Journal of Molecular Structure 966 (2010) 64–68

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Acyclic water pentamer induces novel supramolecular ribbed sheet: Cooperativity and competitiveness of weak and covalent forces?

Atish Dipankar Jana [1], Rajat Saha, Golam Mostafa *

Department of Physics, Jadavpur University, Jadavpur, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 7 October 2009
Received in revised form 4 December 2009
Accepted 8 December 2009
Available online 14 December 2009

Keywords:
Water pentamer
Self-assembly
Cooperativity
Malonate
1,3-Bis(4-pyridyl)propane

ABSTRACT

The 1D chain complex $[\{Cu(II)(bpp)(malonate)(H_2O)\}(H_2O)_4]_n$ (**1**) (bpp = 1,3-bis(4-pyridyl)propane) self-assembles to form a 2D ribbed sheet stabilized by an acyclic pentameric water cluster, which in turn, influences the conformation of the bpp ligand.

1. Introduction

To date a large number of water clusters isolated in a number of crystal hosts including oligomers (tetramer [1,2], pentamer [3], hexamer [4], heptamer [5–7], octamer [8,9], decamer [10], dodecamers [11] etc.) and polymers (1D chain [12], helix [13,14], tape [15] and 2D sheet [16]) have been structurally characterized and provided detailed information about cooperative hydrogen bonding behavior in these diverse geometries. Coordinated water molecules in metal complexes also take part in the cluster formation and even with the participation of coordinated water molecules the cluster attains its regular geometry in many cases [17]. Recently, the advantage of water cluster research, the upsurge in studying small water clusters in different environments by systematically varying the size and the research to understand the properties of the condensed phase have been well-documented in a special issue of Synthesis and Reactivity in Inorganic, Metal–Organic, and Nano-Metal Chemistry [18]. Curiously, it has been seen that water oligomers of even number of water molecules are abundant in metal–organic frameworks whereas odd numbered clusters are scarcely observed [19]. In the current article we present an acyclic water pentamer in the context of self-assembly of a coordination polymer. Till date, only two acyclic water pentamers have been reported in literature [20,21]. The overall self-assembly of a crystalline material is the penultimate outcome of the competitiveness as well as cooperativity of weaker forces (hydrogen bonding, π–π and C–H…π interaction etc.) and stronger forces (coordinative and covalent) in the organization of metal nodes with flexible organic ligands. The present crystal structure nicely represents an example, where this competitiveness and cooperativity has been borne out in the self-assembled supramolecular structure. In this paper we wish to highlight the cooperativity among a set of water molecules, malonate ligands and flexible 1,3-bis(4-pyridyl)propane(bpp) ligands, resulting the organization of water molecules in the form of an acyclic water pentamer.

2. Experimental

2.1. Materials and general methods

All the reagents and solvents for synthesis were commercially available and used as received without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C analyzer.

IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer.

2.2. Synthesis of complex **1**

Copper-malonate was prepared by adding $CuCO_3{\cdot}Cu(OH)_2$ slowly to the aqueous solution of malonic acid with continuous

---

* Corresponding author.
E-mail address: mostafa@phys.jdvu.ac.in (G. Mostafa).

[1] Present address: Department of Physics, Sripat Singh College, Jiaganj, Murshidabad 742 123, India.

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.12.009

Table 1
Hydrogen bonding geometry.

D–H. . .A	D–H (Å)	H...A (Å)	D. . .A (Å)	<D–H–A (Å)
O1W–H1W1...O2^{i}	0.81(3)	1.91(3)	2.703(3)	170(3)
O2W–H1W2...O4^{ii}	0.79(3)	1.99(3)	2.777(3)	176(3)
O5W–H2W5...O4	0.82(3)	1.99(3)	2.773(3)	161(3)
O2W–H2W2...O1W	0.76(5)	2.16(4)	2.866(4)	156(4)
O5W–H1W5...O4W	0.88(4)	1.91(4)	2.766(4)	165(4)
O1W–H2W1...O5W	0.72(4)	1.99(4)	2.705(4)	174(4)
O4W–H2W4...O3^{iv}	0.88(7)	2.09(6)	2.933(4)	161(6)
O3W–H1W3...O2W	0.94(4)	1.94(4)	2.857(4)	165(4)
O3W–H2W3...O1^{v}	0.77(4)	2.25(4)	3.008(4)	167(5)
C1–H1...O3W^{vi}	0.9300	2.3900	3.210(4)	147.00
C13–H13...O5W	0.9300	2.5600	3.478(3)	169.00

