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Two copper(II) complexes with 4-benzoylpyridine ligand: Synthesis, crystal structure and luminescent properties

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ABSTRACT

Two new copper(II) complexes $Cu(NCS)_2(4\text{-Bzpy})_2$ (**1**) and $Cu(NO_3)_2(4\text{-Bzpy})_4$ (**2**) (4-Bzpy = 4-benzoylpyridine) have been synthesized and characterized by IR, UV, elemental analysis and X-ray crystallography. Cu(II) atom has a square planar environment for **1** and an distorted octahedral environment for **2**, respectively. In solid state there are C–H···π interactions and C–H···S hydrogen bonds between adjacent molecules in complex **1**. The molecule of complex **2** is further connected by multiform π–π interactions, C–H···π interactions and C–H···O hydrogen bonds to form a three-dimensional supramolecular structure. The luminescent properties of the complexes **1** and **2** were both investigated in H_2O solution and in solid state at room temperature, respectively.

1. Introduction

The design and construction of functional coordination complexes has attracted considerable attention in recent years for their special functional properties such as optics, magnetism, separation and catalysis as well as the variety of architectures and topologies [1–3]. Among them, owing to the ability of metal-organic complexes to adjust their absorption and emission by altering the metal sphere, construction of metal coordination complexes by the judicious choice of conjugated organic ligands and metal centres can be an efficient method for obtaining new types of luminescent materials [4–6]. Pyridine derivatives are excellent neutral ligands to generate the interesting architectures with metal ions. Moreover, the coordination feature of neutral pyridine derivative ligands in metal complexes is obviously influenced by the nature of different counteranions due to the electroneutrality principle of ligands [7–9]. The chosen ligand L in this paper, 4-benzoylpyridine (4-Bzpy) has been used to assemble a series of the anion dependent copper(I) complexes displaying solid state emission at room temperature, CuX(4-Bzpy) (X = Cl, Br, I, CN, SCN and N_3), $CuX(4\text{-Bzpy})_2$ (X = NO_3 and ClO_4) [10] and other transition metal complexes, such as $Co(N_3)_2(4\text{-Bzpy})_4$, $Co(NCS)_2(4\text{-Bzpy})_4$ and $[Ag(4\text{-Bzpy})_2]NO_3{\cdot}H_2O$ [11]. As a part of our continuing investigations on metal-organic coordination complexes and their photoluminescent properties [12,13], herein we report the synthesis and X-ray single crystal structure of two new copper(II) complexes $Cu(NCS)_2(4\text{-Bzpy})_2$ **1** and $Cu(NO_3)_2(4\text{-Bzpy})_4$ **2** (4-Bzpy = 4-benzoylpyridine). The two complexes both exhibit fluorescent emission at room temperature in H_2O solution and in solid state, respectively.

2. Experimental

2.1. Physical measurements

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. UV–vis spectra were obtained on a Shimadzu UV-250 spectrometer in the range of 500–190 nm in H_2O solution. Luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer. The fluorescence quantum yields were determined in H_2O solution using L-tyrosine ($\Phi_f = 0.14$ in H_2O) [14] as standard.

2.2. Materials

All the chemicals were reagent grade and used without further purification.

2.3. Preparation of the complex 1

A 10 mL aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.242 g, 1.0 mmol) and KSCN (0.194 g, 2.0 mmol) was slowly added to a 10 mL methanol solution of 4-benzoylpyridine (0.183 g, 1.0 mmol). After refluxing for 2 h, the resulting solution was filtered and left for slowly evaporating at room temperature to obtain green block

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crystals suitable for single crystal X-ray structure determination. Yield: 63%. Anal. Calc. For $C_{26}H_{18}CuN_4O_2S_2$ (%): C, 57.18; H, 3.32; N, 10.26. Found (%): C, 57.26; H, 3.37; N, 10.17. IR (KBr pellet, cm^{-1}): 2086(vs), 1661(s), 1613(m), 1593(m), 1578(m), 1550(m), 1449(m), 1415(s), 1327(m), 1312(m), 1280(s), 1225(m), 1180(m), 1155(m), 1065(m), 1024(m), 999(m), 943(m), 934(m), 845(m), 789(m), 748(m), 730(m), 696(s), 648(s), 579(m), 472(m), 455(m).

