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A Magnetically Coupled Three-Dimensional (Terephthalato)manganese(II) Network

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Extensive work has been carried out in the field of molecular magnetism on account of its promising application to diverse areas of technology such as magnetic recording and magnetic optics.[1] In this context, there has been increasing interest in designing two- and three-dimensional magnetic systems which can provide a better understanding of the magneto−structural relationship.[2] Recently, attempts to prepare multidimensional networks have been directed toward systems exhibiting blended magnetic behaviors of ferro- and antiferromagnetic couplings,[3] opening a new fascinating area of molecular magnetism.

Terephthalato (= tp) ligand has been actively studied to elucidate the limiting distance of magnetic exchange between paramagnetic metal centers.[4] In view of the long separation between metal centers bridged by tp, the ability of the ligand to mediate magnetic interactions is in the range from weak ferro- to weak antiferromagnetic exchange parameters. Additional useful feature of the tp ligand is its versatile binding ability as manifested by the formation of dinuclear,[5] tetranuclear,[4] and one-[6] and two-dimensional[7] copper(II) complex systems. In order to develop new three-dimensional networks possibly showing mixed magnetic interactions, the reaction systems of manganese(II) ion with tp as bridging ligand and pyrazoles as end-capping ligand have been explored. Herein, we report the synthesis, structure, and magnetic properties of a new compound $[Mn(5\text{-methylpyrazole})_2(tp)]_n$ (**1**), which constitutes the first example of a three-dimensional terephthalato-bridged network complex.

The reaction of manganese(II) acetate (0.5 mmol, 87 mg) with 2 equiv of 3(5)-methylpyrazole and 1 equiv of dipotassium tp in water afforded analytically pure[8] compound **1** in a yield of 33% (126 mg) based on Mn. The use of different pyrazole end-capping ligand such as unsubstituted pyrazole, 4-methylpyrazole, or 3,5-dimethylpyrazole led to the observation that one-dimensional chain complex[9] was formed for 4-methylpyrazole and no crystalline materials were obtained for the other two pyrazoles, indicating that 3(5)-methylpyrazole is a crucial end-capping ligand for the design of three-dimensional structure.

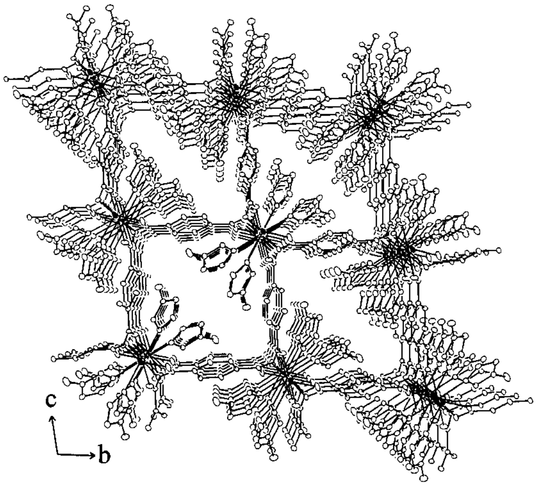

Figure 1. Perspective representation of **1** viewed down the *a* axis.

The occurrence of $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ at 1558 and 1374 cm^{-1}, respectively, in the IR spectra of **1** indicates that all oxygen atoms of both carboxylate groups of tp are coordinated to four manganese(II) ions in the bridging fashion,[10] which is consistent with the X-ray structure.[8] The crystal structure of **1** shows that carboxylato-bridged manganese chains running parallel to the *a* axis are connected along the *b* or *c* axis via benzene rings of extended tp ligands, leading to the formation of a three-dimensional network structure as shown in Figure 1. The shortest intermanganese distances along the *b* and *c* axis are 9.659 and 9.655 Å, respectively.

In the asymmetric unit, depicted in Figure 2 with the atom labeling, two manganese atoms with the interatomic distance of 4.917 Å lie at inversion centers and are bridged by two different tp ligands situating such that dihedral angle of two benzene rings of the bridging tp ligands forms 66.1(1)°. The tp ligands are not planar since dihedral angles of the carboxylate group and the benzene ring of the two bridging tp ligands are 7.53(15) and 7.42(17)°. The manganese(II) ions adopt distorted N_2O_4 octahedral geometry with two pyrazolyl end-capping ligands in trans positions. The interatomic Mn−O distances fall into two classes of short and long bond lengths around 2.158 and 2.233 Å, respectively, indicating that the interactions between manganese ions and the bridging tp oxygen atoms are not symmetric in terms of bond strength.

