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PII: S1386-1425(15)00139-0

DOI: <http://dx.doi.org/10.1016/j.saa.2015.01.118>

Reference: SAA 13286

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 12 October 2014

Revised Date: 22 January 2015

Accepted Date: 31 January 2015



Please cite this article as: J-X. Wang, C. Wang, X. Wang, X-Y. Wang, Y-H. Xing, Q. Sun, Experimental and theoretical investigations of copper (I/II) complexes with triazine-pyrazole derivatives as ligands and their *in situ* C-N bond cleavage, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2015), doi: <http://dx.doi.org/10.1016/j.saa.2015.01.118>

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Experimental and theoretical investigations of copper (I/II) complexes with triazine-pyrazole derivatives as ligands and their *in situ* C-N bond cleavage

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Abstract:

Two copper complexes, $\text{Cu}(\text{SCN})(\text{Mpz}^*\text{T}(\text{EtO})_2)$ (**1**) ($\text{Mpz}^*\text{T}(\text{EtO})_2 = \text{L3}$) and $\text{CuCl}(\text{H}_2\text{O})(\text{Mpz}^*\text{T-O}_2)$ (**2**) ($\text{Mpz}^*\text{T-O}_2 = \text{L4}$) were synthesized by the reaction of 2,4,6-tri(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine (**L1**) or 2,4,6-tri(1H-pyrazol-1-yl)methyl)-1,3,5-triazine (**L2**) with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in anhydrous ethanol and methanol, respectively. The complexes were characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis, single crystal X-ray diffraction and X-ray powder diffraction. The structural characterizations and quantum mechanical calculations of the two complexes were analyzed in detail. It was found that an *in situ* reaction occurred during the synthesis process of complexes **1** and **2**, likely due to catalytic property of copper ions which leads to the C – N bond cleavage to generate new organic species, namely, $\text{Mpz}^*\text{T}(\text{EtO})_2$ (**L3**) and $\text{Mpz}^*\text{T-O}_2$ (**L4**).

Keywords: 1, 3, 5 - Triazine-pyrazole derivative; Copper complexes; Bond cleavage; *In situ* reaction

1. Introduction

1, 3, 5 - triazine and its derivatives have been well known because of their high biological activities and widespread applications in the fields of herbicide, antibacterial and antiphytovirucide[1-4]. Especially, some derivatives can be used as potential functional materials in the fields of magnetic, optical, catalyst, and liquid crystal materials[5-10]. At the same time, pyrazole and its derivatives play a vital role in synthesis of compounds with 1, 3, 5 - triazine and the kind of compound is of particular interest owing to its biological activity[11-13]. In the structures of these compounds, the nitrogen atoms possess larger electronegativities than the carbon atoms. This is the reason that the π -electron located in nitrogen atoms in N-heterocyclic ligands resulting in larger electron cloud density, which can enhance the coordination ability of heterocyclic ligands with metal[14-18]. During the past two decades, some complexes containing 1,3,5 - triazine with pyrazole rings have been reported, for instance, Cu(bpz*eaT)(SCN)₂, Co(bpz*eaT)(SCN)₂ (bpz*eaT: 2,4-dimethyl-1H-pyrazol-1-yl)-6-diethylamino-1,3,5-triazine), [Ni(bpt)₂](ClO₄)₂·H₂O (bpt: 2,4-bis(3,5-dimethylpyrazol)-6-methoxy-1,3,5-triazine), [Zn(mpt)₂(dmp)](ClO₄)₂ (mpt:2,4-dimethoxy-6-(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine and dmp: 3,5-dimethylpyrazole), Hg(TpzT)(SCN)₂·H₂O (TPzT: 2,4,6-tri(pyrazole-1-yl)-1,3,5-triazine), etc. [19-21]. In some of these works, an interesting chemical phenomenon was found: the lability of the C_{triazine} - N_{pyrazole} bond lead to C_{triazine}-N_{pyrazole} being easily fractured in the process of *in situ* reaction system.[22-23] We think that the cause for the C-N bond cleavage likely due to a hydrolysis process with metal ion as a catalyst. To our best knowledge, there are also many other reaction factors influencing C-N bond cleavage, such as pH, metal, temperature, reaction medium, etc. However, there are few investigations of the reaction mechanism of C_{triazine} -N_{pyrazole} bond fracturing so far. In order to further study the key roles of the bond fracturing, it is very necessary to synthesize the complexes related to the C-N bond fracturing. So, we have synthesized two copper complexes with 1, 3, 5 - triazine-pyrazole derivative as ligands. One is Cu(SCN)(Mpz*T-(EtO)₂) (Mpz*T-(EtO)₂=L3) (1), the other is CuCl(H₂O)(Mpz*T-O₂) (2) (Mpz*T-O₂=L4). Although the structure of complex 2 has been reported by J. Manzur[24], its reaction condition is different from

the reported one in the literature. Based on the reaction process of the two complexes, in this paper, we explored the mechanism of C-N bond fracturing about $\text{Mpz}^*\text{T}-(\text{EtO})_2$ (**L3**) and $\text{Mpz}^*\text{T}-\text{O}_2$ (**L4**) in detail.

2. Experimental

2.1 Materials and General methods

All the chemicals used were of analytical grade and used without further purification. **L1** (2,4,6-tri(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine) and **L2** (2,4,6-tri(1H-pyrazol-1-yl)methyl)-1,3,5-triazine) were synthesized according to the literature method [25-26]. Elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. Infrared spectra were recorded on a JASCO FT/IR-480 spectrometer with pressed KBr pellets in the range 4000–200 cm^{-1} and a Bruker AXS TENSOR-27 FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1} . The X-ray powder diffraction data was collected on a Bruker AXS D8 Advance diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of 5–60° with a step size of 0.02° and a scanning rate of 3° min^{-1} . Thermogravimetric analysis for the complexes was recorded on a Perkin Elmer Diamond TG/DTA.

2.2 Synthesis of the complexes

2.2.1 Preparation of complex 1. **L1** (0.048 g, 0.1 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.034 g, 0.2 mmol) and KSCN (0.048 g, 0.5 mmol) were dissolved in anhydrous ethanol (15 ml). The solution was stirred under reflux at 80 °C for 3 h, and then the mixture was cooled down and filtered. The solution was stored at room temperature to be evaporated slowly. After a few days, some green crystals of complex **1** were obtained, filtered off and dried in air. The yield was 74% (based on Cu (II)). Calc. for $\text{C}_{13}\text{H}_{17}\text{N}_6\text{O}_2\text{SCu}$: C, 40.56; H, 4.45; N, 21.83. Found: C, 40.17; H, 4.36; N, 21.36 %.

2.2.2 Preparation of complex 2. **L2** (0.028 g, 0.1 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.017 g, 0.1 mmol) were mixed and stirred at room temperature for 3 h in a solution of anhydrous methanol (15 ml). Then the sky blue solution was filtered and left at room temperature. After a few days, the green

crystals were obtained. The yield was 75% (base on Cu (II)). Calc. for $C_6H_6N_5O_3ClCu$: C, 24.42; H, 2.05; N, 23.73. Found: C, 23.96; H, 2.01; N, 23.15 %. The synthesized condition was much more different from the work of J. Manzur.

2.3 X-ray single crystal structural determinations

Suitable single crystals of complexes **1-2** were mounted on glass fibers for X-ray measurement, respectively. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a ω scan mode. All the measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS program[27]. The structures were solved by the direct method using SHELXL-97[28]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic frameworks were fixed at calculated positions geometrically and refined by using a riding model. Crystallographic data for complex **1** and the structure refinement are given in Table 1. The selected bond lengths and bond angles are listed in Table 2. Short contacts of complexes **1-2** are given in Table 3.

