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Topological structures and properties of two new coordination polymers constructed from biphenyl-3,4′,5-tricarboxylic acid

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$\{[Mn_3(bpt)_2(bib)_2(H_2O)_2]\cdot(H_2O)_2\}_n$ and $\{[Cd(Hbpt)(bib)_{0.5}(H_2O)_2]\cdot(H_2O)_2\}_n$ were obtained under solvothermal reactions of biphenyl-3,4′,5-tricarboxylic acid (H_3bpt) and 1,4-bis(imidazolyl)benzene (bib). In **1**, the fully deprotonated bpt^{3-} is a "Y-shape" and "X-shape" ligand, linking trinuclear manganese ions to generate a 2-D layer. The layer is further bridged by bpt^{3-} to generate a 3-D wave-like zigzag structure. In **2**, $Hbpt^{2-}$ is a "V-shape" ligand, bridging metal centers to generate a sheet. The neighboring sheets are packed together in an ABAB mode to afford a 3-D supramolecular framework. Complex **2** exhibits intense fluorescence at room temperature, which may originate from a ligand-to-metal charge transfer.

Keywords: Biphenyl-3,4′,5-tricarboxylic acid (H_3bpt); Structural analysis; Topology network; Luminescence

1. Introduction

Metal–organic frameworks are of interest for potential applications in magnetism, luminescence, and gas storage [1–7]. The potential for creating intriguing architectures has been recognized by many chemists and resulted in a broad range of topological structures [8–12]. However, the goal of predicting exact structures and topologies remains long-term. It may be affected by many factors such as ligand backbone, solvent, and anions [13, 14].

The connection of carboxylic acid and neutral imidazole-containing ligand provides a strategy to construct frameworks, where the carboxylate balances the positive charge while imidazole completes the coordination geometry of metal centers [15–17]. In this article, biphenyl-3,4′,5-tricarboxylic acid (H_3bpt) is the primary ligand with variable coordination shapes, such as "Y-shape," "X-shape," and "V-shape" [18]. Although various structures and topologies based on H_3bpt have been reported [19–27], the use of imidazole-containing

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ligand as an ancillary remains largely unexplored. Thus, 1,4-bis (imidazol-1-yl)benzene (bib) was chosen as the ancillary ligand as a good candidate for linear linker [28–30].

Herein, we report hydro(solvo)thermal syntheses and structural characterizations of two new coordination polymers, $\{[Mn_3(bpt)_2(bib)_2(H_2O)_2]\cdot(H_2O)_2\}_n$ and $\{[Cd(Hbpt)(bib)_{0.5}(H_2O)_2]\cdot(H_2O)_2\}_n$. H_3bpt significantly influences the topology of resultant coordination complexes. The complexes have been characterized by elemental analysis, IR, thermal stabilities, and X-ray powder diffraction. In addition, fluorescence of **2** has also been explored.

2. Experimental

2.1. *Reagents and physical measurements*

All reagents and solvents were commercially available and used as received. C, H, and N contents were measured by a Vario EL III elemental analyser (Elementar Analysensysteme gmbh, Germany). FT-IR spectra (KBr pellets) were recorded from 4000 to 400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. Luminescence spectra of solid samples were acquired at ambient temperature by using a JOBINYVON/HORIBA SPEX Fluorolog t3 system (slit: 0.2 nm). Thermogravimetric analyses (TGAs) were carried out under nitrogen at 60 cm^3 min^{-1} and heating rate of 10 °C min^{-1}. X-ray power diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA for Cu Kα radiation ($\lambda = 1.5406$ Å), with a scan speed of 2 °C min^{-1} and a step size of 0.02° in 2θ.

