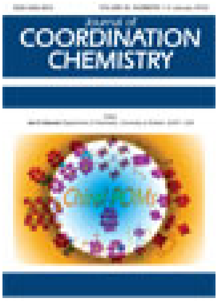
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:40
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Solvothermal synthesis, structure, and luminescence of a 3-D Cd(II) complex assembled with biphenyl-2,5,2′,5′-tetracarboxylic acid involving in situ ligand reaction

Shengqi Guo [a], Dan Tian [a], Yuhui Luo [a] & Hong Zhang [a]
[a] Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China

Published online: 20 Jan 2012.

To cite this article: Shengqi Guo, Dan Tian, Yuhui Luo & Hong Zhang (2012) Solvothermal synthesis, structure, and luminescence of a 3-D Cd(II) complex assembled with biphenyl-2,5,2′,5′-tetracarboxylic acid involving in situ ligand reaction, Journal of Coordination Chemistry, 65:2, 308-315, DOI: 10.1080/00958972.2011.652099

To link to this article: http://dx.doi.org/10.1080/00958972.2011.652099

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 65, No. 2, 20 January 2012, 308–315

Taylor & Francis
Taylor & Francis Group

Solvothermal synthesis, structure, and luminescence of a 3-D Cd(II) complex assembled with biphenyl-2,5,2′,5′-tetracarboxylic acid involving *in situ* ligand reaction

SHENGQI GUO, DAN TIAN, YUHUI LUO and HONG ZHANG*

Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China

(*Received 14 July 2011; in final form 11 November 2011*)

A 3-D metal-organic framework $[Cd_3(L)_2(DMF)_2]\cdot 2H_2O\cdot 2DMF$ (**1**) ($H_3L = $ 2-(dimethylcarbamoyl)biphenyl-5,2′,5′-tricarboxylic acid, DMF = *N*,*N*-dimethylformamide) with trinuclear Cd(II) units has been prepared. Complex **1** is a (3, 6)-connected $(4^2\cdot 6)_2(4^4\cdot 6^2\cdot 8^8\cdot 10)$ coordination net, which results from the solvothermal *in situ* formation of a new asymmetric ligand, 2-(dimethylcarbamoyl)biphenyl-5,2′,5′-tricarboxylic acid (H_3L), through amidation of biphenyl-2,5,2′,5′-tetracarboxylic acid (H_4bptc). Additionally, the luminescence of **1** has been investigated.

Keywords: Trinuclear Cd(II) unit; Amidation reaction; Topology; Photoluminescent

1. Introduction

Metal–organic frameworks (MOFs) have received interest for potential applications, fascinating architectures, and topologies [1–3]. Ligands play crucial roles for design and synthesis of the target coordination polymers. Biphenyl-tetracarboxylic acid ligands have proven to be good candidates in the preparation of MOFs [4, 5] and are versatile ligands for the construction of high-dimensional MOFs with fascinating topologies [6, 7]. The carboxylates can form metal-carboxylate clusters which possess larger sizes, more coordination sites, and smaller steric hindrance for ligands with respect to simple metal centered nodes [8, 9]. Following previous studies [10–12], here we choose biphenyl-2,5,2′,5′-tetracarboxylic acid (H_4bptc) as the ligand for the following reasons: (1) adjacent "dense" carboxyl groups reacting with metal ions can form various coordination modes and have high potential to generate metal clusters and (2) among reported networks of metal carboxylates, biphenyl-2,5,2′,5′-tetracarboxylic acid remains largely unexplored [13, 14].

MOFs are generated by reactions of pre-synthesized or commercially available ligands with metal ions [15]. *In situ* ligand synthesis is of interest in coordination chemistry and organic chemistry for the preparation of crystalline coordination

---

*Corresponding author. Email: zhangh@nenu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.652099

complexes, and for the discovery of new organic reactions [16]. In the past few years, Zhang, Chen and Xiong *et al.* have published reviews about *in situ* ligand syntheses in coordination chemistry [15, 17, 18]. There are few examples on amidation of a carboxylate ligand.

