

由六亚甲基四胺和柔性芳香羧酸构筑的两个一维 配位聚合物的合成及晶体结构

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摘要: 利用六亚甲基四胺分别与苯氧乙酸、 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 及 2,4-二氯苯氧乙酸、 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 反应, 得到了 2 个新的一维配位聚合物, $\{[\text{Cu}_2(\text{pa})_4](\mu_2\text{-hmt})\}_n$ (**1**) 和 $\{[\text{Zn}_3(\text{dcpa})_4(\text{OH})_2](\mu_2\text{-dcpa})_2](\mu_2\text{-hmt})\} \cdot 5\text{H}_2\text{O}\}_n$ (**2**) (Hpa=苯氧乙酸, Hdcpa=2,4-二氯苯氧乙酸, hmt=六亚甲基四胺)。2 个配合物均用元素分析、红外光谱、X 射线单晶衍射及差热分析进行了表征。晶体结构分析表明, 在配合物 **1** 中, 4 个苯氧乙酸根桥联 2 个 Cu^{2+} 形成 $[\text{Cu}_2(\text{COO})_4]$ 双核结构, 相邻的 $[\text{Cu}_2(\text{COO})_4]$ 双核单元由六亚甲基四胺桥联成一维的“zigzag”链; 在配合物 **2** 中, 6 个 2,4-二氯苯氧乙酸根和 2 个 OH^- 桥联 6 个 Zn^{2+} 形成六核 $\{[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})_2](\mu_2\text{-dcpa})_2\}$ 结构单元, 然后相邻的六核单元由 2 个六亚甲基四胺桥联成一维双链结构。

关键词: 六亚甲基四胺; 苯氧乙酸; 2,4-二氯苯氧乙酸; Cu^{2+} ; Zn^{2+} ; 晶体结构

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Syntheses, Crystal Structures of Two 1D Coordination Polymers Based on Hexamethylenetetramine and Flexible Aromatic Acids

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Abstract: Two 1D coordination polymers of $\{[\text{Cu}_2(\text{pa})_4](\mu_2\text{-hmt})\}_n$ (**1**) and $\{[\text{Zn}_3(\text{dcpa})_4(\text{OH})_2](\mu_2\text{-dcpa})_2](\mu_2\text{-hmt})\} \cdot 5\text{H}_2\text{O}\}_n$ (**2**) (Hpa=phenoxyacetic acid, Hdcpa=2,4-dichlorophenoxy acetic acid, hmt=hexamethylenetetramine) were obtained by the reactions of hexamethylenetetramine with phenoxy acetic acid and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, or 2,4-dichlorophenoxy acetic acid and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively. The complexes were characterized by elemental analysis, IR, single X-ray diffraction and thermogravimetric analyses. The crystal structural analysis revealed that, in complex **1**, two Cu^{2+} ions are bridged by four pa ligands to form a $[\text{Cu}_2(\text{COO})_4]$ unit, and the neighboring $[\text{Cu}_2(\text{COO})_4]$ units are further connected by hmt ligands to form a 1D zigzag chain; while in complex **2**, six Zn^{2+} ions are bridged by six dcpa and two OH^- ligands to form hexanuclear $\{[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})_2](\mu_2\text{-dcpa})_2\}$ subunits which are further connected by hmt ligands to form a 1D double chain. CCDC: 1469683, **1**; 1469684, **2**.

Keywords: hexamethylenetetramine; phenoxy acetic acid; 2,4-dichlorophenoxy acetic acid; Cu^{2+} ; Zn^{2+} ; crystal structure