2.2. *Synthesis of 1 and 2*

2.2.1. $\{[Mn_3(bpt)_2(bib)_2(H_2O)_2]\cdot(H_2O)_2\}_n$ (1). A mixture of $MnSO_4\cdot H_2O$ (0.045 mmol, 10.0 mg), H_3bpt (0.0225 mmol, 6.4 mg), and bib (0.0225 mmol, 4.7 mg) was suspended in 8 mL of solvent ($H_2O/C_2H_5OH/CH_3CN = 5/2/1$), then sealed in a 10 mL Teflon with stainless steel container heated to 130 °C for 120 h and cooled to room temperature at a constant rate of 5 °C h^{-1}. Yellow block crystals suitable for X-ray crystal analysis were obtained. Yield: 58% based on H_3bpt. Elemental analysis (%): calcd for $C_{42}H_{32}Mn_3O_{16}N_4$ (Mr = 1013.54): C, 49.77; H, 3.18; N, 5.53. Found: C, 49.61; H, 3.24; N, 5.41. IR (KBr, cm^{-1}): 3119(s), 1613(m), 1530(s), 1490(w), 1400(s), 1301(m), 1255(w), 1150(m), 1113 (m), 1080(m), 929(w), 727(w), 657(w), 617(w), 547(w), 494(w).

2.2.2. $\{[Cd(Hbpt)(bib)_{0.5}(H_2O)_2]\cdot(H_2O)_2\}_n$ (2). The procedure was the same as that for **1** except that $MnSO_4\cdot H_2O$ (0.045 mmol, 10.0 mg) was replaced by $CdCl_2\cdot 2.5H_2O$ (0.045 mmol, 10.0 mg). Colorless block crystals suitable for X-ray crystal analysis were obtained by filtration. Yield: 51% based on H_3bpt. Elemental analysis (%): calcd for $C_{21}H_{19}CdO_{10}N_2$ (Mr = 571.79): C, 44.11; H, 3.35; N, 4.90. Found: C, 43.98; H, 3.12; N, 5.06. IR (KBr, cm^{-1}): 3130(s), 1675(m), 1559(m), 1531(m), 1400(s), 1302(m), 1235(m), 1108(w), 1062(w), 958(w), 838(w), 833(w), 765(m), 650(w), 529(w).

2.3. *Crystallographic data collection and structure determinations*

Single-crystal X-ray diffraction analyses of **1** and **2** were carried out in a Bruker SMART APEX II Diffractometer equipped with graphite monochromatic Mo-Kα radiation

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex no.	**1**	**2**
Formula	$C_{42}H_{32}Mn_3N_4O_{16}$	$C_{21}H_{19}CdN_2O_{10}$
Formula weight	1013.54	571.78
Crystal system, space group	Monoclinic, *P 21/c*	Monoclinic, *C 2/c*
a (Å)	12.7251(12)	24.1485(19)
b (Å)	11.7807(11)	10.0999(8)
c (Å)	26.982(3)	19.5065(15)
α (°)	90	90
β (°)	100.119(2)	116.744(1)
γ (°)	90	90
V (Å^3)	3981.9(7)	4248.7(6)
Density, D_{calcd} (g cm^{-3})	1.691	1.788
μ (mm^{-1})	1.021	1.788
F(000)	2060	2296.0
Reflections collected/unique	20,446/7580	10,421/3800
Independent reflections (R_{int})	0.0341	0.0355
Goodness-of-fit on F^2	0.912	1.054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0361$, $WR_2 = 0.1108$	$R_1 = 0.0367$, $WR_2 = 0.1000$
R indices (all data)	$R_1 = 0.0489$, $WR_2 = 0.1298$	$R_1 = 0.0507$, $WR_2 = 0.1210$

($\lambda = 0.71073$ Å). SAINT software was used for integration of the diffraction profiles. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software [31, 32]. Metal in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogens of organic ligands were generated theoretically onto specific atoms and refined isotropically. However, hydrogens of water were added by difference Fourier maps and refined using a riding model. Crystal parameters and details of the final refinement parameters are shown in table 1; selected bond lengths (Å) and angles (°) for **1** and **2** are listed in Supplementary material.

