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# 含吡咯环的缩氨基硫脲席夫碱镍、铜配合物的晶体结构及与 DNA 的相互作用

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**摘要**: 合成并通过单晶衍射、元素分析及红外光谱表征了配合物[Ni($L^1$)$_2$]·2DMF (**1**),[Cu($L^1$)$_2$]·THF·0.25MeOH·2.25$H_2O$(**2**), [Ni($L^2$)$_2$]·2MeOH(**3**)和[Cu($L^2$)$_2$]·2EtOH (**4**)的结构($HL^1$:5-甲酰基-3,4-二甲基-吡咯-2-甲酸乙酯缩硫代氨基脲,$HL^2$:5-甲酰基-2,4-二甲基-吡咯-3-甲酸乙酯缩 4-异丙基氨基硫脲)。单晶衍射结果表明,除溶剂分子不同外,配合物 **1**~**4** 的结构相似。每个配合物的中心金属离子分别与来自 2 个阴离子 L$^-$配体的 $N_2S_2$ 电子供体配位,采取扭曲的平面正方形配位构型。荧光光谱结果表明,配合物与 DNA 的相互作用强于其配体。

**关键词**: 吡咯; 缩氨基硫脲; 配合物; 晶体结构; DNA 相互作用
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## Ni(Ⅱ)/Cu(Ⅱ) Complexes with Two Pyrrole Thiosemicarbazone Ligands: Crystal Structures and DNA Interaction

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**Abstract**: Two Ni(Ⅱ) and two Cu(Ⅱ) complexes, namely, [Ni($L^1$)$_2$]·2DMF (**1**), [Cu($L^1$)$_2$]·THF·0.25MeOH·2.25$H_2O$ (**2**), [Ni($L^2$)$_2$]·2MeOH (**3**) and [Cu($L^2$)$_2$]·2EtOH (**4**) (where $HL^1$=5-formyl-3,4-dimethyl-1H-pyrrole-2-carboxylate thiosemicarbazone, $HL^2$=5-formyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate *N*(4)-isopropyl thiosemicarbazone) have been synthesized and characterized by single crystal X-ray diffraction, elemental analysis and IR spectroscopy. X-ray diffraction analysis results show that the structures of all complexes are similar while with different solvent molecules. The metal ion in each complex with a distorted square planar geometry is surrounded by two anionic thiosemicarbazone ligands with $N_2S_2$ donor set. In addition, the fluorescence spectra indicate that the interactions of the complexes with DNA are stronger than those of the corresponding ligands. CCDC: 1424498, $HL^1$·0.5$H_2O$; 1424499, **1**; 1424500, **2**; 1427468, $HL^2$·EtOH; 1427469, **3**; 1427470, **4**.

**Keywords**: pyrrole; thiosemicarbazone; complex; crystal structure; DNA interaction

Recently, thiosemicarbazones (TSCs) and their transition metal complexes, have attracted intensity attention in the coordination chemistry because of their high biological and pharmaceutical activities, such as antibacterial, antiviral, antifungal, antitumor activity and so on[1-4]. Recently, there is increasing

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interest in the structure design of thiosemicarbazones derivatives with the purpose of improving the pharmaceutical properties and functions: (i) a heterocyclic ring in the synthesized TSCs plays a major role in extending their pharmacological properties[2-3]; (ii) the presence of a bulky group at the terminal nitrogen N(4) of TSCs could increase the biological activity [5-6,8]. Furthermore, in most cases, coordination to metal ions results in improvement of the pharmacological activity of TSCs. Therefore, a large amount of TSCs metals containing six-member heterocycles have been found to possess considerable antitumor activity[6-8]. However, the studies on antitumor activities of the complexes with TSCs bearing five-member heterocycles, especially pyrrole, are relatively few[9-10].

In fact, our previous work shows that some pyrrole acylhydrazone Cu(Ⅱ) complexes have certain antitumor activity [9-10]. As a continuation of our research on TSC-metals, in this paper, two Cu(Ⅱ) and two Ni(Ⅱ) complexes with two pyrrole TSC ligands have been synthesized and structural determined by single-crystal X-ray diffraction. In addition, the interactions between all compounds and ct-DNA have been studied by ethidium bromide(EB) fluorescence probe.

