

由 2-甲基-4-噻唑甲酸构筑的过渡金属配合物的合成、晶体结构及与 DNA 作用

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摘要: 以 2-甲基-4-噻唑甲酸(HMTZA, C₅H₅NO₂S)为配体合成了 3 种新型过渡金属配合物[Co(MTZA)₂(H₂O)₂] \cdot 3H₂O (**1**), [Cu(MTZA)₂(H₂O)] \cdot 2H₂O (**2**)和[Zn(MTZA)₂(H₂O)₂] \cdot 3H₂O (**3**)。对配合物进行了元素分析、红外光谱和热重分析表征,用单晶 X 射线衍射方法测定了配合物的晶体结构。结果表明,配合物 **1** 属于单斜晶系,空间群为 *P*2₁/*n*,中心金属 Co(II)离子的配位数为 6,配位构型为略为变形的八面体;配合物 **2** 属于三斜晶系,空间群为 *P* $\bar{1}$, Cu(II)离子的配位构型是一个畸变的四方锥;配合物 **3** 属单斜晶系,空间群为 *P*2₁/*n*,中心金属 Zn(II)离子的配位构型为畸变的八面体。用溴化乙锭荧光探针法测定了配体和配合物与 DNA 作用的荧光光谱,结果显示无论配体还是配合物均能使 EB-DNA 复合体系发生不同程度的荧光猝灭,且配合物的作用强度远大于配体。

关键词: 2-甲基-4-噻唑甲酸; 过渡金属配合物; 晶体结构; DNA 作用

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Syntheses, Crystal Structures and DNA-Binding of Transition Metal Complexes Constructed by 2-Methyl-4-thiazolecarboxylic Acid

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Abstract: Three novel transition metal complexes [Co(MTZA)₂(H₂O)₂] \cdot 3H₂O (**1**), [Cu(MTZA)₂(H₂O)] \cdot 2H₂O (**2**) and [Zn(MTZA)₂(H₂O)₂] \cdot 3H₂O (**3**) have been synthesized by using 2-methyl-4-thiazolecarboxylic acid (HMTZA, C₅H₅NO₂S), structurally confirmed by single crystal X-ray diffraction method, and characterized by elemental analysis, IR analysis and TG. The single crystal X-ray diffraction reveals that complex **1** crystallizes in monoclinic system with space group *P*2₁/*n*. Central Co²⁺ is six-coordinated to constitute a slightly distorted octahedral structure. Complex **2** crystallizes in triclinic system with space group *P* $\bar{1}$, and its coordination number is five, forming a slightly distorted pentahedral coordination geometry. Complex **3** crystallizes in monoclinic system with space group *P*2₁/*n*. Each Zn²⁺ is six-coordinated to constitute a distorted octahedral geometry. In addition, DNA-binding of the ligand and complexes were also studied by EtBr fluorescence probe. The interactions of complexes with DNA were stronger than the ligand. CCDC: 1830898, **1**; 1830896, **2**; 1830891, **3**.

Keywords: 2-methyl-4-thiazolecarboxylic acid; transition metal complex; crystal structure; DNA-binding

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0 Introduction

In recent year, the rational design and synthesis of coordination polymers based on metals and organic ligands have attracted remarkable attention due to their structural diversities^[1-2] and potential applications in gas adsorption^[3-4], catalysis^[5], luminescence^[6-7], bioactivity^[8], electronic and magnetic^[9] fields. Extensive investigations show that the formation, molecular structures and properties of coordination polymers are influenced by many factors, such as the nature of the organic ligands, metal-ligand ratio, crystallization conditions. So, it is possible to develop a novel targeted structure with tunable properties through the proper choice of organic ligands and metal ions.

In the previous reports, extensive works have been carried out by using heterocyclic carboxylate ligands^[10-13], because heterocyclic systems are rich in electrons that can coordinate with metal ions, and easily form non-covalent bonds such as hydrogen bonds, aromatic packing, electrostatic and hydrophobic interactions. Carboxylate groups play important roles in many organic ligands, having many different coordinating modes. What is more, deprotonated carboxylate groups could form hydrogen bonds to participate in supramolecular self-assembly with coordination bonds as acceptors. Therefore, heterocyclic carboxylate ligands are potential candidates for novel functional coordination polymers, which offer a self-assembly solution that can be expected and controlled in certain extent.

Thiazole and its derivatives are an important class of heterocyclic compounds containing N, S atoms, exhibiting a variety of biological activities^[14] such as good antibacterial^[15-16], anti-fungal^[17-18], anti-tumor^[19-21], herbicidal^[22-23] properties. Therefore, it is worth carrying out the research concerning about mechanisms and bonding abilities between transition

metal complexes with thiazole carboxylate system and DNA. The further study could help us to design and synthesize DNA secondary structure probes, nucleic acid location reagents and anti-cancer drugs^[24].

In this paper, a novel ligand 2-methyl-4-thiazolecarboxylic acid (HMTZA) were designed and synthesized, thereby three novel transition metal complexes were synthesized and structurally characterized by some measurements. The interactions of ligand and complexes with ct-DNA were also studied by EtBr fluorescence probe.

1 Experimental

1.1 Materials and measurements

All of the reagents and solvents employed were analytical grade and used without further purification. Elemental analyses of C, H, N were performed on elemental analyzer, Elementar Vario EL III. Crystallographic data of the polymers were collected on a Bruker Smart Apex II CCD diffractometer. FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4 000~400 cm^{-1} . A Mettler Toledo thermal analyzer TGA/SDTA 851^o was used to carry out the thermos analysis with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ from 30 to 800 $^{\circ}\text{C}$ in air atmosphere. Fluorescence spectra were measured at room temperature with an Edinburgh FL-FS920 TCSPC system. ^1H NMR spectra of ligand were acquired with Bruker AV400 NMR instrument in DMSO-d_6 solution with TMS as internal standard.

