

由 2-甲基咪唑-4,5-二羧酸构筑的双核平行六面体三维钙配位聚合物

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摘要: 合成了一个双核钙配合物 $\{[\text{Ca}_2(\mu_3\text{-HMIA}^{2-})(\mu_5\text{-HMIA}^{2-})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1**, H_3MIA =2-甲基咪唑-4,5-二羧酸), 并用元素分析、红外光谱和 X-射线单晶衍射等对其进行了表征。结构分析表明, **1** 属单斜晶系, $P2_1/c$ 空间群, 晶胞参数为 $a=0.860\ 67(11)\ \text{nm}$, $b=1.656\ 5(2)\ \text{nm}$, $c=1.269\ 24(16)\ \text{nm}$, $\beta=108.005\ 0(10)^\circ$, $V=1.720\ 9(4)\ \text{nm}^3$, $\text{C}_{12}\text{H}_{10}\text{Ca}_2\text{N}_4\text{O}_{10}$, $M_r=450.40$, $Z=4$, $D_c=1.728\ \text{g}\cdot\text{cm}^{-3}$, $F(000)=920$, $\mu=0.727\ \text{mm}^{-1}$, $S=1.041$, $\lambda(\text{Mo } K\alpha)=0.071\ 073\ \text{nm}$, $R=0.026\ 0$ and $wR=0.063\ 8$ 。在 **1** 晶体结构中, 每个钙(II)离子都是 7 配位的, 但展现 2 个不同的配位环境。4 个 $\mu_3\text{-HMIA}^{2-}$ 配体, 2 个 $\mu_5\text{-HMIA}^{2-}$ 配体和 8 个钙(II)离子形成一个平行六面体结构 $[\text{Ca}_8(\mu_3\text{-HMIA})_4(\mu_5\text{-HMIA})_2]^{4+}$ 。 $\mu_5\text{-HMIA}^{2-}$ 配体采用独特的配位模式并连接周围的平行六面体结构形成一维链结构, 配体 $\mu_3\text{-HMIA}^{2-}$ 连接相邻的一维链形成一种新的蜂窝型的二维层状结构, 相邻的二维层通过 $\mu_3\text{-HMIA}^{2-}$ 配体的 2 个氧原子进一步形成一个三维结构。还研究了配合物 **1** 的热重分析和抑菌活性。CCDC: 869134。

关键词: 配位模式; 钙(II); 2-甲基咪唑-4,5-二羧酸; 水热合成; 晶体结构

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Binuclear Parallelepiped Three-Dimensional Ca(II) Coordination Polymer Constructed by 2-Methylimidazole-4,5-dicarboxylate Ligand

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Abstract: The title complex $\{[\text{Ca}_2(\mu_3\text{-HMIA}^{2-})(\mu_5\text{-HMIA}^{2-})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (**1**, H_3MIA =2-methyl-1H-imidazole-4,5-dicarboxylic acid) was synthesized by hydrothermal synthesis and characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray diffraction. Compound **1** crystallizes in monoclinic system, space group $P2_1/c$ with $a=0.860\ 67(11)\ \text{nm}$, $b=1.656\ 5(2)\ \text{nm}$, $c=1.269\ 24(16)\ \text{nm}$, $\beta=108.005\ 0(10)^\circ$, $V=1.720\ 9(4)\ \text{nm}^3$, $\text{C}_{12}\text{H}_{10}\text{Ca}_2\text{N}_4\text{O}_{10}$, $M_r=450.40$, $Z=4$, $D_c=1.728\ \text{g}\cdot\text{cm}^{-3}$, $F(000)=920$, $\mu=0.727\ \text{mm}^{-1}$, $S=1.041$, $\lambda(\text{Mo } K\alpha)=0.071\ 073\ \text{nm}$, $R=0.026\ 0$ and $wR=0.063\ 8$ for 3 211 observed reflections ($I>2\sigma(I)$). Compound **1** is a unique binuclear Ca(II) parallelepiped MOFs, two Ca(II) cations are seven-coordinated, but show different coordination environments. Four $\mu_3\text{-HMIA}^{2-}$, two $\mu_5\text{-HMIA}^{2-}$ and eight Ca(II) ions form a molecular parallelepiped of $[\text{Ca}_8(\mu_3\text{-HMIA})_4(\mu_5\text{-HMIA})_2]^{4+}$. The $\mu_5\text{-HMIA}^{2-}$ ligand adopts a unique coordination mode and links the neighboring parallelepipeds to form one-dimensional chain. The $\mu_3\text{-HMIA}^{2-}$ ligand links the neighboring one-dimensional chains to yield a two-dimensional honey comb-like network layer architectures, which are further linked through two carboxylate oxygen atoms from $\mu_3\text{-HMIA}^{2-}$ ligand to generate a three-dimensional MOFs. Thermal gravimetric analysis and antibacterial activities of complex **1** were also studied. CCDC: 869134.

