

两个含 3,3'-硫代二丙酸配体的锰和铜配合物的合成、晶体结构与性质

刘继伟^{*1} 关淑霞¹ 谷长生²

(¹ 东北石油大学化学化工学院, 黑龙江省石油与天然气重点实验室, 大庆 163318)

(² 广东海洋大学化学与环境学院应用化学系, 湛江 524088)

摘要: 使用 3,3'-硫代二丙酸、4,4'-联吡啶和硝酸锰在水热条件下反应合成了 1 个锰配合物, 即 $[\text{Mn}(\text{DPA})(4,4'\text{-bipy})\cdot\text{H}_2\text{O}]_n$ (**1**) (DPA=3,3'-硫代二丙酸, 4,4'-bipy=4,4'-联吡啶); 然后又利用 3,3'-硫代二丙酸、1,3-双(4-吡啶基)丙烷和硝酸铜在水热条件下反应合成了 1 个铜配合物, 即 $[\text{Cu}(\text{DPA})(\text{bpp})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]_n$ (**2**) (DPA=3,3'-硫代二丙酸, bpp=1,3-双(4-吡啶基)丙烷)。并对它们分别进行了元素分析、红外光谱、热稳定性、X 射线粉末衍射和 X 射线单晶衍射的表征。结果表明: 配合物 **1** 和 **2** 分别由 3,3'-硫代二丙酸配体和不同氮杂环分子以及金属离子构筑, 形成了二维层状的结构。氢键和 π - π 作用进一步将二维结构拓展成三维超分子网络。

关键词: 3,3'-硫代二丙酸; 1,3-双(4-吡啶基)丙烷; 1,3-双(4-吡啶基)丙烷; 晶体结构

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Syntheses, Crystal Structures and Properties of Mn(II) and Cu(II) Complexes with 3,3'-Thiodipropionic Acid Ligand

LIU Ji-Wei^{*1} GUAN Shu-Xia¹ GU Chang-Sheng²

(¹ College of Chemistry and Chemical Technology, Northeast Petroleum University, Heilongjiang Provincial Key Laboratory of Oil and Chemical Technology, Daqing, Heilongjiang 163318, China)

(² Department of Applied Chemistry, Guangdong Ocean University, Zhanjiang, Guangdong 524088, China)

Abstract: A Mn(II) coordination polymer, $[\text{Mn}(\text{DPA})(4,4'\text{-bipy})\cdot\text{H}_2\text{O}]_n$ (**1**) was prepared with 3,3'-thiodipropionic acid (DPA), 4,4'-bipyridine (4,4'-bipy) and $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ by hydrothermal method, and a Cu(II) coordination polymer, $[\text{Cu}(\text{DPA})(\text{bpp})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]_n$ (**2**) was hydrothermally synthesized by using 3,3'-thiodipropionic acid (DPA), 1,3-bis(4-pyridyl)propane (bpp) and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$. The coordination polymers were characterized by elemental analysis, thermal analysis, IR, XRD and X-ray single crystal diffraction. Complexes **1** and **2** have two-dimensional layer structures. Furthermore, there are hydrogen bonds and π - π stacking interactions contributing three-dimensional supramolecular structures of **1** and **2**, respectively. CCDC: 1841409, **1**; 1545628, **2**.

Keywords: 3,3'-thiodipropionic acid; 1,3-bis(4-pyridyl)propane; 4,4'-bipyridine; crystal structure

0 Introduction

The design of coordination polymers were well developed in recent years^[1-5]. The topologies and

functionalities of such coordination polymers depend on the utilization of appropriate ligands as well as metal salts. The multiple coordination sites of the ligand incline towards forming higher dimensions^[6-8].

