第 35 卷第 4 期
2019 年 4 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.35 No.4
703-710

基于 5-氨基-1*H*-1,2,4-三唑-3-羧酸的锌(Ⅱ)/锰(Ⅱ)配合物的合成、晶体结构及性质

杨 康 谭育慧* 王 宾 周海涛 李 超 杨昌善 刘 艺 高继兴 唐云志*
(江西理工大学冶金与化学工程学院,赣州 341000)

摘要:以 5-氨基-1*H*-1,2,4-三唑-3-羧酸(HAtca)为配体,通过水热法和溶液扩散法分别合成了 2 个新的配合物[Zn(Athy)Br]$_n$ (**1**, HAthy=5-氨基-1*H*-1,2,4-三唑-3-醇)和[Mn(Atca)$_2$(H$_2$O)$_2$] (**2**)。单晶结构分析表明配合物 **1** 和 **2** 分别属于正交和单斜晶系,结晶于 *Pbca* 和 *P*2$_1$/*c* 空间群。配合物 **1** 为 2D 层状结构,**2** 是单核配合物。在配合物 **1** 中不存在氢键,而配合物 **2** 中含有丰富的氢键作用,并且通过氢键的作用形成了一个三维的网格结构。同时在固态下,配合物 **1** 和 **2** 分别在 360、462 nm 和 382、402 nm 处有较强的荧光发射峰。

关键词:三唑配合物;晶体结构;荧光
中图分类号:O614.24$^+$1;O614.71$^+$1 **文献标识码**:A **文章编号**:1001-4861(2019)04-0703-08
DOI:10.11862/CJIC.2019.075

Syntheses, Crystal Structures and Properties of Zn(Ⅱ), Mn(Ⅱ) Complexes Based on 5-Amino-1*H*-1,2,4-triazole-3-carboxylic Acid

YANG Kang TAN Yu-Hui* WANG Bin ZHOU Hai-Tao LI Chao
YANG Chang-Shang LIU Yi GAO Ji-Xing TANG Yun-Zhi*
(*School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, Jiangxi* 341000, *China*)

Abstract: Two coordination polymers [Zn(Athy)Br]$_n$ (**1**, HAthy=5-amino-1*H*-1,2,4-triazol-3-ol) and [Mn(Atca)$_2$(H$_2$O)$_2$] (**2**, HAtca=5-amino-1*H*-1,2,4-triazole-3-carboxylic acid) were separately synthesized by hydrothermal method and solution diffusion method using HAtca, ZnBr$_2$ and MnCl$_2$, respectively. X-ray single crystal diffraction analyses indicate both **1** and **2** have different crystal structures. Complex **1** crystallizes in the orthorhombic system, space group *Pbca*. Complex **2** crystallizes in the monoclinic system, space group *P*2$_1$/*c*. Complex **1** is a 2D grid structure without any hydrogen bonds, but complex **2** has a 3D grid structure constructed by highly stable hydrogen bonds. Moreover, **1** and **2** show strong fluorescence emission at 360, 462 nm and 382, 402 nm at room temperature, respectively. CCDC: 1833088, **1**; 1575499, **2**.

Keywords: triazole complexes; fluorescence; crystal structure

0 Introduction

Coordination polymers (CPs) based on multidentate N-heterocyclic ligands have attracted an upsurge of research interest from past few years owing to their intriguing moleculer topologies and potential applications in gas sorption and storage, catalysis and photoactive devices[1-11]. In this context, the triazole functional groups is particularly prominent in medicinal chemistry and materials science due to metabolically

---

收稿日期:2018-11-13。收修改稿日期:2019-01-13。
国家自然科学基金(No.21471070,21761013,21671086,21461010)资助项目。

*通信联系人。E-mail:tyxcn@163.com,tangyunzhi75@163.com

stable surrogates for a carboxylic acid groups and high density energy materials, respectively[12]. Especially, triazoles have attracted increasing attention in coordination chemistry due to the need for new multifunctional materials and the improvement of research equipment and levels[13-20]. Based on the use of triazoles as a ligand, the researchers synthesized a series of functional complexes with properties of optics, magnetism, ferroelectric, dielectric and adsorption[21].

