

基于三唑配体的金属锰(II)、锌(II)配合物的合成、晶体结构与性质研究

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摘要: 在不同反应条件下, 采用三唑衍生物作为配体与乙酸锰和硝酸锌反应, 合成了 2 个具有三维结构的配位化合物 $\{Mn(pytyba)(H_2O)_3\} \cdot 2H_2O$ (**1**) 和 $\{Zn(pytyba)(H_2O)_3\} \cdot 4H_2O$ (**2**), 并通过元素分析、热重分析、荧光性、X 射线单晶衍射对化合物进行分析。结构分析表明 **1** 和 **2** 有许多共同特征: 两个聚合物的晶体均属于单斜晶系, $C2/c$ 空间群, Mn^{2+} 和 Zn^{2+} 均为六配位畸变八面体配位结构, 具有相似的热稳定性、荧光性以及相近的孔隙率。配体中的氧原子与金属离子配位形成一维链状结构, 然后又通过 $O-H \cdots N$ 、 $O-H \cdots O$ 氢键作用和 $\pi \cdots \pi$ 芳香堆积形成超分子结构。此外, 通过测定化合物抗氧化活性(SOD)的经典方法-Marklund 法对配合物 **1** 和 **2** 的抗氧化活性进行了研究。

关键词: 锰(II); 锌(II); 氢键作用; 1,2,4-三唑; 热重分析; 荧光性质; 抗氧化活性

中图分类号: O614.71+1 O614.24+1 文献标识码: A 文章编号: 1001-4861(2014)08-1938-09

DOI: 10.11862/CJIC.2014.225

Synthesis, Crystal Structure and Properties of Two Manganese (II) and Zinc(II) Coordination Compound Based on 1,2,4-Triazole Derivatives

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Abstract: Under different conditions, a ligand derived from triazole was selected and reacted with acetic manganese or zinc nitrate, producing two coordination compounds $\{[Mn(pytyba)(H_2O)_3] \cdot 2H_2O\}_n$ (**1**) and $\{[Zn(pytyba)(H_2O)_3] \cdot 4H_2O\}_n$ (**2**) (Hpytyba=4-(5-(pyrazin-2-yl)-1H-1, 2,4-triazol-3-yl)benzoic acid), which were characterized by element analysis, TGA, fluorescence properties and single X-ray crystal diffraction. A lot of common characteristics exist in **1** and **2**: both **1** and **2** crystallizes in monoclinic space group $C2/c$. Both Mn^{2+} and Zn^{2+} are six-coordinated and exhibit a distorted-octahedral geometry structure. **1** and **2** show similar thermostability, fluorescence properties and almost the same open channels constitute. One oxygen atom of the ligand coordinated with the metal ion and formed 1D chain, then the 1D structure are further connected by $O-H \cdots N$, $O-H \cdots O$ hydrogen bonds and $\pi \cdots \pi$ interactions to form a 3D supramolecular structure. Superoxide dismutase (SOD) mimetic activity of compound **1** and **2** have been investigated by the modified Marklund method. CCDC: 963156, **1**; 972527, **2**.

Key words: manganese (II); zinc (II); H-bonding interactions; 1, 2, 4-triazole; thermogravimetric analysis; photoluminescence; SOD-like activity

收稿日期: 2013-12-11。收修改稿日期: 2014-03-05。

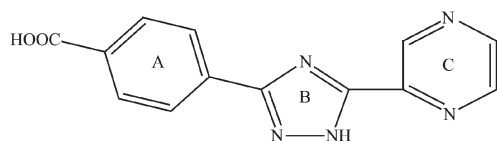
国家自然科学基金(No.21142004), 中央高校基本科研业务费专项资金(SWJTU 2010ZT09, SWJTU12CX048), 四川省科技支撑计划(No. 2013SZ0083)资助。

