

# Three New 3D Coordination Polymers Constructed from Semirigid Tri-carboxylate V-shaped Ligand: Synthesis, Characterization and Magnetic Properties

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Article history: Received: 08 March 2019; revised: 12 April 2019; accepted: 07 May 2019. Available online: 04 July 2019. DOI: <http://dx.doi.org/10.17807/orbital.v11i3.1394>

## Abstract:

Hydrothermal reactions of 2-(2',4'-dicarboxylphenoxy) benzoic acid ( $H_3L$ ) with 1,4-di(pyridin-4-yl)benzene (dpb) and 1,4-bis(2-methylimidazol-3-ium-1-yl)benzene (bimib) in the presence of  $Mn(OAc)_2 \cdot 4H_2O$  and  $Zn(NO_3)_2 \cdot 6H_2O$  yielded three new coordination polymers,  $[Mn_{1.5}(L)(dpb) \cdot H_2O] \cdot H_2O$  (1),  $[Zn_3(L)_2(bimib)]_n$  (2) and  $[Zn_3(L)_2(bmimb)]_n$  (3), complex 1 has a three dimensional structure formed by the combination of mono and binuclear chains, complexes 2 and 3 have identical structures with one only different in the length of the auxiliary ligands, both complexes have 3D structure. All the complexes were characterized by IR, XRD, PXRD, and thermal gravimetric analysis (TGA), furthermore the magnetic behavior of complex 1 was studied; which showed antiferromagnetic behavior.

**Keywords:** metal-organic frameworks; MOFs; coordination polymers; V-shaped ligand

## 1. Introduction

Metal-organic frameworks (MOFs) have recently emerged as an important family of porous materials due to their potential applications in the fields of catalysis, ion exchange, gas absorption, luminescence, nonlinear optics (NLO), and magnetism [1-7]. MOFs can be synthesized by using a wide range of metal ions and organic ligands [8-9]. In this regard, the design of suitable organic ligands favoring structure-specific self-assembly is one of the keys for the construction of coordination architectures. Among the reported structures, organic ligands with carboxylate play an important role in coordination chemistry and can adopt various binding modes such as monodentate, chelating one metal center, bridging two metal centers in a *synsyn*, *syn-anti* and *anti-anti* configuration, and bridging two metal centers in a tridentate form [10-11].

On the other hand, benzene multicarboxylate ligands play a significant role in the design and construction of coordination polymers [12-14] because of their fascinating characteristics including strong coordination ability, diverse coordination modes, various organic skeletons of carboxylate linkers, and extensive hydrogen-bonding interactions. Compared with the rigid aromatic multicarboxylate ligands with one benzene ring as central molecular framework such as 1,4-benzenedicarboxylate, 1, 3,5-benzenetricarboxylate, and 1,2,4,5-benzenetetracarboxylate, Semi-rigid V-shaped multicarboxylate ligands with a nonmetallic atom center connecting two benzene-polycarboxylic moieties are of increasing flexibility since phenyl rings can freely rotate around the bonds formed between carbon atoms and the nonmetallic atom according to the small change in the coordination environment in order to minimize

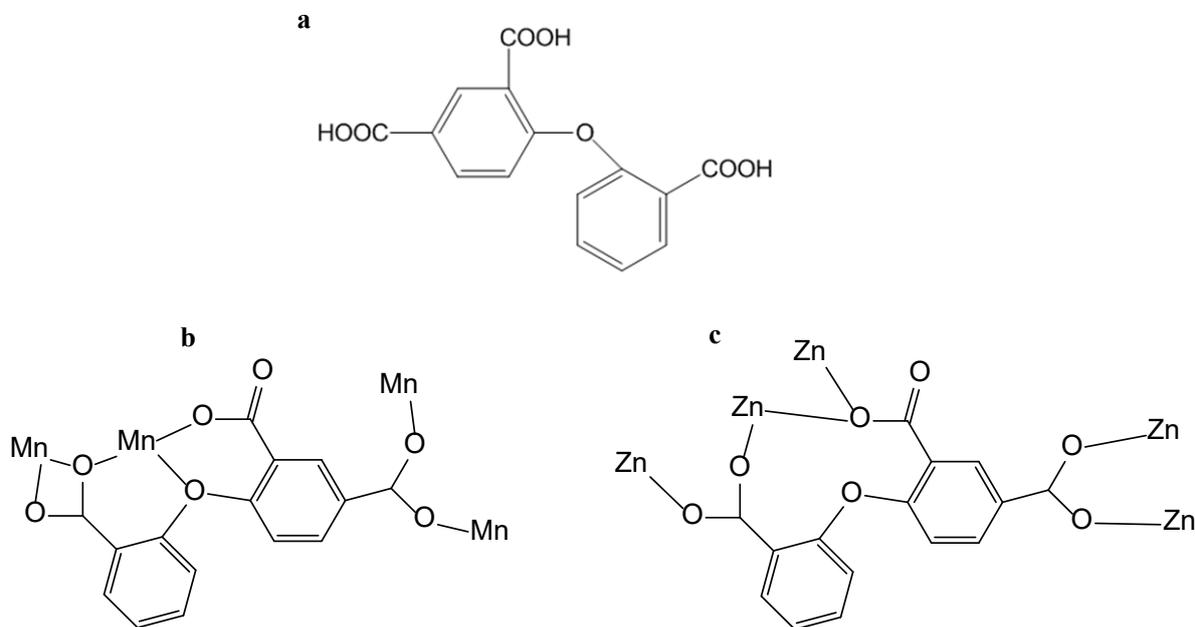
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steric hindrance and therefore leading to metal complexes with diverse structures and potential applications in various fields such as separation, absorption, catalyst, and sensors [15-18], also, in this kind of ligands the carboxylic groups can mediate magnetic coupling by bridging metal ions with the syn-syn bonding mode [19-22]. Furthermore, this kind of ligands can be used as bridging ligand to expand the dimension of coordination polymer. Wang et al have reported a family of the asymmetric semi-rigid V-shaped 3-(4-carboxyphenoxy) phthalic acid with N-donor co-ligands that led to a series of (1D→3D) coordination polymers [18, 23].