## 1 Experimental

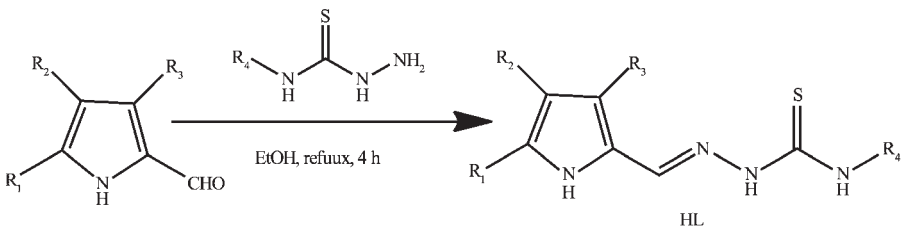
### 1.1 Materials and measurements

Solvents and starting materials for syntheses were purchased commercially and used as received. Elemental analyses were carried out on an Elemental Vario EL analyzer. $^1$H NMR spectra were recorded on a Bruker AV400 NMR spectrometer in DMSO-$d_6$ solution, with TMS as internal standard. The IR spectra ($\nu$=4 000~400 cm$^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. The interactions between the compounds and ct-DNA are measured using literature method[11]. Briefly, upon the addition of varying concentrations of the investigated complexes in 5 mmol·L$^{-1}$ Tris-HCl+50 mmol·L$^{-1}$ NaCl (pH =7.35) into the ethidium bromide (EB)-DNA solution (6.25 μmol·L$^{-1}$ EB and 50 μmol·L$^{-1}$ ct-DNA), emission spectra were recorded on a Varian CARY Eclipse spectrophotometer with the excitation wavelength set at 490 nm.

### 1.2 Preparations of HL$^1$ and HL$^2$

As shown in Scheme 1, the ligand HL$^1$ was prepared by condensation of ethyl 5-formyl-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (1.95 g, 11 mmol) with thiosemicarbazide (0.91 g, 10 mmol) in ethanol solution (30 mL) under reflux condition for 4 h. The yellow powder was filtered and washed three times with ethanol. Yield: 2.48 g (84%). m.p. 258~262 ℃. Anal. Calcd. For HL$^1$ ($C_{11}H_{16}N_4O_2S$) (%): C, 49.24; H, 6.01; N, 20.88; Found (%): C, 49.19; H, 6.08; N, 20.91. $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.306 (1H, s, NH), 11.113 (1H, s, NH), 8.152 (2H, s, NH), 7.882(1H, s, CH=N), 4.090~4.150 (2H, q, $CH_2CH_3$), 2.437 (3H, s, $CH_3$), 2.109(3H, s, $CH_3$), 1.076~1.081(3H, t, $CH_3CH_2$). FTIR (cm$^{-1}$): $\nu$(O=C) 1 656, $\nu$(N=C) 1 536, $\nu$(C=S) 897.

HL$^2$ was synthesized by same method as that of HL$^1$, while using ethyl 5-formyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate and *N*(4)-isopropyl thiosemicarbazide as starting materials. Yield: 2.759 g (89%). m.p.: 238~242 ℃. Anal. Calcd. for HL$^2$ ($C_{14}H_{22}N_4O_2S$)




HL$^1$: $R_1$=COOEt, $R_2$=$CH_3$, $R_3$=$CH_3$, $R_4$=H;
HL$^2$: $R_1$=$CH_3$, $R_2$=COOEt, $R_3$=$CH_3$, $R_4$=$CH(CH_3)_2$;

Scheme 1 Synthetic procedure for two TSC ligands HL$^1$ and HL$^2$

(%): C, 54.17; H, 7.14; N, 18.05; Found (%): C, 53.98; H, 7.24; N, 18.13. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 11.29 (1H, s, NH), 11.26 (1H, s, NH), 8.17~8.19 (1H, d, NH), 7.97 (1H, s, CH=N), 4.41~4.49 (1H, m, CH), 4.20~4.26 (2H, q, $CH_2$), 2.14 (3H, s, $CH_3$), 1.96 (3H, s, $CH_3$), 1.24~1.28 (3H, t, $CH_3CH_2$), 1.18~1.19 (6H, d, $CH_3CH_2$). FTIR ($cm^{-1}$): $\nu$(O=C) 1675, $\nu$(N=C) 1 565, $\nu$(C=S) 930.

Crystals of $HL^1 \cdot 0.5H_2O$ and $HL^2 \cdot EtOH$ suitable for X-ray diffraction analysis were obtained by recrystallization of both TSC ligands from the ethanol solution, respectively.

### 1.3 Preparations of the complexes

The complexes **1**~**2** and **3**~**4** were generated by reaction of $HL^1$ (5 mmol) with equimolar of $Ni(OAc)_2 \cdot 6H_2O$ in MeOH/DMF (20 mL, 3∶1, *V*/*V*) and $Cu(OAc)_2 \cdot 2H_2O$ in MeOH/THF (20 mL, 1∶1, *V*/*V*), $HL^2$ (5 mmol) with equimolar of $Ni(OAc)_2 \cdot 6H_2O$ in MeOH/THF (20 mL, 2∶1, *V*/*V*) and $Cu(OAc)_2 \cdot 2H_2O$ in EtOH/THF (20 mL, 2∶1, *V*/*V*), respectively.

**1**: Brown blocks. Anal. Calcd. for ($C_{28}H_{44}N_{10}O_6S_2Ni$) (%): C, 45.47; H, 6.00; N, 18.94. Found (%): C, 45.52; H, 6.07; N, 18.81. FTIR ($cm^{-1}$): $\nu$(O=C) 1661, $\nu$(N=C-S) 1586, $\nu$(C=N) 1 518, $\nu$(C-S) 863.

