

3-苯氧基甲基-4-(4-甲基苯基)-5-(2-吡啶基)-1,2,4-三唑的铜(II)、镉(II)配合物的合成、晶体结构和光学性质

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摘要: 以 3-苯氧基甲基-4-(4-甲基苯基)-5-(2-吡啶基)-1,2,4-三唑(L)为配体分别合成了 2 个金属配合物即[Cu₂L₂Cl₄]·2H₂O (**1**)和[Cd₃L₂(μ₂-Cl)₆]·2nCH₃CN (**2**), 对其进行了红外、紫外、热重、粉末衍射、元素分析和晶体结构等表征。配合物 **1** 和 **2** 都属于三斜晶系, 空间群都为 $P\bar{1}$, 单晶结构分析表明, 在配合物 **1** 中, 中心铜(II)原子具有畸变三角双锥构型[CuN₃Cl₂]; 配合物 **2** 是配位聚合物, 每个重复单元有 3 个 Cd(II)原子和 2 个不同的 Cd(II)配位中心, Cd1(II)原子具有中心对称的畸变八面体构型 CdCl₄N₂, Cd2(II)原子具有畸变的八面体构型 CdCl₄N₂。

关键词: 铜(II)配合物; 镉(II)配合物; 晶体结构; 三唑

中图分类号: O614.121; O614.24*2 文献标识码: A 文章编号: 1001-4861(2015)02-0405-08

DOI: 10.11862/CJIC.2015.062

Syntheses, Crystal Structures, and Spectral Properties of Copper(II) and Cadmium(II) Complexes with 3-Phenoxymethyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole

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Abstract: Two complexes [Cu₂L₂Cl₄]·2H₂O (**1**) and [Cd₃L₂(μ₂-Cl)₆]·2nCH₃CN (**2**) were obtained by the reaction of 3-phenoxymethyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) with Copper (II) chloride and cadmium (II) chloride respectively. The complexes have been characterized by IR, UV, TGA, powder XRD, elemental analyses and crystal structures. The complexes **1** and **2** crystallize in the triclinic space group $P\bar{1}$. Crystallographic studies reveal that **1** has a distorted trigonal bipyramidal [CuN₃Cl₂] coordination. **2** is a polymeric complex. every repeat unit has three cadmium(II) atoms and two different cadmium(II) centers. Cd1(II) atom possesses a centrosymmetric distorted-octahedral geometry with [CdCl₂Cl' ₂N₂], and Cd2(II) atom has a distorted-octahedral geometries with [CdCl₂Cl'Cl''NN']. CCDC: 1015366, L; 1015367, **1**; 1015368, **2**.

Key words: copper(II) complex; cadmium(II) complex; crystal structures; triazole

收稿日期: 2014-09-29。收修改稿日期: 2014-12-07。

企业合作基金(No.8507040052)资助项目。

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1,2,4-triazole and its derivatives have attracted considerable attention in recent years due to their specific magnetic properties, interesting catalytic activity, various structures^[1-7] and a large number of biological activities such as anticonvulsant, antidepressant, antibacterial, anticancer and antipsychotic^[8-10]. In addition, substituted 1,2,4-triazoles play a prominent role in coordination chemistry since they exhibit versatile and various coordination modes^[11-13]. Some iron(II) complexes with 1,2,4-triazoles show attractive spin-crossover properties which can be applied in molecular-based memory devices as switching material and information storage^[14-17]. 1,2,4-triazoles represent a class of heterocyclic compounds of significant importance in wide areas^[18].

Some metal complexes containing some 4-substituted 3,5-di(2-pyridyl)-1,2,4-triazole have been prepared and characterized in the recent decade^[12,16,19-21]. However, complexes with 3-phenoxyethyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole have not been studied until now. As a continuation of our investigation of the asymmetrical substituted 1,2,4-triazoles^[22-26], herein we report the syntheses, crystal structures and spectroscopic properties of a triazole ligand of 3-phenoxyethyl-4-(4-methylphenyl)-5-(2-pyridyl)-1, 2, 4-triazole (L) and its two complexes, Copper(II) complex **1** and Cadmium(II) complex **2**.

