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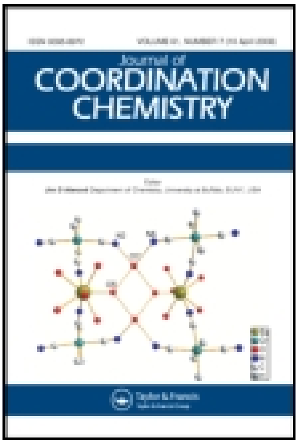

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Crystal structures and luminescence of two cadmium(II) polymers constructed from aromatic polycarboxylate and bis(1,2,4-triazol-1-yl)methane ligands

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Crystal structures and luminescence of two cadmium(II) polymers constructed from aromatic polycarboxylate and bis(1,2,4-triazol-1-yl)methane ligands

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Two new coordination compounds, $\{[Cd_2(btrm)(ip)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**1**) and $\{[Cd_2(btrm)(hip)_2(H_2O)_4]\cdot 3H_2O\}_n$ (**2**) (btrm = bis(1,2,4-triazol-1-yl)methane, H_2ip = isophthalic acid, H_2hip = 5-hydroxy isophthalic acid), have been synthesized and structurally characterized. Compound **1** is a 3-D network with $CdSO_4$ topology. Compound **2** contains 1-D ladder structures, which are interconnected by classical hydrogen-bonding interactions ($O–H\cdots O$) to lead to 3-D supramolecular architectures. Luminescence was performed on **1** and **2**, both of which showed strong fluorescent emissions in the solid state at room temperature.

Keywords: H_2hip; H_2ip; Bis(1,2,4-triazol-1-yl)methane; Fluorescence

1. Introduction

Metal coordination polymers have aroused interest because of their topologies and potential applications in catalysis, adsorption (gas storage), luminescence, magnetism, etc. [1–8]. Luminescent stable metal-organic complexes have been an active research area for their potential applications in material science [9–11]. Because of the diversity of coordination modes and high structural stability, multicarboxylates with suitable spacers, especially benzoic acid-based ligands, are frequently used for metal-organic frameworks (MOFs) [12–16]. Isophthalic acid (H_2ip) and 5-hydroxy isophthalic acid (H_2hip) are rigid, planar molecules and have been widely used as bridging ligands in the synthesis of multidimensional MOFs [17–19]. On the other hand, bis(1,2,4-triazol-1-yl)methane (btrm) is a flexible ligand. The flexibility and conformational freedom of btrm offer the possibility for construction of an unpredictable and interesting framework.

In this contribution, we choose btrm incorporated with isophthalic acid (H_2ip) and 5-hydroxy isophthalic acid (H_2hip) as building blocks. Two new coordination polymeric complexes, $\{[Cd_2(btrm)(ip)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**1**) and $\{[Cd_2(btrm)(hip)_2(H_2O)_4]\cdot 3H_2O\}_n$ (**2**), were fabricated and structurally characterized by X-ray single crystal analyses.

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In particular, d^{10} metal centers and conjugated π systems containing aromatic rings favor the development of fluorescent materials.

2. Experimental

2.1. *General*

Deionized water was used as solvent in this work. The reagents and solvents employed were commercially available and used as received. Ligand btrm was synthesized as reported previously [20]. The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer elemental analyzer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. FT-IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Bio-Rad FTS 135 spectrometer.

2.2. *Synthesis of* $\{[Cd_2(btrm)(ip)_2(H_2O)_2]\cdot 2H_2O\}_n$ *(1) and* $\{[Cd_2(btrm)(hip)_2(H_2O)_4]\cdot 3H_2O\}_n$ *(2)*

Complexes **1** and **2** were prepared by the following method: a mixture of $Cd(NO_3)_2$ (154.24 mg, 0.5 mmol), aromatic multicarboxylic (0.5 mmol, H_2ip for **1**; H_2hip for **2**), btrm (0.5 mmol), NEt_3 (1.0 mmol), and H_2O (12 mL) was poured into a Parr Teflon-lined stainless steel vessel (25 mL), then the vessel was sealed and heated to 140°C for 3 days. The autoclave was cooled to room temperature at a rate of $1.5^\circ C\cdot h^{-1}$. White crystalline products **1** and **2** were filtered off, washed with distilled water, and dried in air.

