

A High-connected Cobalt(II) Pyromellitate MOF Displaying An Uncommon Decadentate Coordination Mode

Chun-lun Ming, Ying-na Zhao, Bao-yi Yu,[†] Kristof Van Hecke,[†] and Guang-hua Cui^{*}

College of Chemical Engineering, Hebei United University, 46 West Xinhua Road, Tangshan 063009, Hebei P.R. China

^{*}E-mail: tscghua@126.com

[†]Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 S3, B-9000 Ghent, Belgium

Received June 16, 2014, Accepted July 18, 2014

Key Words : Cobalt-organic framework, Pyromellitic acid, Trinodal network

Introduction

Metal-organic frameworks (MOFs) from organic ligands and transition metals have become a field of quick growth in supramolecular and material chemistry due to their intriguing structural diversity and potential applications in several aspects such as gas adsorption/separation, catalysis, optics, magnetism, and molecular recognition.¹ In particular, topology focuses on the coordination network connectivity generated *via* the reduction of periodic nets into node-and linker/vertex-and-edge representations, which helps greatly the understanding of the significance of MOFs for theoretical crystal chemistry consists in close relations between their composition, physical properties and topology of the corresponding atomic net. To date, thousands of new MOFs have been synthesized.^{2,3} In these reported coordination networks, the majority are commonly uninodal- and low connected (< 7) nodes, trinodal networks containing highly connected nodes such as (3,4,6)-, (3,4,7)-, (3,6,10)-, (3,8,10)-, (4,4,7)- and (4,8,16)-connected MOFs are relatively rare.^{4,5} The formation of the highly connected MOFs is greatly affected by the organic ligands, the nature of the metal ions, the counterions, and other factors. Among the reported research, organic ligands with carboxylate groups are especially interesting in the field of crystal engineering and coordination chemistry. Pyromellitic acid (H₄pm) as an outstanding organic ligand containing four exo-carboxyl groups around the benzene ring, shows diverse coordination modes and bridges central metal atoms to assemble multidimensional architectures.^{6,7} Therefore, a number of highly connected MOFs based on H₄pm have been synthesized and presented by our group and others during the past several years.⁸ Based on H₄pm, and mixed with bis(pyridyl)-1,2,4-triazolate ligands, two novel 3D zinc(II) coordination polymers were synthesized and characterized by Yu and his co-workers, the topological analysis results reveal the two MOFs can be simplified to a trinodal (3,4,10) and (3,4,5)-connected topology, respectively. Very recently, we found that introduction of rod-like neutral *N,N'*-donor btx (1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene) ligands into the Co-pm system can generate novel compound {[Co₃(pm)₂(btx)(μ₃-OH)₂(H₂O)₂]-2H₂O}_n, which is an unusual 3D binodal (4,10)-connected MOF.⁹ In

continuation of our exploratory research toward developing new coordination polymers constructed from H₄pm with secondary bridging flexible two-connector *N*-containing co-ligands,^{8c} herein, we report the synthesis, crystal structure and characterization of a unique trinodal (4,4,7)-connected 3D MOF, formulated as [Co₂(pm)(bib)_{0.5}(H₂O)_{0.5}]_n (**1**) (bib = 1,4-bis(2-methyl-imidazol-1-yl)butane) with a Schläfli symbol of (4².5².6.7)(4⁴.6²)(4⁹.5⁶.6⁶), in which pyromellitate anions show an unprecedented decadentate coordination mode. In addition, TGA, XRPD and fluorescence spectra determinations were performed for **1**.

Experimental

Materials and Characterization Methods. All reagents were purchased commercially and used without further purification. The *N*-containing ligand bib was synthesized in accordance with previously reported literature.¹⁰ The elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Thermal analysis was performed on a Netzsch TG 209 thermal analyzer from room temperature to 800 °C under N₂ at a heating rate of 10 °C/min. FT-IR spectrum was recorded from KBr pellets in the range of 4000–400 cm⁻¹ on an Avatar 360 (Nicolet) spectrophotometer. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. The X-ray powder diffraction (XRPD) pattern was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator.

