ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2014. Том 55, № 3 *Май – июнь* *С. 591 – 596*

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:547.13:546.73:546.47

INFINITE 1D WATER CHAINS PRESENT IN COMPLEXES OF Co(II) AND Zn(II) WITH 4,4′,6,6′-TETRAMETHYL-2,2′-BIPYRIMIDINE

N. Ma, B.M. Ji

College of Chemistry and Chemical Engineering, Luoyang Normal University, 471022, P. R. China
E-mail: lyhxxjbm@126.com

Received June, 25, 2012

Two new transition metal complexes [Co(tmbpm)$Cl_2(H_2O)$]·$2H_2O$ (**1**) and [Zn(tmbpm)Cl_2]·$2H_2O$ (**2**) (where tmbpm = 4,4′,6,6′-tetramethyl-2,2′-bipyrimidine) are synthesized and characterized by IR and single crystal X-ray diffraction. The tmbpm adopts chelating coordination mode in the two mononuclear complexes. Both **1** and **2** form 2D supramolecular structures containing an infinite 1D water chain through hydrogen bonds.

Keywords: complex, Co(II), Zn(II), tmbpm, crystal structure, intermolecular hydrogen bond, water chain.

Introduction. Water clusters in structures of organic compounds and coordination complexes have been widely studied recently [1—5]. The presence of water molecules in solid state complexes can play an important interconnecting role in some supramolecular structures [6—9]. In most of the reported examples, water clusters are classified as two classes: discrete clusters and polymeric clusters. Discrete clusters containing various $(H_2O)_n$ [10—16] clusters and larger water rings [17], and infinite 1D chains/tapes [18], 2D layers [19], and 3D structures [20] have been observed as polymeric clusters. Among the water clusters, 1D water chains are paid more attention for biological and other reasons [21, 22]. With the interest in the 1D water chains, here we report two infinite 1D water chains in complexes of Co(II) and Zn(II) with 4,4′,6,6′-tetramethyl-2,2′-bipyrimidine (tmbpm).

Experimental. Tmbpm was prepared by the literature method [23]. The C, H, and N microanalyses were carried out on a Flash 1112 elemental analyzer. The FT-IR spectrum (KBr pellets) was recorded in the range 400—4000 cm^{-1} on a Nicolet Avatar-360 spectrometer.

Synthesis of complex 1. A mixture of $CoCl_2 \cdot 6H_2O$ (0.0952 g, 0.4 mmol) and tmbpm (0.0856 g, 0.4 mmol) in H_2O (12 ml) was stirred for 30 min at room temperature. Then the solution was sealed in a Teflon-lined stainless 20 ml-vessel which was heated at 140 °C for three days. After the reaction mixture was cooled to room temperature at a rate of 2.3 °C/h, red crystals of **1** were obtained with the yield of 65 % (based on Co). Anal. Calcd. (%) for $C_{12}H_{20}N_4O_3Cl_2Co$: C, 36.20; H, 5.06; N, 14.07. Found (%): C, 36.09; H, 5.11; N, 14.13. IR (KBr): 3459(b), 2966(w), 2919(w), 1620(s), 1526(w), 1441(m), 1374(w), 1030(w), 572(w), 526(w) cm^{-1}.

Synthesis of complex 2. A mixture of $ZnCl_2$ (0.0272 g, 0.2 mmol) and tmbpm (0.0428 g, 0.2 mmol) in 12 ml of H_2O was stirred for 30 min at room temperature. Then the solution was sealed in a Teflon-lined stainless 20 ml-vessel which was heated at 140 °C for three days. After the reaction mixture was cooled to room temperature at a rate of 2.3 °C/h, colorless crystals of **2** were obtained with the yield of 76 % (based on Zn). Anal. Calcd. (%) for $C_{12}H_{18}N_4O_2Cl_2Zn$: C, 37.28; H, 4.69; N, 14.49. Found (%): C, 37.39; H, 4.66; N, 14.52. IR (KBr): 3441(b), 2961(w), 2915(w), 1599(s), 1531(m), 1439(s), 1358(m), 1265(w), 1026(m), 955(w), 579(w), 559(w) cm^{-1}.