With the aim of understanding this type of ligands coordination chemistry and studying the influence on the framework structures of their complexes, the semi-rigid V-shaped ligands; 2-

(2',4'-dicarboxylphenoxy) benzoic acid ( $H_3L$ ) was used to construct three new coordination polymers with the help of different N-donor ligands as secondary ligands. This ligand is tricarboxylate and possess two benzene rings connected via oxygen atom, the two benzene rings can rotate freely around –O–groups with different angles to meet the requirement of the coordination geometries. The three complexes obtained were characterized by X-ray diffraction, IR and TGA and the magnetic behavior for complex 1 was studied.

For the best of our knowledge the coordination polymers constructed from this asymmetric semirigid V-shaped multidentate O-donor ligand have not been reported thus far.



**Figure 1.**  $H_3L$  ligand (a) and its coordination modes in 1(b), 2 (c) and 3 (c).

## 2. Results and Discussion

### 2.1. X-ray crystallography

X-ray crystallography data for all complexes were collected with an Agilent Technologies SuperNova CCD diffractometer with  $MoK\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) in the  $\omega$  scan mode. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on  $F^2$

by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [24]. The hydrogen atoms positions except for those of water molecules were fixed geometrically and refined isotropically using the riding model. Crystallographic data for **1–3** were summarized in Table 1. The selected bond lengths and angles for **1–3** are supplied in Table 2 and Table 3.

**Table 1.** Crystal Data and Structural Refinement Parameters for 1–3.

Complex	1	2	3
Empirical formula	C <sub>62</sub> H <sub>46</sub> Mn <sub>3</sub> N <sub>4</sub> O <sub>18</sub>	C <sub>44</sub> H <sub>28</sub> N <sub>4</sub> O <sub>14</sub> Zn <sup>3</sup>	C <sub>46</sub> H <sub>32</sub> N <sub>4</sub> O <sub>14</sub> Zn <sub>3</sub>
Formula weight g/mol	1299.85	1032.81	1060.87
Temperature/K	296	296	296
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P -1	P -1
a/Å	20.943(4)	8.7046(10)	8.726(4)
b/Å	16.165(3)	10.9913(13)	11.468(6)
c/Å	16.293(3)	12.5931(13)	12.458(6)
α/°	90	113.076(3)	113.856(8)
β/°	102.144(3)	104.784(3)	100.893(8)
γ/°	90	96.875(4)	97.113(9)
Volume/Å <sup>3</sup>	5392.4(18)	1038.5(2)	1091.5(9)
Z	4	1	1
ρ <sub>calc</sub> /mg/mm <sup>3</sup>	1.601	1.651	1.614
F(000)	2660.0	522.0	538.0
λ (Mo KR) (Å)	0.71073	0.71073	0.71073
Reflections collected	4760	3623	3814
Parameters	398	296	305
Goodness-of-fit on F <sup>2</sup>	1.076	1.048	1.112
R <sub>1</sub> [I ≥ 2σ (I)]	0.0304	0.0265	0.0367
wR <sub>2</sub> [I ≥ 2σ (I)]	0.0821	0.0699	0.1186

