

# Hydrothermal Synthesis and Crystal Structure of [Mn(phen)-(*m*-phth)]<sub>n</sub> (phen=1,10-phenanthroline, *m*-phth=isophthalate)

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Hydrothermal reaction of 1,2,4-benzenetricarboxylic acid, and MnCl<sub>2</sub>•4H<sub>2</sub>O with 1,10-phenanthroline gave the title complex, [Mn(phen)(*m*-phth)]<sub>n</sub>, which crystallizes in the monoclinic system, space group *P2/c* with *a*=0.83582(3) nm, *b*=1.04246(4) nm, *c*=1.87777(7) nm, β=100.314(2)°, *V*=1.60968(10) nm<sup>3</sup>, *Z*=4, and the final *R*=0.0576, *wR*=0.1294. In the complex, each Mn(II) ion is coordinated to four O atoms of carboxylate groups and two N atoms of phen. Isophthalate was generated *in situ* through the loss of one carboxylate group of 1,2,4-benzenetricarboxylic acid under the hydrothermal condition. Each isophthalate is bound to three manganese atoms through O atoms of carboxylate in bridging and chelating fashion, affording manganese(II) pairs that are linked by the isophthalate group to yield a zig-zag chain along the *c*-axis.

**Keywords** hydrothermal synthesis, manganese polymer, crystal structure, π-π stacking interaction

## Introduction

Recently, many novel polymers with a variety of metal ions have been prepared and structurally characterized owing to the versatility of carboxylate ligands.<sup>1-5</sup> Much attention has been devoted to this field partly because polymers of carboxylate ligands are good candidates for the investigation of exchange-coupling interactions between adjacent metal ions. A successful strategy to synthesize these complexes is the reaction of metal salts with properly selected multi-dentate carboxylate ligands under the hydrothermal condition.<sup>6</sup> It is still, however, a challenge to control the final structure of the crystalline compound, due to not only the versatility of the coordination models of carboxylate ligand, but also the change of ligand under the certain condition. Herein reported is a polymeric complex with a chain structure, [Mn(phen)(*m*-phth)]<sub>n</sub> (**1**), isolated from the hydrothermal reaction of MnCl<sub>2</sub>•4H<sub>2</sub>O with 1,2,4-benzenetricarboxylic acid and phen. Strong π-π stacking interactions, which are found between aromatic rings, make the chains form a tight-packed 3D supermolecular structure.

## Experimental

### Preparation of [Mn(phen)(*m*-phth)]<sub>n</sub>

1,2,4-Benzenetricarboxylic acid (0.063 g, 0.30 mmol), MnCl<sub>2</sub>•4H<sub>2</sub>O (0.059 g, 0.30 mmol) and 1,10-phenanthroline (0.046 g, 0.25 mmol) were dis-

solved in 20 mL of H<sub>2</sub>O and the pH value of the solution was adjusted to 8.5 using NaOH solution (0.2 mol/L). Then the mixture was placed in a stainless steel vessel and heated to 160 °C for 72 h. When the mixture was cooled to room temperature during 8 h, light-yellow prism crystals (m.p.>300 °C) of **1** were obtained in about 68% yield. FT-IR (KBr) ν: 3053 (m), 1928 (s), 1854 (s), 1769 (m), 1606 (s), 1543 (s), 1481 (m), 1444 (s), 1390 (s), 1277 (m), 1161 (m), 1101 (m), 864 (m), 849 (s), 786 (s), 727 (m), 698 (m) cm<sup>-1</sup>. Anal. calcd for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>MnO<sub>4</sub>: C 60.17, H 3.03, N 7.02; found C 60.21, H 2.99, N 7.04.

