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### Supramolecular networks with 1-substituted benzotriazole ligands and transition metals

Fei Wang<sup>ab</sup>; Xiao-Yuan Wu<sup>a</sup>; Rong-Min Yu<sup>a</sup>; Zhen-Guo Zhao<sup>ab</sup>; Can-Zhong Lu<sup>a</sup>

<sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China <sup>b</sup> Graduate School, The Chinese Academy of Sciences, Beijing 100039, P.R. China

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## Supramolecular networks with 1-substituted benzotriazole ligands and transition metals

FEI WANG<sup>†‡</sup>, XIAO-YUAN WU<sup>†</sup>, RONG-MIN YU<sup>†</sup>,  
ZHEN-GUO ZHAO<sup>†‡</sup> and CAN-ZHONG LU<sup>\*†</sup>

<sup>†</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China  
<sup>‡</sup>Graduate School, The Chinese Academy of Sciences, Beijing 100039, P.R. China

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1-(2-Pyridyl)benzotriazole (L1) and 1-(4-pyridyl)benzotriazole (L2) with transition metal cations Co(II), Ni(II) and Cu(II) give four coordination complexes, [ $\text{Cu}(\text{L1})_2(\text{H}_2\text{O})_2 \cdot 2\text{NO}_3$ ] (1), [ $\text{Co}(\text{L1})_2(\text{H}_2\text{O})_2 \cdot 2\text{NO}_3$ ] (2), [ $\text{Ni}(\text{L2})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ ] (3), and [ $\text{Cu}_2(\text{L2})_2(\text{CH}_3\text{COO})_4$ ] (4). In 1–4, different supramolecular frameworks are formed through hydrogen bonding and/or  $\pi$ – $\pi$  interactions.

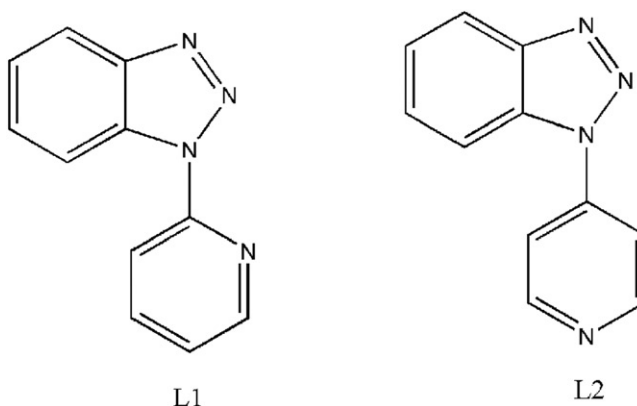
**Keywords:** Benzotriazole; Hydrogen bonding;  $\pi$ – $\pi$  Interactions; Supramolecular networks

### 1. Introduction

Design and synthesis of supramolecular complexes have received much attention [1–3] in the literature. Hydrogen bonding and  $\pi$ – $\pi$  contacts are common interactions in the supramolecular complexes. Assembly of supramolecular architectures is influenced by various factors, including the identity of each component [4], the molar ratio of the reagents [5], the pH [6], and steric requirements of the counterions [7a, 7b]. Great influence of the steric effects of ligands on the structures and catalytic activity of supramolecular complexes [7c, 7d] has been reported. In addition, the influence of the reaction media [7e, 7f] has received attention.

Triazolates compounds have been employed extensively in synthesis of supramolecular complexes and organic–inorganic hybrid materials [8–13]. In this article, we report four complexes based on two 1-substituted benzotriazole ligands (scheme 1): 1-(2-pyridyl)benzotriazole (L1) [8, 14] and 1-(4-pyridyl)benzotriazole (L2) [15], which have four N-atoms providing various possibilities of coordination [16] and supramolecular interactions. Details of the structures and supramolecular interactions are reported.

\*Corresponding author. Email: czlu@fjirsm.ac.cn



Scheme 1. The structure of the ligands.

## 2. Experimental

### 2.1. Materials and physical measurements

L1 and L2 were synthesized following reported procedures [14, 15], and the other reagents were obtained commercially and used directly without purification. IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer.

