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Assistant Effect on Modulating the Two Mn(II) Complexes[1]

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Abstract—Two Mn-based complexes with chemical formulae $\{[Mn(L1)_2(H_2O)(4,4'\text{-Bipy})] \cdot 3H_2O\}$ (**I**) and $[Mn(L2)_2(H_2O)_2(4,4'\text{-Bipy})]$ (**II**) (HL^1 = 3-(4-hydroxyphenyl)propanoic acid, HL^2 = *p*-hydroxy phenylacetic acid, 4,4'-Bipy = 4,4'-bipyridine), have been synthesized and are characterized by single crystal X-ray diffraction (CIF files CCDC nos. 1045594 (**I**), 1045595 (**II**)). Compounds **I** has 1D zigzag chain constructed by bridging bisdentated 4,4'-Bipy linkers, whereas **II** shows mononuclear motif due to the monodentated 4,4'-Bipy mode. The assistant effect of the flexibility of carboxylate may play an important to modulate on the resulting motif.

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INTRODUCTION

Coordination polymers (CPs) have attracted intense attention in recent years because of their intriguing structures and potential applications as functional materials [1–3]. It is well-known that organic ligands play crucial roles in the design and construction of desirable frameworks. The changes in flexibility, length, and uncoordinated functional groups of organic ligands can result in a remarkable class of materials bearing diverse architectures and functions. Thus, the construction of target molecules with properties mentioned above is a challenge for synthetic chemists [4–8].

Recently, the remarkable multidentate ligands 3-(4-hydroxyphenyl)propanoic acid (HL^1) or *p*-hydroxy phenylacetic acid (HL^2) seized our attention for the following reasons [9]: (1) it can act not only as a hydrogen bond acceptor but also as a hydrogen bond donor, depending upon the degree of deprotonation; (2) it holds multipotential groups, which can afford interesting structures with tunable dimensionality; (3) it not only has one rigid hydroxyl group affixed to the aromatic ring but also extends one flexible carboxylic part. On the other hands, the combination of different ligands can result in greater modulation of structural frameworks than single ligand [5–8]. Therefore, mixed-ligands are undoubtedly a good choice for the construction of new polymeric structures. In particular, coordination compounds with flexible ligands exhibit more complex structural peculiarity due to the characteristics of flexible ligands, namely, the configurations of functional groups were changeful [10–13]. In this report, we employed two similar and flexible carboxylate 3-(4-hydroxyphenyl)propanoic acid and *p*-hydroxy phenylacetic acid, to build complexes. We anticipated that increase architecture complexity may be introduced by using bridging aromatic N-donor linkers and there is an opportunity to drive the new modes of network assembly required to satisfy the unique constraints imposed by linker geometries. The reactions of HL^1 and HL^2 with Mn(II) and three well-known dipyridyl linker of 4,4'-bipyridine (4,4'-Bipy) under mild conditions resulted the formation of two new complexes with different motifs—$\{[Mn(L^1)_2(H_2O)(4,4'\text{-Bipy})] \cdot 3H_2O\}$ (**I**) and $[Mn(L^2)_2(H_2O)_2(4,4'\text{-Bipy})]$ (**II**). These compounds are characterized by single crystal X-ray diffraction. Subsequently, the compounds were analyzed for their crystal packing. Furthermore, the stable properties of compounds **I**, **II** were discussed in detail.

EXPERIMENTAL

Materials and methods. All reagents were purchased from commercial sources and used as received. IR spectra were recorded with a PerkinElmer Spectrum One spectrometer in the region 4000–400 cm^{-1} using KBr pellets. Thermogravimetric analysis (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 for CuK_α radiation ($\lambda = 1.5406$ Å) with a scan speed of 2°C/min and a step size of 0.013° in 2θ.

Syntheses of complexes I. A mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.0386 g), HL^1 (0.0190 g), 4,4'-Bipy (0.0232 g), CH_3CH_2OH (5 mL) and deionised water (5 mL) was stirred for 30 min in air. The resulting solu-

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[1] The article is published in the original.