### Crystal structure determination

A light-yellow crystal of dimensions 0.42 mm×0.20 mm×0.14 mm of **1** was mounted on a glass fiber in a random orientation. Diffraction data were collected at room temperature (293 K) on a Siemens SMART-CCD diffractometer equipped with a graphite monochromated Mo Kα radiation (λ=0.071073 nm). A total of 4375 reflections were collected in the range of 1.95°<θ<25.10° using ω-2θ scan mode, in which 2794 independent reflections with *I*<2σ(*I*) were used in the succeeding refinements. The structure was solved by direct method and refined by full-matrix least-squares method. The positions of H atoms were generated geometrically (C—H bond fixed at 0.096 nm), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atom before the final cycle of refinement. The final cycle of refinement included 244 variable parame-

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ters and converged to  $R=0.0576$  and  $wR=0.1294$ . All calculations were performed on a Legend Pentium(IV) computer with Shelxtl 97 software. Crystal parameters and refinement results are summarized in Table 1.

**Table 1** Crystal data and structure refinement for  $\text{MnC}_{20}\text{O}_4\text{N}_2\text{H}_{12}$

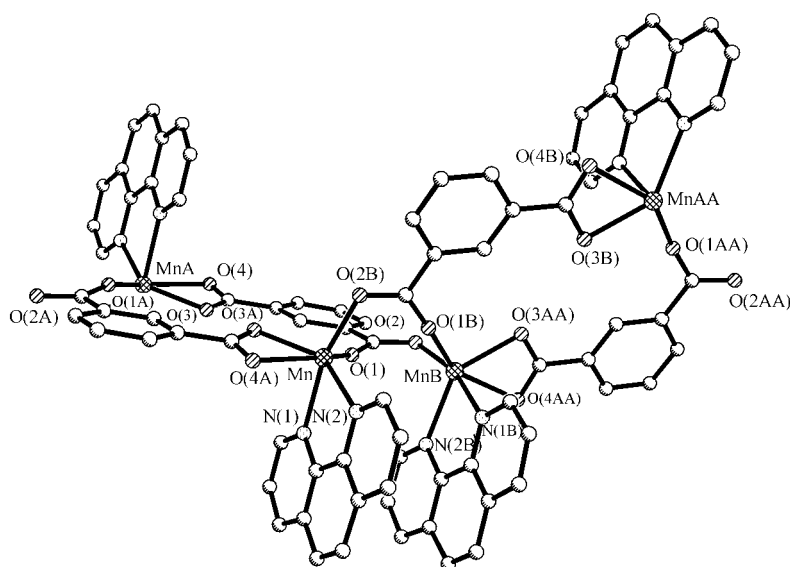
Chemical formula	$\text{MnC}_{20}\text{O}_4\text{N}_2\text{H}_{12}$
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{nm}$	0.83582(3)
$b/\text{nm}$	1.04246(4)
$c/\text{nm}$	1.87777(7)
$B/^\circ$	100.314(2)
$V/\text{nm}^3$	1.60968(10)
$D_c/(\text{g}\cdot\text{cm}^{-3})$	1.647
$Z$	4
$T/\text{K}$	293
Wavelength/nm	0.071073

Continued

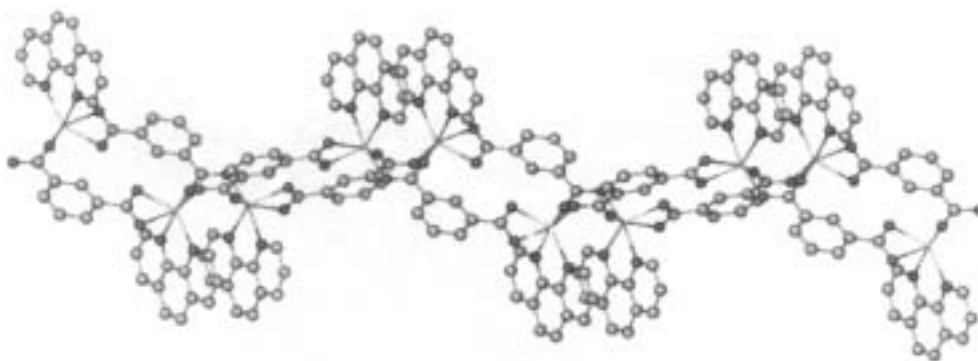
Crystal size/mm	$0.42 \times 0.20 \times 0.14$
$\theta$ range for data collection	$1.95^\circ$ to $25.10^\circ$
Total reflections	4375
Reflections with $I > 2.0\sigma(I)$	2794
$R$	0.0576
$wR$	0.1294