Key words: coordination modes; Ca(II); 2-methyl-1H-imidazole-4,5-dicarboxylic acid; hydrothermal synthesis; crystal structure

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0 Introduction

In recent years, the design and synthesis of metal-organic frameworks (MOFs) have attracted much attention, not only owing to their intriguing variety of architectures but also because of their potential applications as microporous, magnetic, nonlinear optical, and fluorescent materials^[1-5]. The multifunctional organic ligands play an important role in constructing MOFs with unique structures and properties. Thus, considerable efforts have been devoted to choosing or designing various multifunctional bridging ligands^[4-6].

Structures containing metals and *N*-heterocyclic carboxylic acids have attracted much attention as they can function as a multidentate ligand, exhibit diverse structural type and can be potentially used as functional materials^[4-8]. Over the past few years, extensive investigations have focused on the construction of MOFs using 4,5-imidazoledicarboxylic acid as the bridges^[9-17]. However, the reports of coordination polymers with 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid are still rare^[18-23]. Recently, our group reported three 0D transition metal (cadmium, cobalt and nickel) complexes and a 2D (sodium) MOFs with the 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3MIA) ligand^[19-23]. Although cadmium, cobalt and nickel complexes have the same formula, they crystallize in three different crystal systems, and there are many differences in the structures. The 2D sodium MOFs shows a unique coordination mode and interesting 2D topology. Therefore, we have been engaged in synthesizing new MOFs with H_3MIA ligand, and not long ago we obtained a calcium complex with H_3MIA ligand via hydrothermal reaction. Herein, we report the synthesis and structure of the three-dimensional binuclear parallelepiped MOFs constructed by Ca(II) with 2-methyl-1*H*-imidazole-4,5-dicarboxylate building blocks.

1 Experimental

1.1 Materials and measurements

1,2-phenylenediamine, and other reactants of A. R. grade were obtained commercially and used without further purification. Elemental analysis of C,

H and N was performed on a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded (4 000~400 cm^{-1}) as KBr disks on a Nicolet 6700 FT-IR spectrometer. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer TG/DTA 6300 system with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ from temperature to 800 $^{\circ}\text{C}$ under nitrogen atmosphere.

1.2 Synthesis of H_3MIA and complex 1

1.2.1 Synthesis of H_3MIA

2-methylbenzimidazole was prepared from acetic acid and 1,2-phenylenediamine in 4 $\text{mol} \cdot \text{L}^{-1}$ HCl as solvent at reflux for 40 min with a yield of 90%, using a modified Phillips reaction^[24] and was recrystallized from ethanol. Then to 24.5 mL (0.46 mol) H_2SO_4 (98%), 2.64 g (0.02 mol) 2-methylbenzimidazole was added under stirring at ambient temperature. After the reaction mixture became clear, a 10 mL (0.027 5 mol) solution of H_2O_2 (30%) was added dropwise at 100 $^{\circ}\text{C}$ with vigorous stirring, then the temperature was slowly elevated to 145 $^{\circ}\text{C}$ and maintained for 1 h. The resulting mixture was slowly cooled to 100 $^{\circ}\text{C}$ and poured into 100 g ice-cold water with rapidly stirring, then the resulting suspension was filtered and washed with water and ethanol, respectively. 2.38 g (70%) H_3MIA remained after drying in vacuo. m.p. 285 $^{\circ}\text{C}$; IR(KBr, cm^{-1}): 3 541.9, 3 461.6, 2 915.9, 1 591.9, 1 557.6, 1 268.4. MS(ESI) m/z : 169.10 ($M^{+}-1$)(100%). H_3MIA belongs to monoclinic crystal system, $P2_1/c$ space group, $a=0.848\ 97(7)$ nm, $b=1.427\ 31(12)$ nm, $c=0.652\ 81(5)$ nm, $\beta=97.379\ 0(10)^{\circ}$ ^[25].