For **1**: Yield: 38% (based on Cd). Anal. Calcd for $C_{21}H_{22}Cd_2N_6O_{12}$ (%): C, 32.53; H, 2.86; N, 10.84. Found: C, 32.84; H, 3.15; N, 11.02.

For **2**: Yield: 42% (based on Cd). Anal. Calcd for $C_{21}H_{30}Cd_2N_6O_{17}$ (%): C, 29.21; H, 3.50; N, 9.73. Found: C, 29.68; H, 3.27; N, 10.02.

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction measurements of **1** and **2** were carried out with a Bruker Smart CCD diffractometer and a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques using SHELXS-97 and SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically, and hydrogens were located and refined isotropically. Crystallographic data for **1** and **2** are summarized in table 1. Selected bond distances and angles of **1** and **2** are listed in table 2.

3. Results and discussion

3.1. *Structure of* $\{[Cd_2(btrm)(ip)_2(H_2O)_2]\cdot 2H_2O\}_n$ *(1)*

Single-crystal X-ray analysis shows that **1** crystallizes in the monoclinic space group $C2/c$ with the asymmetric unit containing one Cd(II), one ip^{2-}, half of a btrm and one

Table 1. Crystallographic data and structure refinement details for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{21}H_{22}Cd_2N_6O_{12}$	$C_{21}H_{30}Cd_2N_6O_{17}$
Formula weight	775.24	863.3
Crystal system	Monoclinic	$C2/c$
Space group	$C2/c$	$C2/c$
Temperature (K)	293(2)	293(2)
Unit cell dimensions (Å, °)		
a	19.2902(3)	10.1515(2)
b	7.62312(11)	18.4750(3)
c	17.9032(2)	16.1624(3)
α	90	90
β	97.9754(12)	100.441(2)
γ	90	90
Volume (Å^3), Z	2607.24(6), 4	2981.05(9), 4
Calculated density (Mg m^{-3})	1.975	1.924
Absorption coefficient (mm^{-1})	1.706	1.515
F (000)	1528	1720
θ range (°)	2.88 to 25.01	2.46 to 25.01
Limiting indices	$-22 \le h \le 22$;	$-12 \le h \le 7$;
	$-9 \le k \le 9$;	$-14 \le k \le 21$;
	$-21 \le l \le 21$	$-19 \le l \le 18$
Reflections collected/unique	18,571/2291	5827/2629
R(int)	0.0280	0.0217
Goodness-of-fit on F^2	1.062	1.093
R_1/wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0158$, $wR_2 = 0.0389$	$R_1 = 0.0226$, $wR_2 = 0.0543$
R_1/wR_2 (all data)	$R_1 = 0.0178$, $wR_2 = 0.0394$	$R_1 = 0.0278$, $wR_2 = 0.0555$
Largest difference peak and hole (e Å^{-3})	0.341 and −0.258	0.395 and −0.778

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cd(1)–O(2)	2.1966(14)	O(2)–Cd(1)–O(6)	87.59(6)
Cd(1)–O(4)#1	2.2910(15)	N(1)–Cd(1)–O(6)	89.77(6)
Cd(1)–O(6)	2.2995(16)	O(4)#1–Cd(1)–O(6)	88.76(6)
Cd(1)–O(3)#2	2.4465(15)	O(2)–Cd(1)–O(3)#1	85.08(5)
Cd(1)–O(3)#1	2.5967(14)	N(1)–Cd(1)–O(3)#2	90.68(6)
Cd(1)–O(2)	2.7960(12)	O(4)#1–Cd(1)–O(3)#2	98.70(5)
Cd(1)–N(1)	2.2716(16)	O(4)#1–Cd(1)–O(5)	81.83(12)
O(2)–Cd(1)–N(1)	134.24(6)	O(6)–Cd(1)–O(3)#2	170.19(5)
O(2)–Cd(1)–O(4)#1	98.02(6)	O(2)–Cd(1)–O(3)#1	138.27(5)
N(1)–Cd(1)–O(4)#1	127.59(6)		
2			
Cd(1)–O(4)#1	2.2772(18)	O(4)#1–Cd(1)–O(6)	89.16(6)
Cd(1)–O(7)	2.2804(17)	O(7)–Cd(1)–O(6)	84.67(6)
Cd(1)–O(6)	2.3050(17)	O(4)#1–Cd(1)–N(1)	92.41(7)
Cd(1)–O(4)#1	2.2524(18)	O(7)–Cd(1)–N(1)	85.96(7)
Cd(1)–N(1)	2.323(2)	O(6)–Cd(1)–N(1)6)	167.70(7)
Cd(1)–O(2)	2.3615(18)	O(4)#1–Cd(1)–O(2)	83.33(6)
Cd(1)–O(1)	2.448(2)	O(7)–Cd(1)–O(2)	138.95(7)
Cd(1)–O(3)#1	2.627(2)	O(6)–Cd(1)–O(2)	101.68(6)
O(4)#1–Cd(1)–O(7)	137.63(7)	N(1)–Cd(1)–O(2)	90.62(7)