## Results and discussion

The coordination environment around Mn(II) ion in the title compound is shown in Figure 1. The chain structure and packing diagram of  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{MnO}_4$  are shown in Figure 2 and Figure 3, respectively. The selected bond lengths and angles are listed in Table 2. The ligand of 1,2,4-benzenetricarboxylic acid lost one carboxylate group in 1 position under the hydrothermal condition and changed to isophthalate (dianion of benzene-1,3-dicarboxylic acid). This can also be proved by the absorption of FT-IR at  $786$  and  $698\text{ cm}^{-1}$ .



**Figure 1** Coordination environment around Mn(II) ion in the title complex (H atoms have been omitted for clarity).



**Figure 2** Chain structure of  $[\text{Mn}(\text{phen})(m\text{-phth})]_n$  along the  $c$ -axis.

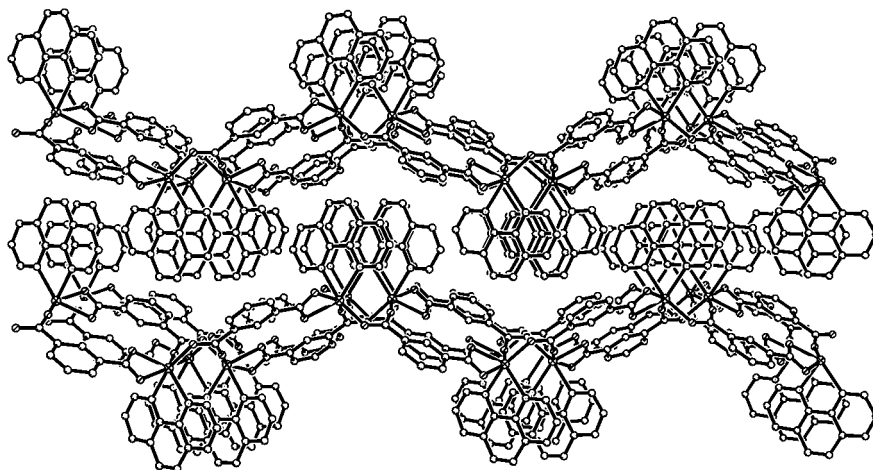


Figure 3 The packing structure of the title compound.

Table 2 Bond lengths (nm) and angles ( $^{\circ}$ ) for  $\text{MnC}_{20}\text{O}_4\text{N}_2\text{H}_{12}$ <sup>a</sup>

Mn—O(1)	0.2104(3)
Mn—O(2)B	0.2124(3)
Mn—O(3)A	0.2188(3)
Mn—N(2)	0.2277(4)
Mn—N(1)	0.2292(4)
Mn—O(4)A	0.2362(3)
O(1)-Mn-O(2)B	97.78(14)
O(1)-Mn-O(3)A	93.97(13)
O(2)B-Mn-O(3)A	103.67(13)
O(1)-Mn-N(2)	119.37(14)
O(2)B-Mn-N(2)	94.56(13)
O(3)A-Mn-N(2)	139.42(13)
O(1)-Mn-N(1)	81.98(14)
O(2)B-Mn-N(1)	164.64(13)
O(3)A-Mn-N(1)	91.65(14)
N(2)-Mn-N(1)	72.58(14)
O(1)-Mn-O(4)A	149.05(12)
O(2)B-Mn-O(4)A	100.34(13)
O(3)A-Mn-O(4)A	57.44(12)
N(2)-Mn-O(4)A	83.99(12)
N(1)-Mn-O(4)A	86.90(13)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: A:  $-x, -y+1, -z-1$ ; B:  $-x, y, -z-1/2$ .

