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Syntheses, crystal structures and magnetic behaviors of three Mn^{II}-terephthalate coordination polymers containing terminal ligands

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ABSTRACT

Three Mn^{II}-terephthalate coordination polymers, $\{Mn^{II}(tp)(bpy)(H_2O)\}_n$ (**1**), $\{Mn^{II}_3(tp)_{6/2}(bpy)_2\cdot(dmf)\}_n$ (**2**) and $\{Mn^{II}(tp)(phen)\}_n$ (**3**) (tp = terephthalic dianion, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been synthesized and characterized by single crystal X-ray diffraction studies and low temperature (2–300 K) magnetic measurements. The structure analysis of **1**–**3** show that they all are coordination polymers composed of Mn atoms as nodes and terephthalate dianions as spacers. Interestingly, compound **1** consists of 1D infinite zigzag chains, while compound **2** consists of 2D sheets and compound **3** has a 3D framework structure. The study of the temperature dependent magnetic susceptibilities revealed that all of the polymers show antiferromagnetism.

1. Introduction

The design and construction of multi-dimensional functional metal-organic coordination polymers with metal ions as nodes and bridging ligands as spacers have attracted much attention from chemists in recent years [1–3]. This has arisen not only for their various intriguing topological structures, but also for their unexpected properties for potential practical applications in material chemistry, such as heterogeneous catalysis, gas sorption, storage and separations, molecular recognition, non-linear optics, luminescent and magnetic properties [4–6].

Selection of the appropriate multidentate ligand to link paramagnetic metal ions is a powerful way for the building of polyfunctional coordination polymers. As a multidentate ligand, terephthalic acid (H_2tp) and its dianion have been used in synthetic systems, not only because they can act as short bridges via one carboxylic group or long bridges via the benzene ring, leading to abundant varieties of multi-dimensional coordination polymers with various kinds of topology, but also terephthalic acid, as an example of a benzenedicarboxylic acid, has a rigid aromatic unit as a spacer which can make give rise to very special systems that can have interesting electronic and magnetic interactions between the metal ions in the network through possible conjugative interactions (shown in Scheme 1) [7,8]. On the other hand, the terminal ligands play an important role in the structures and properties of the coordination polymers [9].

Herein, we report the synthesis, crystal structure and magnetic properties of three manganese coordination polymers, $\{Mn^{II}(tp)(bpy)(H_2O)\}_n$ (**1**), $\{Mn^{II}_3(tp)_{6/2}(bpy)_2\cdot(dmf)\}_n$ (**2**) and $\{Mn^{II}(tp)(phen)\}_n$ (**3**) (tp = terephthalic dianion, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, dmf = *N*,*N*-dimethylformamide), with the terephthalic dianion acting as a bridging ligand and 2,2′-bipyridine (in **1** and **2**) and 1,10-phenanthroline (in **3**) as terminal ligands.

2. Experimental

2.1. Materials and general methods

All reagents for the syntheses and analyses were obtained commercially, were of analytical grade and were used without further purification, and all manipulations were carried out in the laboratory atmosphere. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded as KBr pellets on a Bruker EQUIN0X 55 IR spectrometer. Magnetic measurements were carried out with polycrystalline samples on a Quantum Design MPMS XL-5 SQUID magnetometer. The diamagnetic corrections were evaluated from Pascal's constants.

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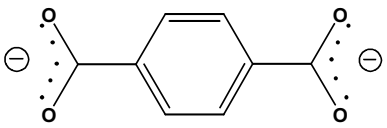

Scheme 1.

2.2. Syntheses of complexes **1** and **3**

2.2.1. $\{Mn^{II}(tp)(bpy)(H_2O)\}_n$ (**1**)

A mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.169 g, 1 mmol) in water (10 ml) and terephthalic acid (0.166 g, 1 mmol) in NaOH (80 mg, 2 mmol) aqueous solution (10 ml) were stirred at room temperature for about 12 h. Yellow crystals of compound **1** were obtained by diffusion of a 10 ml ethanol solution of 2,2′-bipyridine (0.156 g, 1 mmol) and the filtrate of the mixed solution after about 1 week (yield: about 32% based on Mn). *Anal.* Calc. for $\{Mn^{II}(tp)(bpy)(H_2O)\}_n$ (**1**): C, 54.98; H, 3.59; N, 7.12. Found: C, 55.01; H, 3.62; N, 7.16%. IR (KBr, cm^{-1}): 1576.53 s, 1475.14 m, 1438.82 s, 1378.05 s, 1151.97 m, 1058.54 w, 1018.48 m, 866.10 w, 805.18 m, 760.16 s, 736.45 m, 649.63 m, 524.31 m.

