

## 两个由 4-酰基吡唑啉酮衍生物构筑的 Mn(II) 配合物的合成、晶体结构及性质

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**摘要:** 以 4-酰基吡唑啉酮衍生物为配体合成了 2 个 Mn(II)配合物  $[\text{Mn}_2\text{L}_2(\mu\text{-CH}_3\text{OH})_2(\text{CH}_3\text{OH})_2]$  (**1**) 和  $[\text{MnL}(\mu\text{-CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}\cdot\text{CHCl}_3$  (**2**) ( $\text{H}_2\text{L}=\text{N}-(1\text{-苯基-3-苄基-4-丙烯基-5-吡唑啉酮})\text{-异烟酰胺}$ ), 利用元素分析、红外光谱、紫外光谱、热重和 X-射线单晶衍射分析进行了表征。结果表明反应体系的 pH 值影响配体的配位方式, 所得配合物 **1** 为双核结构, 而 **2** 为 2D 网状结构。热重分析表明, 配合物 **1** 的稳定性高于配合物 **2** 的。

**关键词:** 4-酰基吡唑啉酮衍生物; 锰(II)配合物; 晶体结构; 热稳定性

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## Synthesis, Crystal Structure and Properties of Two Mn(II) Complexes with 4-Acyl-pyrazolone Derivative

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**Abstract:** Two manganese complexes,  $[\text{Mn}_2\text{L}_2(\mu\text{-CH}_3\text{OH})_2(\text{CH}_3\text{OH})_2]$  (**1**) and  $[\text{MnL}(\mu\text{-CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}\cdot\text{CHCl}_3$  (**2**) ( $\text{H}_2\text{L}=\text{N}-(1\text{-phenyl-3-benzyl-4-propylene-5-pyrazolone})\text{-isonicotinic hydrazide}$ ) were synthesized and structurally characterized by elemental analyses, IR spectra, UV-Vis spectra, thermogravimetric analyses and single crystal X-ray diffraction. The results show that the pH value of the reaction system has significant effect on the coordination mode of the ligand, which results in a dinuclear structure of **1** and a 2D network of **2**. The thermal gravimetric analyses show that **1** is more stable than **2**. CCDC: 997907, **1**; 997908, **2**.

**Key words:** 4-acyl-pyrazolone derivative; manganese(II) complex; crystal structure; thermostability

### 0 Introduction

The rational design and assembly of metal-organic coordination polymers have received remarkable attention due to their fascinating structural diversities and potential applications in the areas including optical, electronic, magnetic fields, gas storage, ion-

exchange and catalysis<sup>[1-4]</sup>. Investigations show that the designed construction of metal-organic polymers is influenced by many factors such as the nature of the organic building block, the coordination preference of the central metal ion, crystallization conditions, the molar ratio of metal and ligand and preparation methods, etc<sup>[5]</sup>. Among these, proper choice of organic

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ligand is the key factor governing the structure of coordination polymer, as the geometry of ligating atoms within a multi-chelating ligand, the flexibility of the ligand backbone, and the additional functional groups of the ligands all play important roles in directing the extended structure of the resulting complex<sup>[6]</sup>. Thus, considerable efforts have been devoted to choose or design new multidentate ligands to construct novel coordination frameworks with tunable properties.

Pyrazolone-5, especially 4-acyl-pyrazolone, form an important class of organic compounds and widely used in biological, analytical applications, catalysis and extraction metallurgy<sup>[7]</sup>. Moreover, 4-acyl-pyrazolone derivatives can be easily tailored by incorporating other fragment with various complexities, which facilitates the preparation of chelating molecules<sup>[8]</sup>. Due to the various electron-rich donor centers and tautomeric effect of the enol form and keto form of the 4-acyl-pyrazolone derivatives, the coordination behavior of 4-acyl-pyrazolone derivatives has been extensively explored<sup>[7-11]</sup>. Meanwhile, as the compound containing hydrazide moiety and their metal complex always possess biological activities, especially serving as potential inhibitors for many enzymes, the compounds bearing 4-hydrazone moieties have also warranted considerable attention in recent years<sup>[12-13]</sup>. In this paper, two manganese compounds of a new Schiff base derivative of 4-acyl-pyrazolone, *N*-(1-phenyl-3-benzyl-4-propylene-5-pyrazolone)-isonicotinic hydrazide, have been synthesized and characterized. The structural analyses reveal that one is a dinuclear complex, and the other one represents a 2D network based on the dinuclear unit. When a weak organic base was used or not, the ligand performed in different kind of coordination modes, which play an important role in the structure of the final compound. Furthermore, the thermal stabilities of the two manganese complexes are also investigated.

