

## КРАТКИЕ СООБЩЕНИЯ

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## SOLVOTHERMAL SYNTHESSES, CRYSTAL STRUCTURE, AND PHOTOLUMINESCENT PROPERTIES OF TWO Cu(I) COORDINATION POLYMERS CONSTRUCTED BY BISIMIDAZOLE LIGANDS

K.-H. Wang<sup>1</sup>, M.-C. Zhu<sup>2</sup>, D.-L. Wang<sup>1</sup>, J. Bai<sup>1</sup>, Y. Liu<sup>1</sup>, G. Xin<sup>1</sup>,  
T.-C. Li<sup>1</sup>, D.-Y. Hou<sup>1</sup>, E.-J. Gao<sup>2</sup><sup>1</sup>School of Chemistry and Life Science, Anshan Normal University, Anshan, P. R. China

E-mail: khwang16@gmail.com

<sup>2</sup>Laboratory of Coordination Chemistry, Shenyang University of Chemical Technology, Shenyang, P. R. China

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Two Cu(I) coordination polymers  $\{[\text{Cu}_2(\text{bibp})_2] \cdot \text{bdc} \cdot 3\text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Cu}_3(\text{bib})_3] \cdot \text{btc} \cdot 5\text{H}_2\text{O}\}_n$  (**2**), where bibp = 4,4'-bis(1-imidazol-1-yl)biphenyl, H<sub>2</sub>bdc = terephthalic acid, bib = 1,4-bis(1-imidazol-1-yl)benzene, H<sub>3</sub>btc = benzene-1,3,5-tricarboxylic acid, are synthesized under solvothermal conditions and characterized structurally. Complex **1** crystallizes in the triclinic form with the space group *P*-1, and Cu(1) is two-coordinated by two N atoms of bibp, Cu(2) is three coordinated from two N atoms of bibp and one water molecule. Complex **2** crystallizes in the triclinic form with the space group *P*-1; the copper ions are monovalent and two-coordinated by two N atoms of bib. The bdc and btc ligands are not coordinated with Cu ions, but play important roles in the generation of a 3D supramolecular structure of complexes **1** and **2** via weak interactions respectively.

**Keywords:** Cu(I) coordination polymers, crystal structure, bisimidazole ligands.

Supramolecular architectures constructed via coordination bonds or weak interactions have achieved remarkable attention in recent years due to not only their intriguing structure, but also their potential application in gas sorption, ion exchange, magnetism, catalysis, *etc.* [1–4]. Although much progress has been made in the construction of metal-organic frameworks with the desired structure and functions, the rational design of metal-organic frameworks towards targeted products is difficult for chemists because various factors are uncertain in the self-assemble process, excluding reaction conditions such as temperature, pH value, metal-ligand ratio, solvents and templates. The choice of metal ions with various coordination geometry and ligands with different binding preference is generally of primary considerations [5–8]. The divalent copper ion is usually chosen as a center ion because its coordination number could vary from four to six, and it is easily deoxidized to monovalent copper ions under hydro(solvo)thermal synthesis conditions [9–11]. Aromatic polycarboxylic acids are versatile multidentate ligands to construct a variety of interesting structures [12–14]. Recently, the rigid bis(imidazole) ligands such as 1,4-bis(1-imidazol-1-yl)benzene (bib) and 4,4'-bis(1-imidazol-1-yl)biphenyl (bibp) have been reported in the construction of interpenetrating metal-organic architectures [15–17]. On the basis of these considerations, we selected divalent copper ions, terephthalic acid (H<sub>2</sub>bdc), benzene-1,3,5-tricarboxylic acid (H<sub>3</sub>btc), 1,4-bis(1-imidazol-1-yl)benzene (bib), and 4,4'-bis(1-imidazol-1-yl)biphenyl (bibp) as building blocks. Two Cu(I) coordination polymers  $\{[\text{Cu}_2(\text{bibp})_2] \cdot \text{bdc} \cdot 3\text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Cu}_3(\text{bib})_3] \cdot \text{btc} \cdot 5\text{H}_2\text{O}\}_n$  (**2**) have been obtained and characterized by single crystal X-ray diffraction, elemental analyses, and IR spectra. The luminescent properties of two compounds have been studied in a DMF solution at room temperature.