**2**: Brown blocks. Anal. Calcd. for ($C_{26.25}H_{43.5}CuN_8O_{7.5}S_2$) (%): C, 43.86; H, 6.10; N, 15.59. Found (%): C, 44.02; H, 6.19; N, 15.55. FTIR ($cm^{-1}$): $\nu$(O=C) 1 632, $\nu$(N=C-S) 1 558, $\nu$(C=N) 1 508, $\nu$(C-S) 862.

**3**: Brown blocks. Anal. Calcd. for ($C_{30}H_{50}N_8O_6S_2Ni$) (%): C, 48.59; H, 6.80; N, 15.11. Found (%): C, 48.64; H, 6.73; N, 15.14. FTIR ($cm^{-1}$): $\nu$(O=C) 1 663, $\nu$(N=C-S) 1 597, $\nu$(C=N) 1 548, $\nu$(C-S) 910.

**4**: Brown blocks. Anal. Calcd. for ($C_{32}H_{54}N_8O_6S_2Cu$) (%): C, 49.62; H, 7.03; N, 14.47. Found (%): C, 49.53; H, 7.09; N, 14.51. FTIR ($cm^{-1}$): $\nu$(O=C) 1 662, $\nu$(N=C-S) 1 621, $\nu$(C=N) 1 512, $\nu$(C-S) 908.

### 1.3 X-ray crystallography

The X-ray diffraction measurement for $HL^1 \cdot 0.5H_2O$, $HL^2 \cdot EtOH$ and complexes **1** ~**4** were performed on a Bruker SMART APEX Ⅱ CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) by using $\varphi$-$\omega$ scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program [12]. The structures were solved by direct methods and refined by full matrix least-square on $F^2$ using the SHELXTL-97 program [13]. All non-hydrogen atoms were refined anisotropically. H atoms for O3 (situated on special position), O4 and C12-C15 (occupancy value of each atom being 0.5), O5, O6 and C16 (occupancy value of each atom being 0.125) of 2 were not added but directly included in the molecular formula. All the other H atoms were positioned geometrically and refined using a riding model. Details of the crystal parameters, data collection and refinements for $HL^1 \cdot 0.5H_2O$, $HL^2 \cdot EtOH$ and complexes **1**~**4** were summarized in Table 1.

CCDC: 1424498, $HL^1 \cdot 0.5H_2O$; 1424499, **1**; 1424500, **2**; 1427468, $HL^2 \cdot EtOH$; 1427469, **3**; 1427 470, **4**.

**Table 1　Selected crystallographic data for $HL^1$, $HL^2$ and complexes 1~4**

| | $HL^1 \cdot 0.5H_2O$ | **1** | **2** | $HL^2 \cdot EtOH$ | **3** | **4** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{11}H_{17}N_4O_{2.5}S$ | $C_{28}H_{44}N_{10}NiO_6S_2$ | $C_{26.25}H_{43.5}CuN_8O_{7.5}S_2$ | $C_{16}H_{28}N_4O_3S$ | $C_{30}H_{50}N_8NiO_6S_2$ | $C_{32}H_{54}CuN_8O_6S_2$ |
| Formula weight | 277.35 | 739.56 | 718.85 | 356.48 | 741.61 | 774.49 |
| *T* / K | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) | 296(2) |
| size / mm | 0.16×0.15×0.12 | 0.22×0.18×0.16 | 0.12×0.10×0.08 | 0.16×0.15×0.12 | 0.21×0.19×0.16 | 0.15×0.13×0.12 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic | Triclinic | Monoclinic, |
| Space group | *P*2/*n* | *C*2/*c* | *I*2/*m* | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| *a* / nm | 1.221 88(17) | 1.357 5(19) | 1.013 3(7) | 0.872 3(4) | 0.859 68(6) | 0.667 40(10) |
| *b* / nm | 0.810 91(11) | 1.164 7(17) | 2.451 6(7) | 1.033 7(6) | 0.930 84(7) | 2.418 6(4) |
| *c* / nm | 1.458 9(2) | 2.277(3) | 1.590 7(5) | 1.184 8(6) | 1.226 91(9) | 1.242 04(19) |
| $\alpha$ / (°) | 90 | 90 | 90 | 92.327(8) | 95.820 0(10) | 90 |
| $\beta$ / (°) | 104.155(2) | 105.98(3) | 106.124(3) | 104.272(8) | 100.580 0(10) | 96.574(3) |