Variable-temperature magnetic susceptibility data for compound **1** illustrated in Figure 3 were measured in the temperature

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(8) Anal. Calcd for $C_{16}H_{16}N_4O_4Mn$: C, 50.14; H, 4.21; N, 14.62. Found: C, 50.05; H, 4.25; N, 14.59. Crystal data: space group $P\bar{1}$, $a = 9.835(1)$ Å, $b = 10.023(2)$ Å, $c = 10.018(2)$ Å, $\alpha = 68.11(2)°$, $\beta = 71.47(1)°$, $\alpha = 71.47(2)°$, $V = 846.2(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.504$ g cm^{-3}, μ(Mo Kα) = 0.809 mm^{-1}, $2\theta_{max} = 49.92°$, no. of observed reflections ($F_o > 4\sigma(F_o)$) = 2572, no. of parameters = 229, $R_1 = 0.0354$, $wR_2 = 0.1098$.

(9) Crystal data for the antiferromagnetic chain compound $[Mn(4\text{-methylpyrazole})_3(H_2O)(tp)]_n$: $C_{20}H_{24}N_6O_5Mn$, fw = 483.39, space group $P2_1/c$, $a = 17.346(2)$ Å, $b = 12.000(3)$ Å, $c = 11.457(3)$ Å, $\alpha = 90°$, $\beta = 102.81(2)°$, $\alpha = 90°$, $V = 2325.4(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.381$ g cm^{-3}, μ(Mo Kα) = 0.610 mm^{-1}, $R_1 = 0.0779$, $wR_2 = 0.198$.

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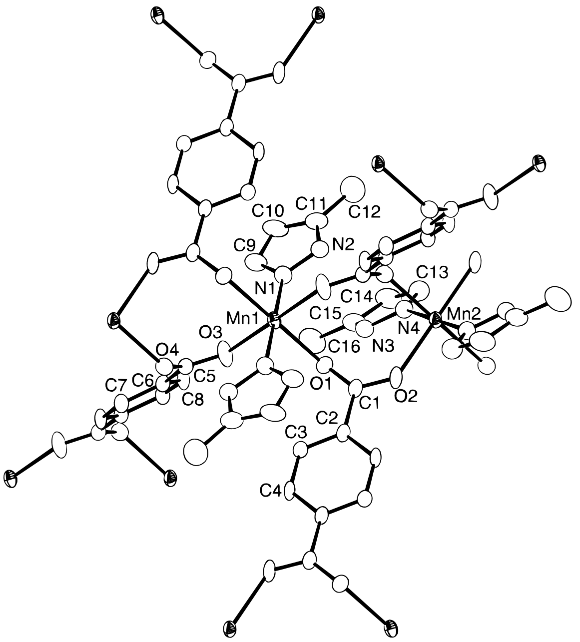

Figure 2. ORTEP view of **1** with atomic numbering scheme and 50% thermal ellipsoids. There are inversion centers at two manganese atoms, Mn1 and Mn2.

range from 301 to 1.8 K with the use of a SQUID magnetometer at a field strength of 0.2 T. The $\chi_m T$ value of 4.29 cm^3 K mol^{-1} at 301 K is slightly smaller than the value of 4.38 cm^3 K mol^{-1} expected for uncoupled Mn(II) ions. As temperature is lowered, the $\chi_m T$ value decreases gradually down to around 50 K and then abruptly down to 1.8 K to reach 0.32 cm^3 K mol^{-1}. In the case of the magnetic susceptibility χ_m, a sharp maximum at about 6 K is observed. Such a magnetic behavior is indicative of overall antiferromagnetic ordering between magnetic centers.