Table1 Crystallographic Data for Complexes **1-2**

complexes	1	2
formula	$C_{13}H_{17}N_6O_2SCu$	$C_6H_6N_5O_3ClCu$
M ($g \text{ mol}^{-1}$)	384.93	295.15
Crystal system	Orthorhombic	Monoclinic
Space group	$Aba2$	$P2_1/n$
$a/\text{\AA}$	10.958(2)	10.999(2)
$b/\text{\AA}$	20.527(4)	6.9933(14)
$c/\text{\AA}$	14.932(3)	12.621(3)
α ($^\circ$)		90
β ($^\circ$)		96.22
γ ($^\circ$)		90
V (\AA^3)	3359.0(12)	965.1(3)
Z	8	4
D_{calc} ($g \text{ cm}^{-3}$)	1.522	2.031
crystal size (mm)	$0.61 \times 0.21 \times 0.27$	$0.54 \times 0.37 \times 0.15$
F(000)	1584	588
μ (Mo-K α)/ mm^{-1}	1.442	2.539
θ ($^\circ$)	3.37 to 27.48	3.34 to 27.46

Reflections collected	15087	7712
Independent reflections ($I > 2\sigma(I)$)	3599(2418)	2200(1760)
Parameters	212	150
$\Delta(\rho)$ ($e \text{ \AA}^{-3}$)	0.383, -0.327	0.469, -0.464
Goodness of fit	1.060	1.168
R^a	0.0654(0.1007) ^b	0.0313(0.0447) ^b
wR_2^a	0.1386(0.1545) ^b	0.0880(0.1073) ^b

*^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$; $[F_o > 4\sigma(F_o)]$.

^b Based on all data

Table 2 Selected bond lengths (\AA) and angles ($^\circ$) for the complexes **1-2**

Complex 1			
Cu-N(1)	2.211(5)	Cu-N(6)	1.904(5)
Cu-N(5)	2.085(6)	Cu-S(1)	2.317(2)
N(5)-Cu-N(1)	75.6(2)	N(6)-Cu-S(1)	117.82(17)
N(6)-Cu-N(1)	120.9(2)	N(5)-Cu-S(1)	102.61(16)
N(6)-Cu-N(5)	123.4(2)	N(1)-Cu-S(1)	108.45(14)
Complex 2			
Cu-N(2)	1.972(2)	Cu-O3W	1.957(2)
Cu-N(3)	2.030(2)	Cu-Cl	2.2568(9)
N(2)-Cu-N(3)	79.54(10)	O(3)-Cu-Cl	94.36(7)
O(3)-Cu-N(2)	168.14(9)	N(2)-Cu-Cl	94.47(8)
O(3)-Cu-N(3)	91.31(10)	N(3)-Cu-Cl	173.71(7)

Table 3 Short contacts (\AA) and bond angles ($^\circ$) of complexes **1-2**

D-H...A	d(D-H)/ \AA	d(H...A)/ \AA	d(D...A)/ \AA	\angle D-H...A/ $^\circ$
Complex 1				
C6-H6...S1	0.93	2.86	3.788(8)	179.0
C8-H8B...O2	0.96	2.47	3.281(10)	141.6
Complex 2				
O3-H3...O2	0.82	1.90	2.701(3)	164.0
O3-H3B...O1	0.80(6)	1.98(5)	2.653(3)	142(5)
N4-H4...O2	0.86	2.01	2.842(3)	161.2

2.4 Quantum chemical calculation

The compounds and the complexes formed by Cu and ligands were fully optimized using a generalized gradient approximation[29] treated with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential and with long rang dispersion correction made using the Grimme's

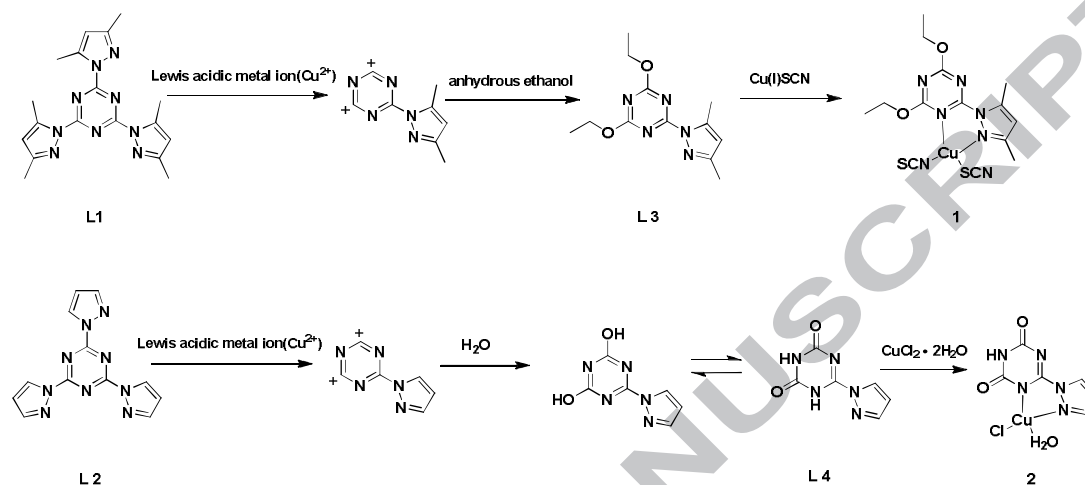
scheme[30]. The molecular structural parameters of the complexes come from the crystal structure data, and the molecular point groups and their symmetry (Cs) are also considered. An all electron double numerical atomic orbital basis set augmented by d-polarization functions (DNP) was used. This level of theory has been used to successfully determine the geometrical, energetic and electronic structural properties of interactions of many small molecules and nano-substrates[31-34]. All the calculations have been performed using DMol3 module in Materials Studio[35-36].

3. Results and discussion

3.1 Synthesis

Complex **1** was synthesized by the reaction of **L1**, KSCN and CuCl₂·2H₂O in anhydrous ethanol system under condition of refluxing at 80 °C, with a molar ratio of **L1**, metal salt, and KSCN equal to 1:2:5. Similarly, complex **2** was synthesized by the reaction of **L2** and CuCl₂·2H₂O in anhydrous methanol, with a molar ratio of **L2** and CuCl₂·2H₂O equal to 1:1. However, it is worthy to note that the organic ligands in the molecular structure of complexes were new species **L3** and **L4** instead of **L1** and **L2**. We thought that as the ligands, **L1** and **L2** were stable in solution, but the introducing of the copper ion lead to C-N bond cleavage in a certain extent. The formation of the heterocyclic molecule **L3** may be explained by the nucleophilic attack of two equivalents of ethanol during release of the leaving group 3,5-dimethylpyrazole, and the oxidation state of the copper ion in the complex **1** was “+1”. We thought that the oxidation state may be deduced from the well know fact that the reaction of the mild reducing agent SCN⁻ with Cu (II) exclusively afford Cu(I)SCN species. Similarly, the formation of **L4** could be explained by the nucleophilic attack of two equivalents of water, followed by a tautomerization of the intermediate 2-(pyrazol-1-yl)-4, 6-dihydroxy-1,3,5 triazole. A presence of water come from the metal salt CuCl₂·2H₂O (Scheme 1). The case is the same as that reported by J. Manzur. Comparing to the synthesized condition of J. Manzur, it is found accidentally that C-N bond fracturing would be less influence by the temperature. According to a large number of experimental studies, we think that there is an *in situ* reaction in the process of synthesizing complexes **1** and **2** during the introducing copper ion, that is, **L1** or **L2** turns into intermediate species (**L3** and **L4**), which immediately

participates in the reaction with the metal salt to produce the final complex. The distinction between **L4** and **L3** is the difference of the substituted groups on the triazine ring (ethoxy for **L3**, carbonyl for **L4**).