Hydro(solvo)thermal reactions provide the capability of *in situ* ligand synthesis due to their reaction conditions [15, 17]. Even insoluble reagents which are unsuitable to synthesize complexes by conventional means can be used in this method, and in the reaction process metastable compounds may be produced and, thus, are available for crystal growth [19–22]. Herein, we report a new metal–organic complex $[Cd_3(L)_2(DMF)_2] \cdot 2H_2O \cdot 2DMF$ (**1**) with trinuclear Cd(II) units, which was obtained by the reaction of $CdCl_2 \cdot 2.5H_2O$ and H_4bptc based on solvothermal reactions. Complex **1** displays a new (3, 6)-connected topology with the Schläfli symbol $(4^2 \cdot 6)_2(4^4 \cdot 6^2 \cdot 8^8 \cdot 10)$. The biphenyl-2,5,2′,5′-tetracarboxylic acid ligand formed through an amidation reaction under solvothermal conditions.

2. Experimental

2.1. *Materials and instrumentation*

Chemicals were purchased from commercial sources and used without purification. The FT-IR spectra were measured in KBr pellets from 4000 to 400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Thermal Analyzer under N_2 with a heating rate of 10°C min^{-1}. Solid-state luminescence spectra were measured on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

2.2. *Synthesis*

2.2.1. Synthesis of $[Cd_3(L)_2(DMF)_2] \cdot 2H_2O \cdot 2DMF$ (1). A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.0206 g, 0.09 mmol), H_4bptc (0.0199 g, 0.06 mmol), H_2O (1 mL), and DMF (20 mL) was placed in a Teflon reactor (20 mL) and heated at 160°C for 4 days. After the sample was gradually cooled to room temperature at a rate of 10°C h^{-1}, colorless block crystals of **1** were obtained in 45% yield based on H_4bptc. Anal. Calcd for $C_{48}H_{56}Cd_3N_6O_{20}$ ($M_r = 1374.19$): C, 41.95; H, 4.11; N, 6.12. Found (%): C, 41.83; H, 4.24; N, 6.01. IR (4000–400 cm^{-1}): 3431(m), 1605(s), 1416(s), 1080(m), 858(s), 811(s), 722(s), 630(s), 500(s).

2.3. *X-ray crystallography*

The X-ray intensity data for **1** were collected on a Bruker SMART APEX CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 273(2) K. The crystal structure was solved by direct methods and refined employing full-matrix least-squares on F^2 (SHELXTL-97). The non-hydrogen atoms were refined with anisotropic displacement

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{48}H_{56}Cd_3N_6O_{20}$
Formula weight	1374.19
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.6784(9)
b	13.5433(9)
c	17.1322(12)
α	77.839(1)
β	76.404(1)
γ	80.614(1)
Volume ($Å^3$), Z	2775.1(3), 2
Absorption coefficient (mm^{-1})	1.218
Calculated density ($g\,cm^{-3}$)	1.645
R(int)	0.0255
Goodness-of-fit on F^2	1.048
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0502
$wR_2{}^b$ $[I > 2\sigma(I)]$	0.1255

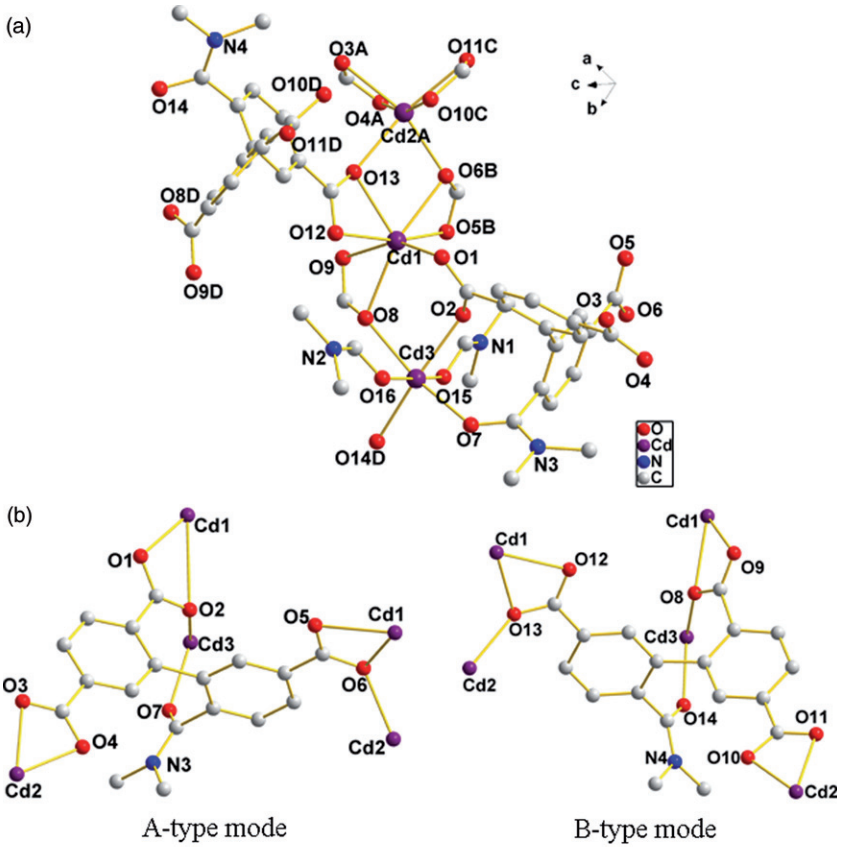
$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $^bwR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