2.4. *Preparation of the complex **2***

A 10 mL aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1.0 mmol) was slowly added to a 10 mL methanol solution of 4-benzoylpyridine (0.183 g, 1.0 mmol). After refluxing for 2 h, the resulting blue solution was filtered and left for evaporating at room temperature to obtain blue block crystals suitable for single crystal X-ray structure determination. Yield: 58%. Anal. Calc. For $C_{48}H_{36}CuN_6O_{10}$ (%): C, 62.64; H, 3.94; N, 9.13. Found (%): C, 62.55; H, 3.89; N, 9.22. IR (KBr pellet, cm^{-1}): 3056(m), 1661(s), 1615(m), 1595(m), 1579(m), 1552(m), 1449(m), 1427(s), 1412(m), 1384(s), 1326(m), 1314(m), 1282(s), 1223(m), 1180(m), 1155(m), 1106(m), 1078(m), 1063(m), 1042(m), 1027(m), 1000(m), 939(m), 850(m), 753(m), 733(m), 702(s), 648(s), 580(m), 462(m).

2.5. *Crystallographic data collection and refinement*

A suitable sample of size 0.15 mm × 0.12 mm × 0.12 mm for **1** and 0.18 mm × 0.16 mm × 0.14 mm for **2** were chosen for the crystallographic study and then mounted on a BRUKER SMART APEX CCD diffractometer with ω and φ scan mode in the range of $1.34^\circ < \theta < 25.00^\circ$ for **1** and $2.09^\circ < \theta < 25.05^\circ$ for **2**, respectively. All diffraction measurements were performed at room temperature using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). For **1**, a total of 6416 (4332 independent, $R_{int} = 0.0234$) reflections were measured. For **2**, a total of 10519 (3663 independent, $R_{int} = 0.0259$) reflections were measured. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXL-97 program package [15]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques and all hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. O(3) and O(4) atoms from the NO_3^- anions in **2** are rotationally disordered over two orientations in the refined ratio 0.5:0.5. CCDC reference numbers: 810698 (**1**) and 810699 (**2**). Space group, lattice parameters and other relevant information are listed in Table 1. The relevant bond lengths and bond angles are listed in Table 2.

3. Results and discussion

3.1. *IR and UV spectra*

In the IR spectrum of the complex **1**, a sharp and strong ν (SCN) absorption band at 2086 cm^{-1} shows the coordination mode of NCS^- anions, which agrees well with the relevant compounds [13]. The band at 1384 cm^{-1} is assigned as the ν (NO_3^-) stretching frequency in the complex **2** [10]. For **1** and **2**, the strong band at 1661 cm^{-1} is assigned to be the stretching C=O frequency of ligand L. Their identity was finally confirmed by X-ray crystallography. The UV spectra of 4-Bzpy, the complexes **1** and **2** in H_2O solution have been measured, respectively. The UV spectrum of 4-Bzpy displays the main absorption peak at 264 nm and a shoulder absorption at 223 nm, which can be assigned to the π–π* and n–π* transition. The UV spectra of two complexes display similar absorption peaks at 222 nm, 263 nm for **1** and 225 nm, 264 nm for **2**, respectively.

Table 1
Crystallographic data and structure refinement for complexes **1** and **2**.

Crystal data	1	2
Chemical formula	$C_{26}H_{18}CuN_4O_2S_2$	$C_{48}H_{36}CuN_6O_{10}$
Formula weight	546.10	920.37
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2(1)/c$
a (Å)	7.5943(11)	9.0247(9)
b (Å)	10.9413(16)	20.769(2)
c (Å)	15.499(2)	11.0487(11)
α (°)	97.961(3)	90.00
β (°)	97.028(3)	90.00
γ (°)	99.516(3)	90.00
Volume (Å^3)	1243.9(3)	2070.9(4)
Z	2	2
D_c (Mg m^{-3})	1.458	1.476
Crystal size (mm)	0.15 × 0.12 × 0.12	0.18 × 0.16 × 0.14
Radiation (Å)	MoKα 0.71073	MoKα 0.71073
Theta Min-Max (°)	1.34–25.00	2.09–25.05
Tot., Uniq. Data, R (int)	6416, 4332, 0.0234	10519, 3663, 0.0259
Observed data [$I > 2.0$sigma(I)]	2922	2910
Nref, Npar	4332, 316	3663, 313
R, wR_2, S	0.0446, 0.1092, 1.030	0.0337, 0.0869, 1.093
Min. and Max. Resd. Dens. [e/Å^3]	−0.348, 0.346	−0.296, 0.222

3.2. *Description of the crystal structure of complex **1***

The title complex **1** crystallizes in the triclinic space group $P\bar{1}$. An ORTEP diagram of the complex **1** with the atomic numbering scheme and the coordination environment of Cu(II) atom is depicted in Fig. 1. The dimer structure of complex **1** is depicted in Fig. 2. The asymmetric unit consists of one Cu(II) centre, two NCS^- anions and two 4-Bzpy ligands. The two 4-Bzpy ligands both adopt a conformation where the benzene ring and pyridine ring twisted with the reference plane C(7)–C(8)–C(9) and C(19)–C(20)–C(21), respectively. The dihedral angles with the reference plane are 14.6° and 16.3° for benzene rings, and 133.3° and 137.0° for pyridine rings. The dihedral angles between the pyridine ring and the benzene ring are 120.8° and 125.3°, respectively.

