faces of the prism, the two triangular faces are not parallel. Thus, the planes defined by  $\text{O}3$ – $\text{N}1$ – $\text{O}5$  and  $\text{O}1$ – $\text{N}2$ – $\text{O}4$  make an angle of  $17.17^\circ$ . The torsion angles about the centroids of the triangular faces and each of the corners (i.e.,  $\text{Ct}1$ – $\text{N}1$ – $\text{N}2$ – $\text{Ct}2$ ) are  $8.08$ ,  $16.07$ , and  $6.70^\circ$ .

It has been shown that the relative abundance of trigonal prismatic complexes for the transition metals is scarcely 1.0% of the six-coordinate central metal atoms.<sup>[13]</sup> Moreover, it has been found that the distribution of this type of arrangement among the transition metals is highly inhomogeneous; the frequency of trigonal prismatic structures is highest for transition metals in groups 3 and 4, Ag and group 12. In addition, there are some metals in groups 5, 6, and 7, and Fe, that also contribute with some examples of trigonal prismatic complexes. Thus, most of the complexes exhibiting trigonal prismatic arrangement belong to those metal–ligand combinations having soft donor atoms and central metal in a high oxidation state, with  $d^0$ ,  $d^1$ , and  $d^2$  configurations. Even more, to the best of our knowledge, there is only one example reported in literature about metaprism complexes with innocent ligands, including an aqua ligand, in their structures,<sup>[14]</sup> and also, one article showing a  $\text{Mn}^{\text{II}}$  coordination polymer having trigonal prismatic environment.<sup>[15]</sup> Therefore, mixed ligands trigonal prismatic complexes or coordination polymers of Mn, using innocent bidentate ligands, are still considered rare. Additionally, muconato bridging-coordination mode in **1** is a combination of monodentate and bidentate chelate at the carboxylate ends (Figure 1). This type of coordination mode is still sporadic among dicarboxylato-bridging complexes or polymers, and it is the first time this particular coordination-bonding mode appears in hybrid polymers assembled with muconato.

In the solid-state, polymer **1** generates a 2D supramolecular structure mainly throughout hydrogen bonding (Figure 2). These interactions are promoted by the presence of the aqua ligand and the non-coordinated oxygen atom of the muco carboxylate. These conditions can be clearly observed in Figure 2, where the main O–H $\cdots$ O hydrogen bonds are formed by the O–H moiety ( $\text{O}5$ ) of the aqua ligand with each of the oxygen atom ( $\text{O}2$ ) of the non-coordinated side of one muco ligand. This is an intramolecular hydrogen bond.

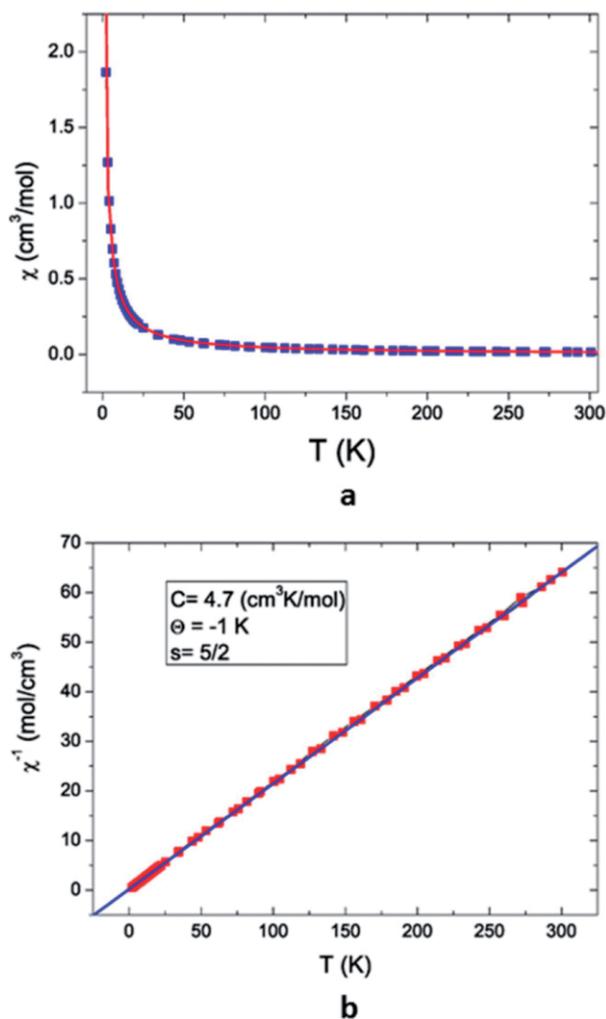


**Figure 2.** Supramolecular 2D array in **1**. Intramolecular and intermolecular hydrogen bonds (a). Hydrogen bonding motif; view perpendicular to  $ab$  plane; dmb ligands removed for clarity (b).