1.2 Synthesis of the ligand

2-Methyl-4-thiazolecarboxylate and 2-methyl-4-thiazolecarboxylic acid (HMTZA) were synthesized according to literature (Fig.1)^[25].

1.2.1 Synthesis of 2-methyl-4-thiazolecarboxylate

Ethyl bromopyruvate (2.6 mL, 20 mmol) was dissolved in absolute ethanol (15 mL). Meanwhile, thioacetamide (1.50 g, 20 mmol) and absolute ethanol

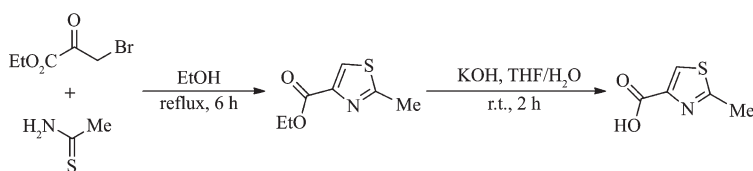


Fig.1 Synthesis of HMTZA

(15 mL) were added to a flask, placed in a water bath at 60 °C and stirred for about 10 min to dissolve completely. Then, the above bromopyruvic acid solution was added dropwise to the flask. After the dropwise addition of it, the temperature of the water bath was raised to 80 °C, and the mixture was further stirred under reflux for 6 hours to obtain a pale yellow transparent liquid, then, cooled to room temperature. The solution was neutralized with NaHCO₃ (3.90 g). The aqueous layer was extracted with Et₂O, and the combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography with petroleum ether/ethyl acetate (2:1, V/V). Yield: 85%.

1.2.2 Synthesis of 2-methyl-4-thiazolecarboxylic acid (HMTZA)

2-Methyl-4-thiazolecarboxylate (3.15 mmol, 0.54 g) was added to the mixture of THF (10 mL) and 10% KOH solution (3.0 mL) at room temperature and stirred continuously for 2 h. HCl (5 mol·L⁻¹) was added until pH=3. The aqueous phase was extracted with ethyl acetate, and dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. Yield: 80%. Anal. Calcd. for C₅H₅NO₂S(%): C, 41.95; H, 3.52; N, 9.78. Found(%): C, 41.87; H, 3.56; N, 9.71. IR(KBr, cm⁻¹): 3 101(s), 1 677(s), 1 500(m), 1 485(m), 1 447(w), 1 411(m), 1 229(s), 1 178(m), 1 109(m), 938(m), 734(w). ¹H NMR: δ 2.82 (3H, s, CH₃); 8.19 (1H, s, H-5); 10.51 (1H, s, COOH).

1.3 Syntheses of the complexes

1.3.1 Synthesis of [Co(MTZA)₂(H₂O)₂]₂·3H₂O (1)

A mixture of HMTZA ligand (0.148 g, 1.0 mmol), Co(CH₃COO)₂·4H₂O (0.125 g, 0.5 mmol) and H₂O (10 mL)/EtOH (10 mL) was put into a 50 mL vessel. Then, KOH solution (10%) was added dropwise until pH=5. And the mixture was stirred and heated in a water bath at 60 °C for about 30 mins. The resulted solution was filtered while hot and cooled to room temperature. After a week, red crystals suitable for single-crystal analysis and physical measurements were obtained. Yield: 40% (based on HMTZA). Anal. Calcd. for C₁₀H₁₈N₂O₉S₂Co(%): C, 27.71; H, 4.16; N,

6.47. Found(%): C, 27.59; H, 4.20; N, 6.42. IR(KBr, cm⁻¹): 3 257(s), 3 121(s), 1 605(s), 1 539(m), 1 489(m), 1 357(s), 1 284(m), 1 197(s), 961(w), 774(w), 752(w), 628(w).

1.3.2 Synthesis of [Cu(MTZA)₂(H₂O)]₂·2H₂O (2)

The preparation method of complex **2** was similar to complex **1** using CuCl₂·2H₂O (0.085 g, 0.5 mmol) instead of Co(CH₃COO)₂·4H₂O, and concentrated ammonia instead of KOH solution was added dropwise until pH=9. After volatilizing naturally for a week, blue crystals suitable for single-crystal analysis and physical measurements were obtained. Yield: 56% (based on HMTZA). Anal. Calcd. for C₁₀H₁₄N₂O₇S₂Cu(%): C, 29.88; H, 3.49; N, 6.97; Found(%): C, 29.79; H, 3.45; N, 6.92. IR (KBr, cm⁻¹): 3 386 (s), 1 638(s), 1 580(s), 1 508(m), 1 444(s), 1 337(m), 1 288(m), 1 185(s), 1 056(w), 853(w), 782(w).

1.3.3 Synthesis of [Zn(MTZA)₂(H₂O)₂]₂·3H₂O (3)

The synthetic method was the same as complex **1**, just replacing Co(CH₃COO)₂·4H₂O with Zn(CH₃COO)₂·2H₂O (0.110 g, 0.5 mmol). After volatilizing naturally for a week, colorless crystals suitable for single-crystal analysis and physical measurements were obtained. Yield: 49% (based on HMTZA). Anal. Calcd. for C₁₀H₁₈N₂O₉S₂Zn(%): C, 27.31; H, 4.10; N, 6.37. Found(%): C, 27.39; H, 4.13; N, 6.31. IR(KBr, cm⁻¹): 3 395 (s), 3 121(s), 1 630(s), 1 527(m), 1 489(s), 1 357(s), 1 286(s), 1 197(s), 1 109(w), 1 006(w), 961(m), 774(m), 753(m), 627(m).