The Cu(II) atom is surrounded by two N atoms from two pyridine rings and two N atoms from two NCS^- anions to attain a square planar coordination geometry with the value of the topological parameter τ of *ca.* 0.04. The Cu(II)–$N_{pyridyl}$ average distance of 2.06 Å is longer than that found (1.992(4) Å) in $[Cu(I)Cl(4\text{-}Bzpy)]_2$ [10]. The Cu(II)–N_{NCS} average distance of 1.93 Å is similar to those found in related complexes [16]. Two NCS^- groups are almost linear with the N–C–S bond angles being 178.5(3)° and 179.7(4).

Table 2
Selected bond distances (Å) and bond angles (°) for complexes **1** and **2**.

1			
Bond length (Å)			
Cu1–N1	1.929(3)	Cu1–N2	1.928(3)
Cu1–N3	2.066(3)	Cu1–N4	2.047(3)
N1–C1	1.153(4)	C1–S1	1.619(4)
N2–C2	1.151(4)	C2–S2	1.628(4)
Bond angle (°)			
N2–Cu1–N1	178.98(12)	N2–Cu1–N4	91.17(12)
N1–Cu1–N4	89.60(13)	N2–Cu1–N3	89.38(13)
N1–Cu1–N3	89.80(13)	N4–Cu1–N3	175.14(11)
N1–C1–S1	178.5(3)	N2–C2–S2	179.7(4)
C1–N1–Cu1	166.9(3)	C2–N2–Cu1	163.8(3)
2			
Bond length (Å)			
Cu1–N1	2.0441(15)	Cu1–N2	2.0318(15)
Cu1–O5	2.5919(18)		
Bond angle (°)			
N2–Cu1–N1[a]	90.09(6)	N2–Cu1–N1	89.91(6)
N2–Cu1–O5[a]	88.59(6)	N2–Cu1–O5	91.41(6)
N1–Cu1–O5	89.25(6)	N1A–Cu1–O5	90.75(6)

[a] Symmetry code, 1 − *x*, −*y*, −*z*.

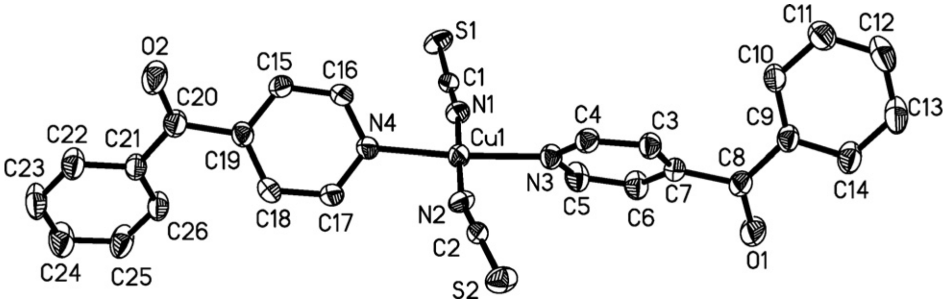

Fig. 1. ORTEP drawing of the complex **1** with the atom numbering scheme. The atoms are represented by 30% probability thermal ellipsoids.

