

## 大空间位阻的 2,9-双噻吩-1,10-菲咯啉-5,6-二酮铜(II)配合物

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**摘要:** 基于 1,10-菲咯啉-5,6-二酮 2,9 位双噻吩的扩展策略, 设计合成了 2 个化合物 **1** 和 **2**。有趣的是, 在大位阻双齿整合配体 **2** 的配位化学研究中发现, 只有铜(II)离子生成了稳定的配合物 **3**·H<sub>2</sub>O。此外, 对 **2**·2·CHCl<sub>3</sub> 和 **3**·H<sub>2</sub>O 的 X-射线单晶结构研究表明, 为了克服空间位阻以满足中心铜(II)离子的配位构型要求, 1,10-菲咯啉-5,6-二酮及其 2,9 位取代的 2 个噻吩环之间的二面角分别从自由配体中的 1.9(2)°、5.2(6)° 和 25.3(3)°、34.9(3)° 增加到了铜(II)配合物中的 5.6(2)°、6.5(6)° 和 27.2(3)°、38.2(3)°。

**关键词:** 铜(II)配合物; 1,10-菲咯啉-5,6-二酮; 噻吩衍生物; 偶联反应

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## A Cu(II) Complex with 2,9-Dithienyl-1,10-phenanthroline-5,6-dione Ligand with Large Steric Hindrance

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**Abstract:** 1,10-Phenanthroline-5,6-dione based molecules (**1** and **2**), extended by two thiophene rings at 2 and 9 positions, have been designed and prepared successfully. It is interesting to mention that the study of coordination chemistry of this large steric ligand **2** with some transition-metal ions reveals that only a Cu(II) complex **3**·H<sub>2</sub>O can be yielded. The conformation of ligand **2** undergoes great alteration after Cu(II) ion complexation, where the dihedral angles between the central 1,10-phenanthroline-5,6-dione and its neighboring two thiophene rings are significantly increased from 1.9(2)°/5.6(2)° in **2** and 5.2(6)°/6.5(6)° in **2**·CHCl<sub>3</sub> to 25.3(3)°/27.2(3)° and 34.9(3)°/38.2(3)° in **3**·H<sub>2</sub>O in order to meet the geometric requirement of four-coordinate Cu(II) centre. CCDC: 1013452, **2**; 1013453, **2**·CHCl<sub>3</sub>; 1013454, **3**·H<sub>2</sub>O.

**Key words:** copper(II) complex; 1,10-phenanthroline-5,6-dione; thiophene derivative; coupling reaction

## 0 Introduction

During the past decades, coordination compounds have attracted much attention because of their potential applications in magnetism, catalysis, molecular

sensing, optics and molecular adsorption<sup>[1-5]</sup>. Particularly, coordination chemistry of 1,10-phenanthroline derivatives having extended  $\pi$  system has become a hot topic of research, and many attempts have been made on the introduction of different donor/acceptor

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units to different substituted positions of 1,10-phenanthroline ring<sup>[6]</sup>. The resultant 1,10-phenanthroline based compounds and their metal complexes can be finely tuned in different aspects, such as size, symmetry, conformation, dihedral angle between adjacent aromatic heterocycles, solubility, reaction activity and optoelectronic properties<sup>[7-11]</sup>.

In thiophene substituted 1,10-phenanthroline compounds, the thiophene ring is  $\pi$  electron rich because of the presence of one sulfur atom in the structure, whereas the phenanthroline part is  $\pi$  electron deficient due to the existence of two nitrogen atoms<sup>[12-13]</sup>. The formation of distinguishable delocalized  $\pi$  system for the whole donor-acceptor molecule can be achieved by altering the substituted positions of 1,10-phenanthroline and thiophene units. Our previous research in this area has been focused mainly on the linear 3,8- and planar 5,6-extended 1,10-phenanthroline based heterocyclic aromatic fluorescent compounds showing semiconducting, photoresponsive and chemosensing properties<sup>[14-21]</sup>. In this work, we have introduced two thiophene rings into 2 and 9 positions of 1,10-phenanthroline-5,6-dione to build a new donor-acceptor molecule (**1**) and explore the coordination chemistry of this 2 and 9 thiophene substituted 1,10-phenanthroline-5,6-dione bedentate ligand with large steric hindrance.