Symmetry transformations used to generate equivalent atoms: for **1**, #1 $x - 1/2$, $y - 1/2$, z; #2 $-x + 1/2$, $-y + 3/2$, $-z$; for **2**, #1 $x - 1$, y, z.

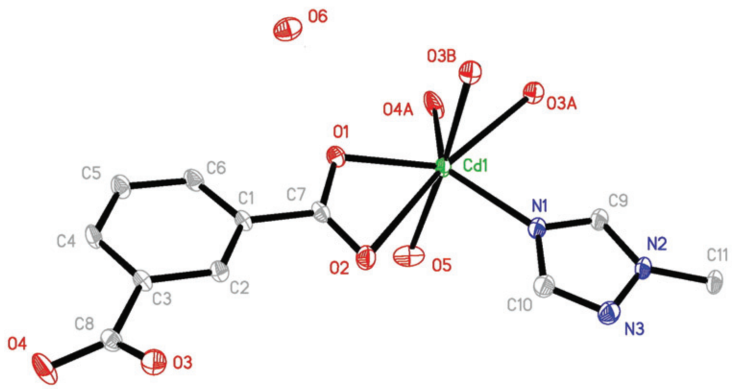

Figure 1. Molecular structure of **1** showing coordination of Cd^{2+}, ip^{2-}, and btrm.

free water molecule. Cd1 is seven-coordinate in a distorted pentagonal bipyramidal coordination sphere (figure 1), defined by one carboxylate oxygen and one water oxygen occupying axial positions, while the equatorial positions are four carboxylate oxygens and one nitrogen from btrm. All Cd–O and Cd–N bond lengths fall in the normal range except that Cd1–O3 and Cd1–O2 bond distances are 2.5967(14) Å and 2.796(12) Å, respectively (table 2), which can be described as a semi-chelating coordination.

In the structure of **1**, carboxylate groups of ip^{2-} have η-O,O′ and μ-O,O-η-O,O′ coordination modes, connecting Cd1 ions to result in a 1-D coordination motif along [0 1 0] with the dimeric $[Cd_2O_2]$ units, with Cd $\cdots$ Cd separation of 4.063(1) Å (figure 2). Such 1-D $[(Cd)(ip)]_n$ arrays are further extended by *trans*-btrm spacers (the dihedral angles between the two triazole ring planes are 57.3°) to afford a 3-D framework (figure 3), in which the Cd $\cdots$ Cd distance separated by btrm is 10.238(1) Å. Each dimeric $[Cd_2O_2]$ unit can be defined as 4-connected nodes. Consequently, the 3-D framework of **1** can be described as a $CdSO_4$-type topological network with one point, $\{6^5.8^3\}$, as shown in figure S3.

3.2. *Structure of* $\{[Cd_2(btrm)(hip)_2(H_2O)_4]\cdot 3H_2O\}_n$ *(2)*

When H_2hip was used instead of H_2ip, a 1-D ladder for **2** is obtained. Compound **2** crystallizes in the monoclinic space group $C2/c$ with the asymmetric unit containing one Cd(II), one hip^{2-}, and half of a btrm (figure 4). For **2,** the distorted pentagonal bipyramidal coordination environment around cadmium(II) is close to those of **1**. However there is some difference about the basic structural units of **1** and **2**. In **2**, cadmium(II) lies in the general position with two lattice water molecules in comparison to that of **1**. The Cd1–O3A bond distance is 2.627(2) Å in **2** (table 2), longer than normal Cd–O, suggesting a semi-chelating coordination. All other Cd–O and Cd–N bond lengths fall in the normal range.

