噻吩和吡啶取代三芳基三唑的两个铜配合物的合成与晶体结构

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摘要:分别以3-(2-吡啶基)-4-苯基-5-(2-噻吩基)-1,2,4-三氮唑(L¹)和3-(2-吡啶基)-4-(4-氯苯基)-5-(2-噻吩基)-1,2,4-三氮唑(L²)作为配体,合成了2个新的单核铜配合物:*trans*-[Cu(L¹)₂(MeOH)₂](ClO₄)₂(1)和*trans*-[Cu(L²)₂(ClO₄)₂]·2MeCN(2),并对其进行了红外、元素分析、单晶结构和粉末X射线衍射表征。2个配合物都属于单斜晶系,*P*2₁/c空间群。单晶结构分析表明,配合物1和2中的铜离子均处于一个扭曲的八面体配位环境[CuN₄O₂],其中1的轴向由2个甲醇分子配位,而2的轴向由2个高氯酸根配位。处于赤道面的配体的吡啶N原子和三氮唑的一个N原子采用螯合双齿模式参与配位,而噻吩不配位。配合物2含2个乙腈客体分子,乙腈与三氮唑环之间存在*π*···*π*堆积作用。配合物1和2中存在O—H···O、C—H···N氢键和C—H···*π*相互作用,从而连接单核配合物形成三维网络。

关键词:合成;铜配合物;晶体结构;三芳基三氮唑
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Syntheses and Crystal Structures of Two Copper Complexes Based on Thienyl and Pyridyl Substituted Triaryltriazoles

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Abstract: Two new copper(II) complexes, *trans*-[Cu(L¹)₂(MeOH)₂](ClO₄)₂ (**1**) and *trans*-[Cu(L²)₂(ClO₄)₂] • 2MeCN (**2**) (L¹ =3-(2-pyridyl)-4-phenyl-5-(2-thienyl)-1,2,4-triazole, L²=3-(2-pyridyl)-4-(*p*-chlorophenyl)-5-(2-thienyl)-1,2,4-triazole), were synthesized and structurally characterized by FT-IR, elemental analyses, single-crystal X-ray crystallography and powder X-ray diffraction. Both **1** and **2** crystallize in monoclinic system with a space group $P2_1/c$. X-ray crystallography analysis reveals that the copper ion in **1** and **2** sits in a distorted octahedral environment [CuN₄O₂] with two MeOH in the *trans*-position in **1** but two ClO₄⁻ in the *trans*-position in **2**. Each L ligand in the equatorial plane adopts a chelating bidentate mode through the pyridyl N atom and one triazole N atom, while the thienyl group does not coordinate. **2** contains two MeCN guest molecules which produce π - π stacking interactions with the triazole ring. In **1** and **2** there are some intermolecular O—H···O, C—H···O and C—H···N hydrogen bonds and C—H··· π interactions, linking the mononuclear complexes to form a 3D framework. CCDC: 2423470, **1**; 2423471, **2**.

Keywords: synthesis; Cu(II) complex; crystal structure; triaryltriazole

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0 Introduction

Over the past few decades, 3,4,5-triarylsubstituted 1,2,4-triazoles have attracted considerable attention in coordination chemistry^[1] because these triazole derivatives can be used as flexible bridging ligands and linkers between transition metal ions^[2-5]. In particular, some Fe (II) complexes with substituted triazoles can show fascinating spin crossover properties and may find potential applications in molecular switches, display devices, sensors and data storages^[6-9]. In our previous work, a series of 3,4,5-triarylsubstituted 1,2,4triazoles with the pyridyl, phenyl, pyrrolyl, imidazolyl, benzimidazolyl and quinolyl groups and their metal complexes have been reported^[10-24]. However, only a Co(II) complex with thienyl substituted triaryltriazoles has been reported until now^[25-26]. As a continuation of our exploration of asymmetrically substituted 1, 2, 4triazoles, we prepared two new triaryltriazoles with a thienyl group: 3-(2-pyridyl)-4-phenyl-5-(2-thienyl)-1,2, 4-triazole (L1) and 3-(2-pyridyl)-4-(p-chlorophenyl)-5-(2-thienyl)-1, 2, 4-triazole (L²) (Scheme 1). Herein we report the syntheses, crystal structures and spectral characterization of two mononuclear copper(II) complexes based on the designed ligands: trans-[Cu(L¹)₂(MeOH)₂] $(ClO_4)_2$ (1) and trans- $[Cu(L^2)_2(ClO_4)_2] \cdot 2MeCN$ (2).



