

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:31

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Synthesis, crystal structures, and properties of copper(II) complexes with 2,6-bis(benzimidazol-2-yl)pyridine

Feng-Mei Nie ^a, Yong Hou ^a & Guan-Nan Li ^a

^a Department of Chemistry, Capital Normal University, Beijing 100048, China

Published online: 09 Mar 2011.

To cite this article: Feng-Mei Nie, Yong Hou & Guan-Nan Li (2011) Synthesis, crystal structures, and properties of copper(II) complexes with 2,6-bis(benzimidazol-2-yl)pyridine, Journal of Coordination Chemistry, 64:6, 1042-1053, DOI: [10.1080/00958972.2011.561429](https://doi.org/10.1080/00958972.2011.561429)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.561429>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synthesis, crystal structures, and properties of copper(II) complexes with 2,6-bis(benzimidazol-2-yl)pyridine

FENG-MEI NIE*, YONG HOU and GUAN-NAN LI

Department of Chemistry, Capital Normal University, Beijing 100048, China

(Received 23 July 2010; in final form 23 December 2010)

Three new mononuclear copper(II) complexes, $[\text{CuL}(2\text{-fca})(\text{CH}_3\text{OH})]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**1**), $[\text{CuL}(\text{m-nba})(\text{CH}_3\text{OH})]\text{ClO}_4$ (**2**), and $[\text{CuL}(\text{pic})(\text{ClO}_4)] \cdot \text{CH}_3\text{OH}$ (**3**), were synthesized and structurally characterized, where L is 2,6-bis(benzimidazol-2-yl)pyridine, while 2-fca, m-nba, and pic are the anions of 2-furoic acid, *m*-nitrobenzoic acid, and picolinic acid, respectively. All of them were characterized by elemental analysis, infrared, UV-Vis, and X-ray crystallography. In **1** and **2**, the Cu(II) resides within a distorted square-pyramidal N_3O_2 coordination sphere with three nitrogens of L, one carboxylate oxygen, and one methanol. In **3**, Cu(II) is coordinated with three nitrogens of L, one nitrogen and one oxygen of picolate, and one oxygen of perchlorate in a distorted octahedral geometry. Two molecules of **1**, **2**, and **3** are interacted by intermolecular hydrogen-bonding interactions and strong π - π stacking interactions to form a dinuclear structural unit. The dinuclear units are further connected by H-bonds *via* perchlorate or lattice methanol to form a 1-D chain for **1** and 2-D network structures for **2** and **3**. Hydrogen-bonding and π - π stacking interactions are important for the stabilization of the final supramolecular structures of the three complexes.

Keywords: Copper(II) complex; 2,6-Bis(benzimidazol-2-yl)pyridine; Crystal structure

1. Introduction

Much attention has been devoted to the construction of supramolecular assemblies by using metal–ligand covalent bonds and multiple weak non-covalent forces like hydrogen bonds and π - π interactions [1–5], since such multidimensional networks may have exciting properties and potential applications as functional materials [6–9]. Multidentate ligands containing two or more benzimidazole donors play an important role in modern chemistry. Complexes containing these ligands have been widely used to prepare structural and spectroscopic models of the active sites of some metalloenzymes [10, 11]. Tridentate 2,6-bis(benzimidazol-2-yl)pyridine (L) containing two benzimidazole units and its complexes with some divalent metals have been reported as simple models [12, 13]. But investigation concerned with the construction of supramolecules *via* this ligand is limited, although it can be used as a multifunctional building block.

*Corresponding author. Email: niefm@mail.cnu.edu.cn

Tridentate L contains two benzimidazole NH groups, which can serve as hydrogen-bond donors. At the same time, it contains one pyridine and two planar benzimidazolyl moieties, which can provide interaction sites for π - π stacking. Therefore, L can be used to construct supramolecular coordination networks incorporating both coordination and non-covalent interactions. A variety of metal complexes of L have been prepared and characterized [14–30]. Several lanthanide(III) complexes of L as a chromophoric ligand were prepared to study the luminescent properties of these complexes [14]. A number of transition metal complexes were also synthesized to model active site structures of relevant metalloenzymes [15, 27, 29]. Most have structures of type ML_2 or MLX_n ($X = Cl, H_2O, CH_3CN, PPh_3, NO_3^-$). Only a few structurally characterized copper(II) complexes with L were reported in which H_2O, CH_3CN, NO_3^- , and Cl^- [27–30] were used as coligands, but carboxylate coligands have not been reported. Here, we describe the synthesis and characterization of three copper complexes containing anions of 2-furoic acid, *m*-nitrobenzoic acid, and picolinic acid as coligands.

2. Experimental

2.1. Reagents and measurements

All chemicals and solvents were purchased from commercial sources and used without purification. Sodium 2-furoate was prepared by reacting 2-furoic acid with a stoichiometric amount of NaOH in water. Ligand L was synthesized according to published procedure [31]. Caution! Salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities. Elemental C, H, and N analyses were performed using an Elemental Vario MICRO CUBE (Germany) elemental analyzer. Infrared (IR) spectra were obtained from KBr pellets with a Bruker TENSOR 27 FT-IR spectrometer from 4000 to 400 cm^{-1} . Electronic spectra were recorded using a TU-1800 PC UV-Vis spectrophotometer.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[CuL(2-fca)(CH_3OH)]ClO_4 \cdot CH_3OH$ (1). A methanol (15 mL) solution of L (0.062 g, 0.2 mmol) was added to a methanol (20 mL) solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.2 mmol) and a clear light blue solution was formed. A methanol (25 mL) solution of sodium 2-furoate (0.027 g, 0.2 mmol) was added to the resulting solution slowly. The mixture was stirred for 4 h and then filtered. Blue crystals were obtained by slow evaporation of the filtrate after 2 weeks. Yield: 0.044 g (34%). FT-IR (KBr pellet, cm^{-1}): 3417s/br, 3069s, 2974s, 1584m, 1557m, 1472s, 1395m, 1115s, 1090s, 749m. Elemental analysis shows that one water molecule was absorbed during storage in air. Anal. Calcd for $C_{26}H_{26}CuN_5O_{10}Cl$ (%): C, 46.78; H, 3.92; N, 10.49. Found (%): C, 46.88; H, 3.44; N, 10.95.