3. Results and discussion

3.1. *Descriptions of structures*

3.1.1. $\{[Mn_3(bpt)_2(bib)_2(H_2O)_2]\cdot(H_2O)_2\}_n$ (1). Single-crystal X-ray diffraction study on **1** reveals a 3-D framework, crystallizing in the monoclinic, and space group *P*2$_1$*/c*. The asymmetric unit contains three crystallographically independent manganese ions, two bpt^{3-}, two bib, two coordinated waters, and two lattice waters. As shown in figure 1(a), Mn1 is six coordinate [O_4N_2] and resides in a distorted octahedral coordination environment of three oxygens from three different bpt^{3-} ligands, one oxygen from a coordinated water and two nitrogens from two bib ligands. Mn2 adopts distorted pentagonal bipyramidal geometry and is coordinated by seven oxygens from four different bpt^{3-} ligands and water. Different from Mn2, Mn3 has distorted octahedral geometry, with six oxygens provided by bpt^{3-}. The Mn–O bond lengths are 2.092(2)–2.415(2) Å and Mn–N lengths are 2.225(3)–2.250(2) Å. The values are in agreement with previous studies [33, 34].

Mn1A, Mn2, and Mn3 are connected by μ–O into a metal cluster, and carboxylate groups adopt three distinct coordination modes, such as chelating/bridging bidentate, chelating, and

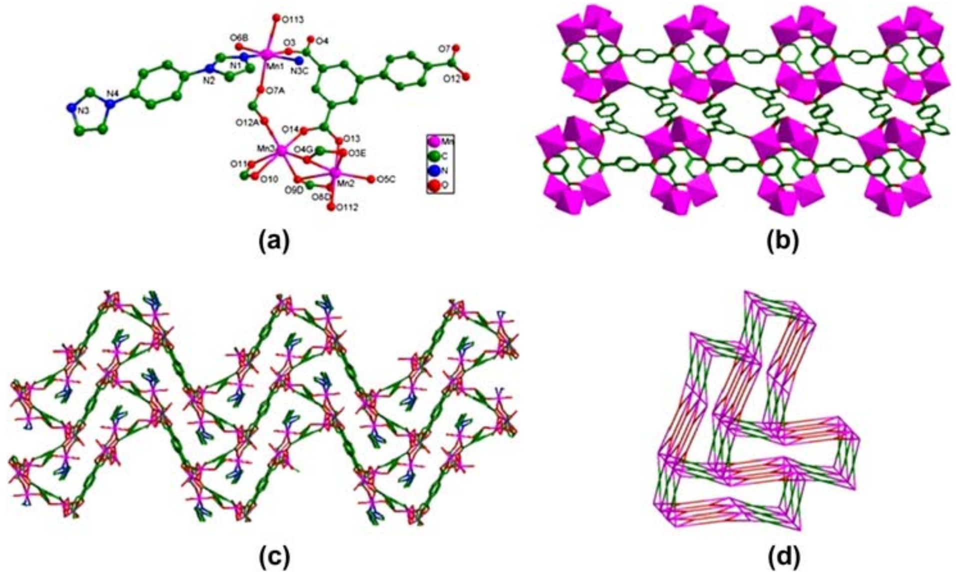

Figure 1. (a) Coordination environment of manganese ions of **1**. Symmetry codes: A: $x+1$, y, z; B: $-x+1$, $y+1/2$, $-z+1/2$; C: $-x-1$, y, z; D: $-x+1$, $-y+1$, $-z+1$; E: $-x$, $y-1/2$, $-z+1/2$; F: $-x$, $y+1/2$, $-z+1/2$; G: $-x+1$, $y-1/2$, $-z+1/2$ (b) 3- and 4-connected bpt^{3-} link to metal clusters generating a 2-D sheet. (c) 3-D wave-like framework. (d) Schematic view of the topology framework.