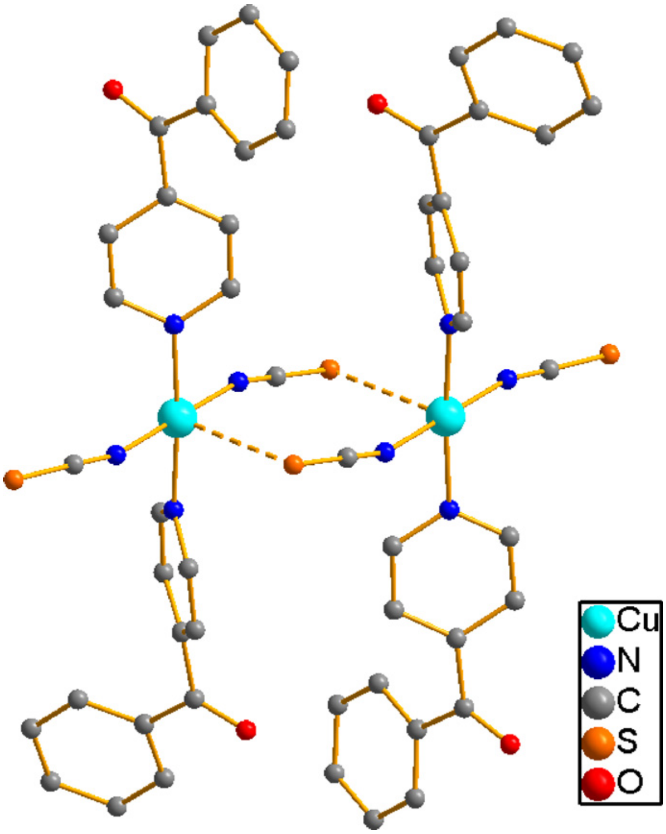

Fig. 2. The dimer structure of the complex **1**.

The connection between Cu(II) and NCS$^-$ group is bent with the Cu(1)–N(1)–C(1) and Cu(1)–N(2)–C(2) bond angles being 166.9(3)° and 163.8(3)°, respectively. The average C–S bond distance of 1.62 Å lies between C–S single bond (1.82 Å) and C═S double bond (1.56 Å) and suggests that it has a partial double bond character. These values are similar to those found in related complexes [12,16]. The two adjacent molecules are connected together through weak Cu···S interactions to form a dimer structure with the Cu···Cu separation of 5.54 Å (Fig. 2). The Cu(1)···S(2A) distance is 2.938 Å and the Cu(1)···S(2A)–C(2A) angle is 92.5°.

It is interesting to note that there are obvious two types of C–H···π interactions involving benzene rings and pyridine rings of adjacent molecules (Fig. 3). The C–H···π interaction between C(22) (symmetry code: $1+x$, y, $-1+z$) and the benzene ring [C(9)–C(14)] is characterized by the C···M separation of 3.55 Å and the C–H···M angle of 121.1° (M, midpoint of the aromatic ring). The C(25)···M separation is 3.97 Å and C–H···M angle is 104.5° for the other type of C–H···π interactions between C(25) (symmetry code: $1+x$, y, z) and the pyridine ring [N(4)C(15)–C(19)]. Additionally, one type of C–H···S hydrogen bonds between the C(3) atoms of pyridine rings and S(2) atoms of NCS$^-$ anions is found with the C···S separation of 3.409(4) Å and C–H···S angle of 119° for C(3)–H(3A)···S(2B) (symmetric code B: $1-x$, $-y$, $-z$).

3.3. Description of the crystal structure of complex 2

The complex **2** crystallizes in the monoclinic space group *P*2(1)/*c*. An ORTEP diagram of the complex **2** with the atomic numbering scheme and the coordination environment of Cu(II) is depicted in Fig. 4. The Cu(II) ion occupies the crystallographic inversion centre special position and is bound to four N atoms from four ligands and two O atoms from two NO$_3$$^-$ anions, forming an enlarged octahedral coordination geometry due to the Jahn–Teller

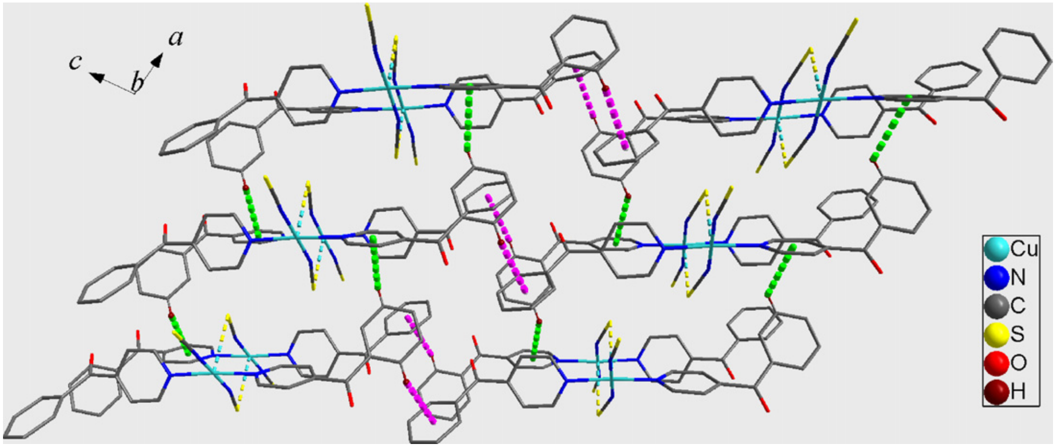

Fig. 3. The supramolecular framework of the complex **1** showing two types of C–H···π interactions in dashed lines.

