

UDC 548.73:547.13:546.48

**A T4(2)6(2) WATER TAPE ENCAPSULATED IN A TWO-DIMENSIONAL
COORDINATION POLYMER CONSTRUCTED BY
2,2'-BIS(1H-1,2,4-TRIAZOLYL)ETHER AND BENZENE-1,4-DIACETIC ACID**

X.J. Xu, J. Wang

Department of Chemistry, Yancheng Teachers University, Yancheng, Jiangsu 224002, P.R. China
E-mail: wjyctu@gmail.com

Received February, 18, 2014

A two-dimensional Cd(II) complex $\{[\text{Cd}(\text{BTE})(\text{PBEA})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**) (BTE = 2,2'-bis(1H-1,2,4-triazolyl)ether, H₂PBEA = benzene-1,4-diacetic acid) has been synthesised and characterised using single crystal X-ray diffraction, IR and elemental analysis. Single-crystal X-ray diffraction analysis revealed that complex **1** is a two-dimensional polymer based on the 24-membered rhomboid subunit $[\text{Cd}_2(\text{BTE})_2]$ with a Cd—Cd separation of 5.354 Å. More interestingly, there is a T4(2)6(2) water tape in complex **1**. The thermal stability and luminescent properties of the title complex have been briefly investigated.

Keywords: Cd(II) complex, benzene-1,4-diacetic acid, 2,2'-bis(1H-1,2,4-triazolyl)ether, crystal structure, luminescence.

INTRODUCTION

In the past decades, more and more researchers have been paying their efforts in the design and preparation of metal-organic frameworks (MOFs) not only due to their intriguing topology matrixes but also owing to their potential applications in gas storage, chemical separations, molecular magnetism, nonlinear optics, heterogeneous catalysis, and so on [1—4]. It is well established that the construction of metal-organic complexes is usually influenced by several factors in the self-assembly process, such as the organic ligands, solvents, temperature, the nature of anions, reaction conditions, and so on [5, 6]. The nature of organic ligands plays a great role in determining the network structure of a complex. In this regard, the versatile multicarboxylic acids and multidentate N-donor ligands were widely used to construct coordination polymers because of their reliable and rich coordination modes.

Benzene-1,4-diacetic acid (H₂PBEA) as a flexible dicarboxylate ligand is a very versatile ligand for the construction of novel metal-organic complexes [7—9]. Meanwhile, because of the presence of a flexible $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$ group in the molecule, 2,2'-bis(1H-1,2,4-triazolyl)ether (BTE) can adopt different conformations compared with the corresponding 1,2,4-triazole ligand [10]. However, to the best of our knowledge, coordination polymers constructed from H₂PBEA and BTE ligands have not been documented so far. In the present case, we have selected the H₂PBEA and BTE as organic ligands, generating the title new Cd(II) coordination polymer, $\{[\text{Cd}(\text{C}_8\text{N}_6\text{OH}_{12})(\text{C}_{10}\text{O}_4\text{H}_8)(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**), the crystal structure of which we now report. In addition, the thermal and luminescent properties of the title complex have been investigated.

EXPERIMENTAL

The 2,2'-bis(1H-1,2,4-triazolyl)ether (BTE) ligand was synthesized according to the literature method [10]. All other reagents and solvents were commercial available and used without further pu-

rification. Infrared spectrum was obtained within the 4000—400 cm^{-1} as KBr disks on a VECTOR 22 spectrometer. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. Thermal gravimetric analysis (TGA) was collected on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 950 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen. Solid-state fluorescence spectra were recorded on a Fluoro Max-P spectrophotometer at room temperature.

Synthesis of $\{[\text{Cd}(\text{BTE})(\text{PBEA})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\}_n$. A mixture of $\text{Cd}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.0345 g, 0.100 mmol), H_2PBEA (0.0195 g, 0.100 mmol), BTE (0.0416 g, 0.200 mmol), and KOH (0.0112 g, 0.200 mmol) in H_2O (10 mL) was sealed in a 16 mL Teflon-lined stainless steel container and heated at 150 $^{\circ}\text{C}$ for 72 h. After cooling to room temperature, white block crystals of complex **1** were collected by filtration and washed by water and ethanol several times. (yield 23.7 %, based on H_2PBEA).