Table 1

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

Parameter	**1**	**2**
Empirical formula	$C_{12}H_{20}Cl_2CoN_4O_3$	$C_{12}H_{18}Cl_2N_4O_2Zn$
Formula weight	398.15	386.57
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/c$
a, b, c, Å	10.6727(14), 7.0189(9), 23.015(3)	12.325(5), 16.184(6), 8.568(3)
α, β, γ, deg.	90, 103.044(2), 90	90, 93.239(4), 90
V, Å^3	1679.6(4)	1706.4(11)
Z	4	4
D_{calcd}, g/cm^3	1.575	1.505
μ, mm^{-1}	1.356	1.760
$F(000)$	820	792
Index ranges	$-12 \le h \le 12, -8 \le k \le 8, -27 \le l \le 27$	$-14 \le h \le 14, -19 \le k \le 19, -10 \le 1 \le 10$
Reflections collected / unique	12032 / 3130	12812 / 3181
Goodness-of-fit on F^2	1.045	1.028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0604, 0.1693	0.0272, 0.0722
R_1, wR_2 [all data]	0.0729, 0.1791	0.0342, 0.0771
Largest diff. peak and hole, e/Å^3	0.803 and –0.541	0.359 and –0.274

Single crystal X-ray diffraction data collections of complex **1** and **2** were performed on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation ($\lambda = 0.071073$ nm). Data collection and reduction were performed using the APEX II software. The structures were solved by direct methods and refined by the least-squared methods with the SHELXL-97 program [24]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules were restrained with O—H = 0.83, H—H = = 1.37 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Crystal data and experimental details of the structure determination, selected bond distances and angles, and hydrogen bonding parameters are listed in Tables 1, 2, and 3 respectively. The X-ray diffraction data were deposited with the Cambridge Crystallographic Data Center (CCDC no. 915048 for **1** and 915047 for **2**) and are available from the authors at www.ccdc.cam.ac.uk/data_request/cif.

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for* **1** *and* **2**

1				**2**	
Cl(1)—Co(1)	2.3121(15)	O(1)—Co(1)—N(1)	101.34(14)	Zn(1)—N(1)	2.0542(19)
Cl(2)—Co(1)	2.3379(16)	O(1)—Co(1)—N(3)	81.70(14)	Zn(1)—N(2)	2.0694(19)
Co(1)—O(1)	2.112(4)	N(1)—Co(1)—N(3)	77.43(13)	Zn(1)—Cl(1)	2.1881(10)
Co(1)—N(1)	2.123(4)	O(1)—Co(1)—Cl(1)	85.18(11)	Zn(1)—Cl(2)	2.2247(10)
Co(1)—N(3)	2.142(3)	N(1)—Co(1)—Cl(1)	117.49(11)	N(1)—Zn(1)—N(2)	80.14(7)
		N(3)—Co(1)—Cl(1)	161.96(11)	N(1)—Zn(1)—Cl(1)	116.89(5)
		O(1)—Co(1)—Cl(2)	154.05(13)	N(2)—Zn(1)—Cl(1)	117.73(6)
		N(1)—Co(1)—Cl(2)	101.04(10)	N(1)—Zn(1)—Cl(2)	108.61(5)
		N(3)—Co(1)—Cl(2)	90.53(11)	N(2)—Zn(1)—Cl(2)	108.99(6)
		Cl(1)—Co(1)—Cl(2)	95.97(6)	Cl(1)—Zn(1)—Cl(2)	118.25(3)

Table 3

Hydrogen bond geometry (Å, deg.) *for* **1** *and* **2**

D—H···A	D—H	H···A	D···A	DH···A	D—H···A	D—H	H···A	D···A	DH···A
1					**2**				
O(3)—H(6W)···O(2)$^{\#1}$	0.84	1.89	2.614(12)	142.7	O(2)—H(4W)···N(3)$^{\#6}$	0.84	2.26	3.009(3)	150.1
O(3)—H(5W)···Cl(1)$^{\#2}$	0.84	2.50	3.254(7)	150.0	O(1)—H(2W)···Cl(2)$^{\#5}$	0.83	2.43	3.233(2)	162.7
O(2)—H(4W)···O(3)$^{\#3}$	0.84	1.77	2.577	160.6	O(1)—H(1W)···O(2)$^{\#7}$	0.83	1.90	2.726(3)	175.6
O(2)—H(3W)···Cl(2)$^{\#2}$	0.86	2.90	3.436(7)	121.8	O(2)—H(3W)···O(1)	0.83	1.93	2.738(3)	161.8
O(2)—H(3W)···Cl(1)$^{\#2}$	0.86	2.38	3.165(8)	151.2					
O(1)—H(2W)···N(4)$^{\#4}$	0.83	2.39	3.069(5)	139.5					
O(1)—H(2W)···N(2)$^{\#4}$	0.83	2.31	3.055(5)	149.6					
O(1)—H(1W)···Cl(2)$^{\#5}$	0.82	2.49	3.228(4)	149.6					