### 2.2. Synthesis

**2.2.1. General method for preparation of (1)–(3).** To a 10 mL ethanol solution of  $M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (0.5 mmol), 10 mL of toluene solution of L1 (0.096 g, 0.5 mmol) was added drop by drop. The resultant solution was allowed to stand at room temperature. Several days later, suitable crystals for X-ray diffraction were produced, collected by filtration and dried in air.

**2.2.2. Synthesis of  $\{[\text{Cu}(\text{L1})_2(\text{H}_2\text{O})_2] \cdot 2\text{NO}_3\}$  (1).** Green block crystals (0.12 g; yield: 40%, based on Cu).  $\text{C}_{22}\text{H}_{20}\text{CuN}_{10}\text{O}_8$ : Anal. Calcd(%): C 43.30, H 3.27, N 22.74; found(%): C 43.91, H 3.49, N 22.85. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3376(w), 3067(w), 1620(s), 1498(m), 1383(s), 1066(w), 1027(w), 786(m), 752(m).

**2.2.3. Synthesis of  $\{[\text{Co}(\text{L1})_2(\text{H}_2\text{O})_2] \cdot 2\text{NO}_3\}$  (2).** Pink block crystals (0.062 g; yield: 20%, based on Co).  $\text{C}_{22}\text{H}_{20}\text{CoN}_{10}\text{O}_8$ : Anal. Calcd(%): C 43.22, H 3.30, N 22.91; found(%): C 43.27, H 3.39, N 22.82. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3276(w), 3060(w), 1594(s), 1476(w), 1384(s), 1073(w), 920(w), 785(w), 648(w).

**2.2.4. Synthesis of  $[\text{Ni}(\text{L2})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  (3).** Green plate crystals (0.153 g; yield: 50% based on Ni).  $\text{C}_{22}\text{H}_{20}\text{N}_{10}\text{NiO}_8$ : Anal. Calcd(%): C 43.24, H 3.30, N 22.92; found(%): C 43.04, H 3.68, N 22.65. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3397(s), 3106(w), 3072(w), 1610(s), 1517(s), 1453(s), 1384(s), 1302(s), 1238(m), 1187(m), 1048(s), 829(m), 770(m), 657(m), 577(m), 532(m).

**2.2.5. Synthesis of  $[\text{Cu}_2(\text{L})_2(\text{CH}_3\text{COO})_4]$  (4).** Complex **4** was synthesized solvothermally in a 23 mL Teflon-lined autoclave by heating a mixture of L2 (0.5 mmol),  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.5 mmol) and ethanol/ $\text{H}_2\text{O}$  (5 mL/5 mL) at 120°C for 4 days and cooled at 5°C h<sup>-1</sup>. Dark green block single crystals were collected for X-ray diffraction.  $\text{C}_{30}\text{H}_{28}\text{O}_8\text{N}_8\text{Cu}_2$ : Anal. Calcd(%): C 47.64, H 3.71, N 14.82; found(%): C 47.04, H 4.18, N 14.65. IR (KBr pellets, cm<sup>-1</sup>): 3398(s), 3114(m), 1629(s), 1559(s), 1508(m), 1454(m), 1428(s), 1299(m), 1237(m), 1182(m), 1045(s), 1013(m), 827(m), 782(m), 742(m), 682(m), 627(m), 531(m).

### 2.3. Crystal structure determination

Suitable single crystals of **1–4** were carefully selected under an optical microscope and glued to thin glass fibers. Crystallographic data for all compounds were collected with a Siemens Smart CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $T = 293(2) \text{ K}$ . Absorption corrections were made using SADABS [17]. The structures were solved using direct methods and refined by full-matrix least squares on  $F^2$  using the SHELX-97 program package [18]. All nonhydrogen atoms were refined anisotropically. Crystal parameters and details of data collection and refinement are given in table 1 and the selected bond lengths and angles are given in table 2.

## 3. Results and discussion

### 3.1. Description of the structure of $[\{\text{Cu}(\text{L}1)_2(\text{H}_2\text{O})_2\} \cdot 2\text{NO}_3]$ (1) and $[\{\text{Co}(\text{L}1)_2(\text{H}_2\text{O})_2\} \cdot 2\text{NO}_3]$ (2)

The structure of **1** is almost identical to that of the corresponding complex with methanol in place of water, described previously [8]. The structure of **1** is shown in figure 1. The copper occupies a special position, sitting on the inversion center.