Synthesis of [Co₂(pm)(bib)_{0.5}(H₂O)_{0.5}]_n. A mixture of CoCl₂·6H₂O (0.1 mmol, 23.8 mg), H₄pm (0.1 mmol, 25.0 mg), bib (0.1 mmol, 22.0 mg), methanol (5 mL) and H₂O (10 mL) was placed in a Teflon-lined stainless steel vessel and then, the pH value was adjusted to 6.5 by NaOH (0.1 M). The mixture was sealed and heated at 140 °C for 3 days under autogenous pressure. After the mixture cooled to room temperature at a rate of 5 °C/h, purple block single crystals of the complex, suitable for X-ray diffraction, were collected by filtration. Yield: 58% (based on Co). Anal. Calc. for C₃₂H₂₄Co₄N₄O₁₇ (%): C, 39.53; H, 2.49; N, 5.76%. Found: C, 39.68; H, 2.31; N, 5.52%. IR (KBr, cm⁻¹): 3435s, 2923w,

1615s, 1565s, 1448s, 1390m, 1272m, 878w, 773w, 696m.

Crystallography. Single crystal X-ray diffraction analysis of the titled compound was carried out on a Bruker Smart 1000 CCD diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) and ω - 2θ scan mode at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multiscan techniques; the structure of the complex was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97.¹¹ Multi-scan absorption corrections were applied to the data using the SADABS program.¹² All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. The H-atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically. The complex showed disorder in N1, N2, C11-C16 of the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining distances with related disordered atoms. The O9 atom is too close to a 2-fold axis, that means, by a 2 symmetry operation, an O9A that are 1.24 angstrom from O9 will be generated (A: $-x+1/2, y-1/2, z$). So the SOF (site occupation factor) of O9 has to be 0.5. CCDC-993735 contains the supplementary crystallographic data. The crystallographic data is summarized in Table S1 (Supporting Information), and the selected bond lengths and angles are listed in Table S2 for the complex.

Results and Discussion

Single-crystal X-ray diffraction analysis reveals that the complex crystallizes in the orthorhombic group $Pbcn$. The coordination environment of the compound is depicted in Figure 1, wherein two crystallographically unique Co(II) cations coexist in the asymmetric unit. The asymmetry unit itself contains two independent cobalt atoms, one pm^4 ligand, half of a coordinated water molecule and half of a neutral bib ligand. Both of the Co(II) centers are hexacoordinated, displaying a distorted octahedral geometry. The Co(1) center is coordinated by six oxygen atoms (O1, O2, O4C, O5B, O8A and O9). A: $-x+1/2, y-1/2, z$; B: $-x+1/2,$

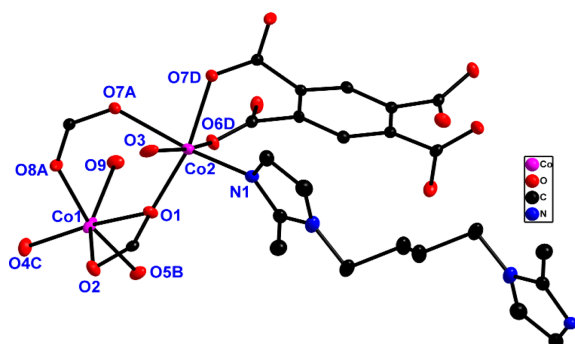


Figure 1. Coordination environment of the two Co(II) centers in **1**. Thermal ellipsoids are drawn at the 30% probability level (All H atoms are omitted for clarity. Symmetry codes: A: $-x+1/2, y-1/2, z$; B: $-x+1/2, -y+1/2, z-1/2$; C: $x, -y, z-1/2$; D: $x-1/2, -y+1/2, -z+1$).