Symmetry transformations used to generate equivalent atoms: $^{\#1}$: $-x+1/2, y-1/2, -z+1/2$; $^{\#2}$: $x-1, y, z$; $^{\#3}$: $x, y+1, z$; $^{\#4}$: $-x+1, -y+1, -z$; $^{\#5}$: $x, y-1, z$; $^{\#6}$: $-x+1, -y+1, -z+1$; $^{\#7}$: $x, -y+1/2, z+1/2$.

Results and discussion. Crystal structure of 1. The asymmetric unit of **1** contains one crystallographically independent Co(II) atom, two Cl anions, one tmbpm ligand, one coordinated water molecule, and two lattice water molecules. The molecular structure of [Co(tmbpm)$Cl_2(H_2O)$] is shown in Fig. 1. The Co atom is five-coordinated by two Cl^- anions, two N atoms from tmbpm, and one O atom from a water molecule, forming a distorted trigonal bipyramidal geometry. The N(1) and N(3) atoms from tmbpm and the Cl(1) anion occupy the equatorial positions, whereas the O(1) atom of the coordinated water molecule and the Cl(2) anion fill the axial sites. The N(1)···N(3) distance (2.668(5) Å) is smaller than N(2)···N(4) (2.720(6) Å) due to the bidentate coordination of tmbpm. The bipyrimidine rings are almost planar, and they form a dihedral angle of 5.26(5)°.

The [Co(tmbpm)$Cl_2(H_2O)$] units are linked by intermolecular O—H···N hydrogen bonds to form dimers (Table 3). These dimers are further connected into an infinite 1D chain along *b*-axis direction by intermolecular O—H···Cl hydrogen bonds (Fig. 3, Table 3). It is worthwhile to mention that the

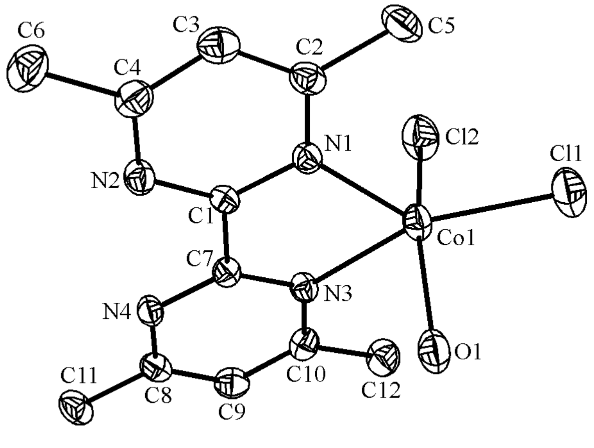

Fig. 1 (*left*). Molecular structure of [Co(tmbpm)$Cl_2(H_2O)$] drawn with 30 % probability displacement ellipsoids (water molecules and all hydrogen atoms are omitted for clarity)

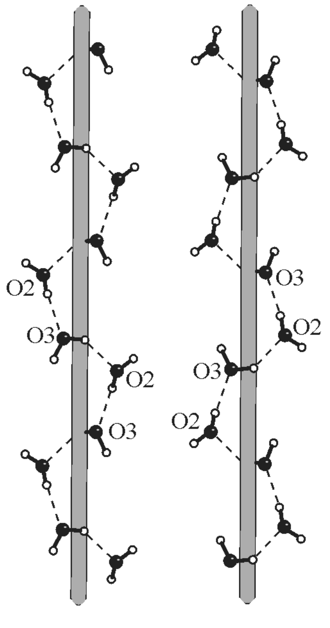

Fig. 2 (*right*). View of alternate left- and right-hand 1D helical water chains in **1** along the *b* axis