1.4 Single X-ray crystallographic study

The single crystals of the complexes with approximate dimensions suitable for single-crystal analysis were selected and mounted on a Bruker Smart Apex II CCD diffractometer. A graphite monochromated Mo Kα radiation (λ=0.071 073 nm) was used to collect the diffraction data at 296(2) K. Absorption corrections were applied using SADABS^[26]. The correction for Lp factors was applied. The structure was solved by using the SHELXS-97^[27] program package and refined with the full-matrix least-squares technique based on F² using the SHELXL-97^[28] program package. All non-H atoms were anisotropically refined. Remaining hydrogen atoms were added in calculated positions and

refined as riding atoms with a common fixed isotropic thermal parameter. Hydrogen atoms on water molecules were located in a difference Fourier map and included in the subsequent refinement using restraints (O-H 0.085 nm) with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$. Detailed information

about the crystal data is summarized in Table 1, and the selected bond lengths and angles are given in Table 2, 3 and 4. All hydrogen bonds are given in Table 5.

CCDC: 1830898, **1**; 1830896, **2**; 1830891, **3**.

Table 1 Crystallographic data for complexes 1~3

Complex	1	2	3
Empirical formula	C ₁₀ H ₁₈ N ₂ O ₉ S ₂ Co	C ₁₀ H ₁₄ N ₂ O ₇ S ₂ Cu	C ₁₀ H ₁₈ N ₂ O ₉ S ₂ Zn
Formula weight	433.31	401.89	439.75
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a / nm	1.306 31(3)	0.758 24(4)	1.306 77(6)
b / nm	0.796 37(2)	1.026 59(5)	0.797 75(4)
c / nm	1.682 79(4)	1.166 17(6)	1.676 67(8)
α / (°)		65.606(2)	
β / (°)	97.277 0(10)	72.307(2)	97.236(2)
γ / (°)		70.962(2)	
V / nm ³	1.736 52(7)	0.766 25(7)	1.733 97(14)
Z	4	2	4
D_c / (g·cm ⁻³)	1.657	1.742	1.685
Absorption coefficient / mm ⁻¹	1.274	1.732	1.703
$F(000)$	892	410	904
$\theta_{\text{min}}, \theta_{\text{max}}$ / (°)	1.86, 27.44	1.96, 27.74	1.87, 27.68
Reflection collected	26 345	25 335	53 181
R_{int}	0.056 8	0.057 1	0.063 9
Data, restraint, parameter	3 952, 15, 217	3 538, 6, 217	3 975, 15, 217
Goodness-of-fit on F^2	1.055	1.276	1.199
R_1, wR_2 [$I > 2\sigma(I)$]	0.038 4, 0.106 0	0.065 9, 0.164 5	0.048 5, 0.126 5
R_1, wR_2 (all data)	0.045 7, 0.112 8	0.071 0, 0.171 8	0.057 4, 0.136 6
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ / (e·nm ⁻³)	630, -667	769, -2 900	592, -1 277

Table 2 Selected bond lengths (nm) and angle (°) of complex 1

Co1-O1W	0.209 55(17)	Co1-O1	0.210 58(16)	Co1-O3	0.210 53(17)
Co1-O2W	0.211 51(18)	Co1-N2	0.212 4(2)	Co1-N1	0.215 0(2)
O1W-Co1-O1	84.22(7)	O1W-Co1-O3	96.57(7)	O1-Co1-O3	179.17(7)
O1W-Co1-O2W	86.17(8)	O1-Co1-O2W	91.37(7)	O3-Co1-O2W	88.94(8)
O1W-Co1-N2	174.06(7)	O1-Co1-N2	100.17(7)	O3-Co1-N2	79.06(7)
O2W-Co1-N2	89.72(8)	O1W-Co1-N1	90.00(8)	O1-Co1-N1	77.59(7)
O3-Co1-N1	102.14(8)	O2W-Co1-N1	168.64(8)	N2-Co1-N1	94.83(8)

Table 3 Selected bond lengths (nm) and angle (°) of complex 2

Cu1-O3	0.195 6(2)	Cu1-N2	0.200 4(3)	Cu1-O1	0.198 3(2)
Cu1-O1W	0.217 3(3)	Cu1-N1	0.199 9(3)		
O3-Cu1-O1	157.49(12)	O3-Cu1-N1	96.11(10)	O1-Cu1-N1	82.78(10)

Continued Table 3

O3-Cu1-N2	83.39(10)	O1-Cu1-N2	96.29(10)	N1-Cu1-N2	176.37(10)
O3-Cu1-O1W	102.67(12)	O1-Cu1-O1W	99.82(11)	N1-Cu1-O1W	90.37(11)
N2-Cu1-O1W	93.25(11)				

Table 4 Selected bond lengths (nm) and angles (°) of complex 3

Zn1-O1W	0.207 2(2)	Zn1-O2W	0.212 4(2)	Zn1-O3	0.211 7(2)
Zn1-O1	0.210 4(2)	Zn1-N2	0.216 9(3)	Zn1-N1	0.213 0(3)
O1W-Zn1-O3	84.99(9)	O1W-Zn1-O1	96.44(9)	O3-Zn1-O1	178.45(9)
O1W-Zn1-N2	90.52(10)	O3-Zn1-N2	77.24(9)	O1-Zn1-N2	102.13(10)
O1W-Zn1-O2W	85.55(10)	O3-Zn1-O2W	77.24(9)	O1-Zn1-O2W	90.33(10)
N2-Zn1-O2W	167.29(10)	O3-Zn1-N1	99.27(9)	O1-Zn1-N1	79.35(9)
N2-Zn1-N1	95.35(10)	O2W-Zn1-N1	89.33(10)		

