ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 9, pp. 579–584. © Pleiades Publishing, Ltd., 2015.

Coordination Polymer $\{[Cd_2(NiL)_2(Btca)_2] \cdot H_2O\}_n$ of Macrocyclic Oxamide with Benzotriazole-5-Carboxylate: Syntheses, Crystal Structures, and Fluorescence Properties[1]

N. Xin[a, b], **Y. F. Zheng**[a, b], **and Y. Q. Sun**[a, b, *]

[a] *Tianjin Key Laboratory of Structure and Performance for Functional Molecule, College of Chemistry, Tianjin Normal University, Tianjin, 300387 P.R. China*

[b] *Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Tianjin Normal University, Tianjin, 300387 P.R. China*

**e-mail: hxxysyq@mail.tjnu.edu.cn*

Received January 20, 2015

Abstract—A novel heterometallic coordination polymer $\{[Cd_2(NiL)_2(Btca)_4] \cdot H_2O\}_n$ (**I**) (H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,13-dien, H_2Btca = benzotriazole-5-carboxylic acid) was synthesized and structurally characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction (CIF file CCDC no. 1043065). Complex **I** exhibits a two-dimensional network structure formed by Cd_2Ni_2 units via the oxamide and benzotriazole-5-carboxylate bridges. It crystallizes in the monoclinic system, space group $P2_1/c$. The lattice parameters are: a = 1.24488(8), b = 2.75370(19), c = 1.49336(10) Å, β = 103.1070(10)° and V = 4.9859(6) Å^3, Z = 4. The fluorescence properties of compound **I** are also discussed.

DOI: 10.1134/S1070328415080102

INTRODUCTION

Coordination polymers are active fields of research, encompassing chemistry, physics, biology, and material science [1–4]. Especially, the heterometallic coordination polymers have recently attracted much attention because of their fascinating structures and their potential application in magnetism, luminescence, adsorption, catalysis [5–10]. However, heterometallic coordination polymers remain relatively scarce because of the coordinative complexity of the heterometallic ions involved in the self-assembly process [11–16]. Recently, some aromatic multicarboxylate as co-ligands were chosen to design and construct diverse oxamido-bridged heteropolynuclear networks [17–20]. However, those containing oxamide and heterocyclic carboxylate mix bridged polynuclear complexes have been made rarely [17–21].

Among various heterocyclic carboxylate ligands, benzotriazole-5-carboxylate ($Btca^{2-}$) has been used to produce metal-organic frameworks owing to their diverse coordination modes and a great ability to satisfy many metal coordination preferences [22]. Furthermore, the strong π-conjugated system of large benzotriazole ring can increase the stability of structures [17, 23]; and five coordination atoms can potentially serve as hydrogen bond acceptors and donors to assemble supramolecular structure.

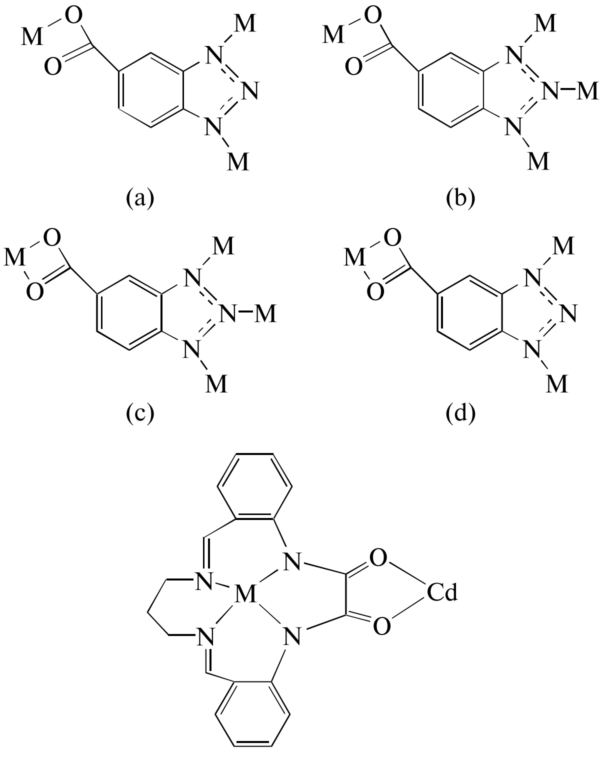
With these facts in mind and in continuation of our interest in heterometallic polynuclear complexes, by using the benzotriazole-5-carboxylate and macrocyclic oxamide complex ligand NiL, a novel 2D heterometallic coordination polymer was firstly obtained. Herein, we report the syntheses, crystal structures and fluorescence properties of the complex $\{[Cd_2(NiL)_2(Btca)_2] \cdot H_2O\}_n$ (**I**). The coordinated modes of the $Btca^{2-}$ (a–d) and the coordinated modes of the macrocylic oxamide complex ligand NiL (e) are given in Scheme:

---

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement of complex **I**

Parameter	Value
Fw	1347.20
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.4488(8)
b, Å	27.5370(19)
c, Å	14.9336(10)
β, deg	103.1070(10)
V, Å^3	4985.9(6)
ρ_{calcd}, g/cm^3	1.795
Z	4
F(000)	2696
μ, mm^{-1}	1.660
Crystal size, mm	0.18 × 0.17 × 0.16
T, K	173(2)
θ Range, deg	1.58–25.01
Index ranges *hkl*	$-14 \le h \le 13$, $-32 \le k \le 31$, $-17 \le l \le 15$
Reflection collected	28729
R_{int}	0.0637
Reflections with $I > 2\sigma(I)$	8792
Number of parameters	739
GOOF	1.063
R_1, wR_2 ($I > 2\sigma(I)$)	0.0423, 0.0882
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	1.205/–0.536



(a) (b) (c) (d)

(e: M = Ni)

Scheme.

EXPERIMENTAL

All the starting reagents were of A. R. grade and were used as purchased. The complex ligand NiL was prepared as described elsewhere [24]. Analyses of C, H, and N were determined on a Perkin-Elmer 240 Elemental analyzer. IR spectrum was recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} range. XRPD spectra for the power were recorded with a Model D/MAX-2550V, Rigaku, Japan. Test the fluorescence properties were recorded with the RF-5301PC fluorescence.

Synthesis of $\{[Cd_2(NiL)_2(Btca)_2] \cdot H_2O\}_n$ (I). A mixture of $CdSO_4 \cdot 6H_2O$ (0.01 mmol, 76.5 mg), H_2Btca (0.01 mmol, 16.0 mg), NiL (0.05 mmol, 19.7 mg), H_2O (10 mL) and CH_3OH (4 mL) was put into an 18 mL Teflon-lined reactor, and the pH value of the solution was adjusted to about 7–8 with triethylamine. After stirring, the mixture was heated at 150°C for 72 h. Then the reaction system was cooled to room temperature during 72 h, and brown-red crystal of the compound was isolated by filtering and washing with water.

For $C_{52}H_{40}N_{14}O_9Cd_2Ni_2$

anal. calcd., %:	C, 46.36;	H, 2.99;	N, 14.56.
Found, %:	C, 46.35;	H, 2.97;	N, 14.54.

Main IR bands: 3436 s. br, 1634 s, 1584 s, 1553 s, 1475 m, 1384 s, 1311 m, 1270 m, 1160 w, 1123 w, 1082 w, 956 w, 846 w, 793 s, 750 s.