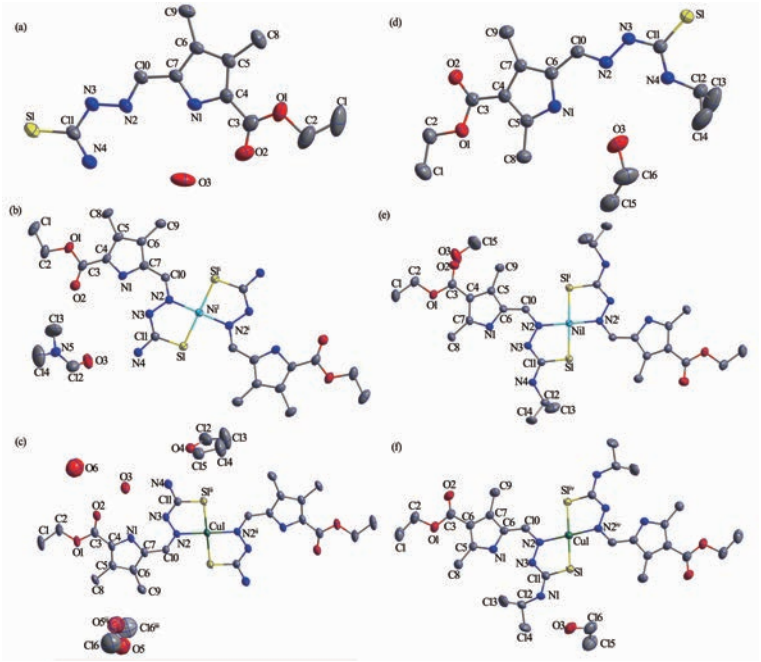
Continued Table 1

| | | | | | | |
|---|---|---|---|---|---|---|
| γ / (°) | 90 | 90 | 90 | 98.601(8) | 99.314 0(10) | 90 |
| $V$ / nm$^3$ | 1.401 7(3) | 3.461(8) | 3.796(3) | 1.020 4(9) | 0.943 65(12) | 1.991 7(5) |
| $Z$ | 4 | 4 | 4 | 2 | 1 | 2 |
| $D_c$ / (g·cm$^{-3}$) | 1.314 | 1.419 | 1.258 | 1.160 | 1.305 | 1.291 |
| $F$(000) | 588 | 1 560 | 1 512 | 384 | 394 | 822 |
| Reflections collected | 6 982 | 8 653 | 9 825 | 5 264 | 4 984 | 10 021 |
| Unique ($R_{int}$) | 2 467(0.026 8) | 3 046(0.052 1) | 3 423(0.054 9) | 3 573(0.016 3) | 3 297(0.015 2) | 3 495(0.029 6) |
| Data, restraint, parameter | 2 467, 2, 178 | 3 046, 4, 214 | 3 423, 24, 227 | 3 573, 224, 218 | 3 297, 1, 216 | 3 495, 3, 224 |
| GOF on $F^2$ | 1.047 | 1.070 | 1.084 | 1.055 | 1.032 | 1.042 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$=0.042 6 | $R_1$=0.055 1 | $R_1$=0.066 4 | $R_1$=0.057 5 | $R_1$=0.041 0 | $R_1$=0.049 2 |
| | $wR_2$=0.114 8 | $wR_2$=0.138 0 | $wR_2$=0.197 5 | $wR_2$=0.158 3 | $wR_2$=0.106 9 | $wR_2$=0.134 0 |
| $R$ indices (all data) | $R_1$=0.064 0 | $R_1$=0.079 4 | $R_1$=0.092 7 | $R_1$=0.076 3 | $R_1$=0.050 9 | $R_1$=0.065 4 |
| | $wR_2$=0.127 9 | $wR_2$=0.152 9 | $wR_2$=0.219 9 | $wR_2$=0.177 4 | $wR_2$=0.115 2 | $wR_2$=0.145 3 |

## 2 Result and discussion

### 2.1 Crystal structures description

A diamond drawing of HL$^1$·0.5H$_2$O, HL$^2$·EtOH and complexes **1**~**4** is shown in Fig.1. Selected bond distances and angles are listed in Table 2. Hydrogen bonds information is in Table 3. As shown in Fig.1a and 1d, HL$^1$ and HL$^2$ in the structures of HL$^1$·0.5H$_2$O and HL$^2$·EtOH, are in a thione form, respectively[11-12]. The lengths of S1-C11 in HL$^1$·0.5H$_2$O, HL$^2$·EtOH are 0.168 7(2) and 0.169 5(3) nm, respectively. However, those change to 0.172 5(3), 0.172 7(5), 0.172 8(3)) and 0.174 5(3) nm in complexes **1**~**4**, respectively, showing that the TSC ligands HL$^1$ and HL$^2$ have thiolated and deprotonated in the complexes[14]. Furthermore, the imine C=N bond (N2-C10) has E configuration in HL$^1$ and HL$^2$, while has Z configuration in the complexes. In the crystal of HL$^1$·



H atoms are omitted for clarity; Symmetry codes: [i] 1–$x$, 2–$y$, –$z$; [ii] –0.5–$x$, 0.5–$y$, 1.5–$z$; [iii] 1–$x$, 1–$y$, 2–$z$; [iv] 3–$x$, 1–$y$, 1–$z$