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*通信联系人. E-mail: liujiwei0706@163.com

The multifunctional thiodicarboxylic acid and its derivatives, which may link metal centers through both carboxylate groups and the S atom, are good ligands for the construction of different extended architecture structures^[9-11]. The carboxylate group can coordinate in multiple ways, either as a monodentate ligand, a bidentate chelating ligand or as a bridging ligand with different coordination numbers to various metal cations, resulting in the assembly of different coordination polymers^[12-13]. Now, based on the use of thiodicarboxylate as a ligand, we have chosen 3,3'-thiodipropionic acid (DPA) to prepare the new coordination polymers. Additionally, N-donor ligands, such as 4,4'-bipyridine (4,4'-bipy) and 1,3-bis(4-pyridyl) propane (bpp), have also been proved to exhibit remarkable properties for their excellent coordinating ability in the design of coordination polymers^[14]. In this context, we present the syntheses, crystal structures and the properties of two coordination polymers, namely $[\text{Mn}(\text{DPA})(4,4'\text{-bipy})\cdot\text{H}_2\text{O}]_n$ (**1**) and $[\text{Cu}(\text{DPA})(\text{bpp})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]_n$ (**2**), which incorporates 4,4'-bipy or bpp ligands.

1 Experimental

1.1 Reagents and instruments

All the reagents were of analytical reagent grade and used without further purification. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. The FT-IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer using KBr pellet at a resolution of 0.5 cm^{-1} ($400\sim 4\,000\text{ cm}^{-1}$). Thermogravimetry analyses were measured on a PERKIN ELMER TG/DTA 6300 thermogravimetric analyzer under a flowing N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ starting at ambient temperature and heating up to $800\text{ }^\circ\text{C}$, using sample weight of 1~5 mg. Powder X-ray diffraction (XRD) patterns were measured at 293 K on a Bruker D8 diffractometer ($\text{Cu K}\alpha$, $\lambda=0.154\,059\text{ nm}$, $U=40\text{ kV}$, $I=10\text{ mA}$), scanning from 5° to 60° .

1.2 Syntheses of the complexes

1.2.1 Synthesis of $[\text{Mn}(\text{DPA})(4,4'\text{-bipy})\cdot\text{H}_2\text{O}]_n$ (**1**)

The complex was prepared by the addition of

4,4'-bipyridine (1.0 mmol), 3,3'-thiodipropionic acid (1.0mmol) and manganese nitrate tetrahydrate (1.0 mmol) to a mixing solution of water and methanol (1:1, V/V , 20 mL), and the pH value was adjusted to 7 with $0.1\text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution. The mixture was sealed in a 50 mL Teflon-lined stainless steel bomb and held at 393 K for 72 h. The bomb was cooled naturally to room temperature, and yellow crystals were obtained from the filtered solution after several days. Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_5\text{SMn}(\%)$: C 47.40, H 4.48, N 6.91; Found(%): C 47.39, H 4.49, N 6.92. IR (KBr, cm^{-1}): 3 424(s), 3 156(s), 1 606(s), 1 567 (s), 1 442(m), 1 401(s), 1 318(m), 1 215(m), 1 063(m), 994(m), 816(s), 630(m), 465(w).

1.2.2 Synthesis of $[\text{Cu}(\text{DPA})(\text{bpp})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]_n$ (**2**)

The synthesis method of complex **2** is same as that of complex **1**. Anal. Calcd. for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_6\text{SCu}(\%)$: C 48.19, H 5.54, N 5.92; Found(%): C 48.20, H 5.55, N 5.91. IR (KBr, cm^{-1}): 3 361(s), 2 915(m), 1 621(s), 1 586(s), 1 428(m), 1 374(m), 1 297(m), 1 077(m), 933(m), 699(m), 520(w).

1.3 X-ray crystallographic determination

The suitable single crystal of these complexes was employed for data collection on a Bruker P4 diffractometer with graphite monochromatized $\text{Mo K}\alpha$ ($\lambda=0.071\,073\text{ nm}$) radiation. All structures were solved by direct method and difference Fourier syntheses. All non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. The C-H atoms were located and included at their geometrically idealized positions, with $d_{\text{C-H}}=0.093\text{ nm}$ and were refined as riding, with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms of water molecules and N-H atoms were located in difference Fourier maps and refined in the riding model approximation, with the O-H, O-H, H \cdots H and N-H distance restrains of 0.085(1), 0.139(1) and 0.090(1) nm, respectively, and with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$. All calculations were carried out with SHELXL 97 program^[15]. The summary of the crystallographic data for the complexes are provided in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 1841409, **1**; 1545628, **2**.

