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An intramolecular antiferromagnetically coupled pentanuclear Mn(II) cluster containing acetate and tetracarboxylate linkers: Synthesis, structure and magnetism

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ABSTRACT

A new Mn(II) complex $\{[Mn_5(CH_3COO)_2(L)_2(DMF)_8](DMF)\}_n$ (**1**), (H_4L = 3,5-bis(3′,5′-dicarboxylphenyl)-1H-1,2,3-triazole), has been synthesized and structurally characterized. The complex **1** have pentanuclear Mn(II) core, where the two sides of metal centers (Mn2 and Mn3) have trigonal bipyramidal arrangement and the middle metal center (Mn1) have octahedral environment utilizing two O atoms from adjacent bridging bidentate carboxylate groups and four O atoms from four coordinated DMF molecules. The planar arrangement of pentanuclear Mn(II) atoms are linked by L linkage to generate two dimensional sheet. The magnetic property of the compound indicates $\chi_M T$ value for the five Mn(II) unit to be 21.3 cm^3 K mol^{-1} at 300 K, which is close to the spin-only value (21.9 cm^3 K mol^{-1}) for the pentamer having $S = 5/2$. Also, the Hirshfeld surface analyses have been performed which indicated the absence of weak Mn···Mn interaction thereby corroborating the results of observed magnetic properties.
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1. Introduction

The current interest in coordination polymers have been extensively expanded in materials chemistry [1–4]. These materials are constructed from metal ions or clusters and functional organic bridging linkers [5,6]. The organic linkers play a pivotal role in the formation of MOFs with certain topology and functionalities as they retain their structures during the assembly process which allows a certain control for the formation of the final product [7–10]. However, it still remains a big challenge for chemists to synthesize MOFs having specified structure and properties.

The design and synthesis of multifunctional ordered porous materials with prime focus on their gas storage properties is gaining interest now-a-days [11–13]. Also, incorporating Mn(II) type system in multifunctional carboxylate group containing ligand may exhibit interesting magnetic properties. The ligand 3,5-bis(3′,5′-dicarboxylphenyl)-1H-1,2,3-triazole comprising of one type of bridging aromatic tetracarboxylate ligand, is rarely used and may result in highly porous frameworks with a low framework density from the crystal engineering point of view. Additionally, its listed structural features inspire our research interest: (i) it has four carboxyl groups, and hence the ligand can expand, shrink and meet different coordination environments, resulting in the formation of new types of coordination polymers with intriguing structures thereby allowing access to a wide variety of structures; (ii) the two phenyl rings in the ligand are almost lying in the same plane, which thereby can generate a rigid node with fixed geometry and enhance the thermal stability and overall rigidity of the net. With these viewpoints and in the quest of new magnetic material comprising of Mn(II) center herein, we wish to report a new pentanuclear complex of Mn(II) comprising of a rigid and multifunctional carboxylate ligand 3,5-bis(3′,5′-dicarboxylphenyl)-1H-1,2,3-triazole.

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2. Experimental

2.1. Materials and method

All chemicals were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. and used without further purification. IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer in the region 4000–400 cm^{-1} using KBr pellets. TGA was carried out with a Metter–Toledo TA 50 in dry dinitrogen (60 mL min^{-1}) at a heating rate of 5 °C min^{-1}. X-ray powder diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60 KV, 300 mA using CuK_α radiation (λ = 1.5406 Å), with a scan speed of 2 °C/min and a step size of 0.013° in 2θ. Magnetic susceptibility data of powdered sample restrained in parafilm were measured on Oxford Maglab 2000 magnetic measurement system in the temperature range 300–1.8 K and at a field of 1 KOe.

2.2. X-ray crystallography

Single crystal X-ray diffraction analysis of the complex **1** was carried out on a *Bruker SMART APEX II CCD* diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using ϕ/ω scan technique at room temperature. Data were processed using the Bruker SAINT package and the structures solution and the refinement procedure was performed using SHELX-97 [14]. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms attached to carbon atoms were calculated and refined with isotropic displacement parameters 1.2 or 1.5 times. Solvent molecule DMF located in the cavities of **1** are disordered. The atoms of disordered DMF molecule have the occupancies of 0.50:0.50. The pertinent crystallographic data for **1** are presented in Table 1. Selected bond distances and bond angles are listed in Table 2. CCDC: 1412683.