Table 1

Crystal data and structure refinement for complex **1**

Parameter	1
Empirical formula	$\text{C}_{18}\text{H}_{28}\text{CdN}_6\text{O}_9$
Formula weight	584.87
System	Monoclinic
Space group	$P2_1/n$
$a, b, c, \text{\AA}$	7.6641(19), 16.864(4), 18.954(5)
$\alpha, \beta, \gamma, \text{deg.}$	90, 98.7700(10), 90
$V, \text{\AA}^3$	2421.1(10)
Z	4
$\rho_{\text{calcd}}, \text{g/cm}^3$	1.605
$\mu(\text{MoK}\alpha), \text{mm}^{-1}$	0.961
Crystal size, mm	0.21 \times 0.19 \times 0.17
θ range, deg.	1.62—25.10
$F(000)$	1192
$R_1^a [I > 2\sigma(I)]$	0.0396
$wR_2^b [I > 2\sigma(I)]$	0.0792
GOOF	1.017

Table 2

Selected bond distances (\AA) and angles (deg.) for complex **1**

Cd(1)—O(1)	2.397(2)	O(1)—Cd(1)—O(2)	53.86(8)	O(1)—Cd(1)—O(3)#1	135.75(8)
Cd(1)—O(3)#1	2.635(3)	O(2)—Cd(1)—O(3)#1	165.86(8)	O(4)#1—Cd(1)—O(1)	85.38(9)
Cd(1)—O(6)	2.304(2)	O(4)#1—Cd(1)—O(2)	139.15(9)	O(4)#1—Cd(1)—O(3)#1	51.29(8)
Cd(1)—N(4)#2	2.334(3)	O(4)#1—Cd(1)—N(4)#2	93.43(11)	O(6)—Cd(1)—O(1)	140.24(9)
Cd(1)—O(2)	2.446(2)	O(6)—Cd(1)—O(2)	86.56(8)	O(6)—Cd(1)—O(3)#1	83.78(8)
Cd(1)—O(4)#1	2.324(2)	O(6)—Cd(1)—O(4)#1	134.29(9)	O(6)—Cd(1)—N(1)	83.69(10)
Cd(1)—N(1)	2.304(3)	O(6)—Cd(1)—N(4)#2	89.81(10)	N(1)—Cd(1)—O(1)	96.36(10)
		N(1)—Cd(1)—O(2)	86.93(10)	N(1)—Cd(1)—O(3)#1	81.78(10)
		N(1)—Cd(1)—O(4)#1	96.04(10)	N(1)—Cd(1)—N(4)#2	170.52(10)
		N(4)#2—Cd(1)—O(1)	84.23(10)	N(4)#2—Cd(1)—O(2)	85.80(10)
		N(4)#2—Cd(1)—O(3)#1	104.43(9)		

#1 $x-1/2, -y+3/2, z+1/2$; #2 $-x+1, -y+2, -z$.

Elemental analysis for $C_{18}H_{28}CdN_6O_9$ ($M_r = 584.86$): C 36.96, H 4.83, N 14.37 %; found: C 37.04, H 4.85, N 14.41 %. Selected IR peaks (cm^{-1}): 3437 (m), 1623 (s), 1463 (s), 1245 (s), 831(w), 776 (w), 701 (w).

X-ray crystallography. The crystal structure of complex **1** was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. Absorption correction was performed by using the SADABS program [11]. The structure was solved by direct method using the program SHELXL-97 and refined by full-matrix least-squares technique on F^2 with SHELXL-97 [12]. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