1.2.2 Synthesis of complex 1

A mixture of $CaCl_2$ (0.021 9 g, 0.1 mmol), H_3MIA (0.034 g, 0.2 mmol), NaOH (0.6 mL, 0.65 $\text{mol} \cdot \text{L}^{-1}$), and distilled water (10 mL) was sealed in a Teflon-lined stainless reactor (25 mL) and heated at 120 $^{\circ}\text{C}$ for 72 h, and then cooled the autoclave to room temperature. The crystals were recovered, then filtered and washed with distilled water. The colorless crystals of **1** were obtained suitable for X-ray diffraction analysis with yield of 80 % based on Ca(II). Elemental Analysis Calcd.(%) for $C_{12}H_{10}N_4Ca_2O_{10}$: C, 31.86; H, 2.67; N, 12.38. Found(%): C, 32.00; H, 2.24; N, 12.44.

IR (KBr, cm^{-1}): 3 418.6, 3 122.4, 1 655.2, 1 560.9, 1 529.5, 1 458.6, 1 408.7, 1 369.7, 1 340.3, 1 262.5, 1 239.2, 1 111.9, 796.4.

1.3 Structure determination

A colorless single crystal with dimensions of 0.26 mm×0.18 mm×0.16 mm was selected and mounted on a glass fiber. Diffraction data were collected at room temperature on a Bruker Smart APEX II CCD area detector diffractometer^[26] equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at

296(2) K. A total of 9 967 reflections were collected in the range of $2.49<\theta<28.31^\circ$ by using an ω - 2θ scan mode, of which 3 211 were unique with $R_{\text{int}}=0.063\ 8$ and used in the succeeding structure calculations. The structure was solved by direct methods and refined against F^2 by full-matrix least-squares technique. All calculations were performed with SHELXTL-97 program^[27-28].

All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses.

Table 1 Crystal and structure refinement data of 1

Empirical formula	$\text{C}_{12}\text{H}_{10}\text{CaN}_4\text{O}_{10}$	Z	4
Formula weight	450.40	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.738
Crystal system	Monoclinic	$\mu (\text{Mo } K\alpha) / \text{mm}$	0.726
Space group	$P2_1/c$	$F(000)$	924
a / nm	0.86 067(11)	Crystal size / mm^3	0.16×0.18×0.26
b / nm	1.656 5(2)	θ range for data collection / $^\circ$	2.49 to 28.31
c / nm	1.26924(16)	Reflections collected	9 967
$\alpha / ^\circ$	90	Independent reflection	3 211 ($R_{\text{int}}=0.018\ 1$)
$\beta / ^\circ$	108.0050(10)	Goodness-of-fit on F^2	1.041
$\gamma / ^\circ$	90	Final R indices [$I>2\sigma(I)$] ^a	$R_1=0.024\ 0$, $wR_2=0.062\ 6$
V / nm^3	1.720 9(4)	R indices (all data) ^a	$R_1=0.026\ 0$, $wR_2=0.063\ 8$

