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HONEYCOMB-LIKE LAYERS CONSTRUCTED BY HYDROGEN BONDS. SYNTHESIS, STRUCTURE, AND PROPERTY OF TWO NEW SUPRAMOLECULAR COMPOUNDS BASED ON POLYOXOTUNGSTATE

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Two new compounds based on polyoxotungstate $[Co_2(PCA)_4(H_2O)_6][SiW_{12}O_{40}]\cdot 8H_2O$ (**1**), $[Cd_2(PCA)_4(H_2O)_6][SiW_{12}O_{40}]\cdot 8H_2O$ (**2**) (PCA = pyridine-4-carboxylic acid) are prepared and characterized by single crystal X-ray diffraction, elemental analysis, IR spectroscopy, and thermal analysis. The results of the single crystal X-ray diffraction analysis reveal that **1** and **2** are isomorphic and two water molecules in the compounds act as the bridging groups of two cobalt or cadmium atoms, forming dinuclear coordination cations. The ligand PCA adopts a monodentate coordination mode and its uncoordinated carboxyl oxygen atom and the protonized nitrogen atom form hydrogen bonds with other ligands, by which the cations are linked into a supramolecular 2D network with hexagonal grids. The polyoxotungstate anions are arranged above and below the cationic grids. A strong emission peak at 420 nm of **2** is attributed to a ligand-metal transition.

Keywords: polyoxotungstate, dimeric coordination cation, hydrogen bonding, supramolecular compound, luminescence.

INTRODUCTION

The design and synthesis of organic-inorganic hybrid materials based on polyoxometalates (POMs) have attracted much attention in recent years not only for their various structures, but also due to their potential applications in many areas such as catalysis, medicine, sorption, electrical conductivity, magnetism, and photochemistry [1—3]. Polyoxometalates (POMs) are considered as an outstanding class of inorganic components to build interesting hybrid materials *via* two kinds of interactions, i.e. coordination covalent bonds and weaker intermolecular forces, due to their rich oxygen atoms in surface. Hydrogen bonding is one of the intermolecular forces leading to supramolecular architectures with versatile organic ligands or metal complex moieties. Recently, the reports on the synthesis of supramolecular compounds increased greatly [4—11].

Recent studies have proven that hydrothermal [12—14] and conventional methods [15, 16] can be used for growing crystals of numerous hybrid compounds based on POMs. Conventional syntheses are always carried out under standard conditions and crystals of good quality are obtained only occasionally. Under hydrothermal conditions, the reduced viscosity of water enhances the diffusion processes so that the solubility and reaction activity of materials increase and a variety of precursors with low solubility may be introduced to the reaction system [17]. Herein we report the synthesis and structures of two new compounds, their thermal stability, and in one case, the luminescent property.

EXPERIMENTAL

All chemicals purchased were of reagent grade and were used without further purification. $H_4SiW_{12}O_{40}$ (SiW_{12}) was synthesized according to the literature [18]. Elemental analyses (Co, Cd, W) were performed on a Leaman inductively coupled plasma (ICP) spectrometer and (C, H, and N) on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectra on KBr pellets were recorded on a Magna-560 FT—IR spectrophotometer in the range 400—4000 cm^{-1}. TG curves were recorded with a Netzsch STA 449C microanalyzer in the nitrogen atmosphere at a heating rate of 10 $°C \cdot min^{-1}$ from 30 °C to 600 °C. The photoluminescence spectrum was measured with a pure solid sample at room temperature using a SPEX FL-2T2 instrument with a 450 W Xenon lamp monochromatized by double grating (1200).

$[Co_2(PCA)_4(H_2O)_6][SiW_{12}O_{40}] \cdot 8H_2O$ (1). Method I: 3.390 g (10 mmol) of $H_4[\alpha\text{-}SiW_{12}O_{40}] \cdot \cdot 20H_2O$, 0.1013 g (4 mmol) $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.2512 g (2 mmol) pyridine-4-carboxylic acid(PCA) were put into 15 ml of distilled water. The pH value of the solution was adjusted to 3.4 with a 1.0 M NaOH solution and then transferred into a 20 ml Teflon-lined autoclave and kept at 160 °C for 4 days. The autoclave was cooled at 10 $°C \cdot h^{-1}$ to room temperature. There was no crystalline product. The reaction mixture was filtered and the filtrate kept at ambient environment for slow evaporation. A week later pink block-shaped crystals of **1** were obtained. The yield based on Co was 42 %. Anal. for $C_{24}H_{44}Co_2N_4O_{62}SiW_{12}$ (**1**) (3732.75): calcd. C 7.72, H 1.19, N 1.50, Co 3.16, W 50.10 (%); found C 7.82, H 0.99, N 1.48, Co 3.21, W 51.05 (%). Selected IR bands (KBr pellet, cm^{-1}): v = 3749 (w), 3422 (vs), 3101 (w), 1596 (m), 1392 (w), 1247 (w), 1014 (w), 971 (m), 923 (s), 795 (vs), 759 (vs), 682 (m), 534 (m).