Table 1. Crystallographic data for **1–4**.

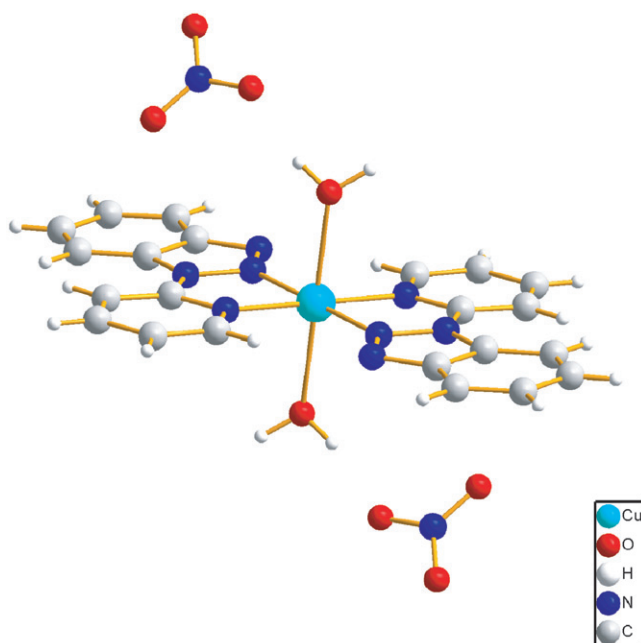
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	$\text{CuC}_{22}\text{H}_{20}\text{N}_{10}\text{O}_8$	$\text{CoC}_{22}\text{H}_{20}\text{N}_{10}\text{O}_8$	$\text{NiC}_{22}\text{H}_{20}\text{N}_{10}\text{O}_8$	$\text{C}_{30}\text{H}_{28}\text{Cu}_2\text{N}_8\text{O}_8$
Formula weight	616.03	611.41	611.19	755.68
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P_21/n$	$P_21/n$	$P_21/n$	$P_21/c$
Unit cell dimensions ( $\text{\AA}$ , °)				
<i>a</i>	7.319(6)	8.158(8)	13.306(7)	14.349(6)
<i>b</i>	11.801(9)	11.550(11)	13.120(7)	13.239(5)
<i>c</i>	14.715(12)	11.550(11)	7.166(4)	8.506(3)
$\beta$	100.296(13)	94.579(19)	95.961(10)	106.695(4)
<i>V</i> ( $\text{\AA}^3$ )	1250.4(17)	1289(2)	1244.1(11)	1548.4(10)
<i>Z</i>	2	2	2	2
<i>T</i> (K)	293(2)	294(2)	293(2)	293(2)
$\rho_c$ ( $\text{g cm}^{-3}$ )	1.636	1.575	1.579	1.621
$\mu$ ( $\text{cm}^{-1}$ )	9.44	7.34	13.73	14.39
$R_1$ ( $\omega R_2$ ) [ $I > 2\sigma(I)$ ]	0.0602 (0.1888)	0.0381 (0.1321)	0.0391 (0.1062)	0.0412 (0.0997)

Table 2. Selected bond lengths (Å) and angles (°) of **1–4**.