Herein, we report the syntheses, crystal structures, thermal and fluorescence properties of two new complexes, $[Zn(Athy)Br]_n$ (**1**, HAthy=HAthy=5-amino-1*H*-1,2,4-triazol-3-ol) and $[Mn(Atca)_2(H_2O)_2]$ (**2**, HAtca=5-amino-1*H*-1, 2, 4-triazole-3-carboxylic acid). The two complexes were synthesized in different ways. Complex **1** was discovered from hydrothermal synthesis, but **2** was synthesied by solution diffusion. One of the carboxyl groups in the ligands was reduced to hydroxyl in the synthesis of complex **1** for synthesis environment with high temperature and high pressure, it is different to the classical reduction of carboxyl reaction[22]. Complex **1** has a 2D mesh structure, and **2** has a 3D framework with rich hydrogen bonding interactions. To our surprise, Complexes **1** and **2** both have strong photoluminescence properties, and might be potential blue fluorescent materials.

1 Experimental

1.1 Materials and physical techniques

All reagents and solvents were obtained from commercial sources and used directly without further purification. PL emission spectra were measured at room temperature on a fluorophotometer (JASCO, FP-6500). The elemental analyses were measured on a Vario EL Ⅲ elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/MAX 2000 PC X-ray diffraction instrument (Cu *Kα*, $\lambda_{\alpha1}$=0.015 405 98 nm, $\lambda_{\alpha2}$=0.015 444 26 nm), under the generator voltage (40 kV) and tube current (40 mA), by using continuous scan type from 5.0° to 50.0° at room temperature.

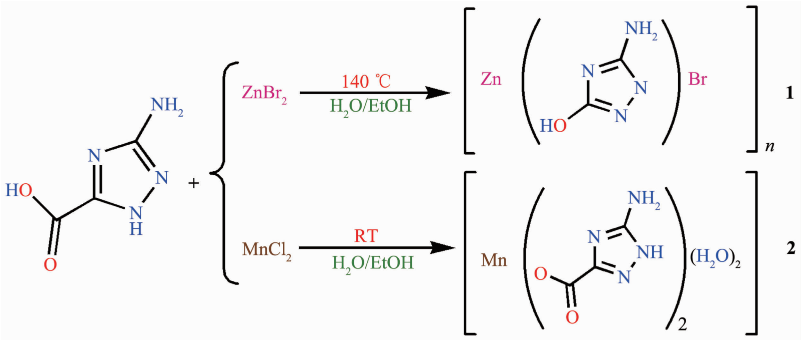
1.2 Syntheses of the complexes

1.2.1 Synthesis of **1**

As shown in Scheme 1, hydrothermal reaction of HAtca (0.025 6 g, 0.2 mmol) and $ZnBr_2$ (0.045 g, 0.2 mmol) in a mixed solution of ethanol (1 mL) and water (6 mL) at 140 ℃ for 2 days gave the colorless block crystals for **1.** Yield: 17.97mg, 70.2% based on HAtca. Anal. Calcd. for $C_{16}H_{18}Br_8N_{32}O_2Zn_8$ (%): C, 10.37; H, 0.98; N, 24.19. Found (%): C, 10.35; H, 0.94; N, 24.09. IR (KBr, cm^{-1}): 3 608(m), 3 450(s), 2 331(m), 1 631(s), 1 487(s), 1 295(s), 1 148(w), 829(w), 712 (m), 463(w).

1.2.2 Synthesis of **2**

As shown in Scheme 1, complex **2** has been synthezied by solution diffusion. Single crystals were obtained by a three-layer crystallization: the lower layer was $MnCl_2$ (0.063 g, 0.5 mmol) dissolved in a mixed solution of ethanol (3 mL) and water (1 mL); the middle layer was a mixed solution of ethanol (3 mL) and water (3 mL); and the top layer was a neutral HAtca aqueous (0.064 g, 0.5 mmol, 5 mL) with pH value adjusted by NaOH (0.10 mL, 1 mol·L^{-1}). Colorless block crystals appeared after 9~10 days. Yield: 13.50 mg, 21.1% based on HAtca. Anal. Calcd. for $C_6H_{10}N_8O_6Mn$(%): C, 20.88; H, 2.92; N, 32.46.



Scheme 1 Preparation of complexes **1** and **2**

Found(%): C, 20.94; H, 2.31; N, 32.52. IR (KBr, cm^{-1}): 3 422(m), 3 370(m), 1 633(s), 1 476(m), 1 411(w), 1 285(s), 1 103(s), 835(w), 719(w), 471(w).