Furthermore, each water molecule is a hydrogen-bond donor to two different hydrogen bonds, the one that is already described above, and another with one muco oxygen atom ( $\text{O}4$ ) already coordinated to  $\text{Mn}^{\text{II}}$  of a neighboring polymeric chain (intermolecular hydrogen bonding) generating, thus, an ex-

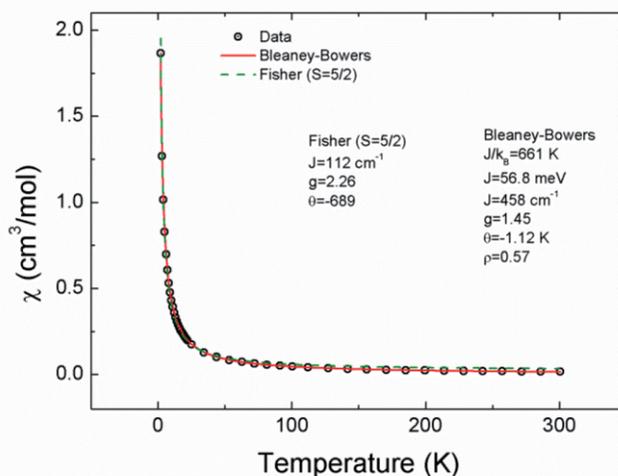
tended 2D supramolecular array (Figure 2). In fact, this bridging-hydrogen bonding performed by the aqua ligand in **1**, can be identified as the key structural factor that allows the formation of a 2D supramolecular structure and, at the same time, provokes the generation of a unique distorted-trigonal prismatic (metaprism) coordination sphere around Mn<sup>II</sup> ions. Similar, supramolecular arrays have been obtained in Co and Zn fumarato complexes<sup>[14]</sup> having also distorted-trigonal prism arrangements. Examples where  $\pi$ -backbonding effects, crystal packing, and rigidity of ligands influence the structure of complexes acquiring the trigonal prismatic arrangement have been reported.<sup>[16,17]</sup> Nonetheless, polymer **1** is one of the first examples where the preference of distorted-trigonal prismatic, over the typical octahedral coordination mode, may be dictated by supramolecular interactions determining the final solid-state structure.

The temperature dependence of the magnetic susceptibility,  $\chi$ , of **1** was determined by measurements performed at zero field cooling (ZFC) and field cooling (FC) from 2–300 K and decreasing. The applied magnetic field was 100 Oe. Plots of  $\chi$  and  $\chi^{-1}$  vs. temperature are shown in Figure 3. The effective



**Figure 3.**  $\chi$  vs.  $T$  plot (a) and  $\chi^{-1}$  vs.  $T$  plot (b) for **1**. Lines correspond to Curie-Weiss law fitting.

magnetic moment [ $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$ ] at room temperature is  $6.11 \mu_{\text{B}}$ , higher than the spin only value of  $5.92 \mu_{\text{B}}$  expected for high-spin Mn<sup>II</sup> in an octahedral crystal field.<sup>[18]</sup> Over the temperature range studied, the magnetic susceptibility data of **1** can be nicely fitted to the Curie-Weiss law,  $\chi = C/(T - \theta)$ , with  $C = 4.7 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  with the Curie-Weiss temperature  $\theta_{(\text{C-W})} = -1.0 \text{ K}$  (Figure 3). Further analyses of the magnetic properties of **1** were performed using Fisher model for a metal atoms chain<sup>[19]</sup> and Bleaney-Bowers model for dinuclear magnetic exchange,<sup>[20]</sup> yielding better fitting results for the latter model throughout the entire temperature range of study (Figure 4). Thus, Bleaney-Bowers model revealed a  $J = 458 \text{ cm}^{-1}$  and a  $\theta = -1.12 \text{ K}$ , this latter value is very similar to that obtained by Curie-Weiss fitting, which proves further that polymer **1** possesses weak antiferromagnetic exchange. This antiferromagnetic coupling between the central metal atoms may arise from the supramolecular structure of **1** (Figure 2b), since in that 2D arrange the Mn $\cdots$ Mn distance is  $6.505 \text{ \AA}$ , whereas the metal distance through the 1D polymer structure (muconato bridging) is  $11.204 \text{ \AA}$ . For a muconato-bridged 3D Ni<sup>II</sup> polymer, weak antiferromagnetic behavior was also reported.<sup>[2]</sup> Moreover, for the other Mn<sup>II</sup> coordination polymer reported having trigonal prismatic arrangement, an antiferromagnetic behavior was also found, but its experimental values did not follow Curie-Weiss law, particularly below 140 K; unexpected high  $C$  and  $\theta$  values were obtained, which was ascribed to the magnetic anisotropy that accompanies to the unusual trigonal prismatic arrangement for Mn<sup>II</sup>.<sup>[15]</sup>



**Figure 4.**  $\chi$  vs.  $T$  plot for **1**. Red line corresponds to Bleaney-Bowers model fitting; green-discontinue line corresponds to Fisher model fitting.