Table 5 Hydrogen bond distances (nm) and bond angles (°) of complexes 1~3

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
Complex 1				
O1W-H1WA...O1#1	0.085	0.185	0.269 0(2)	167.0
O1W-H1WB...O3#2	0.082	0.204	0.284 4(2)	168.2
O2W-H2WA...O2#1	0.081	0.196	0.276 8(3)	173.7
O2W-H2WB...O1W	0.084	0.213	0.287 6(3)	148.0
O3W-H3WA...O4#3	0.081	0.198	0.278 0(3)	169.3
O3W-H3WB...O2W#1	0.084	0.194	0.276 7(3)	168.9
O4W#4-H4WA#4...O3W#4	0.083	0.207	0.288 3(3)	167.3
O4W#4-H4WB#4...O5W#5	0.086	0.198	0.273 3(4)	145.8
O5W#5-H5WA#5...O2#5	0.085	0.194	0.277 1(3)	164.9
O5W#5-H5WB#5...O4W	0.084	0.202	0.275 3(4)	145.7
Complex 2				
O1W-H1WA...O2W	0.086	0.191	0.276 3(4)	169.(5)
O1W-H1WB...O3W	0.085	0.192	0.276 0(4)	172.(5)
O2W-H2WA...O1#1	0.073	0.215	0.288 4(4)	179.(6)
O2W-H2WB...O2#2	0.086	0.192	0.276 3(4)	167.(5)
O3W-H3WA...O2#1	0.083	0.221	0.298 5(5)	158.(6)
O3W-H3WB...O4#3	0.085	0.193	0.276 4(4)	171.(6)
Complex 3				
O1W-H1WA...O3#1	0.085	0.184	0.268 5(3)	168.4
O1W-H1WB...O1#2	0.085	0.201	0.284 4(5)	169.1
O2W-H2WA...O4#1	0.082	0.196	0.277 6(4)	175.0
O2W-H2WB...O3W	0.083	0.195	0.277 6(4)	177.6
O3W-H3WA...O2#3	0.082	0.196	0.278 2(4)	174.4
O3W-H3WB...O2#4	0.083	0.214	0.292 3(5)	157.5
O4W#5-H4WA#5...O5W	0.086	0.193	0.273 6(5)	155.5
O4W#5-H4WB#5...O3W#2	0.085	0.207	0.287 4(5)	159.1
O5W-H5WA...O4W#6	0.084	0.225	0.275 4(5)	119.0
O5W-H5WB...O4	0.084	0.196	0.277 0(4)	160.8

Symmetry codes: #1: $-x+3/2, y+1/2, -z+1/2$; #2: $-x+3/2, y-1/2, -z+1/2$; #3: $x+1/2, -y+5/2, z+1/2$; #4: $-x+5/2, y-1/2, -z+1/2$; #5: $-x+5/2, y+1/2, -z+1/2$ for **1**; #1: $x-1, y, z$; #2: $-x+1, -y+1, -z$; #3: $-x, -y+1, -z+1$ for **2**; #1: $-x+1/2, y+1/2, -z+1/2$; #2: $-x+1/2, y-1/2, -z+1/2$; #3: $-x, -y+1, -z$; #4: $x, y-1, z$; #5: $x+1/2, -y-1/2, z+1/2$; #6: $-x+1, -y, -z$ for **3**.

2 Results and discussion

2.1 Crystal structure analysis of the complexes

2.1.1 Structure analysis of complex 1

Single-crystal X-ray analysis reveals that complex **1** crystallizes in the monoclinic system with space group $P2_1/n$ and $Z=4$. Each asymmetric unit contains one Co^{2+} ion, two independent MTZA⁻ ligands, two coordinated water and three crystal water molecules (Fig. 2). The Co^{2+} ion adopts six-coordinated mode with a distorted octahedral coordinated geometry, by two N atoms from two MTZA⁻ ligands (N1, N2) and two carboxyl O atoms from two MTZA⁻ ligands (O1, O3) and two coordinated water (O1W, O2W). The O1W, O2W, N1, N2 are located in the equatorial plane, and the O1, O3 occupy the axial positions. The distance of Co-O is 0.209 55(17) to 0.211 51(18) nm, Co-N is 0.215 0(2) and 0.212 4(2) nm, respectively, according with the distance of Co-O and Co-N in the literature^[29-30].

Intermolecular hydrogen bonding interactions is listed in Table 5 (Fig.3). Interestingly, the non-

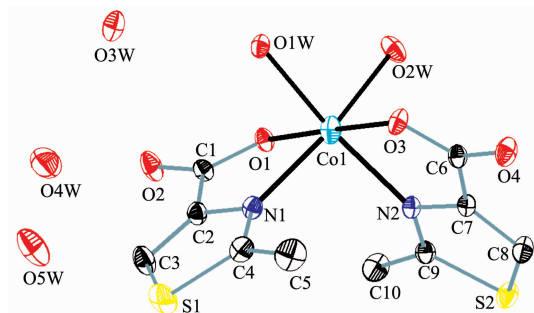
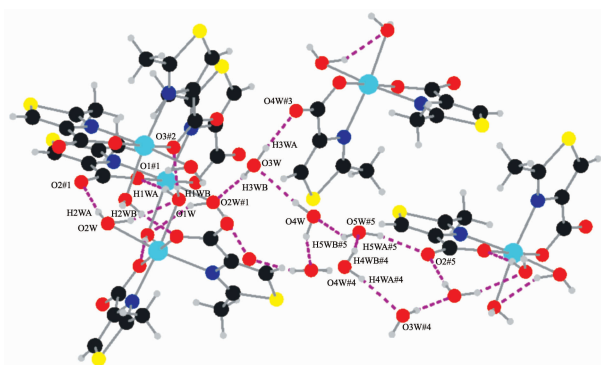


Fig.2 Ellipsoidal structural view of complex **1** with probability level of 30%



Symmetry codes: #1: $-x+3/2, y+1/2, -z+1/2$; #2: $-x+3/2, y-1/2, -z+1/2$; #3: $x+1/2, -y+5/2, z+1/2$; #4: $-x+5/2, y-1/2, -z+1/2$; #5: $-x+5/2, y+1/2, -z+1/2$

Fig.3 Hydrogen bonding interactions of complex **1**

coordinated oxygen atom O2 and O2W from coordinated water and O3W, O4W, O5W from water molecules in complex **1** form a five-membered ring structure through hydrogen bonds. The five-membered rings are regularly connected to each other, forming a 1D chain along the c axis. Rich hydrogen bonds (O1W-H1WA \cdots O1#1, O1W-H1WB \cdots O3#2, O2W-H2WB \cdots O1W, O3W-H3WA \cdots O4#3) make the molecules further connect into a 3D supramolecular network (Fig.4).