1.3 Crystallography

X-ray single crystal diffraction data for **1** and **2** was collected on a Bruker P4 diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 K using φ-ω scan technique and corrected by Lorentz-polarization and absorption corrections[23-24]. Both crystal structures were solved by direct method and refined by full-matrix method based on F^2 by means of SHELXTL software package[25]. Non-H atoms were refined anisotropically using all reflections with $I>2\sigma(I)$. The organic H atoms were generated geometrically; the water H atoms were generated geometrically and refined with isotropic temperature factors. Crystal data and structure refinement parameters for **1** and **2** are listed in Table 1.

CCDC: 1833088, **1**; 1575499, **2**.

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

Complex	**1**	**2**
Empirical formula	$C_{16}H_{18}Br_8N_{32}O_2Zn_8$	$C_6H_{10}N_8O_6Mn$
Formula weight	1 852.86	345.16
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a / nm	0.942 86(8)	0.945 38(9)
b / nm	1.003 95(8)	0.931 54(9)
c / nm	1.228 81(11)	0.679 09(7)
β / (°)		98.005(2)
V / nm^3	1.163 17(17)	0.592 22(10)
D_c / (g·cm^{-3})	2.645	1.936
Z	1	2
μ / mm^{-1}	10.984	1.164
F(000)	874.0	350
Data, restraint, parameter	1 331, 1, 83	2 891, 2, 97
GOF	1.161	1.072
Final R indexes [$I>2\sigma(I)$]	0.054 1, 0.108 7	0.028 1, 0.071 3
Final R indexes (all data)	0.063 5, 0.112 1	0.033 5, 0.074 3
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	1 490, −2 260	652, −327

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

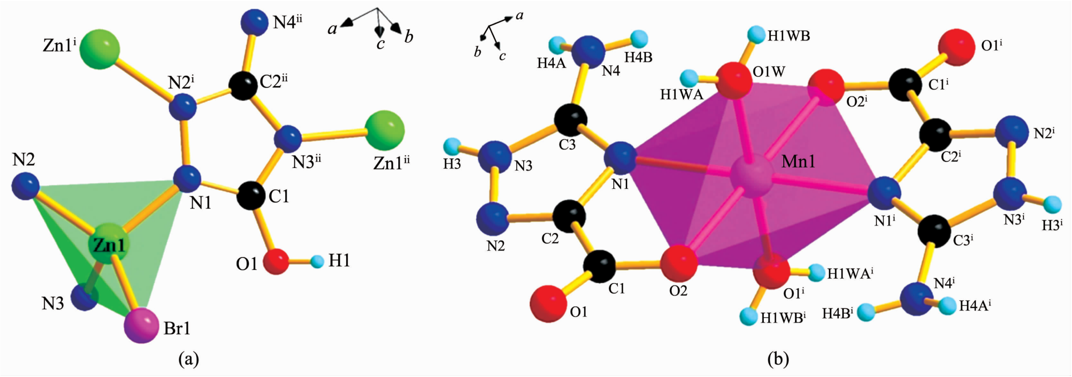
2 Results and discussion

2.1 Crystal structures of 1 and 2

The complexes were synthesized in different ways: **1** was discovered from hydrothermal synthesis, but **2** was synthesized by solution diffusion. It is worth mentioning that HAthy ligand in **1** underwent a de-carbonyl reaction and changed into hydroxyl functional groups under hydrothermal conditions, in which the Zn^{2+} ions act as Lewis acid. The carboxyl groups are prone to de-acidification at high temperature in the presence of Lewis acid. This kind of organic synthesis reaction has been applied in chemical production[26].

Single crystal X-ray diffraction analyses reveal that **1** belongs to orthorhombic crystal system with *Pbca* space group. The asymmetric unit consists of one Zn(Ⅱ) cation, one deprotonated HAthy ligand, and one coordination Br anion. The coordination environment of **1** is depicted in Fig.1a.

Meanwhile, the O atom in the hydroxyl group is not involved in the coordination. Complementary, the N atoms in pyrrol group play a very important role because the deprotonated N atoms balance the charge of complex. As shown in Fig.1a. The center Zn(Ⅱ) cation is coordinated with three N atoms (N2, N3, N4) from HApyo ligand and one Br anion. The selected



Symmetry codes: ^{i} $-x, -y, -z$; ^{ii} $-1/2+x, 1/2-y, -z$ for **1**; ^{i} $-x+1, -y+1, -z+1$ for **2**

Fig.1　Coordinated environment of **1** (a) and **2** (b)