$-y+1/2, z-1/2$; C: $x, -y, z-1/2$). Three of these oxygen atoms (O1, O2 and O4C), originating from two carboxylates of two pm^4 ligands, and one coordinated water molecule (O9) are in the equatorial positions, whereas two oxygen atoms (O5B, O8A), deriving from two symmetry-equivalent pm^4 anions, are in the apical positions (the coordination angle O8A–Co1–O5B is $165.24(9)^\circ$). Co(2) is ligated to one nitrogen atom (N1) of the bib ligand and one oxygen atom (O7A) from one pm^4 in the apical positions, four carboxyl oxygen atoms (O1, O6D, O7D, and O3. D: $x-1/2, -y+1/2, -z+1$) from four carboxyl groups of two pm^4 ligands in the equatorial positions (O7A–Co2–N1 of $169.15(15)^\circ$). The Co–N bond distance is $2.103(5)$ Å and the Co–O bond lengths are in the range of $1.982(2)$ – $2.364(3)$ Å, which are both within acceptable ranges of those observed in other cobalt complexes.¹³

In **1**, the pm^4 ligands take a rare decadentate coordination mode, acting as a $\mu_7-\eta^3:\eta^3:\eta^2:\eta^2$ linker to connect seven Co^{2+} ions and the dihedral angles between the carboxylic groups and the aromatic ring are $36.03(2)^\circ$, $41.22(1)^\circ$, $57.28(2)^\circ$, and $69.60(2)^\circ$, respectively (Figure 2). When searching the Cambridge Structural Database (version 5.35, May 2014)^{13b} for coordination modes of anionic pm ligands, no structures were found, featuring this decadentate coordination mode (Scheme S1 (supporting Information) illustrates the reported versatile coordination modes of the pm^4 ligand). The bib and decadentate pm^4 ligands interconnect the two types of Co atoms into a complicated 3D network with a high density value (1.996 g cm^{-3}) (Figure 3). Calculations from the X-ray structure data of **1** using PLATON¹⁴ program show that this framework contains no residual solvent accessible void. From the topological point of view, the overall topology can be described as a trinodal high-connected network. The pm^4 ligands can be regarded as topologically 7-connected nodes, which connect three Co2 and four Co1 nodes. Each Co1 node links four pm^4 ligands by oxygen atoms of carboxyl groups of pm^4 . As a result, the Co1 center can be simplified as a 4-connected node. The Co2 node fastens another neigh-

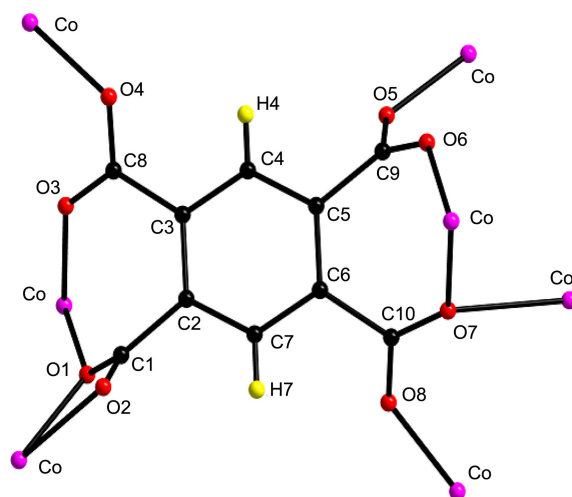


Figure 2. The rare decadentate coordination mode of the pm^4 ligand in **1**.

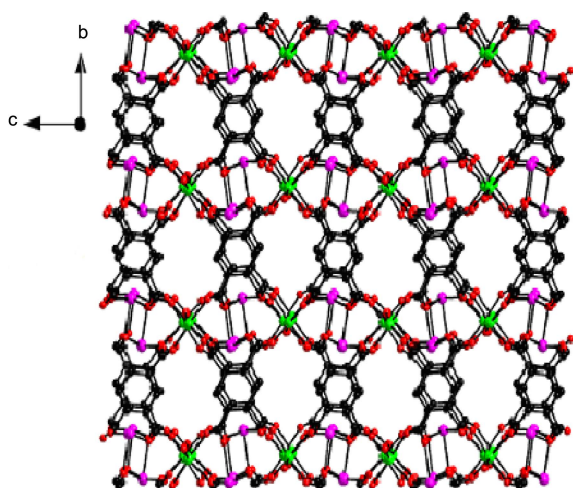


Figure 3. The 3D network of complex 1.