Method II: 3.390 g (10 mmol) of $H_4[\alpha\text{-}SiW_{12}O_{40}] \cdot 20H_2O$ was dissolved in 30 ml of water at room temperature. Then a boiled solution of 0.1013 g (4 mmol) $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.2512 g (2 mmol) PCA was added slowly with stirring. The pH value of the solution was adjusted to 3.4 with a 1.0 M NaOH solution and the solution was stirred at 80 °C for an hour. After cooling down, insoluble materials were filtered off. About three weeks later, pink crystals of **1** were isolated from the filtrate.

$[Cd_2(PAC)_4(H_2O)_6][SiW_{12}O_{40}] \cdot 8H_2O$ (2). Compound **2** was prepared with similar processes, with 0.800 g (4 mmol) $CdSO_4$ instead of $Co(CH_3COO)_2 \cdot 4H_2O$. Colorless block-shaped crystals were obtained from the solution after about two weeks. The yield was 51 % based on Cd. Anal. $C_{24}H_{32}Cd_2N_4O_{62}SiW_{12}$ (**2**) (3825.51): calcd. C 7.53, H 0.84, N 1.46, Cd 5.88, W 57.65 (%); found C 7.56, H 0.79, N 1.58, Cd 5.79, W 57.72 (%). IR-bands (KBr pellet, cm^{-1}): v = 3439 (vs), 1589 (m), 1391 (w), 1244 (w), 1192(w), 1014 (w), 973 (m), 921 (s), 798 (vs), 762 (vs), 684 (m), 532 (m).

X-ray crystallography. Single crystals of **1** and **2** were sealed in glass tubes. Data collection was carried out on a SMART CCD diffractometer with MoK_α monochromatic radiation (λ = 0.071 Å) at 293 K. Empirical absorption corrections were applied. The structures were solved by Directed Methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package [19]. The positions of hydrogen atoms on carbon atoms were calculated. The crystallographic and structure refinement data of **1** and **2** are summarized in Table 1.

CCDC 713141 for **1** and 726037 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Syntheses. It is the characteristics of the hydrothermal method that made us choose this method in trying to synthesize multidimensional compounds with M—O(POM) covalent bonds. As a result, two compounds $[Co_2(PCA)_4(H_2O)_6][SiW_{12}O_{40}] \cdot 8H_2O$ (**1**) and $[Cd_2(PCA)_4(H_2O)_6][SiW_{12}O_{40}] \cdot 8H_2O$ (**2**) without the M—O(POM) covalent bond have been obtained from the filtrates of the hydrothermal reaction. Now that the compounds crystallized from the solution we explored the possibility of obtaining the product *via* a conventional method. Indeed, the two compounds could be crystallized from an aqueous solution when the conventional method was used. This means the hydrothermal conditions in

Table 1

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

	1	**2**
Empirical formula	$C_{24}H_{28}Co_2N_4O_{60}SiW_{12}$	$C_{24}H_{32}Cd_2N_4O_{62}SiW_{12}$
M_r	3684.53	3835.59
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
a, b, c, Å	14.670(3), 21.020(3), 10.3334(18)	14.7588(14), 21.2883(14), 10.3151(8)
β, deg.	96.269(4)	95.0380(10)
V, Å^3	3167.5(10)	3228.4(4)
Z	2	2
D_{calcd}, g·cm^{-3}	3.863	3.946
T, K	293(2)	293(2)
Absorption coeff. (μ), mm^{-1}	22.343	22.071
F(000)	3272	3412
R_{int}	0.071	0.036
Reflections collected / unique	8037 / 2896	9950 / 4134
Refinement parameters	246	263
θ range for data collection, deg.	1.70—25.03	1.68—28.30
Limiting index	$-17 \le h \le 17$, $-24 \le k \le 10$, $-12 \le l \le 11$	$-19 \le h \le 18$, $-27 \le k \le 23$, $-10 \le l \le 13$
Goodness-of-fit on F^2	0.992	0.993
$R1$, $wR2$ [$I \ge 2\sigma(I_0)$]	0.0504, 0.1122	0.0338, 0.0759
$R1$, $wR2$ (all data)	0.0912, 0.1295	0.0469, 0.0822
Largest diff. peak and hole, e·Å^{-3}	2.744, –2.789	1.501, –2.359