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0 Introduction

The rational design and construction of coordination polymers with multidimensional structures are of much interest due to their intriguing topological structures as well as their potential applications such as catalysis, separation, gas storage, luminescence, and magnetism^[1-10]. The common approach for construction of coordination polymers is self-assembly of organic molecules and metal ions. Anionic aromatic acids and neutral N-containing heterocyclic molecules are usually used as organic ligands for extending the structures. For aromatic acids, comparing to the rigid aromatic acids, flexible aromatic ligands have not been studied much. Phenoxyacetic acid (Hpa) and its derivatives have been reported not only as fungicides, plant growth regulators and agricultural herbicides, but also as ligands to build complexes^[11]. For the N-heterocyclic ligands, 4,4'-bipyridine and 2,2'-bipyridine derivatives have been widely used, while heterocyclic hexamethylenetetramine (hmt), which is commercial available, inexpensive, and high soluble, has been explored to a less extent^[12]. However, hmt is a unique ligand, because it has various coordination modes that span from terminal monodentate to μ_2 -, μ_3 -, or μ_4 -bridging mode; moreover, it can act as hydrogen bonding acceptor to generate supramolecular networks^[13-14]. There are some transition metal complexes containing phenoxy or 2,4-dichlorophenoxy acetic acid with bipyridine ligands have been reported, such as, $[\text{Co}(\text{pa})_2(\text{H}_2\text{O})_2]_n$ ^[15], $[\text{Fe}_3\text{O}(\text{pa})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ^[16], $[\text{Cd}_2(2,4\text{-dcpa})_4(2,2'\text{-bipy})_2]$ ^[11], $[\text{Zn}_3(2,4\text{-dcpa})_6(2,2'\text{-bipy})_2]$ ^[17], $[\text{VO}(\text{Tp})(\text{Hpz})(2,4\text{-dcpa})]$ (Tp=hydrotris(pyrazolyl)borate, Hpz=pyrazole)^[18], $[\text{Cu}_3(\text{PhPyCNO})_3(\mu_3\text{-OH})(2,4\text{-dcpa})_2]$ (PhPyCNO=phenyl 2-pyridyl ketoxime)^[19], $[\text{Cd}_2(2,4\text{-dcpa})_4(\text{phen})_2]$ ^[20], however, only one compound comprising phenoxyl and hexamethylenetetramine, $[\text{Ag}_2(2,4\text{-dcpa})_4(\text{hmt})_2]$ ^[21], was found in the current version of the Cambridge Structural Database (CSD)^[22]. In this paper, we report the syntheses and crystal structures of two new complexes containing hmt and phenoxyl/2,4-dichlorophenoxy ligands, $\{[\text{Cu}_2(\text{pa})_4(\mu_2\text{-hmt})]_n\}$ (**1**) and $\{[\text{Zn}_3(\text{dcpa})_4(\text{OH})_2(\mu_2\text{-dcpa})_2](\mu_2\text{-hmt})\} \cdot 5\text{H}_2\text{O}\}_n$ (**2**).

$\{[\text{Zn}_3(\text{dcpa})_4(\text{OH})_2(\mu_2\text{-hmt})]_n\}$ (**2**).

1 Experimental

1.1 Materials and measurements

All reagents and solvents were used as purchased without further purification. IR spectra were recorded on a Perkin-Elmer spectrum one spectrometer with KBr pellet in the region of 4 000~450 cm^{-1} . Elemental analyses of C, H and N were performed on Vario EL III apparatus. Thermogravimetric analysis (TG) data were collected on a Perkin-Elmer Diamond TG/DTA instrument under nitrogen atmosphere with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$.

1.2 Syntheses of the complexes

Synthesis of complex 1. A $\text{H}_2\text{O}/\text{EtOH}$ solution (8 mL, 1:1, $V_{\text{EtOH}}/V_{\text{H}_2\text{O}}$) of phenoxy acetic acid (60 mg, 0.4 mmol) and NaHCO_3 (32 mg, 0.4 mmol) was added into an ethanolic solution (4 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (96 mg, 0.4 mmol). To the resulting solution was added an aqueous solution (4 mL) of hexamethylenetetramine (30 mg, 0.2 mmol). The resulting mixture was stirred for 2 h at room temperature, and then filtered. Green plate crystals suitable for X-ray diffraction were obtained from the filtration (Yield 60 mg, 68%). Anal. Calcd. for $\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_{12}\text{Cu}_2$ (%): C, 52.35; H, 4.62; N, 6.43. Found(%): C, 52.48; H, 4.50; N, 6.40. IR (KBr, cm^{-1}): 3 064(w), 2 958(m), 2 927(m), 1 645(br), 1 600(s), 1 496(vs), 1 460(s), 1 444(s), 1 421(s), 1 336(s), 1 292(w), 1 261(s), 1 225(br), 1 174(s), 1 084(s), 1 064(sh), 1 026(s), 994(s), 930(m), 885(m), 835(w), 822(w), 808(w), 789(s), 756(s), 719(s), 690(s), 663(s), 623(w), 609(w), 511(w).