X-ray crystallography. Single crystal X-ray diffraction analyses of **I** were carried out on a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using ϕ–ω scan technique at room temperature. Semi-empirical absorption corrections were applied using SADABS. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL. Hydrogen atoms were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. Crystal data collection and refinement parameters are given in Table 1, and selected bond lengths and angles for **I** is listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 1043065; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

By using benzotriazole-5-carboxylate and macrocylic oxamide mixed ligands as the metal linker, the new complex **I** has been synthesized under solvothermal condition. The results reported here and previously reported [17, 25], clearly show that the solvothermal

Table 2. Selected bond lengths (Å) and bond angles (deg) for complex **I***

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–O(7)$^{\#1}$	2.212(3)	Cd(2)–O(3)	2.468(3)
Cd(1)–N(9)$^{\#2}$	2.231(4)	Ni(1)–N(7)	1.878(4)
Cd(1)–N(12)	2.254(4)	Ni(1)–N(6)	1.880(4)
Cd(1)–O(2)	2.267(3)	Ni(1)–N(8)	1.881(4)
Cd(1)–O(1)	2.426(3)	Ni(1)–N(5)	1.910(4)
Cd(2)–N(14)	2.226(4)	Ni(2)–N(2)	1.884(4)
Cd(2)–O(5)	2.259(3)	Ni(2)–N(1)	1.886(4)
Cd(2)–O(4)	2.271(3)	Ni(2)–N(3)	1.887(4)
Cd(2)–N(11)$^{\#3}$	2.303(4)	Ni(2)–N(4)	1.905(4)
Cd(2)–O(6)	2.440(3)		
Angle	ω, deg	Angle	ω, deg
O(7)$^{\#1}$Cd(1)N(9)$^{\#2}$	103.20(13)	N(11)$^{\#3}$Cd(2)O(6)	87.08(12)
O(7)$^{\#1}$Cd(1)N(12)	98.76(13)	N(14)Cd(2)O(3)	82.71(12)
N(9)$^{\#2}$Cd(1)N(12)	116.26(13)	O(5)Cd(2)O(3)	94.28(12)
O(7)$^{\#1}$Cd(1)O(2)	145.74(11)	O(4)Cd(2)O(3)	69.05(11)
N(9)$^{\#2}$Cd(1)O(2)	100.04(13)	N(11)$^{\#3}$Cd(2)O(3)	156.84(12)
N(12)Cd(1)O(2)	93.07(13)	O(6)Cd(2)O(3)	97.35(11)
O(7)$^{\#1}$Cd(1)O(1)	78.60(11)	N(7)Ni(1)N(6)	90.85(19)
N(9)$^{\#2}$Cd(1)O(1)	154.93(13)	N(7)Ni(1)N(8)	92.56(18)
N(12)Cd(1)O(1)	87.73(12)	N(6)Ni(1)N(8)	165.46(18)
O(2)Cd(1)O(1)	69.83(11)	N(7)Ni(1)N(5)	161.59(18)
N(14)Cd(2)O(5)	105.81(13)	N(6)Ni(1)N(5)	94.07(18)
N(14)Cd(2)O(4)	102.01(13)	N(8)Ni(1)N(5)	87.10(17)
O(5)Cd(2)O(4)	145.33(12)	N(2)Ni(2)N(1)	91.25(17)
N(14)Cd(2)N(11)$^{\#3}$	99.97(14)	N(2)Ni(2)N(3)	91.48(17)
O(5)Cd(2)N(11)$^{\#3}$	106.89(13)	N(1)Ni(2)N(3)	166.54(17)
O(4)Cd(2)N(11)$^{\#3}$	87.97(13)	N(2)Ni(2)N(4)	162.55(17)
N(14)Cd(2)O(6)	161.98(12)	N(1)Ni(2)N(4)	86.79(17)
O(5)Cd(2)O(6)	56.18(11)	N(3)Ni(2)N(4)	94.45(17)
O(4)Cd(2)O(6)	94.75(11)		

* Symmetry codes: $^{\#1}$ $-x + 1, -y, -z + 2$; $^{\#2}$ $x, y, z + 1$; $^{\#3}$ $x, -y + 1/2, z + 1/2$.

synthesis is a powerful and versatile tool for preparing macrocyclic oxamide and organic acid bridged heterometallic coordination polymers. Considering that the deprotonated degree of H_2Btca may play a vital role in constructing the extended structure, a series of experiments were performed by varying the pH values of the reaction system in the range of 4–9. The results show that the complex was obtained at relatively higher pH (7–8). Complex **I** is stable under the ambient conditions and insoluble in common solvents, such as water, alcohol, and acetonitrile.

