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# 2-(5-甲基-1,3,4-噻二唑)-硫乙酸锌(Ⅱ)配合物的合成、晶体结构和性质

潘兆瑞*,[1,2] 郑和根*,[1]

([1] 南京大学化学化工学院,配位化学国家重点实验室,南京 210023)

([2] 南京晓庄学院环境科学学院,南京 211171)

**摘要**: 合成了 2 个锌配合物[Zn(mtyaa)$_2$(H$_2$O)$_4$]·4H$_2$O (**1**)和[Zn(bpe)(mtyaa)$_2$(H$_2$O)$_2$]$_n$ (**2**)(Hmtyaa=2-(5-甲基-1,3,4-噻二唑)-硫乙酸; bpe=1,2-双(4-吡啶基)乙烷),用 X 射线单晶衍射仪测定了配合物的单晶结构,并对它进行了元素分析、红外光谱、热重和粉末 X 射线衍射等表征。配合物 **1** 和 **2** 的晶体分别属于三斜晶系和单斜晶系,空间群分别为 $P\bar{1}$ 和 $C2/c$。$\pi$-$\pi$ 相互作用以及配位水和游离水分子与羧基氧之间的氢键作用将配合物 **1** 的单分子结构连成三维网状结构。配合物 **2** 中配位水与羧基氧以及配体中的氮原子之间的氢键作用将相邻链连接成二维平面结构。

**关键词**: 2-(5-甲基-1,3,4-噻二唑)-硫乙酸; 晶体结构; $\pi$-$\pi$ 相互作用; 氢键

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# Syntheses, Crystal Structures and Properties of 2-(5-Methyl-1,3,4-thiadiazol-2-ylthio Zinc(Ⅱ) Coordination Compounds

PAN Zhao-Rui*,[1,2] ZHENG He-Gen*,[1]

([1]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing* 210023, *China*)

([2]*School of Environmental Science, Nanjing Xiaozhuang University, Nanjing* 211171, *China*)

**Abstract:** Two coordination compounds [Zn(mtyaa)$_2$(H$_2$O)$_4$]·4H$_2$O (**1**) and [Zn(bpe)(mtyaa)$_2$(H$_2$O)$_2$]$_n$ (**2**) (Hmtyaa=2-(5-methyl-1,3,4-thiadiazol-2-ylthio) acetic acid, bpe=1,2-bis(4-pridyl)ethane) have been synthesized and they were structurally characterized by single-crystal X-ray diffraction, and then were characterized by elemental analysis, FTIR spectra, thermal analysis and powder X-ray diffraction. Compounds **1** and **2** crystallize in the triclinic and monoclinic, space group $P\bar{1}$ and $C2/c$, respectively. Face-to-face $\pi$-$\pi$ interactions and hydrogen bonds between coordinated and free water molecules with carboxylate oxygen atoms connect single molecules in compound **1** into three dimensional network. Compound **2** is connected into three dimensional structure by hydrogen bonds between coordinated water molecules and carboxylate oxygen atoms or nitrogen atoms. CCDC: 653462, **1**; 653467, **2**.

**Keywords:** 2-(5-methyl-1,3,4-thiadiazol-2-ylthio)acetic acid; crystal structure; $\pi$-$\pi$ interaction; hydrogen bonds

## 0 Introduction

The construction of supramolecular architectures are currently of great interest owing to their intriguing structures[1-4] and potential applications in catalysts, electrochemistry, optics, magnetism, gas sorption and so on[5-9]. However, how to construct appropriate crystal structures is the primary issue. The carboxylate

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*通信联系人。E-mail: pzr_2006@163.com,zhenghg@nju.edu.cn;会员登记号:S06N1394M1405。

ligands are widely employed in the design of coordination frameworks for the following reasons: Firstly, because their various coordination modes and flexible molecular backbones can provide a variety of coordination polymers with appealing structures and properties[10]. Secondly, the inherent negative charge of the carboxylate groups can compensate for the charge induced by the metal centers[11-12]. Thirdly, hydrogen bond formation by carboxylate groups reinforces whole architectures[13-15]. On the other hand, the N-donor ligands, such as 4,4′-bipyridine (4,4′-bipy) and 1,2-bis(4-pridyl)ethane (bpe) have also been proven to be useful connectors to formulate high dimensional compounds[16]. Recently, we have successfully synthesized some supramolecular compounds by using 2-(5-methyl-1,3,4-thiadiazol-2-ylthio) acetic acid (Hmtyaa) ligand[17-19]. Herein, we successfully obtained two new coordination compound based on Hmtyaa ligand and N-donor ligands (bpe), namely, $[Zn(mtyaa)_2(H_2O)_4]\cdot 4H_2O$ (**1**) and $[Zn(bpe)(mtyaa)_2(H_2O)_2]_n$ (**2**).