Scheme 1

3.2 Structural description of complexes **1-2**

Cu(SCN)(Mpz*T-(EtO)₂) ($\text{Mpz}^*\text{T}(\text{EtO})_2=\text{L3}$) (**1**). Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the orthorhombic, space group $Aba2$. The molecular structure of the complex **1** shows that the asymmetric unit contains one Cu(I) atom, one specie **L3**, and one thiocyanate anion (Fig. 1a). The coordination environment around Cu(I) atom may be best described as a distorted tetrahedron geometry, and it is coordinated by three nitrogen atoms and one sulfur atom: N1 from 1, 3, 5 - triazine, N5 from pyrazole ring, N6 and S1 from two NCS groups. Specie **L3** links one Cu^+ ion and adopts bidentate coordination mode. The bond distances of Cu-N is in the range of 1.904(5) - 2.211(5) Å, and the distance of Cu-S is of 2.317(2) Å, respectively. Obviously, Cu-N bond length from N- heterocyclic is slightly larger than that from NCS groups. The bond angles of N-Cu-N are in the range of 75.6(2) - 123.4(2)° and the angles of N-Cu-S is in the range of 102.61(16) - 117.82(17)°. The dihedral angles between triazine ring and pyrazole ring is 7.43(0.43)°. The NCS anion acted as a bridging group bonding to two adjacent Cu^+ and formed a polymeric chain with the $\text{Cu}\cdots\text{Cu}$ distance of 5.6167(11) Å along [001] direction (Fig. 1b). These parallel chains are further connected by the hydrogen

bond of C6–H6...S1 and C8–H8B...O2 [C6–H6^{#2}...S1^{#2}, 3.788(8) Å, 179.0°, #2: 2-x, 0.5-y, 0.5+z; C8–H8B...O2^{#3}, 3.281(10) Å, 141.6°, #3: 2.5-x, y, 0.5+z] to form a 2D supermolecular network structure along ac plane (Fig. 1c).

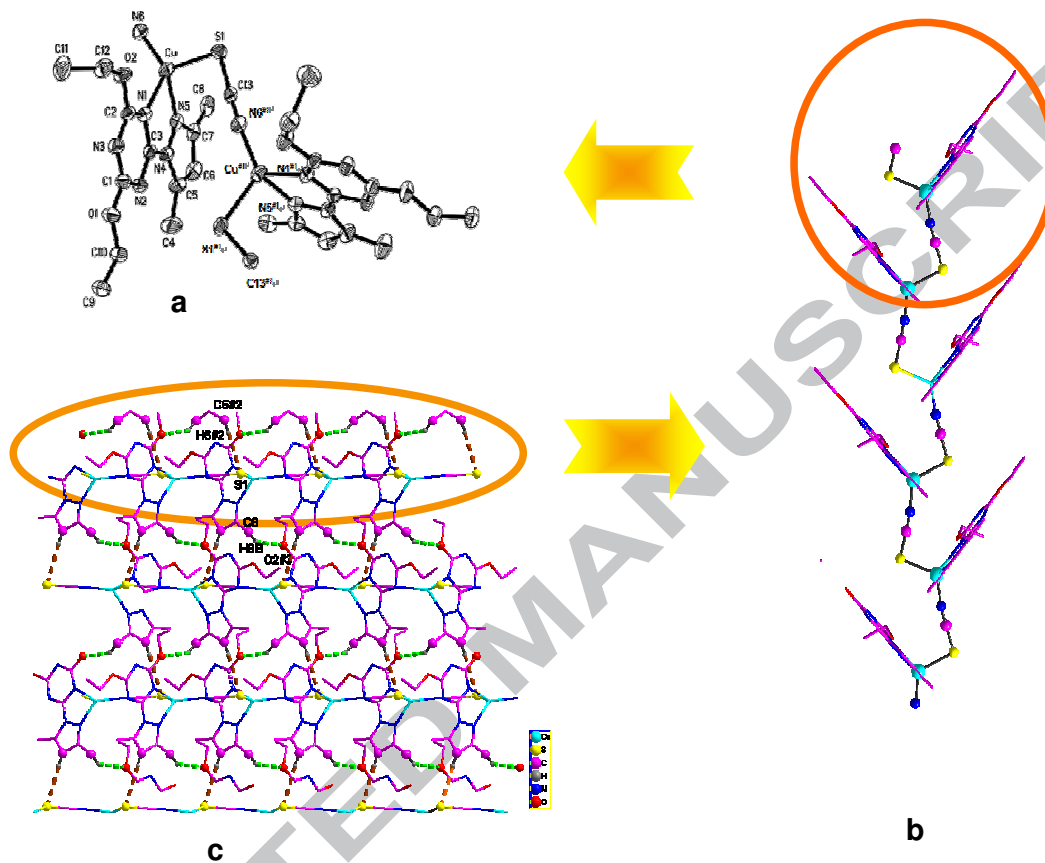


Fig.1 (a) Local coordination environment of Cu(I) atom in **1** (#1: 0.5+x, 0.5-y, z); (b) A view of a polymeric chain along the [001] direction in the complex **1** (the hydrogen atoms are omitted for clarity); (c) A view of a 2D supermolecular network structure formed by the hydrogen bonds linked polymeric chains in the ac plane.(a part of hydrogen atoms are omitted for clarity) (#2: 2-x, 0.5-y, 0.5+z; #3: 2.5-x, y, 0.5+z)

CuCl(H₂O)(Mpz*T-O₂) (Mpz*T-O₂=L4) (2). Single crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the monoclinic, space group $P2_1/n$. The molecular structure of the complex **2** shows that the asymmetric unit is made up of a copper atom, one **L4** anion, one coordinated water molecule and one chlorine atom (Fig. 2a). Each Cu(II) atom coordinates with two nitrogen atoms from **L4** anion (N3 from the triazine ring and N2 from the

pyrazole ring), one coordinated water molecule and one chlorine atom to form a parallelogram geometry coordination environment. The bond distances of Cu-N is in the range of 1.972(2) - 2.030(2) Å, the lengths of Cu-O_w and Cu-Cl are 1.957(2) Å and 2.2568(9) Å, respectively. N-Cu-N bond angle is 79.54(10)°, the angles of O-Cu-N are in the range of 91.31(10) - 168.14(9)°. The bond angles of N-Cu-Cl are in the range of 94.47(8) - 173.71(7)° and the O-Cu-Cl bond angle is 94.36(7)°. The dihedral angle between the triazine ring and the pyrazole ring is 3.93 (0.25)°. Adjacent asymmetric unit is linked by the intermolecular weak interactions between oxygen atom from **L4** group and coordinated water molecule from another asymmetric unit (O3-H3...O2^{#4}, 2.701(3) Å, 164.0°, #4: 0.5+x, 1.5-y, -0.5+z) to form a 1D chain structure (Fig. 2b). Additionally, in the molecular packing, there is a type of hydrogen bond O3-H3B...O1 (O3-H 3B...O1, 2.653(3) Å, 142(5)°), which further enhances the stability of the molecular structure. The adjacent chains are further linked via the hydrogen bond of N4-H4...O2 (N4-H4...O2^{#5}, 2.842(3) Å, 161.2°, #5: -x, 2-y, 2-z) to afford a 2D supermolecular network structure (Fig. 2c).