1 Experimental

1.1 Materials and measurements

All chemicals were analytical grade. Melting points were determined using an X4 digital microscopic melting point apparatus and are uncorrected. C, H, N elemental analyses were performed on a Perkin-Elmer 240 analyzer. ¹H NMR spectra were measured with a Bruker Avance 300 spectrometer at ambient temperature in CDCl₃ using TMS as an internal reference. IR spectra were recorded from 4 000 to 400 cm⁻¹ using KBr pellets on a Vector22 Bruker spectrophotometer. UV/Vis spectra were recorded on a Hitachi-4100 UV-Vis absorption spectrophotometer at room temperature in CH₃CN solution. Fluorescence spectra data for **2** and L were measured on a Fluoromax-4 spectrofluorometer

at room temperature. Thermogravimetric analysis (TGA) measurements were obtained with a NETZSCH STA49F3 thermal analyzer in a nitrogen atmosphere at a heating rate of 10 K·min⁻¹. Powder XRD diffractograms were obtained with a Bruker D8X diffractometer equipped with monochromated Cu K α (λ =0.154 18 nm) radiation at room temperature.

1.2 Synthesis of L

The ligand, 3-phenoxyethyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) was synthesized by the following reaction. To a solution of di(*p*-methylphenyl) phosphazoneanilide (4.0 g, 16.5 mmol) in anhydrous *N,N*-dimethylaniline (30 mL) was added *N*-phenoxyacetyl-*N'*-(2-pyridyl)hydrazine (4.1 g, 15.0 mmol). The mixture was refluxed at 190~200 °C for 3 hours, and then the solvent was removed under reduced pressure. Concentrated hydrochloric acid (4.0 mL) was added to the residue and refluxed for 1 hour. After cooling to room temperature, the solution was filtered, and the filtrate was neutralized to pH=8~9 with K₂CO₃. A precipitate was formed and collected. The crude product was recrystallized from EtOH to give a white solid. Yield: 1.9 g (38.4% based on di(*p*-methylphenyl) phosphazoneanilide), m.p. 146~147 °C. Anal. Calcd. for C₂₁H₁₈N₄O(%): C 73.67, H 5.30, N 16.36; Found(%): C 73.48, H 5.59, N 15.97. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ 2.317(s, 3H), 5.105(s, 2H), 6.992~7.128 (m, 5H), 7.230~7.260 (m, 4H), 7.718~8.343 (m, 4H). UV-Vis (CH₃CN): λ_{max} =221.0, 269.5 nm. IR (KBr pellet, cm⁻¹): 3 075(m), 3 051(w), 2 949(w), 2 870(w), 1 587 (s), 1 518(s), 1 460(s), 1 238(s), 863(m), 827(s), 758 (s), 690(w). ESI-MS: m/z =343.3.

1.3 Synthesis of complex 1

A solution of CuCl₂·2H₂O (0.341 g, 2 mmol) in 10 mL ethanol was added to a warm solution of L (0.342 g, 1 mmol) in 10 mL ethanol. The mixture turned green immediately and a green precipitate formed. The mixture was filtered and the precipitate was collected. Green crystals were obtained by recrystallization from acetonitrile. Yield: 0.371 g (75.2% based on L). Anal. Calcd. for C₄₂H₄₀Cl₄Cu₂N₈O₄(%): C 50.97, H 4.07, N 11.32; Found(%): C 50.89, H 4.21, N 11.07. UV-Vis (CH₃CN): λ_{max} =246.0, 276.5 nm. IR

(KBr pellet, cm^{-1}): 3 448(w), 3 085(m), 1 602(s), 1 523(s), 1 496(s), 1 245(s), 869(m), 784(s), 707(w).

1.4 Synthesis of complex 2

A solution of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.457 g, 2 mmol) in 10 mL acetonitrile was added to a warm solution of **L** (0.342 g, 1 mmol) in 20 mL acetonitrile. A colorless mixture formed and was filtered. The filtrate was left to stand at room temperature for evaporation. Several days later a colorless crystals was collected. Yield: 0.439 g (66.8% based on **L**) Anal. Calcd. for $\text{C}_{46}\text{H}_{42}\text{Cl}_6\text{Cd}_3\text{N}_{10}\text{O}_2$ (%): C 41.96, H 3.21, N 10.64; Found(%): C 42.37, H 3.48, N 10.23. UV-Vis (CH_3CN): λ_{max} =244.5, 282.5 nm. IR (KBr pellet, cm^{-1}): 3 447(w), 3 091(m), 1 607(s), 1 518(s), 1 464(s), 1 242(s), 868(w), 770(s), 702(m).