<b>Complex 1</b>			
Cu(1)–N(2)#1	2.002(3)	Cu(1)–N(4)#1	2.014(3)
Cu(1)–N(2)	2.002(3)	Cu(1)–OW1	2.347(4)
Cu(1)–N(4)	2.014(3)	Cu(1)–OW1#1	2.347(4)
N(2)#1–Cu(1)–N(2)	180.0	N(4)–Cu(1)–OW1	89.73(13)
N(2)#1–Cu(1)–N(4)	100.98(12)	N(4)#1–Cu(1)–OW1	90.27(13)
N(2)–Cu(1)–N(4)	79.02(12)	N(2)#1–Cu(1)–OW1#1	91.96(17)
N(2)#1–Cu(1)–N(4)#1	79.02(12)	N(2)–Cu(1)–OW1#1	88.04(17)
N(2)–Cu(1)–N(4)#1	100.98(12)	N(4)–Cu(1)–OW1#1	90.27(13)
N(4)–Cu(1)–N(4)#1	180.0	N(4)#1–Cu(1)–OW1#1	89.73(13)
N(2)#1–Cu(1)–OW1	88.04(17)	OW1–Cu(1)–OW1#1	180.0
N(2)–Cu(1)–OW1	91.96(17)		
<b>Complex 2</b>			
Co(1)–O(10)	2.070(2)	Co(1)–N(3)#1	2.100(2)
Co(1)–O(10)#1	2.070(2)	Co(1)–N(4)	2.120(2)
Co(1)–N(3)	2.100(2)	Co(1)–N(4)#1	2.120(2)
O(10)–Co(1)–O(10)#1	180.0	N(3)–Co(1)–N(4)	75.52(10)
O(10)–Co(1)–N(3)	89.45(10)	N(3)#1–Co(1)–N(4)	104.48(10)
O(10)#1–Co(1)–N(3)	90.55(10)	O(10)–Co(1)–N(4)#1	89.20(9)
O(10)–Co(1)–N(3)#1	90.55(10)	O(10)#1–Co(1)–N(4)#1	90.80(9)
O(10)#1–Co(1)–N(3)#1	89.45(10)	N(3)–Co(1)–N(4)#1	104.48(10)
N(3)–Co(1)–N(3)#1	180.00(6)	N(3)#1–Co(1)–N(4)#1	75.52(10)
O(10)–Co(1)–N(4)	90.80(9)	N(4)–Co(1)–N(4)#1	180.0
O(10)#1–Co(1)–N(4)	89.20(9)		
<b>Complex 3</b>			
Ni(1)–O(4)#1	2.0722(17)	Ni(1)–O(3)	2.0964(16)
Ni(1)–O(4)	2.0722(17)	Ni(1)–N(4)	2.0969(18)
Ni(1)–O(3)#1	2.0964(16)	Ni(1)–N(4)#1	2.0969(18)
O(4)#1–Ni(1)–O(4)	180.0	O(3)#1–Ni(1)–N(4)	92.18(6)
O(4)#1–Ni(1)–O(3)#1	100.54(7)	O(3)–Ni(1)–N(4)	87.82(6)
O(4)–Ni(1)–O(3)#1	79.46(7)	O(4)#1–Ni(1)–N(4)#1	91.15(7)
O(4)#1–Ni(1)–O(3)	79.46(7)	O(4)–Ni(1)–N(4)#1	88.85(7)
O(4)–Ni(1)–O(3)	100.54(7)	O(3)#1–Ni(1)–N(4)#1	87.82(6)
O(3)#1–Ni(1)–O(3)	180.00(8)	O(3)–Ni(1)–N(4)#1	92.18(6)
O(4)#1–Ni(1)–N(4)	88.85(7)	N(4)–Ni(1)–N(4)#1	180.00(4)
O(4)–Ni(1)–N(4)	91.15(7)		
<b>Complex 4</b>			
Cu(1)–O(3)	1.964(2)	Cu(1)–O(4)	1.971(2)
Cu(1)–O(2)	1.968(2)	Cu(1)–N(4)	2.191(2)
Cu(1)–O(1)	1.970(2)	Cu(1)–Cu(1)#1	2.6338(10)
O(3)–Cu(1)–O(2)	168.18(8)	O(1)–Cu(1)–N(4)	94.26(8)
O(3)–Cu(1)–O(1)	89.36(10)	O(4)–Cu(1)–N(4)	97.61(8)
O(2)–Cu(1)–O(1)	89.13(10)	O(3)–Cu(1)–Cu(1)#1	82.83(6)
O(3)–Cu(1)–O(4)	88.89(10)	O(2)–Cu(1)–Cu(1)#1	85.35(6)
O(2)–Cu(1)–O(4)	90.17(9)	O(1)–Cu(1)–Cu(1)#1	83.73(6)
O(1)–Cu(1)–O(4)	168.12(8)	O(4)–Cu(1)–Cu(1)#1	84.39(6)
O(3)–Cu(1)–N(4)	96.35(8)	N(4)–Cu(1)–Cu(1)#1	177.83(6)
O(2)–Cu(1)–N(4)	95.46(8)		

Symmetry transformations used to generate equivalent atoms: **Complex 1**: (#1)  $-x, -y+1, -z$ ; **Complex 2**: (#1)  $-x, -y, -z+1$ ; **Complex 3**: (#1)  $-x, -y+1, -z$ ; **Complex 4**: (#1)  $-x+2, -y, -z$ .