RESULT AND DISCUSSION

Single crystal X-ray diffraction revealed that complex **1** crystallizes in the monoclinic space group $P2_1/n$, and the asymmetric unit contains a Cd^{II} atom, one fully deprotonated H_2PBEA ligand, one BTE ligand, one coordinated aqua molecule and three water molecules of crystallization. Each $Cd(II)$ center is seven-coordinated by four oxygen atoms from two distinct $PBEA^{2-}$ ligands, ($Cd1-O1 = 2.397(2)$, $Cd1-O2 = 2.446(2)$, $Cd1-O3^i = 2.635(3)$, $Cd1-O4^i = 2.324(2) \text{ \AA}$), one oxygen atom from one aqua ligand ($Cd1-O6 = 2.304(2) \text{ \AA}$) and two nitrogen atoms ($Cd1-N1 = 2.304(3)$, $Cd1-N4^{ii} = 2.334(3) \text{ \AA}$) from two different BTE ligand in a distorted pentagonal-bipyramidal geometry (Fig. 1) [symmetry codes: (i) $-0.5+x, 1.5-y, 0.5+z$; (ii) $1-x, 2-y, -z$]. The average $Cd-O$ and $Cd-N$ distances in complex **1** are comparable to the reported Cd based complexes [13, 14].

In the BTE ligand, the dihedral angles between the two triazole rings is 138.8° and the bond angle $C14O5C15$ is $111.4(3)^\circ$. Two crystallographically equivalent $Cd(II)$ atoms are bridging by two BTE ligands adopting *cis* conformation to form a 24-membered cationic rhomboid subunit $[Cd_2(BTE)_2]_n^{4n+}$ with a $Cd-Cd$ separation of 5.354 \AA . On the other hand, the H_2PBEA ligand is completely deprotonated and acting as a bis(chelating) ligand connects two cadmium (II) atoms to form the $[Cd(PBEA)]_n$ neutral *zig-zig* chain. The $Cd \cdots Cd$ contact distance through the $PBEA^{2-}$ ligand is 11.568 \AA . Thus, cationic rhomboid subunits $[Cd_2(BTE)_2]_n^{4n+}$ are aggregated into $[Cd(BTE)(PBEA)]_n$ 2D coordination polymer layers by $PBEA^{2-}$ ligands which are oriented parallel to the (1 0 1) crystal planes (Fig. 2). Furthermore, the double-layered grid condenses into a 3D supramolecular architecture through $O-H \cdots O$ and $C-H \cdots O$ hydrogen bonds (Fig. 3).

Interestingly, there is a T4(2)6(2) water tape in complex **1** (Fig. 4). The tape water consists of chair-shaped water hexamer and tetramer cyclic arrangements that share two water molecules between

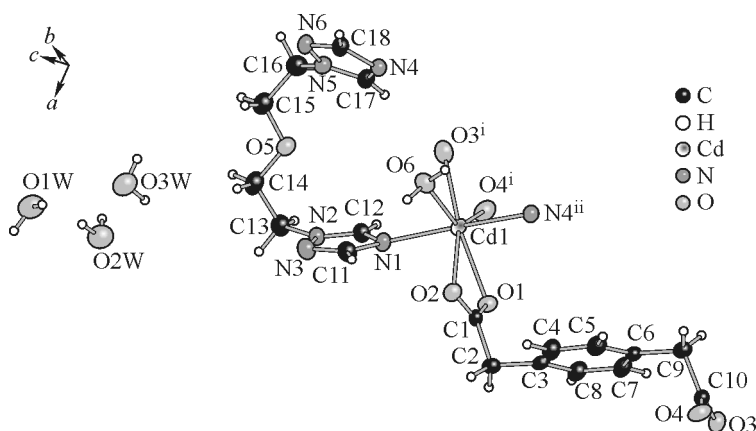


Fig. 1. Coordination environment of the $Cd(II)$ ion in complex **1** showing 30 % ellipsoid probability.