parameters except for disordered guest DMF in **1**. Disordered C, O, N, and H atoms of uncoordinated DMF molecules were split over two positions, with total occupancy of 1, and were refined using DFIX. All hydrogen atoms attached to ligands and DMF molecules were geometrically placed, and those of free water were not located. Crystal data and details of the structure determination for **1** are listed in table 1 and selected bond lengths and angles are listed in table S1.

3. Results and discussion

3.1. *Description of the structure*

$[Cd_3(L)_2(DMF)_2]\cdot 2H_2O\cdot 2DMF$ (1). Single-crystal X-ray diffraction shows that **1** crystallizes in the triclinic space group $P1$ and possesses a 3-D coordination network composed of trinuclear Cd(II) units and two kinds of L^{3-}. As shown in figure 1(a), the non-centrosymmetric linear trinuclear Cd(II) unit consists of a central Cd1 coordinated by seven carboxylate oxygen atoms of four different L^{3-} ligands with pentagonal bipyramidal geometry and two outer Cd2A and Cd3. Cd2 is coordinated by six carboxylate oxygen atoms from four different L^{3-} ligands in a distorted octahedral geometry. Cd3 also exhibits a slightly distorted octahedral geometry, coordinated by two carboxylate oxygen atoms (O2 and O8) and two amide oxygen atoms (O7 and O14D) of two L^{3-} ligands and two amide oxygen atoms (O15 and O16) from two DMF molecules. Cd1 is bridged to neighboring Cd2A and Cd3 atoms by one –O–C–O– bridge and three μ_2–$O_{carboxyl}$ (O6B, O8, and O13) to afford a trinuclear Cd(II) unit with Cd1 $\cdots$ Cd2 and Cd1 $\cdots$ Cd3 distances of 3.660 and 3.971 Å. Each L^{3-} links three trinuclear Cd(II) units using its three carboxylates and one amide to generate a 3-D framework (figure 2b). Trinuclear Cd(II) unit and L^{3-} can be considered as



A-type mode

B-type mode

Figure 1. (a) Coordination environments of Cd(II) in **1**. Hydrogen atoms are omitted for clarity. Symmetry codes: A, $x+1$, y, z; B, $-x+1$, $-y+1$, $-z$; C, x, $y-1$, z; D, $-x+1, -y+1, -z+1$. (b) The coordination modes of L^{3-} in **1**.

six-connected and three-connected nodes, respectively (figure 2a). The 3-D network can be rationalized as a (3, 6)-connected $(4^2 \cdot 6)_2(4^4 \cdot 6^2 \cdot 8^8 \cdot 10)$ topology (figure 2c).

In **1**, two types of μ_5-bridged L^{3-} exist (A-type and B-type, figure 1b) which show the same coordination mode, three carboxylates of each L^{3-} adopt two coordination modes: μ_2-$\eta^1:\eta^2$ tridentate chelating-bridging for the 2′ and 5-substituted carboxylates and μ_1-$\eta^1:\eta^1$ bidentate chelating for the 5′-carboxylate. The dihedral angle between two benzene rings of A-type L^{3-} is 87.46° while for B-type, it is 73.46°.