bouring Co²⁺ via a bridging bib ligand, and three pm⁴⁻ ligands, and can be regarded as a 4-connected node. The bib ligand is a linker (Figure S1 showing three types of nodes). Thus, the 3D high-connected MOF can be simplified as unique mixed nodes, a trinodal (4,4,7)-connected network with a Schläfli symbol of (4².5².6.7)(4⁴.6²)(4⁹.5⁶.6⁶) analyzed by the TOPOS 4.0 program¹⁵ (Figure 4). To the best of our knowledge, the topology of this net has not appeared in MOF chemistry, according to the reticular Chemistry Structure Resource Database.¹⁶

IR Spectrum and XRPD Pattern. The IR spectrum displays characteristic absorption band for water molecule, carboxyl groups of pm⁴⁻, and bib ligand. There is no absorption peak between 1730 and 1690 cm⁻¹, indicating that all carboxyl groups of the organic moieties are deprotonated.¹⁷ The infrared spectra of the title complex represents a broad band centered at ca. 3435 cm⁻¹ which is due to the O-H stretching vibration of water molecules involved in extensive hydrogen bonding interactions or the coordinated water molecule. The bands at 2923 cm⁻¹ and 1272 cm⁻¹ are related to $\nu_{\text{C-H3}}$ and $\nu_{\text{C-N}}$ of the bib ligand, respectively. The splitting of COO⁻ bands suggests the different coordination mode of carboxylate groups from the pm⁴⁻ ligands.¹⁸ This is also in agreement with the crystal structure of the complex.

The simulated and experimental XRPD patterns of compound, obtained at room temperature, are shown in Figure S2. Their peak positions are in good consistency with each other, indicating the phase purity of the as-synthesized samples.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed on a sample of **1** under N₂ atmosphere with a heating rate of 10.0 °C/min. As shown in Figure S3, the complex possessed a two-step weight-loss process. The first step occurred from 110.0 °C to 147.0 °C, with a weight-loss of 2.0%, which can be attributed to the loss of coordinated water molecules (calcd: 1.9%). Furthermore, there is almost no weight loss from 148.0 °C to 358.0 °C. The second step with a weight-loss of 24.9% occurred in a temperature range from 359.0 °C to 579.0 °C, corresponding to the decomposi-

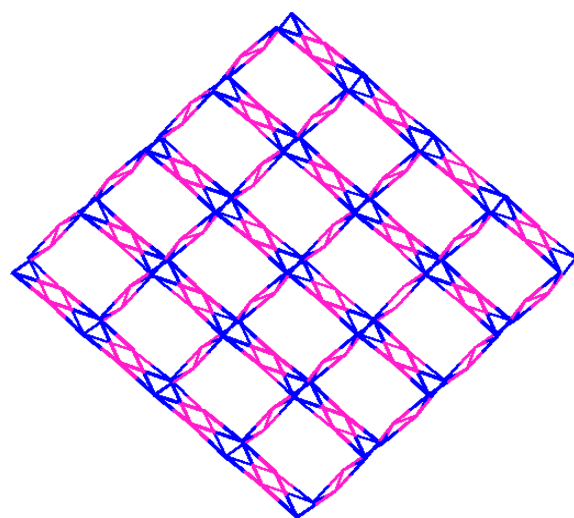


Figure 4. The 3D trinodal (4,4,7)-connected net of complex 1.

tion of the organic ligands. And finally, the remnants are 29.8%, which should be CoO (calcd. 30.9%).

Luminescence Properties. The solid-state photoluminescence spectrum of compound **1** was measured at room temperature, and the result is depicted in Figure S4. The complex exhibits a fluorescent emission band with maximum at 384 nm upon excitation at 235 nm. The main emission peak of H₄pm is at 342 nm ($\lambda_{\text{ex}} = 308$ nm),¹⁹ while the free bib ligand displays very weak fluorescent emission centered at 465 nm ($\lambda_{\text{ex}} = 280$ nm).²⁰ When comparing the title complex with the H₄pm ligand, the emission band of the complex is 42 nm red-shifted, which can be assigned according to intraligand $n-\pi^*$ transitions.²¹

Conclusion

In summary, we present an unusual trinodal (4,4,7)-connected MOF with an uncommon coordination model of pm⁴⁻ ligand. The results clearly reveal that the H₄pm ligand acts as a rich library of tectons in designing and construction of highly-connected MOFs. Furthermore, the bib ligand may influence the functional properties of these coordination polymers.