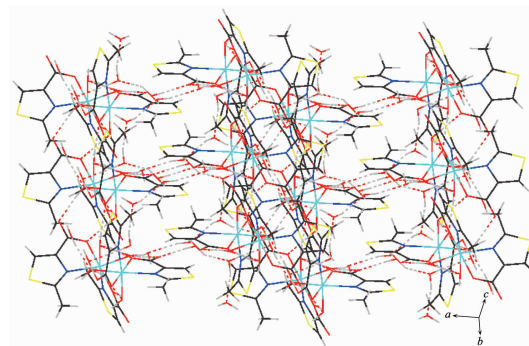


Fig.4 Three-dimensional supramolecular network of complex **1**

2.1.2 Structure analysis of complex 2

Single-crystal X-ray analysis shows that complex **2** crystallizes in the triclinic system with space group $P\bar{1}$, and $Z=2$. Each asymmetric unit consists of one Cu^{2+} ion, two independent MTZA⁻ ligands, one coordinated water and two crystal water (Fig.5). Each Cu^{2+} ion adopts five-coordinated mode with a distorted pentahedral geometry, by one coordinated water (O1W) and two N atoms (N1, N2) from two ligands and two carboxyl O atoms (O1, O3) from the two ligands. The O1, O3, N1 and N2 are located in the

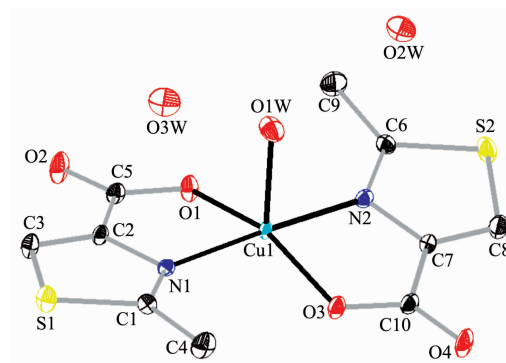
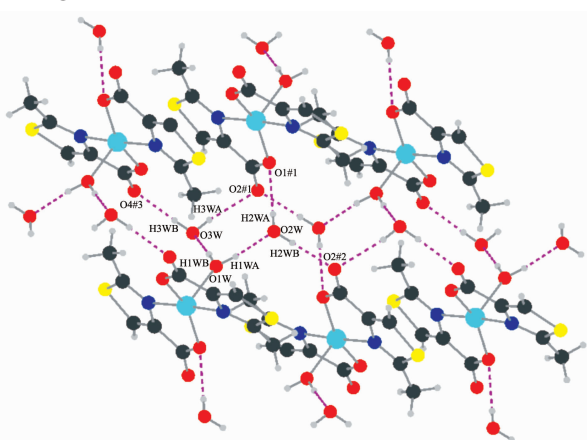


Fig.5 Ellipsoidal structural view of complex **2** with probability level of 30%

basal plane, whereas the O1W from the coordinated water occupies the axial position. The distance of Cu-O is in the range of 0.195 6(2)~0.217 3(3) nm, and Cu-N is 0.199 9(3) and 0.200 4(3) nm, respectively, according with the distance of Cu-O and Cu-N in the literature^[31-32].

As shown in Fig.6, the coordinated water molecule (O1W) and crystal water molecules (O2W and O3W) in complex **2** act as hydrogen donors, contributing hydrogen atoms to O2W, O3W, O1#1, O2#2, O2#1 and O4#3 forming the hydrogen bonds. Interestingly, the abundant hydrogen bonds (H1WA...O2W 0.191 nm, H1WB...O3W 0.192 nm, H2WB...O2#2 0.192 nm, H3WA...O2#1 0.221 nm) form a more stable eight-membered ring chair structure. The more stable structures further connect the molecules into a 2D network through the intermolecular hydrogen bonding interactions.



Symmetry codes: #1: $x-1, y, z$; #2: $-x+1, -y+1, -z$; #3: $-x, -y+1, -z+1$

Fig.6 Hydrogen bonding interactions of complex **2**

2.1.3 Structure analysis of complex **3**

Single-crystal X-ray analysis shows that complex **3** crystallizes in monoclinic, space group $P2_1/n$, and $Z=4$. As shown in Fig.7, each asymmetric unit contains one Zn^{2+} ion, two independent MTZA⁻ ligands, two coordinated water and three crystal water molecules. Each Zn^{2+} ion is six-coordinated with two N atoms from two ligands (N1, N2) and two carboxyl O atoms from the two ligands (O1, O3) and two coordinated water (O1W, O2W). The O1W, O2W, N1, N2 are located in the equatorial plane, whereas the O1, O3

from the ligands occupy the axial positions, forming a distorted octahedral coordinated geometry by considering short-range atomic interactions. The distance of Zn-O ranges from 0.207 2(2) to 0.211 7(2) nm, and Zn-N is 0.216 9(3) and 0.213 0(3) nm, respectively, according with the distance of Zn-O and Zn-N in the literature^[33-34].