Symmetry code: (i) −x, −y, 3 − z; (ii) −x, −y, 2 − z; (iii) 1 + x, y, z; (iv) 1 − x, −y, 2 − z; (v) −x, −y, 3 − z; (vi) x, 1 + y,−1 + z.

stirring. The resulting deep blue solution was evaporated to obtain the blue copper-malonate. 0.5 mmol of the prepared copper-malonate was dissolved 100 mL water. 1,3-Bis-(4-pyridyl)propane (0.5 mmol) dissolved in 50 mL of methanol, was slowly added to this solution and the mixture was stirred at room temperature for 2 h. It was then filtered and the blue filtrate was kept inside a $CaCl_2$ desiccator. After 4 weeks triangular plate shaped deep blue crystals appeared. Yield 85%. Anal. Calcd. for: $C_{16}H_{18}CuN_2O_5$, $4(H_2O)$: C, 42.33; H, 5.77; N, 6.17%. Found: C, 42.23; H, 5.12; N, 5.70%. IR data: 3448.29 (m), 1589.06 (s), 1505.07 (w), 1425.76 (s), 1391.00 (m), 742.32 (w) cm^{-1}.

2.3. X-ray crystallographic studies of complex 1

X-ray single-crystal diffraction measurements for complex **1** were carried out on a Bruker Smart 1000 CCD area detector diffractometer equipped with a graphite crystal monochromator. The determinations of unit cell parameters and data collections were performed with Mo K_α radiation ($\lambda = 0.71073$ Å) by the ω scan mode. There was no evidence of crystal decay during data collection. The program SAINT [22] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS program [23]. The structure was solved by a direct method using the SHELXS program of the SHELXTL package and refined with SHELXL [24]. Metal atoms in complex **1** 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. The water hydrogens were located from difference Fourier map and refined isotropically but the other hydrogen positions were calculated geometrically with a fixed thermal parameter 1.2 times of their parent atoms. Crystallographic data and experimental details for structural analyses are listed in Table S1, selected bond distances/bond angles are listed in Table S2 and H-bonding geometries are listed in Table 1. CCDC No. 606406 contains the supplementary crystallographic data for complex **1**. This material can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/deposit, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

2.4. Ab initio computation

The *ab initio* geometry optimization of bpp in TT, TG and GG′ conformations were performed using Gaussian 03 package at the HF/3-21G level of theory. The optimized geometries are characterized by harmonic-vibrational frequencies, which confirmed that the structures obtained are minimum on the potential energy surface. All calculations were performed with using GAUSSIAN 03 program [25].

3. Results and discussion

3.1. Crystal structure of complex 1

The X-ray structure determination of the synthesized crystal reveals that complex (**1**) consists of 1D polymeric chains of Cu (II) with square pyramidal geometry ($\tau = 0.16$) [26] (Figs. 1 and Table S1). Oxygen (O1, O3) atoms of chelating malonate and nitrogen (N1, N2) atoms of bridging bpp form the basal plane. The oxygen (O1w) atom of coordinated water molecule occupies the axial position (Fig. 1). Selected bond distances and angles have been provided in Table S2 which shows the usual coordination geometry for this kind of system.

Four lattice water molecules combine with the coordinated water molecule to form an acyclic water pentamer (Fig. 2), which folds into two nearly perpendicular directions. One fold forms a cyclic motif **A** [$R_4^4(10)$ in Etter's graph [27] set notation] and propagates the network along *a* axis, whereas the other fold forms another cyclic motif **B** [$R_6^6(16)$] (Figs. 3 and S2) that propagates the network along *c* axis. In motif $R_4^4(10)$ and $R_6^6(16)$, malonate contributes two and four acceptors, respectively whereas water oxygen act as rest of the acceptors.