## 1 Experimental

### 1.1 Materials and general physical measurements

All reagents were purchased from commercial sources and used as received. 1-phenyl-3-benzyl-4-

propionyl-5-pyrazolone and isoniazide were synthesized and purified according to the methods in the literature<sup>[11]</sup>.

Elemental analyses (C, H and N) were performed on a FLASH EA 1112 Series NCHS-O analyzer. Melting point was measured with a TECH XT-6 melting point apparatus. IR spectra were recorded on BRUKER EQUINOX-55 spectrophotometer within 400~4 000 cm<sup>-1</sup> using the samples prepared as pellets with KBr. UV-Vis absorption spectra were measured in solid state at room temperature on a UV-3010 spectrometer equipped with an integrating sphere. Thermal analyses were carried out on NETZSCH STA 449F3 instrument at a temperature range of 30~800 °C with a heating rate of 10 °C·min<sup>-1</sup> in the flowing air atmosphere.

### 1.2 Synthesis of the ligand

The ligand *N*-(1-phenyl-3-benzyl-4-propylene-5-pyrazolone)-isonicotinic hydrazide (H<sub>2</sub>L) was prepared by refluxing equimolar 1-phenyl-3-benzyl-4-propionyl-5-pyrazolone and isoniazide in ethanol at 80 °C for 4 h, adding a few drops of glacial acetic acid as a catalyst. Upon cooling, the yellow precipitate was deposited and collected by filtrating, washed and dried in air. Yield: 75%. m.p. 222.4~225.2 °C. Anal. Calcd. for C<sub>25</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>(%): C, 70.57; H, 5.45; N, 16.46. Found: C, 70.51; H, 5.49; N, 16.52. FT-IR (cm<sup>-1</sup>): 2 967 (b, ν<sub>NH</sub>), 1 623(m, ν<sub>C=O</sub>), 1 591(m, ν<sub>C=O</sub>).

### 1.3 Preparation of the complexes and basic analytical data

#### 1.3.1 [Mn<sub>2</sub>L<sub>2</sub>(μ-CH<sub>3</sub>OH)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>] (1)

To a solution of H<sub>2</sub>L (0.213 g, 0.5 mmol) in 100 mL of methanol was added a solution of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.125 g, 0.5 mmol) in 20 mL of methanol at 80 °C with continuous stirring for 3 h. The resulting solution was allowed to cool in room temperature, and the brown precipitate was collected by suction filtration, washed with methanol and dried in air. The filtrate was left to stand for over one week under ambient conditions to produce brown crystals. Yield: 75%. Anal. Calcd. for C<sub>54</sub>H<sub>58</sub>N<sub>10</sub>O<sub>8</sub>Mn<sub>2</sub> (%): C, 59.78; H, 5.39; N, 12.91. Found: C, 59.55; H, 5.49; N, 13.25. FT-IR (cm<sup>-1</sup>): 1 604, 1 596(m, ν<sub>C=N-N=C</sub>), 1 346(m, ν<sub>C-O</sub>),

534(m,  $\nu_{\text{M-O}}$ ), 458(m,  $\nu_{\text{M-N}}$ ).