**Experimental.** All chemicals were reagent grade commercial samples and were used without further purification. Elemental analyses (C, H, and N) were performed on a model Finnigan EA 1112 instrument. IR spectra were recorded as KBr pellets on a Nicolet IR-470. The fluorescence spectrum was measured on a Perkin-Elmer LS55 fluorescence spectrofluorometer.

**Synthesis of  $\{[\text{Cu}_2(\text{bibp})_2] \cdot \text{bdc} \cdot 3\text{H}_2\text{O}\}_n$  (**1**).** A mixture of  $\text{Cu}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$  (0.1 mmol, 0.0353 g), terephthalic acid ( $\text{H}_2\text{bdc}$ ) (0.1 mmol, 0.0165 g), 4,4'-bis(1-imidazol-1-yl)biphenyl (bibp) (0.1 mmol, 0.0286 g) was dissolved in 9 ml of  $\text{H}_2\text{O}/\text{DMF}$  (2:1, v:v) and was stirred for 0.5 h at room temperature, then the final mixture was placed in a Teflon-lined stainless steel vessel (20 ml) under autogenous pressure and heated at 120 °C for 72 h. After the mixture was cooled to room temperature, a yellow crystal of **1** was obtained. Anal. Calcd for: C, 57.57; N, 12.21; H, 4.17. Found: C, 57.49; N, 12.31; H, 4.15. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3428 (s), 3126 (s), 2977 (s), 2778 (s), 1579 (s), 1515 (m), 1340 (s), 1309 (s), 1261 (s), 1114 (s), 1085 (s), 962 (s), 819 (s), 754 (s), 628 (s), 520 (s).

**Synthesis of  $\{[\text{Cu}_3(\text{bib})_3] \cdot \text{btc} \cdot 5\text{H}_2\text{O}\}_n$  (**2**).** A mixture of  $\text{Cu}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$  (0.1 mmol, 0.0353 g), benzene-1,3,5-tricarboxylic acid ( $\text{H}_3\text{btc}$ ) (0.1 mmol, 0.0210 g), 1,4-bis(1-imidazol-1-yl)benzene (bib) (0.1 mmol, 0.0210 g) was dissolved in 9 ml of  $\text{H}_2\text{O}/\text{DMF}$  (2:1, v:v) and was stirred for 0.5 h at room temperature, then the final mixture was placed in a Teflon-lined stainless steel vessel (20 mL) under autogenous pressure and heated at 120 °C for 72 h. After the mixture was cooled to room temperature, a yellow crystal of **2** was obtained. Anal. Calcd for: C, 48.32; N, 15.03; H, 3.88. Found: C, 48.29; N, 15.12; H, 3.86. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3432 (s), 3114 (s), 2831 (s), 2487 (s), 1618 (w), 1533 (w), 1359 (m), 1305 (m), 1066 (s), 962 (s), 835 (s), 755 (s), 651 (s).

**X-ray crystallography.** The data were collected on a SMART CCD 1000 X-ray single crystal diffractometer with  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K and 296(2) K for complex **1** and **2** respectively. The structures were solved by direct methods using SHELXL97 [18, 19] and all the non-hydrogen atoms were refined with anisotropic thermal parameters by the full-matrix least-squares calculation on  $F^2$ . Crystal data and structure refinement are summarized in Table 1. Selected bond

