

## 4-甲基苯硫乙酸与含氮配体构筑的两个化合物的合成, 晶体结构,热稳定性与发光性质的研究

郑晓咏 何银华 冯云龙\*

(浙江师范大学物理化学研究所,浙江省固体表面反应化学重点实验室,金华 321004)

**摘要:** 合成了 2 个配合物  $[\text{ZnL}_2(\text{Him})_2]$  (**1**) 和  $[(\text{Cu}_2\text{L}_2(\text{phen})_2(\mu_2\text{-Cl})_2) \cdot (\text{Cu}_2(\mu_2\text{-L})_2(\text{phen})_2\text{Cl}_2)]$  (**2**) ( $\text{L}$ =4-甲基苯硫乙酸,  $\text{Him}$ =咪唑,  $\text{phen}$ =1,10-邻菲咯啉), 进行了元素分析、红外、热重等表征, 并测定了其晶体结构。配合物 **1** 晶体属于单斜晶系, 空间群为  $C2/c$ 。配合物 **2** 晶体属于三斜晶系, 空间群为  $P\bar{1}$ 。配合物 **1** 是由  $\text{N-H}\cdots\text{O}$  氢键作用形成的一维带状结构。配合物 **2** 的单胞中含有 2 个分别由氯原子与羧基氧原子桥联的双核独立分子, 通过  $\text{C-H}\cdots\text{O}$ ,  $\text{C-H}\cdots\text{Cl}$  氢键以及  $\text{C-H}\cdots\pi$  作用而构成三维结构。室温固体荧光分析显示配合物 **1** 具有较强荧光吸收。

**关键词:** 4-甲基苯硫乙酸; 晶体结构; 热稳定性; 发光性

中图分类号: O614.24<sup>+</sup>1; O614.121

文献标识码: A

文章编号: 1001-4861(2008)09-1400-06

## Syntheses, Crystal Structures, Thermal Stability and Photoluminescence of Two Complexes Constructed from 4-tolythioacetic Acid and N-donor Ligands

ZHENG Xiao-Yong HE Yin-Hua FENG Yun-Long\*

(Institute of Physical Chemistry, Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces,

Zhejiang Normal University, Jinhua, Zhejiang 321004)

**Abstract:** Two complexes  $[\text{ZnL}_2(\text{Him})_2]$  (**1**) and  $[(\text{Cu}_2\text{L}_2(\text{phen})_2(\mu_2\text{-Cl})_2) \cdot (\text{Cu}_2(\mu_2\text{-L})_2(\text{phen})_2\text{Cl}_2)]$  (**2**) ( $\text{L}$ =4-tolythioacetate,  $\text{Him}$ =imidazole,  $\text{phen}$ =1,10-phenanthroline) were synthesized and characterized by single crystal X-ray diffraction, elemental analysis, IR spectra and TGA. The crystal of complex **1** belongs to monoclinic, space group  $C2/c$ , with  $a=3.101\ 2(6)$  nm,  $b=0.578\ 2(1)$  nm,  $c=1.463\ 8(3)$  nm,  $\beta=100.962(2)^\circ$ ,  $V=2.577\ 0(8)$  nm<sup>3</sup>,  $Z=4$ ,  $M_r=563.98$ ,  $D_c=1.454$  g·cm<sup>-3</sup>,  $F(000)=1\ 168$ ,  $\mu=1.152$  mm<sup>-1</sup>, the final  $R=0.033\ 2$  and  $wR=0.08\ 6$  for 2 154 observed reflections with  $I>2\sigma(I)$ . The crystal of complex **2** belongs to triclinic, space group  $P\bar{1}$ , with  $a=1.0170\ 9(1)$  nm,  $b=1.0464\ 2(1)$  nm,  $c=1.9920\ 2(3)$  nm,  $\alpha=88.649(1)^\circ$ ,  $\beta=84.023(1)^\circ$ ,  $\gamma=66.699(1)^\circ$ ,  $V=1.936\ 25(4)$  nm<sup>3</sup>,  $Z=1$ ,  $M_r=1\ 841.66$ ,  $D_c=1.579$  g·cm<sup>-3</sup>,  $F(000)=940$ ,  $\mu=1.394$  mm<sup>-1</sup>, the final  $R=0.030\ 7$  and  $wR=0.084\ 1$  for 7 495 observed reflections with  $I>2\sigma(I)$ . **1** shows an undulating-ribbon structure constructed from  $\text{N-H}\cdots\text{O}$  hydrogen bonds. **2** consist of two dinuclear molecules bridged via chlorine and carboxylate oxygen atoms, respectively. Furthermore,  $\text{C-H}\cdots\text{O}$ ,  $\text{C-H}\cdots\text{Cl}$  hydrogen bonding and  $\text{C-H}\cdots\pi$  interactions drive **2** to be a 3D architecture. Photoluminescence studies revealed that complex **1** exhibits strong fluorescent emission bands in the solid state at room temperature. CCDC: 690004, **1**; 690005, **2**.