Each copper is in an elongate octahedral coordination environment with axial positions defined by two coordinated waters, and the equatorial plane generated by four nitrogens from two L1 (Cu–N2 2.002(3), Cu–N4 2.013(3), Cu–OW1 2.348(4) Å). Similarly, each cobalt site in **2** is in a slightly distorted octahedron with axial positions occupied by coordinated water, and the equatorial plane generated by the four nitrogens from two L1 (Co–O10(water) 2.070(2), Co–N3 2.100(2), Co–N4 2.120(2) Å).

Figure 1. Coordination environment of Cu(II) in **1**.Table 3. Geometrical parameters of hydrogen bonds of **1–4**.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
<b>Complex 1</b>				
OW1–HW1...O1	0.71(7)	2.06(7)	2.774(7)	179(9)
OW1–HW2...O3#1	0.72(5)	2.27(6)	2.900(7)	147(6)
<b>Complex 2</b>				
O10–H10A...O2#1	0.823(10)	2.078(14)	2.866(4)	160(3)
O10–H10B...O3#2	0.834(10)	1.965(13)	2.782(4)	166(3)
<b>Complex 3</b>				
O4–H4A...O2#1	0.83(4)	1.98(4)	2.790(2)	164(3)
O4–H4B...O2#2	0.85(4)	2.03(4)	2.866(3)	168(3)

Symmetry codes: Complex **1**: (#1)  $-x, y + 1/2, -z + 1/2$ ; Complex **2**: (#1)  $x + 1/2, -y + 1/2, z + 1/2$ , (#2)  $-x, -y, -z + 1$ ; Complex **3**: (#1)  $-x, -y + 1, -z + 1$ , (#2)  $-x, y - 1/2, -z + 1/2$ .

The  $\text{NO}_3^-$ , as counteranions, are involved in  $\text{O}\cdots\text{H}-\text{Ow}$  hydrogen bonds (table 3) with  $\text{O}\cdots\text{O}$  distances between 2.774(7) and 2.900(7) Å, resulting in 2-D networks (figure 2). The 2-D networks in **1** further stack by weak  $\pi-\pi$  interactions (the distance between the ring centroids is *ca* 3.849 Å) forming a 3-D framework (figure 3).

### 3.2. Description of the structure of $[\text{Ni}(\text{L}2)_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ (**3**)

The structure of **3** is composed of one crystallographically independent  $\text{Ni}^{2+}$ , two mono-coordinated L2, two nitrates, and two coordinated waters (figure 4).

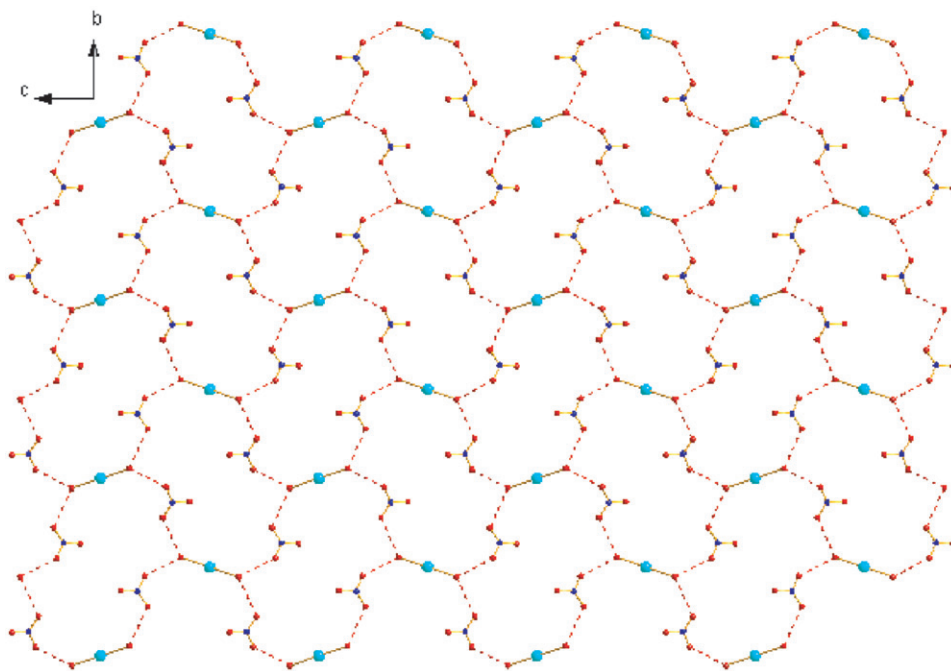


Figure 2. 2-D hydrogen bonding network of **1** (ligands and hydrogen atoms omitted for clarity).