Fig.1 Diamond drawing of HL$^1$·0.5H$_2$O (a), HL$^2$·EtOH (d) and complexes **1**~**4** (b, c, e and f, respectively) with 30% thermal ellipsoids

**Table 2　Selected bond lengths (nm) and angles (°) in $HL^1\cdot0.5H_2O$, $HL^2\cdot EtOH$ and complexes 1~4**

| | | | | | |
|---|---|---|---|---|---|
| | | $HL^1\cdot0.5H_2O$ | | | |
| C11-S1 | 0.168 7(2) | N2-C10 | 0.127 6(3) | N3-C11 | 0.134 4(3) |
| | | **1** | | | |
| C11-S1 | 0.172 5(3) | N3-C11 | 0.127 7(5) | Ni1-N2 | 0.187 7(4) |
| Ni1-S1 | 0.213 2(3) | N2-Ni1-S1i | 94.65(13) | N2-Ni1-S1 | 85.35(13) |
| | | **2** | | | |
| C11-S1 | 0.172 7(5) | N3-C11 | 0.131 2(6) | Cu1-N2 | 0.200 9(4) |
| Cu1-S1 | 0.225 69(15) | N2ii-Cu1-S1 | 95.87(12) | N2-Cu1-S1 | 84.13(12) |
| | | $HL^2\cdot EtOH$ | | | |
| S1-C11 | 0.169 5(3) | N2-C10 | 0.129 1(4) | N3-C11 | 0.135 4(4) |
| | | **3** | | | |
| C11-S1 | 0.172 8(3) | N3-C11 | 0.130 6(3) | Ni1-N2 | 0.191 5(2) |
| Ni1-S1 | 0.217 04(7) | N2-Ni1-S1i | 94.44(6) | N2-Ni1-S1 | 85.56(6) |
| | | **4** | | | |
| C11-S1 | 0.174 5(3) | N3-C11 | 0.131 3(4) | Cu1-N2 | 0.200 8(3) |
| Cu1-S1 | 0.225 18(9) | N2iv-Cu1-S1 | 95.87(7) | N2-Cu1-S1 | 84.13(7) |

Symmetry codes: [i] 1–*x*, 2–y, –*z* for **1** and **3**; [ii] –0.5–*x*, 0.5–*y*, 1.5–*z* for **2**; [iv] 3–*x*, 1–*y*, 1–*z* for **4**

**Table 3　Hydrogen bonds information in $HL^1\cdot0.5H_2O$, $HL^2\cdot EtOH$ and complexes 1~4**

| D-H···A | *d*(D-H) / nm | *d*(H···A) / nm | *d*(D···A) / nm | ∠DHA / (°) |
|---|---|---|---|---|
| | | $HL^1\cdot0.5H_2O$ | | |
| N4-H4B···S1[i] | 0.086 | 0.264 | 0.347 0(2) | 161.1 |
| O3-H3A···O2[v] | 0.084 9(10) | 0.192(2) | 0.273 7(3) | 160(5) |
| N3-H3···S1[vi] | 0.086 | 0.256 | 0.340 6(2) | 169.3 |
| N1-H1···O3 | 0.082(2) | 0.220(3) | 0.299 0(2) | 161(2) |
| | | **1** | | |
| N1-H1···N3 | 0.086 | 0.217 | 0.267 1(5) | 116.9 |
| N4-H4A···O3 | 0.086 | 0.212 | 0.285 4(6) | 143.6 |
| N4-H4B···O3[vii] | 0.086 | 0.202 | 0.288 2(6) | 177.3 |
| | | **2** | | |
| N1-H1···N3 | 0.086 | 0.218 | 0.270 1(5) | 118.3 |
| N4-H4A···O3 | 0.086 | 0.217 | 0.298 3(7) | 157.4 |
| N4-H4B···O4 | 0.086 | 0.212 | 0.297 1(7) | 169.4 |
| O3···O2 | | | 0.281 2 | |
| O3···O3[viii] | | | | 0.299 3 |
| O3···O3[ix] | | | | 0.278 5 |
| | | $HL^2\cdot EtOH$ | | |
| N3-H3A···S1[x] | 0.086 | 0.267 | 0.350 1(3) | 163.6 |
| O3-H3···O2[xi] | 0.082 | 0.204 | 0.285 7(4) | 170.3 |
| N1-H1A···O3 | 0.086 | 0.222 | 0.304 2(4) | 161.1 |
| | | **3** | | |
| O3-H3···O2 | 0.082 | 0.215 | 0.287 0(5) | 147.2 |
| N1-H1A···N3 | 0.086 | 0.222 | 0.271 4(3) | 116.8 |
| N4-H4A···O3[xii] | 0.086 | 0.223 | 0.300 3(4) | 148.7 |