**Table 2.** Selected bond length for complexes 1-3 (Å°).

Complex 1		Complex 2		Complex 3	
Mn1—O3	2.1894	N2—Zn2	1.9859	N2—Zn2	1.9879
Mn1—O3	2.1894	O2—Zn1	2.0832	O2—Zn1	2.0580
Mn1—O8	2.2369	O3—Zn2	1.9669	O2—Zn1	2.0580
Mn1—O8	2.2369	O4—Zn2	1.9634	Zn1—O3	2.1884
Mn1—N2	2.345	O4—Zn1	2.2084	Zn1—O3	2.1884
Mn2—O5	2.0751	O5—Zn2	1.9490	Zn1—O5	2.0695
Mn2—O4	2.1313	O6—Zn1	2.0434	Zn1—O5	2.0695
Mn2—O2	2.1725	Zn1—O6	2.0434	Zn2—O1	1.9648
Mn2—N3	2.3174	Zn1—O2	2.0832	O3—Zn2	1.9644
Mn2—O7	2.4333	Zn1—O4	2.2083	Zn2—O6	1.9654

## 2.2. Structural description

### 2.2.1 Structure Description of [Mn<sub>1.5</sub>(L)(dpb).H<sub>2</sub>O].H<sub>2</sub>O (1)

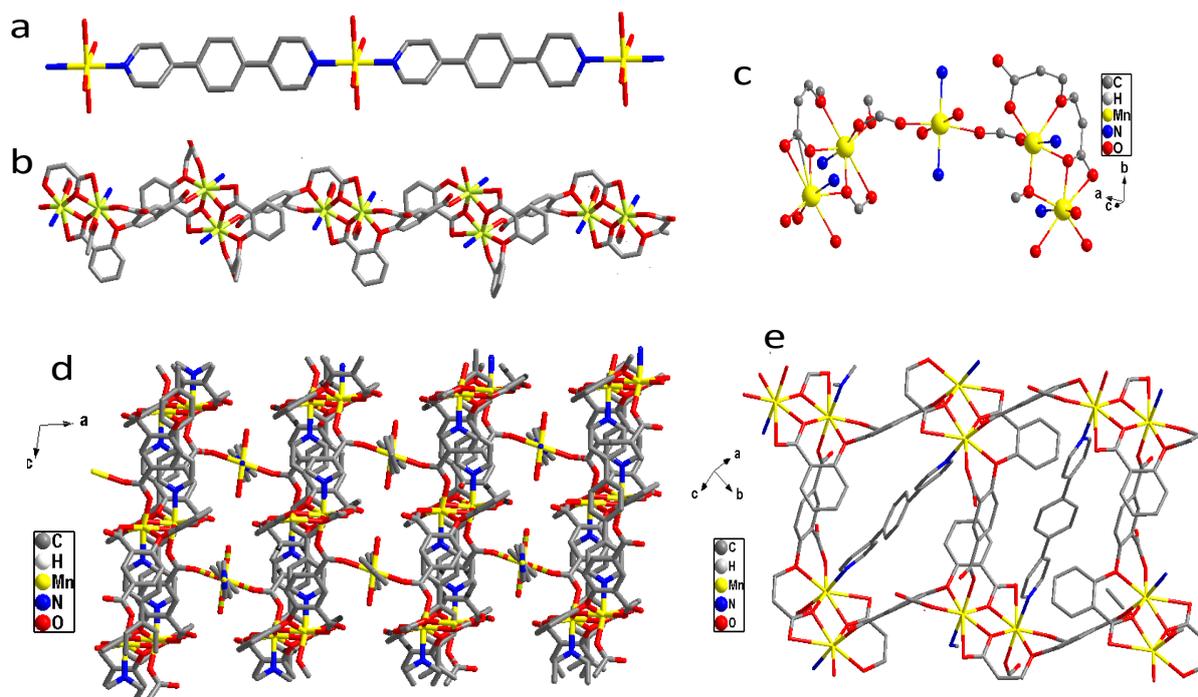
Complex **1** crystallizes in the monoclinic space group C 1 2/c 1 (15). The asymmetric unit of **1** consists of two crystallographically independent units of Mn(II), one coordinated water molecule, one H<sub>3</sub>L, one dpb ligand and one lattice water molecule. Mn1 is six coordinated by two nitrogen from two dpb ligands and four oxygen, two of which from different two H<sub>3</sub>L ligands and two oxygen from two coordinated water molecules to form an octahedral geometry around the metal center. The Mn1 atoms are connected in a linear fashion by two nitrogen atoms from two different

dpb ligands (Mn1– N1=2.313 Å, Mn1–N2=2.345Å) to form a one dimensional linear chain (Figure 2.a).

Mn2 has distorted pentagonal bipyramidal geometry with one nitrogen from one dpb ligand, six oxygen from different three H<sub>3</sub>L ligands, by chelating bidentate, monodentate fashion and by μ<sup>2</sup>-oxygen. Each two neighboring Mn2 form a binuclear unit via 2μ<sup>2</sup> carboxylate bridging oxygen (Mn2–O2= 2.174Å), the distance between the two Mn(II) ions is 3.42 Å, the binuclear units are connected together via O4 carboxylate oxygen (Mn2–N3= 2.318Å, Mn2–O1= 2.767Å, Mn2–O4=2.131Å, Mn2–O5= 2.075Å, Mn2–O7= 2.433Å ), to furnish a one dimensional binuclear chain (Figure 2.b).