**Key words:** 4-tolythioacetic acid; crystal structure; thermal stability; photoluminescence

收稿日期: 2008-01-21。收修改稿日期: 2008-05-23。

浙江省自然科学基金资助项目(No.Y406355)。

\*通讯联系人。E-mail: sky37@zjnu.cn

第一作者: 郑晓咏, 女, 37 岁, 硕士研究生; 研究方向: 结构化学。

In recent years, coordination polymers obtained by reactions of benzenecarboxylate ligands and transition metal centers have attracted considerable interest due to its unique topologies and some potential applications<sup>[1-4]</sup>. As known, flexible carboxylate groups have superiority in plasticity and configuration. So some flexible carboxylate ligands have been adopted to construct unique metal-organic coordination polymers, such as  $[\text{Sr}_2(4\text{-CPOA})_2(\text{H}_2\text{O})_5]_n$ <sup>[5]</sup> and  $[\text{Cu}(\text{CBOAH})(\text{H}_2\text{O})]_n$ <sup>[6]</sup> based on carbxyphenoxycetate ligands,  $[\text{Mn}(\text{BDDA})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ <sup>[7]</sup> derived from benzene-1,2-dioxydiacetic acid and porous lanthanide-organic framework  $[\text{Ln}_2(\text{PDA})_3(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ <sup>[8]</sup> constructed from 1,4-phenyl-endiacetic acid. We are currently interested in using flexible carboxyl ligands to construct metal-organic frameworks with unique network topologies and physical properties. Here, we choose 4-tolythioacetic acid as the main organic ligand. And in this paper, we describe the synthesis, structure, thermal stability and photoluminescence of two new complexes,  $[\text{ZnL}_2(\text{Him})_2]$  (**1**) and  $[(\text{Cu}_2\text{L}_2(\text{phen})_2(\mu_2\text{-Cl})_2) \cdot (\text{Cu}_2(\mu_2\text{-L})_2(\text{phen})_2\text{Cl}_2)]$  (**2**).

## 1 Experimental

### 1.1 Materials and measurement

All starting materials were obtained commercially from Aldrich Chemical Company and used without further purification. Elemental analyses (C, H, N, S) were carried out on a EuroEA3000 element analyzer. IR spectra were obtained from KBr pellets on a Nicolet 5DX FTIR spectrometer. The crystal data collection was carried out on a Bruker SMART APEX-II CCD diffractometer. The thermogravimetric measurements were performed on preweighed samples in an oxygen stream using a Netzsch STA449C apparatus with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . And fluorescent data were collected on a FS920 Spectrofluorometer (Edinburgh Instruments) with a Xe-CW-source (450 W) and RR928P photomultiplier for signal detection.

### 1.2 Synthesis of $[\text{ZnL}_2(\text{Him})_2]$ (**1**)

A mixture of 4-tolythioacetate acid (0.182 g, 1.0 mmol) and NaOH (0.04 g, 1.0 mmol) in  $\text{C}_2\text{H}_5\text{OH}$  (15 mL) /  $\text{H}_2\text{O}$  (5 mL) was stirred for 0.5 h.  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.219 g, 1.0 mmol) and imidazole (0.070 g, 1.0 mmol) were added to the solution. Then the solution was stirred at room temperature for 2 h, resulting in white precipitates. The reaction mixture was filtered and well-shaped colorless crystals of **1** were obtained from the mother liquor by slow evaporation at room temperature for several days (yield 48.1% based on 4-tolythioacetate acid). Ana. Calcd. (%) for  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$ : C 51.11; H 4.65; N 9.93; S 11.37. Found (%): C 51.20; H 4.61; N 10.01; S 11.40.