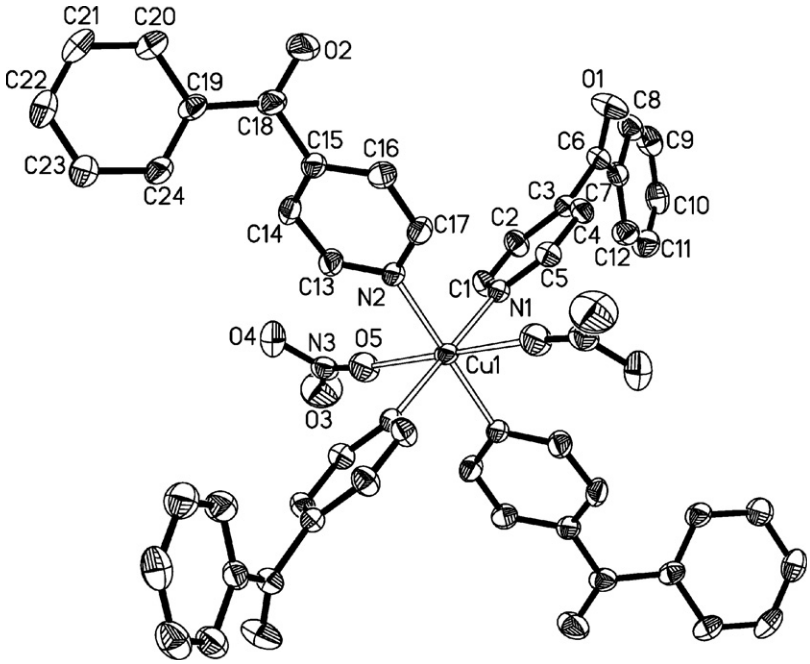

Fig. 4. ORTEP drawing of the complex **2** with the atom numbering scheme. The atoms are represented by 30% probability thermal ellipsoids. Symmetry code, $1-x, -y, -z$.

Table 3
Hydrogen bonding interactions (Å,°)..

D–H···A	d(D–H)	d(H···A)	d(D···A)	∡(DHA)	Symmetry transformation for A
C(1)–H(1A)···O(5)	0.93	2.39	3.106(3)	133	
C(5)–H(5A)···O(1)	0.93	2.59	3.168(3)	120	$-x, 1-y, -z$
C(5)–H(5A)···O(5)	0.93	2.39	3.118(3)	135	$-x, 1-y, 1-z$
C(8)–H(8A)···O(3)	0.93	2.60	3.509(11)	166	$x, y, -1+z$
C(11)–H(11A)···O(3′)	0.93	2.39	3.149(9)	138	$x, 3/2-y, -1/2+z$
C(13)–H(13A)···O(4)	0.93	2.44	3.361(10)	171	
C(13)–H(13A)···O(5)	0.93	2.44	3.156(3)	134	
C(17)–H(17A)···O(5)	0.93	2.37	3.063(3)	131	$-x, 1-y, 1-z$
C(20)–H(20A)···O(4)	0.93	2.50	3.225(10)	135	$x, 1/2-y, -1/2+z$
C(24)–H(24A)···O(2)	0.93	2.57	3.410(3)	150	$x, 1/2-y, 1/2+z$

effect. The axial Cu–O distance is 2.5919(18) Å, whereas the average distance of four equatorial Cu–N is 2.04 Å. The two ligands adopt a conformation where the benzene ring and pyridine ring twisted with the reference plane C(3)–C(6)–C(7) and C(15)–C(18)–C(19), respectively. The dihedral angles with the reference plane are 19.8° and 29.6° for benzene rings and 135.9° and 145.3° for pyridine rings, respectively. The dihedral angles of the pyridine ring and the benzene ring are 120.5° and 121.4°. These results are similar to those found in complex **1** and the related metal complexes [10,11]. In addition, five types of C–H···O hydrogen bonds between the car-