1.5 Crystal structure determination

Well-shaped single crystals of **L**, **1** and **2** were

selected for X-ray diffraction study. The unit cell parameters and the intensity data were collected at 296(2) K on a Bruker Smart APEX II CCD diffractometer with a detector distance of 5 cm and frame exposure time of 10 s using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda=0.071\ 073\ \text{nm}$) radiation. The structures were solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL software^[27]. All nonhydrogen atoms were anisotropically refined and hydrogens were generated geometrically and allowed to ride on their respective parent atoms, but not refined. Crystal data and structure refinement for **L**, **1** and **2** are listed in Table 1. Selected bond lengths and angles for **L**, **1** and **2** are listed in Table 2. Relevant hydrogen-bonding parameters of **L**, **1** and **2** are summarized in Table 3.

CCDC: 1015366, **L**; 1015367, **1**; 1015368, **2**.

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

Compound	L	1	2
Formula	$\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}$	$\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{CuN}_4\text{O}_2$	$\text{C}_{46}\text{H}_{42}\text{Cl}_6\text{Cd}_3\text{N}_{10}\text{O}_2$
Formula weight	342.39	494.85	1 316.80
Crystal size / mm	0.13×0.11×0.10	0.12×0.10×0.10	0.12×0.11×0.10
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / nm	0.918 3(4)	1.029 0(4)	1.087 07(11)
b / nm	0.998 3 (4)	1.047 3 (4)	1.104 87(11)
c / nm	1.084 1(4)	1.171 0(5)	1.153 63(12)
α / (°)	89.344(4)	80.829(5)	83.139 0(10)
β / (°)	69.501(4)	89.582(5)	65.267 0(10)
γ / (°)	79.304(4)	63.540(4)	79.090 0(10)
V / nm^3	0.913 2(6)	1.112 4(8)	1.234 5(2)
Z	2	2	1
D_c / ($\text{g}\cdot\text{cm}^{-3}$)	1.245	1.477	1.771
θ range / (°)	2.01~25.60	1.77~25.59	1.88~25.50
μ / mm^{-1}	0.080	1.247	1.654
$F(000)$	360	506	650
R_{int}	0.025 6	0.019 2	0.023 2
Reflections collected	6 752	8 171	9 043
Independent reflections	3 347	4 056	4 479
Observed reflections	2 518	3 355	3 749
Data / restraints / parameters	3 347 / 0 / 237	4 056 / 0 / 272	4 479 / 0 / 306
Goodness-of-fit on F^2	1.087	1.127	1.003
R_1, wR_2 ($I>2\sigma(I)$)	0.040 8, 0.111 8	0.042 1, 0.123 7	0.027 6, 0.066 3
R_1, wR_2 (all data)	0.055 2, 0.120 4	0.053 0, 0.138 2	0.036 2, 0.070 0
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ / ($\text{e}\cdot\text{nm}^{-3}$)	126, -123	983, -680	358, -421

Table 2 Selected bond lengths (nm) and bond angles (°) for **L**, **1** and **2**

