

# Assembly of a manganese(II) pyridine-3,4-dicarboxylate polymeric network based on infinite Mn–O–C chains †

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Received 24th October 2002, Accepted 18th November 2002

First published as an Advance Article on the web 28th November 2002

A unique metal–organic polymer Mn·PDB·H<sub>2</sub>O (H<sub>2</sub>PDB = pyridine-3,4-dicarboxylic acid), with weak antiferromagnetic interactions both between the manganese(II) centers of an infinite Mn–O–C chain and between the adjacent chains, has been synthesized by the hydrothermal reaction of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O with H<sub>2</sub>PDB; X-ray diffraction shows that the polymer possesses a one-dimensional rectangular channel built up from pyridine rings and pseudo-layers formed by infinite straight Mn–O–C chain building units.

The research on transition metal–organic polymers has been rapidly expanding<sup>1</sup> because of their intriguing topologies and their potential applications, such as in catalysis,<sup>2</sup> adsorption,<sup>3</sup> non-linear optics,<sup>4</sup> fluorescence,<sup>5</sup> electrical conductivity<sup>6</sup> and magnetism.<sup>7</sup> Transition metal–organic compounds may yield a great variety of geometries<sup>1c</sup> and exhibit interesting magnetic<sup>7</sup> and spectroscopic properties.<sup>5b,c</sup> Multi-carboxylate ligands also possess several interesting characteristics: (a) they can exhibit various coordination geometries because of their completely or partially deprotonated carboxylic groups, leading to various structures with higher dimensions; (b) the adjacent carboxylic groups with a special angle (such as 180°, 120° and 60°) may connect metal ions in a particular direction to obtain unique extended networks; (c) they can be regarded not only as hydrogen-bond acceptors but also as hydrogen-bond donors, depending upon the number of deprotonated carboxylic groups. Our interest mainly focuses on the utilization of hydrothermal synthesis to construct transition metal–organic polymers with new structural features from simple ligands and the magnetic properties of these polymers.

More recently, *p*-pyridinecarboxylic acid<sup>8</sup> and *m*-pyridinedicarboxylic acid<sup>4,9</sup> have been used as ligands which showed versatility as manifested by the formation of 1D, 2D and 3D polymeric structure systems. As a ligand, pyridine-3,4-dicarboxylic acid (H<sub>2</sub>PDB)<sup>10</sup> has unique features besides the merits of *p*-pyridinecarboxylic acid and *m*-pyridinedicarboxylic acid. As a result of the steric hindrance between the two adjacent carboxylic groups (separated by a 60° angle), the whole conjugation interaction between the pyridine group and the carboxylic groups is remarkably weakened so that unlike *p*-pyridinecarboxylic acid and *m*-pyridinedicarboxylic acid, H<sub>2</sub>PDB usually acts as a steric ligand instead of a planar one. Therefore, it is more likely that PDB will form high-dimensional frameworks with metals. In this communication, we describe the crystallization of a polymeric open framework compound derived from a hydrothermal system involving manganese ions and H<sub>2</sub>PDB as the reactants.

The hydrothermal reaction of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, H<sub>2</sub>PDB, triethylamine and distilled water at 160 °C for 72 hours under autogenous pressure gave rise to pink rhombohedral

crystals of the polymer in *ca.* 53% yield. Thermogravimetric analysis (TGA) under an atmospheric environment shows that the weight loss of 29.1% between 220 and 315 °C corresponds to the removal of all the organic components and water to yield MnO (calculated: 29.8%). A weight gain of up to about 32.8% occurs at above 315 °C, in accordance with the previously reported conversion of MnO to Mn<sub>3</sub>O<sub>4</sub> (calculated: 32.1%).<sup>11</sup>

An X-ray single crystal diffraction study ‡ on a crystal obtained from the reaction product reveals the presence of a three-dimensional framework that possesses a one-dimensional rectangular channel built up from pyridine rings and infinite Mn–O–C chains. In the asymmetric unit, there is one crystallographically independent Mn ion, one PDB and one water molecule. The Mn atom is located in the centre of a distorted octahedron formed by one pyridine nitrogen atom (Mn(1)–N(1) 2.2845(18) Å) from the PDB unit, four oxygen atoms (Mn(1)–O(1) 2.1593(16) Å, Mn(1)–O(2) 2.1667(15) Å, Mn(1)–O(3) 2.1980(16) Å and Mn(1)–O(4) 2.1770(16) Å) from the carboxylic groups of different PDB units and one oxygen atom (Mn(1)–O(5) 2.3087(17) Å) from the terminal water molecule (Fig. 1). Each carboxylic group of the PDB ligand is bridged

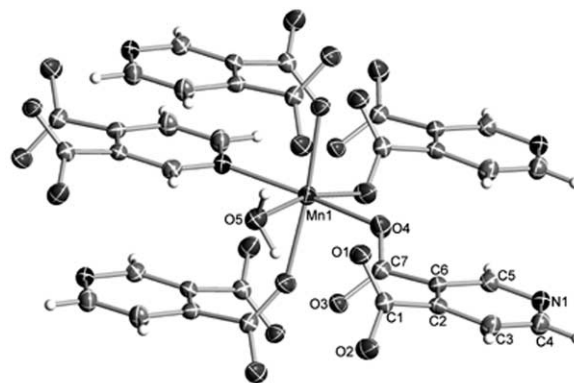


Fig. 1 The Mn(II) coordination environment including the asymmetric unit is represented by thermal ellipsoids drawn to encompass 50% of their electron density.