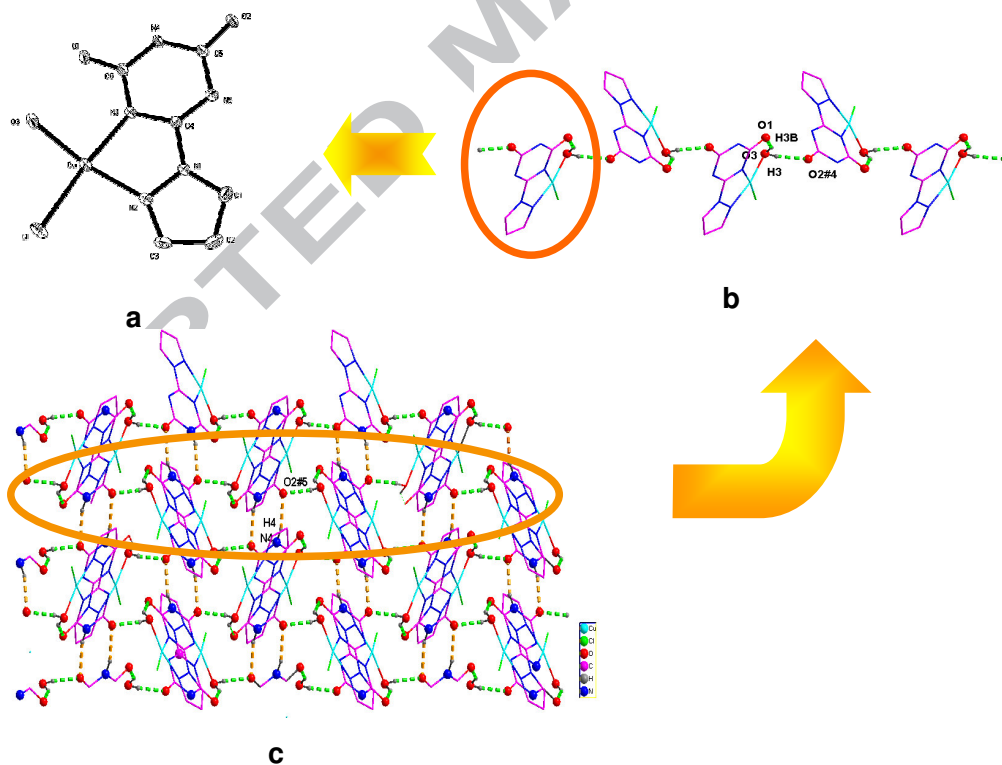


Fig.2 (a) Local coordination environment of Cu(II) atom in **2**; (b) 1D polymeric chain of the complex **2** in ab plane (a part of hydrogen atoms are omitted for clarity) (#4: 0.5+x, 1.5-y, -0.5+z); (c) A view of a 2D supermolecular network structure formed by the hydrogen bonds linked polymeric chains in the ab plane (a part of hydrogen atoms are omitted for clarity) (#5: -x, 2-y,

2-z)

3.3 Quantum chemistry calculations of **L1** - **L4** and complexes **1-2**.

According to molecular orbital theory, the frontiers orbitals and nearby molecular orbitals are the most important factors for the stability. The larger difference between the frontier orbitals, the more stable the molecular structure. For compounds **L1-L4** and complexes **1-2** (the quantum chemistry calculation of compounds **L1-L4** and complexes **1-2** are shown in the supplementary materials Fig. S1), the highest occupied molecular orbital (HOMO) -0.2123, -0.2369, -0.2173, -0.2555, -0.1828 and -0.2098 a.u.; the lowest unoccupied molecular orbital (LUMO) 0.0898, -0.1068, -0.0773, -0.2400, -0.1246 and -0.2088 a.u.. The energy gap value ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) for compounds and complexes is 3.33, 3.54, 3.81, 0.42, 1.58, 0.03 eV, respectively (see Table 4). It is shown that the order of thermodynamic stability about the ligands is **L2** > **L1** and that of complexes is **1** > **2**. For net charges, negative charge is mainly focused on the nitrogen atoms, the oxygen atoms and the coordinated anions. Positive charge is concentrated in the carbon atoms of triazine rings and metal cations. The average net charges of the nitrogen atoms of triazine rings are more negative than that of the nitrogen atoms of pyrazole rings. In the reaction process, it is found that the C-N bonds were broken by the influence of copper ions, in the mean time, the C-O bonds or C=O bonds were formed. This result leads to the net charges of every atoms of compounds change. For compounds **L1**, **L3** and complex **1**, the net charge of respective nitrogen atoms of pyrazole ring for participating in coordination is -0.194, 0.179, 0.0869 e and the net charge of nitrogen atoms of triazine rings for taking part in coordination is -0.429, -0.450, -0.1611e, respectively (see supplementary materials Table S1). It shows that the uncoordinated nitrogen atom is more negative than the coordinated one. Similarly, for compounds **L2**, **L4**, and complex **2**, the net charge of nitrogen atoms of pyrazole rings is -0.174, -0.097, -0.188 e and the net charge of nitrogen atoms of triazine rings is -0.354, -0.340, -0.522 e, respectively. However, it is found that the coordinated nitrogen atom is more negative than the uncoordinated one for the same nitrogen atom. We think the reason about this case is that the C-N bond fracturing and to generate new compounds with different substituted groups.

Table 4 The calculated eigenvalues of HOMO, LUMO (a.u.) and the band gaps (eV) of the compounds and the complexes

	L1	L2	L3	L4	1	2
HOMO (a.u.)	-0.2123	-0.2369	-0.2173	-0.2555	-0.1828	-0.2098
LUMO (a.u.)	-0.0898	-0.1068	-0.0773	-0.2400	-0.1246	-0.2088
Band gap (eV)	3.33	3.54	3.81	0.42	1.58	0.03

3.4 IR Spectra

For complex **1** (Fig. 3), a broad absorption band appearing at 3426 cm^{-1} indicates the presence of water molecules. Absorption occurs at 3096 cm^{-1} should be assigned to the stretching vibrations of $=\text{C}-\text{H}$ on the pyrazolyl rings. The bands at 2989 and 2924 cm^{-1} are characteristic peaks of the $\text{C}-\text{H}$ ($-\text{CH}_3$). The strong peak at 2109 cm^{-1} accounts for the appearance of SCN^- group stretching vibrations. The peaks appear at 1598 , 1545 , 1419 cm^{-1} because of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations of the triazine ring and pyrazolyl rings. $\text{C}-\text{O}$ characteristic band of triazine ring is shown at 1101 cm^{-1} . The bands at 1341 and 1315 cm^{-1} are characteristic of $\text{C}-\text{C}$ and $\text{C}-\text{N}$. The peak at 1029 cm^{-1} is $\text{N}-\text{N}$ stretching vibration of pyrazolyl rings. For complex **2** (Fig. 4), absorption band at 3110 cm^{-1} should be assigned to the $\text{N}-\text{H}$ stretching vibration of the triazine ring. The band at 3020 cm^{-1} is characteristic of $=\text{C}-\text{H}$ on the pyrazolyl rings. Absorption at 1656 cm^{-1} should be assigned to the $\text{C}=\text{O}$ stretching vibration of the triazine rings. The peaks appear at 1577 , 1486 , 1397 cm^{-1} because of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations of the triazine and pyrazolyl rings. The bands at 1321 and 1201 cm^{-1} are characteristic peaks of $\text{C}-\text{C}$ and $\text{C}-\text{N}$. The peak at 1051 cm^{-1} is $\text{N}-\text{N}$ stretching vibration of pyrazolyl rings. In addition, the detailed IR spectra data for the complexes **1-2** are shown in Table 5.