L					
N1-C2	0.130 87(19)	C1-C15	0.147 7(2)	C1-N3	0.137 04(19)
N1-N2	0.138 49(18)	C2-C3	0.147 4(2)	N3-C8	0.144 38(17)
C1-N2	0.130 51(18)	O1-C16	0.137 79(17)	O1-C15	0.142 43(18)
N4-C7-C6	124.3(2)	N2-C1-C15	124.31(13)	N1-C2-N3	110.07(13)
C2-N1-N2	107.65(11)	N3-C2-C3	127.45(13)	C7-N4-C3	116.30(15)
N2-C1-N3	110.50(13)	C2-N3-C8	130.29(12)	C21-C16-O1	124.42(15)
Complex 1					
Cu1-N1 ⁱ	0.199 6(3)	Cu1-Cl1	0.229 13(14)	N1-N2	0.137 7(4)
Cu1-N2	0.214 4(3)	Cu1-Cl2	0.230 34(13)	C1-N1	0.131 3(4)
Cu1-N4	0.201 0(3)	N3-C1	0.135 6(4)	N4-C7	0.133 8(4)
N1 ⁱ -Cu1-Cl1	92.33(9)	N1 ⁱ -Cu1-N2	95.71(11)	N4-Cu1-N2	77.84(11)
N4-Cu1-Cl1	90.71(9)	N2-Cu1-Cl2	115.38(9)	N1 ⁱ -Cu1-N4	173.54(10)
Cl2-Cu1-N1 ⁱ	90.41(9)	Cl1-Cu1-Cl2	130.15(6)	N2-Cu1-Cl1	113.82(10)
N4-Cu1-Cl2	91.98(9)				
Complex 2					
Cd2-N2	0.232 2(2)	Cd1-Cl3	0.264 53(8)	Cd2-Cl3 ⁱ	0.269 67(9)
Cd2-N4	0.249 9(3)	Cd1-Cl2	0.267 65(8)	Cd1-N1	0.233 7(3)
N1-N2	0.137 6(3)	Cd2-Cl1	0.279 67(9)	N1-C1	0.130 9(4)
Cl2 ⁱ -Cd1-Cl2	180.00	N2-Cd2-N4	65.61(9)	N1-Cd1-Cl2	87.27(7)
N1-Cd1-N1 ⁱ	180.00	N1-Cd1-Cl3	92.39(7)	Cl1-Cd2-Cl2	87.74(3)
Cl3-Cd1-Cl2	99.20(3)	Cl2-Cd1-Cl3 ⁱ	80.80(3)	Cd1-Cl3-Cd2 ⁱ	87.71(3)

Symmetry transformations used to generate equivalent atoms: Complex **1**: ⁱ -x+1, -y+1, -z+2; Complex **2**: ⁱ -x, -y+2, -z

Table 3 Hydrogen bonding lengths (nm) and angles (°) for **L**, **1** and **2**

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠DHA
L				
C4-H4...N1 ⁱ	0.093	0.260 39	0.347 91	157.02
Complex 1				
O2w-H2wA...Cl2 ⁱⁱ	0.089	0.266 69	0.314 7(8)	114.96
Complex 2				
C6-H6...N5	0.093	0.250	0.322 9(8)	136.0
C23-H23C...Cl3 ⁱⁱ	0.096	0.271	0.349 1(7)	139.0

Symmetry transformations used to generate equivalent atoms: **L**: ⁱ 2-x, 1-y, -z; Complex **1**: ⁱⁱ -x, 1-y, 2-z; Complex **2**: ⁱⁱ 1-x, 1-y, -z.

2 Results and discussion

2.1 Description of crystal structures

Crystal structure of **L**: X-ray structure analyses reveals that **L** crystallizes in the triclinic space group $P\bar{1}$. Three aromatic rings of 1,2,4-triazole ring, pyridyl ring and phenyl ring (C8, C9, C10, C11, C12, C13)

have planar structures (Fig.1), but they are non-coplanar. The central 1,2,4-triazole ring is oriented at dihedral angles of 41.82 (7)° and 73.84 (6)° with the pyridyl ring and phenyl ring (C8, C9, C10, C11, C12, C13), respectively. There are a weak intermolecular hydrogen bond of C4-H4...N1 and three C-H... π interactions in the **L**. The C-H... π interactions

involve C6–H6 \cdots Cg3, C18–H18 \cdots Cg1 and C20–H20 \cdots Cg3. Three face-to-face $\pi\cdots\pi$ stacking interaction (Fig.2) exists between the two parallel triazole rings. All these interactions assemble the three-dimensional structure of L.