Hydro(solvo)thermal reactions provide the potential of *in situ* ligand synthesis due to reaction conditions [15, 23]. In the synthesis of **1**, the presence of DMF and H_2O under solvothermal conditions results in amidation reaction of biphenyl-2,5,2′,5′-tetracarboxylic acid (H_4bptc). The reaction is shown in scheme 1, at higher temperature DMF slowly hydrolyzes giving formic acid and dimethylamine, and then dimethylamine reacts with H_4bptc to give 2-(dimethylcarbamoyl)biphenyl-5,2′,5′-tricarboxylic acid (H_3L). Therefore, the high temperature, pressure and long reactions promote the *in situ* synthesis of L^{3-} in **1**. To our knowledge, the *in situ* generated L^{3-} is the first ligand derived from H_4bptc under solvothermal conditions.

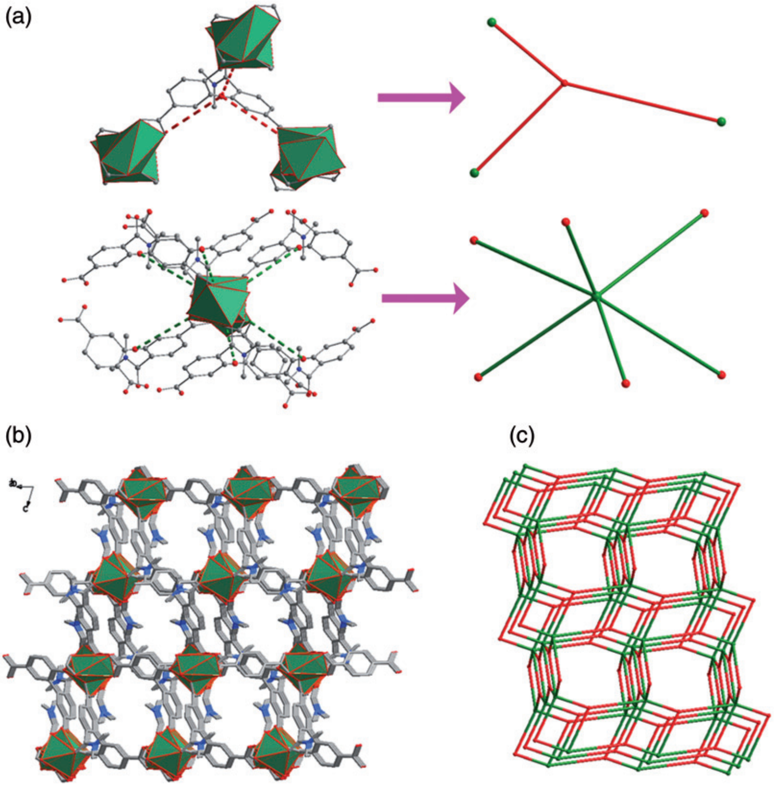
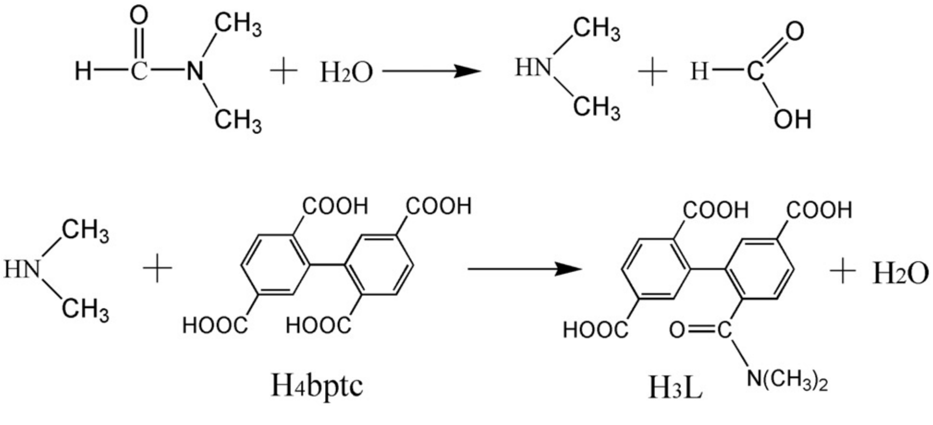


Figure 2. (a) Schematic representations of the three- and six-connected nodes. (b) Polyhedral view of the 3-D structure in **1**. (c) Schematic illustration of the $(4^2 \cdot 6)_2(4^4 \cdot 6^2 \cdot 8^8 \cdot 10)$ topology of the 3-D network of **1**.