Table 1 Crystal data and structure parameters for the complexes

Complex	1	2
Formula	C ₁₆ H ₁₈ N ₂ O ₅ SMn	C ₁₉ H ₂₆ N ₂ O ₆ SCu
Formula weight	405.32	474.02
Temperature / K	293(2)	293(2)
Size / mm	0.20×0.10×0.10	0.21×0.18×0.15
θ range for data collection / (°)	2.16~25.39	2.01~25.37
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> / nm	1.626 4(3)	1.040 8(2)
<i>b</i> / nm	1.163 5(2)	1.233 3(3)
<i>c</i> / nm	1.861 3(4)	1.747 0(4)
β / (°)	99.94(3)	102.99(3)
<i>V</i> / nm ³	3.469(1)	2.185(8)
<i>Z</i>	8	4
<i>D_c</i> / (g·cm ⁻³)	1.552	1.441
μ / mm ⁻¹	0.911	1.131
<i>F</i> (000)	1 672	988
Reflection collected	3 160	4 249
Unique reflection (<i>R_{int}</i>)	1 551 (0.000 0)	4 017 (0.067 2)
<i>R₁</i> , <i>wR₂</i> [<i>I</i> >2 σ (<i>I</i>)]	0.079 6, 0.148 7	0.071 3, 0.197 2
<i>R₁</i> , <i>wR₂</i> (all data)	0.158 1, 0.177 4	0.121 6, 0.277 7
Goodness-of-fit (on <i>F</i> ²)	1.002	1.060
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e·nm ⁻³)	753, -691	1 024, -1 063

Table 2 Selected bond lengths (nm) and angles (°) for the complexes

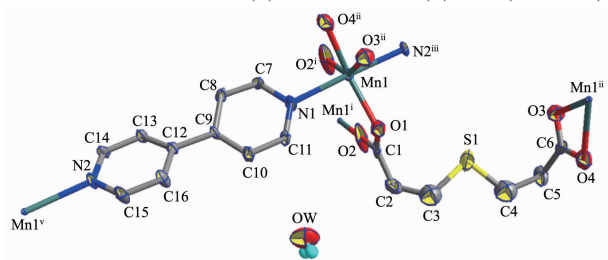
1					
Mn(1)-O(1)	0.216 9(5)	Mn(1)-O(2) ⁱ	0.207 8(6)	Mn(1)-O(3) ⁱⁱ	0.246 8(5)
Mn(1)-O(4) ⁱⁱ	0.221 5(6)	Mn(1)-N(1)	0.226 7(5)	Mn(1)-N(2) ⁱⁱⁱ	0.229 1(5)
O(1)-Mn(1)-O(3) ⁱⁱ	84.1(2)	O(1)-Mn(1)-O(4) ⁱⁱ	136.8(2)	O(1)-Mn(1)-N(1)	89.8(2)
O(1)-Mn(1)-N(2) ⁱⁱⁱ	89.4(2)	O(2) ⁱ -Mn(1)-O(1)	125.8(3)	O(2) ⁱ -Mn(1)-O(3) ⁱⁱ	150.0(3)
O(2) ⁱ -Mn(1)-O(4) ⁱⁱ	97.1(3)	O(2) ⁱ -Mn(1)-N(1)	88.9(2)	O(2) ⁱ -Mn(1)-N(2) ⁱⁱⁱ	88.0(2)
O(4) ⁱⁱ -Mn(1)-O(3) ⁱⁱ	53.6(2)	O(4) ⁱⁱ -Mn(1)-N(1)	85.0(2)	O(4) ⁱⁱ -Mn(1)-N(2) ⁱⁱⁱ	98.5(2)
N(1)-Mn(1)-N(2) ⁱⁱⁱ	175.6(2)	N(1)-Mn(1)-O(3) ⁱⁱ	94.0(2)		
2					
Cu(1)-O(1)	0.195 1(6)	Cu(1)-O(3) ⁱ	0.200 0(5)	Cu(1)-O(4) ⁱ	0.273 0(6)
Cu(1)-O1W	0.226 5(6)	Cu(1)-N(1)	0.200 6(6)	Cu(1)-(N2) ⁱⁱ	0.203 1(7)
O(1)-Cu(1)-O(3) ⁱ	159.4(2)	O(1)-Cu(1)-N(1)	95.9(2)	O(1)-Cu(1)-N(2) ⁱⁱ	86.7(3)
O(1)-Cu(1)-O1W	101.2(3)	O(3) ⁱ -Cu(1)-N(1)	86.3(2)	O(3) ⁱ -Cu(1)-N(2) ⁱⁱ	90.5(2)
O(3)-Cu(1)-O1W	99.2(2)	N(1)-Cu(1)-O1W	92.3(2)	N(1)-Cu(1)-N(2) ⁱⁱ	176.6(3)
N(2) ⁱⁱ -Cu(1)-O1W	89.3(3)	O(3) ⁱ -Cu(1)-O(4) ⁱ	52.8(2)		