### 1.3 Synthesis of $[(\text{Cu}_2\text{L}_2(\text{phen})_2(\mu_2\text{-Cl})_2) \cdot (\text{Cu}_2(\mu_2\text{-L})_2(\text{phen})_2\text{Cl}_2)]$ (**2**)

This complex was prepared similarly to complex **1** by using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.169 g, 1.0 mmol) instead of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , and 1,10-phenanthroline instead of imidazole. Green prism crystals were obtained (yield 62% based on 4-tolythioacetate acid). Anal. Calcd (%) for  $\text{C}_{84}\text{H}_{68}\text{Cl}_4\text{Cu}_4\text{N}_8\text{O}_8\text{S}_4$ : C 54.78; H 3.72; N 6.08; S 6.96. Found (%): C 54.90; H 3.70; N 6.11; S 6.94.

### 1.4 Structural determination

Crystal data were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\text{ nm}$ ) at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structure was solved by direct methods using the SHELXS-97 program<sup>[9]</sup> and refined by full-matrix least-squares method on  $F^2$  using SHELXL-97<sup>[10]</sup>. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. The crystal data and structure refinement parameters are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2. The information of hydrogen bond is listed in Table 3.

Table 1 Crystallographic data for complex **1** and **2**

Empirical formula	$\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$	$\text{C}_{84}\text{H}_{68}\text{Cl}_4\text{Cu}_4\text{N}_8\text{O}_8\text{S}_4$
Formula weight	563.98	1841.66
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$

Continued Table 1

$a / \text{nm}$	3.101 2(6)	1.017 09(1)
$b / \text{nm}$	0.578 2(1)	1.046 42(1)
$c / \text{nm}$	1.463 8(3)	1.992 02(3)
$\alpha / (^{\circ})$		88.649(1)
$\beta / (^{\circ})$	100.962(1)	84.023(1)
$\gamma / (^{\circ})$		66.699(1)
$V / \text{nm}^3$	2.577 0(8)	1.936 25(4)
$Z$	4	1
$\mu / \text{mm}^{-1}$	1.152	1.394
$F(000)$	1 168	940
$\theta$ range / $(^{\circ})$	2.68~27.97	1.03~27.40
Reflections collected / unique	8 348 / 3 076 ( $R_{\text{int}}=0.023$ 9)	25 172 / 8 705 ( $R_{\text{int}}=0.049$ 0)
Observed reflections	2 154	7 495
Parameters refined	164	505
Goodness-of-fit on $F^2$	1.061	1.008
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R=0.033$ 2, $wR=0.086$ 0	$R=0.030$ 7, $wR=0.084$ 9
$R$ indices (all data)	$R=0.051$ 9, $wR=0.090$ 9	$R=0.036$ 7, $wR=0.087$ 7
Max., Min. $\Delta\rho / (\text{e} \cdot \text{nm}^{-3})$	409, -275	355, -468

Table 2 Selected bond distances (nm) and bond angles ( $^{\circ}$ )

Complex 1					
Zn(1)-O(2)	0.195 9(2)	Zn(1)-N(1)	0.199 9(1)		
O(2)-Zn(1)-N(1)#1	104.66(6)	O(2)#1-Zn(1)-N(1)#1	121.80(7)	O(2)-Zn(1)-O(2)#1	101.05(9)
O(2)#1-Zn(1)-N(1)	104.66(6)	N(1)#1-Zn(1)-N(1)	104.30(9)	O(2)-Zn(1)-N(1)	121.80(7)
Complex 2					
Cu(2)-O(4)	0.192 8(1)	Cu(2)-N(3)	0.201 8(2)	Cu(2)-N(4)	0.202 8(2)
Cu(2)-Cl(2)	0.228 3(1)	Cu(2)-Cl(2)#1	0.285 6(1)	Cu(1)-O(2)	0.196 6(2)
Cu(1)-O(2)#2	0.243 2(2)	Cu(1)-N(1)	0.202 9(3)	Cu(1)-N(2)	0.203 2(2)
Cu(1)-Cl(1)	0.226 3(1)				
O(4)-Cu(2)-N(3)	171.97(6)	O(4)-Cu(2)-Cl(2)	93.68(4)	N(3)-Cu(2)-Cl(2)	94.31(4)
N(4)-Cu(1)-Cl(2)	175.70(4)	O(4)-Cu(2)-Cl(2)#1	90.43(1)	Cl(2)-Cu(2)-Cl(2)#1	90.98(2)
O(2)-Cu(1)-N(1)	90.29(6)	O(2)-Cu(1)-N(2)	170.99(6)	Cl(1)-Cu(1)-O(2)#1	98.77(4)
O(2)-Cu(1)-Cl(1)	95.35(4)	N(1)-Cu(1)-Cl(1)	169.68(5)	N(2)-Cu(1)-Cl(1)	93.66(5)
O(2)-Cu(1)-O(2)#1	75.13(6)	N(1)-Cu(1)-O(2)#1	91.03(5)	N(2)-Cu(1)-O(2)#1	103.73(6)