Synthesis of complex 2. A $\text{H}_2\text{O}/\text{MeOH}$ solution (8 mL, 1:1, $V_{\text{MeOH}}/V_{\text{H}_2\text{O}}$) of 2,4-dichlorophenoxy acetic acid (90 mg, 0.4 mmol) and NaHCO_3 (32 mg, 0.4 mmol) was added into a methanolic solution (4 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (120 mg, 0.40 mmol). To the resulting solution was added an aqueous solution (4 mL) of hexamethylenetetramine (30 mg, 0.2 mmol). The resulting mixture was stirred for 2 h at room temperature, and then filtered. Colorless plate crystals suitable for X-ray diffraction were obtained from the filtration (Yield 60 mg, 49%). Anal. Calcd. for $\text{C}_{92}\text{H}_{90}\text{Cl}_{20}\text{N}_8\text{O}_{39}\text{Zn}_6$ (%):

C, 36.43; H, 2.99; N, 3.69. Found (%): C, 36.65; H, 2.84; N, 3.72. IR (KBr, cm^{-1}): 3 579(w), 3 433(w), 3 099(w), 2 966(w), 2 933(w), 1 660(s), 1 645(sh), 1 481(s), 1 429(s), 1 342(m), 1 288(s), 1 265(sh), 1 250(s), 1 236(sh), 1 105(m), 1 077(m), 1 028(m), 991(m), 925(w), 870(w), 837(w), 800(m), 765(m), 717(m), 696(w), 683(w), 656(w), 648(w), 611(w), 557(w), 507(w).

1.3 Crystal structure determination

Crystallographic data of the two complexes were collected at room temperature on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using an φ - ω scan mode at 296(2) K. The crystal structures was solved by direct method, using the program SHELXS-97^[23], and refined on F^2 by full-matrix least-squares techniques using the SHELXTL-97^[24] crystallographic software package. All non-hydrogen atoms except the crystallization water molecules were refined anisotropically. All the hydrogen

atoms were placed in calculated positions and constrained to ride on their parent atoms except that the hydrogen atoms of hydroxyl group and water molecules in complex **2**. The hydrogen atoms of hydroxyl group and water molecules in complex **2** are located from difference maps and refined isotropically. Crystallographic data for both complexes are listed in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC: 1469683, **1**; 1469684, **2**.

2 Results and discussion

2.1 IR spectra

The IR spectra show features attributable to each component of the complexes. The weak bands in the range of 3 064~2 879 cm^{-1} in complex **1**, and 3 099~2 933 cm^{-1} in complex **2**, are attributed to the C-H stretching of hmt molecules, respectively. The band at 994 cm^{-1} in complex **1**, and 991 cm^{-1} in complex **2**,

Table 1 Crystallographic data for the complexes **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{38}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_{12}$	$\text{C}_{92}\text{H}_{30}\text{Cl}_2\text{O}_8\text{N}_8\text{Zn}_6$
Formula weight	871.82	3 032.94
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.191 5(2)	1.332 0(2)
b / nm	1.242 1(2)	1.479 3(3)
c / nm	1.455 5(1)	1.617 0(3)
$\alpha / (^\circ)$	95.279 0(10)	95.497(2)
$\beta / (^\circ)$	106.984 0(10)	90.889(2)
$\gamma / (^\circ)$	109.600 0(10)	112.135(2)
V / nm^3	1.897 1(2)	2.933 3(9)
Z	2	1
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.526	1.717
μ / mm^{-1}	1.190	1.747
$F(000)$	900	1 530
Crystal size / mm	0.20×0.15×0.10	0.20×0.15×0.10
θ range / $(^\circ)$	1.78~26.00	2.21~28.29
Reflections collected	14 646	27 344
Independent reflections (R_{int})	7 283 (0.016 5)	14 047 (0.036 3)
Parameters	505	758
GOF on F^2	1.171	1.023
R_1, wR_2 ($I > 2\sigma(I)$)	0.025 5, 0.075 5	0.051 5, 0.126 2
R_1, wR_2 (all data)	0.034 2, 0.091 8	0.095 5, 0.153 6