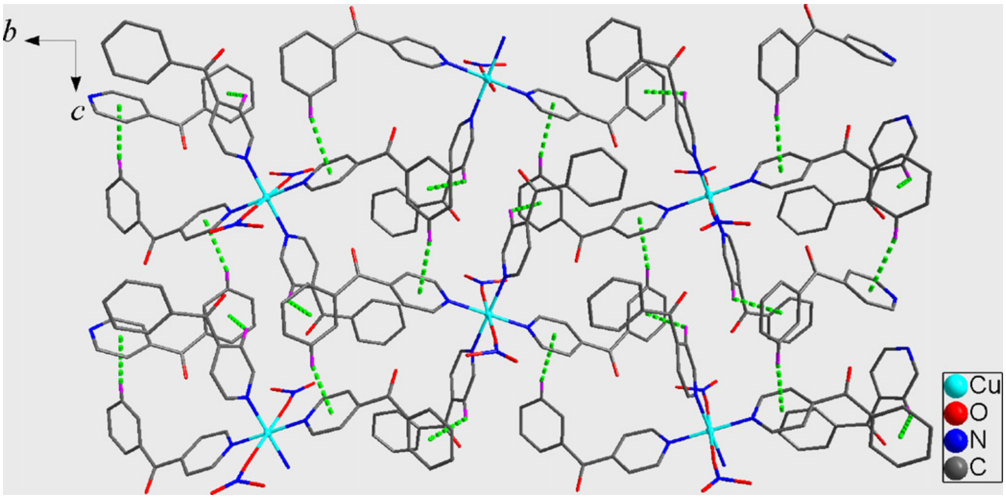

Fig. 5. The supramolecular framework of the complex **2** showing C–H···π interactions in dashed lines.

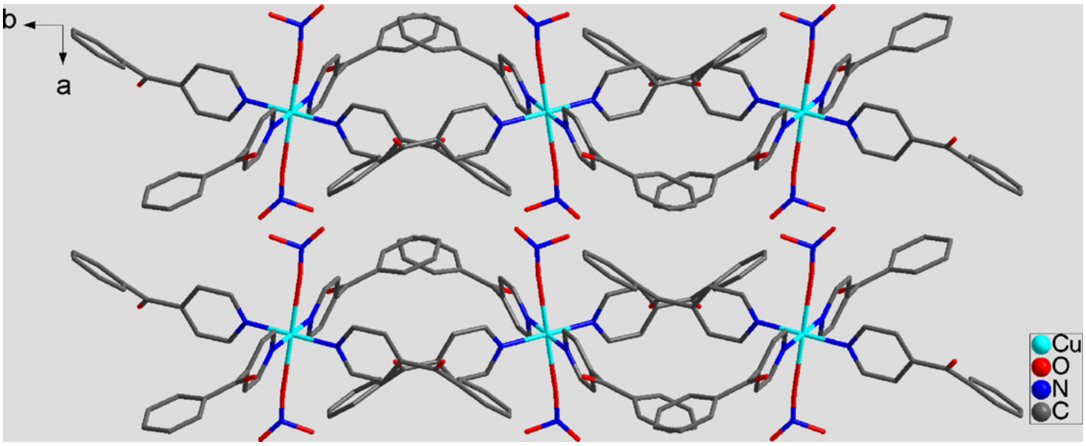

Fig. 6. The crystal packing of the complex **2**.

bon atoms of aromatic rings and the oxygen atoms of two NO_3^- anions are found in the structure and also play an important role in stabilizing the molecule structure (Table 3).

The π–π stacking interaction between two benzene rings [C(7)–C(12)] and [C(19)–C(24)] is found with the centroid–centroid separation of 3.99 Å, the shortest interplanar atom$\cdots$atom separation of 3.48 Å and the dihedral angle of 23.5° (symmetry code, $1-x$, $1/2+y$, $1/2-z$). There are two types of C–H$\cdots\pi$ interactions between benzene ring [C(19)–C(24)] and pyridine ring [N(2)C(13)–C(17)] (Fig. 5). The C–H$\cdots\pi$ interaction between the carbon atom C(4) and adjacent benzene ring [C(19)–C(24)] is characterized by the C(4)$\cdots$M separation of 3.41 Å and C–H$\cdots$M angle of 125°, respectively (symmetry code, $-x$, $1/2+y$, $1/2-z$). The C(23)$\cdots$M separation is 3.67 Å and C–H$\cdots$M angle is 158° for the other type of C–H$\cdots\pi$ interactions between C(23) and the pyridine ring [N(2)C(13)–C(17)] (symmetry code: x, $1/2-y$, $1/2+z$). At the same time, five types of C–H$\cdots$O hydrogen bonds between the carbon atoms of aromatic rings and the oxygen atoms of ligands or NO_3^- anions are found in the crystal packing (Table 3). Although these π–π stacking interactions, C–H$\cdots\pi$ interactions and C–H$\cdots$O hydrogen bonds are weak compared to the metal–nitrogen and metal–oxygen coordination bonds, it could be suggested that these kinds of interactions were important in the formation of the three-dimensional supramolecular network (Fig. 6).