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

Zn1-Br1	0.234 77(12)	N2-C1	0.133 4(8)	N3-N2^{i}	0.138 2(8)
Zn1-N2	0.199 8(6)	N4-C1^{ii}	0.134 3(8)	N3-C2^{iv}	0.132 3(9)
Zn1-N3	0.199 5(6)	N4-C2	0.134 9(8)	C2-N3^{v}	0.132 3(9)
Zn1-N4	0.200 8(5)	C1-N4^{iii}	0.134 3(8)	C2-O1	0.127(3)
N2-N3^{i}	0.138 2(8)	N1-C1	0.133 8(11)		
N2-Zn1-Br1	111.99(17)	C1-N2-N3^{i}	105.6(5)	N1-C1-N4^{iii}	123.5(7)
N2-Zn1-N4	108.2(2)	N3^{i}-N2-Zn1	126.1(4)	N2^{i}-N3-Zn1	125.7(4)
N4-Zn1-Br1	107.45(16)	C1^{ii}-N4-Zn1	130.8(5)	C2^{iv}-N3-Zn1	127.8(5)
N3-Zn1-Br1	114.66(18)	C1^{ii}-N4-C2	103.8(6)	C2^{iv}-N3-N2^{i}	106.5(5)
N3-Zn1-N2	107.7(2)	C2-N4-Zn1	125.4(5)	N3^{v}-C2-N4	111.9(6)
N3-Zn1-N4	107.6(2)	N2-C1-N4^{iii}	112.1(6)	O1-C2-N4	125.7(13)
C1-N2-Zn1	127.5(5)	N2-C1-N1	124.4(7)	O1-C2-N3^{v}	122.2(13)

Symmetry codes: ^{i} $-x, -y, -z$; ^{ii} $1/2+x, 1/2-y, -z$; ^{iii} $-1/2+x, 1/2-y, -z$; ^{iv} $1/2-x, -1/2+y, z$; ^{v} $1/2-x, 1/2+y, z$.

bond lengths and angles for complex **1** are summarized in Table 2. All the data indicate that the center Zn(Ⅱ) adopts slightly distorted tetra-coordinated tetrahedron geometry. The 2D structure of complex **1** can be found that the layers are interlaced with each other through Zn coordinated with the N atoms in deprotonated HAthy ligand observed along *a*, *b* and *c* axis. (Fig.S1).

Four metal ions and four deprotonated HAthy ligand ligands are arranged alternately into a 16-membered big ring (A) structure, and two deprotonated HAthy ligands also form a 6-membered little ring (B) structure with two metal ions, as shown in Fig.2. Each little ring is surrounded by four big rings, meanwhile, each big ring is adjacent to four big rings and four small rings, forming a stable 2D network structure.

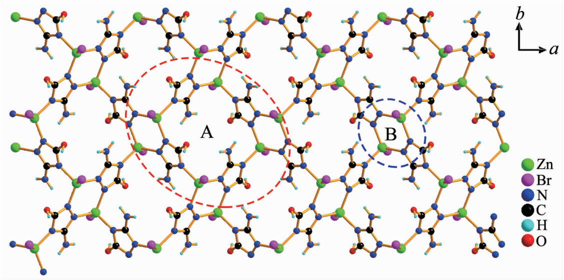


Fig.2　Packing view of 2D sheets along *c* axis in **1**

Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$. The asymmetric unit of **2** is composed of half Mn(Ⅱ) cation, one Atca ligand and one coordinated water molecule. As shown in Fig.1b, the coordination of metal Mn(Ⅱ) and Atca ligands is relatively simple, and the coordinated geometry around Mn(Ⅱ) center can be viewed as a slightly distorted octahedron. The angle between the line L (O1W-Mn-O1W^{i}) and plane S (N1-O2-N1^{i}-O2^{i}) is 86.822(31)°, which is surrounded by two N atoms and two O atoms from two chelating Atca ligands and two coordinated water molecules. Selected bond lengths and angles for **2** are listed in Table 3.

Metal cations are aligned in parallel lines, no matter which axis they are viewed from (Fig.S2). Meanwhile, the alternate arrangement of adjacent pairs of complex can be observed from *a* axis. It can be seen clearly from the structure of **2** that carboxyl group acts as a receptor, amino group as a donor, and the coordinated water as both a receptor and a donor in hydrogen bond. The molecules of each complex are connected to the surrounding molecules by hydrogen bonds (Fig.3a). The bond lengths and bond angles of hydrogen bonds of the complex are 0.25~0.32 nm and 130°~180° (Table 4), respectively, so they can be judged as a moderate hydrogen bond interaction (Fig. 3b). Obviously, two strong hydrogen bonds, O1W⋯O1$^{\rm i}$ and O2$^{\rm iii}$⋯O1W connect two adjacent parts, and form a stable 12-membered ring (#-metal ion-coordination water⋯carboxyl-metal ion-coordination water⋯carboxyl-#), which is then connected into a two-dimensional mesh structure. At the same time, the relatively weak hydrogen bond (N4⋯O1W$^{\rm ii}$) also increases the stability of structure. The other two relatively weak hydrogen bonds, N4⋯N2$^{\rm i}$ and N3⋯O1$^{\rm i}$ connects the two adjacent complex at the upper right to form a 10-membered ring between the two