It is to be noted that motif **A** resembles the planar cyclic water tetramer with one of the water molecules replaced by COO^- functional group of malonate. Similarly, motif B is the replica of cyclic water hexamer in chair conformation in which, COO^- functional

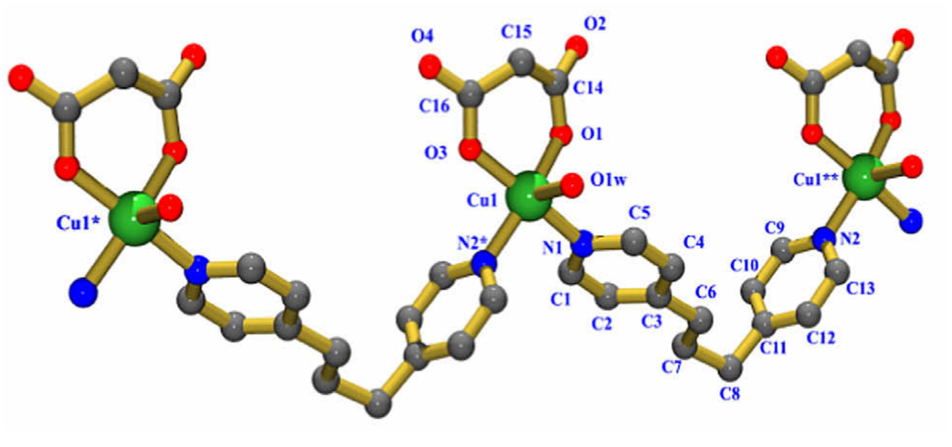

Fig. 1. The 1D polymeric chain of the complex (hydrogen atoms omitted).

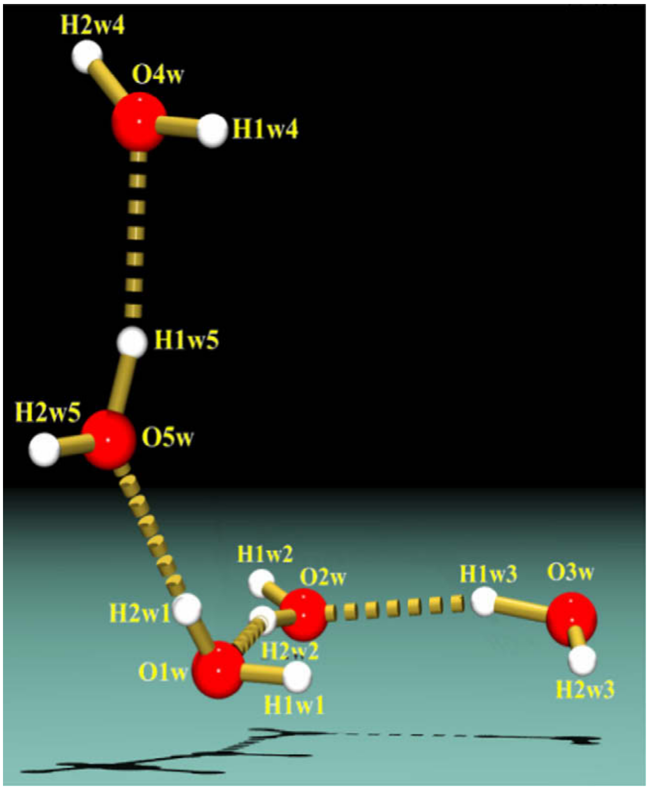

Fig. 2. The acyclic water pentamer.

groups of two malonates replace two water molecules. Motif A is more compact (O5W...O4W = 2.766 Å, <O5W–H1W5–O4W 164°) than motif B (O3W...O2W = 2.858 Å, <O3W–H13W–O2W 165.32°) (Table 1). Strongest association within the acyclic water pentamer is between O1W and O5W (O1W...O5W 2.70 Å, <O1W–H1W1...O5W 174°). O...O distances (2.70–2.86 Å) is comparable to the O. . .O distances observed in other water clusters in metal–organic frameworks [28,29] and the corresponding values in