2.2.2. $\{Mn^{II}_3(tp)_{6/2}(bpy)_2 \cdot (dmf)\}_n$ (**2**)

A solution of $MnCl_2$ (0.136 g, 1 mmol) in 10 ml of water was added to a solution of terephthalic acid (0.249 g, 1.5 mmol) and 2,2′-bipyridine (0.156 g, 1 mmol) in DMF (10 ml), stirring for about 2 h at room temperature. Then the resulting solution was transferred into a Teflon-Steel autoclave inside a programmable electric furnace reactor. The mixed-solvo-thermal reaction lasted for about 3 days at about 423.15 K, and then the mixture was cooled to room temperature naturally. Yellow single crystals were obtained (yield = about 78% based on Mn). *Anal.* Calc. for $\{Mn^{II}_3(tp)_{6/2}(bpy)_2 \cdot (dmf)\}_n$ (**2**): C, 54.14; H, 3.38; N, 6.72. Found: C, 54.28; H, 3.51; N, 6.83%. IR (KBr, cm^{-1}): 1576.76 s, 1474.78 m, 1439.04 s, 1380.86 s, 1313.63 m, 1151.88 m, 1095.69 w, 1058.42 w, 1018.52 m, 971.55 w, 803.94 m, 760.23 s, 668.17 w, 649.94 m, 628.01 w, 524.9 m.

Table 1
Crystallographic data and structure refinement summary for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{18}H_{14}MnN_2O_5$	$C_{47}H_{35}Mn_3N_5O_{13}$	$C_{20}H_{12}MnN_2O_4$
Mr	393.25	1042.62	399.26
Temperature (K)	290(2)	290(2)	290(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*n*	*C*2/*c*	*C*2/*c*
a (Å)	9.8665(3)	18.4033(2)	17.4786(11)
b (Å)	16.3330(6)	25.7135(3)	10.3332(6)
c (Å)	11.3035(4)	9.90320(10)	9.3359(6)
β (°)	111.6760(10)	91.4350(10)	96.173(3)
V (Å^3)	1692.75(10)	4684.86(9)	1676.38(18)
Z	4	4	4
D_{calc} (g cm^{-3})	1.543	1.478	1.582
Crystal size (mm)	0.30 × 0.24 × 0.16	0.32 × 0.24 × 0.20	0.26 × 0.24 × 0.20
Theta range (°)	2.31 to 28.33	2.21 to 28.28	2.29 to 28.28
Reflections collected/ unique	16733/4190	21921/5786	8019/2086
R_{int}	0.0292	0.0203	0.0274
Completeness to theta	99.5% (28.33)	99.5% (28.28)	99.6% (28.28)
Data/restraints/ parameters	4190/0/240	5786/0/325	2086/0/124
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.056	1.030	1.037
Final R_1 and wR_2 indices	R_1 = 0.0317, wR_2 = 0.0868	R_1 = 0.0323, wR_2 = 0.0949	R_1 = 0.0296, wR_2 = 0.0895
R_1 and wR_2 indices (all data)	R_1 = 0.0468, wR_2 = 0.0918	R_1 = 0.0398, wR_2 = 0.0991	R_1 = 0.0379, wR_2 = 0.0924
Min, Max peaks (*e* Å^{-3})	0.321 and −0.244	0.504 and −0.431	0.308 and −0.261

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Mn(1)–O(1)	2.2709(11)	Mn(1)–N(1)	2.2615(14)
Mn(1)–O(2)	2.2854(11)	Mn(1)–N(2)	2.2391(14)
Mn(1)–O(3)#1	2.0985(11)	Mn(1)–O(5)	2.1625(12)
O(1)–Mn(1)–O(2)	57.30(4)	N(1)–Mn(1)–O(2)	95.66(5)
O(1)–Mn(1)–O(3)#1	97.98(5)	N(1)–Mn(1)–O(1)	94.23(5)
O(1)–Mn(1)–O(5)	146.97(5)	N(2)–Mn(1)–O(1)	88.78(5)
O(3)#1–Mn(1)–O(2)	105.69(5)	N(2)–Mn(1)–O(2)	143.80(5)
O(3)#1–Mn(1)–O(5)	86.90(5)	N(2)–Mn(1)–N(1)	72.73(5)
O(3)#1–Mn(1)–N(2)	90.01(5)	O(5)–Mn(1)–O(2)	89.86(5)
O(3)#1–Mn(1)–N(1)	158.63(5)	O(5)–Mn(1)–N(1)	92.37(5)
O(5)–Mn(1)–N(2)	124.01(5)		

Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2$, $-y + 1/2$, $z + 1/2$; #2 $x + 1/2$, $-y + 1/2$, $z - 1/2$.