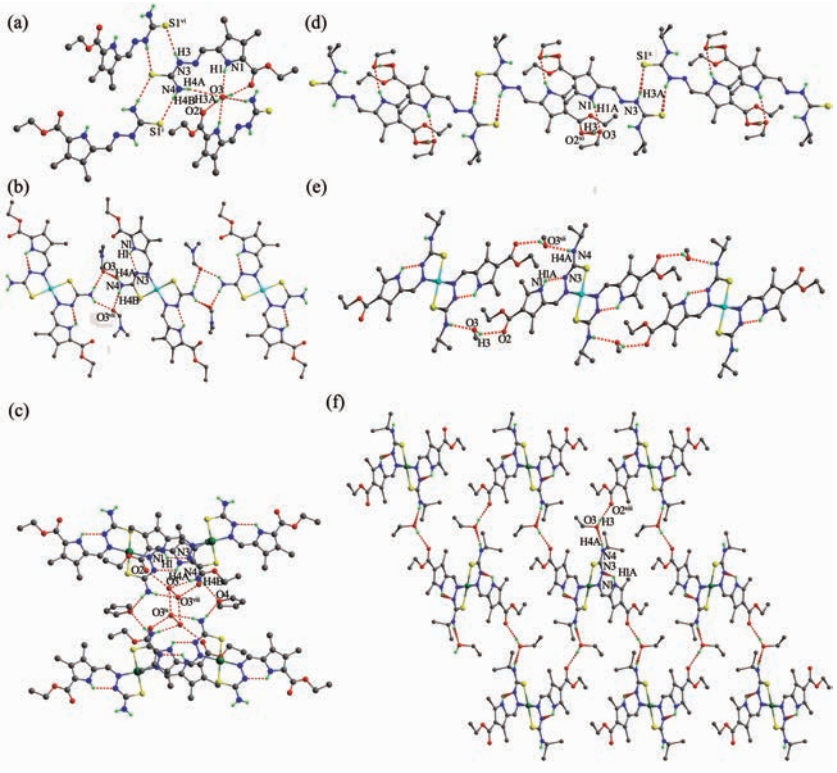
Continued Table 3

| | | | | |
|---|---|---|---|---|
| | | **4** | | |
| O3-H3···O2$^{xiii}$ | 0.082 | 0.203 | 0.283 9(5) | 170.1 |
| N1-H1A···N3 | 0.086 | 0.220 | 0.272 3(4) | 118.8 |
| N4-H4A···O3 | 0.086 | 0.210 | 0.295 1(4) | 168.8 |

Symmetry codes: $^{i}$ 1−*x*, 2−*y*, −*z*; $^{v}$ 0.5−*x*, *y*, 0.5−*z*; $^{vi}$ 1.5−*x*, *y*, 0.5−*z* for $HL^1\cdot0.5H_2O$; $^{vii}$ 1−*x*, *y*, −0.5−*z* for **1**; $^{viii}$ −*x*, *y*, 2−*z*; $^{ix}$ *x*, −*y*, *z* for **2**; $^{x}$ 2−*x*, 1−*y*, 1−*z*; $^{xi}$ 3−*x*, −*y*, 1−*z* for $HL^2\cdot$EtOH; $^{xii}$ 3−*x*, −*y*, −*z* for **3**; $^{xiii}$ 2−*x*, 0.5+*y*, 0.5−*z* for **4**

0.5$H_2O$, one lattice water molecule links two $HL^1$ molecules to form a centrosymmetric dimer via intermolecular N-H···O and O-H···O hydrogen bonds, which are further connected with each other through two pairs of intermolecular N-H···S hydrogen bonds (Fig.2a), giving an extended 3D structure. In the structure of $HL^2\cdot$EtOH, a similar dimer is formed by intermolecular O-H···O and N-H···O hydrogen bonds between $HL^2$ and crystal methanol molecule. Pairs of intermolecular N-H···S hydrogen are helpful to construct an extended one dimentional chain (Fig.2d).

The structures of complexes **1**~**4** are similar while with different solvent molecules. As shown in Fig.1, the central metal ion in each complex is coordinated with two independent thiolated TSC ligands with $N_2S_2$ donor set, thus giving a distorted square planar geometry. The coordination bond lengths of M-N/S of complexes **1**~**4** are comparable with those of some reported complexes with similar donor set[8,15]. In complex **1** (Fig.2b) and **3** (Fig.2d), crystal DMF and methanol molecules link the complexes into chains via the intermolecular N-H···O (additional O-H···O for **3**) hydrogen bonds, respectively. In complex **2** (Fig.2c), an extended 3D




H atoms of C-H bonds and crystal MeOH and water molecules in complex **2** (not involved in hydrogen bonds) are omitted for clarity; Symmetry codes: Symmetry codes: $^{i}$ 1−*x*, 2−*y*, −*z*; $^{v}$ 0.5−*x*, *y*, 0.5−*z*; $^{vi}$ 1.5−*x*, *y*, 0.5−*z* for $HL^1\cdot0.5H_2O$; $^{vii}$ 1−*x*, *y*, −0.5−*z* for **1**; $^{viii}$ −*x*, *y*, 2−*z*; $^{ix}$ *x*, −*y*, *z* for **2**; $^{x}$ 2−*x*, 1−*y*, 1−*z*; $^{xi}$ 3−*x*, −*y*, 1−*z* for $HL^2\cdot$EtOH; $^{xii}$ 3−*x*, −*y*, −*z* for **3**; $^{xiii}$ 2−*x*, 0.5+*y*, 0.5−*z* for **4**