## 1 Experimental

### 1.1 Materials and instruments

All melting points were measured without correction. The reagents of analytical grade were purchased directly from commercial sources and used without any further purification. The starting material was prepared according to the previously reported approach shown in Scheme S11. Column chromatography was carried out on silica gel (300~400 mesh) and analytical thin-layer chromatography (TLC) was performed on glass plates of silica gel GF-254 with detection by UV light. Standard techniques for synthesis were carried out under argon atmosphere. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra (4 000~400

cm<sup>-1</sup>) were collected on a Nicolet FT-IR 170X spectrophotometer at 25 °C using KBr plates. Ultraviolet-Visible (UV-Vis) spectra were recorded on a Shimadzu UV-3100 double-beam spectrometer using a quartz glass cell with a path length of 10 mm at room temperature.

### 1.2 Synthesis of compound 1

Anhydrous K<sub>2</sub>CO<sub>3</sub> (1.379 g, 9.98 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.150 g, 0.13 mmol) and 6,9-dibromo-2,2-dimethyl-1,3-dioxolo[4,5-*f*][1,10]-phenanthroline-5,6-dione (1.853 g, 4.52 mmol) were dissolved in a mixture of H<sub>2</sub>O/DMF (20 mL, 1:1, *V/V*) and transferred to a round-bottom flask under N<sub>2</sub> atmosphere. Then 2-thiophenylboric acid (1.276 g, 9.97 mmol) was carefully added and the mixture was kept to react for 4 h at 110 °C with constant stirring. The reaction mixture was quenched with saturated NH<sub>4</sub>Cl aqueous solution, extracted with CHCl<sub>3</sub>, washed with brine, and purified by silica gel column chromatography (*V*<sub>CHCl<sub>3</sub></sub>:*V*<sub>*n*-hexane</sub>=1:1). Yellow crystalline solid **1** was obtained in a yield of 3.239 g (78%) after removal of the solvent and drying *in vacuo*. m.p. 206~207 °C. Anal. Calcd. for C<sub>61</sub>H<sub>31</sub>Cl<sub>3</sub>N<sub>6</sub>O<sub>6</sub>S<sub>6</sub> (%): C, 58.96; H, 2.51; N, 6.76. Found: C, 58.87; H, 2.65; N, 6.70. Main FT-IR absorptions (KBr pellets, cm<sup>-1</sup>): 3 410, 2 990, 2 931, 1 648, 1 427, 1 368, 1 221, 1 044, 823, 697. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.24 (s, 1H), 8.22 (s, 1H), 8.01 (s, 1H), 7.98 (s, 1H), 7.85 (s, 1H), 7.83 (s, 1H), 7.54 (s, 1H), 7.52 (s, 1H), 7.23~7.18 (m, 2H), 1.90 (s, 6H). ESI-MS in methanol (positive mode), *m/z*: 439.42 (100%), [M+Na]<sup>+</sup>. UV-Vis in CH<sub>3</sub>OH:  $\lambda_{\text{max}}$ =242, 257, 310, 391 and 412 nm.