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) of 1

Ca(1)-O(2) ^{#1}	0.238 04(12)	Ca(1)-O(3) ^{#1}	0.236 20(13)	Ca(1)-O(8) ^{#2}	0.240 13(11)
Ca(1)-O(1)	0.240 52(11)	Ca(1)-O(5)	0.241 94(12)	Ca(1)-N(1)	0.254 76(15)
Ca(1)-N(3)	0.254 76(15)	Ca(2)-O(6) ^{#3}	0.228 17(11)	Ca(2)-O(4) ^{#4}	0.228 28(13)
Ca(2)-O(5)	0.238 85(11)	Ca(2)-O(7) ^{#3}	0.240 69(11)	Ca(2)-O(9)	0.242 14(13)
Ca(2)-O(7) ^{#2}	0.240 69(11)	Ca(2)-O(8) ^{#2}	0.263 29(11)	Ca(1)-Ca(2)	0.395 95(6)
O(3) ^{#1} -Ca(1)-O(2) ^{#1}	75.63(4)	O(3) ^{#1} -Ca(1)-O(8) ^{#2}	137.61(5)	O(2) ^{#1} -Ca(1)-O(8) ^{#2}	79.97(4)
O(3) ^{#1} -Ca(1)-O(1)	81.09(4)	O(2) ^{#1} -Ca(1)-O(1)	119.83(4)	O(8) ^{#2} -Ca(1)-O(1)	81.76(4)
O(3) ^{#1} -Ca(1)-O(5)	131.41(4)	O(2) ^{#1} -Ca(1)-O(5)	77.75(5)	O(8) ^{#2} -Ca(1)-O(5)	74.34(4)
O(1)-Ca(1)-O(5)	147.40(4)	O(3) ^{#1} -Ca(1)-N(3)	80.04(5)	O(2) ^{#1} -Ca(1)-N(3)	100.65(5)
O(8) ^{#2} -Ca(1)-N(3)	138.95(4)	O(1)-Ca(1)-N(3)	128.76(4)	O(5)-Ca(1)-N(3)	65.93(4)
O(2) ^{#1} -Ca(1)-N(1)	171.98(6)	O(3) ^{#1} -Ca(1)-N(1)	111.85(6)	O(8) ^{#2} -Ca(1)-N(1)	95.45(5)
O(1)-Ca(1)-N(1)	65.48(4)	O(5)-Ca(1)-N(1)	95.74(5)	N(3)-Ca(1)-N(1)	78.44(5)
O(6) ^{#3} -Ca(2)-O(4) ^{#4}	85.38(5)	O(6) ^{#3} -Ca(2)-O(5)	94.45(4)	O(4) ^{#4} -Ca(2)-O(5)	86.27(5)
O(6) ^{#3} -Ca(2)-O(7) ^{#3}	77.51(4)	O(4) ^{#4} -Ca(2)-O(7) ^{#3}	104.93(5)	O(5)-Ca(2)-O(7) ^{#3}	165.42(4)
O(6) ^{#3} -Ca(2)-O(9)	81.12(5)	O(4) ^{#4} -Ca(2)-O(9)	160.32(5)	O(5)-Ca(2)-O(9)	80.60(5)
O(7) ^{#3} -Ca(2)-O(9)	86.11(4)	O(6) ^{#3} -Ca(2)-O(7) ^{#2}	144.88(4)	O(4) ^{#4} -Ca(2)-O(7) ^{#2}	95.00(5)
O(5)-Ca(2)-O(7) ^{#2}	120.65(4)	O(7) ^{#3} -Ca(2)-O(7) ^{#2}	68.44(4)	O(9)-Ca(2)-O(7) ^{#2}	104.28(5)
O(6) ^{#3} -Ca(2)-O(8) ^{#2}	161.83(4)	O(4) ^{#4} -Ca(2)-O(8) ^{#2}	83.29(5)	O(5)-Ca(2)-O(8) ^{#2}	70.72(4)
O(7) ^{#3} -Ca(2)-O(8) ^{#2}	119.18(4)	O(9)-Ca(2)-O(8) ^{#2}	105.82(5)	O(7) ^{#2} -Ca(2)-O(8) ^{#2}	50.75(3)

Symmetry transformation: ^{#1} $x, -y+1/2, z+1/2$; ^{#2} $x+1, y, z$; ^{#3} $-x+2, -y, -z+2$; ^{#4} $-x+2, -y, -z+1$; ^{#5} $-1+x, y, z$.