Table 1

Crystallographic data and structure refinement parameters for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Chemical formula	$\text{C}_{44}\text{H}_{38}\text{Cu}_2\text{N}_8\text{O}_7$	$\text{C}_{45}\text{H}_{43}\text{Cu}_3\text{N}_{12}\text{O}_{11}$
Formula weight	917.90	1118.53
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	11.124(9), 12.168(10), 14.329(12)	9.369(16), 11.120(19), 11.349(19)
$\alpha$ , $\beta$ , $\gamma$ , deg.	88.560(9), 88.770(10), 82.427(9)	90.08(2), 101.23(2), 106.12(2)
<i>Z</i>	2	1
$d_{\text{calc}}$ , $\text{g}/\text{cm}^{-3}$	1.586	1.670
$\mu$ , $\text{mm}^{-1}$	1.173	1.500
<i>F</i> (000)	944	572
Reflns collected / unique	10902 / 6660	6322 / 5211
<i>R</i> (int)	0.0218	0.0259
$R_1^a$ [ $I > 2\sigma(I)$ ]	0.0407	0.0481
$wR_2^b$	0.1131	0.1380
GOOF	1.017	0.865

$$^a R = \sum ||F_0| - |F_c|| / \sum |F_0|.$$

$$^b R_w = [\sum [w(F_0^2 - F_c^2)^2] / \sum w(F_0^2)^2]^{1/2}.$$

Selected bond lengths (Å) and angles (deg.) for complex **1**<sup>a</sup> and **2**

<b>1</b>					
Cu(1)—N(5)	1.895(3)	Cu(1)—N(8)#1	1.897(3)	N(5)—Cu(1)—N(8)#1	175.44(11)
Cu(2)—N(1)	1.899(3)	Cu(2)—N(9)#2	1.902(3)	N(1)—Cu(2)—N(9)#2	167.36(11)
Cu(2)—O(5)#1	2.507	Cu(1)—O(3)	2.870		
<b>2</b>					
Cu(1)—N(3)	1.869(8)	Cu(1)—N(9)	1.865(8)	N(3)—Cu(1)—N(9)	175.7(4)
Cu(2)—N(1)	1.871(9)	Cu(2)—N(8)	1.873(9)	N(5)—Cu(3)—N(7)	174.9(4)
Cu(3)—N(5)	1.878(9)	Cu(3)—N(7)	1.877(9)	N(1)—Cu(2)—N(8)	175.8(4)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms for **1**: #1  $x+1, y+1, z$ , #2  $x-1, y-1, z$ .

lengths (Å) and bond angles (deg.) are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 897436, for **1**, 905322 for **2**; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

**Results and discussion. Crystal structure of 1.** The result of the X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic form with the space group  $P-1$ . As shown in Fig. 1, the asymmetric unit consists of two Cu atoms, two bibp, one bdc, and three water molecules. Cu(1) is two-coordinated by two N atoms from two different bibp forming a linear coordination geometry. The Cu(1)—N distances are 1.895(3) Å and 1.897(3) Å, which are compared with the reported Cu—N length in Cu(I) coordination compounds [20], and the Cu(1)—O(3) distance is 2.870 Å; such a weak Cu—O interaction is observed in Cu(I) coordination polymers containing polyoxometalate ligands [21, 22]. The Cu(2) atom adopts a T-shaped coordination geometry; it is coordinated with two N atoms of two different bibp and one water molecule. The bond lengths around Cu(2) are 1.899 Å and 1.902 Å for Cu—N and 2.507 Å for Cu—O. The H<sub>2</sub>bdc ligand is fully deprotonated and not coordinated with Cu ions, but plays a major role in forming the 3D supramolecular structure of complex **1**. It acts as a linker to join the chain-like coordination polymer together through C—H···O and O—H···O hydrogen bonds (C18···O3 3.154 Å; C32···O2 3.546 Å; C20···O6 3.243 Å; C19···O1 3.373 Å; O5···O1 2.700 Å, O5···O6 2.943 Å), generating a 2D layered structure (Fig. 2) [23].