bis (monodentate) bridging. The polycarboxylate bpt^{3-} and metal cluster are both nodes in topological analysis. As shown in figure 2, the fully deprotonated bpt^{3-} has two coordination shapes, "Y-shape" and "X-shape". Each "Y-shape" bpt^{3-} binds to three metals as a 3-connected node, while each "X-shape" bpt^{3-} connects four metals as a 4-connected node. The bpt^{3-} is usually considered a 3-connected node and examples of bpt^{3-} as a 3-connected node and 4-connected node in one complex is rare. Along two different directions, the 3-connected and 4-connected bpt^{3-} link to metals to generate 2-D sheets (figure 1(b)). Two parallel sheets are further pillared by 3-connected bpt^{3-} to afford cuboid-like framework when the sheets are viewed from the side. Interestingly, the cuboid-like frameworks are packed with each other to afford a wave-like zigzag structure (figure 1(c)). The distance from crest to crest of the waves in **1** is 26.9 Å. The buckling of the sheets in **1**, which produces the zigzag structure, is mainly due to the disposition of the carboxylates and the coordination geometry around the manganese atoms. The remaining space within this 3-D

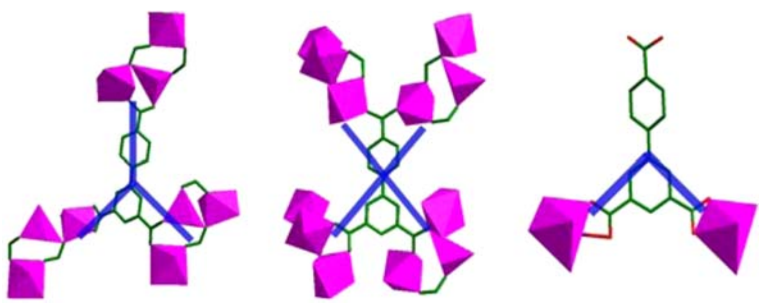

Figure 2. The coordination shapes of H_3bpt.

wave-like framework is occupied by free waters. A topology-simplified strategy as stated above was employed and bib was an additional linear linker. The trimetallic unit is supported by carboxylic groups of seven bpt^{3-}, also connected to another two equivalent units through bib linkers. Thus, the trimetallic unit is a 9-connected node. The topology of the resulting 3-D network can be represented as a new (3, 4, 9)-connected net with the Schäfli symbol of $(3{\cdot}4^2)(3^2{\cdot}4^2{\cdot}5^2)(3^6{\cdot}4^{10}{\cdot}5^7{\cdot}6^{12}{\cdot}8)$ (figure 1(d)).

3.1.2. $\{[Cd(Hbpt)(bib)_{0.5}(H_2O)_2]\cdot(H_2O)_2\}_n$ (2). Single-crystal X-ray structure analysis reveals that **2** contains one crystallographic-independent Cd(II) center. Cd1 resides in a distorted pentagonal bipyramid environment $[NO_6]$ with four oxygens from chelating carboxylic groups of $Hbpt^{2-}$, two oxygens from coordinated water, and one nitrogen of bib (figure 3(a)). The Cd–O bond distances are 2.284(3)–2.451(4) Å and the Cd–N bond distance is 2.260(4) Å, similar to the normal range [35–37].

Each partially deprotonated $Hbpt^{2-}$, acting as a "V-shape" ligand, bridges two Cd(II) centers to form a 1-D chain. The bidentate bib, adopting a trans-coordinated conformation, bridges two adjacent chains into a sheet $[Cd(Hbpt)(bib)_{0.5}]_n$ (figure 3(b)). Neighboring sheets are packed together in an ABAB mode to afford a 3-D supermolecular framework (figure 3(c)) consisting of two types of corrugated ladders, alternatively sharing the Cd(II) centers. One ladder is formed by $Hbpt^{2-}$ lying on the crossbeam and Cd1 on the column. The other type is built from bib ligands bridging Cd(II) centers. Topologically, the Cd(II) centers can be regarded as 3-connected nodes, whereas bib and $Hbpt^{2-}$ are linkers. Complex **2** represents a 3-connected net with Schlafli symbol of (4^3) (figure 3(d)).