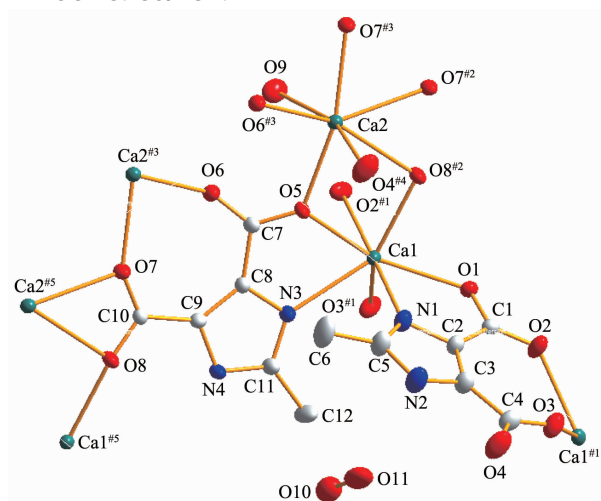
Table 3 Hydrogen bond lengths and bond angles

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O(9)–H(3w)···O(1) ^{#1}	0.078 0	0.203 0	0.276 7	157.54
O(9)–H(4w)···O(3) ^{#2}	0.081 8	0.245 6	0.308 4	134.42
O(9)–H(4w)···O(7) ^{#3}	0.081 8	0.252 7	0.308 5	126.52
N(4)–H(2)···O(1)	0.086	0.192 2	0.277 9	174.46
N(2)–H(1)···O(11) ^{#4}	0.089	0.216	0.277 3	125
O(10)–H(5w)···O(9)	0.082	0.224	0.304 9	172.1
O(10)–H(6w)···O(2) ^{#2}	0.082	0.236	0.316 4	166.0
O(11)–H(7w)···O(9)	0.084	0.202	0.277 5	148.2

Symmetry codes: ^{#1} 1–*x*, –*y*, 1–*z*; ^{#2} 1–*x*, –*y*, 2–*z*; ^{#3} 1–*x*, –1/2+*y*, 3/2–*z*; ^{#4} –*x*+2, –*y*+1, –*z*+2.

The hydrogen atoms bound to carbon were located by geometrical calculations, and their positions and thermal parameters were fixed during the structure refinement. Crystallographic data and pertinent information are given in Table 1, selected bond lengths and angles in Table 2, and geometric parameters of hydrogen bonds in Table 3. The molecular structure with atomic labeling scheme is shown in Fig.1.

CCDC: 869134.



Hydrogen atoms are omitted for clarity; Symmetry codes: ^{#1} *x*, –*y*+1/2, *z*+1/2; ^{#2} *x*+1, *y*, *z*; ^{#3} –*x*+2, –*y*, –*z*+2; ^{#4} –*x*+2, –*y*, –*z*+1; ^{#5} –1+*x*, *y*, *z*

Fig.1 Crystal structure of **1** with 50% thermal ellipsoids

1.4 Antibacterial activities of complex 1

The antibacterial activities of the ligand and its complex was studied using the Kirby-Bauer (K-B) method. The strains selected were the botanical bacteria, including *Penicillium italicum*, *Penicillium digitatum*, and *Magnaporthe oryzae*.