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0 Introduction

In recent years, considerable progress has been made in the design and engineering of multidimensional metal-organic frameworks (MOFs). This is not only because of their various structures, but also because of their enormous potential applications in areas such as electronic, magnetic, optical, absorbent and catalytic areas^[1-6]. Now, many researchers have been devoted to the metal-organic architectures derived from aromatic heterocyclic ligands including the triazole-based ligands which possess five-membered aromatic rings containing three nitrogen heteroatoms so that it can afford coordinate sites to bridge transition metal ions together^[7-9]. Especially, 1,2,4-triazole derivatives can be used to obtain a wide variety of polynuclear molecules and linear coordination polymers based on its bridging function^[10-11], at the same time, a number of metal coordination compounds have been prepared and characterized due to their interesting properties and novel topologies^[12-16].

In this report Hpytyba (Scheme 1) was selected as an organic triazole-based ligand. It contains triazolyl (Ring B), pyrazinyl (Ring C) and carboxyl building-blocks, which can help to provide more nitrogen and oxygen coordination sites to meet considerable requirements for the construction of coordination compounds. Besides, these nitrogen atoms in triazolyl and pyrazinyl also provide many chances for the formation of hydrogen bonds. At the same time, a phenyl (Ring A) is contained in the ligand which can provide π - π stacking opportunity. Both the possible hydrogen bonds and π - π interactions are useful not only favor for the formation of the versatile metal-organic frameworks but also link low-dimensional structures into high-dimensional



Scheme 1 Chemical structure of Hpytyba: 4-(5-(pyrazin-2-yl)-1H-1,2,4-triazol-3-yl)benzoic acid

supramolecular networks. Besides, some mono-zinc compounds are reported in the precious researches to possess SOD-mimic activities may be tested as model or potential substitute.

As we know, the final structures of coordination polymers are decided not only by the geometrical and electronic properties of the metal ions and ligands, but also by other factors such as the counter ion, the solvent system and the metal-to-ligand ratio. In this work, Hpytyba reacted with different transition metal ions under different conditions and two novel coordination compounds obtained. At last, a survey of the literatures reveals that no work has been carried out on the coordination compounds constructed from the Hpytyba ligand.

1 Experimental

1.1 Materials and physical measurements

The ligand Hpytyba was prepared as described in the literature^[17]. Other reagents and solvents employed were commercially available and used as they were received without further purification. Elemental analyses of C, H, and N were determined with a Perkin-Elmer model 240C instrument. Thermal gravimetric analyses (TGA) were performed on a NETZSCHSTA 449C microanalyzer from room temperature to 650 °C under N₂ atmosphere (flow rate 10 mL · min⁻¹) with a heating rate of 5 °C · min⁻¹. Fluorescence spectra were determined on a Varian ~ Cary Eclipse spectrophotometer.

1.2 Synthesis of the title compounds

1.2.1 Synthesis of {[Mn(pytyba)(H₂O)₃] · 2H₂O}_n (1)

The solution of Hpytyba (13.35 mg, 0.05 mmol) in 3 mL of water whose pH value was carefully adjusted to 7 by dilute sodium hydroxide was added to a solution of manganese acetic (12.25 mg, 0.05 mmol) in 2 mL ethanol and stirred for 0.5h at room temperature. Then the mixture was sealed into a 20 mL Teflon-lined autoclave, kept at 120 °C for 3 days. After the autoclave cooled to room temperature, the solution was filtered and volatilized. Two weeks later, light yellow needle-like crystals of **1** were obtained (Yield: 37.3% based on Mn). Elemental analysis (%)

for $C_{13}H_{17}MnN_5O_7$, Found (Calcd.): C, 37.76 (38.02); H, 3.98(4.14); N, 16.89 (17.06).