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

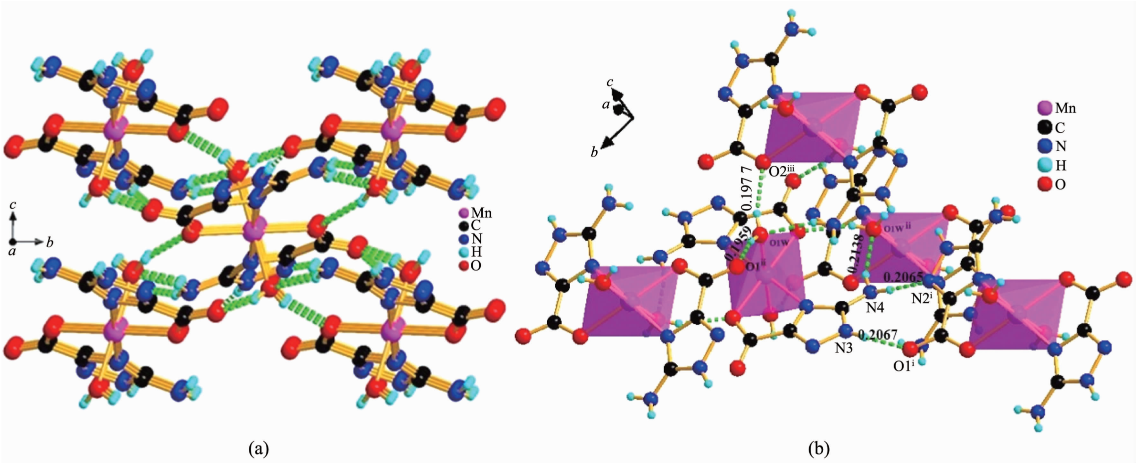
Mn(1)-N(1)	0.220 52(7)	Mn(1)-O(1W)	0.220 86(7)	Mn(1)-O(2)	0.224 06(7)
N(1)-Mn(1)-N(1)$^{\rm i}$	180.0	N(1)-Mn(1)-O(1W)$^{\rm i}$	90.77(3)	O(1W)-Mn(1)-O(2)	86.82(3)
N(1)-Mn(1)-O(1W)	89.23(3)	O(1)-C(1)-O(2)	125.59(8)	O(1W)$^{\rm i}$-Mn(1)-O(1W)	180.0
N(1)-Mn(1)-O(2)$^{\rm i}$	104.66(2)	N(1)$^{\rm i}$-Mn(1)-O(2)$^{\rm i}$	75.34(2)	O(2)$^{\rm i}$-Mn(1)-O(2)	180.00(4)
O(1W)-Mn(1)-O(2)$^{\rm i}$	93.18(3)	N(1)-Mn(1)-O(2)	75.34(2)		

Symmetry codes: $^{\rm i}$ $-x+1$, $-y+1$, $-z+1$.

Table 4　Hydrogen bond parameters of complex 2

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠D–H⋯A/(°)
N(4)–H(4B)⋯O(1W)$^{\rm ii}$	0.085	0.214	0.293 54(12)	159.6
N(4)–H(4A)⋯N(2)$^{\rm i}$	0.084	0.207	0.290 57(12)	168.3
N(3)–H(3)⋯O(1)$^{\rm i}$	0.083	0.207	0.289 30(10)	175.4
O(1W)–H(1WB)⋯O(1)$^{\rm ii}$	0.082	0.196	0.275 41(10)	164.6
O(1W)–H(1WA)⋯O(2)$^{\rm iii}$	0.080	0.198	0.274 94(9)	164.0

Symmetry codes: $^{\rm i}$ x, $1/2+y$, $1/2-z$; $^{\rm ii}$ $1-x$, $-1/2+y$, $1/2-z$; $^{\rm iii}$ x, $3/2-y$, $-1/2+z$.