Scheme 1 Structures of ligands L^1 and L^2

1 Experimental

1.1 Materials and measurements

All chemicals and solvents purchased were of analytical grade. Solvents were purified by conventional methods. Melting points were determined with an X-4 digital microscope melting - point apparatus (Beijing) and are uncorrected. Elemental analyses (C, H, N, S) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. FT-IR spectra were recorded on a Nicolet Avatar 380 FT-IR instrument using KBr disks from 4 000 to 400 cm⁻¹. ¹H NMR spectra were measured on a Bruker AM 400 MHz spectrometer in DMSO -d₆ solution. Electrospray ionization mass spectra (ESI-MS) were recorded with a LCQ ADVANTAGE MAX mass spectrometer. Powder X - ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE diffractometer using Cu $K\alpha$ radiation (λ =0.154 06 nm) at 40 kV and 40 mA in a range of 5°~50°.

1.2 Characterization of ligands L¹ and L²

Ligands L^1 and L^2 were synthesized based on our reported method^[21].

3-(2-pyridyl)-4-phenyl-5-(2-thienyl)-1,2,4-triazole (L¹): m.p. 201~203 °C. Anal. Calcd. for $C_{17}H_{12}N_4S$ (%): C, 67.08; H, 3.97; N, 18.41; S, 10.53. Found (%): C, 67.34; H, 4.24; N, 18.65; S, 10.81. IR (KBr, cm⁻¹): 3 072(w), 1 585(m), 1 489(s), 1 438(m), 1 002(m), 798 (m), 722(m). ¹H NMR (400 MHz): δ 8.31(d, 1H, Py-H), 8.03(d, 1H, Py-H), 7.91(t, 1H, Py-H), 7.66(d, 1H, thienyl-H), 7.54(t, 1H, Ph-H), 7.51(d, 2H, Ph-H), 7.47(d, 2H, Ph-H), 7.35(t, 1H, Py-H), 7.01(d, 1H, thienyl-H), 6.71(d, 1H, thienyl-H). ESI-MS: *m/z*=305.08, [L¹+H]⁺.

3-(2-pyridyl)-4-(*p*-chlorophenyl)-5-(2-thienyl)-1,2, 4 - triazole (L²): m. p. 192~194 °C . Anal. Calcd. for C₁₇H₁₁N₄SCl(%): C, 60.26; H, 3.27; N, 16.54; S, 9.46. Found(%): C, 60.42; H, 3.42; N, 16.39; S, 9.72. IR (KBr, cm⁻¹): 3 054(w), 1 590(m), 1 498(s), 1 443(s), 1 089(m), 997(m), 841(m), 721(m). ¹H NMR (400 MHz): δ 8.33(d, 1H, Py-H), 8.08(d, 1H, Py-H), 7.93(t, 1H, Py-H), 7.69(d, 1H, thienyl-H), 7.59(d, 2H, Ph-H), 7.57(d, 2H, Ph-H), 7.36(t, 1H, Py-H), 7.06(t, 1H, thienyl-H), 6.83(d, 1H, thienyl-H). ESI-MS: m/z=339.05, [L²+H]^{*}.

1.3 Syntheses of complexes 1 and 2

trans - $[Cu(L^1)_2(MeOH)_2](ClO_4)_2$ (1): A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.05 mmol) and $NaClO_4$ (0.1 mmol) in anhydrous MeOH (4 mL) was added to a solution of L¹ (0.1 mmol) in MeOH (4 mL). The mixture was stirred for 4 h at room temperature. The green precipitate was separated by filtration, and washed with water, then dried under vacuum to obtain complex 1 in a yield of 82%. The green block-shaped single crystals of 1 suitable for X-ray diffraction were obtained by slow

evaporation from MeOH solution. Anal. Calcd. for $C_{36}H_{32}Cl_2CuN_8O_{10}S_2(\%)$: C, 46.23; H, 3.45; N, 11.98; S, 6.86. Found(%): C, 46.52; H, 3.51; N, 11.77; S, 6.54. IR (KBr, cm⁻¹): 3 449(m, b), 3 082(w), 2 917(w), 1 617 (w), 1 562(m), 1 493(s), 1 388(m), 1 112(vs), 929(w), 859(w), 731(m), 626(s).