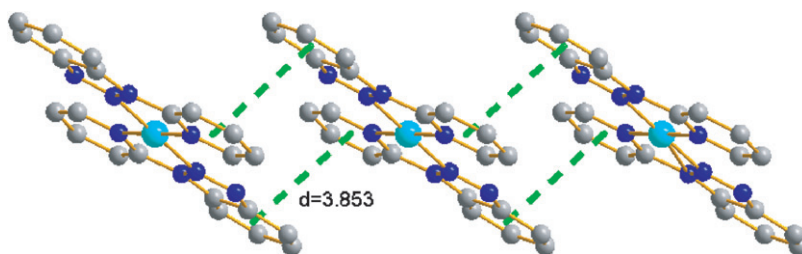


Figure 3. View of the weak  $\pi \cdots \pi$  interactions in **1**. Hydrogen atoms omitted for clarity.

The coordinated  $\text{NO}_3^-$  are also involved in  $\text{O} \cdots \text{H}-\text{Ow}$  hydrogen bonds with  $\text{O} \cdots \text{O}$  distances between 2.790(2) and 2.866(3) Å, resulting in 2-D networks. The ligands play a controlling role over the hydrogen bonding networks. Two types of cycles exist in the hydrogen bonding networks. One has two metal cations, two water molecules and two  $\text{NO}_3^-$ , adjacent cycles link each other by sharing one metal atom to form a 1-D '∞' chain, linked by hydrogen bonding to form the 2-D networks parallel to the  $b$ - $c$  plane. The other kind of cycle exists between two chains, one metal cation, two waters, and two  $\text{NO}_3^-$  (figure 5).

In structure **3** L2 ligands decorate above and below the 2-D sheet. Neighboring L2 ligands, which are almost parallel, are interdigitated with those of neighboring 2-D sheets to form a 3-D network with 1-D channels via  $\pi$ - $\pi$  interactions ( $d_{\text{centroid}}$  is *ca* 3.651 Å) between adjacent triazole rings (figure 6). The 1-D channels are along the  $b$ -axis with the distances of Ni  $\cdots$  Ni atoms in the diagonal about  $13.306 \times 14.423 \text{ \AA}^2$

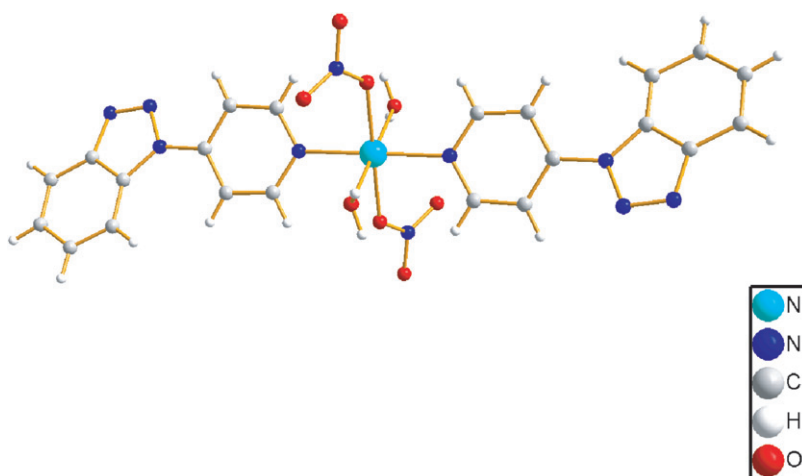


Figure 4. Coordination environment of Ni(II) in **3**.