Symmetry code: (1) #1:  $-x+1, y, -z+1/2$ ; (2) #1:  $-x, -y+1, -z+1$ ; #2:  $-x+1, -y, -z$ .

Table 3 Hydrogen bond distances and bond angles

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle (\text{DHA}) / (^{\circ})$
Complex 1				
N(2)-H(13) $\cdots$ O(1)#2	0.082(3)	0.195(3)	0.273 4(3)	158(3)
Complex 2				
C(18)-H(18) $\cdots$ O(1)#3	0.093	0.238	0.327 5(3)	160.6
C(33)-H(33) $\cdots$ O(3)#4	0.093	0.256	0.344 8(2)	160.6
C(12)-H(12) $\cdots$ Cl(1)#5	0.093	0.286	0.353 3(2)	130.4
C(32)-H(32) $\cdots$ O(4)#6	0.093	0.264	0.348 7(2)	152.1

Symmetry code: (1) #2:  $-x+1, -y, -z+1$ ; (2) #3:  $x, y+1, z$ ; #4:  $x, y-1, z$ ; #5:  $x-1, y, z$ ; #6:  $-x-1, -y+1, -z+1$ .

CCDC: 690004, **1**; 690005, **2**.

## 2 Results and discussion

### 2.1 Structure description

The crystal structure of complex **1** is shown in Fig. 1. The center zinc atom is coordinated by two carboxyl O atoms from different 4-tolythioacetate ligands and two N atoms from two imidazole molecules in a distorted tetrahedral geometry with angles around zinc atom in range from  $101.05(9)^\circ$  to  $121.80(7)^\circ$ . The bond lengths of Zn(1)-O(2) 0.195 9(2) nm and Zn(1)-N(1) 0.199 9(1) nm are comparable with those in other Zn(II) compounds<sup>[11,12]</sup>. There is intermolecular N(2)-H(13)⋯O(1)#2 (symmetry code: #2:  $-x+1, -y, -z+1$ ) hydrogen bonding interaction involving the imidazole nitrogen N(2) and the corresponding carboxylate oxygen O(1) in neighboring 4-tolythioacetate with bond length of 0.273 4(3) nm. It is hydrogen bonds that link these molecules to 1D chains (Fig.2).

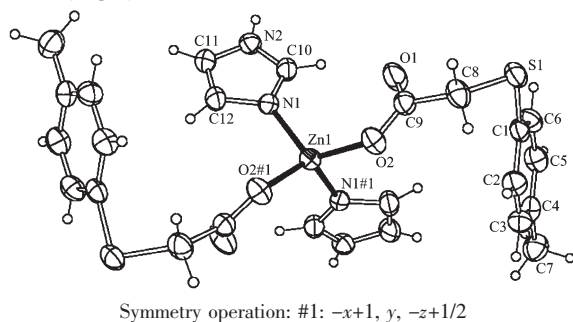
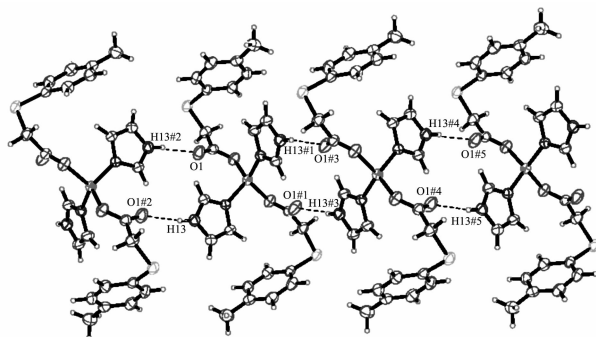