**Crystal structure of 2.** Single crystal X-ray analysis reveals that complex **2** is a sandwich-type supramolecular structure. The asymmetric unit of complex **2** consists of three independent Cu atoms,

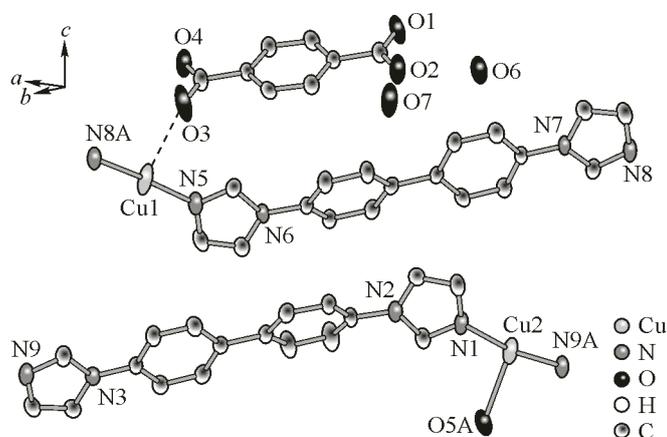


Fig. 1. Coordination environment of Cu(I) in complex **1**

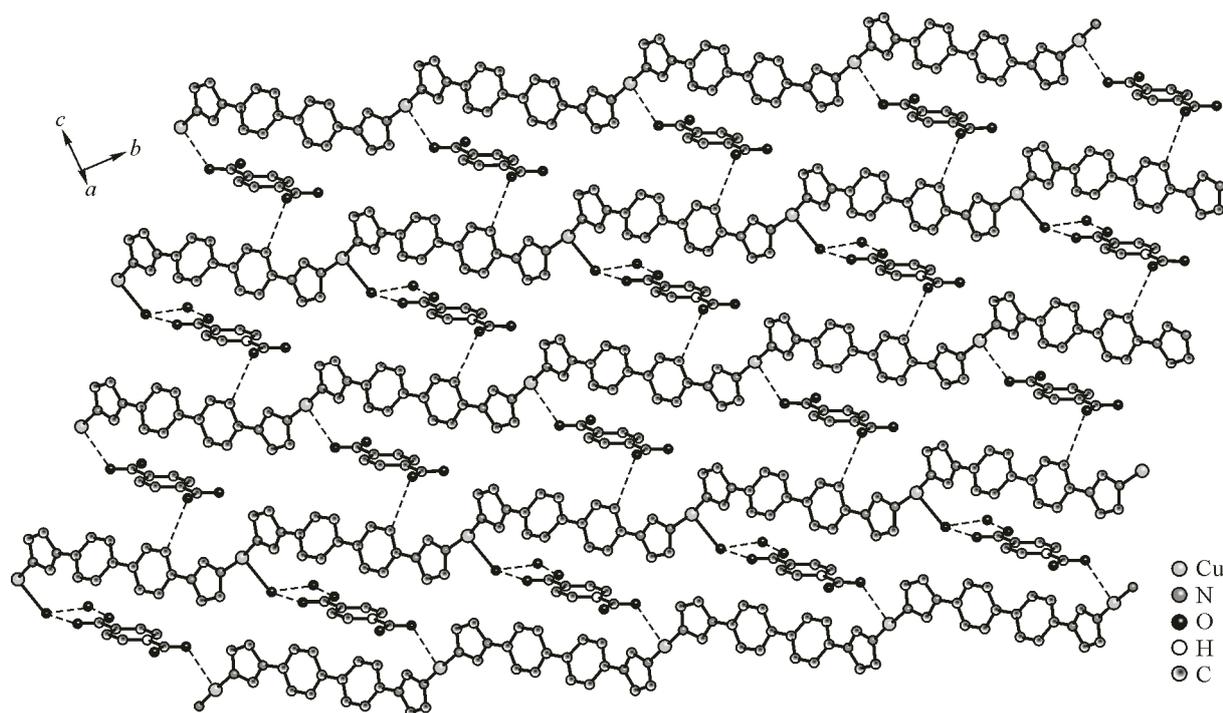


Fig. 2. 2D layer structure of **1** constructed by hydrogen bonds

three halves of bib, one btc, and four lattice water molecules. Each of Cu atoms is monovalent and two-coordinated with two N atoms from two bib. The Cu—N lengths are in range 1.865(8)—1.873(9) Å, comparable to those in the [Cu(BCDC)] PF<sub>6</sub> THF complex [24]. The coordination angles around Cu atoms vary from 174.9(4)° to 175.8(4)°, indicating that these Cu ions display a linear coordination geometry. These chain-like complexes are assembled together via strong  $\pi$ — $\pi$  stacking (the distance of the centroid: 3.660 Å and 3.824 Å) and create a weak Cu—Cu interaction (Cu(2)···Cu(3) 3.550 Å) [25], as shown in Fig. 3. The uncoordinated btc ligand is hydrogen-bonded with each other and lattice water (Table 3), giving rise to a 1D tape structure, which acts as a linker to join the chain-like Cu coordination polymers together through C—H···O hydrogen bonds (C2···O11 3.103 Å, C11···O7 