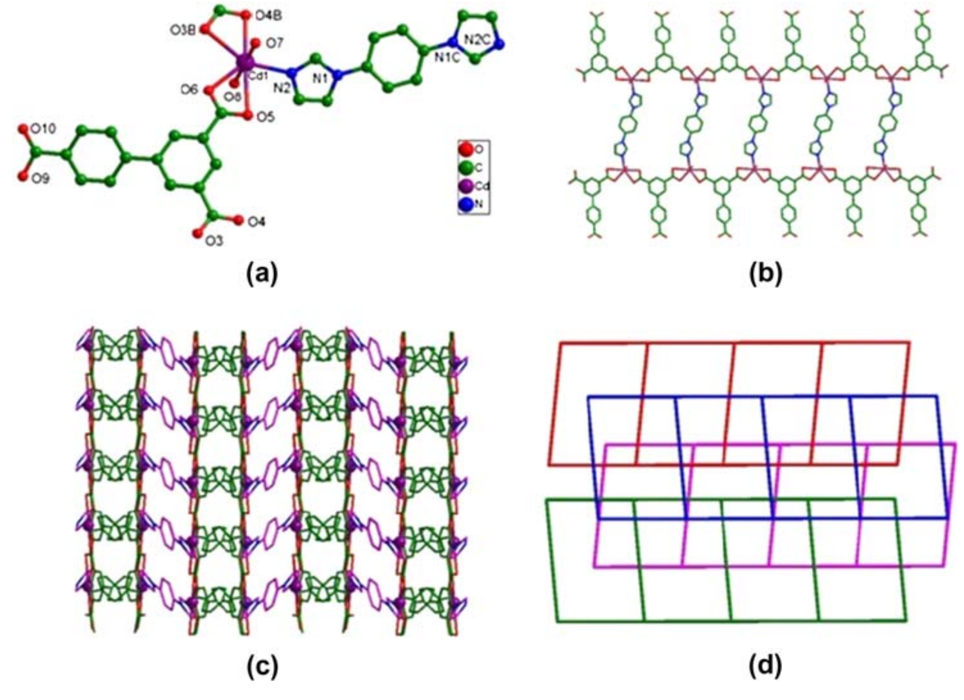

Figure 3. (a) Coordination environment of cadmium ions of **2**. Symmetry codes: A: x, $y+1$, z; B: x, $y-1$, z; C: $-x+3/2$, $-y+1/2$, $-z$. (b) View of the 1-D structure of **2**. (c) 3-D supramolecular framework with two types of corrugated ladders. (d) The topology of 3-connected net with Schlafli symbol of (4^3) in **2**.

3.2. *Factors of structure topology*

Complexes **1** and **2** constructed from H_3bpt and bib illustrate two new networks based on Mn(II) and Cd(II) nodes (figure 4). In self-assembly, bib is neutral and metal centers are bivalent. Different networks drive us to perform a study on the effect of H_3bpt.

In **1**, the fully deprotonated bpt^{3-} is trivalent, needing one and a half metal ions to balance the negative ion, or three halves of metal ion. It is because every half-shared metal ion must site on the center of inversion, thus three symmetric centers appear in a molecule. The bpt^{3-} have two coordination shapes, "Y-shape" and "X-shape," connecting metal centers to form a 3-D topology. For **2**, the partially deprotonated $Hbpt^{2-}$ is bivalent, needing one metal ion to match the charge. Therefore, a unique metal ion is contained in the asymmetric unit of **2**. "V-shape" $Hbpt^{2-}$ are linear linkers, bridging metal centers into a 1-D topology. Comparison of **1** and **2** indicates that the coordination shape of H_3bpt plays an important role in the generation of topological network.