Scheme 1. The possible reaction between biphenyl-2,5,2′,5′-tetracarboxylic acid and DMF under solvothermal condition.

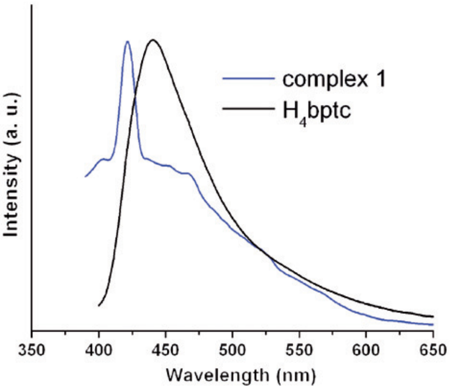


Figure 3. The emission spectra of **1** at room temperature.

A number of Cd(II) coordination polymers from polycarboxylates have been obtained, but both composition and structural features of **1** are different from those reported. For example, a polynuclear complex $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}_n$ (H_2IDC = imidazole-4,5-dicarboxylic acid, Bipy = 4,4′-bipyridine) [24] was prepared under solvothermal condition and the complex exhibited a 3-D structure with channels along the *c*-axis in which free solvent molecules are located. Complexes $[Cd_2(bptc)(bpimb)(H_2O)] \cdot 2H_2O$ and $[Cd_2(bptc)(bpib)] \cdot 4H_2O$ [23] were synthesized by reactions of the corresponding cadmium salts with biphenyl-3,3′,4,4′-tetracarboxylic acid (H_4bptc) and N-containing auxiliary ligands and both present binodal high-connected topologies. Complex $\{[Cd(H_2btc)(terpy)] \cdot H_2O\}_n$ [25] was obtained by reaction of CdO with biphenyl-2,2′,4,4′-tetracarboxylic acid (H_4bptc) and terpyridine in water and features a 3-D supramolecular framework. Complexes $\{[Cd_4(bpea)_4(IP)_8] \cdot 6H_2O\}_n$ and $\{[Cd_{1.5}(suc)_{1.5}(IP)_{1.5}] \cdot 4H_2O\}_n$ (bpea = biphenylethene-4,4′-dicarboxylate, H_2suc = succinic acid and IP = 1H-imidazo[4, 5-f][1, 10]-phenanthroline) [26] also show interesting supramolecular frameworks. Structural differences can be attributed to different ligands used and different synthetic conditions.

3.2. *Photoluminescent property*

The luminescent properties of free H_4bptc and **1** at room temperature are depicted in figure 3. H_4bptc displays an emission at 439 nm upon excitation at 377 nm. Complex **1** exhibits a distinct emission at 423 nm upon excitation at 367 nm, tentatively attributed to intraligand $\pi-\pi^*$ transitions of H_4bptc. Comparing with free H_4bptc, the significantly blue shifted emission for **1** is observed. It is possible that a combination of several factors together, including O-donor ligand chelation to the metal centers, effectively increases the rigidities of the ligands and reduces loss of energy by radiationless decay [25, 26], as well as amidation reaction and deprotonation of H_4bptc.

3.3. *Thermal analysis*

The thermal stability of **1** was investigated by TGA under nitrogen with a heating rate of 10°C min^{-1} (figure S1). In **1**, the first weight loss, 50–130°C, corresponds to loss of two guest water molecules and two guest DMF (Obsd 12.13%, Calcd 13.26%). The second weight loss of 62.79% (Calcd 62.20%) from 180 to 560°C corresponds to decomposition of L^{3-} and coordinated DMF. The remaining weight may be attributed to the formation of CdO (Obsd 25.08%, Calcd 24.54%).