## 1 Experimental

### 1.1 Reagents and physical measurements

Hmtyaa ligand was synthesized as literature reported[20]. All other chemicals were of reagent grade quality from commercial sources and were used without further purification. The IR absorption spectra of the compounds were recorded in the range of 400~4 000 $cm^{-1}$ by means of a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyser. XRD measurements were performed on a Philips X′pert MPD Pro X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda$=0.154 18 nm, $2\theta$=5°~50°), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyser Pyris 1 TGA up to 1 023 K using a heating rate of 20 $K\cdot min^{-1}$ under a $N_2$ atmosphere.

### 1.2 Synthesis

1.2.1 Synthesis of $[Zn(mtyaa)_2(H_2O)_4]\cdot 4H_2O$ (**1**)

A solution of $ZnCl_2$ (54 mg, 0.4 mmol) in $H_2O$ (3 mL) was added to a solution of Hmtyaa (38 mg, 0.2 mmol) in $H_2O$ (5 mL) which was adjusted to pH≈7.0 with dilute sodium hydroxide (1 $mol\cdot L^{-1}$), and the mixture was stirred at room temperature for 12 h to give a colorless solution, which was then filtered. Slow evaporation of the filtrate gave white block-shaped single crystals in two weeks. Yield: 39.98 mg (68%). Anal. Calcd. for $C_{10}H_{26}N_4O_{12}S_4Zn$(%): C, 20.43; H, 4.46; N, 9.53. Found(%): C, 20.45; H, 4.47; N, 9.51. IR (KBr, $cm^{-1}$): 3 487(s), 3 342(s), 1 589(vs), 1 401(m), 1 388(vs), 1 248(m), 1 206(w), 1 093(w), 904(w), 781(w), 689(m), 611(m), 405(w).

1.2.2 Synthesis of $[Zn(bpe)(mtyaa)_2(H_2O)_2]_n$ (**2**)

A solution of $ZnCl_2$ (27 mg, 0.2 mmol) and bpe (36 mg, 0.2 mmol) was added to a solution of Hmtyaa (38 mg, 0.2 mmol) in $H_2O$ (7 mL) which was adjusted to pH≈7.0 with dilute sodium hydroxide (1 $mol\cdot L^{-1}$). The final mixture was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 75 ℃ for 15 h. Little red crystals were obtained and filtered. The filtrate was allowed to slowly evaporate at ambient temperature over 3 days, and quantities of white triangular prism crystals were collected in 95% yield. Anal. Calcd. for $C_{22}H_{26}N_6O_6S_4Zn$(%): C, 39.79; H, 3.95; N, 12.65. Found (%): C, 39.81; H, 3.96; N, 12.62. IR (KBr, $cm^{-1}$): 3 427(s), 1 615(vs), 1 590(vs), 1 428(m), 1 384(vs), 1 219(w), 1 198(w), 1 074(m), 826(w), 685(w), 621(w), 545(w).

### 1.3 X-ray crystallography

X-ray crystallographic data of both compounds were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Smart CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) by using $\varphi$-$\omega$ scan mode at room temperature. The structures were solved by direct methods and refined with the full-matrix least squares technique using the SHELXS-97 and SHELXL-97 programs[21-22]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms bonding to C and N atoms were fixed geometrically at calculated distances and allowed to ride on the parent atoms, and the hydrogen atoms of water molecules were either found from the

difference Fourier map or fixed stereochemically. Crystallographic data and structural refine ment parameters are summarized in Table 1, and the selected bond lengths and angles are given in Table 2 and 3.

CCDC: 653462, **1**; 653467, **2**.

