

Scientific paper

# Synthesis and Crystal Structure of a 4,4'-bipyridine Linked Dinuclear Copper(II) Complex Derived from 2-[[2-(2-hydroxyethylamino)ethylimino]methyl]-6-methylphenol

Xiu-Zhen Zhang,<sup>1</sup> Yitong Gu,<sup>2</sup> Yuntong Li,<sup>2</sup> Andong Liu,<sup>2</sup> Fuyao Liu,<sup>2</sup> Zhonglu You<sup>2,\*</sup> and Hai-Liang Zhu<sup>1,\*</sup>

<sup>1</sup> School of Life Sciences, Shandong University of Technology, Zibo 255049, P. R. China

<sup>2</sup> Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China

\* Corresponding author: E-mail: hailiang\_zhu@163.com; youzhonglu@126.com

Received: 11-03-2016

## Abstract

A novel 4,4'-bipyridine linked dinuclear copper(II) complex,  $[\text{Cu}_2\text{L}_2(\text{bipy})](\text{NO}_3)_2 \cdot \text{bipy}$  ( $\text{L} = 2\text{-}[[2\text{-}(2\text{-hydroxyethylamino)ethylimino]methyl}]\text{-6-methylphenol}$ ;  $\text{bipy} = 4,4'\text{-bipyridine}$ ), was prepared and characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. The Cu...Cu distance is 11.129(2) Å. The Cu<sup>II</sup> atom is coordinated by one phenolate O, one imine N, and one amine N atoms of a Schiff base ligand, and one N atom of the bridging 4,4'-bipyridine ligand, forming a square planar geometry. In the crystal structure of the complex, the dinuclear copper complex cations are linked by 4,4'-bipyridine molecules through intermolecular O-H...N hydrogen bonds, to form 1D chains running in the [2 0 -1] direction.

**Keywords:** Schiff base, Dinuclear structure, Copper complex, Crystal structure

## 1. Introduction

Molecular architectures, prepared by self-assembly of discrete coordination compounds, are attractive direction of modern inorganic and physico-inorganic chemistry, because cooperative behavior of linked units may lead to new properties.<sup>1</sup> Transition metal complexes with Schiff base ligands have received considerable attention for their versatile structures and wide applications in coordination chemistry and biological areas.<sup>2–7</sup> Among the complexes, those with polynuclear structures have been widely studied for their interesting magnetic properties.<sup>8,9</sup> The building block method, because of its directive function of the target structures as well as the expected physical properties, has become one of the most important synthetic strategies for the preparation of polynuclear complexes. The prime method for designing polynuclear complexes is to use suitable bridging ligands, such as carboxylate anions, pseudohalide anions, etc.<sup>10–12</sup> 4,4'-Bipyridine and its analogs have proved especially useful as

bridging ligands, resulting in a large number of polynuclear structures. However, to our knowledge, only 13 Schiff base copper complexes bearing 4,4'-bipyridine bridges have been reported so far.<sup>13–18</sup> As a continuation of such work, we report here a new 4,4'-bipyridine bridged dinuclear copper(II) complex,  $[\text{Cu}_2\text{L}_2(\text{bipy})](\text{NO}_3)_2 \cdot \text{bipy}$  ( $\text{L} = 2\text{-}[[2\text{-}(2\text{-hydroxyethylamino)ethylimino]methyl}]\text{-6-methylphenol}$ ;  $\text{bipy} = 4,4'\text{-bipyridine}$ ).

## 2. Experimental

### 2.1. Materials and Measurements

Commercially available 3-methylsalicylaldehyde, 2-(2-aminoethylamino)ethanol, and 4,4'-dipyridyl were purchased from Aldrich. Other solvents and reagents were made in China. All of the chemicals were used as received. C, H and N elemental analyses were performed with a Perkin-Elmer 240 elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as

KBr pellets in the 4000–400  $\text{cm}^{-1}$  region. Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analyses system.

