TWO-DIMENSIONAL MANGANESE(II) COORDINATION POLYMER BASED ON PHTHALATE AND PYRAZINE BRIDGES EXHIBITING ANTIFERROMAGNETIC PROPERTIES

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Abstract

Magnetic measurements for the 2D coordination polymer $[Mn(Pht)(Pyz)(H_2O)_2]_n$ (**1**), in which metal centres are linked together by pyrazine (Pyz) and 1,6-bridging *o*-phthalate ligand (Pht^{2-}), revealed antiferromagnetic interactions between Mn(II) ions.

1. Introduction

Coordination polymers attract a lot of interest in chemistry and material science due to their unique and highly tailorable properties [1-8]. In particular, coordination polymers exhibiting magnetic properties have a great potential in the development of "intelligent" multifunctional materials, magnetic sensors, and magnetic materials [9]. The most often applied synthetic strategies for the fabrication of magnetic coordination networks are based on using short bridges, such as O- and N-based ligands: carboxylic groups, CN groups, pyrazine, tetrazine, azides, etc., which can effectively transmit magnetic interactions and simultaneously bind several metal centers. We have been extensively investigating the use of *o*-phthalic acid and different ancillary N-donor ligands such as pyridine, imidazole and their derivatives as well as 2,2′-bipyridine in the preparation of Cu(II) and Co(II) chain coordination polymers [10-19]. In continuation of these investigations, herein we report on the preparation of a two-dimensional Mn(II) coordination polymer with the formula $[Mn(Pht)(Pyz)(H_2O)_2]_n$ (**1**) by the interaction of manganese(II) acetate with *o*-phthalic acid (H_2Pht) and a pyrazine ligand (Pyz) in water-ethanole solution under heating. In [20], this complex was prepared under hydrothermal condition and its structure was discussed, but magnetic properties were not investigated.

2. Experimental details

2.1. Synthesis of $[Mn(Pht)(Pyz)(H_2O)_2]_n$

$Mn(CH_3COO)_2 \cdot 4H_2O$ (0.2 mmol, 0.49 g) in 5 ml of water:ethanol (1:1) was added to 15 ml of water:ethanol (1:1) solution of pyrazine (0.2 mmol, 0.16g) and *o*-phthalic acid (0.2 mmol, 0.33g). The resulting mixture was heated under reflux for 1 h. The yellow precipitate was filtrated, washed with ethanol, and dried in air. Yield: 0.78 g, 78.00 %. The crystals suitable for X-ray diffraction were obtained in ten days by the recrystallization of the precipitate from hot

water. Anal. Calc. for $C_{12}H_{12}MnN_2O_6$: 43.00 C, 3.61 H, 8.36 N %. Found: 43.02 C, 3.17 H, 7.60 N %.

2.2. X-ray crystallography

The crystals of **1** are orthorhombic, space group P*ccn* with a = 7.628(3), b = 11.377(5), c = 14.992(7) Å, V = 1301.0(1) Å^3, Z = 4 and D_{calc} = 1.711 g cm^{-3}. The unit cell parameters and experimental data for **1** were collected on a Bruker AXS Smart diffractometer with a graphite monochromated MoKα radiation at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX suite of programs [21]. Refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated ideal positions and refined as rigidly bonded to the corresponding atom.

3. Results and discussion

3.1. X-ray structure of $[Mn(Pht)(Pyz)(H_2O)_2]_n$

The obtained data are in good agreement with those previously reported in [20]. The differences of the unit cell parameters, bond lengths and angles in the two abovementioned refinements are caused by different temperatures of data collections and the quality of the crystals. The N_2O_4 coordination environment of Mn(II) atoms on the base of our data is characterized by the following bond distances: Mn–O_{carb} = 2.140(3) Å, Mn–O_w = 2.163(3) Å, Mn–N = 2.328(5) and 2.371(5) Å. Crystals of **1** consist of two-dimensional polymeric layers (Figure 1) parallel to the *ac* plane. The Mn(II) atoms are connected by 1,6-bridging Pht and endo-bidentate Pyz ligands.