Symmetry codes: $^{\rm i}$ x, $1/2+y$, $1/2-z$; $^{\rm ii}$ $1-x$, $-1/2+y$, $1/2-z$; $^{\rm iii}$ x, $3/2-y$, $-1/2+z$

Fig.3　Hydrogen bonds in complex **2**

ligands. The above two-dimensional mesh structure is connected to form a highly stable 3D grid structure (Fig.S3).

2.2 Fluorescence properties and powder X-ray diffraction analysis

It is generally assumed that transition metal coordination complexes formed by Zn or Mn centers possess excellent luminescent properties, because core-liked *d*-orbitals and *d*-*d* transitions. At the same time, most of the functional complexes constructed by nitrogen heterocyclic organic ligands also have potential applications in the field of fluorescence emission materials. Organic materials can influence the emission of wavelength. So the reasonable selection of organic ligands and central metals (such as Zn(Ⅱ), Cd(Ⅱ), Mn(Ⅱ)) to synthesize functional complexes is an effective way to obtain luminescent materials.

The photoluminescent properties of **1** and **2** were investigated in solid state at room temperature (Fig.4), while the ligand had no photoluminescent properties. When excited at 281 nm (Fig.S4), complex **1** showed two broad emissions at 400 and 490 nm, which is probably due to a mixture of intra-ligand and ligand-to-ligand charge transition (LLCT)[27-28]. Complex **2** exhibited two broad emissions at 382 and 402 nm when excited at 349 nm, similarly. The emissions of **2** also may be a mixture of intra-ligand and ligand-to-ligand charge transition (LLCT). And complex **2** had a hypsochromic shift of 60 nm considered to mainly originate from the influence of the coordination of the ligand to Mn(Ⅱ) ion[29-30].

In addition, the significant increase in fluorescence lifetime of **1** compared with **2** (the fluorescence lifetime of complex **1** is 400 times that of complex **2**) is tentatively attributed to the relative proportion of central metal cations and the difference of coordination Br anions in coordination polymers (Fig.4). It means that the complexes **1** may have better application prospects in blue light materials.

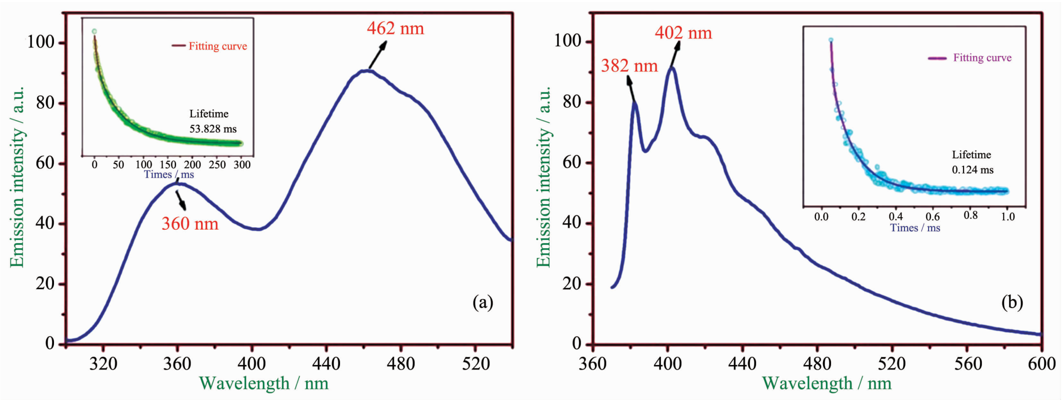


Fig.4 Fluorescence emission spectra and fluorescence lifetime of **1** (a) and **2** (b) in solid-sate at room temperature

2.3 PXRD and thermogravimetric analysis

As shown in Fig.5, the PXRD patterns of complexes of **1** and **2** show that their products are very highly crystalline[31-33].

Complexes **1** and **2** are two-dimensional structures and flexible mononuclear structures respectively, but all have been constructed three dimensions grid structure by hydrogen bonds. Moreover, the hydrogen bonds in the complex **2** also increase the thermal stability of the structure. The thermal stabilities of complex **1** and **2** were tested in a range of 300~1 100 K under a nitrogen atmosphere at a heating of 10 K·min^{-1}, and TGA curves of complexes **1** and **2** are shown in Fig.6.