2.2.2. Synthesis of $[CuL(m-nba)(CH_3OH)]ClO_4$ (2). To a methanol (15 mL) solution containing $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.2 mmol) was added a methanol (10 mL) solution of L (0.062 g, 0.2 mmol) to give a clear light blue solution. A methanol

(25 mL) solution of *m*-nitrobenzoic acid (0.034 g, 0.2 mmol) and triethylamine (0.021 g, 0.2 mmol) was added to the resulting solution slowly. The mixture was stirred for 4 h and then filtered. Blue crystals were obtained by slow evaporation of the filtrate after about 12 days. Yield: 0.053 g (40%). FT-IR (KBr pellet, cm^{-1}): 3452s/br, 3075s, 1606s, 1574m, 1471m, 1380m, 1351s, 1121s, 1086s, 745m. Anal. Calcd for $\text{C}_{27}\text{H}_{21}\text{CuN}_6\text{O}_9\text{Cl}$ (%): C, 48.25; H, 3.14; N, 12.50. Found (%): C, 48.18; H, 3.18; N, 12.54.

2.2.3. Synthesis of $[\text{CuL}(\text{pic})(\text{ClO}_4)] \cdot \text{CH}_3\text{OH}$ (3). Complex **3** was synthesized using the same method as for **2**, with substitution of picolinic acid (0.025 g, 0.2 mmol) for *m*-nitrobenzoic acid. Blue block-shaped crystals were obtained in a yield of 0.021 g (32%). FT-IR (KBr pellet, cm^{-1}): 3441s/br, 1632s, 1597s, 1470m, 1384m, 1371m, 1121s, 1092s, 746m. Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{CuN}_6\text{O}_8\text{Cl}$ (%): C, 48.33; H, 3.58; N, 12.99. Found (%): C, 48.36; H, 3.24; N, 13.50.

2.3. X-ray crystallography

The crystals of **1**, **2**, and **3** were mounted on the Rigaku Saturn 724+ diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) for data collection at 93(2) K. Empirical absorption correction was applied to the collected reflections [32]. First, the structures were solved by direct methods, and then by Fourier difference techniques and refined using full-matrix least-squares methods *via* SHELXL-97 [33, 34]. The non-hydrogen atoms were subjected to anisotropic refinement and hydrogens were located geometrically. The lattice water in **3** was disordered and modeled to locate at three positions with the occupancy of 0.453(8) for O(8), 0.316(6) for O(8'), 0.232(7) for O(8''). The perchlorate in **3** was also disordered with occupancy to be 0.729(6) for Cl(1), O(3), O(4), O(5), O(6) and 0.271(6) for Cl(1'), O(3'), O(4'), O(5'), O(6'). Crystal parameters and details of the data collection and refinement for the three complexes are listed in table 1, and selected bond lengths and angles are summarized in table 2. Bond parameters of hydrogen bonds of the three complexes are summarized in table 3.

3. Results and discussion

3.1. Description of the structures

3.1.1. $[\text{CuL}(2\text{-fca})(\text{CH}_3\text{OH})]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (1). Complex **1** consists of one $[\text{CuL}(2\text{-fca})(\text{CH}_3\text{OH})]^+$, one perchlorate, and one methanol. The perspective drawing of the cation structure is shown in figure 1. The Cu(II) ion is five-coordinate with N_3O_2 coordination sphere in a distorted square-pyramidal environment with the value of Addison τ parameter being 0.10 [$\tau = 0$ (square pyramid) and 1 (trigonal bipyramid)] [35]. The basal plane is defined by N(1), N(2), and N(4) of L and carboxylate O(2) of 2-furoate with bond distances of $\text{Cu}(1)\text{-N}(1) = 1.9778(17) \text{ \AA}$, $\text{Cu}(1)\text{-N}(2) = 2.0038(18) \text{ \AA}$, $\text{Cu}(1)\text{-N}(4) = 2.0293(18) \text{ \AA}$, and $\text{Cu}(1)\text{-O}(2) = 1.9378(14) \text{ \AA}$. The bond length between Cu(II) and pyridine nitrogen is slightly smaller than those observed for the benzimidazole nitrogens. This is also observed in other copper complexes of L, *i.e.*,

Table 1. Crystallographic data and structure refinement for 1–3.