3.481 Å, C16···O4 3.462 Å, C21···O8 3.380 Å, C23···O7 3.301 Å, C25···O1 3.275 Å, C34···O9 3.426 Å, C35···O6, 3.367 Å) and C—H··· $\pi$  (C6···C39 3.482 Å, C5···C43 3.694 Å). So the total structure of complex is the sandwich-type structure in which the 1D tape structure of btc and water are arranged between the adjacent layers of 1D coordination polymers (Fig. 4).

**Infrared spectrum.** In the FI-IR spectra of complexes **1** and **2**, the O—H stretching vibrations of water molecules are observed at 3428 cm<sup>-1</sup> and 3432 cm<sup>-1</sup> respectively. The spectral features at 1579 cm<sup>-1</sup> and 1515 cm<sup>-1</sup> in complex **1** are assigned to the asymmetric and symmetric stretching vibrations of CO<sub>2</sub><sup>-</sup>, and those at 1340 cm<sup>-1</sup> and 1261 cm<sup>-1</sup> are the symmetric stretching of C—O. For complex **2**, asymmetric and symmetric  $\nu$ (CO<sub>2</sub><sup>-</sup>) are found at 1618 cm<sup>-1</sup> and 1533 cm<sup>-1</sup>, and the C—O

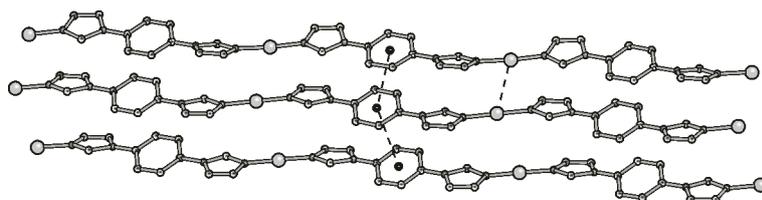


Fig. 3. Coordination environment of Cu(I) in complex **2**

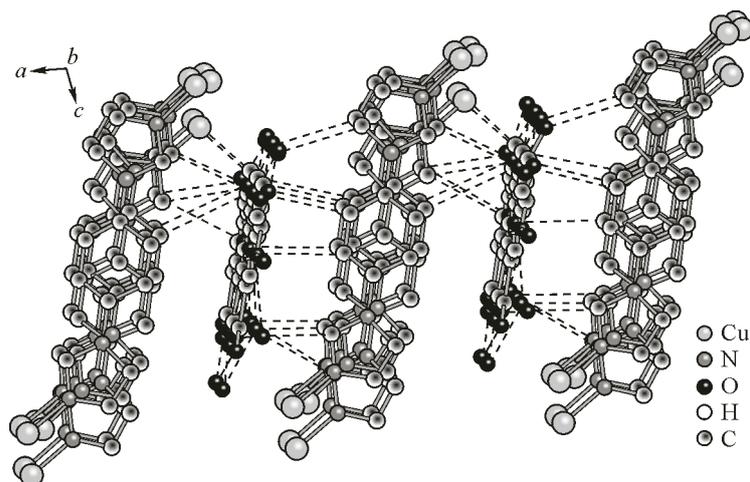


Fig. 4. Sandwich-type supramolecular structure of complex **2** along the *b* axis

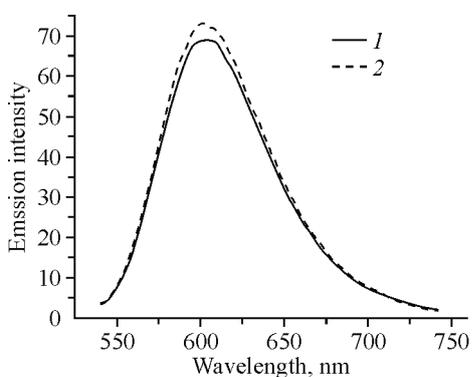
Table 3

Hydrogen bond lengths (Å) and bond angles (deg.)