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

1					
Cu(1)-O(1)	0.197 7(2)	Cu(1)-O(2) ^a	0.198 4(2)	Cu(1)-O(4)	0.198 2(1)
Cu(1)-O(5) ^a	0.198 0(2)	Cu(1)-N(1)	0.217 1(2)	Cu(2)-O(7)	0.197 8(1)
Cu(2)-O(8) ^b	0.196 7(1)	Cu(2)-O(10)	0.197 9(2)	Cu(2)-O(11) ^b	0.197 7(2)
O(1)-Cu(1)-O(2) ^a	166.70(6)	O(1)-Cu(1)-O(4)	88.87(7)	O(1)-Cu(1)-O(5) ^a	88.74(7)
O(4)-Cu(1)-O(2) ^a	89.29(6)	O(5) ^a -Cu(1)-O(2) ^a	90.01(7)	O(5) ^a -Cu(1)-O(4)	166.59(6)
O(1)-Cu(1)-N(1)	103.73(6)	O(2) ^a -Cu(1)-N(1)	89.46(6)	O(4)-Cu(1)-N(1)	90.81(6)
O(5) ^a -Cu(1)-N(1)	102.58(6)	O(7)-Cu(2)-O(10)	88.93(7)	O(8) ^b -Cu(2)-O(7)	167.84(6)
O(8) ^b -Cu(2)-O(10)	89.79(7)	O(8) ^b -Cu(2)-O(11) ^b	89.17(7)	O(11) ^b -Cu(2)-O(7)	89.55(7)
O(11) ^b -Cu(2)-O(10)	167.87(6)	O(7)-Cu(2)-N(2)	101.64(6)	O(8) ^b -Cu(2)-N(2)	90.51(6)
O(10)-Cu(2)-N(2)	97.39(6)	O(11) ^b -Cu(2)-N(2)	94.70(6)		
2					
Zn(1)-N(1)	0.216 5(3)	Zn(1)-O(1)	0.206 6(3)	Zn(1)-O(4)	0.219 1(3)
Zn(1)-O(10)	0.212 6(3)	Zn(1)-O(13)	0.220 0(3)	Zn(1)-O(16)	0.210 7(3)
Zn(2)-O(5)	0.200 3(3)	Zn(2)-O(7)	0.199 5(3)	Zn(2)-O(11)	0.199 9(3)
Zn(2)-O(16)	0.207 9(3)	Zn(2)-N(2)	0.225 0(4)	Zn(3) ^d -O(8)	0.196 0(3)
Zn(3)-O(14)	0.194 0(4)	Zn(3)-O(16)	0.192 6(3)		
Zn(2)-O(16)-Zn(1)	106.65(12)	Zn(3)-O(16)-Zn(1)	113.68(15)	Zn(3)-O(16)-Zn(2)	120.87(15)
O(1)-Zn(1)-O(10)	171.18(13)	O(1)-Zn(1)-O(16)	92.17(12)	O(1)-Zn(1)-N(1)	93.19(12)
O(1)-Zn(1)-O(4)	86.13(12)	O(1)-Zn(1)-O(13)	87.18(13)	O(10)-Zn(1)-O(4)	102.69(13)
O(10)-Zn(1)-O(13)	84.01(13)	O(10)-Zn(1)-N(1)	87.62(12)	N(1)-Zn(1)-O(4)	84.41(13)
O(16)-Zn(1)-O(4)	87.08(12)	O(16)-Zn(1)-O(13)	95.89(12)	O(16)-Zn(1)-O(10)	88.45(11)
O(16)-Zn(1)-N(1)	169.60(13)	N(1)-Zn(1)-O(13)	93.27(13)	O(4)-Zn(1)-O(13)	172.78(12)
O(7)-Zn(2)-O(11)	108.29(13)	O(7)-Zn(2)-O(5)	101.17(13)	O(7)-Zn(2)-O(16)	110.00(12)
O(7)-Zn(2)-N(2) ^c	94.53(12)	O(5)-Zn(2)-O(16)	89.73(12)	O(5)-Zn(2)-N(2) ^c	85.90(13)
O(11)-Zn(2)-O(5)	150.10(13)	O(11)-Zn(2)-O(16)	85.09(13)	O(11)-Zn(2)-N(2) ^c	86.76(14)
O(16)-Zn(2)-N(2) ^c	155.47(12)	O(14)-Zn(3)-O(17)	97.71(17)	O(14)-Zn(3)-O(8) ^d	119.39(17)
O(16)-Zn(3)-O(14)	109.73(14)	O(16)-Zn(3)-O(17)	117.80(18)	O(16)-Zn(3)-O(8) ^d	109.36(14)
O(17)-Zn(3)-O(8) ^d	102.78(15)				