Fig.2 Extend supramolecular structures in $HL^1\cdot0.5H_2O$ (a), $HL^2\cdot$EtOH (d) and complexes **1**~**4** (b, c, e and f, respectively)

structure is formed by intermolecular N-H···O and N-H···O hydrogen bonds involving the complex, lattice water and THF molecules. However, in complex **4**, crystal ethanol molecules link the complexes into an extended 2D supramolecular structure through intermolecular O-H···O and N-H···O hydrogen bonds (Fig.2f). Intramolecular N-H ··· N hydrogen bonds between the nitrogen atom of pyrrole ring and the imine nitrogen atom are also present in complexes **1**~**4**.

### 2.2 IR spectra

The IR spectra for complexes **1**~**4** are more or less similar due to the similarity in coordination modes of the ligands with the metal centre. The $\nu$(C=S) vibration of the free ligand $HL^1$ and $HL^2$ are at 896 and 930 $cm^{-1}$, respectively, while it is absent in the complexes. Meanwhile, new (N=C-S) and (C-S) stretching vibration absorption are observed at 1 586 and 863, 1 558 and 862, 1 597 and 910, 1 621 and 908 $cm^{-1}$ in complexes **1**~**4**, respectively, inferring that the C=S bond has thiolated to N=C-S moiety and the sulphur atom coordinates to the central metal ion in the complexes[16-17]. The $\nu$(N=C) vibration of the free ligand $HL^1$ and $HL^2$ is at 1 536 and 1 565 $cm^{-1}$, respectively, while at 1 518, 1 508, 1 548 and 1 512 $cm^{-1}$ in complexes **1**~**4**, respectively, showing the N=C bond participates in the coordination in each complex[18]. It is in accordance with the crystal structure study.

### 2.3 UV spectra

The UV spectra of the ligands $HL^1$, $HL^2$ and complexes **1**~**4** in DMF solution ($c$=10 μmol·$L^{-1}$) were measured at room temperature (Fig.3). The spectra of $HL^1$ and $HL^2$ features two main bands located around 352 ($\varepsilon$=29 923 L·$mol^{-1}$·$cm^{-1}$) and 368 ($\varepsilon$=27 954 L·$mol^{-1}$·$cm^{-1}$), 340 ($\varepsilon$=39 130 L·$mol^{-1}$·$cm^{-1}$) and 354 nm ($\varepsilon$=33 697 L·$mol^{-1}$·$cm^{-1}$), respectively, which could be assigned to characteristic $\pi$-$\pi$* transitions centered on pyrrole rings and imine unit [14,19]. However, in complexes **1**~**4**, the two main bands were combined along with red shift to 378 ($\varepsilon$=28 759 L·$mol^{-1}$·$cm^{-1}$), 372 ($\varepsilon$=25 139 L·$mol^{-1}$·$cm^{-1}$), 375 ($\varepsilon$=23 566 L·$mol^{-1}$·$cm^{-1}$) and 381 nm ($\varepsilon$=25 389 L·$mol^{-1}$·$cm^{-1}$), respectively, showing that the N=C bond participates in the coordination in each complex. Furthermore,