**Table.3.** Selected bond angles for complexes 1-3(°).

Complex 1		Complex 2		Complex 3	
O3—Mn1—O3	170.28	Zn2—O4—Zn1	103.64	O2—Zn1—O2	179.999
O3—Mn1—O8	78.54	O6—Zn1—O6	180.0	O2—Zn1—O5	94.61
O3—Mn1—O8	78.54	O6—Zn1—O2	86.35	O2—Zn1—O5	85.39
O3—Mn1—O8	101.50	O6—Zn1—O2	93.65	O2—Zn1—O5	85.39
O8—Mn1—O8	179.52	O6—Zn1—O2	93.65	O2—Zn1—O5	94.61
O3—Mn1—N1	85.14	O6—Zn1—O2	86.35	O5—Zn1—O5	180.00
O3—Mn1—N1	85.14	O2—Zn1—O2	180.00	O2—Zn1—O3	91.26
O8—Mn1—N1	90.24	O6—Zn1—O4	89.81	O2—Zn1—O3	88.74
O8—Mn1—N1	90.24	O6—Zn1—O4	90.19	O5—Zn1—O3	88.54
O3—Mn1—N2	94.86	O2—Zn1—O4	90.06	O5—Zn1—O3	91.46
O3—Mn1—N2	94.86	O2—Zn1—O4	89.94	O2—Zn1—O3	88.74
O8—Mn1—N2	89.76	O6—Zn1—O4	90.19	O2—Zn1—O3	91.26
O8—Mn1—N2	89.76	O6—Zn1—O4	89.81	O5—Zn1—O3	91.46
N1—Mn1—N2	180.0	O2—Zn1—O4	89.94	O5—Zn1—O3	88.54
O5—Mn2—O4	88.42	O2—Zn1—O4	90.06	O3—Zn1—O3	180.00
O4—Mn2—O2	85.78	O4—Zn1—O4	180.0	O3—Zn2—O1	109.53
O2—Mn2—O2	76.05	O5—Zn2—O4	112.33	O3—Zn2—O6	104.16
O5—Mn2—N3	94.86	O5—Zn2—O3	105.10	O1—Zn2—O6	106.49
O4—Mn2—N3	166.07	O4—Zn2—O3	100.31	O3—Zn2—N2	125.41
O2—Mn2—N3	93.24	O5—Zn2—N2	107.46	O1—Zn2—N2	103.42
O5—Mn2—O7	80.27	O4—Zn2—N2	122.81	O6—Zn2—N2	106.61
O4—Mn2—O7	86.61	O3—Zn2—N2	107.11		



**Figure 2.** (a) The one dimensional linear chain of Mn1 ions in complex 1. (b) The one dimensional binuclear chain of Mn2 ions in complex 1 (N atoms represent dpb ligands which were deleted for clarity) (c) H<sub>3</sub>L ligand connecting mononuclear and binuclear units in 1 (d) The 3D structure of 1 viewed along b axis (hydrogen atoms and lattice water molecules were omitted for clarity) (e) View of the binuclear units cross-linked by dpb ligands in complex 1.