	1	2	3
Empirical formula	C ₂₆ H ₂₄ ClCuN ₅ O ₉	C ₂₇ H ₂₁ ClCuN ₆ O ₉	C ₂₆ H ₂₃ ClCuN ₆ O ₈
Formula weight	649.49	672.49	646.49
Temperature (K)	93(2)	93(2)	93(2)
Crystal size (mm ³)	0.30 × 0.30 × 0.20	0.43 × 0.37 × 0.30	0.33 × 0.17 × 0.09
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions (Å, °)			
<i>a</i>	8.0494(17)	24.0902(11)	24.850(8)
<i>b</i>	12.020(2)	16.5329(5)	15.692(4)
<i>c</i>	15.168(3)	14.1640(9)	13.959(5)
α	68.797(6)	90	90
β	85.650(9)	105.202(2)	92.283(5)
γ	75.721(7)	90	90
Volume (Å ³), <i>Z</i>	1325.9(5), 2	5443.8(5), 8	5439(3), 8
Calculated density (g cm ⁻³)	1.627	1.641	1.579
Absorption coefficient, μ (mm ⁻¹)	0.990	0.969	0.963
<i>F</i> (000)	666	2744	2648
θ range for data collection (°)	3.00–27.49	3.13–27.48	3.19–27.47
Limiting indices	–9 ≤ <i>h</i> ≤ 10; –15 ≤ <i>k</i> ≤ 15; –19 ≤ <i>l</i> ≤ 19	–31 ≤ <i>h</i> ≤ 30; –21 ≤ <i>k</i> ≤ 21; –14 ≤ <i>l</i> ≤ 18	–32 ≤ <i>h</i> ≤ 32; –20 ≤ <i>k</i> ≤ 19; –18 ≤ <i>l</i> ≤ 15
Reflections collected	13,267	20,826	21,335
Independent reflection	6027 [<i>R</i> (int) = 0.0289]	6135 [<i>R</i> (int) = 0.0271]	6204 [<i>R</i> (int) = 0.0296]
Max. and min. transmission	0.8266/0.7555	0.7598/0.6791	0.9158/0.7398
Data/restraints/parameters	6027/0/386	6135/0/403	6204/13/448
Goodness-of-fit on <i>F</i> ²	1.001	0.999	1.002
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.0860	<i>R</i> ₁ = 0.0380, <i>wR</i> ₂ = 0.1180	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.0966
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0488, <i>wR</i> ₂ = 0.0914	<i>R</i> ₁ = 0.0414, <i>wR</i> ₂ = 0.1220	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.1025
Largest difference peak and hole (e Å ⁻³)	0.545 and –0.324	0.416 and –0.606	0.648 and –0.339

1.980(2) Å [27], 1.966(2) Å [28]. The bond angles in the equatorial sites range from 79.19(7)° to 102.99(7)°. The apical site is occupied by O(4) of methanol with Cu(1)–O(4) distance of 2.2331(18) Å. Cu(1) deviates from the mean plane by 0.171 Å in the direction of the axial O(4).

Two molecules of **1** are interlinked by intermolecular H-bonds through the NH of L and the uncoordinated carboxylate of 2-furoate [N(5)–H(5)⋯O(3), 2.727(2) Å] to form a dinuclear cation unit (figure 2), which are also stabilized by π – π stacking interactions from pyridine and benzene of adjacent molecules with the shortest distance of 3.519 Å (center-to-center) with a dihedral angle of 7.09° (Cg1 = C14–C15–C16–C17–C18–C19, Cg2 = C8–C9–C10–C11–C12–N1). The dinuclear units are further connected through hydrogen bonding from NH of L, lattice methanol, the two oxygens of perchlorate and coordinated methanol [N(3)–H(3)⋯O(9), 2.769(3) Å; O(9)–H(9O)⋯O(7), 2.973(2) Å; O(4)–H(4O)⋯O(8), 2.792(3) Å] to form a 1-D chain structure (figure 3).

3.1.2. [CuL(m-nba)(CH₃OH)]ClO₄ (2). Complex **2** consists of one [CuL(m-nba)(CH₃OH)]⁺ and one perchlorate. The perspective drawing of the cation structure is shown in figure 4. The Cu(II) center is five-coordinate with three nitrogens of L,

Table 2. Selected bond lengths (Å) and angles (°) for 1–3.

Complex 1			
Cu(1)–O(2)	1.9378(14)	Cu(1)–N(4)	2.0293(18)
Cu(1)–N(1)	1.9778(17)	Cu(1)–O(4)	2.2331(18)
Cu(1)–N(2)	2.0038(18)	N(2)–Cu(1)–N(4)	158.78(7)
O(2)–Cu(1)–N(1)	164.82(7)	O(2)–Cu(1)–O(4)	94.97(7)
O(2)–Cu(1)–N(2)	96.83(7)	N(4)–Cu(1)–O(4)	93.59(7)
N(1)–Cu(1)–N(2)	79.70(7)	N(2)–Cu(1)–O(4)	92.14(7)
N(1)–Cu(1)–N(4)	79.19(7)	N(1)–Cu(1)–O(4)	99.90(7)
O(2)–Cu(1)–N(4)	102.99(7)	–	–
Complex 2			
Cu(1)–O(1)	1.9332(14)	Cu(1)–N(4)	2.0273(16)
Cu(1)–N(1)	1.9831(16)	Cu(1)–O(5)	2.2489(16)
Cu(1)–N(2)	2.0195(16)	N(2)–Cu(1)–N(4)	158.39(7)
O(1)–Cu(1)–N(1)	166.94(6)	O(1)–Cu(1)–O(5)	90.75(6)
O(1)–Cu(1)–N(2)	101.00(6)	N(1)–Cu(1)–O(5)	102.32(6)
N(1)–Cu(1)–N(2)	78.94(7)	N(2)–Cu(1)–O(5)	90.65(7)
O(1)–Cu(1)–N(4)	99.46(6)	N(4)–Cu(1)–O(5)	96.00(7)
N(1)–Cu(1)–N(4)	79.56(7)	–	–
Complex 3			
Cu(1)–N(1)	1.9709(19)	Cu(1)–N(2)	2.0468(19)
Cu(1)–N(6)	1.988(2)	Cu(1)–O(1)	2.2825(18)
Cu(1)–N(4)	2.043(2)	Cu(1)–O(3')	2.41(2)
N(1)–Cu(1)–N(6)	174.92(8)	N(4)–Cu(1)–O(1)	95.19(7)
N(1)–Cu(1)–N(4)	80.19(8)	N(2)–Cu(1)–O(1)	93.71(7)
N(6)–Cu(1)–N(4)	97.67(8)	N(1)–Cu(1)–O(3')	84.9(3)
N(6)–Cu(1)–O(1)	77.84(7)	O(1)–Cu(1)–O(3')	177.3(3)
N(6)–Cu(1)–N(2)	103.18(8)	N(4)–Cu(1)–O(3')	84.9(4)
N(4)–Cu(1)–N(2)	158.64(8)	N(2)–Cu(1)–O(3')	87.1(3)
N(1)–Cu(1)–O(1)	97.71(7)	N(6)–Cu(1)–O(3')	99.5(3)
N(1)–Cu(1)–N(2)	79.40(8)	–	–