between two manganese ions to form infinite straight Mn–O–C chains running along the [101] direction (Fig. 2). The intrachain Mn–Mn distance and the interchain distance are *ca.* 4.8 Å and *ca.* 5.7 Å, respectively. These straight chains are aligned in the *ac* plane to form pseudo-layers and the interlayer distance is *ca.* 7.6 Å. Meanwhile, all of the manganese ions of each pseudo-layer are coplanar. The chains are cross-linked by pyridine rings, leading to the topology of a three-dimensional extended network in which the terminal water molecules point into the one-dimensional rectangular straight channels running along the [001] direction (Fig. 3). The distance of the adjacent pyridine rings between the Mn–O–C pseudo-layers is *ca.* 3.3 Å. The observed interatomic distances of O(5)–O(2)#3 and O(5)–O(3)#2 associated with the H-bonding are 2.877(2) and 2.723(2) Å, indicative of strong H-bonding interactions.

† Electronic supplementary information (ESI) available: experimental details; table of selected bond lengths and angles; TGA and DSC curves; experimental magnetic data. See <http://www.rsc.org/suppdata/dt/b2/b210462h/>

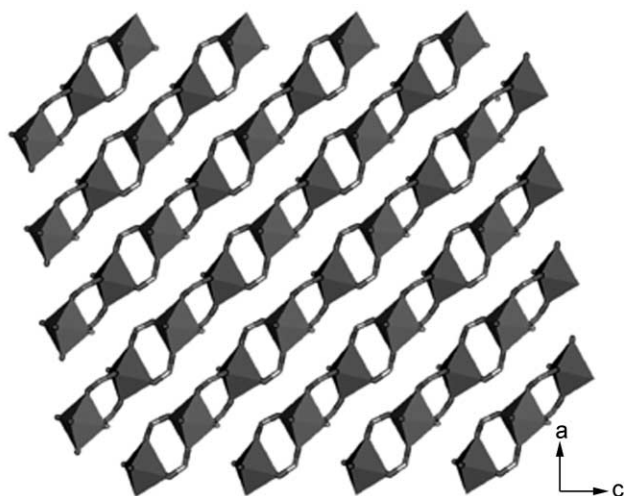


Fig. 2 The pseudo-layer parallel to the *ac* plane, which is made up of infinite Mn–O–C chain building units, viewed along the [010] direction (pyridine rings have been omitted for clarity).

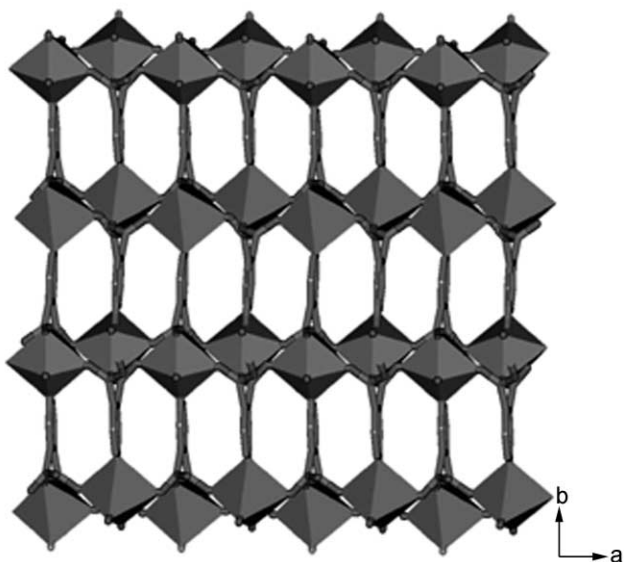


Fig. 3 The three-dimensional framework of the polymer that possesses a one-dimensional rectangular channel built from the conjugated system of pyridine rings and the pseudo-layers viewed along the [001] direction.

Temperature-dependent magnetic susceptibility measurements for the polymer were performed on the polycrystalline sample. In Fig. 4, the value of  $\chi_M T$  is shown to be  $7.58 \text{ cm}^3 \text{ K mol}^{-1}$  at room temperature, which is larger than that expected for an uncoupled manganese(II) ion ( $g = 2.0$ ,  $4.38 \text{ cm}^3 \text{ K mol}^{-1}$ ). As the temperature decreases, the value of  $\chi_M T$  decreases continuously upon cooling and reaches  $1.65 \text{ cm}^3 \text{ K mol}^{-1}$  at 4 K, indicating the occurrence of an antiferromagnetic interaction between the manganese ions. According to the structural data, the polymer may exhibit two types of Mn(II)–Mn(II) magnetic exchange interaction: type one is through a short bridge *via* the carboxylate groups of PDB between the manganese(II) centers of an infinite Mn–O–C chain, which is treated as the intra-chain interaction; and type two is through a long bridge *via* the pyridine ring of PDB between the adjacent chains, which is taken as the interchain interaction. The  $\chi_M$  data are well interpreted based on the expression of Fisher's model for the classical spin chain system [eqn. (1), (2)] and the molecular field approximation [eqn. (3)].<sup>12</sup> Taking into account the TIP term, a satisfactory least-squares fitting§ of the observed data at 4–298 K led to  $J/k = -0.81 \text{ K}$ ,  $zJ'/k = -0.13 \text{ K}$ ,  $g = 2.19$ , TIP(1) =  $6.46 \times 10^{-3}$  and TIP(2) =  $3.05 \times 10^{-3}$  with the agreement