1.2.2 Synthesis of $\{[Zn(pytyba)(H_2O)_3] \cdot 4H_2O\}_n$ (**2**)

The solution of $Zn(NO_3)_2 \cdot 6H_2O$ (14.87 mg, 0.05 mmol) in 5 mL of ethanol was layered slowly onto a solution of Hpytyba (13.35 mg, 0.05 mmol) in 5 mL of water whose pH value was carefully adjusted to 6.5 by dilute sodium hydroxide. The resulting mixture was kept at room temperature and light primrose yellow needle-like crystals were obtained after about two weeks (Yield: 45.3% based on Zn). Elemental analysis (%) for $C_{13}H_{21}ZnN_5O_9$, Found (Calcd.): C, 35.24 (34.17); H, 4.15(4.60); N, 14.83 (15.33).

1.2 Structure Determination and Refinement

Data collection for **1** and **2** was carried out on a Bruker SMART APEX II CCD diffractometer

equipped with a graphite-monochromated Mo $K\alpha$ radiation with radiation wavelength 0.071 073 nm at 293 (2) K. The intensity data were collected by the ω scan technique. The structure was solved by direct method and refined with the full-matrix least-squares technique using the SHELXS-97^[18] and SHELXL-97^[19] programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2.

CCDC: 963156, **1**; 972527, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	$C_{13}H_{17}N_5O_7Mn$	$C_{13}H_{21}N_5O_9Zn$
Formula weight	410.26	456.72
Temperature / K	293(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system, Space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$
a / nm	2.003 50(18)	1.930 0(3)
b / nm	1.569 76(8)	1.606 83(14)
c / nm	1.458 25(11)	1.457 24(18)
β / (°)	115.088(9)	115.261(10)
V / nm ³	4.153 5(5)	4.087 0(9)
Z	8	8
D_c / (g·cm ⁻³)	1.312	1.485
Absorption coefficient / mm ⁻¹	0.675	1.255
$F(000)$	1 688	1 888
Crystal size / mm	0.04×0.02×0.02	0.03×0.03×0.02
θ / (°)	2.60 to 25.02	2.97 to 25.02
Limiting indices	$-23 \leq h \leq 20, -18 \leq k \leq 18, -17 \leq l \leq 16$	$-22 \leq h \leq 22, -19 \leq k \leq 19, -17 \leq l \leq 17$
Reflections collected/unique(R_{int})	7 846 / 3 666(0.047 0)	8 934 / 3 592 (0.079 7)
Completeness to $\theta=25.02^\circ$	99.90%	99.90%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Max. and min. transmission	0.986 6 and 0.973 5	0.975 3 and 0.963 3
Data /restraints/parameters	3 666 / 606 / 254	3 592 / 588 / 253
Goodness of fit on F^2	1.112	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1=0.094$ 4, $wR_2=0.289$ 6	$R_1=0.083$ 4, $wR_2=0.209$ 8
R indices (all data)	$R_1=0.152$ 3, $wR_2=0.346$ 5	$R_1=0.157$ 2, $wR_2=0.265$ 9
Largest diff. peak and hole / (e·nm ⁻³)	856 and -450	773 and -654