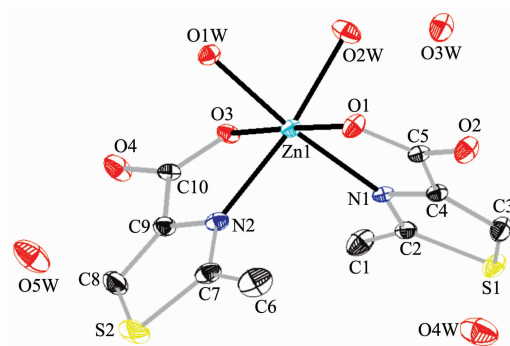
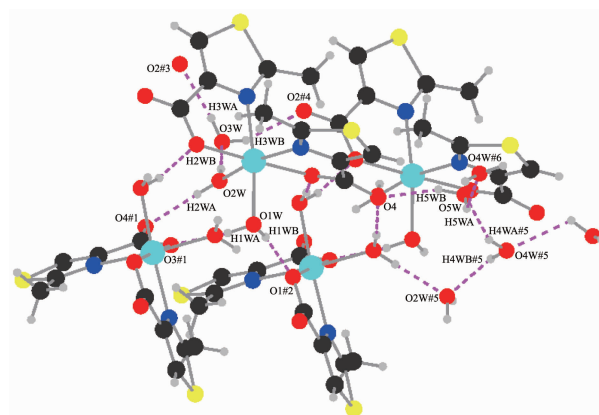


Fig.7 Ellipsoidal structural view of complex **3** with probability level of 30%

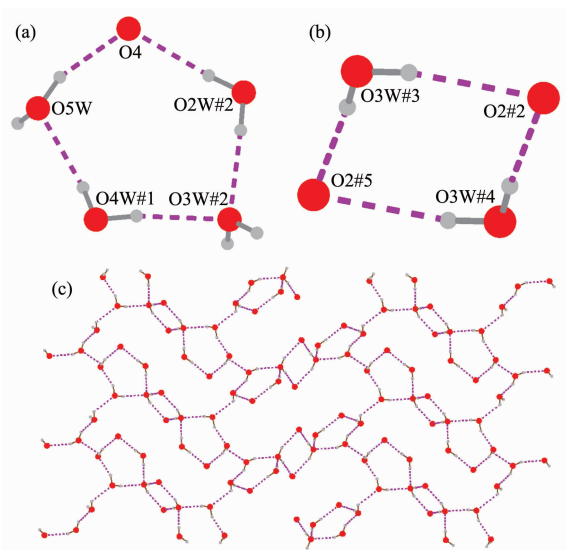
Intermolecular hydrogen bonding interactions is observed in complex **3** (Fig.8). As shown in Fig.9(a) and (b), respectively, a non-coordinated oxygen atom O4 and O2W#2 from coordinated water and O3W#2, O4W#1, and O5W from water molecules in complex **3** form a five-membered ring structure through hydrogen bonding, meanwhile, O2#2, O2#5, O3W#3 and O3W#4 form a four-membered ring structure. It is worth noting that the four-membered ring and the five-membered ring are connected to each other through abundant hydrogen bonds, eventually forming a two-



Symmetry codes: #1: $-x+1/2, y+1/2, -z+1/2$; #2: $-x+1/2, y-1/2, -z+1/2$; #3: $-x, -y+1, -z$; #4: $x, y-1, z$; #5: $x+1/2, -y-1/2, z+1/2$; #6: $-x+1, -y, -z$

Fig.8 Hydrogen bonding interactions of complex **3**

dimensional network (Fig.9(c)). The two-dimensional network structure further connects the entire structure into a 3D supramolecular network through hydrogen bonding ($\text{O1W}-\text{H1WA}\cdots\text{O3\#1}$, $\text{O1W}-\text{H1WB}\cdots\text{O1\#2}$) (Fig.10).



Symmetry codes: #1: $x+1/2, -y-1/2, z+1/2$; #2: $-x+1/2, y-1/2, -z+1/2$; #3: $-x+1/2, y+1/2, -z+1/2$; #4: $x+1/2, -y+1/2, z+1/2$; #5: $x+1/2, -y+3/2, z+1/2$

Fig.9 (a) Hydrogen bonding interaction forming a five-membered ring structure in complex **3**; (b) Hydrogen bonding interaction forming a four-membered ring in complex **3**; (c) Two-dimensional network of hydrogen bonding in complex **3**