Table 3. Hydrogen bond parameters for 1–3.

D–H...A	<i>d</i> (H...A) (Å)	∠(DHA) (°)	<i>d</i> (D...A) (Å)	Symmetry codes
Complex 1				
N(3)–H(3)...O(9)	1.91	164	2.769(3)	<i>x</i> , –1 + <i>y</i> , <i>z</i>
O(4)–H(4O)...O(8)	2.04(4)	163(3)	2.792(3)	1 + <i>x</i> , –1 + <i>y</i> , <i>z</i>
N(5)–H(5)...O(3)	1.88	160	2.727(2)	1 – <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>
O(9)–H(9O)...O(7)	2.26	143	2.973(2)	–
Complex 2				
N(3)–H(3)...O(2)	1.91	158	2.7479	1/2 – <i>x</i> , 1/2 – <i>y</i> , – <i>z</i>
N(5)–H(5)...O(9)	2.11	142	2.8535	1/2 – <i>x</i> , –1/2 + <i>y</i> , 1/2 – <i>z</i>
O(5)–H(5O)...O(8)	2.15	172	2.8934	–
Complex 3				
N(3)–H(3N)...O(1)	1.96	146	2.7335	1/2 – <i>x</i> , 1/2 – <i>y</i> , 1 – <i>z</i>
N(5)–H(5N)...O(7)	1.84	169	2.7047	<i>x</i> , 1 – <i>y</i> , 1/2 + <i>z</i>
O(7)–H(7O)...O(2)	1.81	175	2.6468	–

one carboxylate oxygen of *m*-nitrobenzoate and methanol. The coordination geometry of Cu(II) can be described as distorted square pyramidal with Addison τ parameter of 0.14. The basal plane is formed by N(1), N(2), and N(4) of L and one oxygen of *m*-nitrobenzoate with Cu(1) being 0.152 Å out-of-plane toward O(5) of methanol. The bond distances are 1.9831(16) Å for Cu(1)–N(1), 2.0195(16) Å for Cu(1)–N(2),

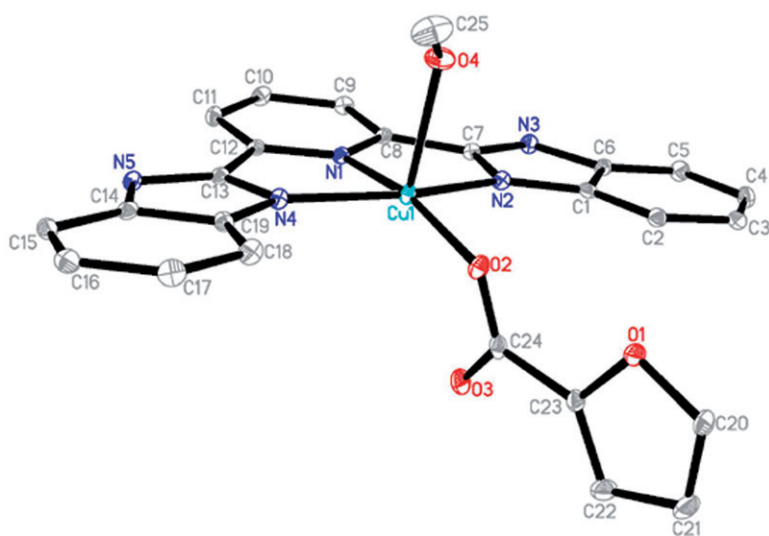


Figure 1. Cation structure of **1** showing 30% probability thermal ellipsoids.

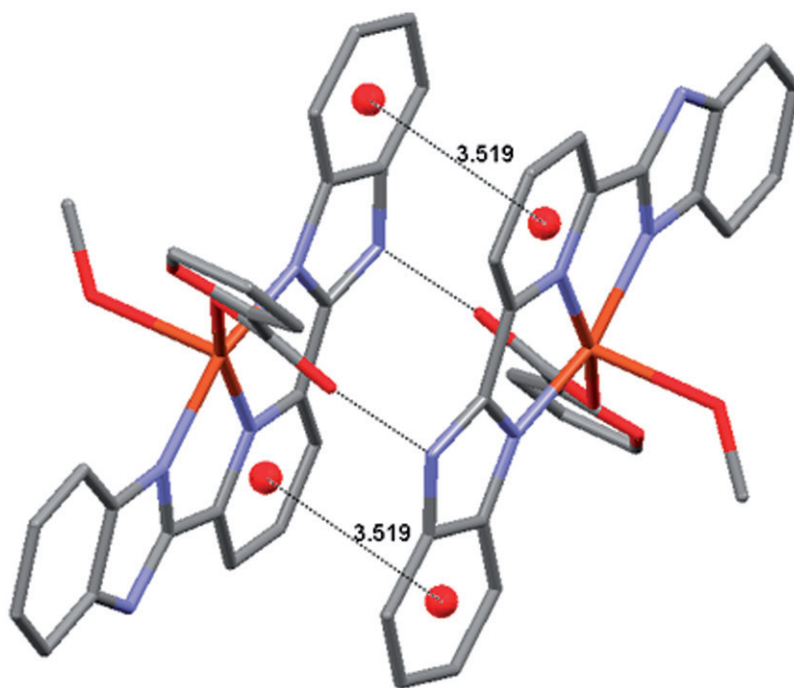


Figure 2. Dinuclear cation unit *via* H-bonds and π - π stacking interactions in **1**.