Symmetry codes: ^a -x+1, -y+1, -z; ^b -x+2, -y+1, -z+1 for **1**; ^c -x+1, -y, -z+1; ^d -x, -y, -z+1 for **2**

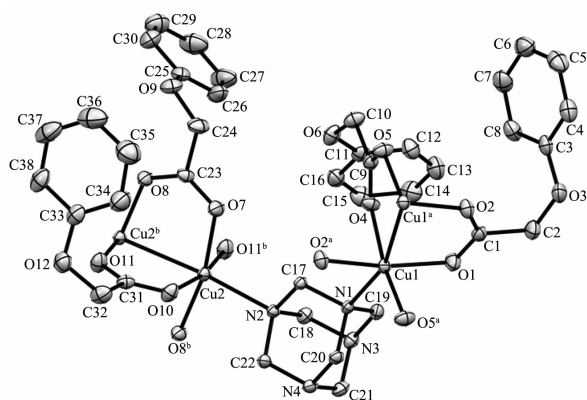
due to the C-N stretching of hmt, further confirms the existence of the hmt ligand in two complexes. The strong vibrations at 1 645, 1 496 cm^{-1} in complex **1**, and 1 660, 1 481 cm^{-1} in complex **2**, are attributed to the asymmetric and symmetric stretching vibrations of the carboxylate group, suggesting that the pa or deca exist in complex **1** or **2**. In addition, the bands at 3 579, and 3 433 cm^{-1} are also observed in complex **2**, which could be assigned to the O-H stretching vibrations of the bridging hydroxyl group and water molecules involved in hydrogen bonding.

2.2 Crystal structures

2.2.1 Crystal structure of complex **1**

X-ray crystal structural analysis revealed that the asymmetric unit of complex **1** is comprised of two crystallographically independent Cu^{2+} ions, Cu1 and Cu2, four pa ligands, and one hmt ligand. As shown in Fig.1, each Cu^{2+} ion is five coordination in a square-pyramidal geometry with four oxygen atoms from four pa ligands that are occupying the equatorial positions and one nitrogen atom from hmt ligand that is at the axial position. The Cu^{2+} ions are deviated by 0.151 7(1)

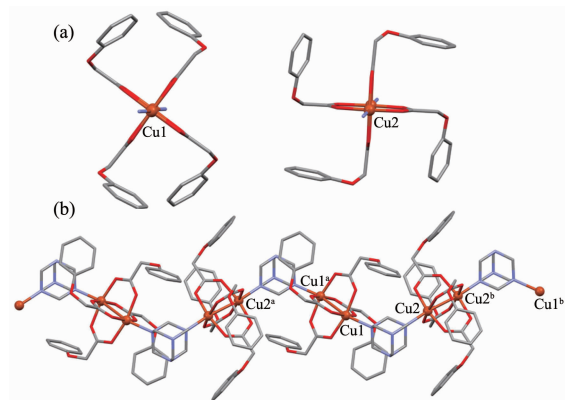
nm for Cu1 and 0.209 7(2) nm for Cu2 from the equatorial plane toward the axial N atoms, respectively.



Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ^a -x+1, -y+1, -z; ^b -x+2, -y+1, -z+1

Fig.1 View of the coordination environment of the Cu(II) centers in complex **1**

The four pa ligands using four carboxylate groups link two Cu²⁺ ions with distances of 0.268 6(1) for Cu1...Cu1^a and 0.264 7(1) nm for Cu2...Cu2^b, respectively, to form [Cu₂(COO)₄] paddlewheel molecular building blocks. The oxyacetate groups are almost twisted out of the phenyl ring planes, with the torsion angles of C1-C2-O3-C3, C9-C10-O6-C11, C23-C24-O9-C25, and C31-C32-O12-C33 being 66.2(3)°, 74.6(3)°, 67.6(3)°, and 67.7(3)°, respectively. The four phenyl groups around Cu2...Cu2^b are arranged in the same direction, thus, the shape of [Cu₂(COO)₄] paddlewheel in Cu2...



Hydrogen atoms are omitted for clarity; Symmetry code: ^a -x+1, -y+1, -z; ^b -x+2, -y+1, -z+1

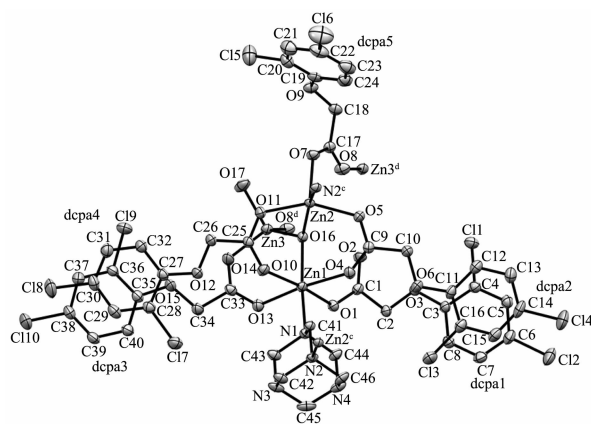
Fig.2 (a) Shapes of [Cu₂(COO)₄] paddlewheels viewed through Cu-Cu vectors; (b) 1D zigzag chain structure of complex **1**

Cu2^b units looks like “卐” character viewed through Cu2-Cu2^b vector, which is different from the [Cu₂(COO)₄] paddlewheel in Cu1-Cu1^a units. Hexamethylenetetramine ligands link the vertices of [Cu₂(COO)₄] paddlewheel units using μ_2 -bridging mode. Therefore, a 1D zigzag chain structure forms in complex **1** (Fig.2).

2.2.2 Crystal structure of complex **2**

The asymmetric unit of complex **2** consists of three Zn²⁺ ions, five dcpa⁻ ligand, one OH⁻ ion, one hmt ligand, and two and a half water molecules. As shown in Fig.3, Zn1 is six coordination in a distorted octahedral geometry with four oxygen atoms from four different dcpa ligands at the equatorial position (O1, O4, O10, and O13), one oxygen atom of OH⁻ ion (O16) and one nitrogen atom from an hmt ligand (N1) which occupy the axial position. Zn2 is five coordinated with four oxygen atoms (O5, O7, O11, and O16) and one nitrogen atom (N2) in a square-pyramidal geometry, in which O5, N2^c, O11, and O16 are at the equatorial plane and the O7 is at the axial position. Zn3 is four coordination in a tetrahedral geometry with carboxylate oxygen atoms of O8^d and O14, one oxygen atom of OH⁻ ion O16, and one water molecule O17. As described above, it is interested to find that there are four-, five-, and six-coordination Zn²⁺ ions in the same units, and OH⁻ ion bridges the three Zn²⁺ ions.