Fig.1 Molecular structure of complex **1** with ellipsoids at 30% probability

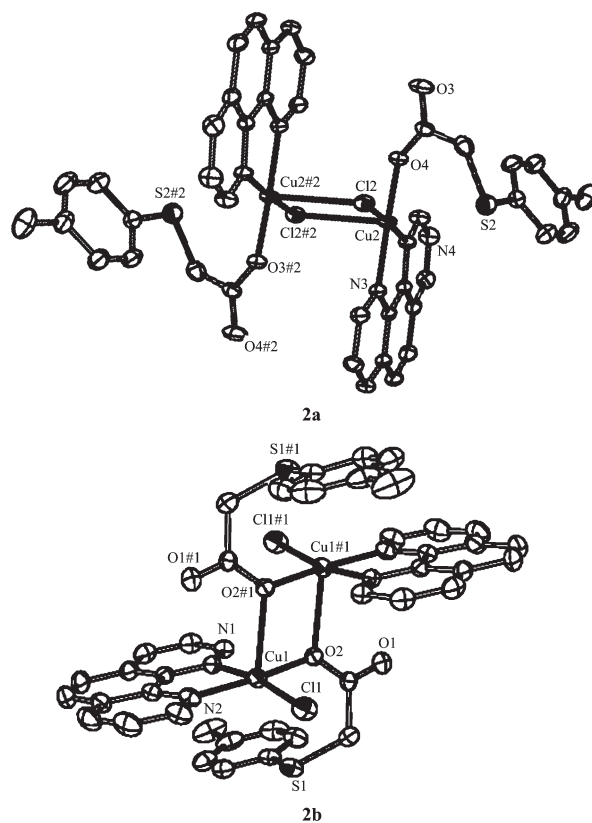


Symmetry operation: #1:  $-x+1, y, -z+1/2$ , #2:  $-x+1, -y, -z+1$ , #3:  $x, -y, z-1/2$ , #4:  $-x+1, -y, -z$ , #5:  $-x, y, z-1$

Fig.2 1D chain structure bridged by N-H⋯O hydrogen bonds

In complex **2**, there are two crystallographically independent molecules  $[\text{Cu}_2\text{L}_2(\text{phen})_2\text{Cl}_2]$  in unit cell,

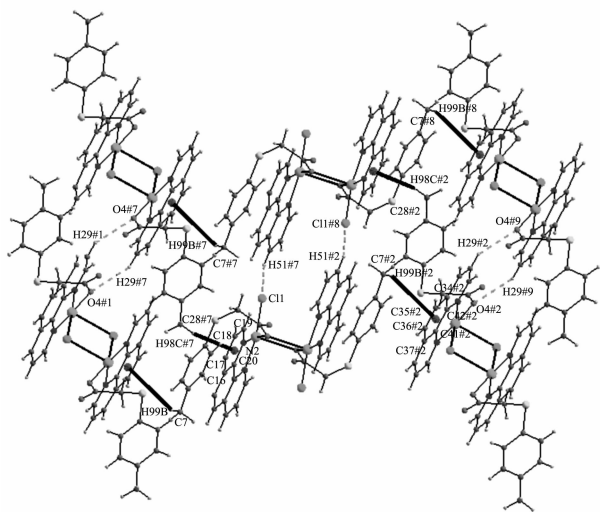
which labeled as **2a** and **2b** with different molecule configuration. A perspective view of two independent molecules is illustrated in Fig.3 which shows that each molecule has an inverse centre at the middle of two Cu atoms. The coordination polyhedron around each Cu(II) can be best described as (4+1) distorted square pyramid. Each Cu(II) in **2a** is coordinated in the equatorial plane by one carboxylate O atom of 4-tolythioacetate, two N atoms of phen and one Cl atom, while the axial coordination site is occupied by one symmetrically related Cl atom of the other monomeric unit. Comparing with the reported complex  $[\text{Cu}_4(18\text{py}2\text{pz})_2(\mu\text{-Cl})_4\text{Cl}_2]\text{Cl}_2$ <sup>[13]</sup> with Cu-Cl bond length of 0.302 9(2) nm, the Cu-Cl bond length of 0.285 6(1) nm in **2a** is acceptable. While in **2b**, the carboxylate group of 4-tolythioacetate ligand adopts bridging monodentate mode and chlorine atom is in the equatorial plane. Similar as complex **1**, hydrogen bonds play an important role in constructing complex **2**. Hydrogen bond C-H⋯O assuming of carbon from phen and oxygen belonging to undentate carboxylate. Studies