2.3. Synthesis of {[$Mn_5(CH_3COO)_2(L)_2(DMF)_8$](DMF)}$_n$ (**1**)

A mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.255 g), H_4L (0.021 g) was dissolved in DMF (4 mL) in a screw-capped vial. Then, 0.25 mL HNO_3 (63%, aq.) was added into the mixture. The vial was capped and placed in an oven at 110 °C for 3 days, the solution was then cooled to room temperature at rate of 5 °C h^{-1}. The resulting single crystals were washed thrice with absolute ethanol (3 × 10 mL) to obtain **1**. IR (KBr, cm^{-1}): 3270 (vs); 2860 (v); 2470 (m); 1589 (vs); 1453 (v); 1342 (vs); 1018 (v); 771 (m); 724 (m); 573 (m). Elemental analysis (%) Calcd for **1** ($C_{67}H_{83}Mn_5N_{15}O_{29}$): C, 43.80; H, 4.55; N, 11.44. Found: C, 43.93; H, 4.60; N, 11.35.

Table 1
Crystal data and structure refinement information for compound 1.

Formula	$C_{67}H_{83}Mn_5N_{15}O_{29}$
Crystal system	Triclinic
Space group	*P*-1
a, Å	8.6957(9)
b, Å	14.4473(14)
c, Å	16.9100(17)
α, °	82.6690(10)
β, °	86.2570(10)
γ, °	76.9150(10)
V, Å^3	2050.9(4)
Z	1
ρ_{calMn}, g/cm^3	1.488
μ, mm^{-1}	0.837
F(000)	947
θ Range, °	2.42–24.01
Reflection collected	19757
Independent reflections (R_{int})	0.0395
Reflections with $I > 2\sigma(I)$	9210
Number of parameters	5877
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0520, 0.1182
R_1, wR_2 (all data)**	0.0967, 0.1358

*$R = \sum(F_o - F_c)/\sum(F_o)$, ** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) of structure 1.

1			
Mn1– O1	2.124(2)	Mn1– O1	2.124(2)
Mn1– O11	2.151(3)	Mn1– O11	2.151(3)
Mn1– O12	2.191(3)	Mn1– O12	2.191(3)
Mn2– O2	2.076(2)	Mn2– O9	2.118(3)
Mn2– O8	2.119(2)	Mn2– O3	2.194(2)
Mn2– O13	2.222(3)	Mn3– O7	2.058(2)
Mn3– O4	2.103(2)	Mn3– O10	2.104(3)
Mn3– O6	2.121(2)	Mn3– O14	2.210(3)
O1– Mn1– O1#1	179.998(1)	O11– Mn1– O11	179.999(1)
O12 –Mn1– O12#2	180	O2– Mn2– O9	91.89(10)
O8 –Mn2– O3	159.08(10)	O2 –Mn2 –O13	85.81(10)
O9– Mn2– O13	175.60(11)	O7 –Mn3– O4	94.88(10)
O7– Mn3– O10	98.04(13)	O4– Mn3– O6	161.87(9)
O10– Mn3– O6	91.48(11)	O10– Mn3– O14	173.24(11)

#1: x, y, z; #2: −x, −y, −z.

3. Results and discussion

3.1. Molecular structure description

Single-crystal structural determinations reveal that **1** crystallizes in the triclinic system having *P*-1 space group. The asymmetric unit of **1** contains five Mn(II) centers, two acetate anions, two L ligands, eight coordinated DMF molecules and one free DMF molecule. The dications (Mn2 and Mn3) have a crystallographically imposed inversion center, with a core consisting of a planar array of metal atoms required by the imposed symmetry. As shown in Fig. 1, the Mn2 and Mn3 have the same geometries that are coordinated by five oxygen atoms from four bridging carboxyl groups and one coordinated DMF molecule, completing trigonal bipyramidal geometries, while Mn1 has six oxygen atoms from two bridging carboxyl groups and four coordinated DMF molecules, forming an octahedral geometry. The Mn1–O distances falls in range from

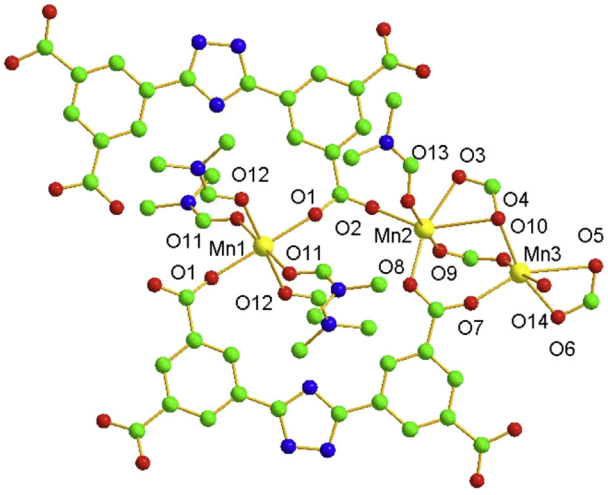

Fig. 1. The coordination geometries of the metal centers and the ligands geometries in 1. Displacement ellipsoids are drawn at the 20% probability level and H atoms are omitted for clarity.

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