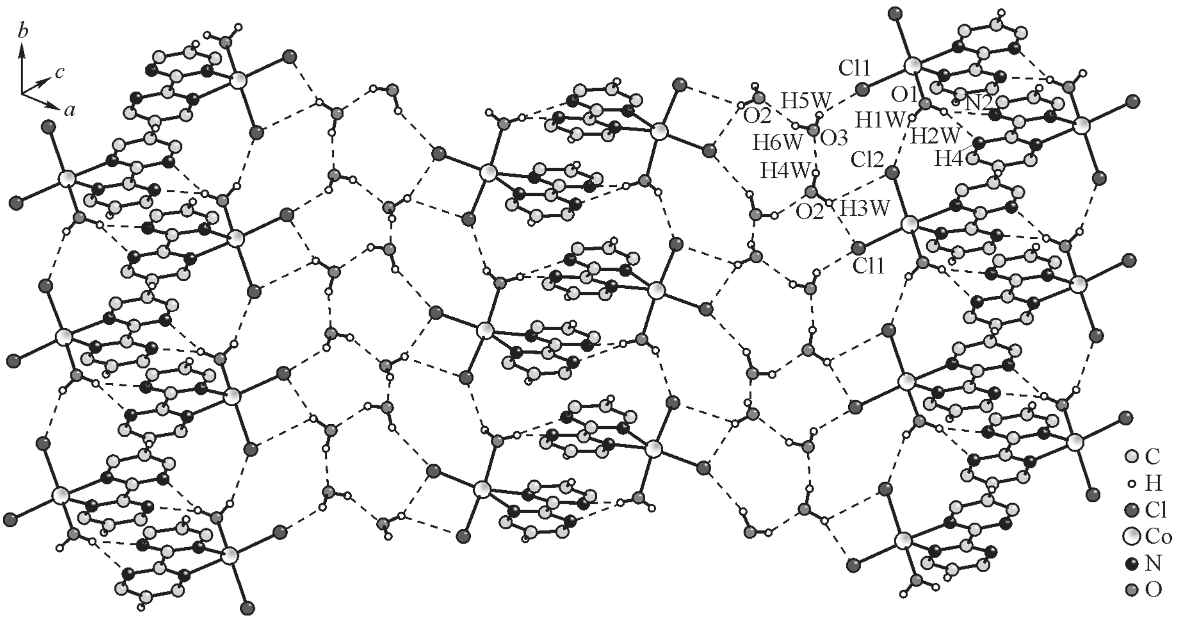

Fig. 3. 2D supramolecular structure of **1** (some C and H atoms are omitted for clarity)

two lattice water molecules are linked to each other by intermolecular O—H···O hydrogen bonds to form alternate left- and right-hand 1D helical chains along the *b* axis (Fig. 2, Table 3). The O···O distances (O(2)···O(3) = 2.577(12) Å, O(3)···O(2) = 2.614(12) Å) are significantly shorter than the value of 2.759 Å in ice I_h at 183 K. These two types of 1D helical water chains are bridged by the above mentioned 1D complex chains *via* O—H···Cl hydrogen bonds, generating a 2D supramolecular structure in the *ab* plane (Fig. 3, Table 3).

Crystal structure of 2. The asymmetric unit of **2** consists of one crystallographically independent Zn atom, two Cl^- anions, one tmbpm ligand, and two lattice water molecules. The molecular structure of $[Zn(tmbpm)Cl_2]$ is shown in Fig. 4. The Zn atom is four-coordinated by two Cl^- anions and two N atoms from tmbpm with a slightly distorted tetrahedral geometry. The bidentate coordination mode makes the ligand slightly distort with a bite distance of 2.654(2) Å and 2.762(3) Å for N(1)···N(2) and N(3)···N(4), respectively. The bipyrimidine rings are almost planar, and they form a dihedral angle of 8.70(7)°.