3.3. *TGA and XRPD patterns*

To study the thermal stability of **1** and **2**, TGA was performed on polycrystalline sample under nitrogen atmosphere between 30 and 900 °C (Supplementary material). For **1**, the first weight loss of 3.99% was observed from 35 to 95 °C, corresponding to loss of lattice molecules (calcd: 3.55%). Then two consecutive steps of weight loss follow, till 20.74% residue remains, corresponding to MnO (calcd: 20.99%). The TG curve of **2** exhibits two well-separated weight loss stages. The first of 30.19% at 45–192 °C agrees with loss of water and bib (calcd: 30.98%). The second from 359 to 564 °C indicates decomposition of the coordination framework. The final residue of 20.81% is close to the calculated 22.45% based on CdO.

To confirm phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiments have been carried out. The XRPD experimental and computer-simulated patterns, shown in Supplementary material, are in good agreement with the corresponding simulated one, indicating phase purity of the products.

3.4. *Luminescence property*

Considering luminescent properties of d^{10} metal complexes, such as Zn(II), Cd(II), and Cu (I), luminescence of **2** was investigated (figure 5). The luminescence of free ligands exhibits fluorescent emission with maxima at 410 nm ($\lambda_{ex} = 370$ nm) for H_3bpt [21] and 456 nm

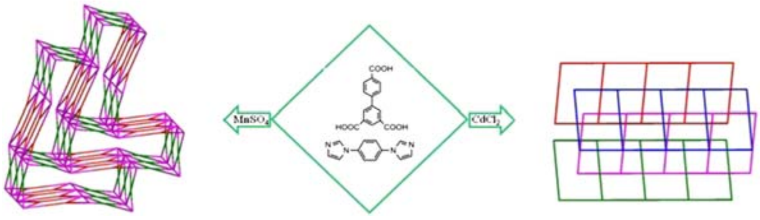

Figure 4. Synthesis of **1** and **2**.

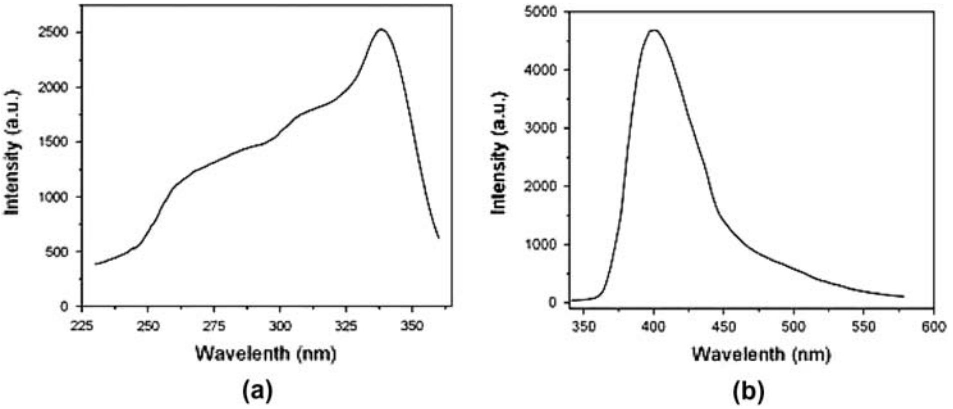

Figure 5. (a) Excitation spectra of **2** for emission at 430 nm. (b) The solid-state emission spectra of **2** at room temperature.

($\lambda_{ex} = 341$ nm) for bib [9]. For excitation spectra (figure 5(a)), **2** exhibits an absorbance maxima at 338 nm for emission at 430 nm. Upon excitation at 338 nm, **2** exhibits an intense fluorescence emission at 397 nm (figure 5(b)). In comparison to the free carboxylic acid, the emission maximum of **2** was blue-shifted relative to free ligand. The change may be assigned to ligand-to-metal charge transfer transitions [38–41]. Enhancement of fluorescence intensity in **2** is likely due to rigidity of Hbpt^{2-} and bib with regard to metal centers, effectively increasing rigidity and conjugation upon metal coordination and then affects nonradiative decay of the intraligand (π–π^*) excited state [42]. These observations indicate that **2** may be a candidate for photoactive materials.