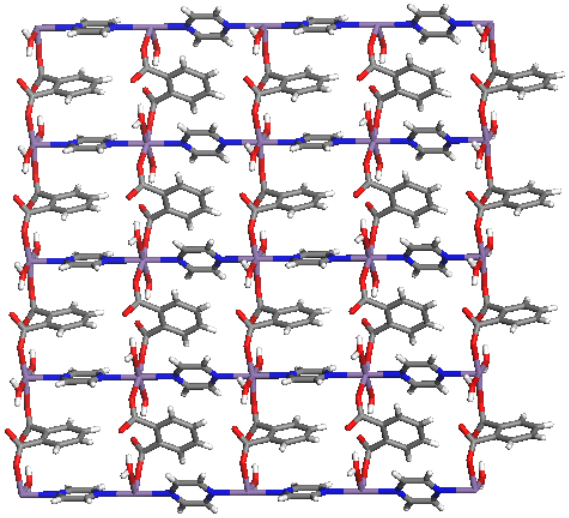

Fig. 1. Polymer layer in the structure of $[Mn(Pht)(Pyz)(H_2O)_2]_n$. Color scheme: C, grey; N, blue; O, red; H, white sticks.

The Mn…Mn separations are 7.628 Å along the *a* axis (Pht-bridge) and 7.496 Å along the *c* axis (Pyz-bridge). Also, in the $[Mn(Pht)]_n$ chain, it can be noted that there is a short hydrogen bond between the coordinated water molecule and the uncoordinated oxygen atom of Pht-molecule [the distances O–H…O = 2.721(4) Å]. The layers are shifted relative each other on the

½ *c* axis and united into 3D network by the other hydrogen bond from the coordinated water molecule and carboxylate oxygen of the neighboring layer (2.759(4) Å) (Fig. 2).

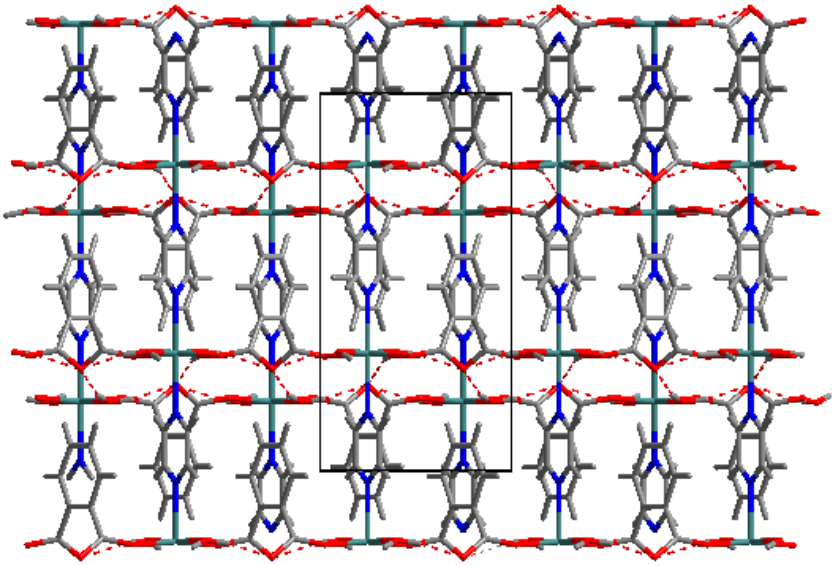

Fig. 2. Crystal packing diagram of **1**.