D—H···A	<i>d</i> (D—H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠DHA
O(8)—H(8C)···O(1)	0.851	1.800	2.649	175.14
O(7)—H(7D)···O(8)	0.850	1.894	2.737	170.71
O(11)—H(11H)···O(7)	0.850	1.934	2.771	167.96
O(11)—H(11G)···O(2)	0.850	1.857	2.694	167.39
O(7)—H(7C)···O(3)	0.849	1.949	2.790	170.20
O(8)—H(8D)···O(9)	0.850	1.837	2.648	174.73
O(9)—H(9C)···O(3)	0.850	1.802	2.642	169.45
O(9)—H(9D)···O(6)	0.850	1.846	2.686	169.33
O(10)—H(10D)···O(6)	0.850	1.993	2.84	176.98
O(10)—H(10C)···O(4)	0.850	2.073	2.922	177.05

symmetric stretching appears at  $1359\text{ cm}^{-1}$  and  $1305\text{ cm}^{-1}$ . The C—N stretching is observed at  $1114\text{ cm}^{-1}$ ,  $1085\text{ cm}^{-1}$  for **1** and  $1066\text{ cm}^{-1}$  for **2**.

**Photoluminescent properties.** It is well known that Cu(I) complexes with both discrete or multi-dimensional structures exhibit excellent luminescence. Hence, we studied the photoluminescent properties of complexes **1** and **2** in a DMF solution at room temperature. As shown in Fig. 5, it can be observed that intense emissions occur at 603 nm ( $\lambda_{\text{ex}} = 320\text{ nm}$ ) for **1** and 601 nm ( $\lambda_{\text{ex}} = 330\text{ nm}$ ) for **2**.



Compared with free bibp and bib ligands [ $\lambda_{\text{em}} = 462\text{ nm}$  ( $\lambda_{\text{ex}} = 328\text{ nm}$ ) for bibp,  $\lambda_{\text{em}} = 455\text{ nm}$  ( $\lambda_{\text{ex}} = 341\text{ nm}$ ) for bib], the clear red shift of the emission bands of **1** and **2** may originate from the excited states of ligands-to-metal charge transfer (LMCT) between the Cu(I) atoms and ligands, which is observed in other Cu(I) coordination polymers [26].

Two monovalent copper coordination polymers have been successfully synthesized and characterized. In complex

Fig. 5. Emission spectra of complexes **1** and **2** measured in a DMF solution

**1**, the Cu(1) ion is two-coordinated with two N atoms of bibp, the Cu(2) ion is three-coordinated with two N atoms of bibp and one water molecule. In complex **2**, the Cu ions are two-coordinated with two N atoms from bib. The uncoordinated bdc and btc ligands play important roles in the formation of 3D framework for **1** and **2** via weak interactions such as hydrogen bonds.