### 1.3.2 $\{[\text{MnL}(\mu\text{-CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}\cdot\text{CHCl}_3\}_n$ (2)

4,4'-bipyridine (0.047 g, 0.3 mmol) was added to a 100 mL methanol solution of  $\text{H}_2\text{L}$  (0.128 g, 0.3 mmol) at reflux temperature, followed by the addition of a 20 mL methanol solution of  $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  (0.075 g, 0.3 mmol) after fifteen minutes. The mixture was stirred for 4 h, the resulting solution was cooled to room temperature and then filtered off. The dark brown single crystals suitable for analyses were obtained by slowly evaporating the mixed solution of filtrate and  $\text{CHCl}_3$  at room temperature for a few days. Yield: 52%. Anal. Calcd. for  $\text{C}_{28}\text{H}_{30}\text{Cl}_3\text{N}_5\text{O}_4\text{Mn}$ (%): C, 50.81; H, 4.57; N, 10.58. Found: C, 51.33; H, 4.46; N, 10.34. FT-IR ( $\text{cm}^{-1}$ ): 1 607, 1 595(m,  $\nu_{\text{C=N=C}}$ ), 1 360 (m,  $\nu_{\text{C-O}}$ ), 537(m,  $\nu_{\text{M-O}}$ ), 473(m,  $\nu_{\text{M-N}}$ ).

### 1.4 X-ray crystallography

The single crystal X-ray diffraction data of complexes **1** and **2** were performed on a Rigaku R-axis Spider diffractometer with graphite monochromatic Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ) at 153 and 296 K.

The crystal structure was solved by direct method using SHELXS-97 program and all non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the SHELXTL-97 crystallographic software package<sup>[14]</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined using the riding model. Details of the data collection parameters and crystallographic information for complex **1** and **2** are summarized in Table 1. Selected bond lengths and angles with their estimated standard deviations are listed in Table 2. Summary for hydrogen bond data are listed in Table 3.

CCDC: 997907, **1**; 997908, **2**.

## 2 Results and discussion

### 2.1 Synthesis

The ligand *N*-(1-phenyl-3-benzyl-4-propylene-5-pyrazolone)-isonicotinic hydrazide ( $\text{H}_2\text{L}$ ), possessing an adequate number of coordination sites, was designed to fabricate manganese(II) complex, as shown in

Table 1 Crystallographic data and structure refinements for **1** and **2**

Compound	<b>1</b>	<b>2</b>
<i>T</i> / K	153(2)	296(2)
Formula	$\text{C}_{54}\text{H}_{58}\text{N}_{10}\text{O}_8\text{Mn}_2$	$\text{C}_{28}\text{H}_{30}\text{Cl}_3\text{N}_5\text{O}_4\text{Mn}$
Formula weight	1 084.98	661.86
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
<i>a</i> / nm	1.014 13(3)	1.500 59(3)
<i>b</i> / nm	1.088 88(4)	1.287 68(2)
<i>c</i> / nm	1.349 79(4)	1.663 65(3)
$\alpha$ / (°)	78.919 0(1)	
$\beta$ / (°)	70.9450(1)	111.541 0(1)
$\gamma$ / (°)	67.858 0(1)	
<i>V</i> / nm <sup>3</sup>	1.300 88(7)	2.990 11(9)
<i>Z</i>	1	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.385	1.470
$\mu$ / mm <sup>-1</sup>	0.550	0.752
Reflections collected	12 829	24 656
Unique reflections ( <i>R<sub>int</sub></i> )	5 902 (0.032 9)	5 850 (0.027 0)
Observed reflections	4 272	4 951
GOF on $F^2$	1.136	1.069
Final <i>R</i> indices [ $I>2\sigma(I)$ ]	$R_1=0.042\ 9$ , $wR_2=0.121\ 4$	$R_1=0.050\ 9$ , $wR_2=0.140\ 4$
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub> / (e·nm <sup>-3</sup> )	−891, 731	−942, 1 435