3.4. Luminescence properties

The luminescent properties of a series of copper(I) complexes with 4-Bzpy have been investigated previously[10]. Herein, the luminescent properties of the copper(II) complexes **1**, **2** and ligand 4-Bzpy were investigated in H_2O solution and in solid state at room temperature, respectively (Table 4).

As shown in Fig. 7, excited at 240 nm, the complex **1** shows the main emission peak at 366 nm (quantum yield $\Phi \approx 0.08$) in H_2O solution. The excitation spectrum of **1** (λ_{em} = 366 nm) exhibit two strong peaks at 240 nm and 287 nm. The 240 nm excitation was chosen because it is suitful for the **1** to exist the strong emission peak. Upon excitation at 296 nm, the complex **2** shows luminescent emission maximum at 448 nm (quantum yield $\Phi \approx 0.06$) in H_2O solution, while the emission maximum of 4-Bzpy is at 450 nm (quantum yield $\Phi \approx 0.10$) upon excitation at 316 nm in H_2O solution. Comparably, complex **2** and 4-Bzpy display similar emission band except that the fluorescent intensity decreases markedly. It is also observed that the emission peak changes from 448 nm for $CuL_4(NO_3)_2$ (**2**) to 366 nm for $CuL_2(SCN)_2$ (**1**), i.e., the emission maximum is shifted to a lower energy on going from the SCN^- coordinated complex to the NO_3^-. Interestingly, the luminescent spectrum of complex **1** shows very strong emission peak and indicates SCN^- anion play a key role in fluorescent emission of **1**. The SCN^- group is a good electron donor and the electron transfer from SCN^- to Cu(II), therefore, the emission band at 366 nm for the **1** might be attributed to ligand-to-metal charge transfer, which has been observed in other metal thiocyanate system [12].

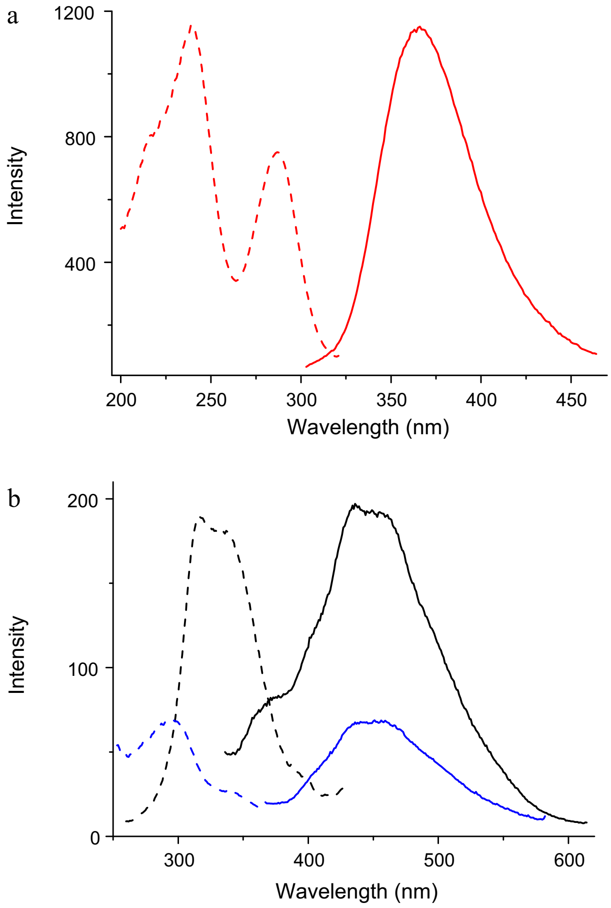

Fig. 7. (a) The excitation spectrum (dash, λ_{em} = 240 nm and 287 nm) and emission spectrum (solid, λ_{ex} = 240 nm) of **1** in H_2O solution at room temperature; (b) the excitation spectrum (dash, L: λ_{em} = 448 nm; **2**: λ_{em} = 450 nm) and emission spectrum (solid, L: λ_{ex} = 316 nm; **2**: λ_{ex} = 296 nm) of L (black) and **2** (blue) in H_2O solution at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 4
Emission spectra of the free 4-benzoylpyridine and the two complexes.