Table 1. Crystal data and structure refinement information for compound **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	611.50	705.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Crystal color	Colorless	Colorless
a, Å	8.752(9)	5.7015(16)
b, Å	15.694(15)	7.780(2)
c, Å	22.705(19)	36.404(10)
β, deg	109.99(3)	94.437(4)
V, Å^3	2931(5)	1609.9(8)
Z	4	2
ρ_{calcd}, g/cm^3	1.386	1.456
μ, mm^{-1}	0.509	0.471
F(000)	1276	734
θ Range, deg	2.01–28.12	2.26–28.56
Reflection collected	17638	8104
Independent reflections (R_{int})	0.0550	0.0218
Reflections with $I > 2\sigma(I)$	6966	2926
Number of parameters	3609	2746
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0525, 0.0864	0.0468, 0.1503
R_1, wR_2 (all data)**	0.1205, 0.1030	0.0516, 0.1587

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

tion was kept at room temperature for one week, the crystals formed were filtered off, washed with water and dried in air.

For $C_{28}H_{34}MnN_2O_{10}$ ($M = 613.50$)

anal. calcd., %:	C, 54.81;	H, 5.59;	N, 4.57.
Found, %:	C, 54.60;	H, 5.47;	N, 4.39.

IR spectrum (KBr; ν, cm^{-1}): 3505 v, 3164 v, 2969 m, 1600 m, 1503 v, 1395 v.s, 1212 v, 995 v, 870 v.s, 807 v.s, 625 m.

Syntheses of complexes II was carried out by the same method used for **I** except that HL^1 was replaced with HL^2 (0.0156 g).

For $C_{36}H_{34}MnN_4O_8$ ($M = 705.61$)

anal. calcd., %:	C, 61.28;	H, 4.86;	N, 7.94.
Found, %:	C, 61.21;	H, 4.55;	N, 7.53.

IR spectrum (KBr; ν, cm^{-1}): 3083 v, 2809 m, 1560 v.s, 1451 v.s, 1406 v., 1206 v.s, 1140 v.s, 1058 v.s, 995 v, 792 v.s, 619 v.s, 522 v.

X-ray crystallography. Single crystal X-ray diffraction analysis of the title compounds were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 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. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The hydrogen atoms of lattice water molecule in compounds were located using the different Fourier method. Table 1 shows crystallographic data of **I**, **II**. Selected bond distances and bond angles are listed in Table 2. Some H-bonded parameters are listed in Table 3.

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1045594 (**I**), 1045595 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 2. Selected bond distances (Å) and angles (deg) of structurse **I** and **II***

Bond	d, Å	Bond	d, Å
I			
Mn(1)–O(1w)	2.183(3)	Mn(1)–O(1)	2.199(2)
Mn(1)–N(2)	2.293(3)	Mn(1)–N(1)	2.295(3)
Mn(1)–O(4)	2.311(3)	Mn(1)–O(5)	2.349(3)
II			
Mn(1)–O(2)	2.1487(18)	Mn(1)–O(1w)	2.210(2)
Mn(1)–N(1)	2.286(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**
I			
O(1w)Mn(1)O(1)	133.81(9)	O(1w)Mn(1)N(2)	91.12(9)
O(1)Mn(1)N(2)	94.45(10)	O(1w)Mn(1)N(1)	85.82(9)
O(1)Mn(1)N(1)	88.18(10)	N(2)Mn(1)N(1)	176.87(9)
O(1w)Mn(1)O(4)	85.87(9)	O(1)Mn(1)O(4)	139.93(9)
II			
O(2)Mn(1)O(2)$^{\#1}$	180.0	O(2)Mn(1)O(1w)	90.57(8)
O(2)Mn(1)O(1w)	89.43(8)	O(1w)Mn(1)O(1w)$^{\#1}$	180.0
O(2)Mn(1)N(1)	90.90(8)		

* Symmetry code: $^{\#1}$ $-x + 1, -y + 1, -z$.