Table 2 Selected bond lengths(nm) and angles(°) of compound **1** and **2**

1					
Mn(1)-O(1A)	0.208 8(5)	Mn(1)-O(4)	0.219 7(6)	Mn(1)-N(3)	0.219 1(5)
Mn(1)-O(3)	0.220 5(5)	Mn(1)-O(5)	0.221 1(5)	Mn(1)-N(1)	0.236 2(6)
O(1A)-Mn(1)-N(3)	157.6(2)	N(3)-Mn(1)-N(1)	71.3(2)	O(3)-Mn(1)-O(5)	175.3(2)
O(1A)-Mn(1)-O(4)	103.1(3)	N(3)-Mn(1)-O(5)	89.30(19)	O(3)-Mn(1)-N(1)	90.8(2)
O(1A)-Mn(1)-O(5)	88.9(2)	N(3)-Mn(1)-O(3)	91.68(19)	O(4)-Mn(1)-O(3)	88.5(2)
O(1A)-Mn(1)-N(1)	86.5(2)	N(3)-Mn(1)-O(4)	99.1(2)	O(4)-Mn(1)-O(5)	86.8(2)
O(1A)-Mn(1)-O(3)	91.9(2)	O(5)-Mn(1)-N(1)	93.8(2)	O(4)-Mn(1)-N(1)	170.4(2)
2					
Zn(1)-O(1A)	0.200 8(5)	Zn(1)-O(4)	0.211 9(6)	Zn(1)-N(3)	0.206 4(6)
Zn(1)-O(5)	0.219 0(6)	Zn(1)-O(3)	0.214 9(6)	Zn(1)-N(1)	0.228 3(6)
O(1A)-Zn(1)-N(2)	163.6(2)	O(5)-Zn(1)-N(1)	88.9(2)	N(3)-Zn(1)-O(3)	90.7(2)
O(1A)-Zn(1)-O(4)	96.5(2)	O(4)-Zn(1)-O(3)	86.6(3)	N(3)-Zn(1)-O(5)	92.5(2)
O(1A)-Zn(1)-O(3)	89.1(2)	O(4)-Zn(1)-O(5)	87.2(2)	N(3)-Zn(1)-O(1)	99.8(2)
O(1A)-Zn(1)-O(5)	89.5(2)	O(3)-Zn(1)-O(5)	173.5(2)	N(3)-Zn(1)-N(1)	75.3(2)
O(1A)-Zn(1)-N(1)	88.5(2)	O(3)-Zn(1)-N(1)	97.5(2)	O(4)-Zn(1)-N(1)	173.6(2)

1.3 Determination of SOD-like Activity

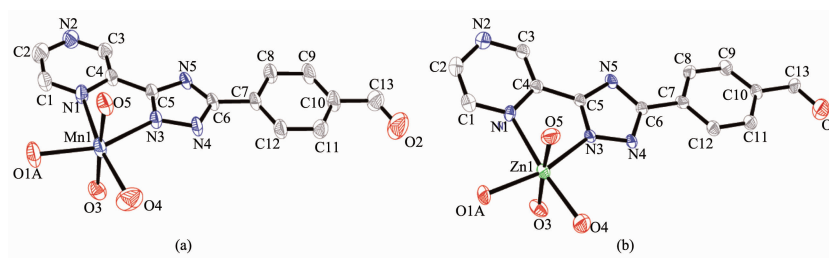
SOD-like activity of compound **1** and **2** were investigated with modified Marklund method^[20]. The solutions of **1** and **2** were prepared in dimethyl sulfoxide before adding the Tris-HCl buffer (pH=8.2). All the reagents were added according to Table 3. Then put them respectively into 25 °C water bath for 10 min after homogeneous mixing and 0.30 mL of pyrogalllic acid solution (4.0 mmol·mL⁻¹) which was also held in 25 °C water bath was added to the mixture immediately. Then the well-mixed mixture was quickly turned into 1 cm quartz cuvette. Finally, the absorbance values of the resulting solutions were measured at 320 nm every 30 seconds after adding in pyrogalllic acid for one minute.

2 Results and discussion

2.1 Crystal structure of **1**

An ORTEP drawing of the structure with atomic numbering are shown in Fig.1a. Single-crystal X-ray diffraction analysis reveals that compound **1** crystallized in monoclinic space group *C2/c*. Two nitrogen atoms, one oxygen atom of the ligand and one oxygen atom of the coordinated water molecule occupying the equatorial position, while the other two water molecules in the axial position, thus exhibited an distorted-octahedral structure.