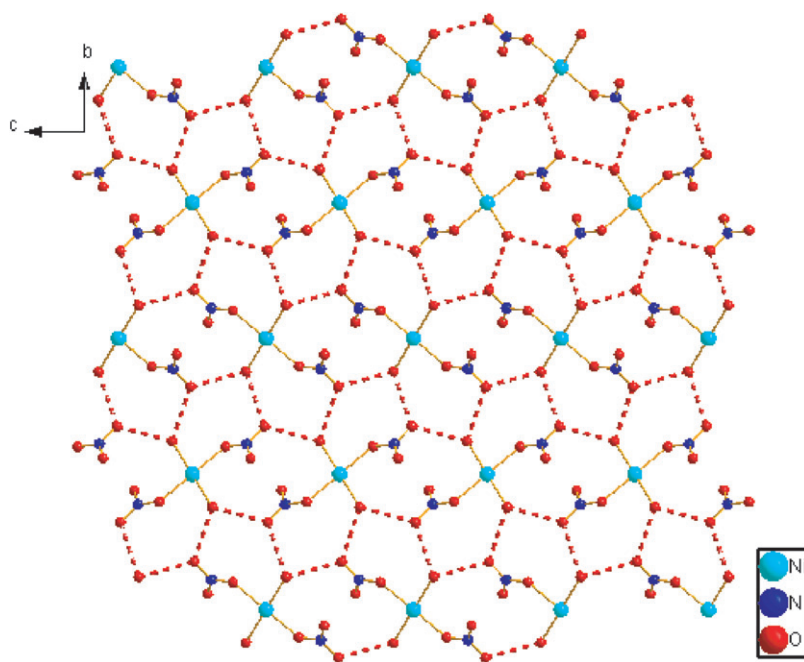


Figure 5. 2-D hydrogen bonding network of **3** (ligands and hydrogen atoms omitted for clarity).

(channel size is measured without considering van der Waals radii for constituting atoms).

### 3.3. Description of the structure of $[Cu_2(L2)_2(CH_3COO)_4]$ (**4**)

The structure of **4** is composed of paddlewheel dinuclear  $\{Cu_2(COO)_4\}$  units. Similar to complex **3**, the L2 ligands are coordinated to the center metal by pyridyl-N atoms,



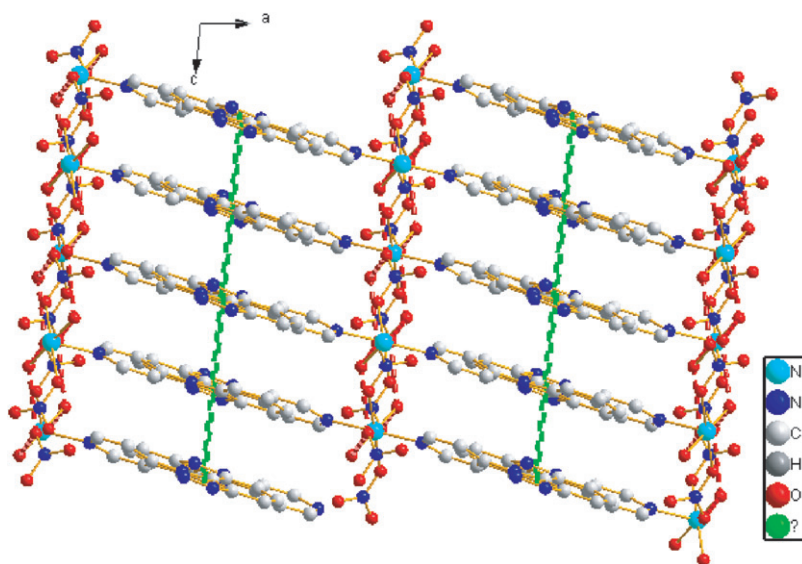


Figure 6. 3-D framework of **3** formed by hydrogen bond and  $\pi \cdots \pi$  interactions including 1-D channel along *b*-axis (hydrogen atoms omitted for clarity).