Symmetry codes: ⁱ $-0.5+x, 1.5-y, 0.5+z$; ⁱⁱ $1-x, 2-y, -z$

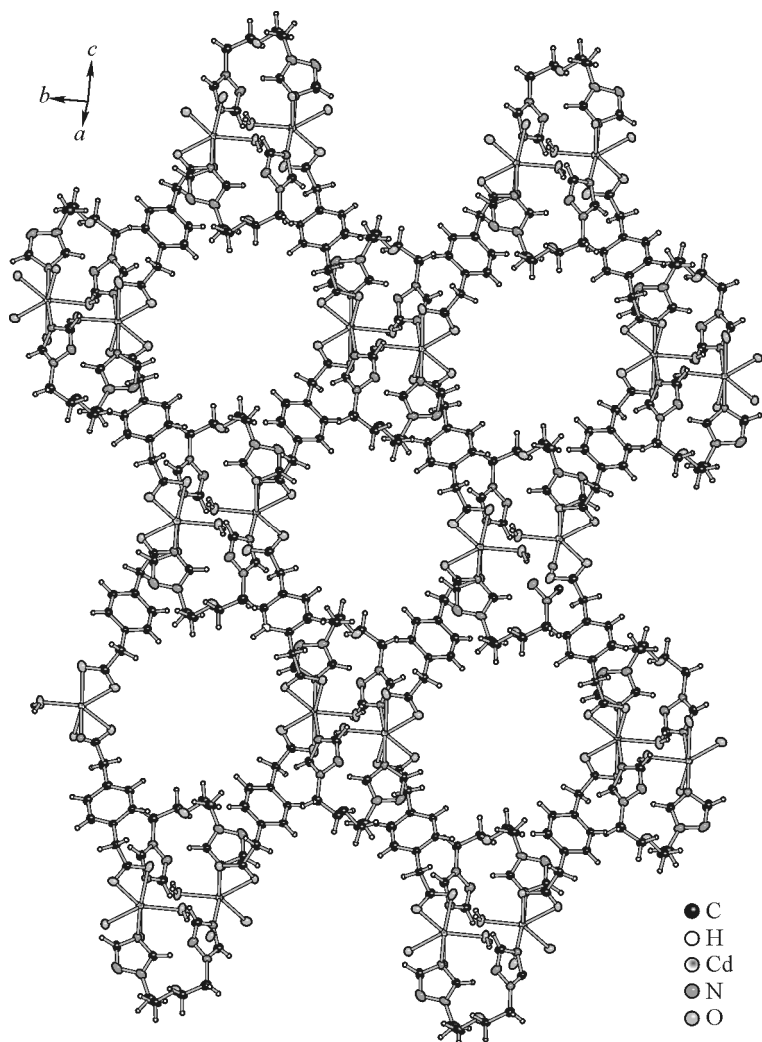


Fig. 2. View of 2D framework of complex **1**

the adjacent rings. The O—O distance is 2.820, 2.821, 2.854, and 2.946 Å, respectively (and the average distance is 2.860 Å), which is significantly longer than the corresponding value of 2.85 Å in liquid water. The water tape connected with the host framework with strong hydrogen-bond interactions of O1W—H1WB···O1, O3W—H3WA···O4.

The thermal stability of complex **1** was investigated. As shown in Fig. 5, the water molecules were ejected from 98 °C to 110 °C (12.68 % weight loss observed, 12.32 % calcd). The removal of the organic ligands occurs in the temperature range of 145 to 695 °C. The final residue was proved to be CdO. The calculated result (21.96 %) is basically comparable with the observed one (21.94 %).

The fluorescent property of complex **1** was studied in the solid state at room temperature. The free H₂PBEA shows emission peaks at 454 nm ($\lambda_{\text{ex}} = 365$ nm) [15]. Irradiation of crystalline samples of complex **1** with ultraviolet light ($\lambda_{\text{ex}} = 330$ nm) in the solid state resulted in intense emission violet visible light emission with a λ_{max} of 390 nm (Fig. 6). According to a recent review of d^{10} metal coordination polymer luminescence, the emissive behavior of **1** can be ascribed to ligand-centered electronic transitions [16, 18].

In summary, we have presented the synthesis and crystal structure of a new two-dimensional Cd(II) complex $\{[\text{Cd}(\text{BTE})(\text{PBEA})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**). Single-crystal X-ray diffraction analysis revealed that complex **1** is a two-dimensional polymer based on the 24-membered rhomboid subunit