4. Conclusion

We have demonstrated a 3-D framework with (3, 6)-connected topology, in which trinuclear Cd(II) unit and L^{3-} are six-connected and three-connected nodes. In this study, a new 2-(dimethylcarbamoyl)biphenyl-5,2′,5′-tricarboxylic acid (H_3L) from biphenyl-2,5,2′,5′-tetracarboxylic acid (H_4bptc) precursor has been synthesized through *in situ* ligand transformation under solvothermal conditions, providing a useful strategy to construct coordination complexes or MOFs *via in situ* ligand synthesis.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 804581 for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgments

We gratefully acknowledge financial support by the NSF of China (Nos. 21071027 and 20771023), the China High-Tech Development 863 Program (No. 2007AA03Z218), and analysis and testing foundation of Northeast Normal University.

References

[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange. *Acc. Chem. Res.*, **38**, 217 (2005).
[2] N. Guillou, C. Livage, M. Drillon, G. Férey. *Angew. Chem. Int. Ed.*, **42**, 5314 (2003).
[3] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato. *Chem. Commun.*, 1198 (2001).
[4] L.J. Gao, P.X. Cao, J.J. Wang, Y.P. Wu, F. Fu, M.L. Zhang, Y.X. Ren, X.Y. Hou. *J. Coord. Chem.*, **64**, 1299 (2011).
[5] R.H. Cui, G.J. Xu, Z.H. Jiang. *J. Coord. Chem.*, **64**, 222 (2011).
[6] S.Q. Zang, Y. Su, Y.Z. Li, H.Z. Zhu, Q.J. Meng. *Inorg. Chem.*, **45**, 2972 (2006).
[7] F. Luo, Y.X. Che, J.M. Zheng. *Inorg. Chem. Commun.*, **9**, 1045 (2006).
[8] X.M. Zhang, R.Q. Fang, H.S. Wu. *J. Am. Chem. Soc.*, **127**, 7670 (2005).
[9] J.W. Cheng, S.T. Zheng, W. Liu, G.Y. Yang. *CrystEngComm.*, **10**, 765 (2008).
[10] D. Tian, Y. Pang, Y.H. Zhou, L. Guan, H. Zhang. *CrystEngComm.*, **13**, 957 (2011).
[11] D. Tian, Y. Pang, S.Q. Guo, X.F. Zhu, H. Zhang. *J. Coord. Chem.*, **64**, 1006 (2010).
[12] D. Tian, Y.H. Zhou, L. Guan, X.F. Zhu, Y. Pang, H. Zhang. *Chinese J. Struct. Chem.*, **30**, 120 (2010).

[13] R.Z. Chen, F.J. Guo, F.L. Meng. *Acta Cryst.*, **E64**, m761 (2008).
[14] R.Z. Chen, F.J. Guo, F.L. Meng. *Acta Cryst.*, **E64**, m855 (2008).
[15] X.M. Zhang. *Coord. Chem. Rev.*, **249**, 1201 (2005).
[16] R.A. Michelin, M. Mozzon, R. Bertani. *Coord. Chem. Rev.*, **147**, 299 (1996).
[17] X.M. Chen, M.L. Tong. *Acc. Chem. Res.*, **40**, 162 (2007).
[18] H. Zhao, Z.R. Qu, H.Y. Ye, R.G. Xiong. *Chem. Soc. Rev.*, **37**, 84 (2008).
[19] L. Pan, X. Huang, J. Li, Y. Wu, N. Zheng. *Angew. Chem. Int. Ed.*, **39**, 527 (2000).
[20] Y.C. Liang, R. Cao, W.P. Su, M.C. Hong, W.J. Zhang. *Angew. Chem. Int. Ed.*, **39**, 3304 (2000).
[21] R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi, Q. Shi. *Inorg. Chem.*, **41**, 2087 (2002).
[22] Y.H. Wan, L.P. Jin, K.Z. Wang, L.P. Zhang, X.Z. Zheng, S.Z. Lu. *New J. Chem.*, **26**, 1590 (2002).
[23] R.H. Cui, G.J. Xu, Z.H. Jiang. *J. Coord. Chem.*, **64**, 222 (2011).
[24] K. Yang, Z.Z. Wang, Z.H. Liu. *J. Coord. Chem.*, **63**, 2286 (2010).
[25] L.J. Gao, P.X. Cao, J.J. Wang, Y.P. Wu, F. Fu, M.L. Zhang, Y.X. Ren, X.Y. Hou. *J. Coord. Chem.*, **64**, 1299 (2011).
[26] J.Q. Liu. *J. Coord. Chem.*, **64**, 1503 (2011).