Symmetry codes: ⁱ -*x*+1, *y*, -*z*+3/2; ⁱⁱ -*x*+1/2, *y*-1/2, -*z*+3/2; ⁱⁱⁱ *x*, *y*+1, *z* for **1**; ⁱ *x*-1, *y*, *z*; ⁱⁱ *x*+1, -*y*+1/2, *z*+1/2 for **2**.

2 Results and discussion

2.1 Crystal structure of $\{[\text{Mn}(\text{DPA})(4,4'\text{-bipy})]\cdot\text{H}_2\text{O}\}_n$ (1)

Crystal data, data collection and structure refinement details are summarized in Table 1. The molecular structure of complex **1** is depicted in Fig.1 and the selected bond distances and bond angles are given in Table 2. The asymmetric unit of **1** contains one Mn(II) ion, one 3,3'-thiodipropionate ligand, and one 4,4'-bipy molecule and one free water molecule. The carboxyl groups of 3,3'-thiodipropionate show two coordination modes: one carboxyl group is bound to two Mn(II) ions in a double-monodentate coordination fashion; whereas the other carboxyl group is coordinated to one Mn(II) ion in a bidentate chelating mode. Each Mn(II) ion lies on a distorted octahedral coordination configuration, defined by four O atoms from three different 3,3'-thiodipropionate ligands and two N atoms from two 4,4'-bipy molecules. Atoms O1, O2ⁱ, O3ⁱⁱ and O4ⁱⁱ comprise the equatorial plane, and N1 and N2ⁱⁱⁱ atoms occupy the apical sites (N(1)-Mn(1)-N(2)ⁱⁱⁱ 175.6(2)°). The Mn-O distances fall in the range of 0.207 8 (6)~0.246 8 (5) nm, while the Mn-N distances are 0.226 7(5) and 0.229 1(5) nm (Table 2).



Symmetry codes: ⁱ $-x+1, y, -z+3/2$; ⁱⁱ $-x+1/2, y-1/2, -z+3/2$; ⁱⁱⁱ $x, y+1, z$; ^v $x, y-1, z$

Fig.1 Molecular structure of **1** with ellipsoids drawn at 30% probability level

Adjacent Mn(II) ions are bridged by the 4,4'-bipy molecules in the bis-monodentate mode, with the Mn...Mn separation distance of 1.163 5 nm, resulting in a one-dimensional infinite chain structure. The chains are further connected by the O atoms of 3,3'-thiodipropionate ligands to give a two-dimensional layer structure, with the Mn...Mn separation distance of 0.387 0 nm (Fig.2). There exist π - π stacking interac-

tions between adjacent pyridine rings (Cg1...Cg2 0.361 0 nm; Cg1: C7, C8, C9, C10, C11, N1 (Symmetry codes: $1.5-x, 0.5+y, 1.5-z$); Cg2: C7, C8, C9, C10, C11, N1 (Symmetry codes: $0.5+x, 0.5+y, z$); the dihedral angle = 0.3°) and an intermolecular hydrogen bond (O1W...O4^{iv} 0.282(1) nm, Symmetry codes: ^{iv} $-x+1/2, -y+5/2, -z+2$).