The IR spectra of complex I clearly show the existence of benzotriazole-5-carboxylate and macrocyclic oxamido moieties in the molecules respectively. The IR spectra of **I** exhibit broad absorption bands in the range 3360–3450 cm^{-1}, demonstrating the existence of wa-

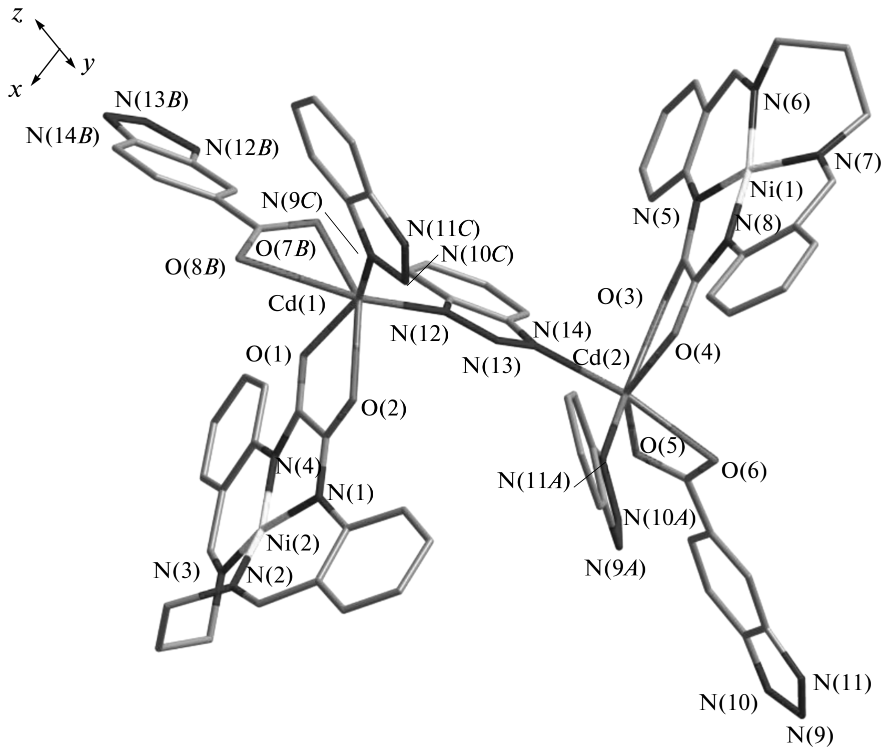


Fig. 1. Perspective view of asymmetric structure of Cd_2Ni_2 unit in **I**: (*A*) $x, 0.5 - y, 0.5 + z$; (*B*) $1 - x, -y, 2 - z$; (*C*) $x, y, 1 + z$.

ter [26], and the spectra exhibit strong absorption bands in the region 1629–1613 and 1588–1563 cm^{-1} due to the ν(C=O) and the ν(C=N) vibrations, respectively [26, 27]. The IR spectra of it show no bands in the region 1680–1720 cm^{-1}, indicating complete deprotonation of the carboxyl groups.

To confirm the phase purity of the obtained complex, the original samples were characterized by XRPD at room temperature. The experimental spectra of complex **I** is almost consistent with those of simulated based on the structure models derived from single-crystal X-ray diffraction data, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the power.