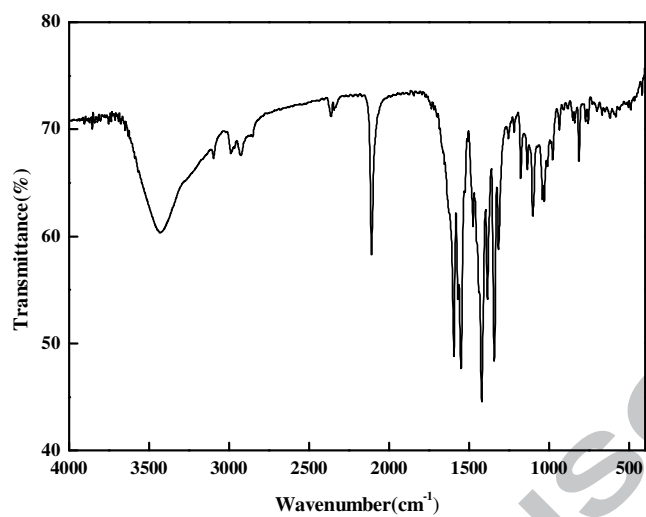


Fig. 3 The Solid-state IR spectra of complex **1** at a room temperature

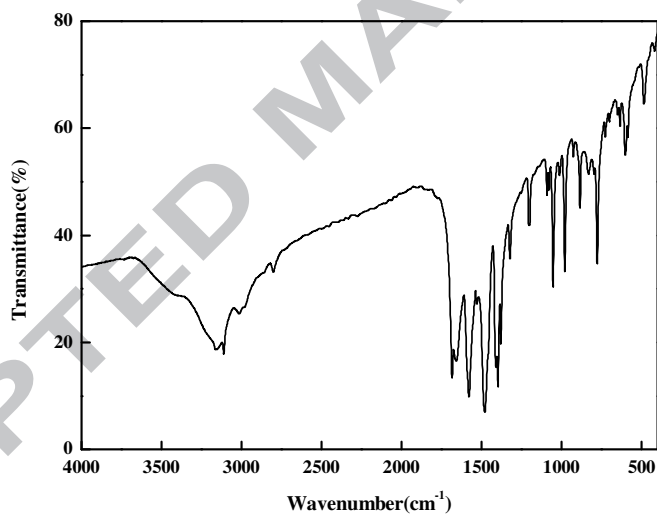


Fig. 4 The Solid-state IR spectra of complex **2** at a room temperature

Table 5 The IR data (cm^{-1}) for complexes **1** and **2**

Complexes	1	2
$\nu_{\text{N-H}}$		3110
$\nu_{\text{=C-H}}$	3096	3020
$\nu_{\text{-CH}_3, \text{-CH}}$	2989, 2924	
$\nu_{\text{SCN-}}$	2109	
$\nu_{\text{C=O}}$		1656
$\nu_{\text{C=C, C=N}}$	1598, 1545, 1419	1577, 1486, 1397
$\nu_{\text{C-O}}$	1101	

$V_{C-C, V_{C-N}}$	1341,1315	1321,1201
V_{N-N}	1029	1051
δ_{C-H}	812	882,771
V_{Cu-N}	414,382,362	310,277

3.5 XRD analysis

The composition of the complexes **1-2** (Fig. 5-6) was confirmed by X-ray powder diffraction (PXRD). It was used to confirm the phase purity of the bulk materials. The experiment results prove that all the peaks presented in the measured patterns closely match the simulated patterns generated from single crystal diffraction data.

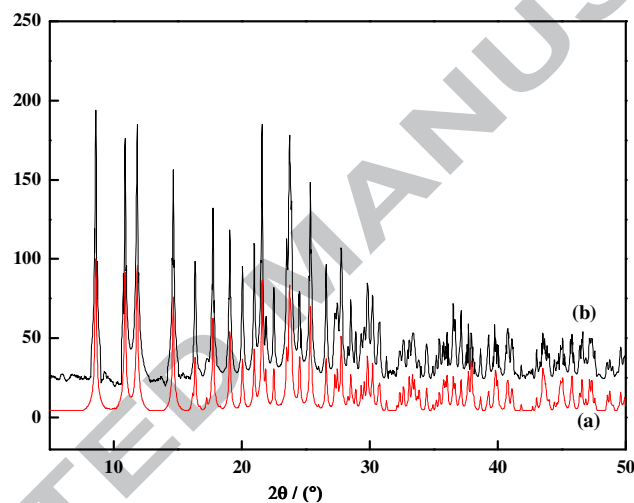


Fig. 5 (a) experimental powder X-ray diffraction (PXRD) of **1**; (b) the simulated powder X-ray diffraction (PXRD) of **1**

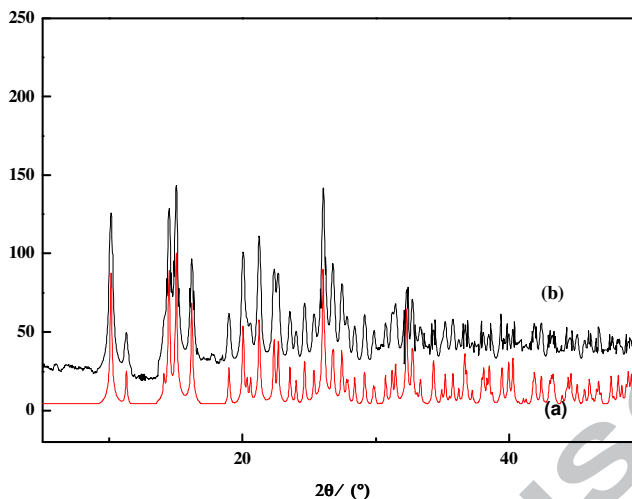


Fig. 6 (a) experimental powder X-ray diffraction (PXRD) of **2**; (b) the simulated powder X-ray diffraction (PXRD) of **2**

3.6 Thermal properties

To examine the thermal stability of complexes **1-2**, thermogravimetric analysis (TG) was carried out at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen in the temperature range of 35-1000 $^{\circ}\text{C}$ (Fig. 7). In complex **1**, the result show that the initial mass loss of 61.43% before 340 $^{\circ}\text{C}$ is due to the release of the species **L3** (calc. 61.13%). The second mass loss 13.58% occurs in the range of 340 - 1000 $^{\circ}\text{C}$, which is ascribed to the release of two coordinated nitrogen atoms and the coordinated NCS group (calc. 14.04%). The final residue corresponds to copper sulfide. In **2**, the first mass loss of 50.82% is attributed to the species **L4** (calc. 50.86%) in the temperature range of 90 - 350 $^{\circ}\text{C}$. The second mass loss of 15.13% should be attributed to the release of two coordinated nitrogen atoms and one coordinated water molecule (calc. 15.59%) in the temperature range of 350 - 1000 $^{\circ}\text{C}$. The residues correspond to the copper chloride compound.