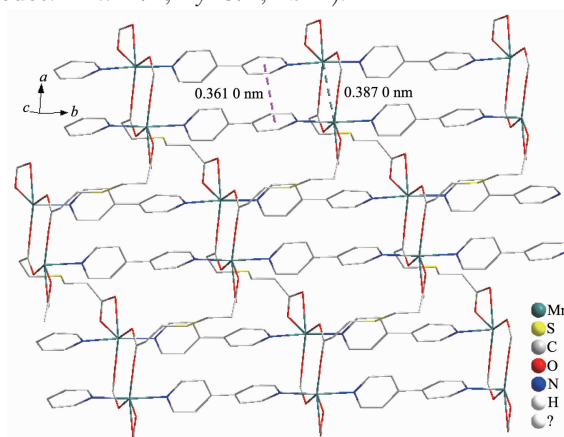


Fig.2 Two-dimensional structure of **1**

Furthermore, there exist other π - π stacking interactions between adjacent layers (C...Cg 0.325 6 nm), leading to the formation of a three-dimensional supramolecular network (Fig.3).

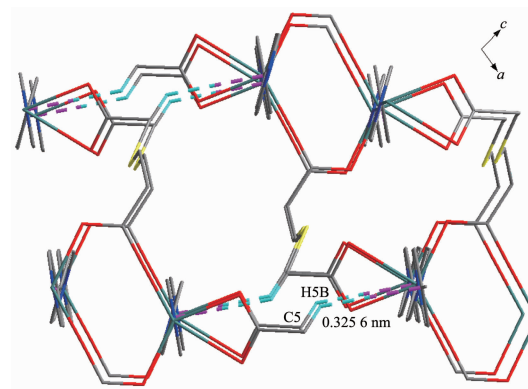
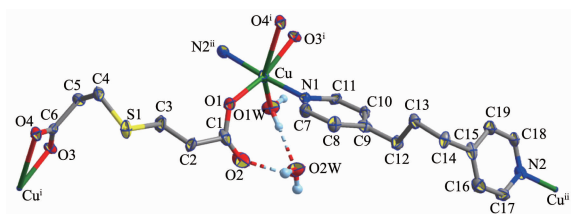


Fig.3 Three-dimensional structure of **1**

2.2 Crystal structure of $\{[\text{Cu}(\text{DPA})(\text{bpp})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (2)

As depicted in Fig.4, the Cu(II) ion exists in a distorted octahedral coordination configuration, defined by two N-atom donors from two monodentate 1,3-bis(4-pyridyl)propane co-ligands, three O-atom donors from two different 3,3'-thiodipropionate ligands, where one carboxylate group (O3ⁱ-C-O4ⁱ) coordinates in a bidentate mode and the other group (O1-C-O2)



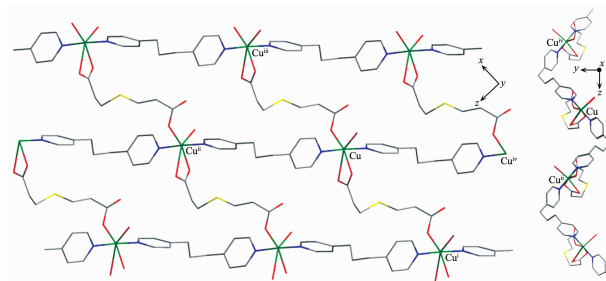
Symmetry codes: ⁱ $x-1, y, z$; ⁱⁱ $x+1, -y+1/2, z+1/2$

Fig.4 Molecular structure of **2** with the ellipsoids drawn at the 30% probability level

coordinates in a monodentate mode, as well as one coordination water molecule. Differing from **1**, the carboxylate O2 of **2** is uncoordinated to Cu(II) ion. Atoms O1, O3ⁱ, O4ⁱ and O1W comprise the equatorial plane, and atoms N1 and N2 occupy the axial positions (N(1)-Cu(1)-N(2) 176.6(3)°). The bond lengths of Cu-N are 0.200 6(6) and 0.203 1(7) nm, respectively, and the bond lengths of Cu-O are 0.195 1(6), 2.000(5), 0.226 5(6) and 0.273 0(6) nm, respectively (Table 2). It is noted that the Cu-O (4) distance is much longer than other Cu-O distances^[16-17]. Two kinds of intra-molecular hydrogen bonds are observed in the complex: O(1W)⋯O(2W) 0.276 4(1) nm and O(2W)⋯O(2) 0.265 2(1) nm, as shown in Table 3.