As shown in Fig.6a, when the temperature was less than 750 K, complex **1** had higher thermal stability. Complex **1** had a downward peak near 769 K in the DTA curve, which may be due to high nitrogen content and high energy content of complex **1**. As well, it was preliminarily determined that the decomposition rate of **1** near 769K was the fastest, and then the structure completely collapsed and

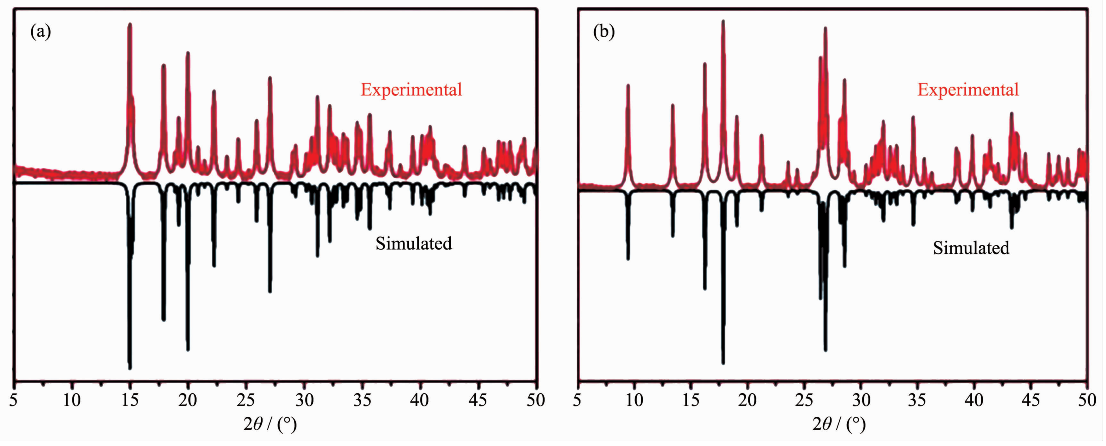


Fig.5　Powder XRD patterns of complexes **1** (a) and **2** (b)

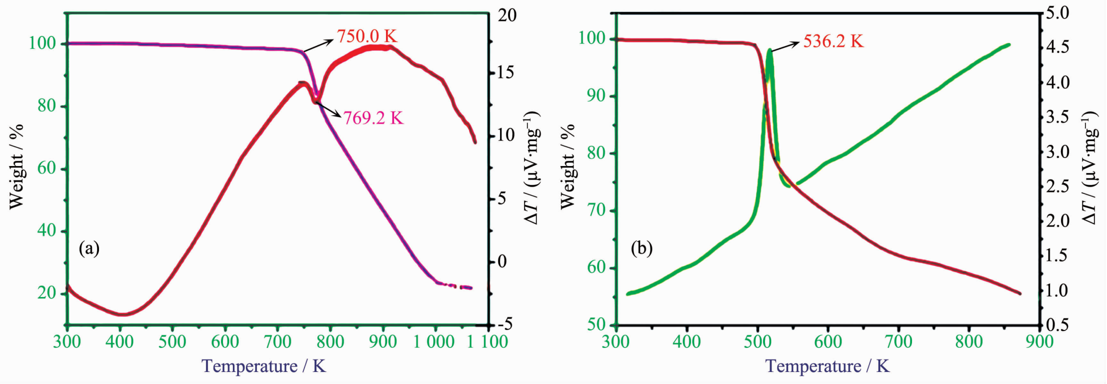


Fig.6　TG and DTA curves of complexes **1** (a) and **2** (b)

decomposed. However, the DTA curve of complex **2** had an upward peak in vicinity of 536 K (Fig.6b), which may be caused by coordination of complex **2** with more water and a relatively high proportion of water in **2**.

The results indicate that complex **1** has better thermal stability than **2**, and the changes of their structure with temperature are represented by DSC, respectively (Fig.S5).

3　Conclusions

In summary, we have successfully synthesized two novel transition metal triazole carboxylic complexes $[Zn(Athy)Br]_n$ (**1**) and $[Mn(Atca)_2(H_2O)_2]$ (**2**) through hydrothermal method and diffusion method, respectively. In the process of hydrothermal synthesis, the carboxyl group on triazole of complex **1** was reduced to the hydroxyl group. Complexes **1** and **2** have blue and violet fluorescence properties, respectively, indicating potential applications in photoluminescence materials.

Acknowledgments: Dr. Tan is grateful for the support from the National Natural Science Foundation of China (Grants No. 21471070, 21761013, 21671086, 21461010), the Academic leader Foundation of Jiangxi Province and Jiangxi Science and Technology Department (Grant No.20153BCB22006).