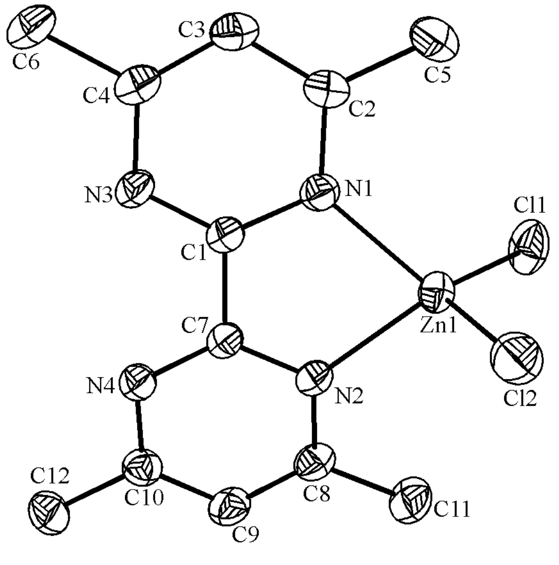

Fig. 4. Molecular structure of $[Zn(tmbpm)Cl_2]$ drawn with 30 % probability displacement ellipsoids (water molecules and all hydrogen atoms are omitted for clarity)

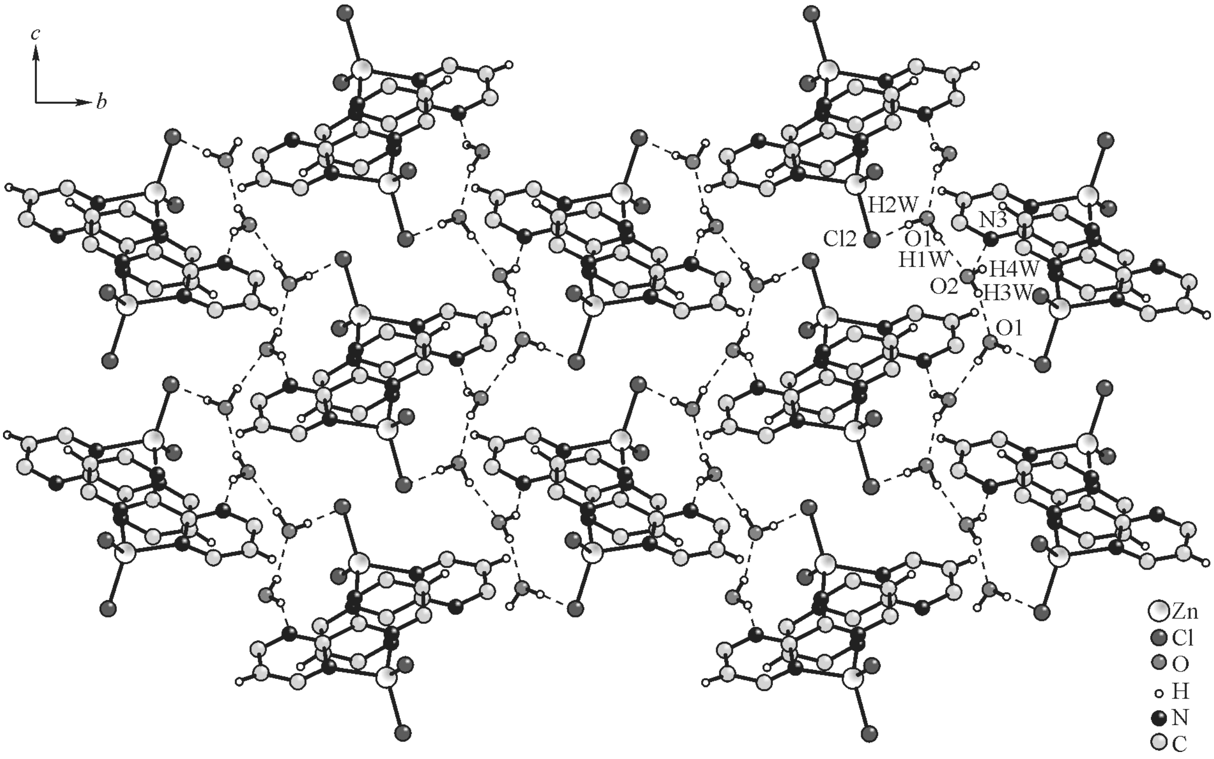

Fig. 5. 2D structure of **2** (some C and H atoms are omitted for clarity)

The lattice water molecules in complex **2**, O(1) and O(2), are connected with each other through intermolecular hydrogen-bonding interactions into an infinite 1D water chain in an ABAB fashion along the *c* axis (Fig. 5, Table 3). The O···O distances (O(1)···O(2) = 2.726(3) Å, O(2)···O(1) = =2.738(3) Å) are about the same as the value of 2.759 Å in ice I_h at 183 K. These 1D water chains are connected by the complex [Zn(tmbpm)Cl_2] units *via* intermolecular O—H···N and O—H···Cl hydrogen bonds, generating a 2D supramolecular structure in the *bc* plane (Fig. 5, Table 3).