3.2. Magnetic properties

A plot of χ(T) for $[Mn(Pht)(Pyz)(H_2O)_2]_n$ (**1**) shows an increasing susceptibility over the entire temperature range with a value of 2.023 $cm^3 \cdot mol^{-1}$ at 1.9 K. An inverse susceptibility plot fitted with the Curie-Weiss equation between 300 - 54 K gives C = 4.446(1) $cm^3 \cdot K \cdot mol^{-1}$ and θ = −0.16(3) K (Fig. 3). The χT(T) plot shows a decreasing moment below ~50 K and a room temperature value of 4.44 $cm^3 \cdot K \cdot mol^{-1}$ (Fig. 4). From C and χT_{300k}, it is possible to derive a g-value of 2.01.

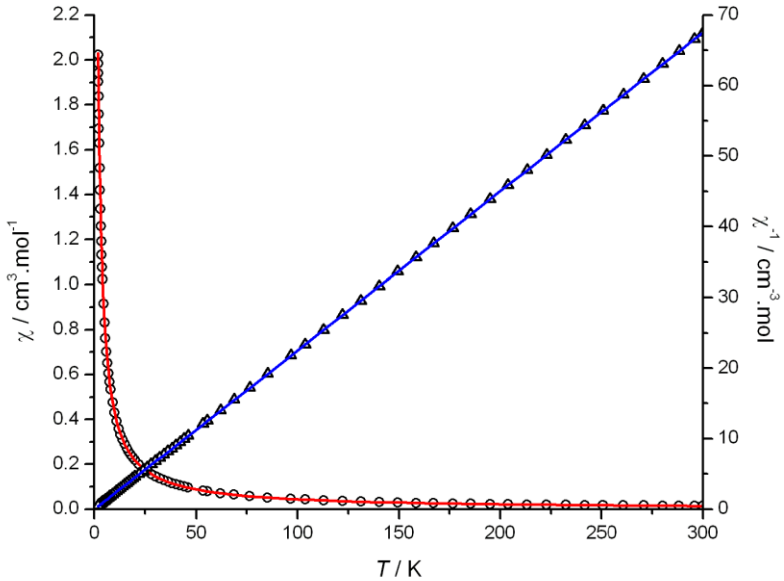

Fig. 3. χ(T) (open circles) plot for **1** with fit to S = 5/2 Fisher chain equation (red line, g =2.014(1) and $2J/k_B$ = −0.051(3)K) and χ^{-1}(T) plot (triangles) with Curie-Weiss fit (blue line, 300-54K, C = 4.446(1) $cm^3 \cdot K \cdot mol^{-1}$ and θ = −0.16(3) K).

The field-dependent magnetization curve (Fig. 5) is similar to that of the Brillouin curve for g = 2.01. From the value of M at 50,000 G (M = 27,987 $cm^{3}{\cdot}G{\cdot}mol^{-1}$), we find g = 2.00. The negative Weiss constant and the decrease in the value of χT with temperature indicate an antiferromagnetic interaction. Given the structure of **1**, the largest likely coupling would be through the pyrazine bridge forming one-dimensional chains. The coupling pathway through the phthalic acid is longer by two atoms and should be correspondingly much weaker; so, for the treatment of these data, it can be discarded.

The χ(T) and χT(T) data were fitted using the Fisher 1-D chain equation (eqs. 1a and 1b) over the entire temperature range and gave values g = 2.014(1) and $2J/k_B$ = −0.051(3) K:

$$\chi = \frac{N g^2 \mu_B^2 S(S+1)}{3 k_B T} \cdot \frac{1-u}{1+u} \qquad \text{eq. 1a}$$

$$\chi T = \frac{N g^2 \mu_B^2 S(S+1)}{3 k_B} \cdot \frac{1-u}{1+u} \qquad \text{eq. 1b}$$

where $u = (T / T_0) - \coth(T_0 / T)$ and $T_0 = 2JS(S+1) / k_B$.