RESULTS AND DISCUSSION

The asymmetric unit of **I** consists of one Mn^{2+} ion, two L^1 anions, one neutral 4,4-Bipy, one coordinative water molecule and three free water molecules. As shown in Fig. 1a, the octahedral sphere of Mn(1) is defined by one chelated carboxylate group, one monodentated carboxylate group and one terminal coordinative water molecule in the equatorial plane, as well as two N atoms from 4,4'-Bipy at the axial sites. As a result, the 4,4'-Bipy acting as bridging linker connects the Mn centers to result in a 1D coordination motif (Fig. 2a). Whereas the L^1 ligands take as the terminal pendants to decorate the 1D array along the two sides. Notably, the coordinative water molecule O(1w) is H-bonded to two free water molecules (O(2w) and O(3w)). Multiform H-bonds also exists between lattice water/carboxylate/phenolic, in which result in 1D chain along the y axis (Fig. 2b).

To investigate the influence of the flexibility ligand on the complex networks, the L^1 was deliberately replaced by the little flexibility of L^2 ligand. A new compound **II** was obtained. Complex **II** displays a mononuclear unit structure. The structure of **II** contains one Mn^{2+} ion, two L^2 ligands, one bismonodentate 4,4'-Bipy ligands, and two coordinative water molecules. The Mn(II) atom is coordinated by four oxygen atoms from two symmetric monodentate carboxylic group of L^2 ligands and two coordinative water molecules, and two N atoms from two symmetric 4,4'-Bipy ligands, completing a octahedral geometry (Fig. 1b and Table 2). The Mn–O/N distance are in the normal ranges and are agreed with the reported Mn polymers [15].

In addition, careful analysis reveals that the hydrogen bonded interaction association of water molecules, phenolic groups, pyridyl rings and carboxylate groups in **II** leads to the formation of 2D supramolecular network (Fig. 3 and Table 3). The oxygen atom (O(3)) of phenolic group could take as donor to bind with N(2) from pyridyl ring of 4,4'-Bipy. Also, the O(1w) taking as donor involves in O(1) of carboxylate group, which stabilize the full network. It should be noted that there is not any packing interaction between rings from adjacent 4,4'-Bipy molecules.

From a molecular level, the structural discrepancy for these complexes will be assigned to the assistant effect of length of carboxylate ligands. For instance, although the Mn(II) centers also have the same coordinative number, whereas **I** and **II** have some different in packing modes. The L^1 anions in **I** two different binding mode, L^2 only have one monodentate coordinative fashion. Furthermore, the same bridging N-donor ligand and coordinative numbers of Mn centers, but they show different bridging functions, which may be induced by the flexibility of carboxylates L^1 and L^2.