The symmetric unit in **1** contains one Mn(II) ion, one pytyba anion, three coordinated water molecules and two free water molecules. The average distance of

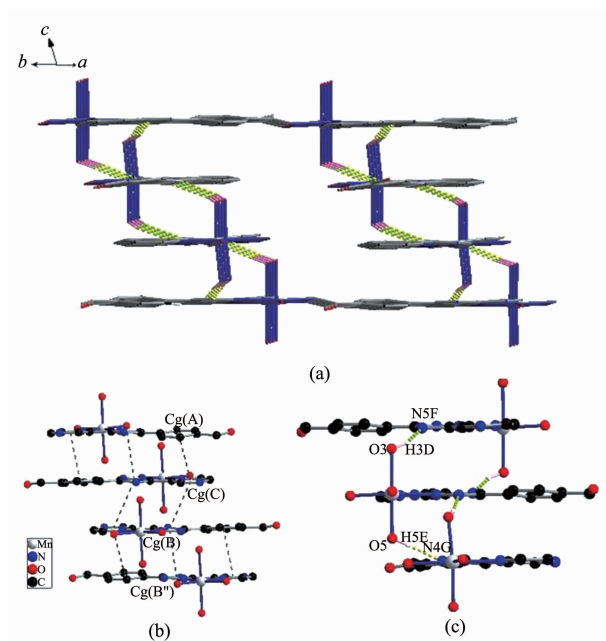


All hydrogen atoms and free H₂O molecular are omitted for clarity, 30% thermal ellipsoids

Fig.1 Molecular structure of **1(a)** and **2(b)**

Mn-O is 0.217 5 nm and that of Mn-N is 0.227 6 nm, similar to those observed in the reported complexes^[21-22]. Triazolyl plays important roles in the crystallization of **1** (Fig.2a). Besides N (3) coordinated with the metal ion, the other two nitrogen[N(4) and N (5)] atoms formed two hydrogen bonds with other two water molecules in the axial position (Fig.2c). Hydrogen bonds are as follows: O (3)-H (3D) \cdots N(5F) 0.277 9(7) nm; O(5)-H(5E) \cdots N(4G) 0.274 0(7) nm; \angle O(3)-H(3D) \cdots N(5F) 136.2°; \angle O(5)-H(5E) \cdots N(4G) =170.9°.

Besides, π - π interactions also exist. The phenyl, triazolyl and pyrazinyl formed three π plane: A, B and C. Each ligand molecule has three kinds of π - π interactions with its upper and lower neighbors (Fig. 2b), thus **1** further stacked and formed 3D architecture. The center distance and dihedral angles between the aromatic rings are as follows: Cg(A) \cdots Cg(C) 0.3649 nm [dihedral angle 3.962(262)°]; Cg(B) \cdots Cg(C) 0.369 3 nm [dihedral angle 3.592(257)°]; Cg(B) \cdots Cg(B) 0.337 1 nm [dihedral angle 4.808(248)°].



Symmetry code: A: x, y, z ; B: $x, 1-y, -0.5+z$; B': $-x, 1-y, -z$; C: $-x, y, 0.5-z$; D: $1-x, -y, 1-z$; E: $1-x, y, 0.5-z$

Fig.2 (a) The packing structure of complex **1**, (b) π - π interactions between neighboring molecules in **1**, (c) O-H \cdots N hydrogen-bond between neighboring molecules in **1**

2.2 Crystal structure of **2**

In the crystal of **2**, the Zn^{2+} has the same coordination environment with the Mn^{2+} , the ORTEP drawing of the structure with atomic numbering are shown in Fig.1b, but two more free water molecules included in symmetric unit than **1** and more hydrogen bonds appeared. The average distance of Zn-O is 0.211 3 nm and the Zn-N is 0.217 3 nm, similar to those observed in the reported complexes^[23]. Hydrogen bonds and π - π interactions also exist in polymer **2**, the distance of some of the hydrogen bonds are as follows: O(3)-H \cdots N(4a) 0.273 8(8) nm; O(5b)-H \cdots N

(5a) 0.282 3(8) nm (Fig.3). Also the phenyl, triazolyl and pyrazinyl formed three π plane: A, B and C, but compared with **1**, only two types of π - π interactions exist between the intersected 1D chains: Cg(B) \cdots Cg(B) 0.337 4(3) nm [dihedral angle 2.748(302)°]; Cg(A) \cdots Cg(C) 0.365 4(3) nm [dihedral angle 4.340(275)°] (Fig. 4). Hydrogen bonds and π - π interactions data in **1** and **2** are listed in Table 4.