2 Results and discussion

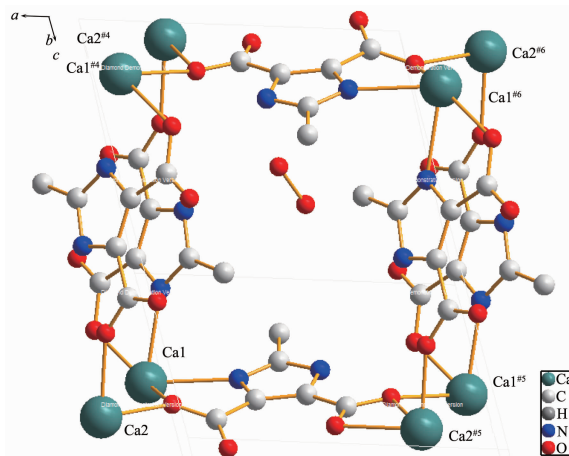
2.1 Description of the structure

Single crystal X-ray diffraction analysis reveals that the structure of the title complex **1**, $\{[\text{Ca}_2(\mu_3\text{-HMIA}^{2-})(\mu_5\text{-HMIA}^{2-})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (H_3MIA =2-methyl-1*H*-imidazole-4,5-dicarboxylic acid) is binuclear complex, each asymmetric unit composed of two Ca(II) cations, two bidentate HMIA²⁻ ligands ($\mu_3\text{-HMIA}^{2-}$ and $\mu_5\text{-HMIA}^{2-}$), one coordinated water and one uncoordinated water (Fig.1). Interestingly, two Ca(II) cations are seven-coordinated, but two Ca(II) cations show different coordination environments. It is rare that the same metal ions have different coordination environments in one molecular building block of one compound^[29-32]. Each Ca(1) cation is coordinated with one nitrogen atom (N(1)) and three oxygen atoms (O(1), O(2)^{#1}, O(3)^{#1}) from $\mu_3\text{-HMIA}^{2-}$ ligand, and one nitrogen atom (N(3)) and two oxygen atoms (O(5), O(8)^{#2}) from $\mu_5\text{-HMIA}^{2-}$ ligand, forming a distorted pentagonal bipyramidal geometry. The Ca–N bond distances are 0.249 39(16) and 0.254 74(18) nm, the Ca–O bond distances are in the range of 0.236 16(16)~0.241 93(14) nm, the N–Ca–N bond angles is 78.46(6)°, the N–Ca–O bond angles vary from 65.46(5) to 171.99(6)° and the O–Ca–O bond angles vary from 74.34 (5) to 147.38(5)° (Table 1). Each Ca(2) cation is coordinated with one oxygen atom (O(4)^{#4}) from $\mu_3\text{-HMIA}^{2-}$ ligand, four oxygen atoms (O(5), O(6)^{#3}, O(7)^{#2}, O(7)^{#3}, O(8)^{#4}) from $\mu_5\text{-HMIA}^{2-}$ ligand and one oxygen atom (O(9)) from coordinated water, yielding a distorted pentagonal bipyramidal geometry. The Ca–O bond distances are

in the range of 0.228 08(14)~0.248 09(13) nm, and the O-Ca-O bond angles vary from 68.45(5) to 165.42(5) $^{\circ}$ (Table 1). These angles further confirm the distorted coordination geometry of Ca(II) in **(1)**. μ_3 -HMIA $^{2-}$ and μ_5 -HMIA $^{2-}$ are full deprotonated, and Each μ_3 -HMIA $^{2-}$ and μ_5 -HMIA $^{2-}$ is quasi-planar, with the mean deviations from the planes being 0.003 7 and 0.007 93 nm, respectively. The μ_3 -HMIA $^{2-}$ and μ_5 -HMIA $^{2-}$ bridge the Ca(II) ions in a asymmetrical mode, in which the μ_3 -HMIA $^{2-}$ and μ_5 -HMIA $^{2-}$ lies in a C_2 symmetry (Fig.1).