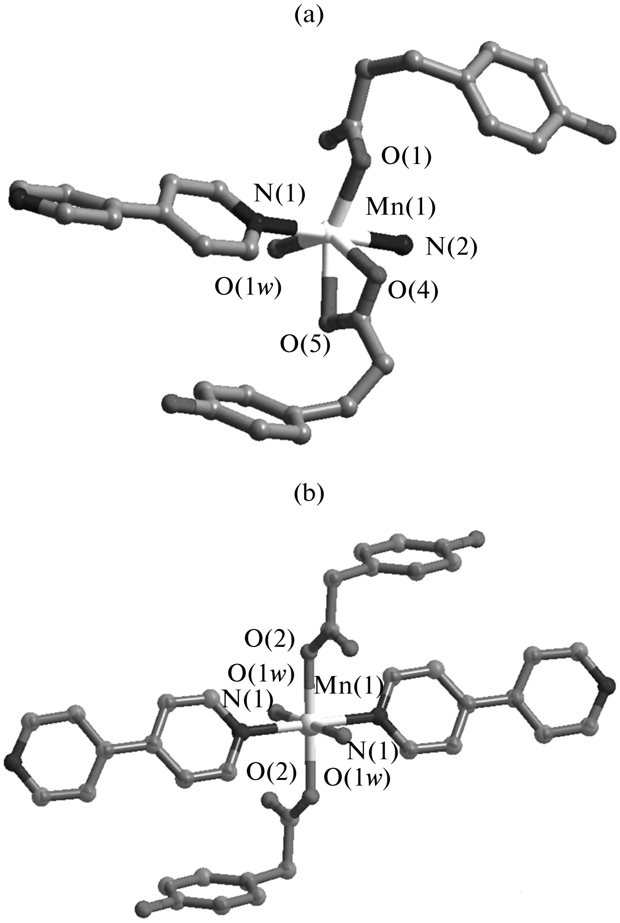

Fig. 1. The coordination geometries of the metal centers and the ligands geometries in **I** (a) and **II** (b) (displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity).

In the FTIR spectra, all the compounds show a broad band centered around 3300 cm^{-1} attributable to the O–H stretching frequency of the water. The asymmetric stretching vibration $\nu(COO^-)$ appear around 1600 cm^{-1} for **I**, **II**, and the symmetric stretching vibration $\nu(COO^-)$ are observed 1450/1400 cm^{-1}. For the complexes, the difference between the asymmetric and symmetric stretches, $\Delta\nu_{as}(COO^-) - \nu_s(COO^-)$, are on the order of 150/200 cm^{-1} indicating that carboxyl groups are coordinated to the metal in a monodentate/bidentate modes [16], consistent with the observed X-ray crystal structures of **I**, **II**.

To study the stability of the polymers, TGA of complexes **I**, **II** were performed (Fig. 4). The TGA diagram of **I** shows two weight loss steps. The first weight loss began at 35°C and completed at 115°C. The observed weight loss of 11.4% is corresponding to the loss of the coordinative water molecule (calcd. 11.7%). After 240°C, the deposition of all the ligands starts on. The second weight loss occurs in the range 216–650°C, which can be attributed to the elimination of L^1 and Bipy ligands. The complex **II** has also two weight loss steps. The first weight loss began at 35°C and completed at 145°C. The observed weight loss of 5.3% is corresponding to the loss of all the water molecules (calcd. 5.1%). The framework then starts the decomposition when the coordinative water molecules were removed.

Additionally, to confirm the phase purity and stability of compounds **I**, **II**, all the original samples were characterized by XRPD. Although the experimental patterns have a few unindexed diffractions lines and some are slightly broadened in comparison to those simulated from single-crystal models, it can still to be considered that the bulk synthesized materials and as-grown crystal are homogeneous for compounds **I**, **II**.

In conclusion, we have presented synthetic strategy that successfully achieved four Mn-based complexes of **I** and **II**, which show the length of carboxylate on the modulation of resulting motifs. Further systematic work towards fabricating more polymers with interesting structures and functionalities is in progress.

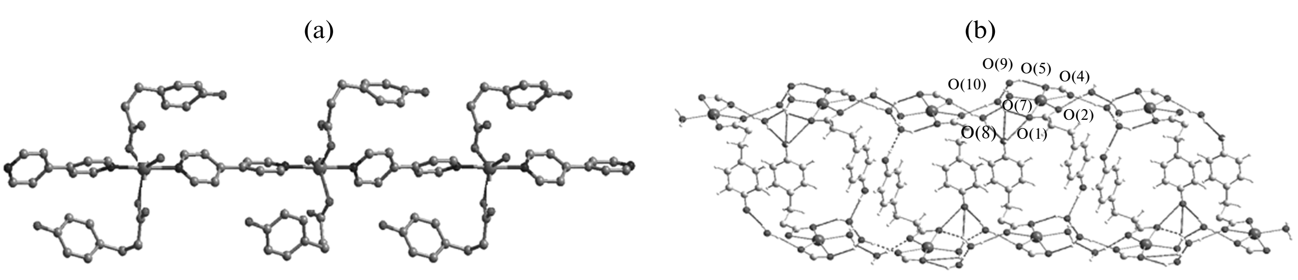

Fig. 2. The 1D chain constructed by 4,4'-Bipy in **I** (displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity) (a); view of the 1D packing framework directing by weak interactions (b).