**Table 2** Selected bond lengths (nm) and angles ( $^{\circ}$ ) for **1** and **2**

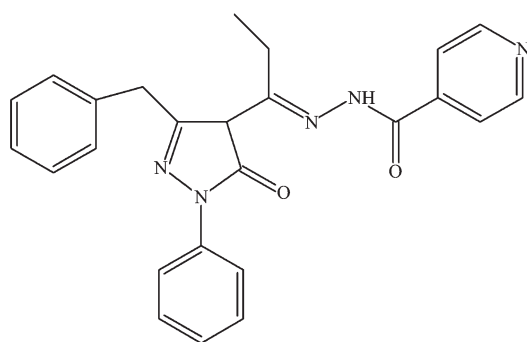
<b>1</b>					
Mn-O3	0.187 6(2)	Mn-O1	0.192 6(2)	Mn-O2	0.193 5(2)
Mn-N3	0.200 2(2)	Mn-O3A	0.218 3(2)	Mn-O4	0.224 5(2)
Mn-MnA	0.312 1(8)	O1-C7	0.129 5(3)	O2-C20	0.130 4(3)
C17-N3	0.130 2(2)	C20-N4	0.130 5(3)		
O1-Mn-O2	170.95(7)	O3-Mn-N3	171.59(9)	O3-Mn-O1	94.52(8)
O3-Mn-O2	93.60(8)	O1-Mn-N3	92.04(8)	O2-Mn-N3	80.26(8)
O3-Mn-O3A	79.75(8)	O1-Mn-O3A	95.08(8)	O2-Mn-O3A	90.28(8)
N3-Mn-O3A	94.44(8)	O3-Mn-O4	93.38(8)	O1-Mn-O4	88.90(8)
O2-Mn-O4	86.65(8)	N3-Mn-O4	92.01(8)	O3A-Mn-O4	172.29(7)
Mn-O3-MnA	100.25(8)				
<b>2</b>					
Mn1-O1	0.189 9(2)	Mn1-O2	0.191 2(2)	Mn1-O3	0.189 8(2)
Mn1-N3	0.199 1(2)	Mn1-O3A	0.228 4(2)	Mn1-N5B	0.232 6(2)
Mn1-Mn1A	0.314 5(8)	O1-C7	0.129 1(3)	O2-C20	0.130 0(3)
C17-N3	0.131 2(3)	C20-N4	0.130 3(3)		
O3-Mn1-O1	93.54(8)	O3-Mn1-O2	92.41(8)	O1-Mn1-O2	174.04(8)
O3-Mn1-N3	171.17(9)	O1-Mn1-N3	93.47(9)	O2-Mn1-N3	80.64(9)
O3-Mn1-O3A	82.87(8)	O3A-Mn1-N5B	177.63(8)	O1-Mn1-O3A	90.68(8)
O2-Mn1-O3A	90.41(8)	N3-Mn1-O3A	91.67(8)	O3-Mn1-N5B	95.32(8)
O1-Mn1-N5B	90.99(9)	O2-Mn1-N5B	88.10(8)	N3-Mn1-N5B	89.93(9)

Symmetry mode: For **1**, A:  $1-x$ ,  $2-y$ ,  $1-z$ ; For **2**, A:  $1-x$ ,  $2-y$ ,  $1-z$ ; B:  $0.5+x$ ,  $1.5-y$ ,  $-0.5+z$ .

**Table 3** Lengths (nm) and angles ( $^{\circ}$ ) of hydrogen bonds for **1** and **2**

	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle \text{D-H}\cdots\text{A}$
<b>1</b>				
O4-H40 $\cdots$ N5C	0.082 1	0.188	0.269 3(5)	173.00
<b>2</b>				
C27-H27 $\cdots$ N2M	0.098 0	0.253	0.341 6(5)	150.00
C14-H14A $\cdots$ Cl2P	0.093 0	0.283	0.349 3(7)	130.00

Symmetry transformations used to generate equivalent atoms: For **1**, C:  $2-x$ ,  $1-y$ ,  $1-z$ ; For **2**, M:  $3/2-x$ ,  $1/2+y$ ,  $3/2-z$ ; P:  $-0.5+x$ ,  $3.5-y$ ,  $0.5+z$ .