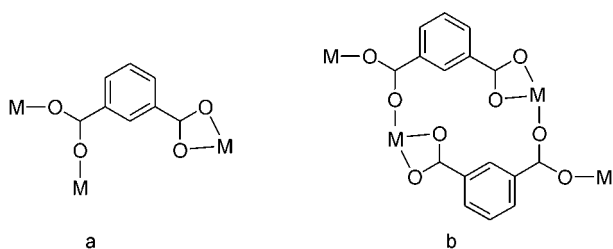
As shown in Figure 1, two nitrogen atoms from phen and four oxygen atoms from three different *m*-phth ligands, forming a distorted octahedral geometry, coordinate the central manganese ion. The lengths of Mn—O bonds range from 0.2104(3) to 0.2362(3) nm, similar to those observed in the previous reported complexes.<sup>7-9</sup> Each *m*-phth ligand connects with three Mn(II) ions through its two carboxylate groups in chelating and

Table 3 Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{nm}^2 \times 10^5$ ) for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Mn	1366(1)	6748(1)	-3274(1)	30(1)
C(1)	3431(6)	8585(5)	-2054(3)	45(1)
C(2)	4031(7)	9735(6)	-1735(3)	58(2)
C(3)	3445(8)	10860(6)	-2025(3)	62(2)
C(4)	2247(7)	10877(5)	-2650(3)	48(1)
C(5)	1575(9)	12024(6)	-3014(4)	68(2)
C(6)	398(9)	11964(6)	-3604(4)	64(2)
C(7)	-221(7)	10767(5)	-3907(3)	52(1)
C(8)	-1459(7)	10640(7)	-4518(3)	63(2)
C(9)	-1955(7)	9454(7)	-4765(3)	60(2)
C(10)	-1194(6)	8389(6)	-4429(3)	48(1)
C(11)	447(6)	9631(4)	-3585(3)	38(1)
C(12)	1700(6)	9683(4)	-2945(3)	35(1)
C(13)	-2180(6)	5453(4)	-3119(2)	33(1)
C(14)	-3129(5)	4675(4)	-3713(2)	30(1)
C(15)	-4632(5)	4150(4)	-3651(2)	34(1)
C(16)	-5503(6)	3433(4)	-4206(2)	36(1)
C(17)	-4870(6)	3230(4)	-4834(2)	35(1)
C(18)	-3399(5)	3764(4)	-4916(2)	30(1)
C(19)	-2537(5)	4488(4)	-4356(2)	31(1)
C(20)	-2754(6)	3565(4)	-5602(2)	33(1)
O(1)	-1009(4)	6094(3)	-3258(2)	47(1)
O(2)	-2620(4)	5463(3)	-2511(2)	42(1)
O(3)	-1507(4)	4181(3)	-5695(2)	46(1)
O(4)	-3440(4)	2785(4)	-6060(2)	46(1)
N(1)	-20(5)	8460(4)	-3851(2)	36(1)
N(2)	2285(5)	8547(4)	-2642(2)	34(1)

bridging fashion (Scheme 1a). Every two Mn(II) ions, which are coordinated to one phen in each, are joined by two *m*-phth ligands to form a basic unit,  $[\text{Mn}_2(\text{phen})_2(\text{m-phth})_2]$ , (Scheme 1b), in which two *m*-phth ligands are coplanar. Each two basic units are linked by the remainder oxygen atom of the bridging carboxylate group in the basic units  $[\text{Mn}-\text{O}(2)\text{B}$ , 0.2124(3) nm] to form a zig-zag chain along the *c*-axis (Figure 2), in which the dihedral angle of the adjacent basic units is  $68.4^\circ$ . The minimum distance of the two phen ligands is 0.3650 nm, indicating the existence of strong  $\pi$ - $\pi$  stacking interactions between aromatic rings. The  $\pi$ - $\pi$  interactions (0.3618 nm) between the phenyl rings of the carboxylate ligands in two chains allow them to extend into a two-dimensional wave-like layer.

Scheme 1



The final 3D supramolecular architecture (as shown in Figure 3) shows that the layers are geared with each other in a tight packing fashion without any guest solvent molecule.

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