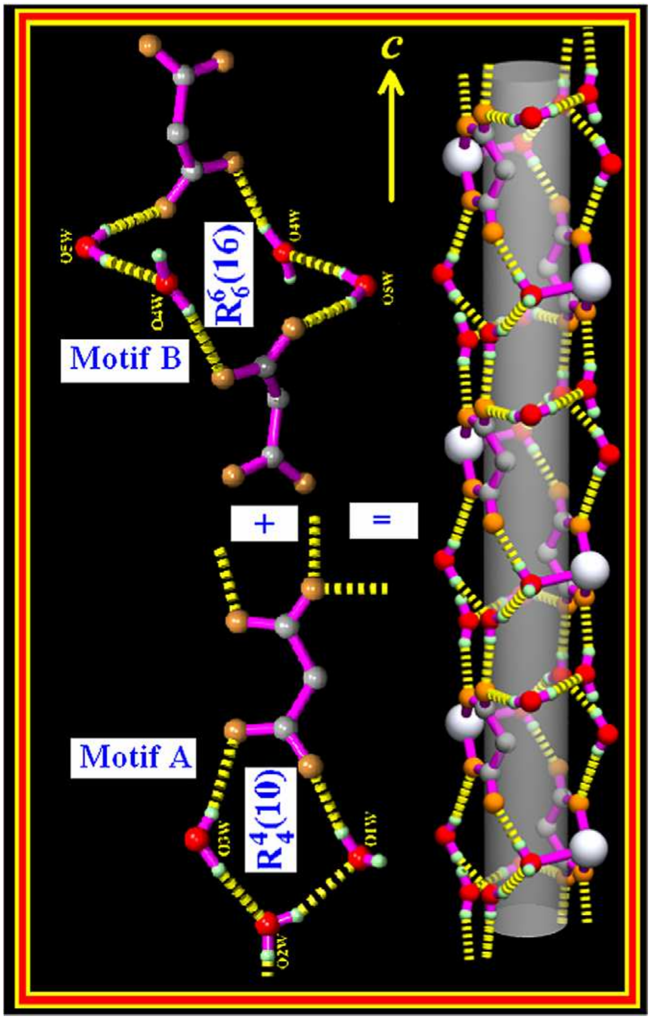

Fig. 3. The supramolecular channel assembled by motif A and B [color code: Cu-Cyan; O(water)-Red, C-Gray]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

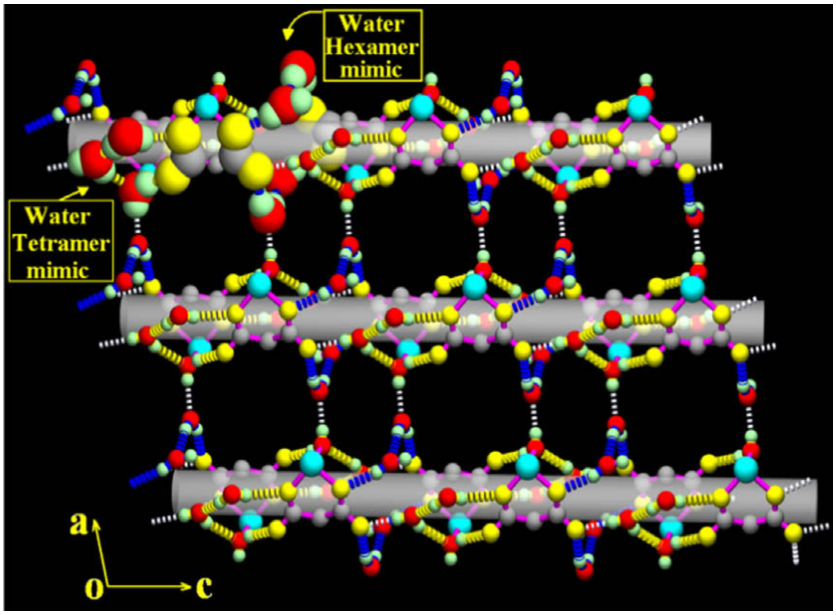

Fig. 4. The supramolecular ribbed sheet with wide and narrow grids and the channels as its ribs (color code: Cu-Cyan; O(water)-Red, C-Gray; O(malonate)-Yellow), bpp omitted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