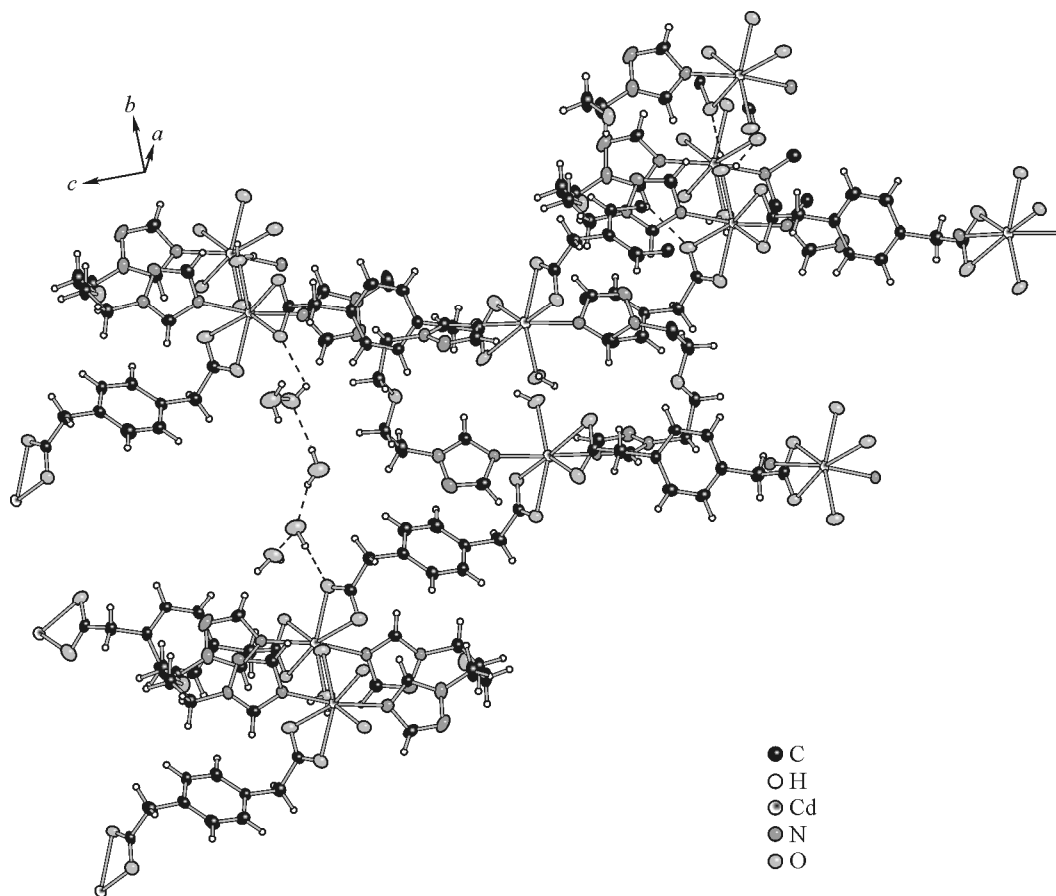


Fig. 3. A perspective view of the three-dimensional supramolecular structure of complex **1**, incorporating O—H...O and C—H...O hydrogen bonds (dashed lines)

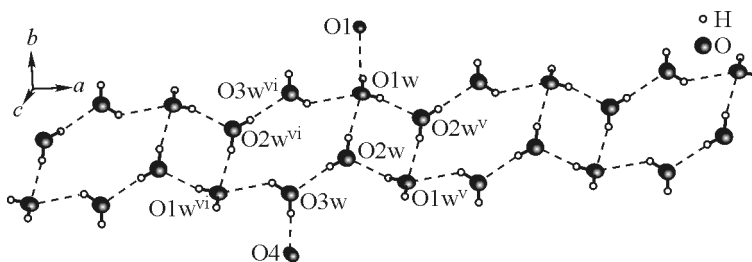


Fig. 4. Perspective view of the T4(2)6(2) water tape showing hydrogen bonding interactions.

Symmetry codes: (vi) $1-x, 1-y, 2-z$; (v) $2-x, 1-y, 2-z$

[Cd₂(BTE)₂] with a Cd—Cd separation of 5.354 Å. More interestingly, there is a T4(2)6(2) water tape in complex **1**. Moreover, the thermal stability and luminescent properties of the title complex have been briefly investigated.