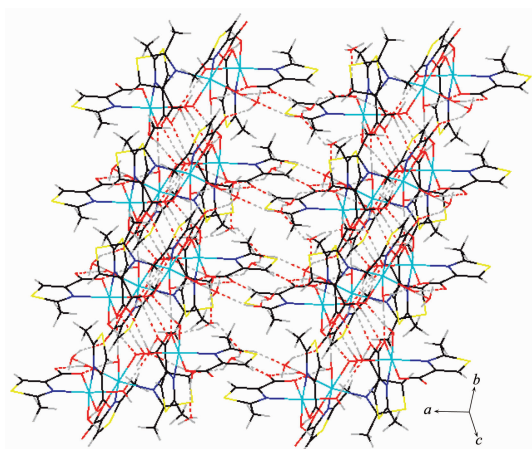


Fig.10 Three-dimensional supramolecular network of complex **3**

2.2 IR spectrum

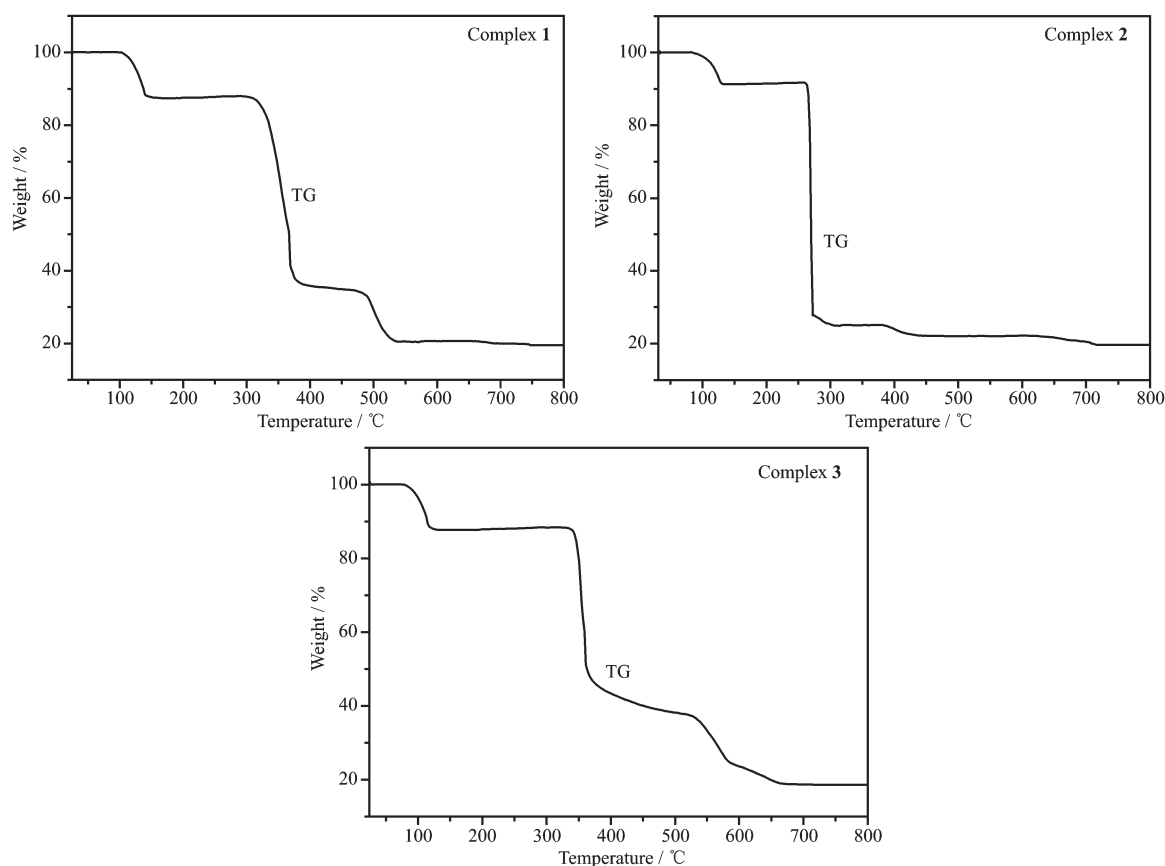
The IR spectrum of complexes and the ligand (HMTZA) can be seen that all complexes have broad

and strong absorption peaks in the range of $3\ 500\sim 3\ 200\ \text{cm}^{-1}$. It can be seen that there is a stretching vibration of the water molecule ($\nu(\text{O-H})$), indicating the presence of water in the complexes^[35].

In the IR spectrum of complexes, the asymmetric and symmetric stretching of COO^- appeared at $1\ 605\ \text{cm}^{-1}$ ($\nu_{\text{asym}}(\text{OCO})$) and $1\ 357\ \text{cm}^{-1}$ ($\nu_{\text{sym}}(\text{OCO})$) for **1**, $1\ 638\ \text{cm}^{-1}$ ($\nu_{\text{asym}}(\text{OCO})$) and $1\ 444\ \text{cm}^{-1}$ ($\nu_{\text{sym}}(\text{OCO})$) for **2**, $1\ 630\ \text{cm}^{-1}$ ($\nu_{\text{asym}}(\text{OCO})$) and $1\ 357\ \text{cm}^{-1}$ ($\nu_{\text{sym}}(\text{OCO})$) for **3**, respectively, which shows the presence of monodentate carboxylate linkage. The C=N characteristic stretching vibration appeared at $1\ 489, 1\ 508, 1\ 489\ \text{cm}^{-1}$, respectively, which shows the coordination of nitrogen atoms from the ligands. Besides, the peak at $750\sim 800\ \text{cm}^{-1}$ is the C-H stretching vibration of the thiazole heterocycle, indicating the presence of the thiazole heterocycle.

2.3 Thermal analysis

Thermal gravimetric (TG) analysis was carried out from 30 to $800\ ^\circ\text{C}$. The TG curves of the title complexes are shown in Fig.11. For **1**, the first weight loss of 12.12% up to $145\ ^\circ\text{C}$ can be assigned to the removal of water molecules (Calcd. 12.46%). A quick weight loss in the temperature range of $315\sim 375\ ^\circ\text{C}$ was observed, indicating the framework of complex **1** starts to collapse. Over $490\ ^\circ\text{C}$, continuous weight loss was also found. The remaining weight of 19.57% corresponds to CoO (Calcd. 19.29%). Complex **2** was stable up to $85\ ^\circ\text{C}$, and the first weight loss of 8.52% in the range of $85\sim 130\ ^\circ\text{C}$ can be assigned to the removal of water molecules (Calcd. 8.96%). The second step in the range of $260\sim 272\ ^\circ\text{C}$ with a quick weight loss corresponds to the decomposition of the ligand. Finally, the remaining weight of 19.64% seems likely to correspond to CuO (Calcd. 19.79%). Complex **3** was stable up to about $78\ ^\circ\text{C}$, and the observed weight loss (12.06%) in the temperature range of $78\sim 125\ ^\circ\text{C}$ can be assigned to the loss of water molecules (Calcd. 12.28%). Then, no significant weight loss was observed until the decomposition of complex **3** occurred at about $335\ ^\circ\text{C}$. A quick weight loss in the range of $335\sim 365\ ^\circ\text{C}$ is observed, which means complex **3** begins to decompose with the collapse of the ligand.

Fig.11 TG curves of complexes **1**, **2** and **3**

Over 365 up to 665 °C, continuous weight loss was also found. The final residue weight of 18.98% corresponds to ZnO (Calcd. 18.42%).