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## REFERENCES

1. *Suh M.P., Park H.J., Prasad T.K., Lim D.W.* // Chem. Rev. – 2012. – **112**. – P. 782 – 835.
2. *Nouar F., Eckert J., Eubank J.F., Forster P., Eddaoudi M.* // J. Amer. Chem. Soc. – 2009. – **13**. – P. 2864 – 2870.
3. *Harbuzaru B.V., Rey F., Antienzar P., Jordá J.L.* // Angew. Chem. Int. Ed. – 2008. – **47**. – P. 1080 – 1083.
4. *Lu W.G., Yuan D.Q., Yakovenko A., Zhou H.C.* // Chem. Commun. – 2011. – **47**. – P. 4986 – 4988.
5. *Du M., Jiang X.J., Zhao X.J.* // Inorg. Chem. – 2007. – **46**. – P. 3984 – 3995.
6. *Carlucci L., Ciani G., Macchi P., Proserpio D.M., Sironi A.* // Chem. Commun. – 1997. – P. 631 – 632.
7. *Wu S.T., Long L.S., Huang R.B., Zheng L.S.* // Cryst. Growth Des. – 2007. – **7**. – P. 1746 – 1752.
8. *Zhang T.L., Kong J.X., Hu Y.J., Meng X.G., Yin H.B., Hu D.S., Ji C.P.* // Inorg. Chem. – 2008. – **47**. – P. 3144 – 3149.
9. *Zhang J.P., Lin Y.Y., Huang X.C., Chen X.M.* // J. Amer. Chem. Soc. – 2005. – **127**. – P. 5495 – 5506.
10. *Zhang J.P., Zheng S.L., Huang X.C., Chen X.M.* // Angew. Chem. Int. Ed. – 2003. – **43**. – P. 206 – 209.
11. *Lu H.J., Zhu Y.Y., Chen N., Gao Y.C., Guo X.F., Li G., Tang M.S.* // Cryst. Growth Des. – 2011. – **11**. – P. 5241 – 5252.
12. *Gao C.Y., Liu S.X., Xie L.H., Ren Y.H., Cao J.F., Sun C.Y.* // CrystEngComm. – 2007. – **9**. – P. 545 – 547.
13. *He J., Zhang J.X., Tan G.P., Yin Y.G., Zhang D., Hu M.H.* // Cryst. Growth Des. – 2007. – **7**. – P. 1508 – 1513.
14. *Choi E.Y., Kwon Y.U.* // Inorg. Chem. – 2005. – **44**. – P. 538 – 545.
15. *Li Z.X., Chu X., Cui G.H., Liu Y., Li L., Xue G.L.* // CrystEngComm. – 2011. – **13**. – P. 1984 – 1989.
16. *Wen L.L., Wang F., Feng J., Lv K.L., Wang C.G., Li D.F.* // Cryst. Growth Des. – 2009. – **9**. – P. 3581 – 3589.
17. *Wang F., Ke X.H., Zhao J.B., Deng K.J., Leng X.K., Tian Z.F., Wen L.L., Li D.F.* // Dalton Trans. – 2011. – **40**. – P. 11856 – 11865.
18. *Sheldrick G.M.* SHELXS 97 program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997.
19. *Sheldrick G.M.* SHELXS 97 program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.
20. *Zhu A.X., Xu Q.Q., Liu F.Y., Li Z., Qi X.L.* // Inorg. Chim. Acta. – 2011. – **370**. – P. 333 – 339.
21. *Liu H.Y., Wu H., Yang J., Liu Y.Y., Ma J.F., Bai H.Y.* // Cryst. Growth Des. – 2011. – **11**. – P. 1786 – 1797.
22. *Tian A.X., Ying J.Y., Peng J., Sha J.Q., Pang H.J., Zhang P.P., Chen Y., Zhu M., Su Z.M.* // Cryst. Growth Des. – 2008. – **8**. – P. 3717 – 3724.
23. *Hou G.F., Bi L.H., Li B., Wang B., Wu L.X.* // CrystEngComm. – 2011. – **13**. – P. 3526 – 3535.
24. *Anthony S.P., Radhakrishnan T.P.* // Cryst. Growth Des. – 2004. – **4**. – P. 1223 – 1227.
25. *Allen F.H., Davies J.E., Galloy J.J., Johnson O., Kennard O., Macrae C.F., Mitchell E.M., Mitchell G.F., Smith J.M., Watson D.G.* // J. Chem. Inf. Comput. Sci. – 1991. – **31**. – P. 187 – 204.
26. *Li M.X., Wang H., Liang S.W., Shao M., He X., Wang Z.X., Zhu S.R.* // Cryst. Growth Des. – 2009. – **9**. – P. 4626 – 4633.