Supplementary material. Crystallographic data for the structural analysis of complex **1** has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 985977. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EQ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

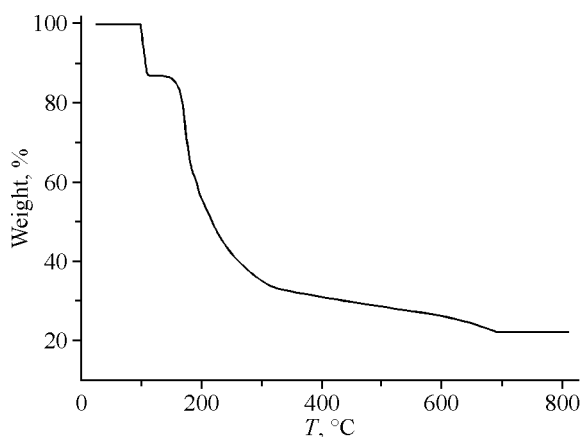


Fig. 5. The TG curve of complex **1**

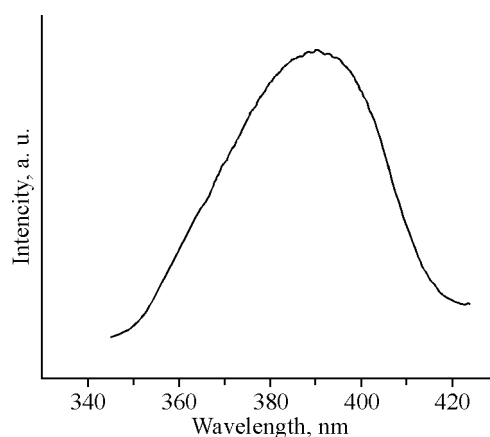


Fig. 6. Solid-state emission spectrum of complex **1** at room temperature

REFERENCES

1. Kitagawa S., Kitaura R., Noro S. // *Angew. Chem. Int. Ed.* – 2004. – **43**. – P. 2334 – 2375.
2. Ferey G., Mellot-Draznieks C., Serre C. *et al.* // *Acc. Chem. Res.* – 2005. – **38**. – P. 217 – 225.
3. Roy S., Mahata G., Biradha K. // *Cryst. Growth Des.* – 2009. – **9**. – P. 5006 – 5008.
4. Zhang Y.B., Zhang W.X., Feng F.Y. *et al.* // *Angew. Chem., Int. Ed.* – 2009. – **48**. – P. 5287 – 5290.
5. Kan W.-Q., Liu B., Yang J. *et al.* // *Cryst. Growth Des.* – 2012. – **12**. – P. 2288 – 2298.
6. Liu Y.-Y., Li J., Ma J.-F. *et al.* // *CrystEngComm.* – 2012. – **14**. – P. 169 – 177.
7. Pan L., Adams K.M., Hernandez H.E. *et al.* // *J. Amer. Chem. Soc.* – 2003. – **125**. – P. 3062 – 3067.
8. Braverman M.A., LaDuca R.L. // *Cryst. Growth Des.* – 2007. – **7**. – P. 2343 – 2351.
9. Wang L.-Y., Yang Y., Liu K., Li B.-L. *et al.* // *Cryst. Growth Des.* – 2008. – **8**. – P. 3902 – 3904.
10. Luo S.-C., Lin I.J.B. // *J. Chin. Chem. Soc.* – 2010. – **57**. – P. 893 – 895.
11. Sheldrick G.M. SADABS, An empirical absorption correction program. – Madison, WI: Bruker Analytical X-ray Systems, 1996.
12. Sheldrick G.M. SHELXL-97, Program for refinement of crystal structures. – University of Göttingen, Germany, 1997.
13. Wang J., Xu X.-J., Tao J.-Q. // *Acta Crystallogr.* – 2011. – **C67**. – P. m137 – m139.
14. Wang J., Tao J.-Q., Xu X.-J. *et al.* // *Z. Anorg. Allg. Chem.* – 2012. – **638**. – P. 1261 – 1264.
15. Luo L., Wang P., Xu G.-C. *et al.* // *Cryst. Growth Des.* – 2012. – **12**. – P. 2634 – 2645.
16. Wen L.L., Li Y.Z., Lu Z.D. *et al.* // *Cryst. Growth Des.* – 2006. – **6**. – P. 530 – 537.
17. Lin J.G., Zang S.Q., Tian *et al.* // *CrystEngComm.* – 2007. – **9**. – P. 915 – 921.
18. Yang Y., Du P., Ma J.F. *et al.* // *Cryst. Growth Des.* – 2011. – **11**. – P. 5540 – 5553.