Acknowledgments. Publication cost of this paper was supported by the Korean Chemical Society.

Supplementary Material. CCDC number: 993735 for the complex. The data can be obtained free of charge via https://services.ccdc.cam.ac.uk/structure_deposit (or from the Cambridge Cryst allographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033(44); or deposit@ccdc.cam.ac.uk).

References

- (a) Du, M.; Li, C. P.; Liu, C. S.; Fang, S. M. *Coord. Chem. Rev.* **2013**, 257, 1282. (b) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.;

- Yaghi, O. M. *Science* **2013**, *341*, 1230444. (c) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. *Chem. Rev.* **2012**, *112*, 1001. (d) Cook, T. R.; Zheng, Y. R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734. (e) Gladysz, J. A. *Chem. Rev.* **2011**, *111*, 1167.
2. (a) Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247. (c) LaDuca, R. L. *Coord. Chem. Rev.* **2009**, *253*, 1759. (d) O'Keefe, M. *Chem. Soc. Rev.* **2009**, *38*, 1215. (e) Cui, G. H.; He, C. H.; Jiao, C. H.; Geng, J. C.; Blatov, V. A. *CrystEngComm* **2012**, *14*, 4210. (f) Oganov, A. R. *Modern Methods of Crystal Structure Prediction*; Wiley-VCH: Weinheim, 2011; (g) Liu, T. F.; Lü J.; Guo, Z. G.; Proserpio, D. M.; Cao, R. *Cryst. Growth Des.* **2010**, *10*, 1489.
3. (a) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Solid State Chem.* **2005**, *178*, 2452. (b) Baburin I. A.; Blatov, V. A. *Acta Crystallogr., Sect. B: Struct. Sci.* **2007**, *63*, 791. (c) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *Cryst. Growth Des.* **2008**, *8*, 519. (d) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2008**, *10*, 1822. (e) O'Keefe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3. (f) Lian, Z. X.; Cai, J. W.; Chen, C. H.; Luo, H. B. *CrystEngComm* **2007**, *9*, 319. (g) Hsiao, H. L.; Wu, C. J.; Hsu, W.; Yeh, C. W.; Xie, M. Y.; Huang, W. J.; Chen, J. D. *CrystEngComm* **2012**, *14*, 8143.
4. (a) O'Keefe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 675. (b) Rajput, L.; Hong, S.; Liu, X.; Oh, M.; Kim, D.; Lah, M. S. *CrystEngComm* **2011**, *13*, 6926. (c) Datta, A.; Das, K.; Lee, J. Y.; Jhou, Y. M.; Hsiao, C. S.; Huang, J. H.; Lee, H. M. *CrystEngComm* **2011**, *13*, 2824. (d) Cai, S. L.; Zheng, S. R.; Pan, M.; Tan, J. B.; Fan, J.; Zhang, W. G. *CrystEngComm* **2012**, *14*, 1193. (e) Zhang, W. G.; Cui, G. H.; Xiao, S. L.; Du, X. *Bull. Korean Chem. Soc.* **2013**, *34*, 1243.
5. (a) Liu, G. X.; Li, X. L.; Ren, X. M. *Chinese J. Struct. Chem.* **2011**, *30*, 1239. (b) Liu, G. Z.; Li, X. L.; Xin, L. Y.; Wang, L. Y. *CrystEngComm* **2012**, *14*, 5315. (c) Zhang, M. D.; Qin, L.; Yang, H. T.; Li, Y. Z.; Guo, Z. J.; Zheng, H. G. *Cryst. Growth Des.* **2013**, *13*, 1961. (d) Geng, J. C.; Wang, C. J.; Wang, F.; Luo, H. R.; Yang, C. C.; Cui, G. H. *Chin. J. Inorg. Chem. (Wu Ji Huaxue Xuebao)* **2012**, *28*, 1060.