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

Mn(1)–O(2)	2.1323(11)	O(1)–C(11)	1.266(2)
Mn(1)–O(4)	2.2104(10)	O(2)–C(11)	1.240(2)
Mn(1)–O(6)	2.1094(12)	O(4)–C(15)	1.288(2)
Mn(2)–O(1)	2.1162(11)	O(3)–C(15)	1.242(2)
Mn(2)–O(4)	2.2057(11)	O(5)–C(19)	1.257(2)
Mn(2)–O(5)	2.0912(11)	C(19)–O(6)	1.243(2)
Mn(2)–N(1)	2.2534(14)	C(23)–O(7)	1.73(3)
Mn(2)–N(2)	2.2959(15)	O(4)–Mn(2)–N(2)	87.53(5)
O(2)#1–Mn(1)–O(2)	180.00(5)	N(1)–Mn(2)–N(2)	71.70(5)
O(4)–Mn(1)–O(4)#1	180.0	C(1)–N(1)–Mn(2)	123.09(12)
O(6)#1–Mn(1)–O(6)	180.00(6)	C(5)–N(1)–Mn(2)	118.52(12)
O(6)–Mn(1)–O(2)	93.64(6)	C(19)–O(5)–Mn(2)	121.26(10)
O(2)–Mn(1)–O(4)	88.08(4)	C(10)–N(2)–Mn(2)	123.69(13)
O(6)–Mn(1)–O(4)	89.58(5)	C(6)–N(2)–Mn(2)	117.11(12)
O(5)–Mn(2)–O(1)	101.82(5)	C(11)–O(1)–Mn(2)	126.39(10)
O(5)–Mn(2)–O(4)	109.14(4)	C(11)–O(2)–Mn(1)	140.47(12)
O(1)–Mn(2)–O(4)	93.89(4)	O(2)–C(11)–O(1)	125.66(15)
C(19)–O(6)–Mn(1)	148.96(12)	C(15)–O(4)–Mn(2)	95.04(9)
O(5)–Mn(2)–N(1)	88.34(5)	C(15)–O(4)–Mn(1)	128.26(10)
O(1)–Mn(2)–N(1)	105.10(5)	Mn(2)–O(4)–Mn(1)	105.74(4)
O(4)–Mn(2)–N(1)	151.12(5)	O(3)–C(15)–O(4)	120.69(15)
O(5)–Mn(2)–N(2)	159.42(5)	O(6)–C(19)–O(5)	125.12(15)
O(1)–Mn(2)–N(2)	88.58(5)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2$, $-y + 1/2$, $-z + 1$; #2 $-x$, y, $-z + 3/2$; #3 $-x + 1/2$, $-y + 1/2$, $-z$; #4 $-x + 1$, y, $-z + 3/2$.

Table 4
Selected bond lengths (Å) and angles (°) for complex **3**

Mn(1)–O(1)	2.1387(8)	O(2)–C(7)	1.2506(12)
Mn(1)–O(2)#1	2.1183(8)	N(1)–C(1)	1.3273(14)
Mn(1)–N(1)	2.3499(9)	N(1)–C(6)	1.3554(13)
O(1)–C(7)	1.2519(13)		
O(2)#4–Mn(1)–O(2)#1	99.63(4)	C(7)–O(1)–Mn(1)	145.24(7)
O(2)#1–Mn(1)–O(1)	98.24(3)	C(7)–O(2)–Mn(1)#1	144.24(7)
O(2)#4–Mn(1)–O(1)	85.32(3)	C(1)–N(1)–Mn(1)	125.84(7)
O(1)#2–Mn(1)–O(1)	174.51(4)	C(6)–N(1)–Mn(1)	116.60(6)
N(1)#2–Mn(1)–N(1)	70.88(4)	O(2)–C(7)–O(1)	126.41(9)
O(2)#4–Mn(1)–N(1)	94.83(3)	O(1)#2–Mn(1)–N(1)	89.93(3)
O(2)#1–Mn(1)–N(1)	165.28(3)	O(1)–Mn(1)–N(1)	85.59(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 1$, $-z + 1$; #2 $-x$, y, $-z + 3/2$; #3 $-x + 1/2$, $-y + 1/2$, $-z + 1$; #4 x, $-y + 1$, $z + 1/2$.