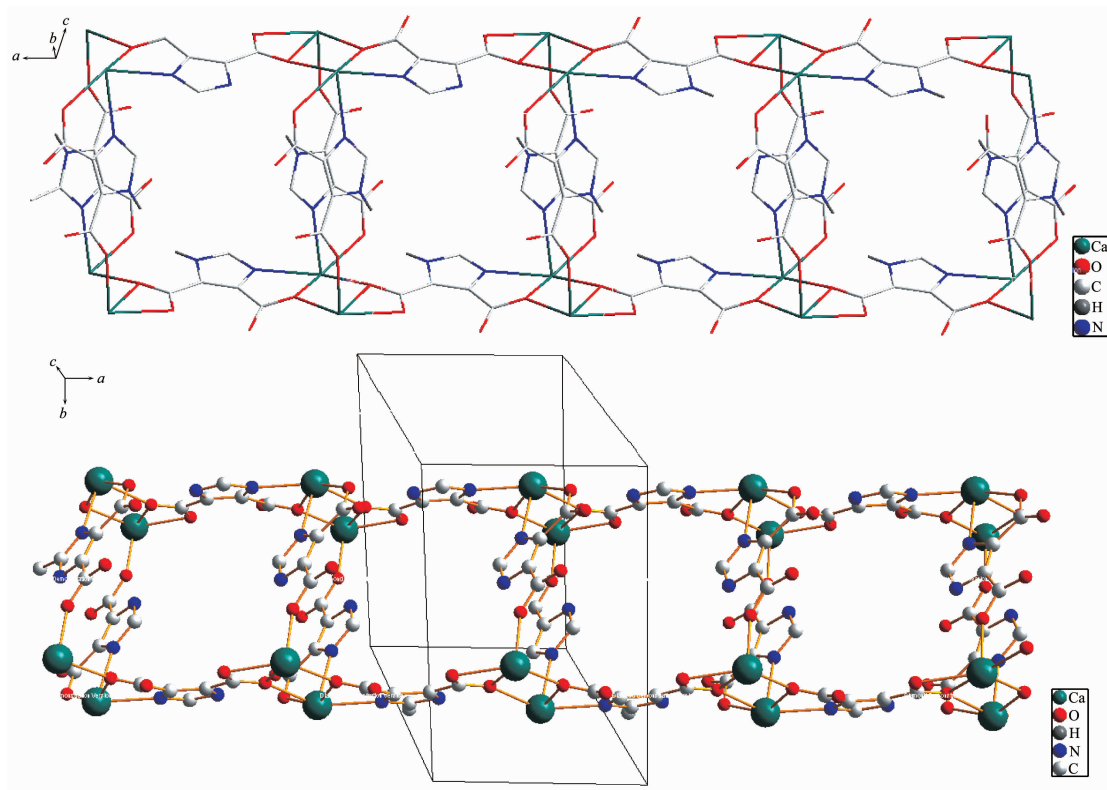
In **1**, four μ_3 -HMIA $^{2-}$, two μ_5 -HMIA $^{2-}$ and eight Ca(II) ions form a molecular parallelepiped of $[\text{Ca}_8(\mu_3\text{-HMIA})_4(\mu_5\text{-HMIA})_2]^{4+}$ (Fig.2), in which eight calcium are distributed in the vertices of the parallelepiped, two μ_3 -HMIA $^{2-}$ is on the equatorial plane, four μ_5 -HMIA $^{2-}$ is on the axial plane with the dihedral angles of 38.111 $^{\circ}$. The distances of Ca(1) \cdots Ca(2), Ca(1) \cdots Ca(2) $^{\#4}$, and Ca(1) \cdots Ca(1) $^{\#5}$ are 0.395 95, 0.860 67, and 0.915 6 nm and the angles Ca(1) \cdots Ca(2) \cdots Ca(2) $^{\#5}$, Ca(1) \cdots Ca(2) \cdots Ca(1) $^{\#4}$ Ca(2) $^{\#5}$ \cdots Ca(2) \cdots Ca(1) $^{\#4}$ are 75.485, 91.039, 100.676 $^{\circ}$, respectively. The μ_5 -HMIA $^{2-}$

ligand acts as octadentate (N107) in **1** and adopts a unique $\mu_5\text{-}\kappa\text{N},\text{O}:\kappa\text{O}:\kappa\text{O},\text{O}':\kappa\text{O},\text{O}':\kappa\text{O}$ coordination mode. Each carboxylate oxygen atom (O(5), O(6) $^{\#3}$ and O(8) $^{\#2}$) and imidazole nitrogen atom (N(3)) from μ_5 -HMIA $^{2-}$ links the neighboring parallelepipeds to form one-dimensional chain (Fig.3). The μ_3 -HMIA $^{2-}$ ligand



Hydrogen atoms are omitted for clarity; Symmetry codes: $^{\#4} -x+2, -y, -z+1$; $^{\#5} -1+x, y, z$; $^{\#6} 1-x, y, z$