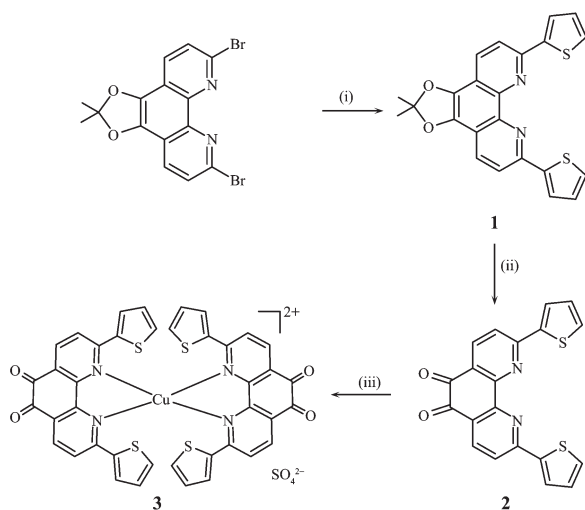
### 1.3 Synthesis of compound 2

Compound **1** (1.250 g, 3.00 mmol) was dissolved in a mixture of H<sub>2</sub>O/trifluoroacetic acid (TFA) (15 mL, 1:2, *V/V*) solution and heated at 50 °C under N<sub>2</sub> for 5 h. After being cooled to room temperature, the resultant mixture was washed with water and the residue was extracted with CHCl<sub>3</sub> (5×30 mL). The organic layer was separated, dried by anhydrous sodium sulfate, and evaporated to dryness. The reaction mixture was extracted with CHCl<sub>3</sub>, washed with brine, and purified by silica gel column chromatography

( $V_{\text{CHCl}_3}:V_{n\text{-hexane}}=1:2$ ). Red crystalline solid **2** was finally obtained in a yield of 0.784 g (70%) after removal of the solvent and drying *in vacuo*. m.p. 255~256 °C. Anal. Calcd. for  $\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2$ : C, 64.15; H, 2.69; N, 7.48%. Found: C, 64.05; H, 2.60; N, 7.40%. Main FT-IR absorptions (KBr pellets,  $\text{cm}^{-1}$ ): 3 444, 1 671, 1 578, 1 437, 1 118, 715, 537.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  8.41 (d,  $J=10.1$  Hz, 2H), 8.18 (d,  $J=8.3$  Hz, 2H), 8.11 (d,  $J=3.6$  Hz, 2H), 7.93 (d,  $J=4.9$  Hz, 2H), 7.30 (m, 2H). ESI-MS in methanol (positive mode),  $m/z=396.24$  (100%),  $[\text{M}+\text{Na}]^+$ ; UV-Vis in  $\text{CH}_3\text{OH}$ :  $\lambda_{\text{max}}=234$ , 259 and 322 nm. The red single crystals of **2** and **2**·CHCl<sub>3</sub> suitable for X-ray diffraction determination were grown from a mixture of  $\text{CH}_3\text{CN}$  and  $\text{CHCl}_3$  by slow evaporation in air at room temperature, respectively.

#### 1.4 Synthesis of complex **3**·H<sub>2</sub>O

A mixture of  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  (0.025 g, 0.10 mmol) and **2** (0.047 g, 0.10 mmol) was dissolved in a mixture of  $\text{CH}_3\text{CN}/\text{CH}_3\text{Cl}$  (15 mL, 2:1, *V/V*). The mixture was refluxed for 2 h and cooled to room temperature, and then the red block single crystals of **3**·H<sub>2</sub>O were collected in a yield of 0.037 g (46%) (based on **2**) after slow evaporation in air for five days. Anal. Calcd. for  $\text{C}_{40}\text{H}_{22}\text{CuN}_4\text{O}_9\text{S}_5$  (%): C, 51.85; H, 2.39; N, 6.05. Found: C, 51.78; H, 2.51, N, 5.99.



Reaction conditions: (i) 2-thiophenylboronic acid,  $\text{K}_2\text{CO}_3$ ,  $\text{Pd}(\text{PPh}_3)_4$ ,  $V_{\text{CH}_3\text{CN}}:V_{\text{CHCl}_3}:V_{\text{DMF}}=1:1:1$ ; (ii)  $V_{\text{H}_2\text{O}}:V_{\text{TFA}}=1:2$ , 50 °C, 5 h; (iii)  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ,  $V_{\text{CH}_3\text{CN}}:V_{\text{CHCl}_3}=1:1$ , reflux, 4 h

Scheme 1 Synthetic route of compound **1-3**

Main FT-IR absorptions (KBr pellets,  $\text{cm}^{-1}$ ): 3 404, 1 688, 1 572, 1 266, 1 092, 801. UV-Vis in  $\text{CH}_3\text{OH}$ :  $\lambda_{\text{max}}=323$  nm.