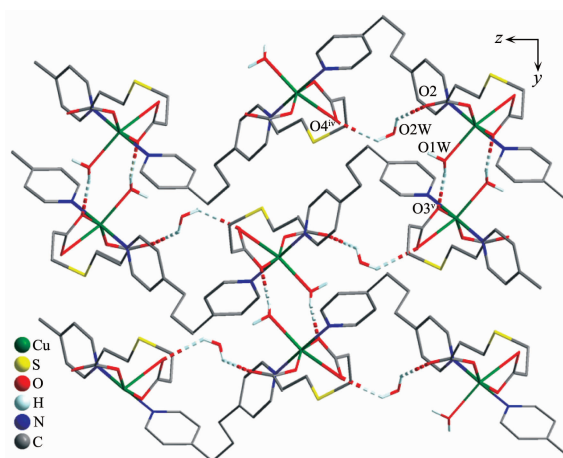
Adjacent Cu(II) ions are bridged by 1,3-bis(4-pyridyl)propane molecules, resulting in a one-dimensional infinite chain structure. In the chain, the adjacent Cu⋯Cu distance is 1.211 2 nm. The adjacent chains are further linked by the 3,3'-thiodipropionate ligands to give a two-dimensional layer structure, with the Cu⋯Cu separation distance of 1.040 8 nm (Fig.5). In addition, it is observed that there exist intermolecular hydrogen bonds: O-H⋯O (O(1W)⋯O(3)^v 0.273 9(8) nm and O(2W)⋯O(4)^{iv}

0.280 1(9) nm; Symmetry codes: ^{iv} $x-1, -y+1/2, z-1/2$; ^v $-x+2, -y, -z+1$), resulting in a three-dimensional supramolecular network structure (Fig.6).



Symmetry codes: ⁱⁱ $x+1, -y+1/2, z+1/2$; ⁱⁱⁱ $x+1, y, z$; ^{iv} $x-1, -y+1/2, z-1/2$

Fig.5 Two-dimensional layer structure of complex **2**



Symmetry code: ^{iv} $x-1, -y+1/2, z-1/2$; ^v $-x+2, -y, -z+1$

Fig.6 Three-dimensional structure of complex **2**

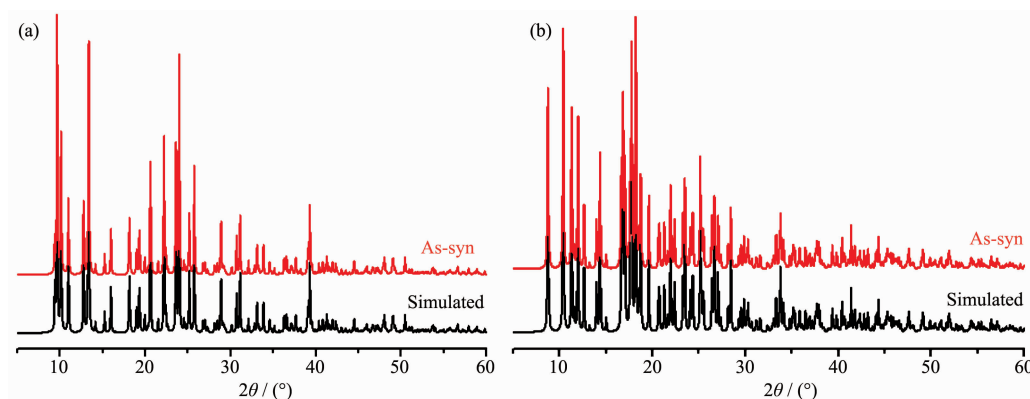
2.3 XRD and thermogravimetric analysis

Powder X-ray diffraction (XRD) patterns for solid samples of complexes **1** and **2** are measured at room temperature as illustrated in Fig.7. The patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that