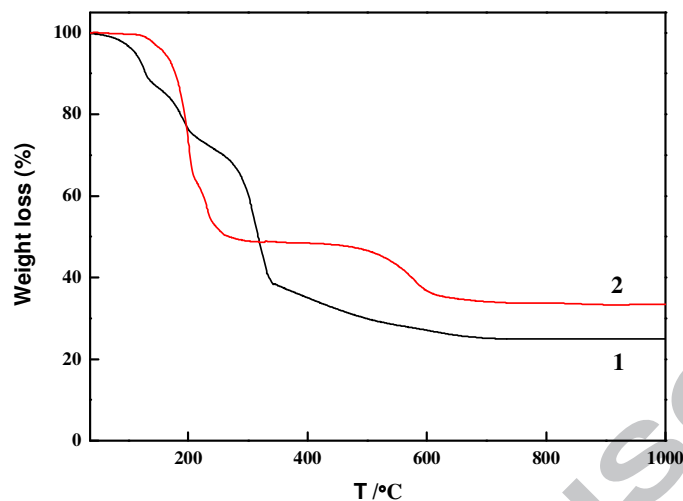


Fig.7 TG curves of complexes 1-2

4. Conclusion

In this work, two complexes supported by 1, 3, 5-pyrazolyl triazine ligand were successfully synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis, X-ray powder diffraction and single crystal X-ray diffraction. Both form 2D sheet structures via intermolecular hydrogen bonds. It is interesting to note that an *in site* reaction occurs during the synthesis process of complexes **1** and **2** likely due to catalytic property of copper ions, which leads to C – N bond cleavage to generate new organic species with different substituted groups.

Supplementary material

Tables of atomic coordinates, an isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC: 981969 for **1** and 981970 for **2** from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

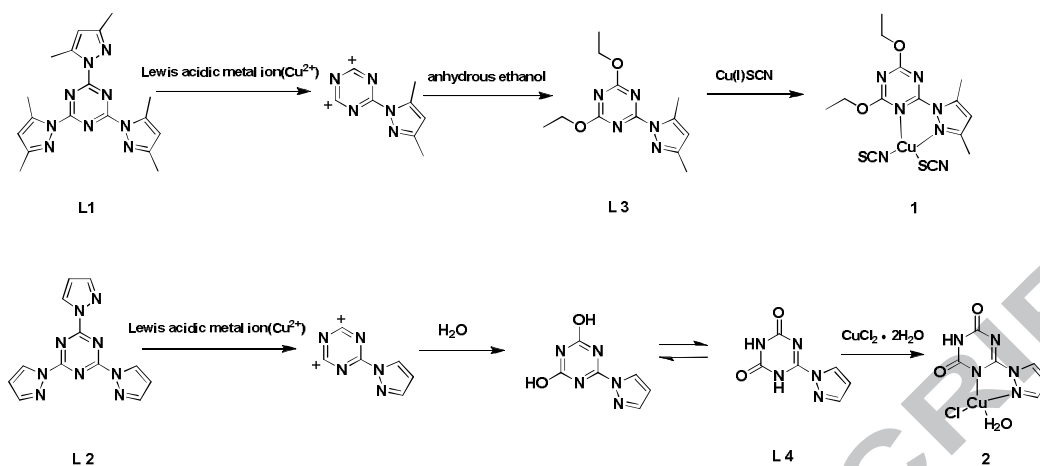
Acknowledgements

We acknowledge National Natural Science Foundation of China (No.21371086 and No. 21071071) for the financial support.

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Scheme 1

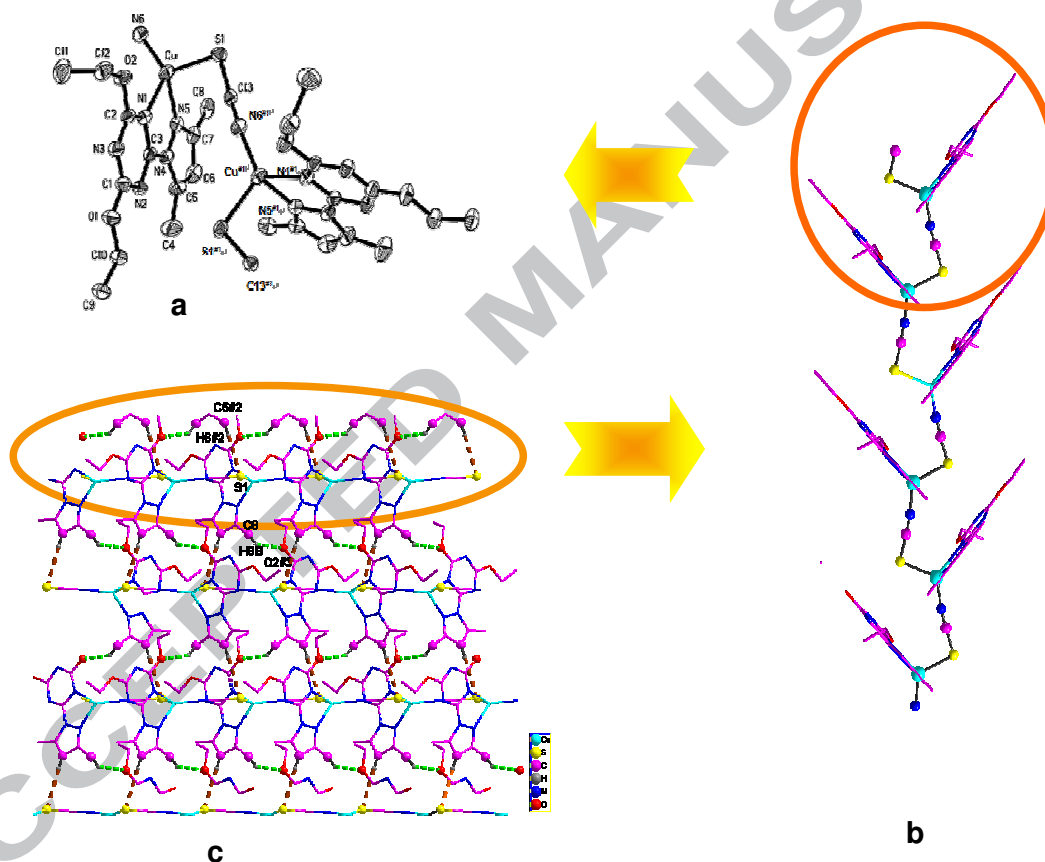


Fig 1

Fig.1 (a) Local coordination environment of Cu(I) atom in **1** (#1: $0.5+x$, $0.5-y$, z); (b) A view of a polymeric chain along the $[001]$ direction in the complex **1** (the hydrogen atoms are omitted for clarity); (c) A view of a 2D supermolecular network structure formed by the hydrogen bonds linked polymeric chains in the ac plane.(a part of hydrogen atoms are omitted for clarity) (#2: $2-x$, $0.5-y$, $0.5+z$; #3: $2.5-x$, y , $0.5+z$)