our experiments do not lead to a multidimensional structure with the M—O(POM) covalent bonds, which is consistent with our early works [20].

Crystal structures of compounds 1 and 2. The structure analyses have revealed that compounds **1** and **2** are isomorphic and contain one discrete Keggin-type polyoxoanion $[SiW_{12}O_{40}]^{4-}$ (abbreviated as SiW_{12}, Fig. 1). In the crystals, due to the orientational disorder of the polyoxoanion the central Si atom in the polyoxoanion is at the center of a cube defined by eight oxygen atoms with half-site occupancy. This kind of disorder often appears in $[XM_{12}O_{40}]^{n-}$ Keggin clusters, already explained by Evans and Pope [21].

Due to the isomorphism, only the structure of **1** is described in details here. In **1**, there is one crystallographically independent cobalt atom that is six-coordinated by two carboxyl oxygen atoms from two PCAs, two terminal and two bridging H_2O molecules. A butterfly-like dinuclear cation

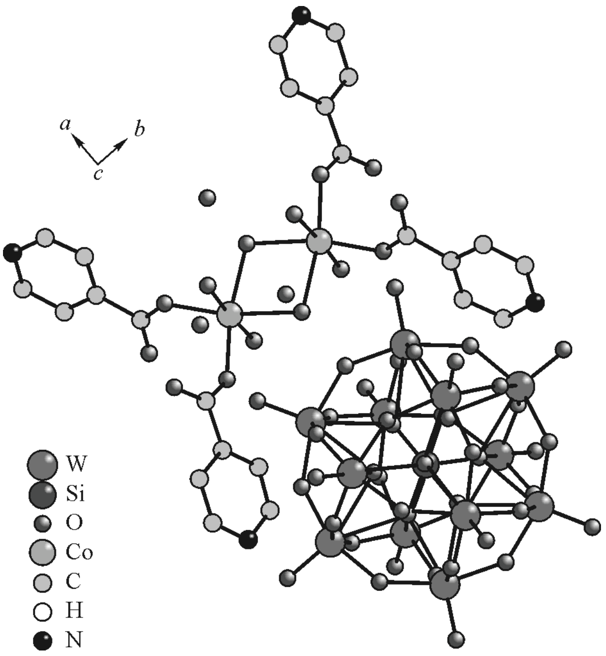

Fig. 1. Ball-stick representation of **1**. All hydrogen atoms are omitted for clarity

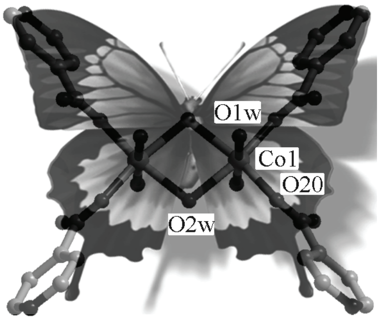

Fig. 2. Dinuclear cation $[Co_2(PCA)_4(H_2O)_4(\mu_2\text{-}H_2O)_2]^{4+}$

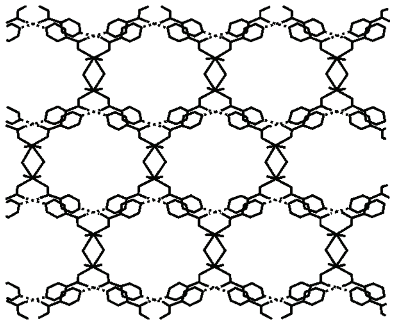

Fig. 3. Layer with hexagonal grids in **1** viewed from the *c* axis

$[Co_2(PCA)_4(H_2O)_4(\mu_2\text{-}H_2O)_2]^{4+}$ is formed (Fig. 2). In the cation, PCA exists in the form of an amphoteric ion: $^{-}OOCC_5H_4NH^{+}$. One of the carboxyl oxygen atoms coordinates to the Co atom, while the another and the protonized nitrogen atom form double hydrogen bonds ($d(N\cdots O) = 2.702$ Å) with other cations in a supramolecular layer with a hexagonal grid in the [002] plane (Fig. 3).