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

Fig.3 Molecular structure of complex **2** with ellipsoids at 30% probability

have revealed that the C $\cdots$ O distance ( $D$ ) in C–H $\cdots$ O hydrogen bond is in the range of 0.30~0.40 nm. The C–H $\cdots$ O angle  $\theta$  in the range of 110°~180° is acceptable, although a linear C–H $\cdots$ O bond (150°< $\theta$ <180°) is structurally more important<sup>[14]</sup>. C(33) $\cdots$ O(3)#4 (symmetry code: #4:  $x, y-1, z$ ) distance of 0.344 8(2) nm and C(33)–H(33) $\cdots$ O(3)#4 angle of 160.6° indicate a strong C–H $\cdots$ O hydrogen bond to join **2a** molecules to 1D chains and resulting chains are further connected through C(32)–H(32) $\cdots$ O(4)#6 (symmetry code: #6:  $-x-1, -y+1, -z+1$ ) hydrogen bonding interactions. Similarly, **2b** molecules are joined by C(18)–H(18) $\cdots$ O(1)#3 (symmetry code: #3:  $x, y+1, z$ ) hydrogen bonds to 1D chains which are further linked via C(12)–H(12) $\cdots$ Cl(2)#5 (symmetry code: #5:  $x-1, y, z$ ). All hydrogen bond distances are summarized in Table 3 and are within the ranges reported for other structures<sup>[15–17]</sup>. Furthermore, edge-to-face C–H $\cdots$  $\pi$  interactions (H $\cdots$  $\pi$  0.271 nm and C–H $\cdots$  $\pi$  167°) are observed between methyl hydrogen atoms and the neighboring pyridine rings of phen ligands, leading to the formation of a 3D supermolecular network.



Symmetry operation #1:  $-x+1, -y, -z$ ; #2:  $-x, -y+1, -z+1$ , #7:  $x+1, y, z$ , #8:  $-x+2, -y, -z$ , #9:  $x+2, y-1, z-1$

Fig.4 3D network of **2** formed by C–H $\cdots$ O, C–H $\cdots$ Cl hydrogen bonds indicated by dashed lines and C–H $\cdots$  $\pi$  interactions indicated by bold lines, respectively; And front ellipse balls represent centroids of the benzene ring (C34–C37/C41/C42) and the pyridine ring (N2/C16–C20) of phen ligands

## 2.2 FTIR spectroscopy

IR spectra show the characteristic bands of the carboxyl group at 1 654, 1 610  $\text{cm}^{-1}$  and 1 610, 1 580  $\text{cm}^{-1}$  for the antisymmetric stretching vibrations, 1 450, 1 400  $\text{cm}^{-1}$  and 1 411, 1 351  $\text{cm}^{-1}$  for the symmetric stretching vibrations in complex **1** and **2**, respectively. The separation ( $\Delta$ ) between  $\nu_{\text{asym}}$  ( $\text{CO}_2$ ) and  $\nu_{\text{sym}}$  ( $\text{CO}_2$ ) of 204 and 199  $\text{cm}^{-1}$  indicates the presence of monodentate coordination modes in complex **1** and **2**<sup>[18]</sup>, which is consistent with the crystal structure determined by X-ray diffraction. The absence of the expected characteristic bands at 1 730~1 690  $\text{cm}^{-1}$  attributed to the protonated carboxylate groups accounts for the deprotonation of 4-tolythioacetic acid. The band at 3 440  $\text{cm}^{-1}$  assigned to the  $\nu$  (N–H) stretch from the imidazole and phen ligands, while hydrogen bonding of the type N–H $\cdots$ O and C–H $\cdots$ O is supported by the presence of broad strong bands centered at 3 200 and 3 000  $\text{cm}^{-1}$  for complex **1** and **2**. The band around 1 180  $\text{cm}^{-1}$  can be assigned to the  $\nu$ (C–S–C) stretching vibrations.

## 2.3 Thermal properties

The TGA curve of complex **1** shows two weight loss. The first stage of weight loss 56.5% from 200 to 400 °C corresponding to the loss of 4-tolythioacetate ligands. The second stage is 29.4 % in the temperature range of 400 to 700 °C described as the release of the imidazole ligands. The whole weight loss (85.9%) is according to the calculated value (85.7%), giving the final solid product of ZnO. The TGA curve of complex **2** shows one main weight loss from 329 to 637 °C corresponding to the burning of the ligands. The final residuals are CuO. The observed total weight loss of 82.7% matches with the theoretical one (82.1%).