trans-[Cu(L²)₂(ClO₄)₂] •2MeCN (2): The prepared procedure for **2** was the same as that for **1** except using L² (0.1 mmol) to replace L¹. The well-shaped single crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation from MeCN solution. Yield: 87%. Anal. Calcd. for $C_{38}H_{28}Cl_4CuN_{10}O_8S_2(\%)$: C, 44.65; H, 2.76; N, 13.70; S, 6.27. Found(%): C, 44.27; H, 2.93; N, 13.82; S, 6.41. IR (KBr, cm⁻¹): 3 077 (w), 2 921(w), 2 347(w), 1 613(m), 1 566(m), 1 493(s), 1 114(vs), 1 098(s), 930(w), 859(m), 726(m), 621(s).

1.4 Crystal structure determination

Suitable single crystals of **1** and **2** were selected for lattice parameter determination and collection of intensity data on a Bruker SMART APEX II CCD diffractometer with a graphite-monochromated Mo $K\alpha$ $(\lambda = 0.071 \ 073 \ \text{nm})$ radiation using a $\varphi - \omega$ scan mode at 296(2) K. Multi-scan absorption corrections were applied to all intensity data using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL software^[27]. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were fixed in calculated positions and refined isotropically. The ClO_4^- ions in 1 were disordered over two positions with an occupancy of 0.677(14) for O2, O3, O4 and O5 and 0.323(14) for O2A, O3A, O4A and O5A. The two O atoms of coordinated ClO_4^{-} in 2 were also disordered over two positions with an occupancy of 0.548(7) for O2 and O3 and 0.452(7) for O2A and O3A. The crystallographic data of 1 and 2 are summarized in Table 1 and the selected bond lengths and angles are given in Table 2.

CCDC: 2423470, 1; 2423471, 2.

Complex	1	2
Empirical formula	$C_{36}H_{32}Cl_2CuN_8O_{10}S_2$	$C_{38}H_{28}Cl_4CuN_{10}O_8S_2$
Formula weight	935.25	1 022.16
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_{1}/c$
<i>a</i> / nm	0.846 57(19)	0.830 66(11)
<i>b</i> / nm	1.547 9(4)	1.541 0(2)
<i>c</i> / nm	1.566 7(4)	3.404 6(5)
β / (°)	98.002(3)	93.925(2)
V / nm^3	2.033 0(8)	4.347 8(10)
Ζ	2	4
$D_{\rm c} /({\rm g} \cdot {\rm cm}^{-3})$	1.528	1.562
μ / mm $^{-1}$	0.838	0.908
<i>F</i> (000)	958	2 076
Crystal size / mm	0.17×0.13×0.09	0.15×0.12×0.09
heta range / (°)	1.86~25.00	1.20~25.00
Reflection collected	14 399	30 959
Independent reflection	3 569 (R_{int} =0.033 3)	7 645 (R _{int} =0.033 9)
Reflection observed $[I > 2\sigma(I)]$	2 877	6 127
Data, restraint, parameter	3 569, 67, 306	7 645, 30, 589
Goodness-of-fit on F^2	1.066	1.071
$R_1, wR_2 [I > 2\sigma(I)]$	0.039 3, 0.102 5	0.050 7, 0.135 8
R_1, wR_2 (all data)	0.053 0, 0.108 8	0.064 9, 0.143 6
$(\Delta \rho)_{\rm max}, (\Delta \rho)_{\rm min} / ({\rm e} \cdot {\rm nm}^{-3})$	409, -332	654, -471

 Table 1
 Crystal data and structure refinements for 1 and 2

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1					
Cu1—N1	0.205 6(2)	Cu1—N2	0.198 4(2)	Cu1-01	0.240 6(2)
N2—N3	0.138 2(3)	S1—C8	0.171 7(3)	S1—C11	0.170 0(4)
N1—Cu1—N2	79.42(9)	N1-Cu1-01	84.20(9)	N2—Cu1—O1	92.75(9)
C1—N1—Cu1	126.4(18)	C5—N1—Cu1	115.5(17)	C6—N2—Cu1	115.3(3)
2					
Cu1—N1	0.205 3(3)	Cu1—N2	0.197 4(3)	Cu1-01	0.252 9(3)
Cu1—N5	0.205 3(3)	Cu1—N6	0.196 7(5)	Cu1-05	0.242 8(3)
N2—N3	0.137 2(4)	S1—C8	0.170 6(4)	C15—Cl1	0.173 4(4)
N6—N7	0.137 3(2)	S2—C25	0.171 2(4)	C32—Cl2	0.174 0(4)
N1—Cu1—N2	80.46(11)	N1-Cu1-01	86.45(13)	N2—Cu1—O1	89.08(12)
N5—Cu1—N6	80.09(8)	N5—Cu1—O5	91.69(7)	N6—Cu1—O5	90.74(11)
C1—N1—Cu1	127.4(2)	C5—N1—Cu1	114.0(2)	C6—N2—Cu1	113.8(2)
C18—N5—Cu1	127.12(5)	C22—N5—Cu1	114.49(8)	C23—N6—Cu1	115.0(5)