Table 3 Hydrogen bond parameters for the complexes

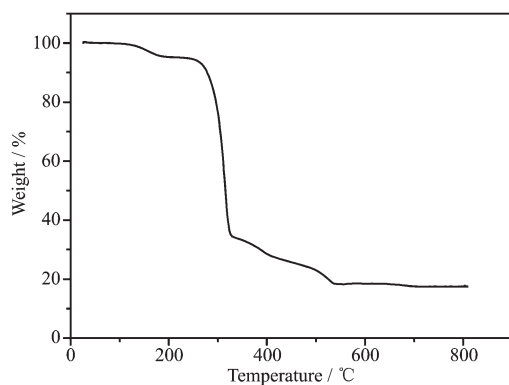
D-H⋯A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}⋯\text{A}) / \text{nm}$	$d(\text{D}⋯\text{A}) / \text{nm}$	$\angle \text{D-H}⋯\text{A} / (^\circ)$
Complex 1				
O(1W)-HWA⋯O(4) ^{iv}	0.085	0.237	0.281 9(1)	113.4
Complex 2				
O(1W)-H(1WA)⋯O(3) ^v	0.085(1)	0.193(4)	0.273 9(8)	159(1)
O(1W)-H(1WB)⋯O(2W)	0.085(1)	0.192(2)	0.276 4(1)	175(9)
O(2W)-H(2WA)⋯O(4) ^{iv}	0.085(1)	0.217(1)	0.280 1(9)	131(1)
O(2W)-H(2WB)⋯O(2)	0.085(1)	0.196(1)	0.265 2(1)	138(1)

Symmetry codes: ^{iv} $-x+1/2, -y+5/2, -z+2$ for **1**; ^{iv} $x-1, -y+1/2, z-1/2$, ^v $-x+2, -y, -z+1$ for **2**.

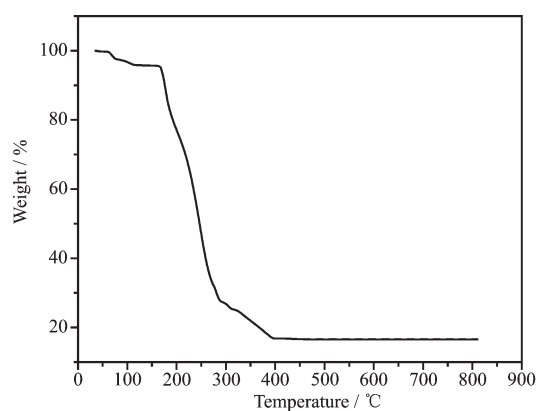
Fig.7 PXRD patterns for complexes **1** (a) and **2** (b)

the single-crystal structures are really representative of the bulk of the corresponding samples.

From the thermal analysis curves of complex **1** (Fig.8), we can see that there are three weight-loss steps. Above 26 °C up to 186 °C, a small amount of molecular fragment is found (Obsd. 4.50%, Calcd. 4.44%), which is attributed to the dehydration of the uncoordinated water molecules. A rapid weight loss can be detected from 186 to 537 °C, which is attributed to the dehydration of 4,4'-bipy molecules and carboxyl groups. After gradually burning decomposition, the final residue may be MnO (Obsd. 17.68%, Calcd. 17.50%).

Fig.8 TG curve of complex **1**

The result of TG analysis of complex **2** is showed in Fig.9. The first weight loss can be detected from 33 to 168 °C (Obsd. 4.40%, Calcd. 7.60%), which is attributed to the dehydration of the uncoordinated and coordinated water molecules. The weight loss occurring between 168 and 432 °C corresponds to decomposition of 1,3-bis(4-pyridyl)propane molecules and carboxyl groups. The final residual is CuO (Obsd.

Fig.9 TG curve of complex **2**

16.54, Calcd. 16.78%).

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