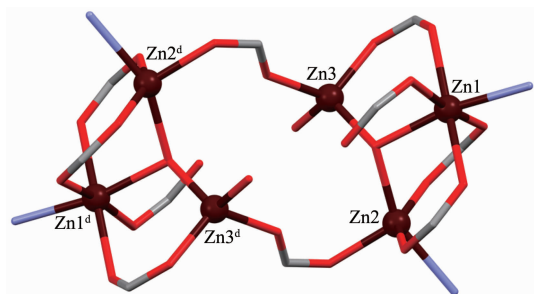
The torsion angles of C1-C2-O3-C3, C9-C10-O6-



Hydrogen atoms and lattice water molecules are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ^c -x+1, -y, -z+1; ^d -x, -y, -z+1

Fig.3 View of the coordination environment of the Zn(II) centers in complex **2**

C11, C25-C26-O12-C27, and C33-C34-O15-C35 are $163.4(3)^\circ$, $175.4(3)^\circ$, $-173.4(3)^\circ$, and $179.9(3)^\circ$, respectively, indicating that the oxyacetate groups are almost in the same planes with the phenyl rings in dcpa1, dcpa2, dcpa3, and dcpa4 ligands. On the other hand, the oxyacetate group is almost out of the phenyl ring plane in dcpa5 ligand, with the torsion angle of C17-C18-O9-C19 being $83.8(4)^\circ$. There are two coordination modes of the carboxylate groups in complex **2**. Only the carboxylate group in dcpa1 ligand coordinates to Zn1 using monodentated coordination mode. The carboxylate groups in dcpa2, dcpa3, and dcpa4 using monodentate-bridged coordination modes to connect the three Zn^{2+} ions. Thus, a trinuclear $[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})]^+$ unit is formed, and the $[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})]^+$ units are bridged by the carboxylate groups of two dcpa5 ligands using monodentate-bridged coordination mode to form a hexanuclear $\{[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})]_2(\mu_2\text{-dcpa})_2\}$ units (Fig.4). Furthermore, the $\{[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})]_2(\mu_2\text{-dcpa})_2\}$ units are connected by two hexamethylenetetramine ligands that use μ_2 -bridging mode. Therefore, a 1D double chain structure forms in complex **2** (Fig.5).



Only the coordinated atoms and carboxylate groups are remained for clarity; Symmetry code: $d -x, -y, -z+1$

Fig.4 A perspective view of hexanuclear $\{[\text{Zn}_3(\text{dcpa})_4(\mu_3\text{-OH})]_2(\mu_2\text{-dcpa})_2\}$ unit

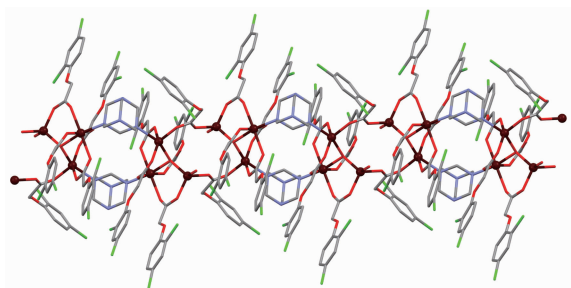
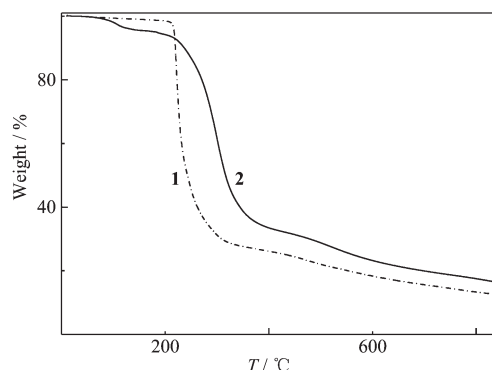


Fig.5 1D double chain structure of complex **2**

2.3 TGA

The thermogravimetric analyses were carried out to examine the thermal stability of the two complexes (Fig.6). Complex **1** started to decompose at 205°C . The weight loss of 69.38% from 205 to 320°C is attributed to the loss of four pa ligands (Calcd. 69.34%). Complex **2** is found to exhibit a two-step weight loss process. The first step is in the range of $80\sim 135^\circ\text{C}$, with the weight loss of 3.23%, which is attributed to the loss of five crystallized water molecules (Calcd. 2.97%). The weight loss of 62.03% in the range of $190\sim 420^\circ\text{C}$ was observed, corresponding to the loss of two OH^- , two coordination water molecules, two hmt and seven dcpa ligands (Calcd. 62.33%).



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