## 2.4 Photoluminescent properties

The luminescent properties of 4-tolythioacetic acid, complex **1** and **2** in the solid state were measured at ambient temperature. The emission with maximum at 383 and 404 nm were observed for complex **1** as illustrated in Fig.5, while no clear photoluminescence was observed for 4-tolythioacetic acid and complex **2**. It is known, imidazole does not emit any luminescence in the range of 400~800 nm. So the emissions of **1** may be due to  $\sigma$ -donation from the coordination environments

of the metal centers and may be assigned to ligand-to-metal charge transfer (LMCT). But the copper ions in **2** quench the fluorescence of the phen ligand which has the emission bands at 365 nm<sup>[19]</sup>. This result indicates that the photoluminescence properties of the metal-organic complexes depend on the nature of the organic ligand as well as the metal ions.

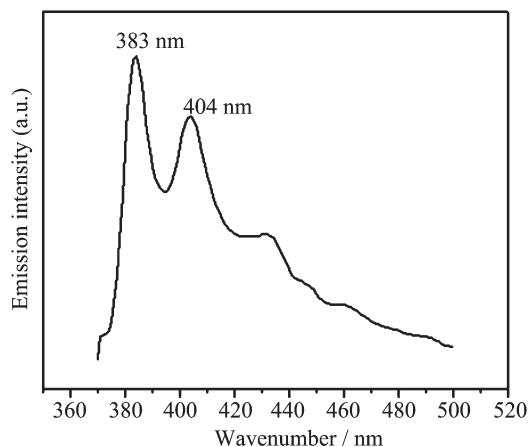


Fig.5 Photoluminescent spectra of complex **1** in solid state at room temperature

## References:

- [1] Yaghi O M, Li H, Davis C, et al. *Acc. Chem. Res.*, **1998**,**31**(8): 474~484
- [2] Hargman P J, Hargman D, Zubieta J. *Angew. Chem. Int. Ed.*, **1999**,**38**(18):2639~2684
- [3] HE Yin-Hua(何银华), FENG Xia(封霞), FENG Yun-Long(冯云龙), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2007**,**23**(10):1805~1808
- [4] XIE Jing(谢静), CHEN Xuan(陈轩), LIU Guang-Xiang(刘光祥), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2007**,**23**(7):1295~1298
- [5] GAO Shan(高山), HUO Li-Hua(霍丽华), ZHAO Hui(赵辉), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2005**,**21**(8):1245~1248
- [6] GAO Shan(高山), YUE Yu-Mei(岳玉梅), MA Dong-Sheng(马东升), et al. *Chinese J. Struct. Chem. (Jiegou Huaxue)*, **2004**,**23**(7):825~828
- [7] Smith G, O'Reilly E J, Kennard C H L. *Polyhedron*, **1987**,**6**: 871~879
- [8] Pan L, Adams K M, Hernandez H E, et al. *J. Am. Chem. Soc.*, **2003**,**125**:3062~3067
- [9] Sheldrick G M. *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, **1997**.
- [10] Sheldrick G M. *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, **1997**.
- [11] LI Bin(李彬), SUN Yue-Fei(孙跃飞), GOU Shao-Hua(苟少华), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2001**,**17**(6):917~920
- [12] Li J, Zhou J H, Li Y Z, et al. *Inorg. Chem. Commun.*, **2004**,**7**: 538~541
- [13] Schuitema A M, Aubel P G, Koval I A, et al. *Inorg. Chim. Acta*, **2003**,**355**:374~385
- [14] Desiraju G R. *Acc. Chem. Res.*, **1996**,**29**:441~449
- [15] Jose J C, Herbert H, Miguel P. *Inorg. Chim. Acta*, **2008**,**361**: 248~254
- [16] Jayaraman A, Balasubramaniam V, Valiyaveetil S. *Cryst. Growth Des.*, **2006**,**6**:636~642
- [17] Reger D L, Semeniuc R F, Smith M D. *Inorg. Chem.*, **2001**, **40**:6545~6546
- [18] Nakamoto K. *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compound*. New York: Wiley, **1986**.
- [19] Shi X, Zhu G S, Fang Q R, et al. *Eur J. Inorg. Chem.*, **2004**,**1**: 185~191