Table 2 gives some bond lengths and bond angles around the M^{2+} ions in the complex cations. The Co^{2+} and Cd^{2+} ions are all in the center of a distorted octahedron, but the $CdO_2(H_2O)_2(\mu_2\text{-}H_2O)_2$ octahedron is more distorted than the $CoO_2(H_2O)_2(\mu_2\text{-}H_2O)_2$ octahedron due to the increase in the radius of the Cd^{2+} ion.

Between the SiW_{12} anions there are hydrogen bonds formed through water molecules, O1···Ow3···O13 and O10···Ow5···O9, with O···O distance of 2.77—2.94 Å, so that the SiW_{12} anions also form supramolecular layers. The anion and cation layers are arranged alternatively, stacked in a supramolecular architecture *via* hydrogen bonds ($d(O13\cdots O2w) = 2.891$ Å) between the polyanions and coordinating water molecules (Fig. 4).The hydrogen bonding interactions of water molecules have lead to a 3D supramolecular architecture of **1**. The structure of **2** is very similar to that of **1**.

Thermal analysis. Thermogravimetric (TG) analyses of **1** and **2** were carried out in the N_2 atmosphere from 30 °C to 600 °C with a heating rate of 10 $°C\cdot min^{-1}$. In the TG curves, the weight losses of 7.9 % for **1** (Fig. 5, *a*) and 8.8 % for **2** (Fig. 5, *b*) below 200 °C are attributed to the loss of absorption,

Table 2

Bond lengths (Å) *and bond angles* (deg.) *around* M^{2+} *ions* [a]

Co^{2+}		Cd^{2+}	
Co—O20#2	1.97(2)	Cd—O14#2	2.171(10)
Co—O20	1.97(2)	Cd—O14	2.171(10)
Co—O1w	2.22(3)	Cd—O1w	2.324(11)
Co—O1w#2	2.22(3)	Cd—O1w#2	2.324(11)
Co—O2w	2.22(18)	Cd—O2w	2.495(7)
Co—O2w#5	2.22(18)	Cd—O2w#5	2.495(7)
O20—Co—O20#2	101.3(15)	O14—Cd—O14#2	124.1(8)
O1W—Co—O1w#2	177.0(2)	O1w—Cd—O1w#2	168.6(5)
O20—Co—O2w#5	89.1(9)	O14—Cd—O2w#2	82.0(5)
O2w—Co—O2w#5	81.1(11)	O2w—Cd—O2w#5	74.0(4)
Co—O2w—Co1#5	98.9(11)	Cd—O2w—Cd1#5	106.0(4)

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[a] Symmetry operation: #2 $-x, y, -z$; #5 $-x, -y, -z$.