In view of the structure of **1**, there are two possible exchange pathways: one through the carboxylate bridge and the other through the extended terephthalato ligand. Thus, it is possible to interpret the observed magnetic behavior by using the modified analytical expression (eq 1). The eq 1 was derived

$$\chi_m = Ng^2\beta^2\, F(S,T)/\{1 - 2zJ'F(S,T)\} \tag{1}$$

$$F(S,T) = S_A(S_A + 1)/3kT\{(1 + u)/(1 - u)\}$$

$$u = \coth[JS_A(S_A + 1)/kT] - [kT/JS_A(S_A + 1)]$$

by combining the infinite chain model ($H = -J\sum_{i=1}^{n-1} S_{A_i} \cdot S_{A_{i+1}}$) by Fisher[11] and interchain interactions (J') under the molecular field approximation.[12]

Ignoring interchain interactions (zJ'), the best agreement for the $S_A = {}^5/_2$ system is obtained with a set of parameters $g = 2.03$ and $J = -1.06$ cm^{-1}. The measure of the goodness of fit R, defined as $R = [\Phi/(n - k)]^{1/2}$, where n is the number of data points, k is the number of parameters, and $\Phi = \sum[(\chi_m)_i^{obs} - (\chi_m)_i^{calc}]^2$, is equal to 1.71×10^{-3}. With allowance for all the parameters to vary, the best least-squares fit shown in Figure 3 gives $g = 2.02$ ($g_{exp} = 2.01$ by EPR), $J = -1.11$ cm^{-1}, $zJ' = 0.21$ cm^{-1}, and $R = 1.48 \times 10^{-3}$. The J value, which is in the usual range of doubly bridged carboxylate Mn(II) compounds,[13] indicates the presence of a weak antiferromagnetic coupling through the short pathway of carboxylate bridge of the tp. In the case of inclusion of interchain parameter, the experimental data points as described above are better fitted with the theoretical result and the positive zJ' value may be assigned to a weak ferromagnetic contribution from the long pathway via the benzene rings of the tp ligands. It would be interesting to consider possible explanations for a weak ferromagnetic interaction. The pair contribution $J_{\mu\nu}$ in a simple exchange scheme between pairs of magnetic orbitals ($J = 1/n^2\sum J_{\mu\nu}$) can be expressed in terms of coexisting ferromagnetic ($J_{\mu\nu}^F > 0$) and antiferromagnetic term ($J_{\mu\nu}^{AF} < 0$).[14] The latter part can be minimized by reducing the overlap integral between magnetic orbitals.[15] In the case of **1**, the overlap integral between magnetic orbitals seems to be reduced as judged by large dihedral angle of 66.1(1)° between two benzene rings of the bridging tp ligands in cis-positions and dihedral angles of 51.3(1) and 68.6(1)° between the MnO_4 core plane and two different benzene rings, allowing the $J_{\mu\nu}^F$ term to be slightly dominant over the $J_{\mu\nu}^{AF}$ term to give the positive zJ' value.[5,6] Thus, a weak ferromagnetic behavior through the long pathway of tp present in **1** may not be completely ruled out.

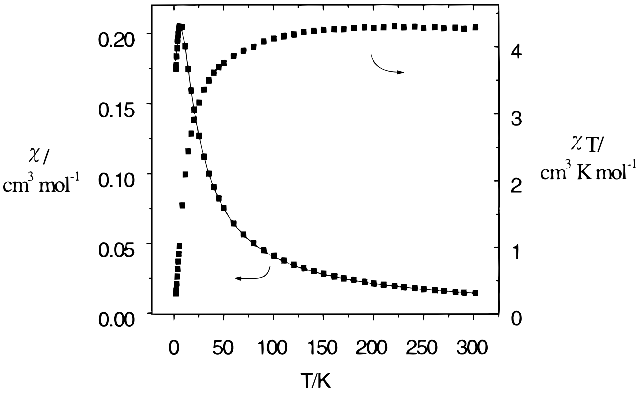

Figure 3. Plots of observed χ_m and $\chi_m T$ versus T for **1**. The solid line represents the best theoretical fit.

To our knowledge, compound **1** is the first three-dimensional example for terephthalato systems and is very interesting with respect to the investigation into the magnetic exchange mechanism of magnetically coupled compounds. In order to further our initial goal of developing new multidimensional tp systems showing diverse magnetic interactions, it may be necessary to tune the capping ligand.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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