2.0273(16) Å for Cu(1)–N(4), and 1.9332(14) Å for Cu(1)–O(1). The angles of the basal plane are 101.00(6)° for O(1)–Cu(1)–N(2), 78.94(7)° for N(1)–Cu(1)–N(2), 99.46(6)° for O(1)–Cu(1)–N(4), and 79.56(7)° for N(1)–Cu(1)–N(4). The axial position is occupied by O(5) of methanol with bond length 2.2489(16) Å for Cu(1)–O(5).

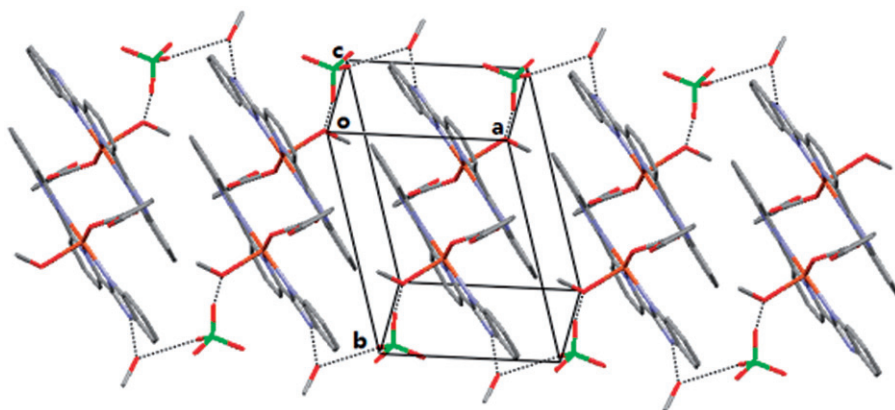


Figure 3. The 1-D chain through hydrogen-bonding interactions in **1**.

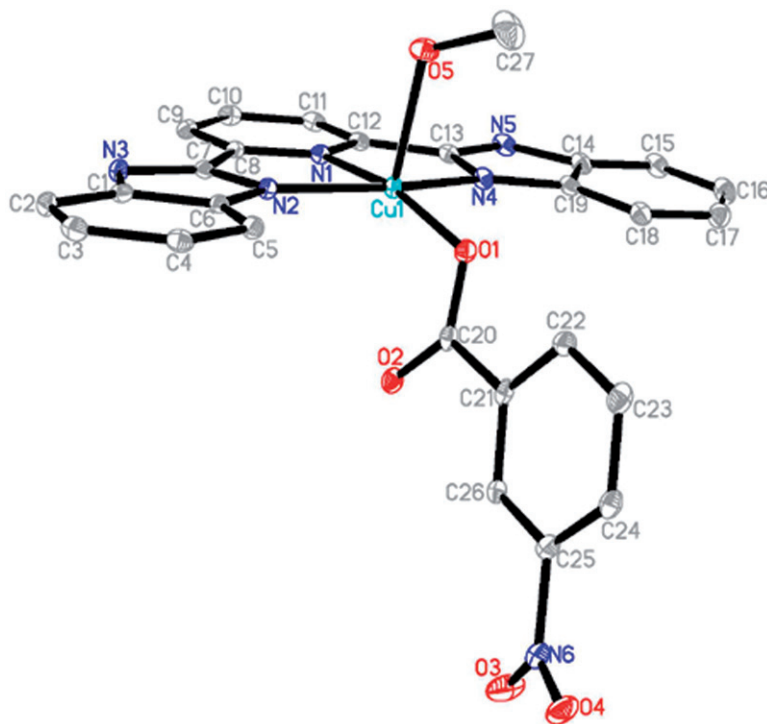


Figure 4. Cation structure of **2** showing 30% probability thermal ellipsoids.

Similar to **1**, two adjacent molecules of **2** are interlinked by two intermolecular H-bonds through NH of L and uncoordinated carboxylate of *m*-nitrobenzoate [N(3)–H(3)···O(2), 2.7479 Å] to form a dinuclear cation unit, further stabilized by π – π stacking interactions from pyridine ring and benzene ring of adjacent molecules with the shortest distance of 3.521 Å (center-to-center) with a dihedral angle of 1.84°