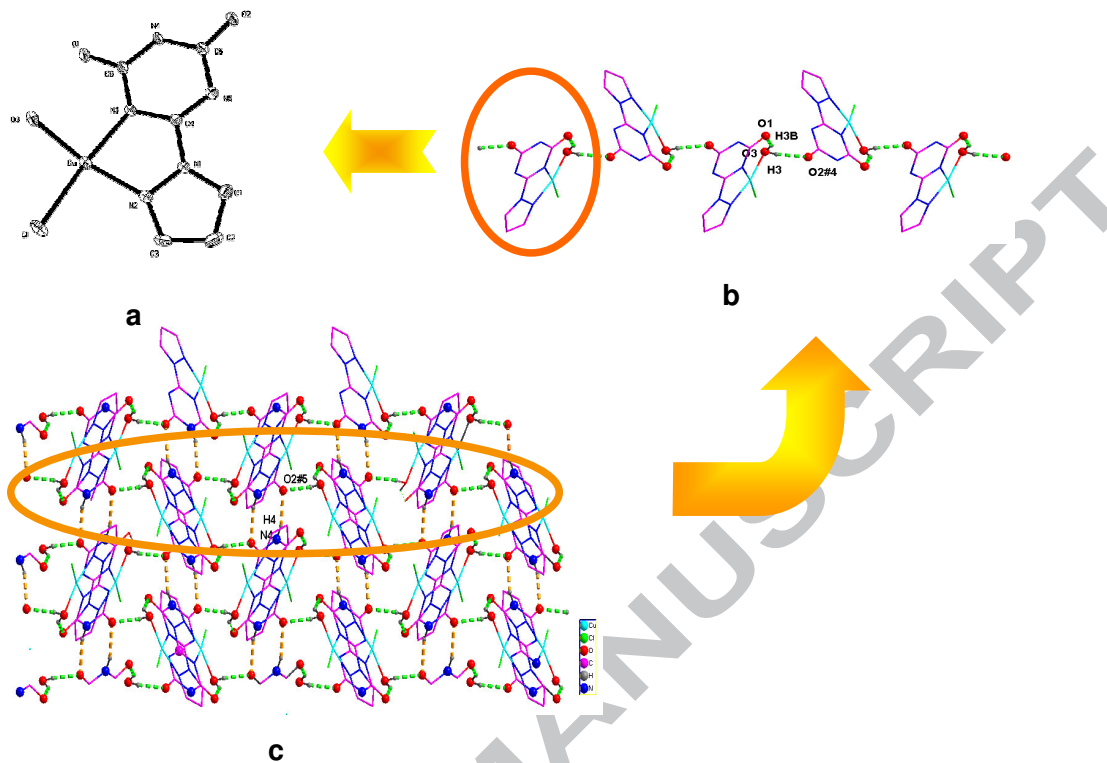


Fig.2 (a) Local coordination environment of Cu(II) atom in **2**; (b) 1D polymeric chain of the complex **2** in *ab* plane (a part of hydrogen atoms are omitted for clarity) (#4: $0.5+x, 1.5-y, -0.5+z$); (c) A view of a 2D supermolecular network structure formed by the hydrogen bonds linked polymeric chains in the *ab* plane. (a part of hydrogen atoms are omitted for clarity) (#5: $-x, 2-y, 2-z$)

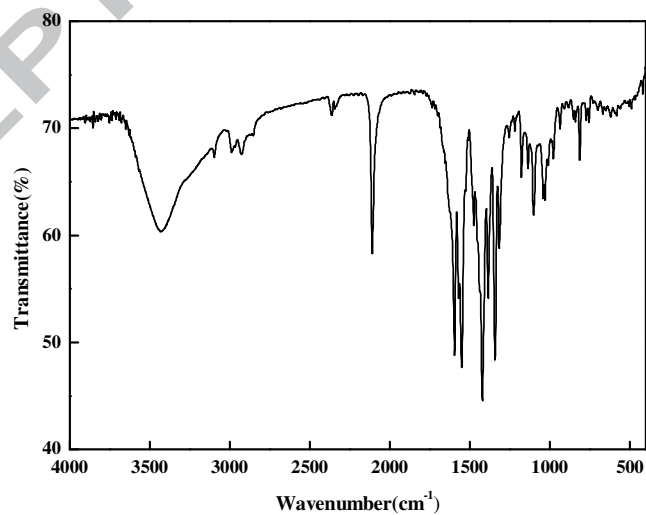


Fig. 3 The Solid-state IR spectra of complex **1** at a room temperature

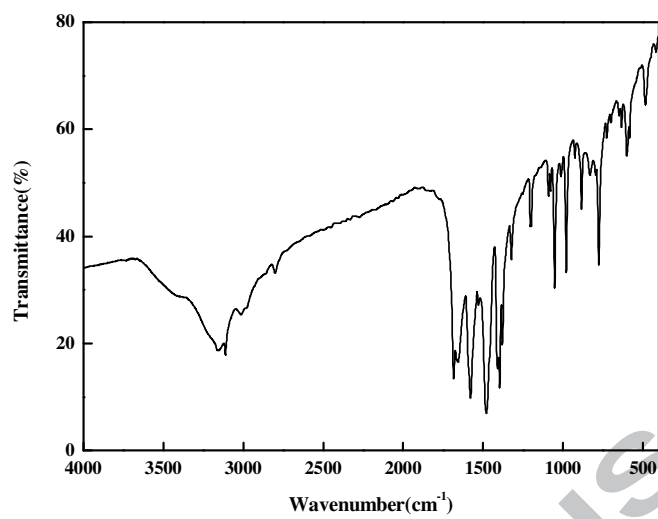


Fig. 4 The Solid-state IR spectra of complex 2 at a room temperature

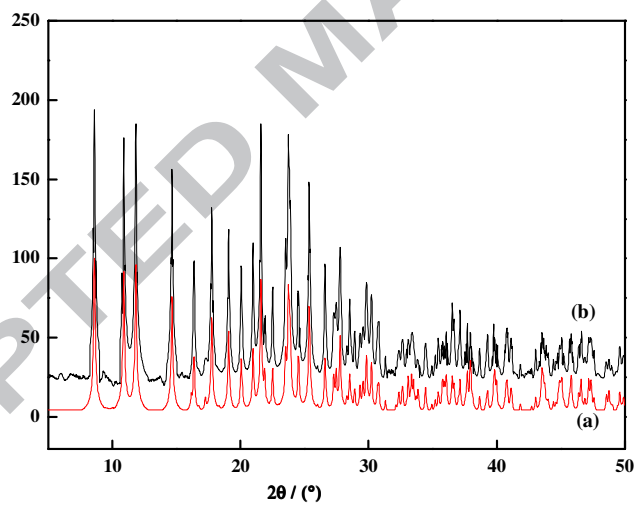


Fig. 5 (a) experimental powder X-ray diffraction (PXRD) of 1; (b) the simulated powder X-ray

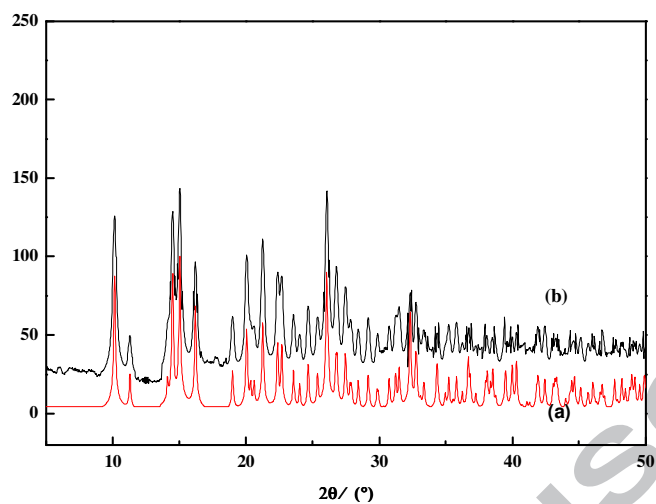


Fig. 6 (a) experimental powder X-ray diffraction (PXRD) of **2**; (b) the simulated powder X-ray diffraction (PXRD) of **2**

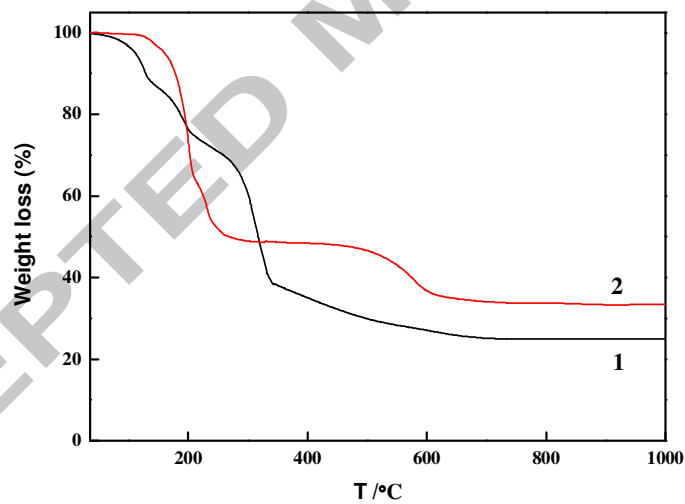


Fig.7 TG curves of complexes **1-2**

Graphical Abstract

Experimental and theoretical investigations of copper (I/II) complexes with triazine-pyrazole derivatives as ligands and their *in situ* C-N bond cleavage