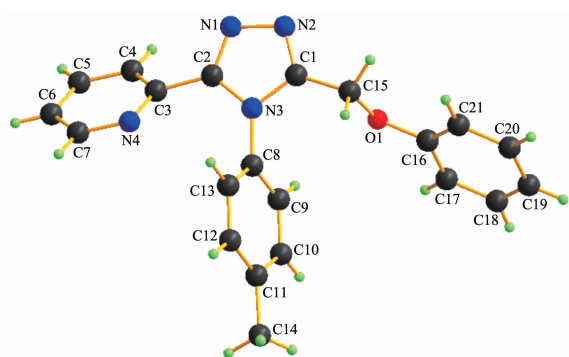


Fig.1 Structure of L with the atomic labeling

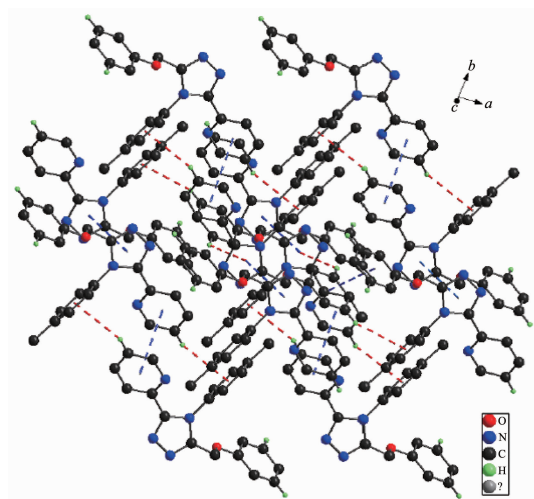
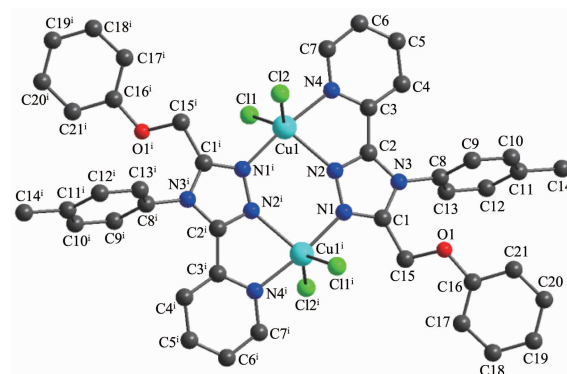


Fig.2 Packing diagram of L showing the $\pi\cdots\pi$ and C–H $\cdots\pi$ interactions

Crystal Structure of 1: Complex **1** is a double-bridged binuclear copper(II) complex (Fig.3) crystallizing in the triclinic space group $P\bar{1}$. Two Cu(II) atoms are double-bridged together by four nitrogen atoms (N1, N2) of two triazole rings in L, and the bond lengths of Cu1–N1ⁱ and Cu1–N2 are 0.199 6(3) and 0.214 4(3) nm, respectively. Each Cu(II) atom is also coordinated by another nitrogen atom (N4) of pyridyl ring and two chloride atoms (Cl1, Cl2), and the bond lengths of Cu1–N4, Cu1–Cl1 and Cu1–Cl2 are 0.201 0(3), 0.229 13(14) and 0.230 34(13) nm, respectively. All these nitrogen atoms (N1, N2, N4) and chloride atoms (Cl1, Cl2) make the center Cu(II) atoms form distorted



Symmetry codes: ⁱ –x+1, –y+1, –z+2

Fig.3 Structure of **1** with the atomic labeling

trigonal-bipyramidal geometries[CuN₃Cl₂].

As the nitrogen atom (N4) of pyridyl ring coordinated to the center Cu1 (II) atom, it makes the 1,2,4-triazole ring and pyridyl ring almost coplanar with an dihedral angle of 5.97(19)°. There are a weak intermolecular hydrogen bond of O2W–H2WB \cdots Cl2 and several C–H $\cdots\pi$ interactions in complex **1**. The C–H $\cdots\pi$ interactions involve O2W–H2WA \cdots Cg2, O2W–H2WB \cdots Cg2, C9–H9 \cdots Cg6, C12–H12 \cdots Cg6 and C20–H20 \cdots Cg2. An offset face-to-face $\pi\cdots\pi$ interaction (Fig.4) exists between the two parallel pyridyl rings with a centroid-centroid distance of 0.370 8(3) nm. There is also another $\pi\cdots\pi$ interaction between the triazole ring and phenyl rings (C16, C17, C18, C19, C20, C21). All these interactions assemble the complex