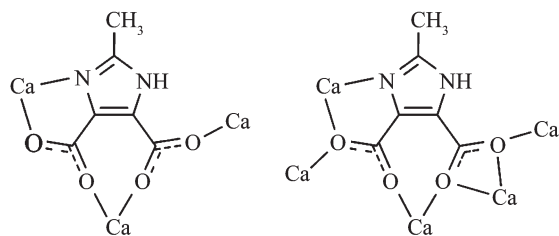
Fig.2 Parallelepiped structure of **1** with 50% thermal ellipsoids



Hydrogen atoms are omitted for clarity

Fig.3 One dimensional metal-organic frameworks (MOFs) of **1**

acts as pentadentate (N1O4) in **1** and adopts a $\mu_3\text{-}\kappa\text{N}, \text{O}:\kappa\text{O}, \text{O}':\kappa\text{O}$ coordination mode^[4] (Scheme 1). Each carboxylate oxygen atom (O(1), O(4)[#]) and imidazole nitrogen atom (N(1)) from $\mu_3\text{-HMIA}^{2-}$ ligand links the neighboring one-dimensional chains yielding a two-dimensional network layer framework. Two carboxylate oxygen atoms (O(2), O(3)) from $\mu_3\text{-HMIA}^{2-}$ ligand links the Ca(1) from the neighboring two-dimensional network layer framework to form a three-dimensional metal-organic frameworks (MOFs). The 3D MOFs is also stabilized by the intermolecular O—H \cdots O hydrogen bonds between the coordination water and the carboxyl group and the intermolecular N—H \cdots O hydrogen bonds between imidazole ring and the carboxyl group (Table 2).



Scheme 1 Coordination codes of $\mu_3\text{-HMIA}^{2-}$ and $\mu_5\text{-HMIA}^{2-}$ ligand

2.2 TGA analysis

The TGA data of **1** indicate two obvious weight losses shown in Fig.4. The first weight loss starts at 200~300 °C to give a total weight loss of 11.13% (Calcd. 8.04%), corresponding to the loss of coordinated water and uncoordinated water molecules.

And then at 300~800 °C to give a total weight loss of 63.97% (Calcd. 66.95%), attributed to the removal of H₃MIA ligands and the final product is CaO with the weight of 24.90% (Calcd. 25.01%).

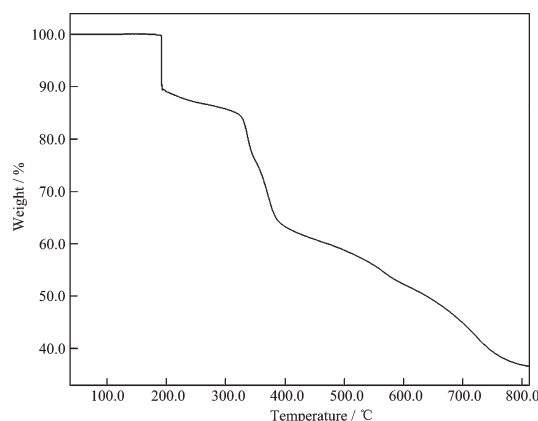


Fig.4 TGA curve of **1**

2.3 Biological activity

The result of the bacterial growth inhibition study is reported in Table 4 in terms of the average diameter of inhibition zone. The result shows that the ligand and complex show antimicrobial activity to *Penicillium italicum*, *Penicillium digitatum*, and *Rhizoctonia solani*, and the effect strengthens with increasing of the concentration. The complex shows better activity than the ligand to *Penicillium italicum* and *Rhizoctonia solani*, but shows poorer activity than the ligand to *Penicillium digitatum*, calcium ions may have promoting effect of on the growth to *Penicillium digitatum*.

Table 4 Antibacterial data for the ligand and its complex

Agent	Concentration / (mg·mL ⁻¹)	Average value of diameter of inhibition zone / mm		
		<i>Penicillium italicum</i>	<i>Penicillium digitatum</i>	<i>Rhizoctonia solani</i>
Ligand	2.5	13	14.5	14
	5	14	15	14.5
	10	14.5	15	16.5
	20	16	15.5	19.5
Complex	2.5	12	12	15.5
	5	13.5	12	16
	10	15	12.5	22
	20	17	13.5	26

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