## 2. 2. Synthesis of the Complex

3-Methylsalicylaldehyde (0.10 mmol, 13.6 mg) and hydroxyethylethylenediamine (0.10 mmol, 10.4 mg) were dissolved in methanol (10 mL). The mixture was stirred at room temperature for 10 min to give a yellow solution. To this solution was added with stirring a methanolic solution (10 mL) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.10 mmol, 24.2 mg) and 4,4'-bipyridine (0.10 mmol, 15.6 mg). The mixture was stirred for another 10 min at room temperature. After keeping the filtrate on air for a few days, blue block-shaped crystals suitable for X-ray crystal structure determination, were formed at the bottom of the vessel. The crystals were isolated by filtration, washed three times with methanol and dried in a vacuum desiccator containing anhydrous  $\text{CaCl}_2$ . Yield 38% on the basis of copper salt. Analysis: Found: C 52.7, H 5.1, N 13.7%. Calculated for  $\text{C}_{44}\text{H}_{50}\text{Cu}_2\text{N}_{10}\text{O}_{10}$ : C 52.5, H 5.0, N 13.9%. IR data (KBr,  $\text{cm}^{-1}$ ): 3437m, 3166m, 1637s, 1601m, 1548w, 1440m, 1416m, 1375s, 1322s, 1221w, 1074w, 1026w, 821m, 752w, 627w, 563w, 465w.

## 2. 3. X-ray Crystallography

Diffraction intensities for the complex were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with Mo  $\text{K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The collected data were reduced using SAINT program,<sup>19</sup> and multi-scan absorption corrections were performed using SADABS program.<sup>20</sup> Structure of the complex was solved by direct methods and refined against  $F^2$  by full-matrix least-squares methods using SHELXTL.<sup>21</sup> All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

## 3. Results and Discussion

### 3. 1. General

The complex was prepared by the reaction of equimolar quantities of 3-methylsalicylaldehyde, hydrox-

**Table 1.** Crystallographic data and refinement parameters for the complex

Parameter	Value
Chemical formula	$\text{C}_{44}\text{H}_{50}\text{Cu}_2\text{N}_{10}\text{O}_{10}$
$M_r$	1006.02
Crystal color, habit	Blue, block
Crystal size ( $\text{mm}^3$ )	$0.27 \times 0.23 \times 0.22$
Crystal system	Triclinic
Space group	$P-1$
$a$ ( $\text{\AA}$ )	9.0937(6)
$b$ ( $\text{\AA}$ )	10.9261(7)
$c$ ( $\text{\AA}$ )	12.2102(8)
$\alpha$ ( $^\circ$ )	102.230(2)
$\beta$ ( $^\circ$ )	95.456(2)
$\gamma$ ( $^\circ$ )	102.278(2)
$V$ ( $\text{\AA}^3$ )	1146.0(1)
$Z$	1
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.458
Temperature (K)	298(2)
$\mu$ ( $\text{mm}^{-1}$ )	0.996
$F(000)$	522
Number of unique data	4346
Number of observed data [ $I > 2\sigma(I)$ ]	3838
Number of parameters	299
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0337, 0.0826
$R_1, wR_2$ (all data)	0.0404, 0.0876
Goodness of fit on $F^2$	1.051

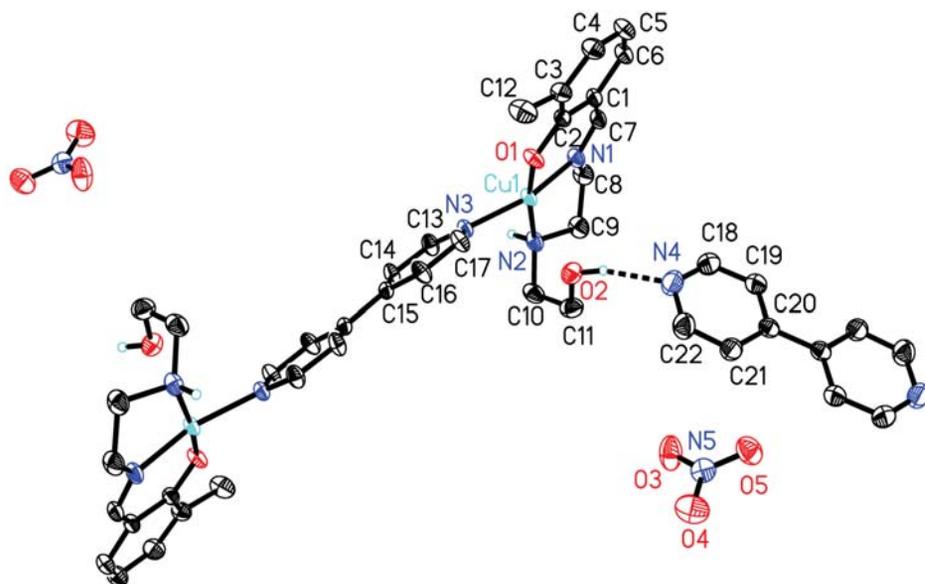
yethylethylenediamine, 4,4'-bipyridine and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in methanol. Crystals of the complex are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile.