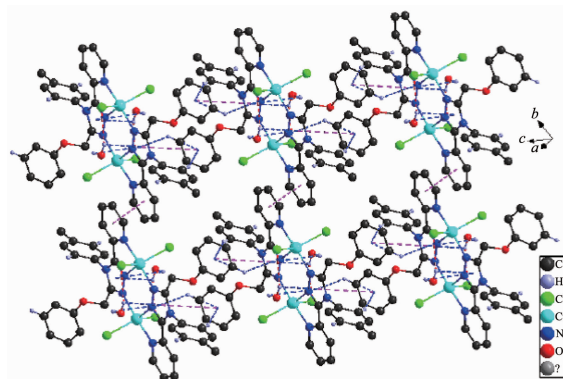


Fig.4 Packing diagram of complex **1** showing the $\pi\cdots\pi$ and C–H $\cdots\pi$ interactions

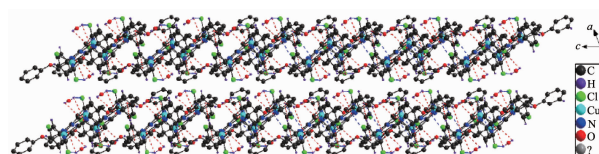


Fig.5 One-dimensional network of complex **1**

1 into a one-dimensional chain structure (Fig.5).

Crystal Structure of 2: Complex **2** is a cadmium(II) polymeric complex (Fig.6) crystallizing in the triclinic space group $P\bar{1}$. The Cd(II) atoms are bridged by the nitrogen atoms(N1, N2) of triazole rings in L and chloride atoms. Every repeat unit has three Cd(II) atoms and two different Cd(II) centers ($\text{Cd2}-\text{Cd1}-\text{Cd2}^i$) (Fig.7). Two Cd(II) atoms (Cd2 , Cd2^i) are bridged together by two chloride atoms (Cl1 , Cl1^i) between every repeat units. The distance of two adjacent Cd(II) atoms(Cd1 , Cd2) in the repeat units is 0.370 13 (4) nm, and that of two adjacent Cd2(II) atoms between every repeat units is 0.394 13(5) nm. The Cd1(II) atom possesses centre-symmetrical distorted-octahedral geometries [$\text{CdCl}_2\text{Cl}'_2\text{N}_2$], and the bond lengths of Cd1-N1, Cd1-Cl2 and Cd1-Cl3 are 0.233 7(3), 0.267 65(8) and 0.264 53(8) nm, respectively. The Cd2(II) atoms have asymmetrical distorted-octahedral geometries [$\text{CdCl}_2\text{Cl}'\text{Cl}''\text{NN}'$].

In complex **2** there are two weak hydrogen bond

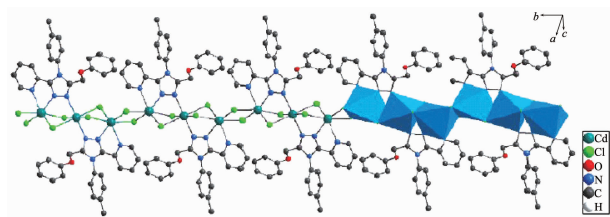
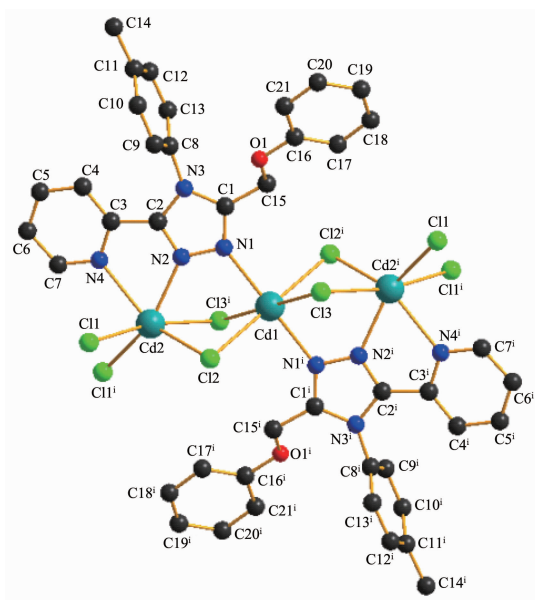