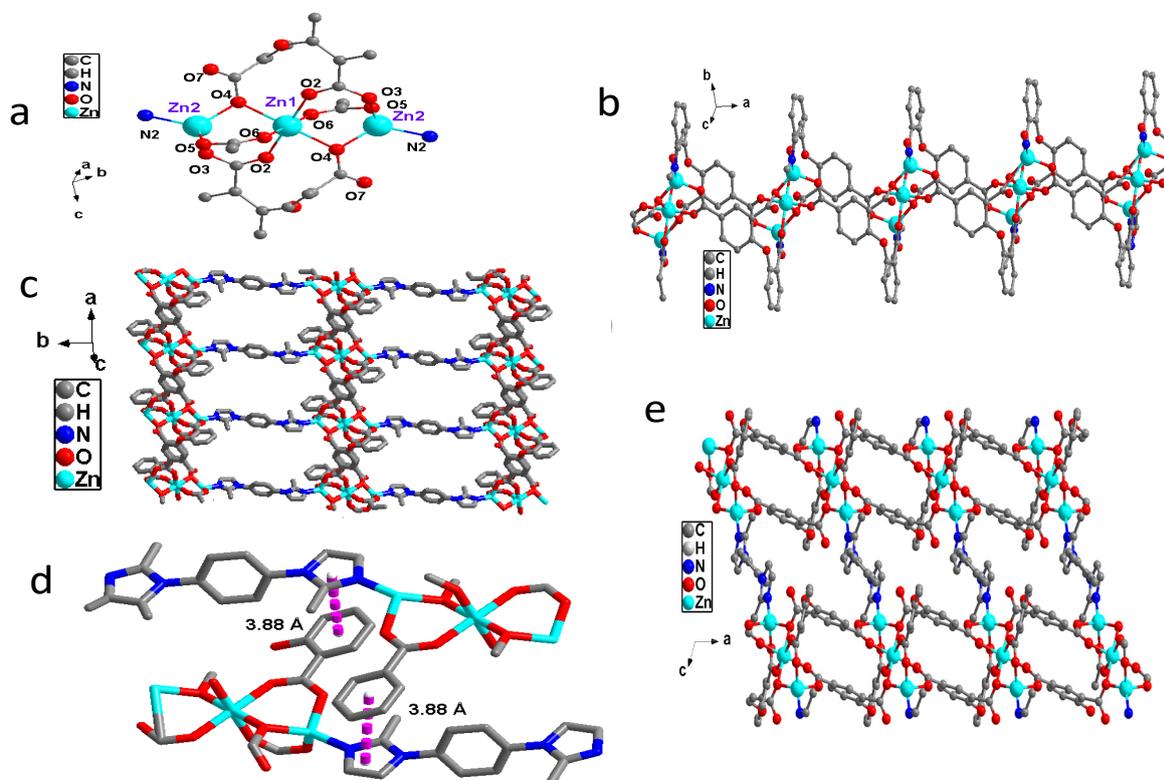
The linear one dimensional chain formed by Mn1 ions and the binuclear chain formed by Mn2 ions are linked by H<sub>3</sub>L ligand via O3 and O4 carboxylate oxygen by syn, syn bridging mode (figure 2.c) to build up the three dimensional complex (Figure 2.d). On the other hand, dpb ligands also cross link the binuclear units to further support the 3D framework (Figure 2.e). The lattice water molecule O1W forms hydrogen bonds with O8W coordinated to Mn1. Hydrogen bonds were also observed between O8W---O5, O8W---O6.

### 2.2.2. Structure Description of [Zn<sub>3</sub>(L)<sub>2</sub>(bimib)]<sub>n</sub> (2)

Complex **2** crystallizes in the triclinic space group P-1 (2). The asymmetric unit of **2** consists of one and half crystallographically independent Zn(II) ions, one H<sub>3</sub>L and a half of bimib ligand. One of Zn(II) ion is situated at the center of symmetry therefore has half occupancy. The structure forms a unit of three Zn(II) ions

coordinated by bridging carboxylates (figure 3.a). In this trinuclear cluster, each terminal metal center shows a tetrahedral ZnNO<sub>3</sub> coordination geometry from three bridging carboxylate O (Zn2-O3= 1.967Å, Zn2-O4=1.963Å and Zn2-O5= 1.949Å) and one N atom of bimib ligand (Zn2-N2=1.986Å). The middle metal atom shows an octahedral ZnO<sub>6</sub> coordination geometry from six bridging carboxylate O (Zn1-O= 2.043-2.208Å). All the bond distances fall in the range found for Zn(II) ions.

The trimeric units are connected together via H<sub>3</sub>L ligands to form a one dimensional trimeric Zn(II) chain (Figure 3.b). The ligands bimib extend the structure via the N atoms coordinated to Zn2 to form a 2D layered structure (Figure 3.c). Intermolecular π...π interactions through face-to-face fashion between phenyl rings from H<sub>3</sub>L ligands and imidazole rings from bimib ligands [intercentroid distance = 3.88Å,] (Figure 3.d) lead to the construction of the 3D structure of **2** (Figure 3.e).



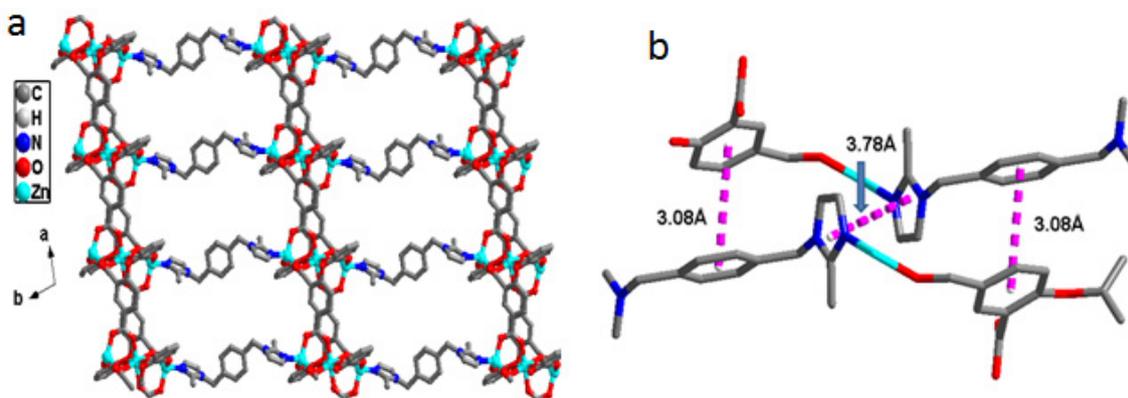
**Figure 3.** (a) View of trinuclear cluster in complex 2. (b) View of the one dimensional trimeric Zn(II) chain in complex 2.(c) View of the 2D layer in complex 2.(d) The π...π interactions in complex 2(e) View of the 3D structure in complex 2 along b axis.