Deprotonated hip bianions bridge Cd^{2+} centers to form a 1-D chain running along the *a*-axis (figure 5); two such chains are bridged by μ_2 *trans*-btrm ligands (the dihedral angles between the triazole ring planes are 83.7°) to produce a 1-D ladder, in which the

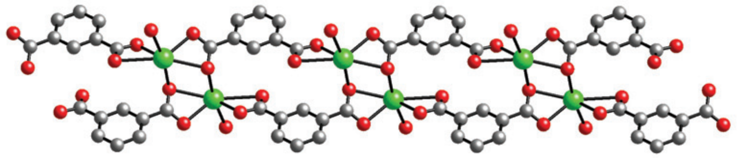

Figure 2. The extended 1-D chain along the *a* direction linked by ip^{2-} in **1**.

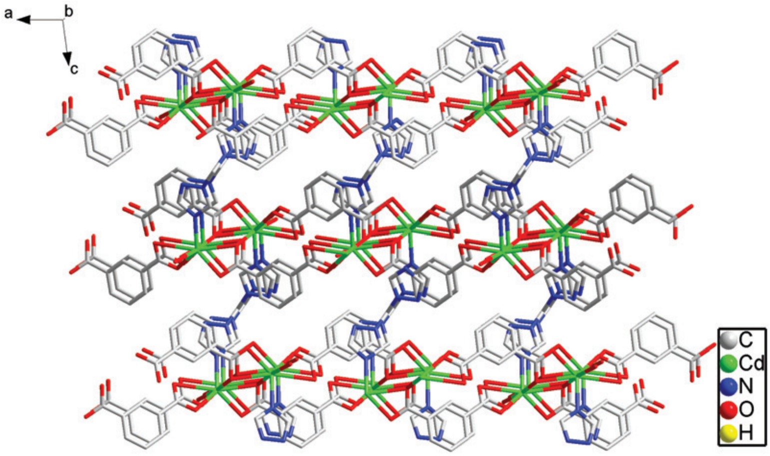

Figure 3. The 3-D framework of **1** viewed along the *b* direction linked by ip^{2-} and btrm.

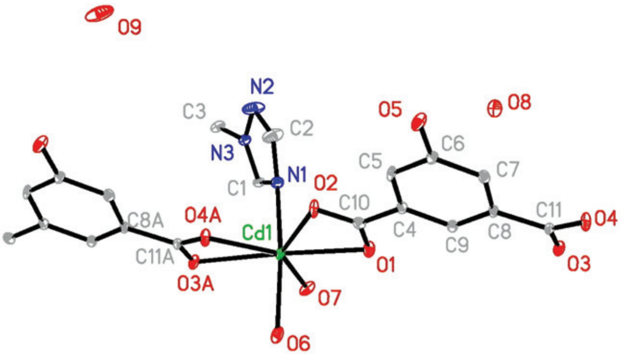

Figure 4. Molecular structure of **2** showing coordination of Cd^{2+}, hip^{2-}, and btrm.

Cd ··· Cd distance separated by btrm is 9.077(1) Å. The 1-D ladders are further linked *via* hydrogen-bonding interactions (O7 ··· O3 = 2.694, O–H ··· O = 175.98; O6 ··· O2 = 2.657, O–H ··· O = 176.60; O6 ··· O5 = 2.878, O–H ··· O = 126.89) between coordinated water molecules and the carboxylate oxygens of hip^{2-}, coordinated water molecules or the hydroxy oxygens of hip^{2-}, thus constructing a 3-D supramolecular framework, as shown in figure 6. Lattice water guests (O8 and O9) located in the 3-D framework are

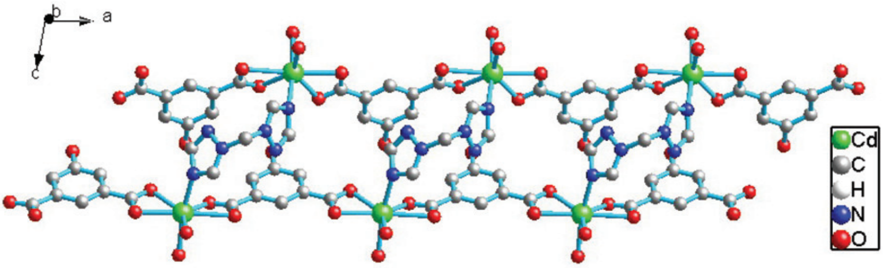

Figure 5. The 1-D ladder structure of **2** linked by hip^{2-} and btrm.