4. Conclusions

By utilizing H_3bpt and bib with different metal centers, we have produced two coordination frameworks, including examples of 3-D and 1-D topology. The different structures demonstrate the influence of H_3bpt on assembly of coordination polymers. Complex **2** exhibits strong emission in the solid state at room temperature.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 886041 and 886042. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or email: deposit@ccdc.cam.ac.uk.

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References

[1] N. Hoshino, Y. Sekine, M. Nihei, H. Oshio. *Chem. Commun.*, **46**, 6117 (2010).

[2] S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai, S. Kitagawa. *Nature Mater.*, **8**, 831 (2009).

[3] H.L. Wu, J.K. Yuan, Y. Bai, G.L. Pan, H. Wang, X.B. Shu, G.Q. Yu. *J. Coord. Chem.*, **65**, 616 (2012).

[4] Z.G. Guo, R. Cao, X. Wang, H.F. Li, W.B. Yuan, G.J. Wang, H.H. Wu. J. Li. *J. Am. Chem. Soc.*, **131**, 6894 (2009).

[5] H.L. Wu, X.C. Huang, B. Liu, F. Kou, F. Jia, J.K. Yuan, Y. Bai. *J. Coord. Chem.*, **64**, 4383 (2011).

[6] Y.P. Wu, D.S. Li, F. Fu, W.W. Dong, J. Zhao, K. Zou, Y.Y. Wang. *Cryst. Growth Des.*, **11**, 3850 (2011).

[7] D.S. Li, F. Fu, J. Zhao, Y.P. Wu, M. Du, K. Zou, W.W. Dong, Y.Y. Wang. *Dalton Trans.*, **39**, 11522 (2010).

[8] J.S. Hu, L. Qin, M.D. Zhang, X.Q. Yao, Y.Z. Li, Z.J. Guo, H.G. Zheng, Z.L. Xue. *Chem. Commun.*, **48**, 681 (2012).

[9] Y.W. Li, H. Ma, Y.Q. Chen, K.H. He, Z.X. Li, X.H. Bu. Cryst. *Growth Des.*, **12**, 189 (2012).

[10] L.M. Fan, D.C. Li, P.H. Wei, P.Q. Tang, M.H. Li, D. Yuan, G.Z. Liu, X.T. Zhang, J.M. Dou. *J. Coord. Chem.*, **64**, 3031 (2011).

[11] S. Wang, R.R. Yun, Y.Q. Peng, Q.F. Zhang, J. Lu, J.M. Dou, J.F. Bai, D.C. Li, D.Q. Wang. *Cryst. Growth Des.*, **12**, 79 (2012).

[12] D.S. Li, P. Zhang, J. Zhao, Z.F. Fang, M. Du, K. Zou, Y.Q. Mu. Cryst. *Growth Des.*, **12**, 1697 (2012).

[13] T.L. Hu, Y. Tao, Z. Chang, X.H. Bu. *Inorg. Chem.*, **50**, 10994 (2011).

[14] B. Zheng, J.F. Bai, Z.X. Zhang. *Cryst. Eng. Comm.*, **12**, 49 (2010).

[15] Y.N. Zhang, P. Liu, Y.Y. Wang, L.Y. Wu, L.Y. Pang, Q.Z. Shi. *Cryst. Growth Des.*, **11**, 1531 (2011).

[16] H.Y. Bai, J.F. Ma, Yang, B. Liu, L.P. Zhang, J.C. Ma, Y.Y. Liu. *Eur. J. Inorg. Chem.*, 5709 (2010).

[17] L.Y. Xin, G.Z. Liu, X.L. Li, L.Y. Wang. *Cryst. Growth Des.*, **12**, 147 (2012).

[18] Y.L. Lu, W.J. Zhao, Y. Liu, B. Liu, X. Feng, J.T. Tan, X. Li, X.W. Yang. *J. Solid State Chem.*, **192**, 144 (2012).