### 3. 2. Crystal Structure Description of the Complex

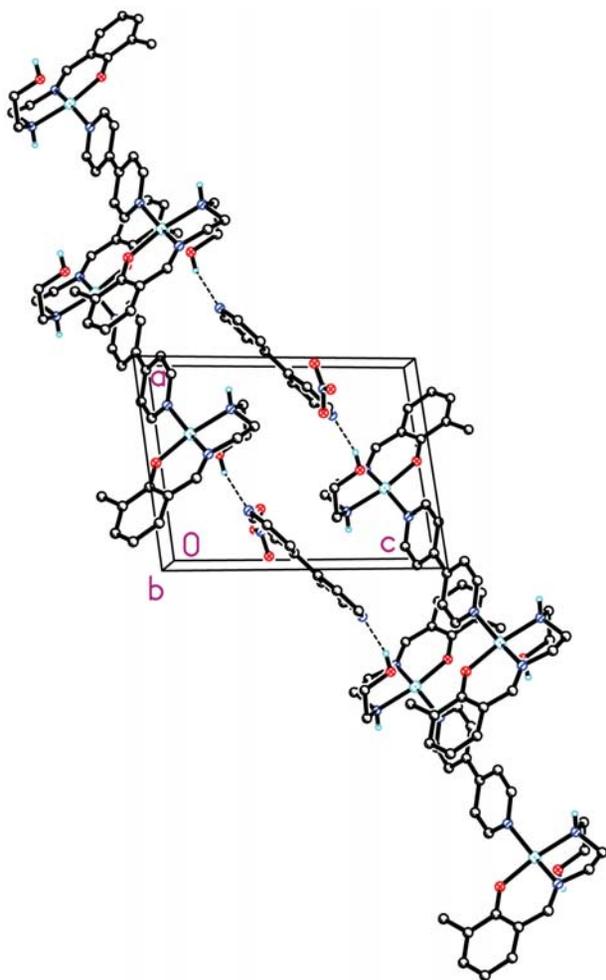
Molecular structure of the complex is shown in Figure 1 together with the atom numbering scheme. X-ray crystallography indicates that the asymmetric unit of the complex contains a 4,4'-bipyridine bridged centrosymmetric dinuclear copper(II) complex cation, a hydrogen bonded 4,4'-bipyridine molecule, and two nitrate anions. The inversion center of the dinuclear complex cation is located at the midpoint of the 4,4'-bipyridine ligand. The Cu...Cu distance is 11.129(2)  $\text{\AA}$ . The  $\text{Cu}^{\text{II}}$  atom is coordinated by one phenolate O, one imine N, and one amine N atoms of a Schiff base ligand, and one N atom of the bridging 4,4'-bipyridine ligand, forming a square planar geometry. The significant distortion of the square planar coordination is mainly revealed by the bond angles. The bond angle

**Table 2.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the complex

Cu(1)–O(1)	1.904(2)	Cu(1)–N(1)	1.934(2)
Cu(1)–N(2)	2.045(2)	Cu(1)–N(3)	2.035(2)
O(1)–Cu(1)–N(1)	93.34(7)	O(1)–Cu(1)–N(3)	89.36(6)
N(1)–Cu(1)–N(3)	164.99(8)	O(1)–Cu(1)–N(2)	170.33(7)
N(1)–Cu(1)–N(2)	84.19(7)	N(3)–Cu(1)–N(2)	95.44(7)



**Figure 1.** The structure of the complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are at the symmetry position  $(2-x, 1-y, -z)$ .