Scheme 1

Scheme 1. The reactions of manganese(II) acetate with  $\text{H}_2\text{L}$  in the different pH value of the reaction system produced  $[\text{Mn}_2\text{L}_2(\mu\text{-CH}_3\text{OH})_2(\text{CH}_3\text{OH})_2]$  (**1**) and  $[\{\text{MnL}(\mu\text{-CH}_3\text{OH})\}\cdot\text{CH}_3\text{OH}\cdot\text{CHCl}_3]_n$  (**2**) in good yield. 4,4'-Bipyridine was used as a weak organic base to modulate the pH value of the reaction system.

## 2.2 IR and UV-Vis spectra

IR spectroscopy usually provides valuable information on the coordination modes of the ligand and metal ions. The IR spectrum of the ligand shows

strong peaks at 2 967, 1 623 and 1 591  $\text{cm}^{-1}$ , which are assigned to  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})$  of the lateral chain and  $\nu(\text{C=O})$  of the pyrazolone-ring, respectively<sup>[15-17]</sup>. These results suggest that the free ligand in the solid state is in di-keto form. Compared with the spectrum of the free ligand, the most notable changes in the spectra of **1** and **2** are the disappearance of  $\nu(\text{NH})$  and  $\nu(\text{C=O})$  of the pyrazolone-ring and the lateral hydrazide chain. Meanwhile, new bands are observed between 1 607~1 595  $\text{cm}^{-1}$  and 1 346~1 360  $\text{cm}^{-1}$ , which are assigned to  $\nu(\text{-C=N-N=C-})$  of hydrazone and  $\nu(\text{C-O}^-)$ , respectively. Weak bands in the region of 534~537  $\text{cm}^{-1}$  and 458~473  $\text{cm}^{-1}$  are also observed, which are assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  stretching vibrations. These results indicate that the ligand undergoes isomerization from di-keto form to the enol form during the coordination, and then lose two protons to coordinate with Mn(II) atoms as double negative charged units. The results are coincident with the crystal structural analyses below.

The UV-Vis absorption spectra of the ligand and manganese(II) complexes were recorded in solid state and displayed in Fig.1. The electronic absorption spectrum of the ligand gives bands at 219, 329 and 413 nm correspond to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The spectra of manganese(II) complexes **1** and **2** do not exhibit significant differences between each other and the broad bands at around 320 and 450 nm might be due to intra ligand charge transfer type and  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition respectively, in an octahedral structure<sup>[18]</sup>.

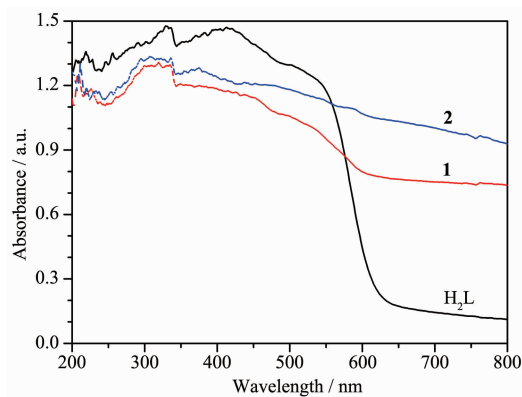
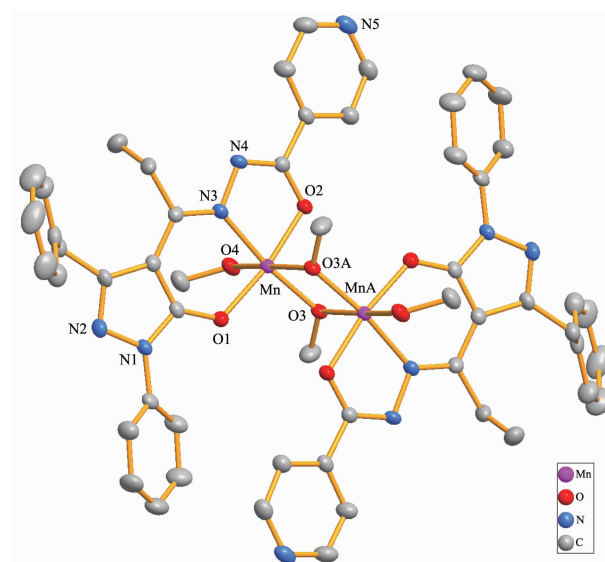