#### 1.5 X-ray crystallography

Single-crystal samples of **2**, **2**·CHCl<sub>3</sub> and **3**·H<sub>2</sub>O were covered with glue and mounted on glass fibers for data collection with Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm) on a Bruker SMART 1K diffractometer equipped with a CCD camera. Data collection was performed by using SMART program and cell refinement and data reduction were made with the SAINT program<sup>[22]</sup>. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP, and then the structures were solved by direct method and refined by least-squares method on  $F^2$  by using full-matrix least squares methods with SHELXTL version 6.10<sup>[23]</sup>. All non-H atoms were anisotropically refined, and all hydrogen atoms except two water protons in **3**·H<sub>2</sub>O were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic  $U$  of the atoms to which they are attached and allowed to ride on their respective parent atoms. Two water protons were located in the difference synthesis first and their positions were fixed geometrically and the distances to oxygen atom were set as 0.085 nm. Furthermore, the two protons were assigned fixed isotropic thermal parameters at 1.5 times the equivalent isotropic  $U$  of the oxygen atom. Two oxygen atoms (O5 and O7) of sulfate anion in **3**·H<sub>2</sub>O are refined disorderly with the site occupancy factors of 0.706(12) and 0.294(12). In addition, three sulfur atoms (S1, S3 and S4) of four thiophene rings in **3**·H<sub>2</sub>O are refined disorderly with the site occupancy factors of 0.646(5):0.354(5), 0.311(5):0.689(5) and 0.700(5):0.300(5). All calculations were carried out by the SHELXTL PC program package and molecular graphics were drawn by using XSELL and DIAMOND software<sup>[24]</sup>. The summary of the data collection and refinement for **2**, **2**·CHCl<sub>3</sub> and **3**·H<sub>2</sub>O is given in Table 1.

CCDC: 1013452, **2**; 1013453, **2**·CHCl<sub>3</sub>; 1013454, **3**·H<sub>2</sub>O.

**Table 1** Crystal data and structure refinement parameters for **2**, **2**·CHCl<sub>3</sub> and **3**·H<sub>2</sub>O

Compound	<b>2</b>	<b>2</b> ·CHCl <sub>3</sub>	<b>3</b> ·H <sub>2</sub> O
Chemical formula	C <sub>20</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>61</sub> H <sub>31</sub> Cl <sub>3</sub> N <sub>6</sub> O <sub>6</sub> S <sub>6</sub>	C <sub>40</sub> H <sub>22</sub> CuN <sub>4</sub> O <sub>9</sub> S <sub>5</sub>
Formula weight	374.44	1242.69	926.52
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>R</i> 3 <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / nm	0.744 8(1)	3.149 9(13)	0.187 0(2)
<i>b</i> / nm	1.786 2(2)	3.149 9(13)	2.328 2(5)
<i>c</i> / nm	1.314 4(2)	0.944 9(4)	2.181 4(5)
$\beta$ / (°)	105.056(2)		91.421(4)
<i>V</i> / nm <sup>3</sup>	1.688 5(3)	8.119 0(26)	3.995 7(16)
<i>Z</i>	4	6	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.473	1.525	1.540
<i>F</i> (000)	768	3 804	1 884
$\mu$ (Mo <i>K</i> $\alpha$ ) / mm <sup>-1</sup>	0.333	0.463	0.869
Reflections collected	5 014	3 054	7 018
Reflections [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	3 843	941	3 893
Parameters	235	248	590
<i>R</i> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.058 9	0.078 7	0.071 0
<i>wR</i> <sub>2</sub> (all data)	0.183 8	0.199 4	0.215 2
Goodness of fit on <i>F</i> <sup>2</sup>	1.01	1.09	1.01
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub> / (e·nm <sup>-3</sup> )	640, -590	380, -410	480, -430