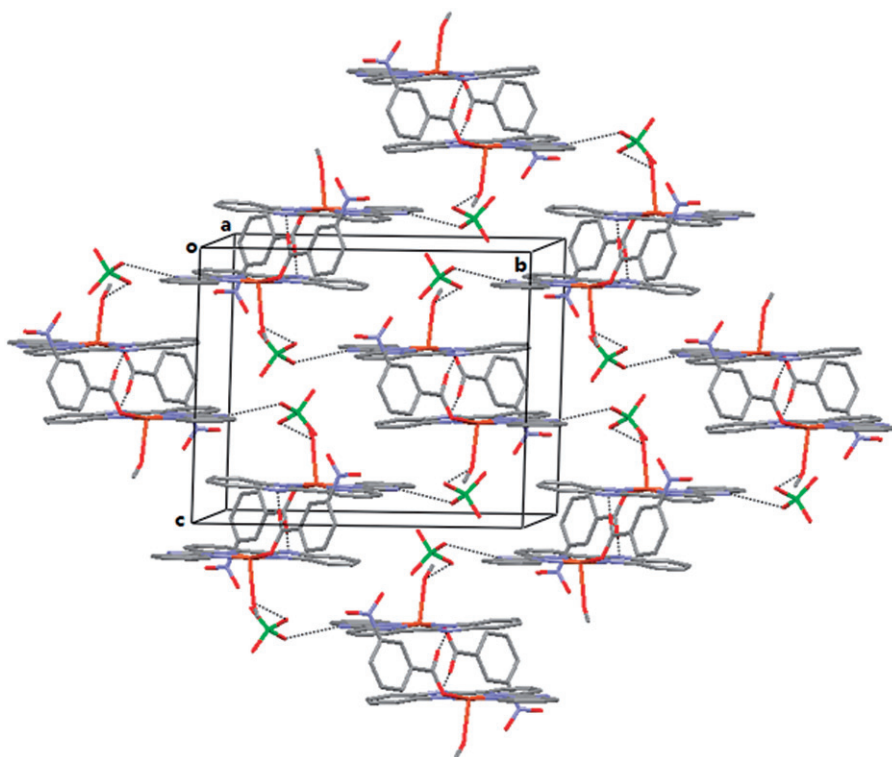


Figure 5. The 2-D structure formed through hydrogen-bonding interactions in **2**.

(Cg1 = C1–C2–C3–C4–C5–C6, Cg2 = C8–C9–C10–C11–C12–N1). Dinuclear units are further connected through hydrogen bonding of perchlorate to form a 2-D network (figure 5). Two H-bonds are formed for each perchlorate, one between the perchlorate O(8) and the coordinated methanol [O(5)–H(5O)···O(8), 2.8934 Å] and the other between the NH of L and the perchlorate O(9) [N(5)–H(5)···O(9), 2.8535 Å].

3.1.3. [CuL(pic)(ClO₄)] · CH₃OH (3**).** The structure of **3** consists of a [CuL(pic)(ClO₄)] unit in which the copper has a distorted octahedral coordination geometry. A perspective drawing of **3** is shown in figure 6. The octahedron around Cu(II) is achieved by three nitrogens of L, one perchlorate oxygen O(3'), one pyridine N(6), and one carboxylate O(1) of picolinate in bidentate μ_2 -N,O chelating mode. The equatorial plane of Cu(II) is formed by N(6) of picolinate and three nitrogens N(1), N(2), and N(4) of L. The bond lengths in the equatorial plane are 1.9709(19) Å for Cu(1)–N(1), 2.0468(19) Å for Cu(1)–N(2), 2.043(2) Å for Cu(1)–N(4), and 1.988(2) Å for Cu(1)–N(6). The equatorial bond angles are from 79.40(8)° to 103.18(8)°. Apical sites are occupied by carboxylate O(1) of picolinate and O(3') from disordered perchlorate with O(1)–Cu(1)–O(3') bond angle of 177.3(3)°. The bond distance of Cu(1)–O(3') is 2.41(2) Å, longer than Cu(1)–O(1) of 2.2825(18) Å. The long bond lengths are caused by the Jahn–Teller effect.

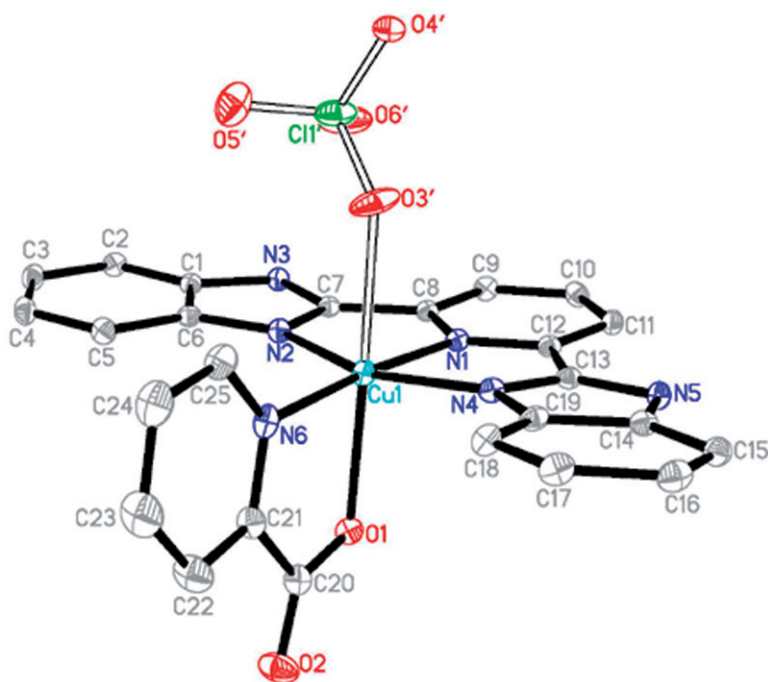


Figure 6. Structure of **3** showing 30% probability thermal ellipsoids.