Fig.1 UV-Vis absorption spectra of the ligand, **1** and **2** in solid state

## 2.3 Crystal structural description

### 2.3.1 Crystal structure of **1**

The crystal structure of **1** is shown in Fig.2 with atom numbering scheme. The asymmetric unit contains two Mn(II) centers, two ligand anions  $\text{L}^{2-}$ , two coordinated methanol molecules and two  $\mu_2$ -bridged methanol molecules. The ligand anions act as negative bivalent tridentate chelating units and bond with the Mn(II) atoms. The two Mn(II) atoms (Mn and MnA) are bridged by two  $\mu_2$ -O atoms of the methanol molecules and form a dinuclear unit. Each Mn(II) is hexa-coordinated by O1, N3 and O2 atoms from one ligand anion  $\text{L}^{2-}$ , one O4 atom from methanol molecule, and two O atoms (O3 and O3A) from two bridging methanol molecules to form an octahedron geometry with N1O5 donor sets. The O1, N3, O2 and O3 atoms consist of the equatorial plane with the least square plane deviation of 0.008 32 nm, and the Mn(II) ion strays from the equatorial plane 0.000 97 nm, which indicates that the Mn(II) atom nearly lies in the equatorial plane. The bond distances of Mn-O1, Mn-N3, Mn-O2 and Mn-O3 in the equatorial plane are 0.192 6(2), 0.200 2(2), 0.193 5(2) and 0.187 6(2) nm, respectively. The axial positions are occupied by O3A and O4 atoms with the bond distances of 0.218 3(2)

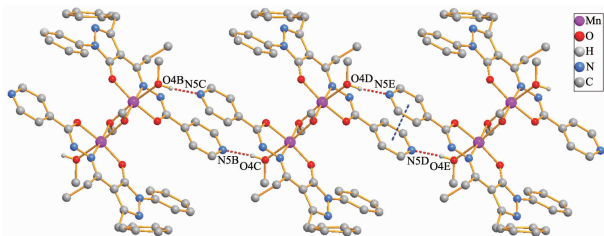


Hydrogen atoms were omitted for clarity; Symmetry transformations used to generate equivalent atoms: A: 1-x, 2-y, 1-z

Fig.2 Crystal structure of **1** with 50% probability displacement ellipsoids

and 0.224 5(2) nm. It is obvious that the axial bond distances are longer than the bond distances of the equatorial plane. The bond angles of O1-Mn-O2, O3-Mn-N3 and O3A-Mn-O4 are  $170.95(7)^\circ$ ,  $171.59(9)^\circ$  and  $172.29(7)^\circ$ , respectively, which are deviated from the theoretical value of  $180^\circ$ . All these observations implied that the geometry around the Mn(II) atom in **1** should be an elongated distorted octahedron. In the dinuclear unit, two Mn(II) atoms are bridged by two  $\mu_2$ -O atoms (O3 and O3A) from methanol molecules to define a planar centrosymmetric parallelogram, in which the side lengths are 0.187 6(2) and 0.218 3(2) nm. The Mn $\cdots$ Mn intermetallic distance is 0.312 1(8) nm. The bond angles of Mn-O3-MnA and O3A-Mn-O3 are  $100.25(8)^\circ$  and  $79.75(8)^\circ$ . On the other hand, the ligand functions as tridentate chelating agent coordinated to the Mn(II) atom with its ONO donor atoms in meridional fashion.

Furthermore, the dinuclear units are further linked into 1D chain via O-H $\cdots$ N intermolecular hydrogen bond between the O4 atom of the coordinated methanol molecule and N5 atom from neighboring ligand (O4-H40 $\cdots$ N5C, 0.269 3 (5) nm,  $173.00^\circ$ , Symmetry mode: C: 2-x, 1-y, 1-z), as shown in Fig.3. In addition, there are weak face to face  $\pi$ - $\pi$  interactions between the parallel pyridine rings of the ligands with a centroid-to-centroid distance of 0.373 8 nm.