**Figure 2.** The crystal packing of the complex, viewed along the  $b$  axis. Hydrogen bonds are shown as dashed lines.

$\text{N1-Cu1-N2}$  deviates from  $90^\circ$  by  $5.81(7)^\circ$ , which is due to the strain created by the five-membered chelate ring  $\text{Cu1/N1/C8/C9/N2}$ . The  $\text{Cu-O}$  and  $\text{Cu-N}$  bond lengths are comparable to the corresponding values observed in the Schiff base copper(II) complexes cited above. The dihedral angle between the planes defined by the bridging 4,4'-bipyridine ligand and the  $\text{C1-C6}$  benzene ring is  $31.8(3)^\circ$ .

In the crystal structure the dinuclear copper complex cations are linked by 4,4'-bipyridine molecules through intermolecular  $\text{O-H}\cdots\text{N}$  hydrogen bonds [ $\text{O2-H2}\cdots\text{N4}$ :  $\text{O2-H2} = 0.88 \text{ \AA}$ ,  $\text{H2}\cdots\text{N4} = 1.90 \text{ \AA}$ ,  $\text{O2}\cdots\text{N4} = 2.751(3) \text{ \AA}$ ,  $\text{O2-H2}\cdots\text{N4} = 163^\circ$ ;  $\text{N2-H2A}\cdots\text{O5}$ :  $\text{N2-H2A} = 0.89 \text{ \AA}$ ,  $\text{H2A}\cdots\text{O5} = 2.12 \text{ \AA}$ ,  $\text{N2}\cdots\text{O5} = 2.976(3) \text{ \AA}$ ,  $\text{N2-H2A}\cdots\text{O5} = 160^\circ$ ], to form 1D chains running in the  $[2\ 0\ -1]$  direction (Figure 2).

### 3. 3. IR Spectra

The bands in the range of  $2850\text{--}2990 \text{ cm}^{-1}$  are characteristic of aliphatic  $\nu(\text{C-H})$  vibrations for the complex and the bands observed at  $3030\text{--}3090 \text{ cm}^{-1}$  are attributed to the aromatic  $\nu(\text{C-H})$  vibrations.<sup>22</sup> The medium and broad band centered at  $3437 \text{ cm}^{-1}$  is assigned to the  $\nu(\text{O-H})$  vibration, while the medium and sharp band at  $3166 \text{ cm}^{-1}$  is assigned to the  $\nu(\text{N-H})$  vibration.<sup>23</sup> The strong absorption band at  $1637 \text{ cm}^{-1}$  can be attributed to  $\nu(\text{C=N})$ .<sup>24</sup> The  $\text{C-O}$  (phenolic) stretching band is observed at  $1221 \text{ cm}^{-1}$  in the complex.<sup>25</sup> Nitrate complexes show IR bands in the range  $1410\text{--}1448 (\nu_3)$ ,  $1290\text{--}1322 (\nu_1)$ , and  $1073\text{--}1077 \text{ cm}^{-1} (\nu_2)$  due to  $\text{NO}$  stretches. The value of  $\Delta(\nu_3 - \nu_1)$ , i.e.,  $102\text{--}131 \text{ cm}^{-1}$ , suggests monodentate coordination. For monodentate coordination of  $\text{NO}_3^-$ ,

the separation of first NO stretching vibrations is low ( $100\text{--}130\text{ cm}^{-1}$ ), whereas these bands show larger separation ( $180\text{--}225\text{ cm}^{-1}$ ) when  $\text{NO}_3^-$  is bidentate.<sup>26</sup> IR spectrum of the complex shows a band at  $1375\text{ cm}^{-1}$  due to ionic nitrate.<sup>27</sup>

### 3. 4. Thermal Property

Thermal gravimetric analysis (TG) were conducted from 25 to  $1000\text{ }^\circ\text{C}$  under air atmosphere at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  to examine the stability of the complex (Figure 3). The first step started at  $202\text{ }^\circ\text{C}$  and completed at  $326\text{ }^\circ\text{C}$ , probably corresponding to the loss of the coordinated and uncoordinated bipy ligands and methylbenzylidene moiety of the Schiff base ligands. The observed weight loss of 51.5% is close to the calculated value (52.3%). The second step, from  $326\text{ }^\circ\text{C}$  to  $473\text{ }^\circ\text{C}$ , probable corresponds to the loss of the remaining moieties of the Schiff base ligands and the nitrate anions, and the formation of the final product CuO. The total observed weight loss of 85.0% agrees well with the calculated value (84.1%).