Crystal **1** and **2** have many common features but not identical. Both **1** and **2** formed infinite one-dimensional (1D) ribbon-shaped chains by means of coordination effect between carboxyl and metal ion

environment did not lead to virtually identical crystal structure, there are less π - π interactions than **1**, but extra hydrogen bonds can make up for it and also formed stable crystal structure. Another interesting issue is, in the crystallization stacking process of both **1** and **2**, the 1D chains are parallel to each other in the same layer, but in different layers the 1D chains have different tendency. Each 1D chain is parallel to the chain in the upper layer but intersects with the chain in the layer below.

Table 4 Hydrogen bonds and π - π interactions in **1** and **2**

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
1				
O(3)-H(3D) \cdots N(5F)	0.085	0.21	0.277 9(7)	136.2
O(5)-H(5E) \cdots N(4G)	0.085	0.19	0.274 0(7)	170.9
2				
O(3)-H(3C) \cdots N(5)	0.085	0.201	0.282 3(8)	159.1
O(5)-H(5H) \cdots N(4'')	0.085	0.224	0.273 8(8)	117.7
O(3)-H(3D) \cdots O(7)	0.085	0.229	0.026 7(2)	143
O(5)-H(5G) \cdots O(6)	0.085	0.211	0.275 5(0)	132
O(6)-H(6E) \cdots O(7)	0.085	0.208	0.292 0(4)	173
O(7)-H(7A) \cdots O(9)	0.085	0.212	0.289 4(3)	151
O(6)-H(6F) \cdots N(2')	0.085	0.207	0.289 3(5)	162
O(9)-H(9B) \cdots O(2)	0.085	0.183	0.267 1(6)	173
Cg \cdots Cg	$d(\text{Cg(i)}-\text{Cg(j)}) / \text{nm}$	$\alpha / (^\circ)$	$\beta / (^\circ)$	$\gamma / (^\circ)$
1				
B \cdots B	0.3371(4)	10.44	10.44	-3.316(3)
B \cdots C	0.3693(4)	3.7(4)	24.48	27.85
C \cdots A	0.364 9(5)	3.9(4)	21.22	17.44
2				
B \cdots B'	0.337 4(3)	3.374(3)	10.52	10.52
A \cdots C	0.365 4(3)	4.351(5)	19.11	23.25

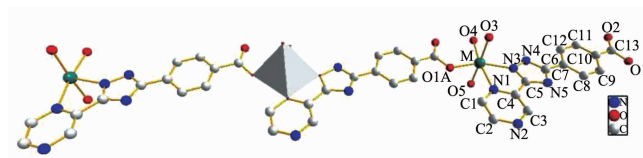
H atoms were omitted for clarity; Symmetry code: A: $x+0.5, y-0.5, z$

Fig.5 View of the coordination of metal atom(M=Mn or Zn) and 1D ribbon-like structure of the complex

2.3 Thermal Gravimetric Analyses

Thermal gravimetric analyses (TGA) of **1** and **2** were performed under N_2 atmosphere with a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range of $30 \sim 650^\circ\text{C}$ (Fig.S1). The TG curves of both compound **1** and **2** show three distinct weight loss steps: the first weight loss step occurs below 100°C with percentage of 9.1% and 13.4%, corresponding to the loss of the free water molecules (Calcd. 8.7% and 14.2%). The second weight loss step in the range of $280 \sim 310^\circ\text{C}$ with percentage of 20.6% and 28.7%, corresponding to the loss of the crystal water molecules (Calcd. 21.9% and 27.6%). When the temperature reached 480°C , the skeleton of compound **1** and **2** collapsed and get the final weight of 22.1% and 18.6%. The end product

might be MnO_2 and ZnO (Calcd. 21.2% and 17.7%).