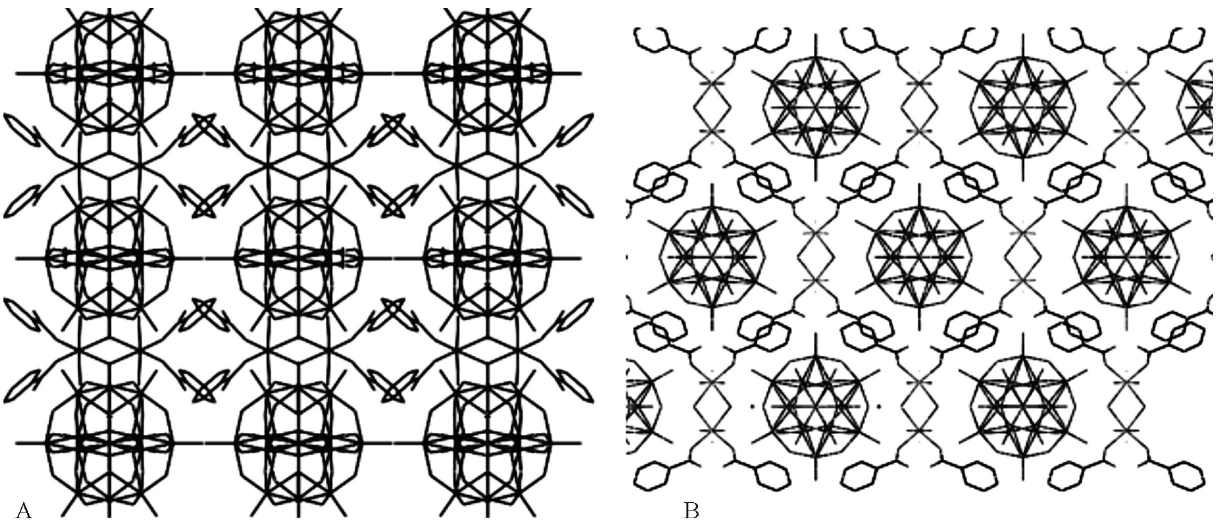

Fig. 4. Stacking of layers in **1** viewed from the *a* axis (A) and from the *c* axis (B). All hydrogen atoms are omitted for clarity

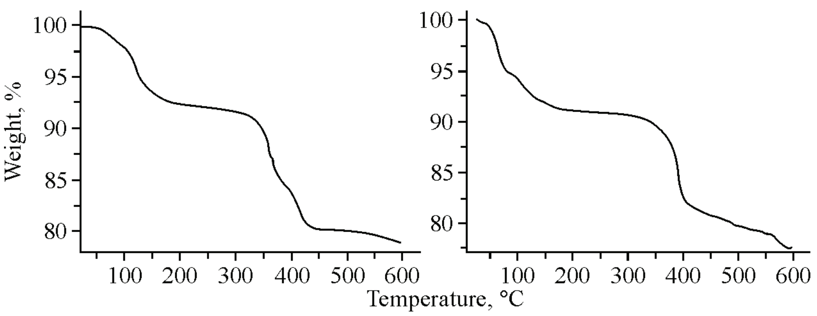

Fig. 5. TG curves of **1** (left) and **2** (right)

lattice and coordinated water molecules (calculated value 6.75 % for the lattice and coordinated water molecules for **1** and 6.6 % for **2**). The release of organic molecules occurred at 300—600 °C with a weight loss of 13.2 % in **1** and 12.6 % in **2** corresponding to the mass of four PAC molecules (13.19 %) for **1** and 12.6 % for **2**.

Luminescence properties The presence of d^{10} metal ions may be one of the important factors contributing to the photoluminescence property, owing to their ability to enhance, shift, or quench the luminescence of organic ligands coordinated to the metal ions. Therefore, the solid-state photoluminescence of **2** at room temperature was investigated. **2** exhibits strong photoluminescence and its emission bands are centered at $\lambda_{\max} = 420$ nm and 469 nm upon excitation at 360 nm (Fig. 6). In order to understand the photoluminescence nature

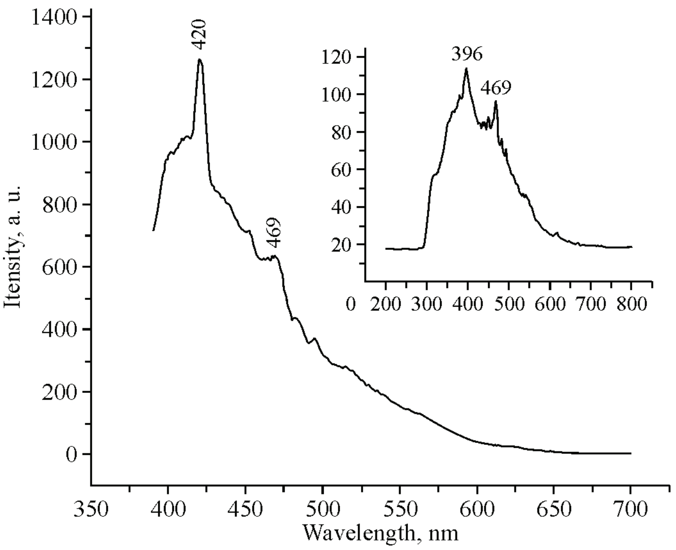

Fig. 6. Emission spectra of **2** and free PCA (inset)

of **2**, the emission spectrum of free PCA was also measured under the same condition (inset in Fig. 6). It displays two emission bands at 396 nm and 469 nm when excited at 254 nm. Comparing the two emission spectra, it becomes clear that the intensity of the emission peaks of **2** are nearly 10 times of that of free PAC; the band (395 nm) of free PCA is quenched or overlapped by the peak at 420 nm; the peak at 420 nm in **2** can be attributed to the ligand-metal transition [22].