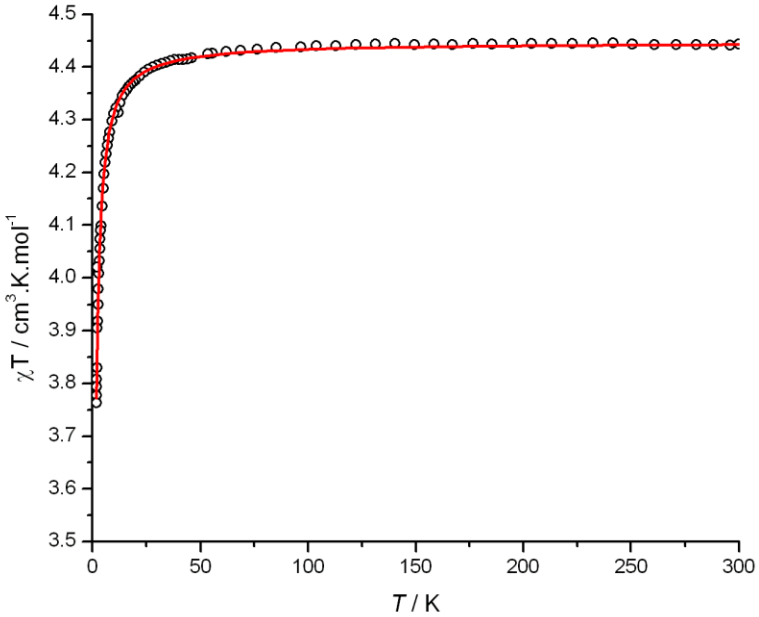

Fig. 4. χT(T) plot for **1** with fit to S = 5⁄2 Fisher chain equation (red line, g = 2.014(1) and $2J/k_B$ = −0.051(3)K).

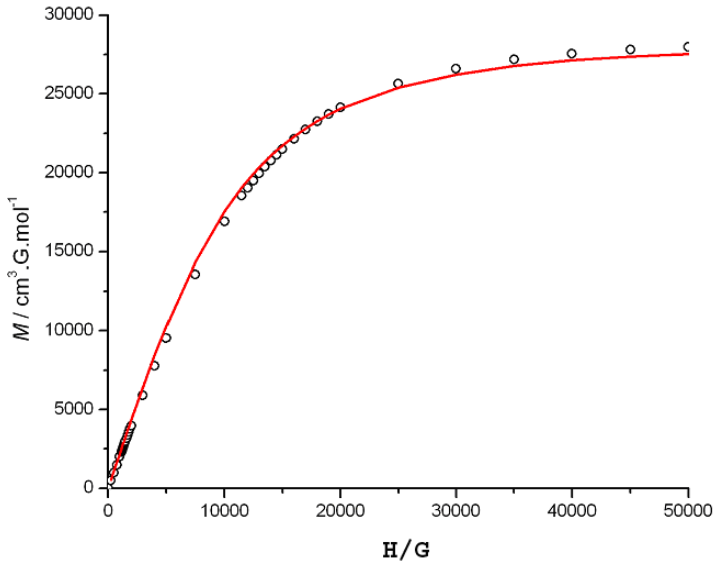

Fig. 5. Magnetisation curve (open circles) for **1** with Brillouin $S = 5/2$ curve (red line).

It is not practicable to attempt a Mean Field approximation to account for any coupling through the phthalate molecules as any effect is likely to occur at much lower temperatures than 1.9 K.

4. Conclusions

We have presented a simpler synthetic route to the two-dimensional coordination polymer $[Mn(Pht)(Pyz)(H_2O)_2]_n$ (**1**) from manganese acetate, *o*-phthalic acid, and pyrazine under refluxing in a water/ethanol solution. The metal atoms are connected by two kinds of bridges: the shorter linkers, such as pyrazine, and the longer ones via 1,6-bridging deprotonated phthalic acid. Magnetic measurements indicate the presence of weak antiferromagnetic interactions between Mn(II) atoms with $g = 2.014(1)$ and $2J/k_B = -0.051(3)$K) and these interactions occur via shorter pyrazine linkers within the two-dimensional layers.

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