Table 2 Selected bond distances (nm) and bond angles (°) for 1 and 2

2 Results and discussion

2.1 Synthesis

Asymmetrically thienyl substituted 3,4,5-triaryl-1, 2,4-triazoles (L¹ and L²) reacted with Cu(NO₃)₂·3H₂O and NaClO₄ in molar ratio of 2:1:2 to lead the formation of two mononuclear complexes, *trans*-[Cu(L¹)₂ (MeOH)₂](ClO₄)₂ (**1**) and *trans*-[Cu(L²)₂(ClO₄)₂]·2MeCN (**2**), which are stable in air. The yields for **1** and **2** were 82% and 87%, respectively. The elemental analyses were satisfactory and indicate that **1** contains one Cu(II), two L¹ ligands, two MeOH molecules and two ClO₄⁻ ions, and **2** has one Cu(II), two L² ligands, two MeCN molecules and two ClO₄⁻ anions.

2.2 Crystal structures of 1 and 2

Although both 1 and 2 crystallize in the monoclin-

ic space group $P2_1/c$ (Fig.1), Z=2 and c=1.566 7(4) nm in 1 while Z=4 and c=3.404 6(5) nm in 2. Thus, there is an inversion center at the Cu (II) ion in 1 but none occurs in 2. The asymmetric unit of 1 is composed of half Cu (II) cation, one L¹ ligand, one coordinated MeOH molecule and one ClO₄⁻ anion, which is consistent with the elemental analysis result. The Cu1 ion of 1 is coordinated by four nitrogen atoms from two L¹ ligands in the equatorial plane and two oxygen atoms from two MeOH molecules in the axial positions to form a distorted octahedral [CuN₄O₂] geometry. Each L¹ ligand coordinates to Cu1 ion via N1 atom of the pyridyl and N2 atom of the triazole, similar to the coordinated modes in some related Cu (II) complexes^[14,16,24]. The thienyl group of L¹ ligand does not take part in



All H atoms, MeCN solvent and disordered O atoms are omitted for clarity; Symmetry code: i 1–x, 1–y, 1–z for 1

Fig.1 Projection of structures of 1 and 2 with 30% thermal ellipsoids probability

coordination, which is similar to the Co(II) complex with a thienyl substituted triaryltriazole: trans-[CoL₂ $(NCS)_2$] (L=3-(2-pyridyl)-4-(p-methoxyphenyl)-5-(2thienyl)-1,2,4-triazole)^[25]. However, the S1 atom of thienyl group in 1 does not orient to the phenyl ring, which is quite distinct from that observed in the trans-[CoL₂(NCS)₂] complex^[25]. The distance of Cu1-O1 is 0.240 6(4) nm. The Cu-N bond lengths are within the normal ranges found for the octahedral Cu(II) complexes^[28-31]. Nevertheless, the Cu-N bond to the triazole nitrogen is 0.007 3 nm shorter than that to the pyridyl one. The analogous feature has been observed in the similar Cu(II) complexes^[24]. The ligand L¹ in **1** is nonplanar. The triazole makes dihedral angles of $6.2(4)^{\circ}$, $29.7(6)^{\circ}$ and $64.6(3)^{\circ}$ with the pyridyl ring, the thienyl ring and phenyl ring, respectively.