### 2.2.3. Structure Description of $[Zn_3(L)_2(bmimb)]_n$ (3)

Complexes 2 and 3 have identical structures; the only different between the two structures is that the auxiliary ligand (bmimb) used in 3 is

longer than bimib ligand used for complex 2 by 2 -ch<sub>2</sub>- groups.

Figures 4.a and 4.b show the 2D structure and the  $\pi \dots \pi$  interactions in complex 3.

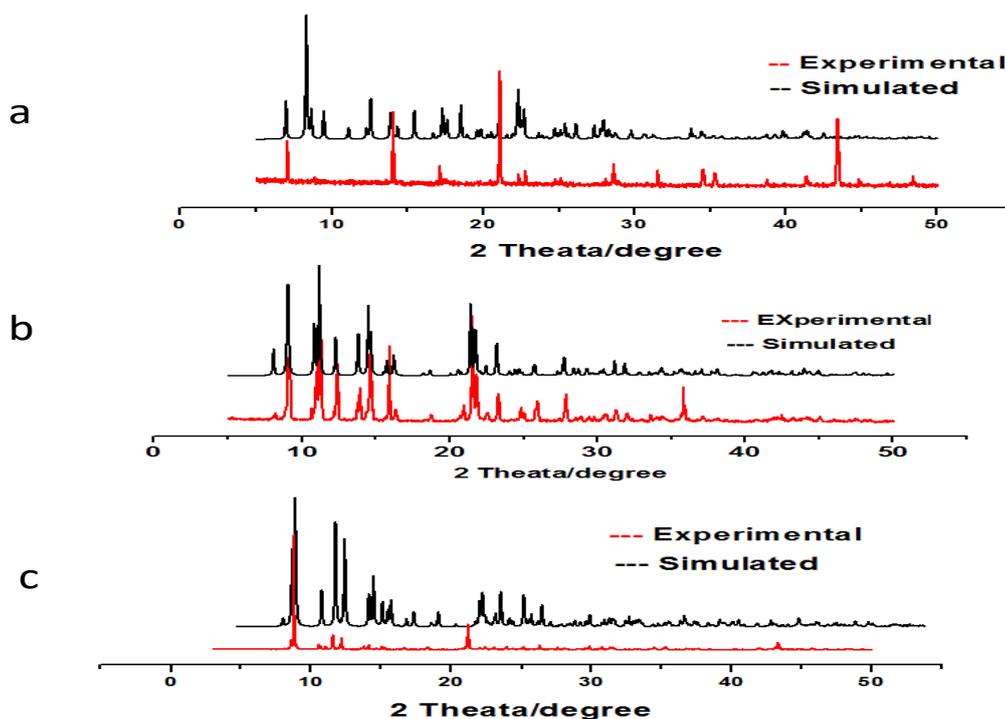


**Figure 4.** (a) View of the 2D layer in complex 3 (b) The  $\pi \dots \pi$  interactions in complex 3.

### 2.3 PXRD and thermogravimetric analysis

The phase purity of all complexes was checked by X-ray powder diffraction (PXRD) at

room temperature. The observed powder X-ray diffraction (PXRD) patterns for 1-3 are in good accordance with those simulated on the basis of the single-crystal X-ray diffraction data (Figure 5).



**Figure 5.** Patterns of complexes 1(a), 2(b) and 3(c), simulated from X-ray single-crystal structure and as synthesized.

The TGA shows that compound 1 was stable up to 310°C then it shows a weight loss of about

75% between 310 °C-480 °C suggesting the decomposition of the organic framework, the

remaining weight is assigned to Manganese oxide (25%) (Figure 6).

Compound **2** was stable up to 420 °C then we have the decomposition of the organic skelton between 420 °C-480 °C (65% loss of weight), the remaining weight is assigned to Zinc oxide (35%) (Figure 6). Compound **3** was stable up to 450 °C then we have the decomposition of the organic skelton between 450 °C-480 °C (55% loss of weight), the remaining weight is assigned to Zinc oxide (45%) (Figure 6).