The ligands involved in this research are listed in Scheme (d) and (e). Single-crystal X-ray analysis revealed that **I** was a complicated two-dimensional polymer consisting of crystallographic independent two cadmium(II) and two nickel(II) ions. A perspective view of the structure is depicted in Fig. 1. In structure **I**, each Ni^{2+} ion is coordinated by four nitrogen atoms from the macrocyclic organic ligand, and the coordination geometry of Ni(II) is a distorted square planarity. The Ni(1) ion is displaced from the least-square plane by 0.0249 Å, and the deviations of the four donor atoms (N(5), N(6), N(7), N(8)) from their mean plane are –0.2750, 0.2553, –0.2742 and 0.2689 Å, respectively. The Ni(2) ion is displaced from the least-square plane by –0.0235 Å, and the deviations of the four donor atoms (N(1), N(2), N(3), N(4)) from their mean plane are –0.2536, 0.2554, –0.2347 and 0.2565 Å, respectively. The Cd^{2+} ion coordinates with two oxygen atoms of the macrocyclic oxamide ligand, two nitrogen atoms from two $Btca^{2-}$ anions and two oxygen atoms from another $Btca^{2-}$ anion. The coordination spheres of the cadmium centers are distorted octahedral geometry. Two adjacent metal ions (Cd(1), Cd(2)) are connected by a benzotriazole-5-carboxylate to construct a bimetallic unit [Cd_2], in which the non-bonding distance of Cd···Cd is 6.3489(5) Å. Two nickel ions and [Cd_2] unit are interlinked through the macrocyclic oxamide ligand to form heterotetranuclear [Ni_2Cd_2] unit. Adjacent [Cd_2Ni_2] units are connected by $Btca^{2-}$ bridging ligands to form 2D infinite plane, as shown in Fig. 2. In 2D plane structure, the $Btca^{2-}$ ligand acts as a tetradentate connector to bridge three Cd^{2+} ions (Scheme, d), and the relationship of the adjacent $Btca^{2-}$ with respect to each other is *anti*. Furthermore, the 2D infinite plane are linked together with C–H···O hydrogen bonding to form a 3D framework (Fig. 3). The data of hydrogen bonds of complex **I** are listed in Table 3.

The excitation and fluorescence spectra of the complex as well as ligands are measured in their DMF solutions (the experimental concentration of ligands and complexes is 4×10^{-3} mmol L^{-1}). In order to understand the nature of the emission bands of complex **I**, the

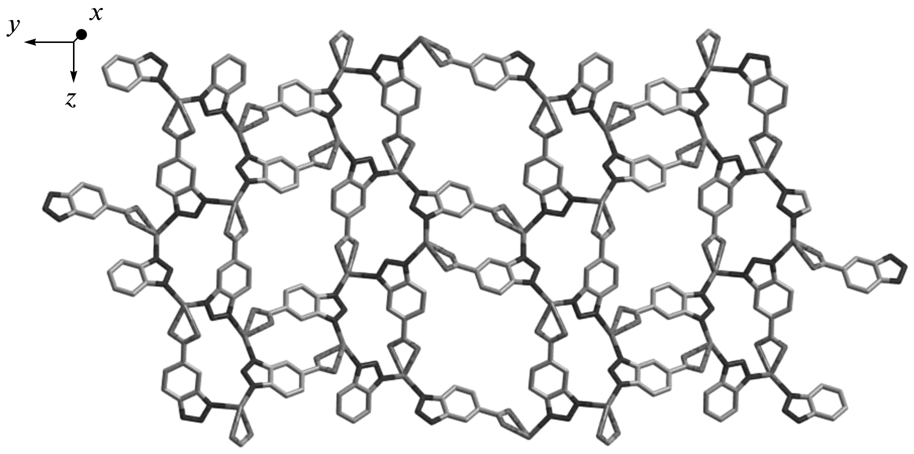


Fig. 2. View of the two-dimensional network structures of **I** through a $Btca^{2-}$ quadridentate connector (some hydrogen atoms and NiL ligands were removed for clarity).