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

**Table 2** Selected bond distances (nm) and angles (°) for **2**, **2**·CHCl<sub>3</sub> and **3**·H<sub>2</sub>O

<b>2</b>					
O1-C5	0.121 1(4)	O2-C6	0.121 7(3)	C5-C6	0.153 8(4)
<b>2</b> ·CHCl <sub>3</sub>					
O1-C5	0.123 1(11)	O2-C6	0.123 7(10)	C5-C6	0.152 8(14)
<b>3</b> ·H <sub>2</sub> O					
Cu1-N1	0.205 3(4)	Cu1-N3	0.203 3(4)	Cu1-N4	0.206 6(4)
Cu1-N2	0.206 2(4)				
N1-Cu1-N2	82.0(2)	N1-Cu1-N4	112.5(2)	N2-Cu1-N4	140.0(2)
N1-Cu1-N3	133.6(2)	N2-Cu1-N3	115.7(2)	N3-Cu1-N4	81.9(2)

## 2 Results and discussion

### 2.1 Syntheses and spectral characterizations

Our strategy here is to synthesize **2** and 9 thiophene substituted 1,10-phenanthroline-5,6-dione derivatives and their possible metal complexes, and relative synthetic strategy is based on the routes shown in Scheme 1. Different synthetic methods, such as Suzuki-Miyaura and Grignard reagents<sup>[25-26]</sup>, have been used to optimize the experimental conditions for

obtaining 2,9-dithiophene substituted 1,10-phenanthroline-5,6-dione compound **2**, and it is found that Suzuki-Miyaura coupling could give a higher yield. However, the protection of 1,10-phenanthroline-5,6-dione by 2-nitropropane is necessary to guarantee the smooth proceeding of Suzuki-Miyaura coupling between 6,9-dibromo-2,2-dimethyl-1,3-dioxolo[4,5-f][1,10]-phenanthroline-5,6-dione and 2-thiophenylboric acid.

Mononuclear Cu(II) complex **3** with a molar ratio

$n_{\text{metal}}:n_{\text{ligand}}$  of 1:2 was synthesized under reflux 4 h in the mixture of acetonitrile and chloroform. Considering that **2** is a bidentate chelating ligand with large steric hindrance, the formation of its metal complexes is difficult since 2 and 9 substituted thiophene rings will block the metal ion complexation. A series of metal ions with different charge and size, such as  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ag}^+$  and  $\text{Cd}^{2+}$  ions, has been used to react with compound **2**, but only the Cu(II) ion can overcome the steric hindrance by pushing two side thiophene rings to larger dihedral angles and a mononuclear four-coordinate Cu(II) complex **3**·H<sub>2</sub>O can be isolated successfully.

UV-Vis spectra of **1**~**3** have been recorded and plotted together in Fig.SI1 for comparison. They show characteristic absorptions at 300~450 nm corresponding to the  $\pi$ - $\pi^*$  transitions between adjacent aromatic heterocycles. The difference of  $\lambda_{\text{max}}$  may arise from the variation of delocalized  $\pi$  system of **1**, **2** and **3**. Compared with 2-nitropropane protected compound **1**, 2,9-dithiophene substituted 1,10-phenanthroline-5,6-dione compound **2** and **3** display similar UV-Vis spectra, and the interring  $\pi$ - $\pi^*$  transitions of **2** and **3** have 69 and 68 nm hypochromatic shifts, indicative of worse conjugating system after the dissociation of acetal.