CONCLUSIONS

Supramolecular compounds **1** and **2** could be obtained by a hydrothermal method and the conventional method. The bridging of Co and Cd atoms respectively by water molecules results in dinuclear cations in which the organic components PCA act as monodentate ligands and hydrogen bond donors as well as acceptors. The hydrogen bonds between the dinuclear cations create a layer with a hexagonal grid, and the hydrogen bonds between the layers, SiW_{12} anions, and water molecules lead to a supramolecular structure. The combination of the Cd^{2+} ion and PCA gives strong blue luminescence.

REFERENCES

1. *Katsoulis D.E.* // Chem. Rev. – 1998. – **98**. – P. 359 – 387.
2. *Dolbecq A., Dumas E., Mayer C.R., Mialane P.* // Chem. Rev. – 2010. – **110**. – P. 6009 – 6048.
3. *Long D.-L., Tsunashima R., Cronin L.* // Angew. Chem. – 2010. – **122**. – P. 1780 – 1803; Angew. Chem. Int. Ed. – 2010. – **49**. – P. 1736 – 1758.
4. *Pradeep C.P., Long D.-L., Newton G.N.* // Angew. Chem. – 2008. – **120**. – P. 4460 – 4463; Angew. Chem. Int. Ed. – 2008. – **47**. – P. 4388 – 4391.
5. *Li J., Chen Y.-G., Zhang C.-J.* // J. Mol. Struct. – 2009. – **921**. – P. 233 – 238.
6. *Xie Y.-M., Zhang Q.-S., Zhao Z.-G.* // Inorg. Chem. – 2008. – **47**. – P. 8086 – 8090.
7. *Zhao X.-L., Mak T.C.W.* // Inorg. Chem. – 2010. – **49**. – P. 3676 – 3678.
8. *Wang L., Zhu L., Yin P.* // Inorg Chem. – 2009. – **48**. – P. 9222 – 9235.
9. *Duval S., Floquet S., Simonnet-Jégat C.* // J. Amer. Chem. Soc. – 2010. – **132**. – P. 2069 – 2077.
10. *Li Y.-W., Li L.-G., Wang Y.-H.* // Inorg. Chem. – 2009. – **48**. – P. 6452 – 6458.
11. *Nomiya K., Yoshida T., Sakai Y.* // Inorg. Chem. – 2010. – **49**. – P. 8247 – 8254.
12. *Zhai Q.G., Wu X.Y., Chen S.M.* // Inorg. Chim. Acta. – 2007. – **360**. – P. 3484 – 3492.
13. *Yu H.H., Cui X.B., Lu J.* // J. Mol. Struct. – 2008. – **879**. – P. 156 – 161.
14. *Yi Z.H., Cui X.B., Zhang X.* // J. Mol. Struct. – 2008. – **891**. – P. 123 – 128.
15. *Proust A., Thouvenot R., Gouzerh P.* // Chem. Commun. – 2008. – P. 1837 – 1852.
16. *Hu M.-X., Chen Y.-G., Zhang C.-J.* // Cryst. Eng. Comm. – 2010. – **12**. – P. 1454 – 1460.
17. *Xu R., Pang W.* Inorganic Synthesis and Preparation Chemistry. – Beijing: Higher Education Press, 2001. – P. 128 – 130.
18. *Thouvennot R., Fournier M., Franck R., Rocchiccioli-Deltchff C.* // Inorg. Chem. – 1984. – **23**. – P. 596 – 604.
19. *Sheldrick G.M.* // Acta Crystallogr. – 2008. – **A64**. – P. 112 – 122.
20. (a) *Zhang C.-J., Pang H.-J., Hu M.-X.* // J. Solid State Chem. – 2009. – **182**. – P. 1772 – 1779; (b) *Li J., Chen Y.-G., Zhang C.-J., Kong Q.-J.* // J. Mol. Struct. – 2009. – **92**. – P. 233 – 238; (c) *Pang H.-J., Zhang C.-J., Shi D.-M., Chen Y.-G.* // Cryst. Growth & Des. – 2008. – **8**. – P. 4476 – 4480.
21. *Evans H.T. Jr., Pope M.T.* // Inorg. Chem. – 1984. – **23**. – P. 501 – 510.
22. *Sun Y.-Q., Zhang J., Yang G.-Y.* // Chem. Commun. – 2006. – P. 4700 – 4702.