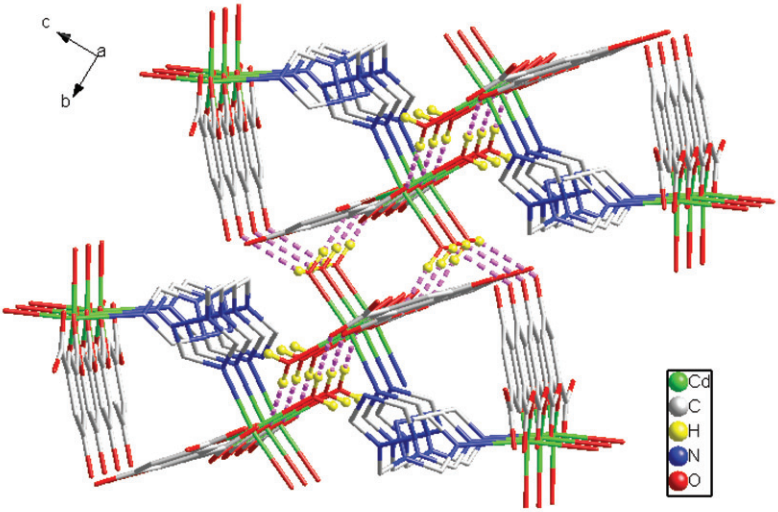

Figure 6. The 3-D supramolecular structure of **2** (pink dotted line: hydrogen-bonding).

involved in host–guest (O7-H7A $\cdots$ O9 and O8-H8B $\cdots$ O5) and guest–guest (O8-H8A $\cdots$ O9) H-bonding interactions.

The synthesis conditions for **1** and **2** were very similar, but the structures of **1** and **2** are very different. The first reason is that ip^{2-} in **1** has η-O,O′ and μ-O,O-η-O,O′ coordination modes, and hip^{2-} in **2** displays only η-O,O′ coordination. The other reason may be due to the flexibility of btrm, which makes the ligand take different dihedral angles. This work can be compared with previous results, in which we used btrp instead of btrm and two 2-D and one 1-D cadmium(II) compounds $\{[Cd(btrp)(ip)(H_2O)]\cdot 2.5H_2O\}_n$, $\{[Cd(btrp)(hip)(H_2O)]\cdot 3H_2O\}_n$, and $\{[Cd(btrp)_2(H_2O)_2]\cdot H_2O\cdot 2H_2btc\}_n$ were isolated [21]. The result is quite different from the framework structures of **1** and **2**. The btrp ligands adopt TG and TT conformations [22]; the btrp has much more flexibility than btrm and cadmium(II) in reference [21] has different coordination modes in comparison to those in **1** and **2**. The results show that ligand conformations and coordination modes of the central ions are important for various framework structures in crystal engineering.

3.3. *IR spectra*

In the IR spectra of **1** and **2** (figures S1 and S2), broad peaks centered at *ca* 3400 cm^{-1} indicate O–H stretch of water, hydroxyl, and/or carboxyl. The absence of absorption of carboxyl (*ca* 1700 cm^{-1}) in **1** and **2** confirms complete deprotonation of aromatic multicarboxylic. As a consequence, the antisymmetric and symmetric stretching vibrations of carboxylate appear at 1580–1530 and 1375–1395 cm^{-1}, respectively.

3.4. *Luminescence*

Syntheses of MOFs can be an efficient method for obtaining new types of electroluminescent materials, especially for Zn(II) and Cd(II) compounds. Luminescent properties of ligands, **1** and **2** were investigated in the solid state, as shown in figure S4. Both **1** and **2** have emission bands with maxima at 491 and 485 nm, respectively, if excited at 370 nm. The solid-state photoluminescence of free H_2ip and H_2hip (H_2ip: $\lambda_{em} = 382$ nm, $\lambda_{ex} = 340$ nm; H_2ip: $\lambda_{em} = 375$ nm, $\lambda_{ex} = 340$ nm) was also analyzed. It is clear that the emission bands of **1** and **2** are blue shifted compared with free H_2ip and H_2hip ligands, suggesting charge-transfer transitions between the ligand and the metal [23].