Different from 1, the asymmetric unit of 2 consists of a Cu(II) cation, two L^2 ligands, two ClO₄⁻ ions and two MeCN molecules. The Cu(II) ion of **2** is coordinated by four nitrogen atoms from two L² ligands in the equatorial plane and two oxygen atoms from two ClO_4^- in the axial positions to build a distorted octahedral [CuN₄O₂] geometry. Each L² ligand coordinates to Cu1 atom via N1 (or N5) atom of the pyridyl and N2 (or N6) atom of the triazole whereas the thienyl group of L^2 ligand is also uncoordinated, which is very similar to the coordination mode of L^1 in **1**. The distance of Cu1-01(0.253 nm) is longer than that of the Cu1-O5 (0.242 8 nm). The Cu-N bond lengths are within the normal ranges observed for some octahedral Cu(II) complexes, whereas Cu-N bond to the triazole nitrogen is 0.008 6 nm shorter than that to the pyridyl one. The triazole

ring containing N2 atom forms dihedral angles of $2.4(2)^{\circ}$, $6.9(9)^{\circ}$ and $89.2(8)^{\circ}$ with the pyridyl ring with N1 atom, the thienyl ring with S1 atom and phenyl ring with Cl1 atom, respectively. And the triazole ring having N6 atom makes dihedral angles of $4.1(7)^{\circ}$, $9.6(4)^{\circ}$ and $87.6(3)^{\circ}$ with the pyridyl ring with N5 atom, the thienyl ring with S2 atom and phenyl ring with Cl2 atom, respectively. Therefore, the pyridyl, triazole and thienyl ring of L² in **2** is almost coplanar. Notably, the S atoms (S1 and S2) of thienyl groups in **2** orient to the *p*-chlorophenyl ring, which is similar to that found in the trans-[CoL₂(NCS)₂] complex^[25].

There are abundant intermolecular hydrogen bonds interactions in **1**: (1) between MeOH and ClO₄⁻ anion (O1—H1A···O4); (2) between pyridyl and triazole ring (C1—H1···N3ⁱ); (3) between phenyl and ClO₄⁻ anion (C13—H13···O2ⁱⁱⁱ and C17—H17···O2ⁱ); (4) between pyridyl and ClO₄⁻ anion (C3—H3···O5ⁱⁱ). In addition, there are an intramolecular edge-to-face C—H··· π interaction involving C4—H4 and phenyl ring (H4··· π 0.308 nm and \angle C4—H4··· π =148°) and an intermolecular edge-to-face C—H··· π interaction involving MeOH and pyridyl ring (H18C··· π 0.326 nm and \angle C18—H18C··· π =139°) (Fig. 2, Table 3). These interactions further connect the mononuclear **1** to form a 3D framework (Fig.3).

Complex **2** has richer C—H···O interactions including: (1) between pyridyl and ClO_4^- (C2—H2··· $O2^i$, C19—H19···O7ⁱⁱ and C20—H20···O6^v); (2) between thienyl and ClO_4^- (C9—H9···O7ⁱⁱ and C26—H26 ···O1ⁱ); (3) between phenyl and ClO_4^- (C16—H16··· $O4^{iv}$ and C17—H17···O3^{iv}). There are two kinds of C—



Symmetry codes: ⁱ 1-*x*, 1-*y*, 1-*z*; ⁱⁱ 2-*x*, 1-*y*, 1-*z*; ⁱⁱⁱ *x*, 1/2-*y*, 1/2+*z* for **1**; ⁱ *x*-1, *y*, *z*; ⁱⁱⁱ 1+*x*, *y*, *z*; ⁱⁱⁱ 2-*x*, 1-*y*, 1-*z*; ^{iv} 1-*x*, *y*-1/2, 1.5-*z*; ^v 1-*x*, 1-*y*, 1-*z*; ^{vi} -*x*, 1-*y*, 1-*z* for **2**

Fig.2 Hydrogen-bonding, C—H $\cdots \pi$ and $\pi \cdots \pi$ interactions in **1** and **2**

H····N interactions in **2** including: (1) between pyridyl and triazole (C1—H1····N7 and C18—H18····N3); (2) between thienyl and MeCN (C10—H10····N9ⁱⁱⁱ and C27—H27···N10ⁱⁱ). In addition, there are two kinds of π - π stacking interactions between triazole rings and the MeCN molecules $(\pi \cdots \pi (C \equiv N9)^{\circ} 0.331 \text{ 6 nm}, \pi \cdots \pi (C \equiv N10)^{\circ} 0.330 \text{ 4 nm})$ (Table 3, Fig. 2). All the interactions assemble the mononuclear **2** into a 3D network (Fig.3).