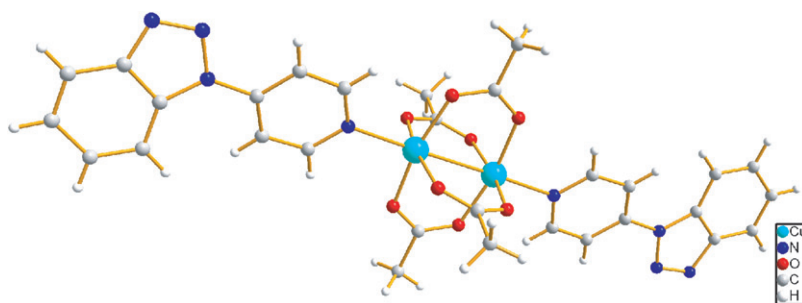


Figure 7. The paddlewheel dinuclear  $\{\text{Cu}_2(\text{COO})_4\}$  units of **4**.

occupying axial sites of the  $\{\text{Cu}_2(\text{COO})_4\}$  paddle wheels (figure 7). There are weak intermolecular  $\pi$ - $\pi$  stacking interactions between the triazole and phenyl rings from adjacent L2 ligands. The distance between the ring centroids is *ca* 3.978 Å. There is no hydrogen bonding among the isolated molecules. The weak intermolecular  $\pi$ - $\pi$  stacking interactions and the van der Waals' force contribute to the stability of the crystal packing (figure 8).

### 3.4. Temperature and steric effects of the ligands

The ligands (L1 and L2) contain three potential coordinate sites offering possibilities to form metal-organic coordination polymers. Surprisingly, the reactions of these ligands with  $\text{M}^{2+}$  produced simple discrete transition complexes.

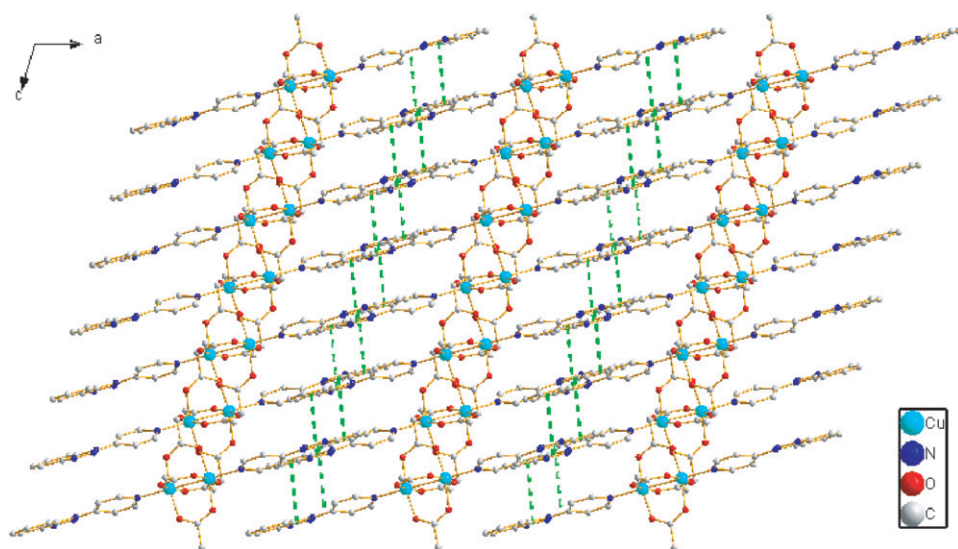


Figure 8. Packing diagram of **4**. Hydrogens omitted for clarity.

L1 in **1** and **2** coordinate to  $M^{2+}$  using triazolate nitrogen, but L2 uses pyridyl-N atoms to link  $M^{2+}$  cations in **3** and **4**. The difference in coordination is ascribed to the steric effect [8]. Complex **4** was synthesized under solvothermal conditions at 120°C. The yields and quality of crystals decreased when the reactions were performed at higher temperature, indicating a great influence of the temperature on the formation of the compounds.

#### 4. Conclusion

We report here four complexes obtained by traditional solution or solvothermal methods. Structure determinations of these complexes demonstrate that temperature, steric effects of ligands, and coordination sphere of the metal center could greatly affect the structures through hydrogen bonding and/or  $\pi$ - $\pi$  interactions. Selection of appropriate ligands and temperature would be an ideal way to construct coordination structures and supramolecular networks [16, 19].

#### Supplementary material

CCDC 676324 (**1**), 676325 (**2**), 676329 (**3**), 686181(**4**), contain the supplementary crystallographic details for these complexes.

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