**Table 1 Crystallographic data and structure refinement details for compounds 1 and 2**

| Compound | **1** | **2** |
|---|---|---|
| Formula | $C_{10}H_{26}N_4O_{12}S_4Zn$ | $C_{22}H_{26}N_6O_6S_4Zn$ |
| Formula weight | 587.96 | 664.10 |
| Temperature / K | 293(2) | 293(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $C2/c$ |
| $a$ / nm | 0.675 5(2) | 1.933 1(5) |
| $b$ / nm | 0.859 2(3) | 1.203 4(3) |
| $c$ / nm | 1.063 3(3) | 1.489 1(4) |
| $\alpha$ / (°) | 96.452(5) | 90 |
| $\beta$ / (°) | 100.038(5) | 125.713(4) |
| $\gamma$ / (°) | 103.392(5) | 90 |
| $V$ / nm$^3$ | 0.583 6(3) | 2.812 7(12) |
| $Z$ | 1 | 4 |
| Crystal size / mm | 0.26×0.24×0.23 | 0.32×0.28×0.26 |
| $D_c$ / (g·cm$^{-3}$) | 1.673 | 1.568 |
| $\mu$ / mm$^{-1}$ | 1.471 | 1.219 |
| $F$(000) | 304 | 1 368 |
| $\theta$ range for data collection / (°) | 1.97~25.00 | 2.13~25.00 |
| Reflection collected, unique | 2 915, 2 020 ($R_{int}$=0.078 3) | 6 848, 2 467 ($R_{int}$=0.067 8) |
| Observed reflections [$I>2\sigma(I)$] | 1 794 | 2 051 |
| Parameter refined | 142 | 179 |
| Goodness-of-fit on $F^2$ | 1.002 | 1.002 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$=0.045 2; $wR_2$=0.125 42 | $R_1$=0.037 8; $wR_2$=0.095 3 |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm$^{-3}$) | 671, −657 | 425, −369 |

**Table 2 Selected bond lengths (nm) and angles (°) in compounds 1 and 2**

| Compound **1** | | | | | |
|---|---|---|---|---|---|
| O2-Zn1 | 0.203 8(2) | O3-Zn1 | 0.217 0(2) | O4-Zn1 | 0.206 5(2) |
| O2a-Zn1-O2 | 180 | O2-Zn1-O4a | 90.63(10) | O2-Zn1-O4 | 89.37(10) |
| O4a-Zn1-O4 | 180 | O2-Zn1-O3 | 90.49(10) | O4-Zn1-O3 | 88.86(10) |
| O2-Zn1-O3a | 89.51(10) | O4-Zn1-O3a | 91.14(10) | O3-Zn1-O3a | 180 |
| Compound **2** | | | | | |
| N3-Zn1 | 0.216 2(2) | O2-Zn1 | 0.2152 2(19) | O3-Zn1 | 0.211 54(18) |
| O3-Zn1-O3a | 180 | O3-Zn1-O2 | 90.87(7) | O3a-Zn1-O2 | 89.13(7) |
| O2-Zn1-O2a | 180 | O3-Zn1-N3 | 92.06(8) | O3a-Zn1-N3 | 87.94(8) |
| O2-Zn1-N3 | 89.58(8) | O2a-Zn1-N3 | 90.42(8) | O3a-Zn1-N3a | 92.06(8) |
| N3-Zn1-N3a | 180 | | | | |

Symmetry codes: a: $-x+1$, $-y+2$, $-z+2$ for **1**; a: $-x+1/2$, $-y+3/2$, $-z+1$ for **2**.

**Table 3　Hydrogen-bonding parameters in compounds 1 and 2**

| D–H···A | *d*(D-H) / nm | *d*(H···A) / nm | *d*(D···A) / nm | ∠DHA / (°) |
|---|---|---|---|---|
| Compound **1** | | | | |
| O6–H6A···N2 | 0.085 | 0.225 | 0.286 6(4) | 129.2 |
| O6–H6B···O3a | 0.085 | 0.241 | 0.283 1(4) | 111.3 |
| O5–H5B···O1a | 0.085 | 0.217 | 0.290 0(5) | 143.3 |
| O6–H6B···O4b | 0.085 | 0.254 | 0.338 8(4) | 173.5 |
| O4–H4B···N1b | 0.085 | 0.203 | 0.286 1(4) | 168.5 |
| O4–H4A···O1c | 0.085 | 0.195 | 0.271 8(4) | 150.9 |
| O3–H3A···O5d | 0.085 | 0.194 | 0.275 0(5) | 158.3 |
| O4–H4A···S1e | 0.085 | 0.300 | 0.349 4(3) | 119.2 |
| O3–H3B···O1e | 0.085 | 0.200 | 0.282 6(4) | 164.1 |
| Compound **2** | | | | |
| O3–H3B···O1 | 0.095 | 0.170 | 0.260 3(3) | 158.4 |
| O3–H3A···N1a | 0.093 | 0.189 | 0.282 1(3) | 175.7 |