## Conclusions

1D coordination polymer **1** represents the first example of a Mn<sup>II</sup>-muconato bridged extended structure, and also the first one exhibiting a distorted-trigonal prismatic coordination arrangement having innocent bidentate ligands and, in particular, an aqua ligand in its coordination sphere. Magnetic properties

of **1** follows well the Curie-Weiss law and the Bleaney-Bowers model, with a  $\theta = -1.0$  K and  $J = 458$  cm<sup>-1</sup>, demonstrating the existence of antiferromagnetic interactions. Both, coordination arrangement and magnetic properties of **1**, can be attributed to its 2D supramolecular array in the crystalline state.

## Experimental Section

**Materials and Instrumentation:** All chemicals were of analytical grade, purchased commercially (Aldrich) and were used without further purification. Elemental analyses for C, H, and N were carried out for standard methods with a Vario Micro-Cube analyzer. IR spectra of the complexes were determined as KBr disks with an Avatar 360 FT-IR Nicolet spectrophotometer from 4000–400 cm<sup>-1</sup>. Crystallographic data for **1** were collected with a Bruker SMART APEX DUO three-circle diffractometer equipped with an Apex II CCD detector using Mo- $K_{\alpha}$  ( $\lambda = 0.71073$  Å, Incoatec I $\mu$ S microsource) at 100 K.<sup>[21]</sup> The crystal was coated with hydrocarbon oil (Parabar), picked up with a nylon loop, and mounted in the cold nitrogen stream (100 K) of the diffractometer. The structure was solved by direct methods (SHELXS-97)<sup>[22]</sup> and refined by full-matrix least-squares on  $F^2$ <sup>[29]</sup> using the shelXle GUI.<sup>[23]</sup> The hydrogen atoms of the C–H bonds were placed in idealized positions whereas the hydrogen atoms from H<sub>2</sub>O molecule were localized from the difference electron density map, and their position was refined with  $U_{iso}$  tied to the parent atom with distance restraints at distances standard (0.84 Å for O–H bond) using distance restraints (dfix). Magnetic characteristics of **1** were determined in a MPMS Quantum Design magnetometer with measurements performed at zero field cooling (ZFC) and field cooling (FC) from 2–300 K and decreasing. The applied magnetic field was 100 Oe, and the total diamagnetic corrections were estimated using Pascal's constants as  $-250 \times 10^{-6}$  cm<sup>3</sup>·mol<sup>-1</sup>.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1474257 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

**Synthesis of 1:** A 10 mL solution of sodium hydroxide (0.5 mmol) was added to a methanol-water solution (60 mL) of *trans,trans*-mucic acid (0.25 mmol) while stirring. This solution was heated at 60 °C for 5 min. Afterwards, a methanol solution (5 mL) of 5,5'-dimethyl-2,2'-bipyridine (0.25 mmol) was poured while stirring. After 5 min, this ligands solution was added to a water solution (5 mL) of MnCl<sub>2</sub>·4H<sub>2</sub>O (0.25 mmol). Finally, a light-yellow translucent solution was obtained. After 2 d, yellow small crystals were obtained, filtered, washed with a 50:50 deionized water-methanol solution, and air-dried. Yield: 65.54% based on metal precursor. C<sub>18</sub>H<sub>18</sub>MnN<sub>2</sub>O<sub>5</sub>: calcd. C 54.41; H 4.56; N 7.05%; found: C 54.17; H 4.56; N 7.03%. **IR** (KBr):  $\tilde{\nu} = 3271$  (vs, br), 3051 (m), 2904 (m), 1936 (w), 1921 (w), 1840 (w), 1620 (s), 1527 (s), 1531 (s), 1373 (s), 1292 (m, sh), 1246 (m, sh), 1161 (m), 1022 (s,sh), 957 (m, sh), 879 (m), 698 (m, br), 563 (m,sh), 417 (m, sh), 413 (s,sh) cm<sup>-1</sup>.

**Supporting information** (see footnote on the first page of this article): Characterization data, including IR spectroscopy and X-ray crystallography.

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**Keywords:** Coordination polymer; Trigonal prismatic; Manganese; Metaprism; Antiferromagnetism; Supramolecular chemistry

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