2.4 Photoluminescent property

As shown in Fig.6, the emission spectrum of the

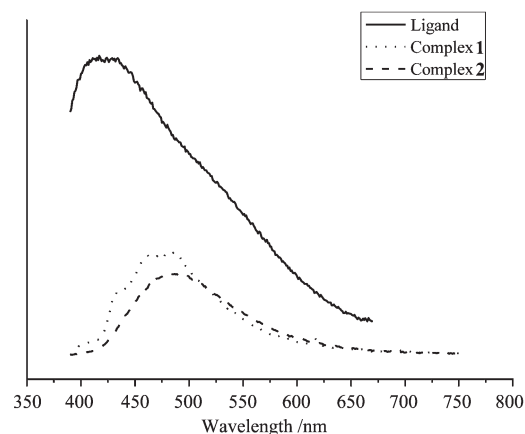


Fig.6 Fluorescence spectra of ligand and complexes

complexes and the Hpytyba was also investigated in the solid state at room temperature. Upon excitation at wavelength of 300 nm, the ligand shows an intense emission peak at 423 nm, which is assigned to the $\pi \cdots \pi^*$ electronic transitions. Compared with the photoluminescence spectra of free ligand, the intraligand $\pi \cdots \pi^*$ transition between the heterocyclic rings in complex **1** and **2** show an obvious bathochromic shift from 423 nm to 486 nm(**1**) and 488 nm (**2**), that's because the ligand coordinated with the metal ions increases electron delocalization on the complexes backbone. On the other hand, the two complexes show weaker photoluminescence emission than the ligand, this might result from a static quenching process, where a non-luminescence coordination compound formed when the ligand coordinated with the metal ions.

2.5 SOD-like Activity

The SOD-like activity of **1** and **2** were assayed according to its anti-oxidation ability of pyrogalllic acid, and the absorbance values were determined at 320 nm and the relationship between the time and the absorbance value were shown in Fig.7 and the equation of linear regression was $A = K_0 t + K_1$, A is the absorbance, K_0 is the speed of auto-oxidation of pyrogalllic acid, t is the time of auto-oxidation, K_1 is

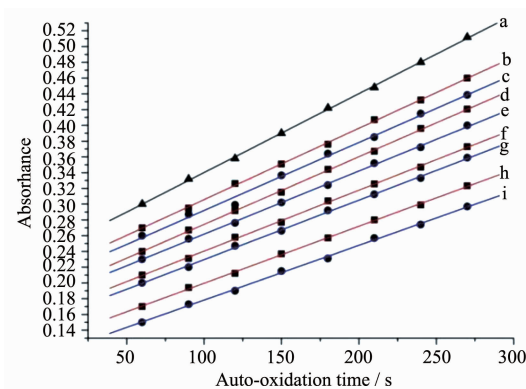


Fig.7 Absorbance vs. auto-oxidation time of pyrogalllic acid in Tris-HCl buffer solution(pH=8.2)

the intercept of the straight line.

As shown in Fig.7, with the increase of the concentration of compound **1** or **2**, the slope of the line exhibits a slightly decreasing tendency which represents the decline of the speed of auto-oxidation. On the other hand, inhibition ratio (η) is calculated from the formula: $\eta = (1 - K_0/K_{\text{auto}}) \times 100\%$. The relationship between inhibition ratio and the concentration of compound **1** and **2** are listed in Table 5, from which it shows the greater the concentration of compound **1** or **2**, the lower velocity of auto-oxidation of pyrogalllic acid, thus indicated that both the Manganese and Zinc compound presented a certain SOD-like activity.

Table 5 Relationship between inhibition ratio and the concentration of **1** and **2**

Compound		1				2			
$C / (\mu\text{g} \cdot \text{mL}^{-1})$		10	20	40	80	10	20	40	80
K_0 / s^{-1}		0.000 9	0.000 86	0.000 77	0.000 73	0.000 84	0.008	0.000 77	0.000 7
$\eta / \%$		10	14	23	27	16	20	23	30

$K_{\text{auto}} = 0.001 \text{ s}^{-1}$

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