4. Conclusion

Combination of bis(1,2,4-triazol-1-yl)methane(btrm) and deprotonated isophthalate (ip^{2-}) or 5-hydroxy isophthalate (hip^{2-}) with cadium(II) leads to 3-D and 1-D MOFs. Compound **1** features 3-D networks with $CdSO_4$ topology. The 1-D ladders in **2** assemble into 3-D supramolecular architectures interconnected by hydrogen-bonding interactions. Both **1** and **2** display strong blue emissions at room temperature.

Supplementary material

CCDC-**1** 816373 and CCDC-**2** 816374 contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; or email: deposit@ccdc.cam.ac.uk).

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References

[1] T. Savaki, T. Dewa, Y. Aoyama. *J. Am. Chem. Soc.*, **120**, 8539 (1998).
[2] G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr. *Coord. Chem. Rev.*, **196**, 165 (2000).
[3] O. Ikkala, G. Brinke. *Science*, **295**, 2407 (2002).
[4] N. Ishikava, M. Sugita, T. Ishikawa, S.Y. Koshihara, Y. Kaizu. *J. Am. Chem. Soc.*, **125**, 8694 (2003).
[5] J.P. Zhang, Y.Y. Lin, W.X. Zhang, X.M. Chen. *J. Am. Chem. Soc.*, **127**, 14162 (2005).
[6] S. Kitagawa, S.I. Noro, T. Nakamura. *Chem. Commun.*, **11**, 701 (2006).
[7] J. Zhang, X.H. Bu. *Angew. Chem. Int. Ed.*, **46**, 6115 (2007).
[8] W. Morris, C.J. Doonan, H. Furukawa, R. Banerjee, O.M. Yaghi. *J. Am. Chem. Soc.*, **130**, 12626 (2008).
[9] B.H. Ye, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **249**, 545 (2005).
[10] V.A. Friese, D.G. Kurth. *Coord. Chem. Rev.*, **252**, 199 (2008).
[11] K. Biradha, M. Sarkar, L. Rajput. *Chem. Commun.*, **11**, 4169 (2006).
[12] Q.H. Zhao, H.F. Li, X.F. Wang, Z.D. Chen. *New J. Chem.*, **26**, 1709 (2002).
[13] D.F. Sun, R. Cao, Y.Q. Sun, W.H. Bi, X.J. Li, Y.Q. Wang, Q. Shi, X. Li. *Inorg. Chem.*, **42**, 7512 (2003).
[14] B. Li, X. Zhu, J. Zhou, Y. Peng, Y. Zhang. *Polyhedron*, **23**, 3133 (2004).
[15] C.D. Wu, W.B. Lin. *Angew. Chem. Int. Ed.*, **44**, 1958 (2005).
[16] L. Yi, X. Yang, T.B. Lu, P. Cheng. *Cryst. Growth Des.*, **5**, 1215 (2005).
[17] H. Abourahma, G.J. Bodwell, J. Lu, B.I. Moulton, R.R. Pottie, B. Walsh, M.J. Zaworotko. *Cryst. Growth Des.*, **3**, 513 (2003).
[18] B. Moulton, H. Abourahma, M.W. Bradner, J. Lu, G.J. McManus, M.J. Zaworotko. *Chem. Commun.*, **8**, 1342 (2003).
[19] A.C. Sudik, A.P. Ĉtée, O.M. Yaghi. *Inorg. Chem.*, **44**, 2998 (2005).
[20] J. Torres, J.L. Lavandera, P. Cabildo, R.M. Claramunt, J. Elguero. *J. Heterocycl. Chem.*, **25**, 771 (1988).
[21] L. Tian, L. Yan, L.P. Wang, Z.H. Liang. *J. Mol. Struct.*, **998**, 30 (2011).
[22] X.Q. Liang, D.P. Li, X.H. Zhou, Y. Sui, Y.Z. Li, J.L. Zuo, X.Z. You. *Cryst. Growth Des.*, **9**, 4872 (2009).
[23] Q.G. Zhai, C.Z. Lu, X.Y. Wu, S.R. Batten. *Cryst. Growth Des.*, **7**, 2332 (2007).