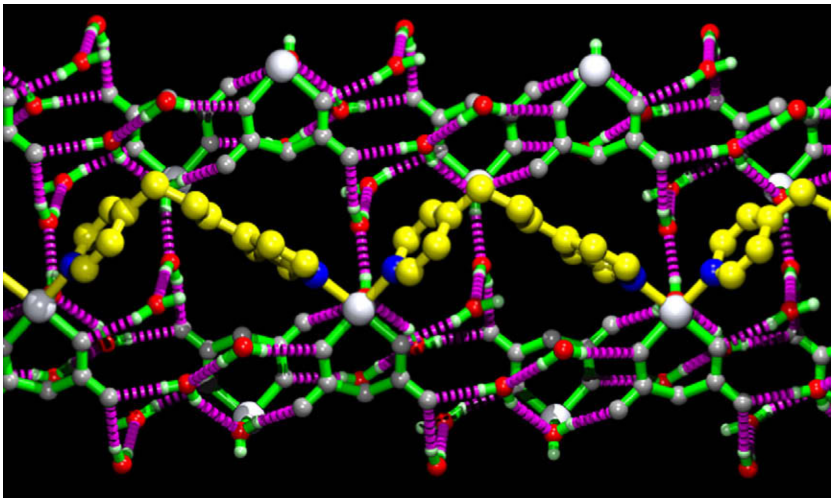

Fig. 5. The correlation between wide-narrow grid topology and long-short flex of bpp in TG mode demonstrates that even in certain cases weaker forces can cooperatively compete with covalent forces and may be suitably used to influence the conformation and coordination mode of ligands.

regular ice, in liquid water, and in the vapor phase are 2.74, 2.85 and 2.98 Å, respectively.

The motifs formed by the pentamer play two important roles: (i) two oppositely running supramolecular chains, formed by the self-assembly of motif A, link each other through motif B to form a tubular assembly along the *c* axis (Figs. 3 and S3) and (ii) these tubes line up side by side along the *a* axis and are connected to each other through hydrogen bonding interactions between O5W of motif A and O1w of motif B leading to a 2D ribbed sheet in the *ac* plane (Fig. 4). The tubes form the rib of the supramolecular sheet and in-between two ribs alternate narrow and wider grids are present (Fig. S4). The total width of successive narrow and wide grid along a rib is equal to the distance between successive Cu (II) centers (11.269 Å separation) (Fig. 5). This distance is just right for the trans-gauche (TG) mode of flexible bpp ligand. The obvious correlation between the wide-narrow network topology of the supramolecular sheet and the long-short flex of the bpp ligand in its TG conformation is clearly evident in Fig. 5. At this point we were curious about this particular conformation of bpp which generally adopts two other conformations trans–trans (TT) and guche–antiguche (GG) [30]. To find the lowest energy conformation among these three modes, we have performed the *ab initio* geometry optimization of bpp in these three modes. The optimized energies of the respective conformations are found to be $E_{TT} = -605.9330633$, $E_{GG'} = -605.9328347$ and $E_{TG} = -605.9298547$ Hartree, showing TT as lowest energy conformation. Thus the supramolecular ribbed sheet architecture, is the result of the self-assembly of bpp, malonate and water molecules around Cu centers, in which the cooperativity between water molecules, malonates and bpp ligands has been borne out in the generation of $R_4^4(10)$ and $R_6^6(16)$ water–malonate cluster motifs and the adoption of higher energy TG (Δ[TG–TT] = 2.01 kcal/mol; Δ[GG′–TT] = 1.87 kcal/mol) conformation of bpp.

In general, the Cu-malonate moieties have a tendency to assemble into a 2D coordination polymeric sheet [31–33]. By the introduction of a competing ligand bpp, and the participation of water in the coordination sphere of Cu, the donor atoms of malonate preferred to form novel motifs A and B with water molecules that compete over the tendency of malonate O-atoms to coordinatively bind to adjacent metal centers. This inhibits the malonate O-atoms to opt for the coordination bonds to adjacent Cu centers and the sheet formation is disrupted, instead a 2D supramolecular ribbed sheet is preferred. The synchronization of strong and weak interactions is further evidenced by the adoption of a high-energy TG conformation (than TT conformation) of bpp. This investigation focuses on the importance of both strong and weak interactions simultaneously in the assembly of crystalline materials.

Interestingly, in the present crystal structure motif A mimics the planar water tetramer and motif B mimics the cyclic water hexamer with chair conformation. From literature survey, we realized that when a number of water molecules are present in the crystal structure, they often tend to self-organize themselves in the form of regular water clusters such as tetramer, hexamer etc. The self-assembly of the water clusters are so robust that they can withstand appreciable amount of strain arisen from the penetration of perturbing organic ligands and they preserve their regular cluster geometry. The observation, that the malonate penetrates the motif A (tetramer) and motif B (hexamer), nicely substantiates above view.