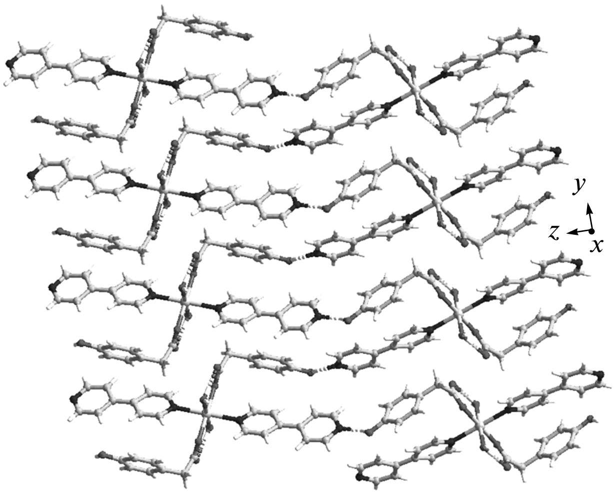

Fig. 3. View of the 1D packing chain directing by weak interactions along the *yz* plane.

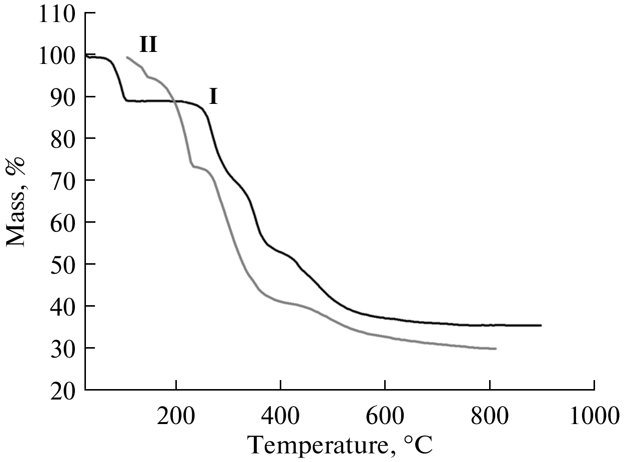

Fig. 4. The TGA curves of **I** and **II**.

Table 3. Hydrogen bonding geometry for complexes **I** and **II**

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
O(1*w*)–H(1*A*)···O(3*w*)	0.83(3)	1.89(3)	2.718(4)	178(4)
O(1*w*)–H(1*B*)···O(2*w*)	0.82(3)	2.03(3)	2.828(5)	166(3)
O(2*w*)–H(2*C*)···O(4*w*)	0.81(3)	1.96(3)	2.719(5)	158(3)
O(2*w*)–H(2*D*)···O(3)	0.815(18)	1.95(2)	2.752(4)	170(3)
O(3*w*)–H(3*C*)···O(1)	0.82(3)	2.02(3)	2.809(4)	160(4)
O(3*w*)–H(3*D*)···O(6)	0.83(4)	1.92(3)	2.700(4)	156(3)
O(4*w*)–H(4*A*)···O(5)	0.835(14)	2.02(2)	2.819(5)	159(4)
O(4*w*)–H(4*B*)···O(2)	0.84(2)	2.56(3)	3.004(5)	114(2)
		II		
O(1*w*)–H(1*A*)···O(1)	0.8100	1.7900	2.591(3)	171.00
O(1*w*)–H(1*B*)···O(2)	0.8200	2.0300	2.816(3)	160.00
O(3)–H(2*A*)···N(2)	0.791(19)	1.96(2)	2.721(4)	163(2)

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