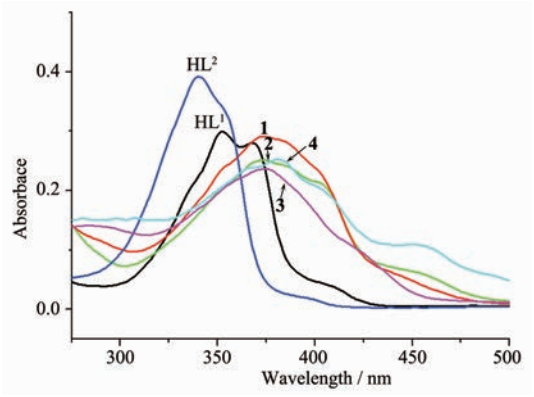
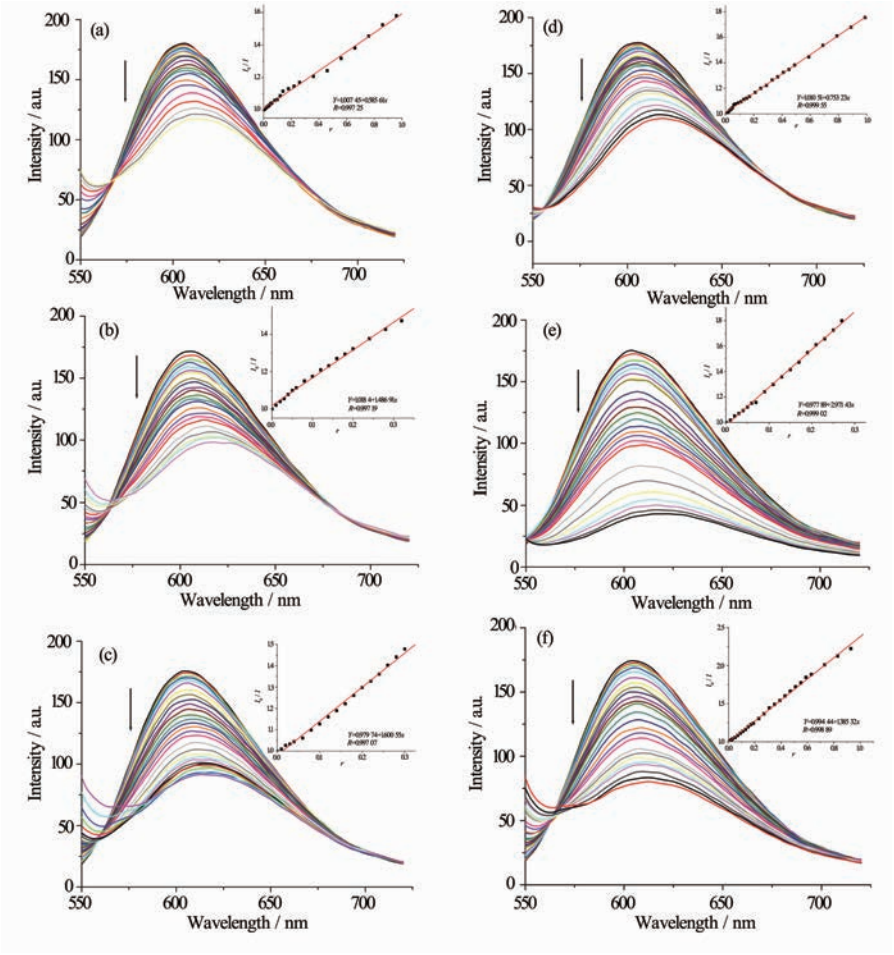



Fig.3 UV spectra of the ligands $HL^1$, $HL^2$ and complexes **1**~**4** in the DMF solution at room temperature

there is a new absorbance band of **2** (452 nm, $\varepsilon$=6 401 L·$mol^{-1}$·$cm^{-1}$) and **4** (453 nm, $\varepsilon$=10 982 L·$mol^{-1}$·$cm^{-1}$), which is probably due to *d*-*d* transition of the centre Cu(Ⅱ) ions[20].

### 2.4 EB-DNA binding study by fluorescence spectrum

It is well known that EB can intercalate nonspecifically into DNA, which causes it to fluoresce strongly. Competitive binding of other drugs to DNA and EB will result in displacement of bound EB and a decrease in the fluorescence intensity[15]. The effects of the ligand and complexes on the fluorescence spectra of EB-DNA system are presented in Fig.3, the fluorescence intensities of EB bound to ct-DNA at about 600 nm show remarkable decreasing trends with the increasing concentration of the tested compounds, indicating that some EB molecules are released into solution after the exchange with the compounds. The quenching of EB bound to DNA by the compounds is in agreement with the linear Stern-Volmer equation: $I_0/I = 1 + K_{sq}r$ [11], where $I_0$ and $I$ represent the fluorescence intensities in the absence and presence of quencher, respectively, $K_{sq}$ is the linear Stern-Volmer quenching constant, $r$ is the ratio of the concentration of quencher and DNA. In the quenching plots of $I_0/I$ versus $r$, $K_{sq}$ values are given by the slopes. The $K_{sq}$ values are 0.586, 1.487 and 1.601 for $HL^1$, complexes **1** and **2**, respectively, while those for $HL^2$, complexes **3** and **4** are tested to be 0.753, 2.971 and 1.385, respectively. The results indicate that interactions of the complexes with DNA are stronger than those of the corresponding TSC ligands, probably




Arrow shows the fluorescence intensities change of EB-DNA system upon increasing tested compound concentration; Inset: plot of $I_0/I$ versus $r$

Fig.3 Emission spectra of EB-DNA system in the presence of $HL^1$ (a), $HL^2$ (d) and complexes **1~4** (b, c, e and f, respectively)

due to the higher rigidity of the complexes, which is in accordance with the literature[11]. In addition, complex **3** has the highest quenching ability among the tested complexes, this could be explained from three aspects: (i) metal-ligand synergism effect may be more effective in **3** than in other complexes[18]; (ii) the isopropyl at the terminal nitrogen N(4) of $HL^2$ is helpful to enhance the quenching ability, which is in agreement with the fact that interaction of $HL^2$ with DNA is stronger than that of $HL^1$; (iii) the positions of the substitutes in the pyrrole ring may be also responsible for the DNA interaction ability in some content.

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