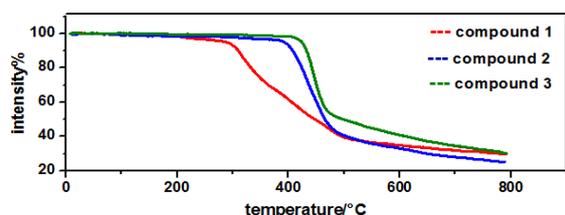


Figure 6. TGA Curves for 1–3.

## 2.4. Magnetic behavior of complex (1)

To investigate magnetic properties for **1**, magnetic susceptibility was measured with an applied magnetic field of 1000 Oe from 2 to 300K. The thermal dependence of  $\chi_M T$  and  $1/\chi_m$  in **1** is shown in (Figure 7), the experimental  $\chi_M T$  at 300K of  $8.47 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  is smaller than that expected for two spin-only case of Mn(II) ions ( $8.75 \text{ cm}^3 \text{ K mol}$ ,  $g=2.0 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $S=5/2$ ), with lowering of temperature, the  $\chi_M T$  product decreases slightly, until a rapid decrease is observed below 50 K, The  $\chi_M T$  value is  $8.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 50 K and finally drops to  $2.5 \text{ cm}^3 \text{ K mol}^{-1}$ . This behavior suggests the existence of weak antiferromagnetic exchange between Mn ions.

The structure of **1** can be considered as mono nuclear unit connected to a binuclear unit by carboxylate oxygen (Figure 6), two Mn(II) ions was linked by carboxylate oxygen to form the binuclear unit (Mn1...Mn2 =  $5.29\text{\AA}$ , Mn2...Mn2= $3.42\text{\AA}$ ). Based on this structural characteristic the alternating chain model ( $J_1$ ... $J_1$ ... $J_2$ ) can be used, taking into account the molecular field approximation ( $zJ'$ ), magnetic susceptibility equation can be expressed as the following equation [25-28].

$$\chi_m = \frac{Ng^2\beta^2 S(S+1)}{3kT} \frac{3(1-u_1^4 u_2^2) + 4u_1(1-u_1^2 u_2^2) + 2u_2(1+u_1)^2(1-u_1^2) + 2u_1^2(1-u_2^2)}{(1-u_1^2 u_2^2)^2}$$

$$u_i = \coth[J_i S(S+1) / kT] - kT / [J_i S(S+1)] \quad (i = 1, 2; S = 5/2)$$

$$\chi_m T = T \left[ \frac{\chi_m}{1 - \chi_m (2zJ' / (Ng^2\beta^2))} \right]$$

The best fit of the experimental data in the range above 30K gives  $J_1 = -0.86 \text{ cm}^{-1}$ ,  $J_2 = -1.67 \text{ cm}^{-1}$ ,  $g=1.95$  and  $zj' = 0.1159$ . The negative values of  $J_1$  and  $J_2$  indicate the existence of antiferromagnetic coupling between Mn(II) ions. According to the Curie-Weiss law of  $\chi_M = C / (T - \theta)$ , the linear fit was obtained  $\theta = -9.9 \text{ K}$  and  $C = 10 \text{ cm}^3 \text{ K mol}^{-1}$ . The negative value of  $\theta$  further confirms the antiferromagnetic interactions (Figure 8).

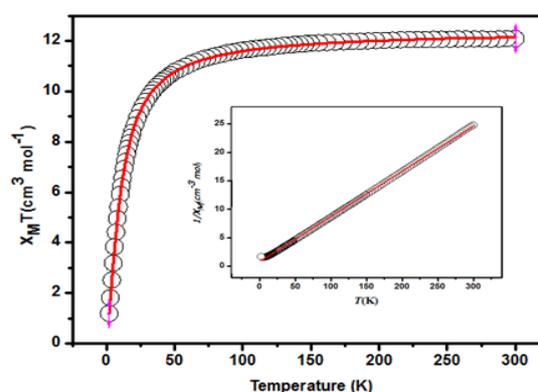


Figure 7. Plots of  $\chi_M T$  and  $1/\chi_m$  versus T for complex 1.

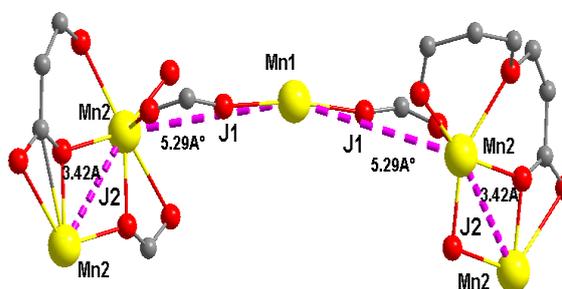


Figure 8. Mono and binuclear units linked via carboxylates oxygen in **1**.