Two molecules of **3** are interlinked by intermolecular H-bonds through NH of L and the coordinated carboxylate of picolinate [N(3)–H(3N)···O(1), 2.7335 Å] to form a dinuclear unit, which are also stabilized by π – π stacking interactions from the pyridine and benzene of adjacent molecules with the shortest distance of 3.647 Å (center-to-center) and a dihedral angle of 4.13° (Cg1 = C1–C2–C3–C4–C5–C6, Cg2 = C8–C9–C10–C11–C12–N1). The dinuclear units are further connected through hydrogen bonding of methanol to form a 2-D network (figure 7). The methanol is involved in two hydrogen bonds, both as a donor [O(7)–H(7O)···O(2), 2.6468 Å] and as an acceptor [N(5)–H(5N)···O(7), 2.7047 Å].

3.2. Characterizations of the complexes

3.2.1. IR spectra. All three complexes exhibit a broad band at 3000–3500 cm^{-1} , which may be ascribed to hydrogen bonded $\nu(\text{O–H})$ and $\nu(\text{N–H})$, and may also include $\nu(\text{C–H})$ [17, 27]. The $\nu_{\text{as}}(\text{COO}^-)$ is assigned to strong bands at 1584 (**1**), 1606 (**2**), and 1632 cm^{-1} (**3**), whereas the $\nu_{\text{s}}(\text{COO}^-)$ is attributed to the 1395 (**1**), 1380 (**2**), and 1384 cm^{-1} (**3**) peaks, suggesting the presence of coordinated 2-furonate, *m*-nitrobenzionate, and picolinate, respectively [10]. The fairly strong broad absorptions at 1115 (**1**), 1121 (**2**), and 1121 cm^{-1} (**3**) indicate that ionic perchlorate is present [17, 36].

3.2.2. UV-Vis spectra. The electronic spectra of **1–3** in DMF from 300 to 1100 nm all display one broad absorption. The absorption maxima are at 676 nm for **1**, 676 nm for **2**,

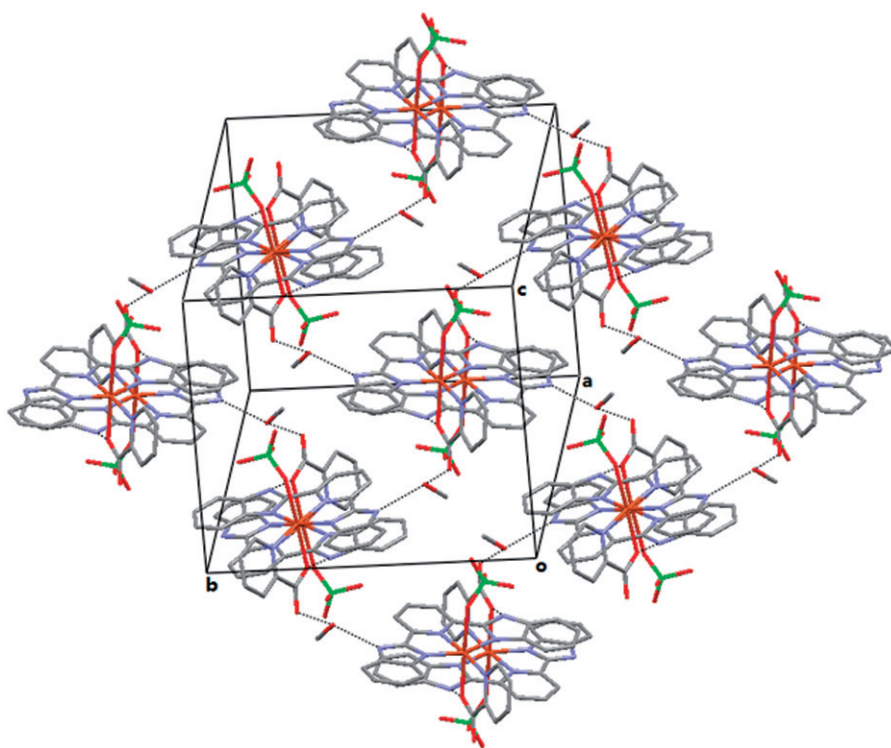


Figure 7. The 2-D structure formed through hydrogen-bonding interactions in **3**.

and 677 nm for **3**. For **3**, similar spectral behavior to **1** and **2** was observed, probably from dissociation of the weakly coordinated perchlorate ($\text{Cu}1\text{O}3'$, (perchlorate) = $2.41(2)$ Å) from **3** in polar DMF. The solution spectra of the three complexes can be adequately explained by d–d transitions in Cu(II) in a distorted square-pyramidal geometry with C_{4v} symmetry [37–39].

4. Conclusion

Three new mononuclear copper(II) complexes of 2,6-bis(benzimidazol-2-yl)pyridine have been synthesized and characterized. All are mononuclear with the carboxylates coordinated monodentate to copper(II) in **1** and **2** and bidentate O,N-chelating in **3**. In the three complexes, a dinuclear structural unit is formed by intermolecular hydrogen bonds through the NH of L and carboxylate of the corresponding aromatic carboxylate. The dinuclear units are further connected by H-bonds *via* perchlorate or lattice methanol to form a 1-D chain for **1** and 2-D network structures for **2** and **3**.

Supplementary material

CCDC 780708, 780709, and 780710 contain the supplementary crystallographic data for **1**, **2**, and **3** in CIF format. These data can be obtained free of charge

via <http://www.ccdc.cam.ac.uk> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This study was supported by Beijing Natural Science Foundation (Grant No. 2092010), Beijing Municipal Education Commission research program (KM200810028009) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government.