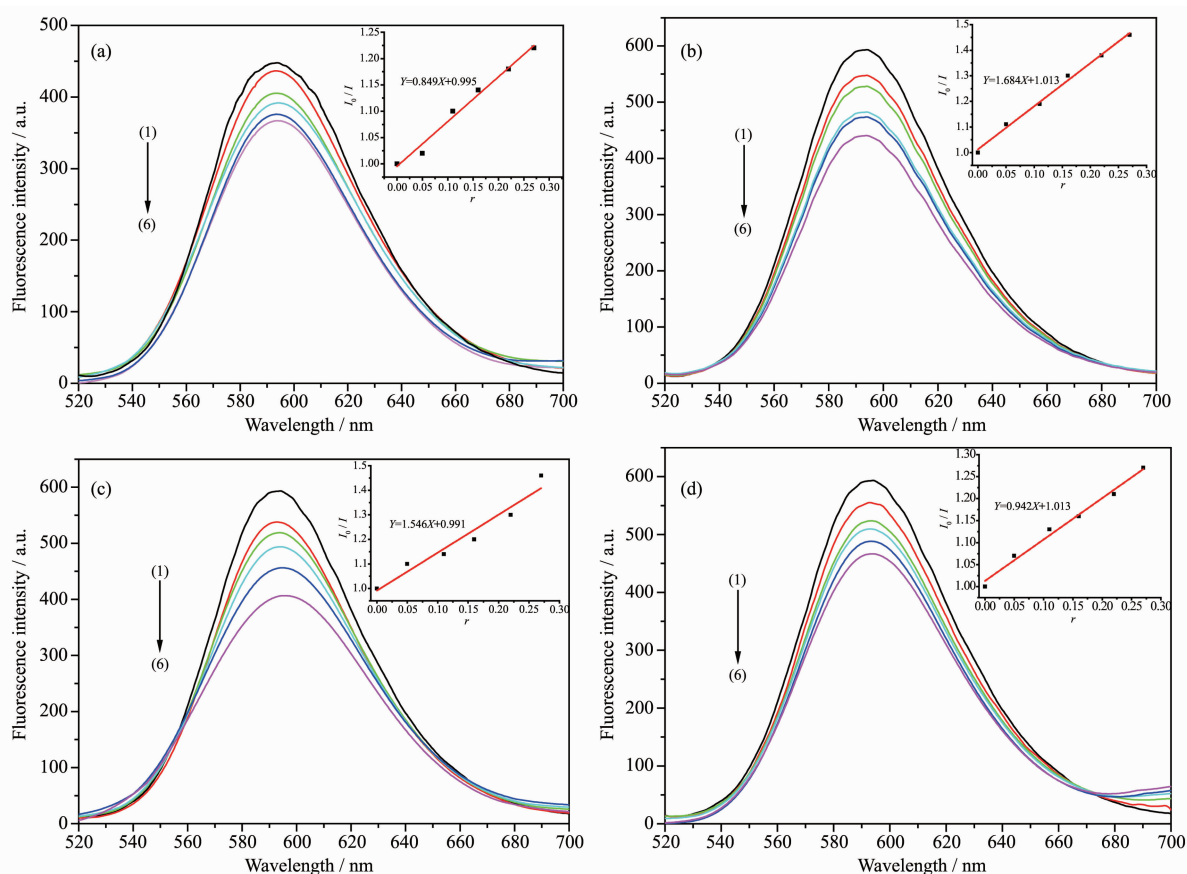
2.4 EB-DNA binding study by fluorescence spectrum

The interactions of the ligand (HMTZA) and complexes with calf thymus DNA (ct-DNA) were studied by ethidium bromide fluorescent probe. The experiment was carried out by adding different volumes of compound solution to 10 mL colorimetric tube, which contained 1.0 mL 200 $\mu\text{g} \cdot \text{mL}^{-1}$ ct-DNA, 1.0 mL 200 $\mu\text{g} \cdot \text{mL}^{-1}$ EB and 2.0 mL Tris-HCl buffer solution (pH=7.40). And then, different amounts of ligand and complexes solution ($0.10 \text{ mmol} \cdot \text{L}^{-1}$) were diluted with distilled water to the scale. The reactions were carried out for 12 h at room temperature. The fluorescence spectra of the composite system were obtained at the wavelength of 530~690 nm with 255 nm as the excitation wavelength.

The effects of the ligand and complexes on the

fluorescence spectra of EB-DNA system are presented in Fig.12. With the increasing concentration of the complexes, the fluorescence intensities of EB bound to ct-DNA at 592 nm showed remarkable decreasing trend, indicating that some EB molecules are released into solution after the exchange with the compounds that result in the fluorescence quenching of EB. According to the classical Stern-Volmer equation^[36]: $I_0/I = 1 + K_{\text{sq}}r$, where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. K_{sq} is the linear Stern-Volmer quenching constant, r is the ratio of the concentration of quencher and DNA. And K_{sq} was obtained as the slope of I_0/I versus r plot.

From the inset of Fig.12, the K_{sq} values are 0.849, 1.684, 1.546 and 0.942 for the HMTZA ligand and complexes **1**, **2** and **3**. The results indicate that the interactions of the complexes with DNA are stronger than the ligand, because the complexes have higher rigidity to bind the base pairs along DNA.



(a) Ligand, (b) Complex **1**, (c) Complex **2**, (d) Complex **3**; $r = c_{\text{compound}} / c_{\text{DNA}}$, from (1) to (6): $r = 0, 0.05, 0.11, 0.16, 0.22, 0.27$, respectively

Fig.12 Influence of the compounds on the fluorescence spectra of EB-DNA system

3 Conclusions

In summary, one kind of thiazole derivative HMTZA was purposely synthesized based on ethyl bromopyruvate. Its three novel complexes, $[\text{Co}(\text{MTZA})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{MTZA})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**2**) and $[\text{Zn}(\text{MTZA})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**3**), were synthesized. The complexes **1** and **3** exhibit extended 3D framework by rich intermolecular hydrogen bonding interactions. Complex **2** displays a 2D framework by intermolecular hydrogen bonding interactions. Complexes **1** and **2** have more stronger interactions with DNA than complex **3**, which can release more free EB molecules from EB-DNA.

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