## 2.2 Crystal structures

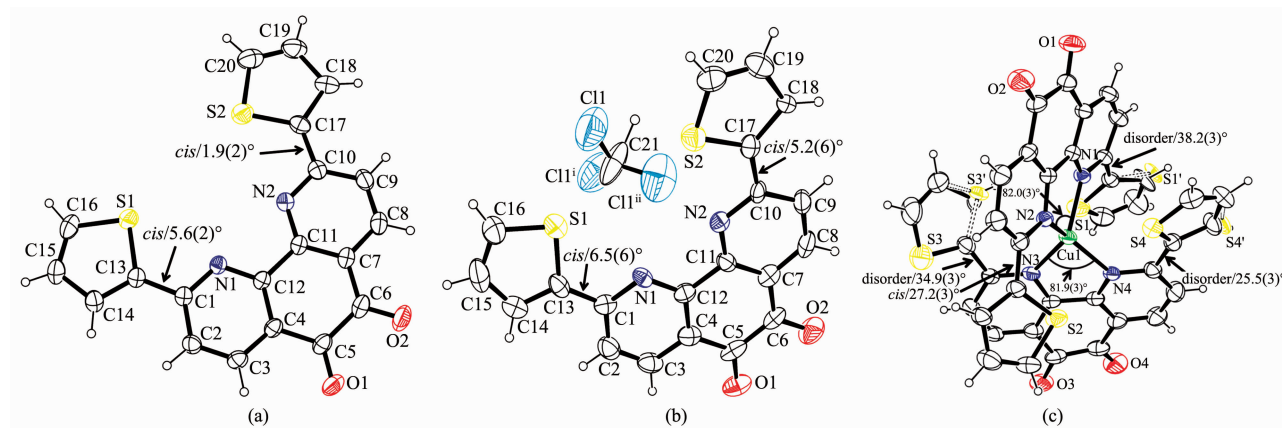
### 2.2.1 Compound **2** and **2**·CHCl<sub>3</sub>

X-ray single-crystal diffraction studies for **2** and

its chloroform solvate compound **2**·CHCl<sub>3</sub> reveal that both of the thiophene rings at 2 and 9 positions of 1,10-phenanthroline-5,6-dione centre adopt the same *cis* conformation, as shown in Fig.1a and Fig.1b, respectively.

Compound **2** crystallizes in the monoclinic space group *P2<sub>1</sub>/c*, while **2**·CHCl<sub>3</sub> belongs to the trigonal space group *R3c*. The C-C bond distance between two carbonyl groups at 5 and 6 positions of 1,10-phenanthroline unit in **2** is 0.153 8(4) nm, indicative of character of single bond, which is similar to that in **2**·CHCl<sub>3</sub> (0.152 8(14) nm). The 1,10-phenanthroline-5,6-dione ring is essentially coplanar with adjacent two thiophene rings in both **2** and **2**·CHCl<sub>3</sub>, where the dihedral angles between the central 1,10-phenanthroline-5,6-dione and its neighboring two thiophene rings in **2** are 5.6(2)° and 1.9(2)°, as depicted in Fig. 1a. In contrast, the corresponding dihedral angles in **2**·CHCl<sub>3</sub> are 6.5(6)° and 5.2(6)°, respectively. Moreover, intermolecular  $\pi$ - $\pi$  stacking interactions are found for both structures. In compound **2**, the centroid-to-centroid separations between adjacent 1,10-phenanthroline-5,6-dione and thiophene rings from different molecules are 0.382 9(9) and 0.387 3(9) nm (Fig.2a), while there are four types of  $\pi$ - $\pi$  stacking interactions in **2**·CHCl<sub>3</sub> with the centroid-to-centroid separations of 0.383 3(3), 0.361 8(3), 0.309 4(3) and 0.356 6(3) nm in **2** (Fig.2b).

### 2.2.2 Cu(II) complex **3**·H<sub>2</sub>O



Protons are shown as small spheres of arbitrary radii

Fig.1 ORTEP diagrams (30% thermal probability level ellipsoids) of the molecular structures of three compound **2** (a), **2**·CHCl<sub>3</sub> (b) and **3**·H<sub>2</sub>O (c) with the atom-numbering scheme