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Two copper complexes: $\text{Cu}(\text{SCN})(\text{Mpz}^*\text{T}(\text{EtO})_2)$ (**1**) and $\text{CuCl}(\text{H}_2\text{O})(\text{Mpz}^*\text{T}-\text{O}_2)$ (**2**) ($\text{Mpz}^*\text{T}(\text{EtO})_2=2$ - (3,5 - dimethyl pyrazole) -4, 6 - diethanol -1,3,5 - triazine, $\text{Mpz}^*\text{T}-\text{O}_2=2$ - pyrazole 4, 6 - dioxo-1 ,3,5-triazine) have been synthesized. They are characterized by elemental analysis, IR spectroscopy, single crystal X-ray diffraction, X-ray powder diffraction and quantum mechanical calculations of the two complexes are analyzed in detail.

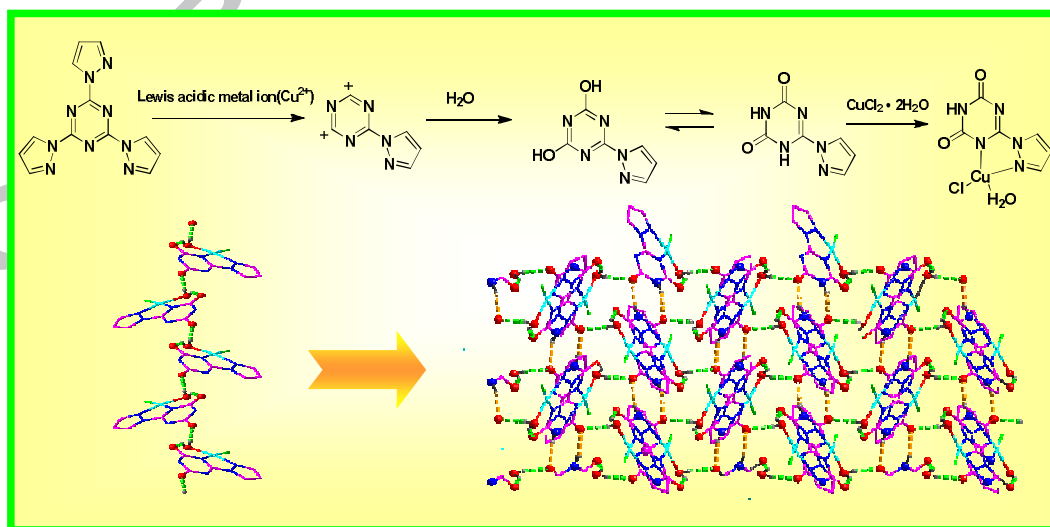


Table1 Crystallographic Data for Complexes **1-2**

complexes	1	2
formula	C ₁₃ H ₁₇ N ₆ O ₂ SCu	C ₆ H ₆ N ₅ O ₃ ClCu
<i>M</i> (g mol ⁻¹)	384.93	295.15
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Aba2</i>	<i>P2₁/n</i>
<i>a</i> /Å	10.958(2)	10.999(2)
<i>b</i> /Å	20.527(4)	6.9933(14)
<i>c</i> /Å	14.932(3)	12.621(3)
α (°)		90
β (°)		96.22
γ (°)		90
<i>V</i> (Å ³)	3359.0(12)	965.1(3)
<i>Z</i>	8	4
<i>D</i> _{calc} (g cm ⁻³)	1.522	2.031
crystal size (mm)	0.61 × 0.21 × 0.27	0.54 × 0.37 × 0.15
F(000)	1584	588
μ (Mo-K α)/mm ⁻¹	1.442	2.539
θ (°)	3.37 to 27.48	3.34 to 27.46
Reflections collected	15087	7712
Independent reflections (<i>I</i> > 2 σ (<i>I</i>))	3599(2418)	2200(1760)
Parameters	212	150
$\Delta(\rho)$ (e Å ⁻³)	0.383, -0.327	0.469, -0.464
Goodness of fit	1.060	1.168
<i>R</i> ^a	0.0654(0.1007) ^b	0.0313(0.0447) ^b
<i>wR</i> ₂ ^a	0.1386(0.1545) ^b	0.0880(0.1073) ^b

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2 c^{1/2}]; [F_o > 4\sigma(F_o)]\}$.

^b Based on all data

Table2 Selected bond lengths (Å) and angles (°) for the complexes **1-2**

Complex 1			
Cu-N(1)	2.211(5)	Cu-N(6)	1.904(5)
Cu-N(5)	2.085(6)	Cu-S(1)	2.317(2)
N(5)-Cu-N(1)	75.6(2)	N(6)-Cu-S(1)	117.82(17)
N(6)-Cu-N(1)	120.9(2)	N(5)-Cu-S(1)	102.61(16)
N(6)-Cu-N(5)	123.4(2)	N(1)-Cu-S(1)	108.45(14)
Complex 2			
Cu-N(2)	1.972(2)	Cu-O3W	1.957(2)
Cu-N(3)	2.030(2)	Cu-Cl	2.2568(9)
N(2)-Cu-N(3)	79.54(10)	O(3)-Cu-Cl	94.36(7)
O(3)-Cu-N(2)	168.14(9)	N(2)-Cu-Cl	94.47(8)
O(3)-Cu-N(3)	91.31(10)	N(3)-Cu-Cl	173.71(7)

Table 3 Short contacts (Å) and bond angles (°) of complexes **1-2**

D-H...A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	∠D-H...A/°
Complex 1				
C6-H6...S1	0.93	2.86	3.788(8)	179.0
C8-H8B...O2	0.96	2.47	3.281(10)	141.6
Complex 2				
O3-H3...O2	0.82	1.90	2.701(3)	164.0
O3-H3B...O1	0.80(6)	1.98(5)	2.653(3)	142(5)
N4-H4...O2	0.86	2.01	2.842(3)	161.2

Table 4 The calculated eigenvalues of HOMO, LUMO (a.u.) and the band gaps (eV) of the compounds and the complexes

	L1	L2	L3	L4	1	2
HOMO (a.u.)	-0.2123	-0.2369	-0.2173	-0.2555	-0.1828	-0.2098
LUMO (a.u.)	-0.0898	-0.1068	-0.0773	-0.2400	-0.1246	-0.2088
Band gap (eV)	3.33	3.54	3.81	0.42	1.58	0.03

Table 5 The IR data (cm⁻¹) for complexes **1** and **2**

Complexes	1	2
$\nu_{\text{N-H}}$		3110
$\nu_{\text{C-H}}$	3096	3020
$\nu_{\text{CH}_3-\text{CH}}$	2989,2924	
$\nu_{\text{SCN-}}$	2109	
$\nu_{\text{C=O}}$		1656
$\nu_{\text{C=C}}, \nu_{\text{C=N}}$	1598,1545,1419	1577,1486,1397
$\nu_{\text{C-O}}$	1101	
$\nu_{\text{C-C}}, \nu_{\text{C-N}}$	1341,1315	1321,1201
$\nu_{\text{N-N}}$	1029	1051
$\delta_{\text{C-H}}$	812	882,771
$\nu_{\text{Cu-N}}$	414,382,362	310,277

- C-N bond cleavage
- *In situ* reaction
- The mechanism for C-N bond fracturing was explored.

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