## 3. Material and Methods

### 3.1. General Physical Measurements

Fourier transform infrared (FT-IR) spectra were obtained in the range  $400\text{--}4000 \text{ cm}^{-1}$  on an FTS 3000 (the United States DIGILAB)

spectrometer using KBr pellets. Thermogravimetric analysis (TGA) experiments were taken on a Perkin-Elmer TG-7 analyzer heated from 25 to 800 °C with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. Powder X-ray diffraction (PXRD) analyses were obtained on a Philips PW 1710-BASED diffractometer at 293 K.

### 3.2. Materials and General Methods

The ligand 2-(2',4'-dicarboxylphenoxy) benzoic acid (H<sub>3</sub>L) and all other Chemicals were purchased from commercial sources and used without further purification.

### 3.3 Synthesis

#### 3.3.1 Synthesis of complex [Mn<sub>1.5</sub>(L)(dpb).H<sub>2</sub>O].H<sub>2</sub>O (1)

A mixture containing 2-(2',4'-dicarboxylphenoxy) benzoic acid (H<sub>3</sub>L) (0.1 mmol), Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.2 mmol), and 1,4-di(pyridin-4-yl)benzene (dpb) (0.1 mmol) was placed in a Teflon reactor (15 mL), which was heated at 120 C° for 3 days and then gradually cooled to room temperature, yellow crystals of **1** were isolated from the mother liquid, washed with water, and then dried at ambient temperature. IR/cm<sup>-1</sup>(KBr): 3865(w), 3805(w), 3750(w), 3676(w), 3650(w), 3413(m), 3202(w), 3055(w), 3922(w), 1940(w), 1590(s), 1546(m), 1480(m), 1416(m), 1424(m), 1390(w), 1360(w), 1227(m), 1077(w), 995(w), 870(w), 705(m), 572(m), 465(m), (figure S1).

#### 3.3.2 Synthesis of complex [Zn<sub>3</sub>(L)<sub>2</sub>(bimib)]<sub>n</sub> (2)

A mixture containing 2-(2',4'-dicarboxylphenoxy) benzoic acid (H<sub>3</sub>L) (0.2 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.3 mmol), and 1,4-bis(2-methylimidazol-3-ium-1-yl)benzene (bimib) (0.1 mmol) was placed in a Teflon reactor (15 mL), which was heated at 125 C° for 3 days and then gradually cooled to room temperature, yellow crystals of **2** were isolated from the mother liquid, washed with water, and then dried at ambient temperature. IR/cm<sup>-1</sup>(KBr): 3429(w), 3141(m), 1656(s), 1613(s), 1570(w), 1514(s), 1390(s), 1328(s), 1296(m), 1231(s), 1158(s), 1090(s), 1011(m), 965(w), 927(w), 902(w), 856(m),

822(w), 802(w), 760(s), 713(w), 680(m), 658(m), 575(m), 532(m), 503(w), 451(w), 430(w), (figure S2).

#### 3.3.3 Synthesis of complex [Zn<sub>3</sub>(L)<sub>2</sub>(bmimb)]<sub>n</sub> (3)

A mixture containing 2-(2',4'-dicarboxylphenoxy) benzoic acid (H<sub>3</sub>L) (0.2 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.3 mmol), and 1,4-bis((2-methyl-1H-imidazol-1-yl)methyl)benzene (bmimb) (0.1 mmol) was placed in a Teflon reactor (15 mL), which was heated at 125 C° for 3 days and then gradually cooled to room temperature, yellow crystals of **2** were isolated from the mother liquid, washed with water, and then dried at ambient temperature. IR/cm<sup>-1</sup>(KBr): 3439(w), 3139(m), 370(w), 1657(s), 1614(s), 1571(w), 1475(w), 1393(s), 1335(s), 1291(m), 1259(w), 1233(s), 1163(s), 1088(s), 1008(m), 911(w), 879(w), 826(m), 798(w), 759(s), 714(w), 685(m), 654(m), 605(w), 530(s), 438(M), (figure S3).

## 4. Conclusions

In summary, three new coordination polymers based on 2-(2',4'-dicarboxylphenoxy) benzoic acid (H<sub>3</sub>L) were successfully prepared under hydrothermal conditions. complex **1** has a 3D structure formed by the combination of mono and binuclear chains, complexes **2** and **3** have identical structures with one only difference in the length of the auxiliary ligands. The complexes were structurally characterized by single-crystal X-ray diffraction. IR spectra and the thermal stability was also studied. The magnetic behavior of complex **1** was studied; which showed antiferromagnetic behavior.

## Supporting Information

[Figure S1. IR spectra for complex 1; Figure S2. IR spectra for complex 2; Figure S3. IR spectra for complex; Crystallographic Information File \(CIF\).](#)

## Acknowledgments

We are very grateful for the support of this study by the National Natural Science Foundation of China (Nos.21461023 and 21361023),

Fundamental Research Funds for the Gansu Universities.

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