Supporting information is available at http://www.wjhxxb.cn

References:

[1] Fermi A, Bergamini G, Roy M, et al. *J. Am. Chem. Soc.*, **2014**,**136**(17):6395-6400

[2] Huang Y B, Wang Q, Liang J, et al. *J. Am. Chem. Soc.*, **2016**,**138**(32):10104-10107

[3] Decadt R, Hecke K V, Depla D, et al. *Inorg. Chem.*, **2012**, **51**(21):11623-11634

[4] Tian D, Chen Q, Li Y, et al. *Angew. Chem. Int. Ed.*, **2014**,**53**: 837-841

[5] He K H, Song W C, Li Y W, et al. *Cryst. Growth Des.*,

2012,**12**:1064-1068

[6] Li L, Zhang S, Han L, et al. *Cryst. Growth Des.*, **2013**,**13**: 106-110

[7] Wang H, Yang W, Sun Z M, et al. *Chem. Asian J.*, **2013**,**8**: 982-989

[8] Hasegawa S, Horike S, et al. *J. Am. Chem. Soc.*, **2007**,**129**(9):2607-2614

[9] Zhang Y J, Liu T, Kanegawa S, et al. *J. Am. Chem. Soc.*, **2010**,**132**(3):912-913

[10]Singh R, Mrozinski J, Bharadwaj P K. *Cryst. Growth Des.*, **2014**,**14**(7):3623-3633

[11]Kusaka S, Sakamoto R, Kitagawa Y, et al. *Chem. Asian J.*, **2012**,**7**:907-910

[12]Zhao H, Qu Z R, Ye H Y, et al. *Chem. Soc. Rev.*, **2008**,**37**: 84-100

[13]Gao J X, Xiong J B, Tang Y Z, et al. *Cryst. Growth Des.*, **2016**,**16**:1559-1564

[14]Tang Y Z, Yu Y M, Xiong J B, et al. *Sci. China Chem.*, **2014**,**57**(11):1516-1519

[15]Tan Y H, Yu Y M, Xiong J B, et al. *Polyhedron*, **2014**,**70**: 47-51

[16]Tang Y Z, Xiong J B, Tan Y H, et al. *Inorg. Chim. Acta*, **2014**,**10**:82-87

[17]Tang Y Z, Huang J, Zhou M, et al. *Z. Anorg. Allg. Chem.*, **2013**,**639**(2):409-413

[18]Tan Y H, Wu J S, Yang C S, et al. *Polyhedron*, **2013**,**57**:24-29

[19]Tang Y Z, Huang J, Zhou M, et al. *Bull. Korean Chem. Soc.*, **2013**,**34**(1):295-297

[20]Tang Y Z, Zhou M, Huang J, et al. *Inorg. Chem.*, **2013**,**52**: 1679-1681

[21]Huang D, Zhao P, Astruc D. *Coord. Chem. Rev.*, **2014**,**272**: 145-165

[22]GAO Hong Bin(高鸿宾). *Organic Chemistry*(有机化学). Beijing: Higher Education Press, **2005**:438-439

[23]Sheldrick G M. *SHELXS*-97, *Program for X-ray Crystal Structure Determination*, University of Göttingen, Germany, **1997**.

[24]Sheldrick G M. *SHELXL*-97, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[25]Flack H D. *Acta Crystallogr. Sect. A: Found. Crystallogr.*, **1983**,**A39**:876-881

[26](a)Fraga-Dubreuil J, Garcia-Serna Juan, Garcia-Verdugo Eduardo, et al. *J. Supercrit. Fluids*, **2006**,**39**(2):220-227
(b)Buijs W. *J. Mol. Catal. A: Chem.*, **1999**,**146**(1/2):237-246

[27]JIANG Zheng-Jing(蒋正静), YIN Jing-Zhou(殷竞洲), LI Rong-Qing(李荣清), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2018**,**34**(4):719-727

[28]MAO Pan-Dong(毛盼东), CHEN Ze-Hua(陈泽华), WANG Yuan(王媛), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2017**,**33**(10):1849-1854

[29]Su Z, Fan J, Chen M, et al. *Cryst. Growth Des.*, **2011**,**11**: 1159-1169

[30]Wan X Y, Jiang F L, Chen L, et al. *CrystEngComm*, **2015**, **17**:3829-3837

[31]Xu Z, Ma Y, Xiao Y, et al. *Cryst. Growth Des.*, **2015**,**15**: 5901-5909

[32]Li M, Li D. *Chem. Commun.*, **2008**,**29**:3390-3392

[33]Tan Y H, Xiong J B, Gao J X, et al. *J. Mol. Struct.*, **2015**, **1086**:49-55