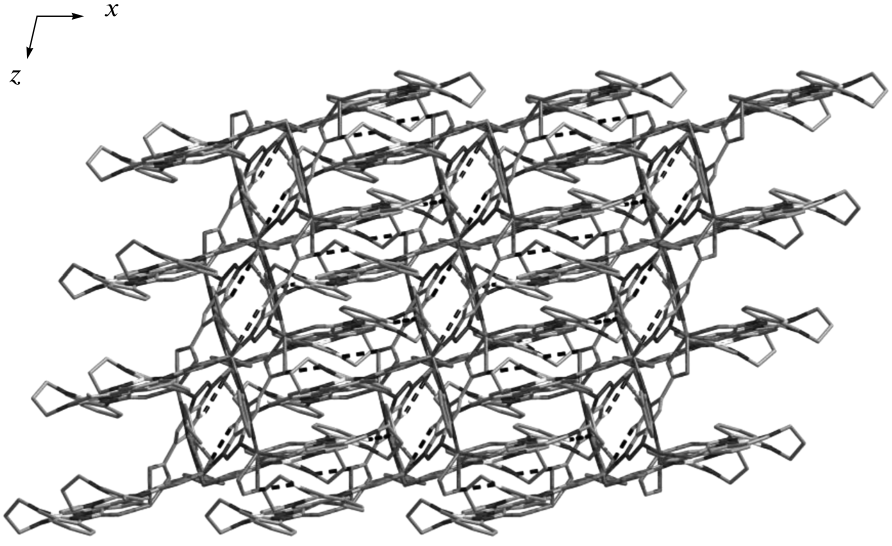


Fig. 3. View of the self-assembly 3D superamolecular architecture through C–H···O hydrogen bond interactions in **I**.

fluorescent spectra of complex **I**, H_2Btca, and NiL were measured using the excitation wavelength of 306 nm under room temperature. The fluorescence spectra were given in Fig. 4. The main emission band for the H_2Btca is at 368 nm. The main emission bands for complex **I** are at 337 and 364 nm. For H_2Btca and complex **I**, these bands may be attributed to the $\pi^* \to \pi$ and/or $\pi^* \to n$ transitions [28, 29]. Compared with the emission spectra of the H_2Btca, the fluorescence intensity decreased slightly in complex **I**. The reasons of fluorescence quenching are that H_2Btca coordinated with Cd^{2+} ions. Moreover, the tidy blue-shifted emissions were observed in complex **I** comparing with the emission spectra of the H_2Btca and NiL (339 nm). Thus, coordination polymer $\{[Cd_2(NiL)_2(Btca)_2] \cdot H_2O\}_n$ adjust the emission wavelength and intensity of H_2Btca through incorporation of Cd(II) and Ni(II) centers.

Table 3. Geometric parameters of hydrogen bonds for complex **I**

D–H···A	Diatance, Å			Angle DHA, deg
	D–H	H···A	D···A	
C(12)–H(12)···O(6)	0.95	2.33	3.139(6)	143
C(37)–H(37)···O(8)	0.95	2.34	3.174(7)	146
C(43)–H(43)···O(7)	0.95	2.37	3.253(11)	143

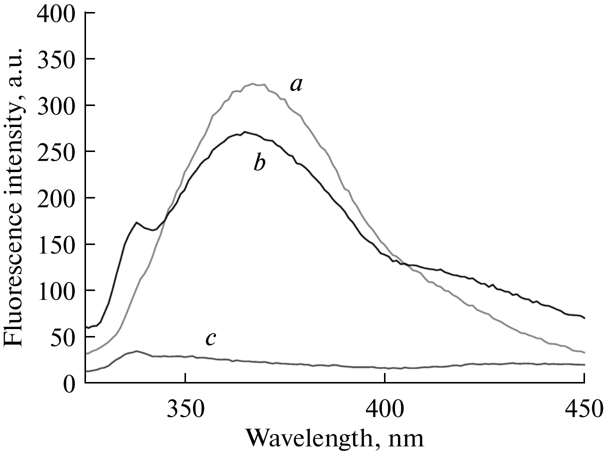


Fig. 4. The fluorescence spectrum of H_2Btca (*a*), complex **I** (*b*), and NiL (*c*) (λ_{ex} = 306 nm).