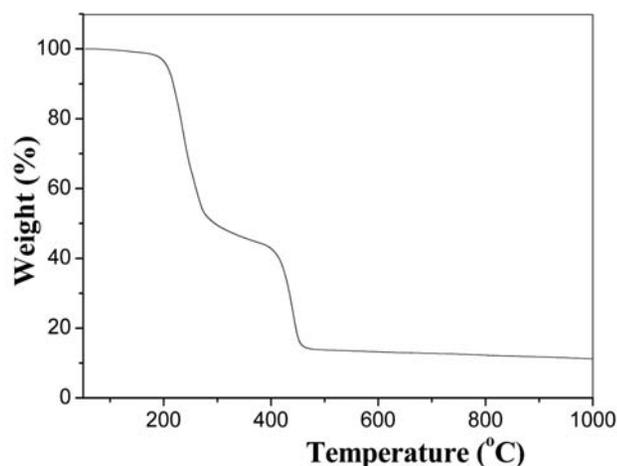


Figure 3. TG curve of the complex.

## 4. Conclusions

A novel dinuclear copper(II) complex has been prepared and characterized by elemental analyses, IR spectroscopy, and single crystal X-ray diffraction. The  $\text{Cu}^{\text{II}}$  atom is coordinated by one phenolate O, one imine N, and one amine N atoms of a Schiff base ligand, and one N atom of the bridging 4,4'-bipyridine ligand, forming a square planar geometry. Crystal structure of the complex are stabilized by intermolecular O–H...N hydrogen bonds. Thermal analysis indicates that the complex is stable up to  $202\text{ }^\circ\text{C}$ .

## 5. Supplementary Information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data

Centre (CCDC-956327). Copy of this information can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## 6. References

- S. V. Kolotilov, O. Cadour, S. Golhen, O. Shvets, V. G. Ilyin, V. V. Pavlishchuk, L. Ouahab, *Inorg. Chim. Acta* **2007**, *360*, 1883–1889. <http://dx.doi.org/10.1016/j.ica.2006.09.025>
- T. Mukherjee, J. C. Pessoa, A. Kumar, A. R. Sarkar, *Dalton Trans.* **2013**, *42*, 2594–2607. <http://dx.doi.org/10.1039/C2DT31575K>
- T. Rosu, E. Pahontu, D. C. Ilies, R. Georgescu, M. Mocanu, M. Leabu, S. Shova, A. Gulea, *Eur. J. Med. Chem.* **2012**, *53*, 380–389. <http://dx.doi.org/10.1016/j.ejmech.2012.03.046>
- R. N. Patel, A. Singh, V. P. Sondhiya, Y. Singh, K. K. Shukla, D. K. Patel, R. Pandey, *J. Coord. Chem.* **2012**, *65*, 795–812. <http://dx.doi.org/10.1080/00958972.2012.662592>
- S.-S. Qian, X. Zhao, J. Wang, Z. You, *Acta Chim. Slov.* **2015**, *62*, 828–833.
- D. Zhang, L. Kong, H. Zhang, *Acta Chim. Slov.* **2015**, *62*, 219–224.
- K.-H. Yang, *Acta Chim. Slov.* **2014**, *61*, 629–636.
- P. Bhowmik, N. Aliaga-Alcalde, V. Gomez, M. Corbella, S. Chattopadhyay, *Polyhedron* **2013**, *49*, 269–276. <http://dx.doi.org/10.1016/j.poly.2012.10.017>
- L. Rigamonti, A. Forni, R. Pievo, J. Reedijk, A. Pasini, *Inorg. Chim. Acta* **2012**, *387*, 373–382. <http://dx.doi.org/10.1016/j.ica.2012.02.030>
- C. Biswas, M. G. B. Drew, E. Ruiz, M. Estrader, C. Diaz, A. Ghosh, *Dalton Trans.* **2010**, *39*, 7474–7484. <http://dx.doi.org/10.1039/c0dt00331j>
- S. Naiya, C. Biswas, M. G. B. Drew, C. J. Gomez-Garcia, J. M. Clemente-Juan, A. Ghosh, *Inorg. Chem.* **2010**, *49*, 6616–6627. <http://dx.doi.org/10.1021/ic1005456>
- P. Talukder, S. Shit, A. Sasmal, S. R. Batten, B. Moubaraki, K. S. Murray, S. Mitra, *Polyhedron*, **2011**, *30*, 1767–1773. <http://dx.doi.org/10.1016/j.poly.2011.03.049>
- Q. Cheng, Z. Pan, H. Zhou, J. Chen, *Inorg. Chem. Commun.* **2011**, *14*, 929–933. <http://dx.doi.org/10.1016/j.inoche.2011.03.034>
- L. Rigamonti, A. Forni, R. Pievo, J. Reedijk, A. Pasini, *Dalton Trans.* **2011**, *40*, 3381–3393. <http://dx.doi.org/10.1039/c0dt01304h>
- R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadiou, S. Shova, *Chem. Eur. J.* **2006**, *12*, 187–203. <http://dx.doi.org/10.1002/chem.200500321>
- R. Karmakar, C. R. Choudhury, S. Mitra, L. Dahlenburg, *Struct. Chem.* **2005**, *16*, 611–616. <http://dx.doi.org/10.1007/s11224-005-7573-4>
- M. Niu, Z. Cao, R. Xue, S. Wang, J. Dou, D. Wang, *J. Mol. Struct.* **2011**, *996*, 101–109. <http://dx.doi.org/10.1016/j.molstruc.2011.04.025>
- D. Visinescu, M. Andruh, A. Muller, M. Schmidtman, Y.