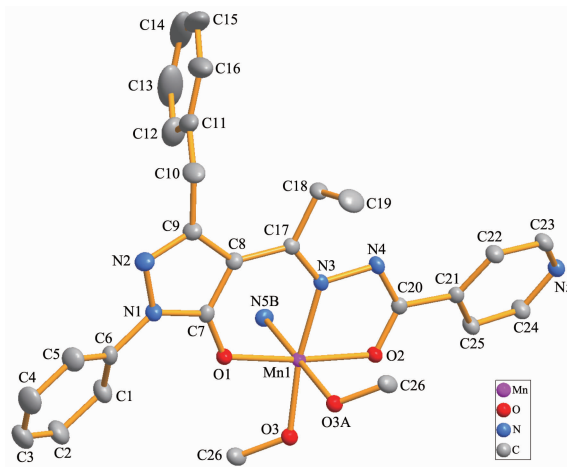
Symmetry transformations used to generate equivalent atoms: B: 2-x, -y, 1-z; C: x, -1+y, z; D: 1-x, 1-y, 1-z; E: -1+x, y, z

Fig.3 1D chain of **1**

### 2.3.2 Crystal structure of **2**

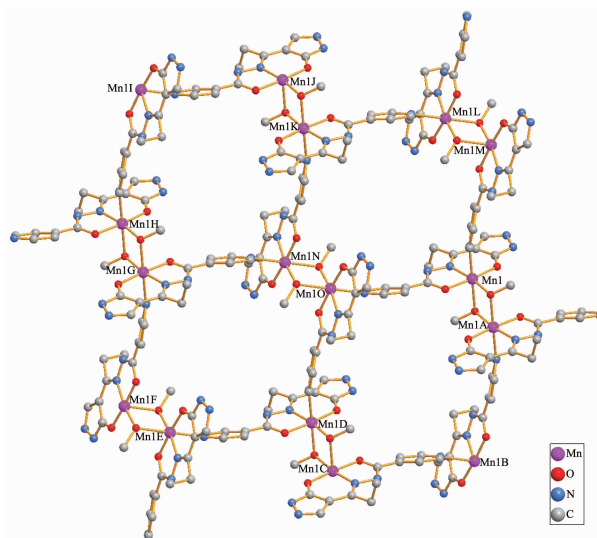
The crystal structure of **2** is shown in Fig.4 with atom numbering scheme. The asymmetric unit contains one crystallographically independent Mn(II) center, one ligand anion  $L^{2-}$  and one  $\mu_2$ -bridged methanol molecule. Similar with **1**, the two Mn(II) atoms (Mn1

and Mn1A) are bridged by two  $\mu_2$ -O atoms of the methanol molecules and form a dinuclear unit. However, the most interesting thing in **2** is that the ligand  $H_2L$  functions as a negative bivalent tetradentate chelating-bridging unit. The pyridyl groups of the ligands take part in the coordination and bridge the neighboring dinuclear units, which give rise to a 2D network as indicated in Fig.5. Each Mn(II) is hexa-



Hydrogen atoms were omitted for clarity; Thermal ellipsoids are at the 50% probability level; Symmetry transformations used to generate equivalent atoms: A: 1-x, 2-y, 1-z

Fig.4 Crystal structure of **2** with the coordination environment around the Mn(II) center



Symmetry transformations used to generate equivalent atoms: A: 1-x, 2-y, 1-z; B: 0.5+x, 1.5-y, -0.5+z; C: 1-x, 1-y, 1-z; D: x, -1+y, z; E: 1.5-x, -1.5+y, 1.5-z; F: 0.5+x, 0.5-y, 0.5+z; G: 2-x, 1-y, 2-z; H: 1+x, -1+y, 1+z; I: 2.5-x, -0.5+y, 2.5-z; J: 1+x, y, 1+z; K: 2-x, 2-y, 2-z; L: 0.5+x, 2.5-y, 0.5+z; M: 1.5-x, 0.5+y, 1.5-z; N: 0.5-x, 1.5-y, 0.5+z; O: 1.5-x, -0.5+y, 1.5-z