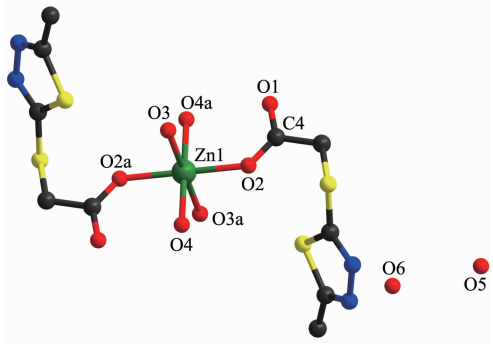
Symmetry codes: a: *x*, *y*, *z*−1; b: −*x*+1, −*y*+2, −*z*+1; c:−*x*+1, −*y*+2, −*z*+2; d: −*x*+1, −*y*+1, −*z*+1; e: *x*−1, *y*, *z* for **1**; a: *x*, −*y*+1, *z*−1/2 for **2**.

## 2　Results and discussion

### 2.1　Structure description of compounds 1 and 2

2.1.1　Crystal structure of $[Zn(mtyaa)_2(H_2O)_4]\cdot 4H_2O$ (**1**)

Each Zn(Ⅱ) ion is six coordinated and exhibits a distorted octahedral geometry. Two oxygens O2 and O2a from two ligands and two coordinated water donor O4 and O4a form the equatorial plane with an average length of 0.205 17 nm and an average O2-Zn1-O4 angle of 90.00(1)°, and the other two water molecules O3, O3a, occupy axial positions with an average length of 0.217 0(2) nm and the O3-Zn1-O3a angle of 180° ( Fig.1). As depicted in Fig.1, mtyaa ligand acts as a monodentate ligand. Numerous hydrogen-bonding interactions occurred such as O(water)···O(carboxyl), O(water)···O(water), O(water)···N and O(water)···S, connect compound 1 into a 2D structure network (Fig. 2). The center-to-center separation for the parallel-arranged ring are 0.354 and 0.344 nm, respectively, indicating the presence of strong face-to face $\pi$-$\pi$ stacking interactions in compound **1**, which further stabilize the 2D crystal structure. The two dimensional planar is further connected into three dimensional network by hydrogen bonds (Fig.3).




Hydrogen atoms have been omitted for clarity; Symmetry codes: a: 1–*x*, 2–*y*, 2–*z*

Fig.1　Structural unit of $[Zn(mtyaa)_2(H_2O)_4]\cdot 4H_2O$ (**1**) with atom numberings

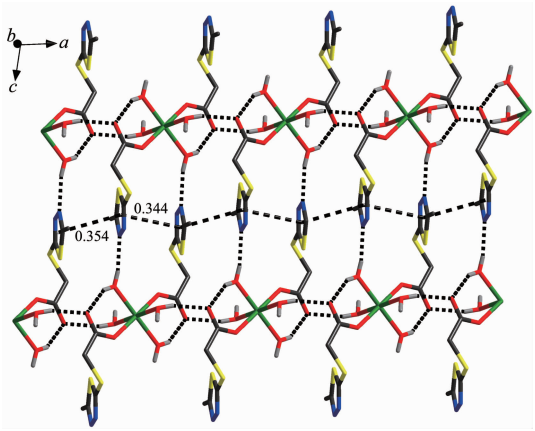
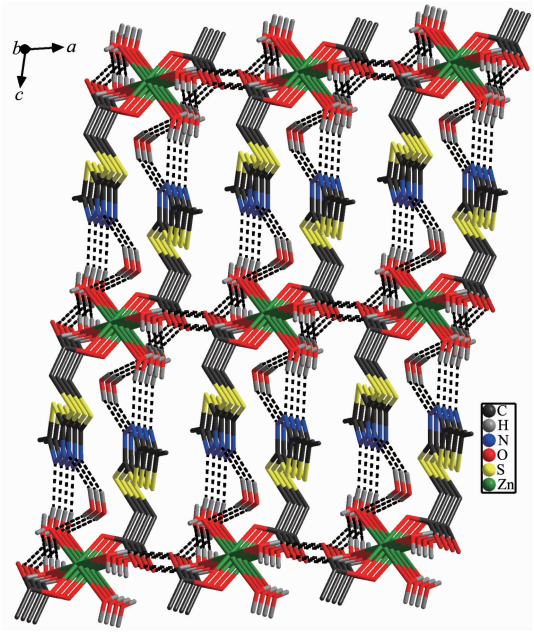