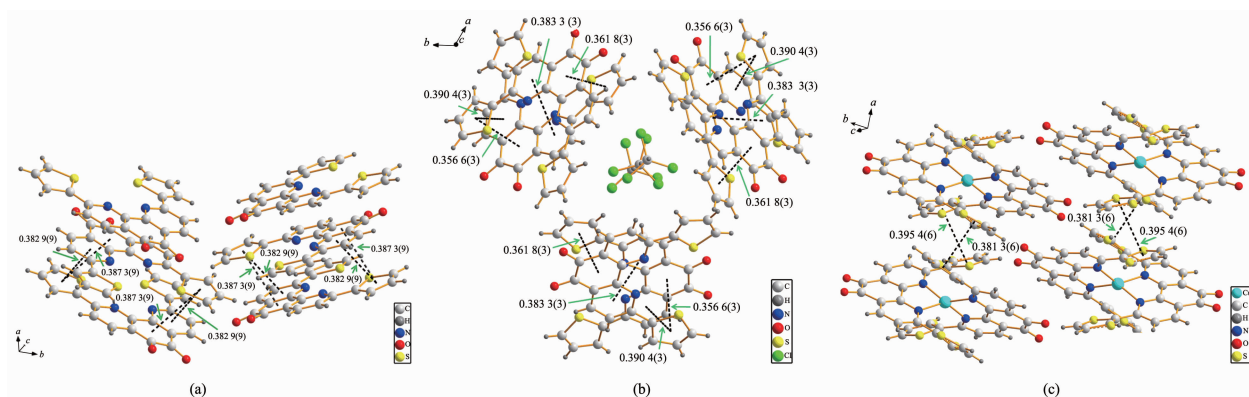


Fig.2 Perspective view of the packing structures of **2** (a), **2**·CHCl<sub>3</sub> (b) and **3**·H<sub>2</sub>O (c) showing stacking interactions

The structural analysis of **3**·H<sub>2</sub>O indicates that it consists of one Cu(II) coordination centre and two bidentate chelating ligands **2**, and the coordination geometry around central Cu(II) ion can be described as a slightly distorted tetrahedron, as depicted in Fig.1c. Interestingly, it is found that the conformation of each 2,9-dithienyl-1,10-phenanthroline-5,6-dione ligand has changed after Cu(II) ion complexation. In comparison with the free ligand **2** and its chloroform solvate compound **2**·CHCl<sub>3</sub>, which have essentially planar molecular structures, the dihedral angles between the central 1,10-phenanthroline-5,6-dione and its neighboring two thiophene rings are significantly increased from 1.9 (2)°/5.6 (2)° in **2** and 5.2 (6)°/6.5 (6)° in **2**·CHCl<sub>3</sub> to 25.3(3)°/27.2(3)° and 34.9(3)°/38.2(3)° in **3**·H<sub>2</sub>O because of the geometric requirement of four-coordinate Cu(II) centre. In addition, three of four thiophene rings of two ligands are found to be disordered with different site occupancy factors to further reduce the spacial crowding around the Cu(II) centre. The dihedral angle between two chelating 1,10-phenanthroline-5,6-dione rings in **3**·H<sub>2</sub>O is 55.43(3)°. Furthermore, strong  $\pi$ - $\pi$  stacking interactions are observed in the crystal packing of **3**·H<sub>2</sub>O between adjacent two thiophene rings from different molecules with the centroid-to-centroid separations of 0.381 3(6) and 0.395 4(6) nm, as can be seen in Fig.2c.

### 3 Conclusions

In summary, planar 2,9-dithienyl-1,10-phenanthroline-5,6-dione (**2**) and its entwined concave-shaped mononuclear four-coordinate Cu(II) complex **3** have

been firstly synthesized and structurally characterized. Because of the large spacial crowding effect of two thiophene rings at 2 and 9 positions of 1,10-phenanthroline-5,6-dione, our experimental results reveal that only its Cu(II) coordination complex can be isolated successfully, in comparison with other transition-metal ions such as Fe<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Ag<sup>+</sup> and Cd<sup>2+</sup>. Further studies are being undertaken on the aromatic heterocyclic extension of 5,6-dione unit of **2** via Radziszewski reaction with certain thiophene based aldehydes.

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