[19] C.C. Ji, J. Li, Y.Z. Li, Z.J. Guo, H.G. Zheng. *Cryst. Eng. Comm.*, **13**, 459 (2011).

[20] M. Meng, D.C. Zhong, T.B. Lu. *Cryst. Eng. Commun.*, **13**, 6794 (2011).

[21] Z.J. Lin, B. Xu, T.F. Liu, M.N. Cao, J. Lu, R. Cao. *Eur. J. Inorg. Chem.*, **3842**, (2010).

[22] A.G. Wong-Foy, O. Lebel, A.J. Matzger. *J. Am. Chem. Soc.*, **129**, 15740 (2010).

[23] C.S. Lim, J.K. Schnobrich. *Inorg. Chem.*, **49**, 5271 (2010).

[24] L. Li, J.X. Ma, C. Song, T.L. Chen, Z.H. Sun, S.Y. Wang, J.H. Luo, M.C. Hong. *Inorg. Chem.*, **51**, 2438 (2012).

[25] Z.Y. Guo, H. Xu, S.Q. Su, J.F. Cai, S. Dang, S.C. Xiang, G.D. Qian, H.J. Zhang, M. O'Keeffe, B.L. Chen. *Chem. Commun.*, **47**, 5551 (2011).

[26] Z.Y. Guo, G.H. Li, L. Zhou, S.Q. Su, Y.Q. Lei, S. Dang, H.J. Zhang. *Inorg. Chem.*, **48**, 8069 (2009).

[27] L. Li, J.H. Luo, S.Y. Wang, Z.H. Sun, T.L. Chen, M.C. Hong. *Cryst. Growth Des.*, **11**, 3744 (2011).

[28] Z.X. Li, Y.F. Zeng, H. Ma, X.H. Bu. *Chem. Commun.*, **46**, 8540 (2010).

[29] P.C. Wang, F.L. Meng, C. Liu, K.Y. Zou, Z.X. Li. *Inorg. Chem. Commun.*, **17**, 95 (2012).

[30] Z.X. Li, X. Chu, G.H. Cui, Y. Liu, L. Li, G.L. Xue. *Cryst. Eng. Comm.*, **13**, 1984 (2011).

[31] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Solution*, University of Götingen, Germany (1997).

[32] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[33] J. Zhao, X.L. Wang, X. Shi, Q.H. Yang, C. Li. *Inorg. Chem.*, **50**, 3198 (2011).

[34] A.R. Fout, Q.L. Zhao, D.J. Xiao, T.A. Betley. *J. Am. Chem. Soc.*, **133**, 16750 (2011).

[35] L.F. Ma, L.Y. Wang, M. Du. *Cryst. Eng. Comm.*, **11**, 2593 (2009).

[36] D.C. Zhong, W.X. Zhang, F.L. Cao, L. Jian, T.B. Lu. *Chem. Commun.*, **47**, 1204 (2011).

[37] S.A. Barnett, A.J. Blake, N.R. Champness, C. Wilson. *Dalton Trans*., 3852 (2005).

[38] L.F. Ma, J.H. Qin, L.Y. Wang, D.S. Li. *RSC Adv.*, **1**, 180 (2011).

[39] G.J. Yin, B.M. Ji, C.X. Du. *Inorg. Chem. Commun.*, **15**, 21 (2012).

[40] H.Y. Bai, J.F. Ma, J. Yang, B. Liu, L.P. Zhang, J.C. Ma, Y.Y. Liu. *Eur. J. Inorg. Chem.*, **5709**, (2010).

[41] Y.F. Zhou, W.T. Xu, M.Y. Wu, A.J. Lan, L.J. Zhang, R. Feng, F.L. Jiang, M.C. Hong. *Inorg. Chem. Commun.*, **15**, 140 (2012).

[42] H.S. Deka, R.P. Sarma, S.C. Kumari, A.K. Khare, J.B. Baruah. *J. Solid State Chem.*, **184**, 1726 (2011).