6. (a) Cao, R.; Sun, D. F.; Liang, Y. C.; Hong, M. C.; Tatsumi, K.; Shi, Q. *Inorg. Chem.* **2002**, *41*, 2087. (b) Ruiz-Pérez, C.; Lorenzo-Luis, P.; Hernández-Molina, M.; Laz, M. M.; Delgado, F.; Gili, P.; Julve, M. *Eur. J. Inorg. Chem.* **2004**, *2004*, 3873. (c) Ren, C.; Hou, L.; Liu, B.; Yang, G. P.; Wang, Y. Y.; Shi, Q. Z. *Dalton Trans.* **2011**, *40*, 793. (d) Wang, J. L.; Hou, K. L.; Xing, Y. H.; Deng, Z. Y.; Shi, Z. *J. Coord. Chem.* **2011**, *64*, 3767.
7. (a) Fabelo, O.; Pasán, J.; Lloret, F.; Julve, M.; Ruiz-Pérez, C. *CrystEngComm* **2007**, *9*, 815. (b) Feng, S. Z.; Jing, J.; Lei, L.; Heng, X. Y.; Yun, N. S. *Acta Phys. Chim. Sin.* **2009**, *25*, 2011. (c) Zhang, L. J.; Xu, J. Q.; Shi, Z.; Zhao, X. L.; Wang, T. G. *J. Solid State Chem.* **2003**, *173*, 32. (d) Hua, Q.; Zhao, Y.; Xu, G. C.; Chen, M. S.; Su, Z.; Cai, K.; Sun, W. Y. *Crys. Growth Des.* **2010**, *10*, 2553.
8. (a) Zhang, W. G.; Cui, G. H.; Xiao, S. L.; Du, X. *Bull. Korean Chem. Soc.* **2013**, *34*, 1243. (b) Ma, P. J.; Li, Y. H.; Qin, L.; Cui, G. H. *Bull. Korean Chem. Soc.* **2013**, *34*, 3843. (c) Ming, C. L.; Zhang, H.; Li, G. Y.; Cui, G. H. *Bull. Korean Chem. Soc.* **2014**, *35*, 651. (d) Liu, J. F.; Huang, F. P.; Bian, H. D.; Yu, Q. Z. *Anorg. Allg. Chem.* **2013**, *639*, 2347.
9. Hao, J. M.; Wang, L. N.; Van Hecke, K.; Cui, G. H. *Inorg. Chem. Commun.* **2013**, *41*, 43.
10. Luo, G. G.; Xiong, H. B.; Dai, J. C. *Cryst. Growth Des.* **2011**, *11*, 507.
11. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
12. Sheldrick, G. M.; SADABS (version 2.03), *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen (Germany) 1996.
13. (a) Zhou, H.; Liu, G. X.; Wang, X. F.; Wang, Y. *CrystEngComm* **2013**, *15*, 1377. (b) Allen, F. H. *Acta Cryst.* **2002**, *B58*, 380.
14. Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7.
15. Blatov, V. A. *Struct. Chem.* **2012**, *23*, 955.
16. Reticular Chemistry Structure Resource (RCSR), <http://rcsr.anu.edu.au/>.
17. (a) Liu, G. C.; Huang, J. J.; Zhang, J. W.; Wang, X. L.; Lin, H. Y. *Transition Met. Chem.* **2013**, *38*, 359. (b) Tao, B.; Lei, W.; Cheng, F. R.; Xia, H. *Bull. Korean Chem. Soc.* **2012**, *33*, 1929.
18. (a) Lyszczek, R. *J. Therm. Anal. Calorim.* **2007**, *90*, 533. (b) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.
19. Hou, Y.; Wang, S.; Shen, E.; Wang, E.; Xiao, D.; Li, Y.; Xu, L.; Hu, C. *Inorg. Chem. Acta* **2004**, *357*, 3155.
20. Guo, F. *J. Coord. Chem.* **2012**, *65*, 4005.
21. Jiao, C. H.; Cui, G. H.; He, C. H.; Geng, J. C. *J. Mol. Struct.* **2012**, *1020*, 134.