- Journaux, *Inorg. Chem. Commun.* **2002**, 5, 42–45.  
[http://dx.doi.org/10.1016/S1387-7003\(01\)00344-6](http://dx.doi.org/10.1016/S1387-7003(01)00344-6)
19. Bruker, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, **2002**.
20. G. M. Sheldrick, SADABS. Program for Empirical Absorption Correction of Area Detector, University of Göttingen, Germany, **1996**.
21. G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112–122.  
<http://dx.doi.org/10.1107/S0108767307043930>
22. C. Demetgül, M. Karakaplan, S. Serin, M. Diğrak, *J. Coord. Chem.* **2009**, 62, 3544–3551.  
<http://dx.doi.org/10.1080/00958970903082192>
23. A. Ray, G. Pilet, C. J. Gómez-García, S. Mitra, *Polyhedron* **2009**, 28, 511–520.  
<http://dx.doi.org/10.1016/j.poly.2008.11.054>
24. S. Sreedaran, K. S. Bharathi, A. K. Rahiman, R. Prabu, R. Jegadeesh, N. Raaman, V. Narayanan, *J. Coord. Chem.* **2009**, 62, 3073–3084.  
<http://dx.doi.org/10.1080/00958970902870886>
25. M. Sebastian, V. Arun, P. P. Robinson, P. Leeju, D. Varghese, G. Varsha, K. K. M. Yusuff, *J. Coord. Chem.* **2010**, 63, 307–314. <http://dx.doi.org/10.1080/00958970903342117>
26. S. Chandra, A. K. Sharma, *J. Coord. Chem.* **2009**, 62, 3688–3700. <http://dx.doi.org/10.1080/00958970903121305>
27. S. Chandra, A. K. Sharma, *Spectrochim. Acta A* **2009**, 72, 851–857. <http://dx.doi.org/10.1016/j.saa.2008.12.022>

## Povzetek

Sintetiziran je nov dvojedrni bakrov(II) kompleks z mostovnim 4,4'-bipiridinskim ligandom,  $[\text{Cu}_2\text{L}_2(\text{bipy})](\text{NO}_3)_2 \cdot \text{bipy}$  (L = 2-[2-(2-hidroksietilamino)etilimino]metil]-6-metilfenol; bipy = 4,4'-bipiridin), in okarakteriziran z elementno analizo, IR spektroskopijo in monokristalno rentgensko difrakcijo. Razdalja Cu...Cu je 11.129(2) Å. Cu<sup>II</sup> atom je koordiniran z enim fenolatnim O, enim iminskim N in enimaminskim N atomom Schiffove baze in enim N atomom mostovnega 4,4'-bipiridina, ki tvorijo kvadratno-planarno geometrijo. V kristalni strukturi kompleksa je kationski dvojedrni bakrov kompleks povezan z molekulami 4,4'-bipiridina preko intermolekularnih O–H...N vodikovih vezi, ki tvorijo 1D verige v [2 0 –1] smeri.