Fig.5 2D network of **2**



coordinated by O1, N3 and O2 atoms from one ligand anion  $L^{2-}$ , one N5B atom from another ligand anion, and two O atoms (O3 and O3A) from two bridging methanol molecules to form an octahedron geometry with N2O4 donor set. The O1, O2, N3, O3 atoms consist of the equatorial plane and the axial positions are occupied by O3A and N5B atoms. The Mn-O/N bond distances in equatorial plane are in the range of 0.189 8(2) to 0.199 1(2) nm, which are shorter than the axial bond lengths (Mn-O3A: 0.228 4(2) nm, Mn-N5B: 0.232 4(2) nm). Therefore, the local coordination geometry around the Mn(II) center in **2** can be described as highly distorted octahedron.

In comparison, the structure of **2** is quite different from **1**. The coordination mode of the ligand plays a vital role in the formation of multidimensional structure. In **1**, the ligand functions as a tridentate chelating unit to bond with one Mn(II) atom. While in **2**, it is noteworthy to note that the pyridine N atoms of the ligands take part in the coordination, and the ligand acts as a tetradentate chelating-bridging unit coordinated with two Mn(II) atoms to form a 2D network. The results indicated that the pH value of the solution has a certain effect on coordination mode of the ligand and structure of the resulting complex. Moreover, in both complexes the O1-C7 and O2-C20 distances are consistent with a single bond while the C17-N3 and C20-N4 are consistent with a double bond, which confirm that the ligand is in the deprotonated tautomeric enolic form to bond with Mn atom.

## 2.4 Thermal analyses

To estimate the stability of the complexes, thermal gravimetric measurements for **1** and **2** were carried out. The TG curves of complex **1** and **2** are shown in Fig.6. For **1**, no weight loss is observed from room temperature to 200 °C. After that temperature, **1** begins to decompose following a process of continuous weight loss of the coordinated methanol molecule and ligand anion. The observed weight loss is 84.0%, which is well consistent with the theoretical value of 83.9%. The decomposition completes at 430 °C and the end product, estimated as  $MnO_2$ , has the observed mass of 16.2% as against the calculated value of

16.1%. The TG curve of **2** shows a weight loss of 6.0% from 110 to 185 °C, corresponding to the removal of one lattice MeOH molecule of each formula unit (Calcd.: 4.8%). Then the decompositions of lattice chloroform, two coordinated methanol molecules and the ligand were followed. Weight constancy is attained at around 430 °C. The end product, estimated as  $MnO_2$ , has an observed mass of 14.8% compared with the calculated value of 13.1%. The thermal gravimetric analyses show that **1** is more stable than **2**.

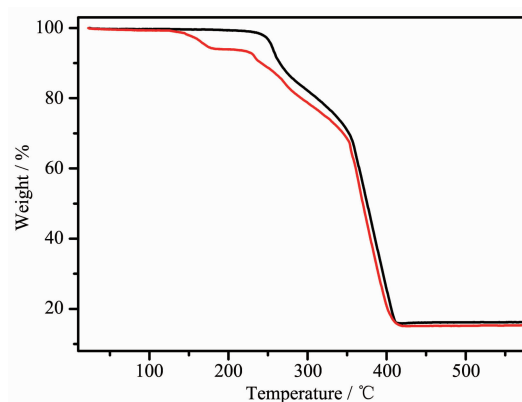


Fig.6 TG curves of **1** and **2**

## 3 Conclusions

In this work, two Mn(II) complexes based on the 4-acyl-pyrazolone derivative have been successfully synthesized. The results show that the pH value of the reaction system has significant effect on the coordination mode of the ligand, which result in a dinuclear or a 2D network of the final complexes. This study promotes to understand how the resulting molecular structure and coordination networks can be manipulated by the coordination mode of the 4-acyl-pyrazolone ligand.

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