This work was supported by the National Natural Science Foundation of China (projects no. 21072089).

REFERENCES

1. *Infantes L., Motherwell S.* // CrystEngComm. – 2002. – **4**, N 75. – P. 454 – 461.
2. *Infantes L., Chisholm J., Motherwell S.* // CrystEngComm. – 2003. – **5**, N 85. – P. 480 – 486.
3. *Ghosh S.K., Ribas J., Bharadwaj P.K.* // Cryst. Growth. Des. – 2005. – **5**, N 2. – P. 623 – 629.
4. *Ghosh S.K., Bharadwaj P.K.* // Inorg. Chem. – 2005. – **44**, N 16. – P. 5553 – 5555.
5. *Cheruzel L.E., Pometun M.S., Cecil M.R. et al.* // Angew. Chem. Int. Ed. – 2003. – **42**, N 44. – P. 5452 – 5455.
6. *Ghosh S.K., Ribas J., Bharadwaj P.K.* // CrystEngComm. – 2004. – **6**, N 45. – P. 250 – 256.
7. *Ghosh S.K., Bharadwaj P.K.* // Inorg. Chem. – 2004. – **43**, N 17. – P. 5180 – 5182.
8. *Zhao B., Cheng P., Chen X.Y. et al.* // J. Amer. Chem. Soc. – 2004. – **126**, N 10. – P. 3012 – 3013.
9. *Ma B.Q., Sun H.L., Gao S.* // Chem. Commun. – 2005. – **18**. – P. 2336 – 2338.
10. *Manikumari S., Shivaiah V., Das S.K.* // Inorg. Chem. – 2002. – **41**, N 26. – P. 6953 – 6955.
11. *MacGillivray L.R., Atwood J.L.* // J. Amer. Chem. Soc. – 1997. – **119**, N 10. – P. 2592 – 2393.
12. *Supriya S., Manikumari S., Raghavaiah P. et al.* // New. J. Chem. – 2003. – **27**, N 2. – P. 218 – 220.
13. *Rodríguez-Cuamatzi P., Vargas-Díaz G., Höpfl H.* // Angew. Chem. Int. Ed. – 2004. – **43**, N 23. – P. 3041 – 3044.
14. *Mir M.H., Vittal J.J.* // Angew. Chem. Int. Ed. – 2007. – **46**, N 31. – P. 5925 – 5928.
15. *Atwood J.L., Barbour L.J., Ness T.J. et al.* // J. Amer. Chem. Soc. – 2001. – **123**, N 29. – P. 7192 – 7193.

16. *Barbour L.J., Orr G.W., Atwood J.L.* // Nature. – 1998. – **393**. – P. 671 – 673.
17. *Raghuraman K., Katti K.K., Barbour L.J. et al.* // J. Amer. Chem. Soc. – 2003. – **125**, N 23. – P. 6955 – 6961.
18. *Banerjee S., Murugavel R.* // Cryst. Growth. Des. – 2004. – **4**, N 3. – P. 545 – 552.
19. *Lakshminarayanan P.S., Suresh E., Ghosh P.* // J. Amer. Chem. Soc. – 2005. – **127**, N 38. – P. 13132 – 13133.
20. *Carballo R., Covelo B., Lodeiro C.* // CrystEngComm. – 2005. – **7**, N 48. – P. 294 – 296.
21. *Lee Y.S., Krauss M.* // J. Mol. Struct. – 2004. – **700**, N 1-3. – P. 243 – 246.
22. *Hummer G., Rasaiah J.C., Noworyta J.P.* // Nature. – 2001. – **414**. – P. 188 – 190.
23. *Vlád G., Horváth I.T.* // J. Org. Chem. – 2002. – **67**, N 18. – P. 6550 – 6552.
24. *Sheldrick G.M.* SHELXS-97 and SHELXL-97. Programs for Crystal Structure Refinement. – Univ. Göttingen, Germany, 1997.