References

- [1] J. Dai, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, M. Munakata. *Inorg. Chem.*, **36**, 2688 (1997).
- [2] X.-J. Zheng, L.-P. Jin. *J. Mol. Struct.*, **655**, 7 (2003).
- [3] J.M. Casas, B.E. Diosdado, L.R. Falvello, J. Forniés, A. Martín, A.J. Rueda. *Dalton Trans.*, 2733 (2004).
- [4] G. Marinescu, M. Andruh, M. Julve, F. Lloret, R. Llusar, S. Uriel, J. Vaissermann. *Cryst. Growth Des.*, **5**, 261 (2005).
- [5] C.-L. Ma, J.-F. Sun. *Polyhedron*, **23**, 1547 (2004).
- [6] K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume, Y. Ohashi. *J. Am. Chem. Soc.*, **118**, 1803 (1996).
- [7] K. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda, Y. Aoyama. *J. Am. Chem. Soc.*, **119**, 4117 (1997).
- [8] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994).
- [9] T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi. *Inorg. Chem.*, **36**, 576 (1997).
- [10] F.-M. Nie, F. Lu, J. Chen, Y.-L. Yang. *Inorg. Chim. Acta*, **362**, 4198 (2009).
- [11] A.W. Addison, H.M.J. Hendriks, J. Reedijk, L.K. Thompson. *Inorg. Chem.*, **20**, 103 (1981).
- [12] Z.-Z. Yan, Z.-H. Xu, G.-L. Dai, H.-D. Liang, S.-L. Zhao. *J. Coord. Chem.*, **63**, 1097 (2010).
- [13] N.M. Aghatabay, A. Neshat, T. Karabiyik, M. Somer, D. Hacıu, B. Dülger. *Eur. J. Med. Chem.*, **42**, 205 (2007).
- [14] S. Wang, Y. Zhu, Y. Cui, L. Wang, Q. Luo. *J. Chem. Soc., Dalton Trans.*, 2523 (1994).
- [15] S.-X. Wang, Y.-X. Cui, R.-X. Tan, Q.-H. Luo, J.-Q. Shi, Q.-J. Wu. *Polyhedron*, **13**, 1661 (1994).
- [16] S.-G. Liu, J.-L. Zuo, Y.-Z. Li, X.-Z. You. *J. Mol. Struct.*, **705**, 153 (2004).
- [17] S.-X. Wang, Y. Zhu, F.-J. Zhang, Q.-Y. Wang, L.-F. Wang. *Polyhedron*, **11**, 1909 (1992).
- [18] R. Rajan, R. Rajaram, B.U. Nair, T. Ramasami, S.K. Mandal. *J. Chem. Soc., Dalton Trans.*, 2019 (1996).
- [19] S.-X. Wang, S.-Y. Yu, Q.-H. Luo, Q.-Y. Wang, J.-Q. Shi, Q.-J. Wu. *Transition Met. Chem.*, **19**, 205 (1994).
- [20] S.-M. Yue, H.-B. Xu, J.-F. Ma, Z.-M. Su, Y.-H. Kan, H.-J. Zhang. *Polyhedron*, **25**, 635 (2006).
- [21] T.-R. Chen. *Acta Cryst.*, **E60**, m1544 (2004).
- [22] S.-G. Liu, J.-L. Zuo, Y. Wang, Y.-Z. Li, X.-Z. You. *J. Phys. Chem. Solids*, **66**, 735 (2005).
- [23] R. Boča, P. Baran, L. Dlhán, H. Fuess, W. Haase, F. Renz, W. Linert, I. Svoboda, R. Werner. *Inorg. Chim. Acta*, **260**, 129 (1997).
- [24] T.A. Gerber, P. Mayer, Z.R. Tshentu. *J. Coord. Chem.*, **58**, 1271 (2005).
- [25] D. Mishra, S. Naskar, S.K. Chattopadhyay, M. Maji, P. Sengupta, R. Dinda, S. Ghosh, T.C.W. Mak. *Transition Met. Chem.*, **30**, 352 (2005).
- [26] F.-Y. Meng, Y.-L. Zhou, H.-H. Zou, M.-H. Zeng, H. Liang. *J. Mol. Struct.*, **920**, 238 (2009).
- [27] J. Garcia-Lozano, J. Server-Carrió, E. Coret, J.V. Folgado, E. Escrivá, R. Ballesteros. *Inorg. Chim. Acta*, **245**, 75 (1996).
- [28] S.B. Sanni, H.J. Behm, P.T. Beurskens, G.A. Van-Albada, J. Reedijk, A.T.H. Lenstra, A.W. Addison, M. Palaniandavar. *J. Chem. Soc., Dalton Trans.*, 1429 (1988).
- [29] S. Dey, S. Sarkar, H. Paul, E. Zangrando, P. Chattopadhyay. *Polyhedron*, **29**, 1583 (2010).
- [30] G. Bernardinelli, G. Hopfgartner, A.F. Williams. *Acta Crystallogr.*, **C46**, 1642 (1990).
- [31] A.W. Addison, P.J. Burke. *J. Heterocycl. Chem.*, **18**, 803 (1981).

- [32] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1997).
- [33] G.M. Sheldrick. *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany (1997).
- [34] G.M. Sheldrick. *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany (1997).
- [35] A.W. Addison, T.N. Rao, J. Reedjik, J. Van Rijn, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
- [36] F.-M. Nie, J. Chen, Z. Li, F. Lu. *J. Coord. Chem.*, **63**, 1711 (2010).
- [37] S.S. Massoud, F.A Mautner. *Inorg. Chim. Acta*, **358**, 3334 (2005).
- [38] S.S. Massoud, F.A Mautner, R. Vicente, H.N. Sweeney. *Inorg. Chim. Acta*, **359**, 1489 (2006).
- [39] F.R.Y. Louka, F.A Mautner, R. Vicente, S.S. Massoud. *Inorg. Chem. Commun.*, **11**, 438 (2008).