Fig.6 A partial chain of complex **2**



Symmetry codes: $i -x, -y+2, -z$

Fig.7 Structure of **2** with the atomic labeling

interactions ($\text{C6}-\text{H6}\cdots\text{N5}$ and $\text{C23}-\text{H23C}\cdots\text{Cl3}$) and several $\text{C}-\text{H}\cdots\pi$ interactions (Fig.8). The $\text{C}-\text{H}\cdots\pi$ interactions involve $\text{C4}-\text{H4}\cdots\text{Cg11}$, $\text{C9}-\text{H9}\cdots\text{Cg12}$, $\text{C18}-\text{H18}\cdots\text{Cg10}$, $\text{C20}-\text{H20}\cdots\text{Cg9}$ and $\text{C23}-\text{H23B}\cdots\text{Cg12}$. A face-to-face $\pi\cdots\pi$ interaction exists between the two parallel pyridyl rings with a centroid-centroid distance of 0.368 0(2) nm. Another $\pi\cdots\pi$ interaction involves the triazole ring and phenyl rings (C16 , C17 , C18 , C19 , C20 , C21). Complex **2** forms a three-dimensional structure through these interactions.

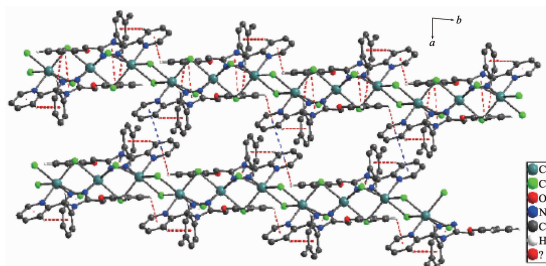


Fig.8 Packing diagram of complex **2** showing the $\pi\cdots\pi$ and $\text{C}-\text{H}\cdots\pi$ interactions

2.2 Spectral characterization

The IR spectrum of the free L shows two medium intensity bands at 1 587 and 1 566 cm^{-1} , which are attributed to pyridine ring vibrations. As the nitrogen atoms of pyridyl rings coordinate to metal atoms, the higher band shifted about 15 cm^{-1} [28]. So we can find a band at 1 601 cm^{-1} (or 1 606 cm^{-1}) in the spectrum of **1** (or **2**), which can be assigned to the coordinated pyridyl rings, indicating that the ligands of L in complexes **1** and **2** are chelating to metal atoms. In addition, the bands at 1 238, 1 245 and 1 242 cm^{-1} are attributed to the C-O stretching vibrations in L, complex **1** and **2**, respectively. These features are in consistent with the results of X-ray analyses.

The UV-Vis spectra of ligand L, complex **1** and **2** were performed in dilute acetonitrile solution. The ligand L exhibits two strong bands at 221.0 and 269.5 nm. The complex **1** (or **2**) shows two bands at 246.0 and 276.5 nm (or 244.5 and 282.5 nm), which are attributed to the L $\pi-\pi^*$ and $n-\pi^*$ electronic transitions.

The photoluminescent properties of complex **2** and the free ligand L have been studied in the solid state at room temperature (Fig.9). The complex **2**

exhibits an emission band at 403 nm with excitation at 314 nm, while free ligand L displays an emission at 422 nm upon excitation at 327 nm. Compared with the free ligand L, the emission band of complex **2** is blue-shifted about 19 nm. As the Cd^{2+} has d^{10} configuration, the luminescence emission of complex **2** is contributed to the intra-ligand fluorescent emission of the ligand L^[29]. This performance indicates that complex **2** could be potential photoluminescent materials and electron-transport materials.

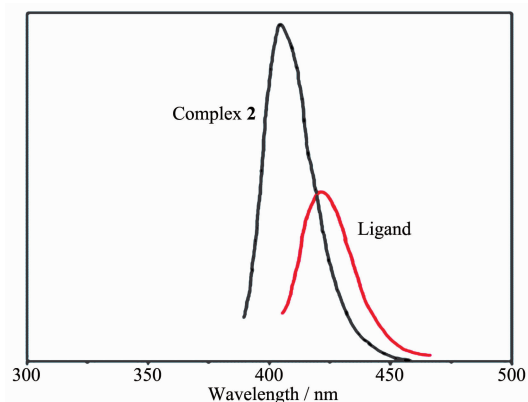


Fig.9 Solid-state emission spectra of free Ligand L and **2** at room temperature

2.3 Thermogravimetric analysis(TGA) and PXRD

Thermogravimetric analysis (TGA) of complex **1** and **2** were performed in the temperature range of 40~800 °C in nitrogen atmosphere with a heating rate of 10 K·min⁻¹ to investigate their thermal stabilities (Fig.