Fig.2　Two dimensional planar structure of compound **1** formulated by hydrogen bonds and $\pi$-$\pi$ stacking interactions

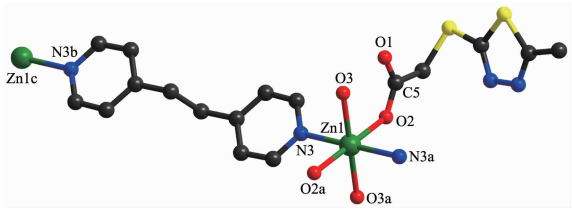
2.1.2　Crystal Structure of $[Zn(bpe)(mtyaa)_2(H_2O)_2]_n$ (**2**)

As illustrated in Fig.4, in compound **2**, each Zn(Ⅱ) is six coordinated and exhibits a distorted octahedral geometry. Two carboxylate oxygens O2 and O2a from




Hydrogen atoms, except for the O-H, have been omitted for clarity

Fig.3 Three dimensional network formed through the O(water)···O(carboxyl) and O(water)···N hydrogen bonds in **1** viewed along *b* axis




Hydrogen atoms have been omitted for clarity; Symmetry codes: a: 0.5−*x*, 1.5−*y*, 1−*z*; b: −*x*, 2−*y*, −*z*; c: −0.5+*x*, 0.5+*y*, −1+*z*

Fig.4 Structural unit of {[Zn(bpe) $(mtyaa)_2(H_2O)_2$]}$_n$ (**2**) with atom numberings

two mtyaa ligands and two coordinated water molecules O3 and O3a form the equatorial plane with an average length of 0.213 38(18) nm and the average angle of O(2)-Zn1-O(3) is 90.00°. Two nitrogen molecules N3 and N3a from two bpe ligands occupy axial positions with the length of 0.216 2(2) nm and the N3-Zn1-N3a angle of 180°. The adjacent Zn(Ⅱ) ions are bridged into one dimensional chain structure by nitrogen atoms coming from mtyaa ligands (Fig.5). Numerous hydrogen-bonding interactions such as O(water)···O(carboxyl) and O(water)···N, connect the adjacent chains into three dimensional network (Fig.6 and 7).

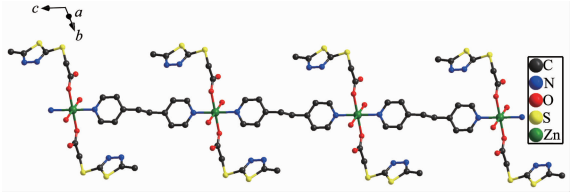
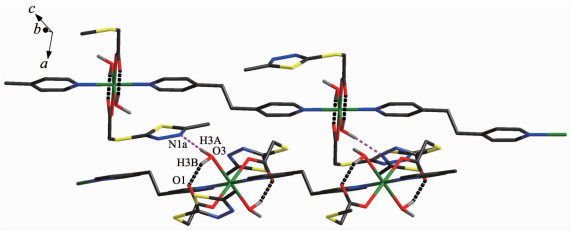
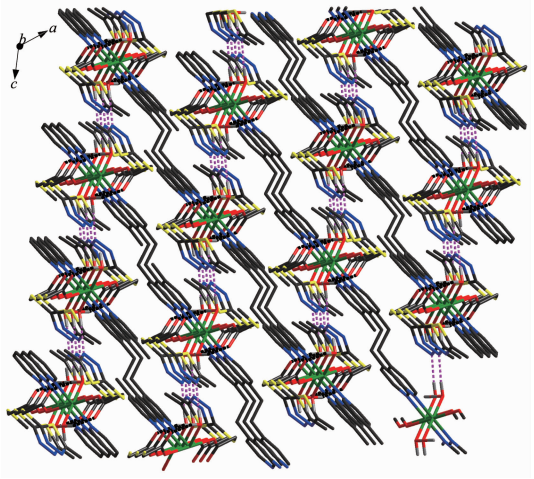



Fig.5 One dimensional chain structure of compound **2**




Symmetry codes: a: 0.5−*x*, 0.5+*y*, 1.5−*z*

Fig.6 Intra and inter chain hydrogen bonds of compound **2**




Hydrogen atoms, except for the O-H, have been omitted for clarity

Fig.7 Three dimensional network formed through the O(water)···O(carboxyl) and O(water)···N hydrogen bonds in **2** viewed along *b* axis