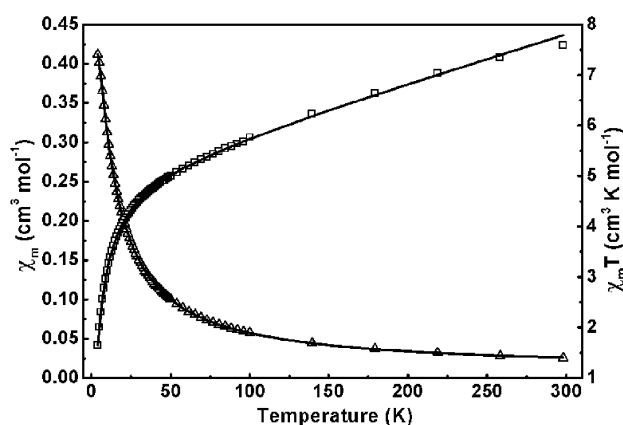


Fig. 4 Temperature dependence of  $\chi_M$  ( $\Delta$ ) and  $\chi_M T$  ( $\square$ ) values for the polymer. The solid line corresponds to the best-fit curves using the parameters described in the text.

factor  $R = 1.77 \times 10^{-6}$  [eqn. (4)].  $J$  may be assigned to type one and  $zJ'$  to type two. The small negative  $J$  and  $zJ'$  values imply the existence of a weak antiferromagnetic interaction both between the manganese(II) centers of an infinite Mn–O–C chain and between the adjacent chains. The possible reason that the magnetic exchange interaction in the polymer is weakened is that the whole conjugacy of the PDB molecules is weakened by the steric hindrance between the pyridine group and the carboxylic groups.

In summary, we have demonstrated a unique open-framework metal–organic polymer that possesses a one-dimensional rectangular channel with a diameter of *ca.*  $7.6 \times 3.3 \text{ \AA}$  built from pyridine rings and infinite straight Mn–O–C chain building units. In addition, the analysis of the magnetic properties suggests that the magnetic exchange interactions both between the Mn(II) centers of an infinite Mn–O–C chain and between the adjacent chains are weakly antiferromagnetic.

We thank Professor Li-Min Zheng (Nanjing University) for helpful discussions on magnetic properties and the National Natural Science Foundation of China for financial support.

## Notes and references

‡ Crystal data for the polymer:  $\text{C}_7\text{H}_2\text{MnNO}_5$ ,  $M = 238.06$ , monoclinic, space group =  $P2_1/n$  (no. 14),  $a = 6.7055(14) \text{ \AA}$ ,  $b = 14.783(3) \text{ \AA}$ ,  $c = 7.9166(15) \text{ \AA}$ ,  $\beta = 100.724(3)^\circ$ ,  $V = 771.0(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $F(000) = 476$ ,  $D = 2.051 \text{ g cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 293(2) \text{ K}$ ,  $\mu(\text{Mo-K}\alpha) = 1.705 \text{ mm}^{-1}$ ,  $R = 0.0328$ ,  $R_w = 0.0859$ ,  $R_{\text{int}} = 0.0199$ , 1780 unique reflections with  $I > 2\sigma(I)$ , maximum/residual peak of  $0.716/-0.292 \text{ e \AA}^{-3}$ . CCDC reference number 192268. See <http://www.rsc.org/suppdata/dt/b2/b210462h/> for crystallographic data in CIF or other electronic format.

§ Magnetic model:

$$H_{\text{chain}} = -J \sum_{i=1}^{n-1} S_i \cdot S_{i+1} \quad (1)$$

$$\chi_M^J = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{1+u}{1-u} + \text{TIP}(1)$$

$$u = \coth \left[ \frac{JS(S+1)}{kT} \right] - \left[ \frac{kT}{JS(S+1)} \right] \quad (2)$$

$$\chi_M^{J+J'} = \frac{\chi_M^J}{1 - (2zJ' \times \chi_M^J / Ng^2 \beta^2)} + \text{TIP}(2) \quad (3)$$

$$R = \frac{\sum \left[ (\chi_M^{J+J'})_i^{\text{obs}} - (\chi_M^{J+J'})_i^{\text{calc}} \right]^2}{\sum \left[ (\chi_M^{J+J'})_i^{\text{obs}} \right]^2} \quad (4)$$

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