Table 3	Hydrogen-bond	geometry and	ІС—Н…	π interactions in	1 and 2
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D—H…A	$d(\mathrm{D}-\mathrm{H})$ / nm	$d(\mathbf{H}\cdots\mathbf{A})$ / nm	$d(\mathbf{D}\cdots\mathbf{A})$ / nm	$\angle D$ —H····A / (°)
		1		
01—H1A…04	0.086	0.203	0.279 6(6)	148
$C1$ — $H1$ ··· $N3^{i}$	0.093	0.236	0.316 1(4)	144
С3—Н3…05"	0.093	0.261	0.335 9(3)	138
C4—H4···· π (Ph)	0.093	0.308	0.389 7(2)	148
С13—Н13…О2 ^{ііі}	0.093	0.257	0.342 8(7)	154
C17—H17…O2 ⁱ	0.093	0.260	0.349 2(8)	162
C18—H18C… <i>π</i> (Ру)	0.096	0.326	0.402 9(8)	139
		2		
C1—H1…N7	0.093	0.233	0.310 2(5)	140
$C2$ — $H2$ ··· $O2^{i}$	0.093	0.237	0.307 0(7)	131
C4—H4···· π (Ph)	0.093	0.284	0.368 6(7)	152
С9—Н9…07"	0.093	0.246	0.337 6(6)	168
C10—H10…N9 ⁱⁱⁱ	0.093	0.268	0.354 0(7)	154
C16—H16…O4 ^{iv}	0.093	0.256	0.334 7(5)	142
C17—H17…O3 ^{iv}	0.093	0.251	0.310 0(9)	122
C18—H18…N3	0.093	0.239	0.318 6(5)	143
C19—H19…O7 ⁱⁱ	0.093	0.263	0.331 4(5)	130
C20—H20····O6 ^v	0.093	0.258	0.350 8(7)	173
C21—H21···· π (Ph)	0.093	0.302	0.384 6(6)	150
C26—H26…O1 ⁱ	0.093	0.270	0.331 4(8)	123
$C27$ — $H27$ ···· $N10^{vi}$	0.093	0.259	0.350 5(6)	168

Symmetry codes: ⁱ 1-*x*, 1-*y*, 1-*z*; ⁱⁱ 2-*x*, 1-*y*, 1-*z*; ⁱⁱⁱ *x*, 1/2-*y*, 1/2+*z* for **1**; ⁱ *x*-1, *y*, *z*; ⁱⁱⁱ 1+*x*, *y*, *z*; ⁱⁱⁱ 2-*x*, 1-*y*, 1-*z*; ^{iv} 1-*x*, *y*-1/2, 1.5-*z*; ^v 1-*x*, 1-*y*, 1-*z*; ^{vi} -*x*, 1-*y*, 1-*z*; ^{iv} 1-*x*, *y*-1/2, 1.5-*z*;



Fig.3 Three dimensional frameworks of 1 and 2

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2.3 IR spectra

In the IR spectra of **1** and **2**, a broad band at 3 447 cm⁻¹ in **1** is due to the O—H stretching vibrations of MeOH, while a weak band at 2 347 cm⁻¹ in **2** is assigned to characteristic C==N stretching vibrations of MeCN^[32]. A medium band at 1 562 cm⁻¹ in **1** or 1 566 cm⁻¹ in **2** can be assigned to the coordinated pyridyl ring vibrations. In **1** (or **2**), the bands around 1 112 (or 1 114), 929 (or 930), 626 (or 621) cm⁻¹ can be assigned to the IR-allowed ν mode, IR-forbidden ν mode and the non-degenerate ClO₃ symmetrical bending frequency of the ClO_4^- anions, respectively^[33]. Additionally, the stretching vibration of Cl - C(Ph) in **2** is found at 1 098 cm^{-1[34]}. These features are in consistent with the X-ray analysis results.

2.4 PXRD

The PXRD patterns and simulated ones of **1** and **2** are shown in Fig. 4. The experimental patterns are in well agreement with the simulated ones from the single X-ray crystal data, revealing that the high phase purity of the bulk products of **1** and **2**.



Fig.4 PXRD patterns of **1** and **2**

3 Conclusions

Two new Cu (II) complexes based on the thienyl and pyridyl substituted triarytriazole, trans-[Cu(L¹)₂ (MeOH)₂](ClO₄)₂ (1) and trans-[Cu(L²)₂(ClO₄)₂] • 2MeCN (2), have been synthesized and characterized by IR, PXRD and X-ray crystallography. The structural analyses reveal that two complexes have a similar pseudooctahedral [CuN₄O₂] core with two MeOH molecules in the *trans*-positions in 1 but two ClO₄⁻ ions in the *trans*positions in 2.

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