## 2.2 Thermal and XRD analysis

To confirm whether the crystal structures are truly representative of the bulk materials, XRD experiments were carried out for **1** and **2**. The XRD experimental and computer-simulated patterns of the corresponding compounds are shown in Fig.8, which show that the bulk synthesized materials and the measured single crystals are the same. In order to investigate the thermal stability of the complex, their thermal behaviours were studied by TGA (Fig.9). For compound **1**, a rapid weight loss is observed from 30

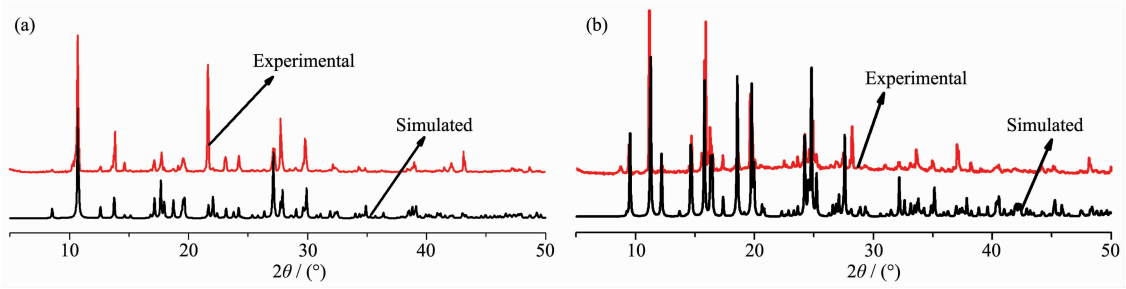



Fig.8　Experimental and simulated powder X-ray diffraction patterns of compound **1** (a) and compound **2** (b) at 293 K

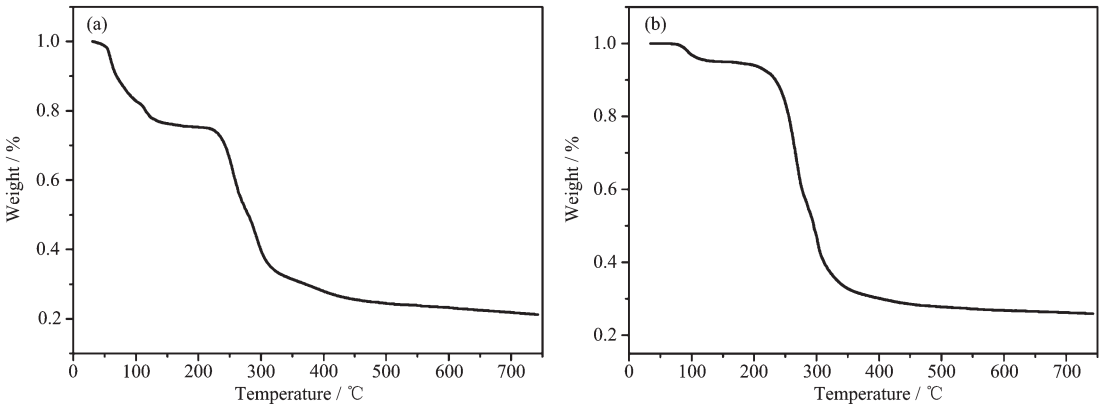



Fig.9　TGA curves of compounds **1** (a) and **2** (b)

to 159 ℃, which is attributed to loss of the coordinated water molecules and free water, with a weight loss of 24.28% (Calcd. 24.49%). The TGA curve of **2** shows that **2** undergoes dehydration between 78 and 135 ℃, which is attributed to loss of the lattice water molecules, with a weight loss of 5.28% (Calcd. 5.42%). The decomposition of the anhydrous residue of **1** and **2** occurs at 221 and 198 ℃, respectively.

## 3　Conclusions

In summary, by using N-donor ligand (bpe) and Hmtyaa ligand, we have synthesized two new coordination compounds $[Zn(mtyaa)_2(H_2O)_4]\cdot 4H_2O$ (**1**) and $[Zn(bpe)(mtyaa)_2(H_2O)_2]_n$ (**2**). Both compounds are connected into three dimensional network by hydrogen bonds between coordinated and free water molecules with carboxylate oxygen atoms.

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