Sample	$\lambda^{ex\ a}$ (nm)	λ^{em}_{max} ^{a} (nm)	$\lambda^{ex\ b}$ (nm)	λ^{em}_{max} ^{b} (nm)
4-Bzpy	306	450	220 392	315 425, 456, 491, 532
$Cu(NCS)_2(4\text{-}Bzpy)_2$ **1**	240	366	220	320
$Cu(NO_3)_2(4\text{-}Bzpy)_4$ **2**	296	448	220	313

[a] Measured in H_2O solution.
[b] Measured in the solid state.

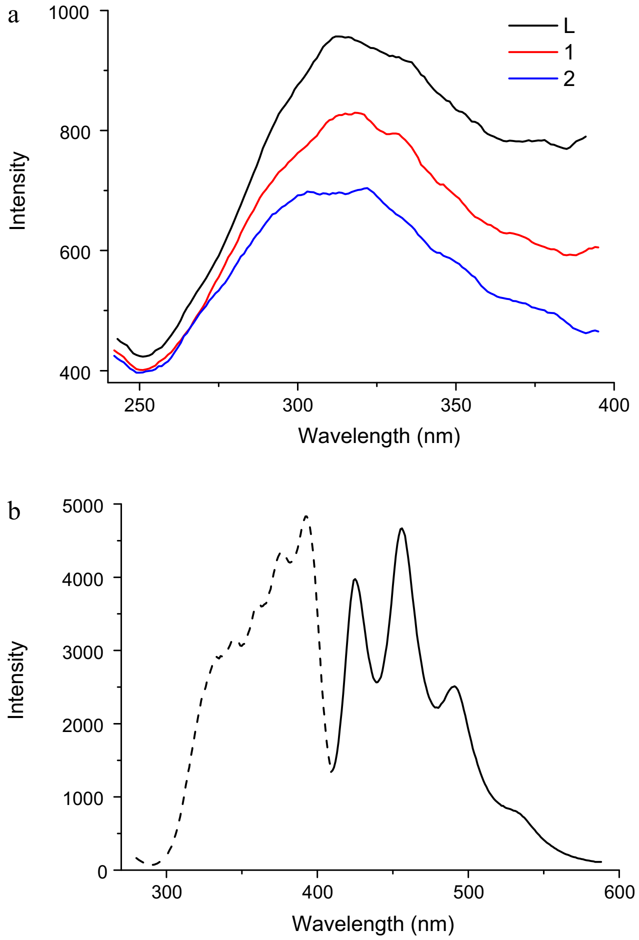

Fig. 8. (a) The emission spectra of L, **1** and **2** (λ_{ex} = 220 nm) in solid state at room temperature; (b) the excitation spectrum (dash, λ_{em} = 425 nm) and emission spectrum (solid, λ_{ex} = 392 nm) of L in solid state at room temperature.

As shown in Fig. 8, the ligand L exhibits the main emission peak at 315 nm with exciting wavelength of 220 nm and four emission maximum at 425 nm, 456 nm, 491 nm and 532 nm upon excitation at 392 nm in the solid state, respectively. Upon excitation at 220 nm, the complexes **1** and **2** show the similar luminescent emission maximum at 320 nm and 313 nm, respectively. Such emission bands are compared to that of the corresponding ligand L except that the fluorescence signals are slightly weaker.

4. Conclusion

In summary, we presented two new copper(II) complexes $Cu(NCS)_2(4\text{-}Bzpy)_2$ (**1**) and $Cu(NO_3)_2(4\text{-}Bzpy)_4$ (**2**) based on 4-benzoylpyridine ligand. The structures of the complexes have been established by single-crystal X-ray diffraction analysis and also characterized by IR, UV and luminescent properties. The Cu(II) atom has a square planar coordination geometry with N_4 donor set in **1** and an enlarged octahedral coordination geometry with N_4O_2 donor set in **2**, respectively. C–H···π interactions and C–H···S hydrogen bonds are observed in complex **1**. And complex **2** forms a three-dimensional supramolecular structure in the solid state through multiform C–H···O hydrogen bonds, π–π interactions and C–H···π interactions. The fluorescence measurement of **1** showed a strong emission peak at 366 nm in H_2O solution, indicating that it may be excellent candidate for potential photoactive materials.

Supplementary material

CCDC-810698 (**1**) and 810699 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 01223 336033; email: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.04.065.

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