REFERENCES

1. Desiraju, G.R., *Angew. Chem. Int. Ed. Engl.*, 1995, vol. 34, p. 2311.
2. Lehn, J.M., *Superamol. Chem.*, Weinheim: VCH, 1995.
3. Desiraju, G.R., *Chem. Commun.*, 1997, p. 1475.
4. Tang, J.K., Li, Y.Z., Wang, Q.L., et al., *Inorg. Chem.*, 2002, vol. 4, p. 2188.
5. Guo, Z.G., Cao, R., Wang, X., et al., *J. Am. Chem. Soc.*, 2009, vol. 131, p. 6894.
6. Yoshizawa, M., Tamura, M., and Fujita, M., *Science*, 2006, vol. 312, p. 251.
7. James, S.L., *Chem. Soc. Rev.*, 2003, vol. 32, p. 276.
8. Rosi, N.L., Eckert, J., Eddaoudi, M., et al., *Science*, 2003, vol. 300, p. 1127.
9. Nune, S.K., Thallapally, P.K., Dohnalkova, A., et al., *Chem. Commun.*, 2010, vol. 46, p. 4878.
10. Thallapally, P.K., Tian, J., Kishan, M.R., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, p. 16842.
11. Stork, J.R., Thoi, V.S., and Cohen, S.M., *Inorg. Chem.*, 2007, vol. 46, p. 11213.
12. Zhang, Y., Chen, B., Fronczek, F.R., and Maverick, A.W., *Inorg. Chem.*, 2008, vol. 47, p. 4433.
13. Westerhausen, M., *Dalton Trans.*, 2006, p. 4755.
14. Zhang, B., Ni, Z.H., Cui, A.L., and Kou, H.Z., *New J. Chem.*, 2006, vol. 30, p. 1327.
15. Chen, B., Fronczek, F.R, and Maverick, A.W., *Inorg. Chem.*, 2004, vol. 43, p. 8209.
16. Chen, B., Fronczek, F.R., and Maverick, A.W., *Chem. Commun.*, 2003, p. 2166.
17. Sun, Y.Q., Fan, L.L., Gao, D.Z., et al., *Dalton Trans.*, 2010, vol. 39, p. 9654.
18. Sun, Y.Q., Fan, L.L., Gao, D.Z., and Zhang, G.Y., *Z. Anorg. Allg. Chem.*, 2010, vol. 636, p. 846.
19. Sun, Y.Q., Gao, D.Z., Xu, Y.Y., et al., *Dalton Trans.*, 2011, vol. 40, p. 5528.
20. Sun, Y.Q., Xu, Y.Y., Gao, D.Z., et al., *Dalton Trans.*, 2012, vol. 41, p. 5704.
21. Sun, Y.Q., Gao, D.Z., Dong, W., et al., *Eur. J. Inorg. Chem.*, 2009, p. 2825.
22. Xiao, Juan, Liu, Bao-Yu, Wei, Gang, and Huang, Xiao-Chun, *Inorg. Chem.*, 2011, vol. 50, p. 11032.
23. Chen, P.K., Che, Y.X., Zheng, J.M., and Batten, S.R., *Chem. Mater.*, 2007, vol. 19, p. 2162.
24. Black, D.S.C. and Corrie, H., *Inorg. Nucl. Chem. Lett.*, 1976, vol. 12, p. 65.
25. Sun, Y.Q., Fan, L.L., Gao, D.Z., and Zhang, G.Y., *Z. Anorg. Allg. Chem.*, 2010, vol. 636, p. 846.
26. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: John Wiley, 1997.
27. Lloret, F., Journaux, Y., and Julve, M., *Inorg. Chem.*, 1990, vol. 29, p. 3967.
28. Allendorf, M.D., Bauer, C.A., Bhakta, R.K., and Houk, R.T., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1330.
29. Hathaway, B.J., *Struct. Bond.*, 1973, vol. 14, p. 49.