10). For complex **1**, the first weight loss of 3.52% between 40 and 95 °C is observed, due to the loss of two lattice water molecules (Calcd. 3.64%). Practically no weight loss was found between 95 and 245 °C. A rapid weight loss was observed above 245 °C with the residue of CuCl_2 (Obsd. 26.20 % , Calcd. 27.28%). For complex **2**, the TGA curve shows that no obvious weight loss is found until the abrupt decomposition of the framework occurs at about 260 °C. Powder X-ray diffraction (PXRD) experiments were carried out on the ligand L, complex **1** and **2**. The experimental and simulated XRD patterns generated from single-crystal diffraction data of ligand L, complex **1** and **2** are shown in Fig.11. The experimental peak position are in agreement with the corresponding simulated XRD patterns, which indicate the single phase purity of ligand L, complex **1** and **2**.

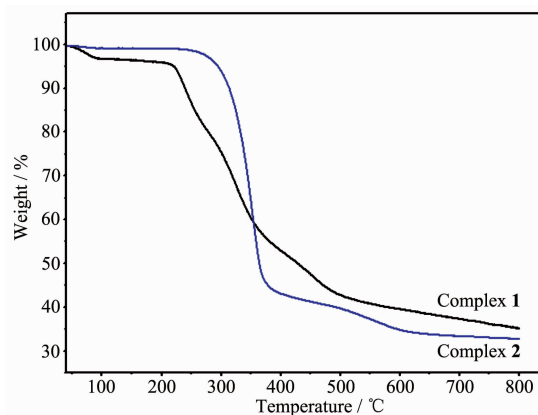


Fig.10 TGA curves of the complexes **1** and **2**

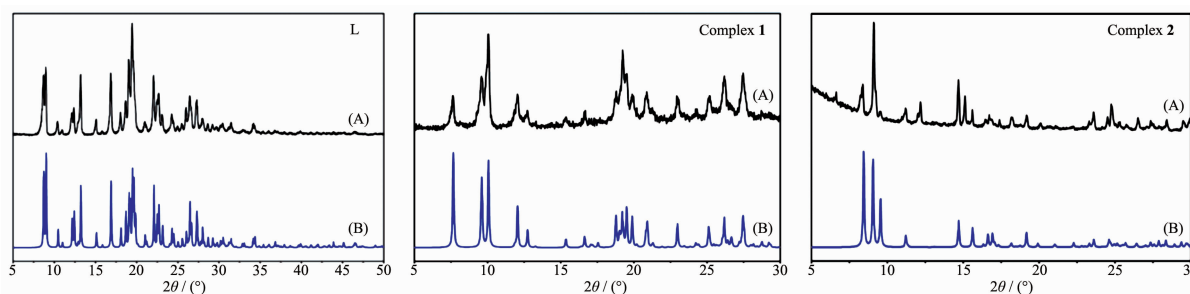


Fig.11 Experimental (A) and simulated (B) X-ray powder diffraction patterns of L, **1** and **2**

3 Conclusions

Two complexes, $[\text{Cu}_2\text{L}_2\text{Cl}_4] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Cd}_3\text{L}_2(\mu_2\text{-Cl})_6]_n \cdot 2n\text{CH}_3\text{CN}$ (**2**), with 3-phenoxyethyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) have been synthesized, and their molecular structures were

determined by X-ray crystallography, element analysis, IR, UV/Vis, fluorescence measurement, TGA and powder XRD. Crystallographic studies reveal that complex **1** has a distorted trigonal bipyramidal geometry $[\text{CuN}_3\text{Cl}_2]$. However, complex **2** is a polymeric, and every repeat unit has three Cd (II)

atoms and two different Cd(II) centers(Cd2-Cd1-Cd2²). The centre Cd(II) atoms possess distorted-octahedral geometries.

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