3.2. Thermogravimetric analysis

The thermal stability of the water pentamer was studied. The compound was heated up to 200 °C at a rate of heating

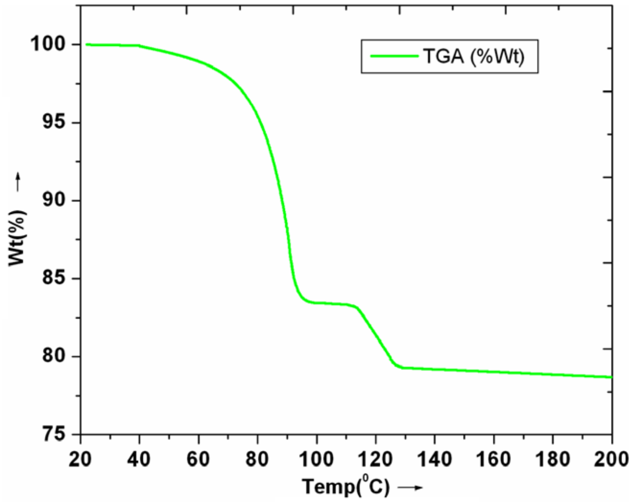

Fig. 6. The thermal analysis of compound **1** was plotted.

10 °C/min. The thermal analysis was plotted in Fig. 6. The water loss of the compound was happening in two steps. The weight loss starts from 45 °C, four water molecules were lost between 45 and 100 °C and the coordinated water molecule was lost within 110–130 °C.

4. Conclusion

In summary, the self-assembly of an acyclic water pentamer with malonate induces a supramolecular ribbed sheet by cooperativity and competitiveness of weak and covalent forces. The adoption of high-energy TG conformation by bpp indicates that the weak forces can compete the strong covalent forces and act in unison cooperatively. Further, an interesting observation is that the water clusters preserve their regular geometry even with the replacement of some water molecules by the acceptor atoms of perturbing ligands.

Acknowledgements

R.S. acknowledges financial support from the Council of Scientific and Industrial Research (CSIR), New Delhi under the JRF program (09/096(0565)2008-EMR-I). G.M. acknowledges Jadavpur University for a research grant under the "Nano Science and Technology Programme" with the University with Potential for Excellence Scheme of UGC (India).

Appendix A. Supplementary data

ORTEP diagram of the complex and figures of grid topology have been supplied as supplementary materials (Figs. S1–S4). CIF file for complex **1** bears the CCDC No. 606406. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.12.009.

References

[1] L.-S. Long, Y.-R. Wu, R.-B. Huang, L.-S. Zheng, Inorg. Chem. 43 (2004) 3798.
[2] G. Jiang, J. Bai, H. Xing, M. Scheer, Y. Li, X. You, Cryst. Growth Des. 6 (2006) 1264.
[3] B.-Q. Ma, H.-L. Sun, S. Gao, Chem. Commun. 19 (2004) 2220.
[4] S.K. Ghosh, P.K. Bharadwaj, Inorg. Chem. 42 (2003) 8250.
[5] M.H. Mir, J.J. Vittal, Cryst. Growth Des. 8 (2008) 1478.
[6] M.H. Mir, J.J. Vittal, Angew. Chem. 46 (2007) 5925.
[7] M.H. Mir, L. Wang, M.W. Wong, J.J. Vittal, Chem. Commun. (2009) 4539.
[8] J.L. Atwood, L.J. Barbour, T.J. Ness, C.L. Raston, P.L. Raston, J. Am. Chem. Soc. 123 (2001) 7192.
[9] S.-N. Wang, Y. Yang, J. Bai, Y.-Z. Li, M. Scheer, Y. Pan, X.-Z. You, Chem. Commun. 42 (2007) 4416.
[10] L.J. Barbour, G.W. Orr, J.L. Atwood, Chem. Commun. 10 (2000) 859.
[11] S.K. Ghosh, P.K. Bharadwaj, Angew. Chem. Int. Ed. 43 (2004) 3577.
[12] Q.-Y. Liu, L. Xu, CrystEngComm 7 (2005) 87.
[13] B.K. Saha, A. Nangia, Chem. Commun. 24 (2005) 3024.
[14] B. Sreenivasulu, J.J. Vittal, Angew. Chem. Int. Ed. 43 (2004) 5769.
[15] J.P. Naskar, M.G.B. Drew, A. Hulme, D.A. Tocher, D. Datta, CrystEngComm 7 (2005) 67.
[16] B.-Q. Ma, H.-L. Sun, S. Gao, Angew. Chem. Int. Ed. 43 (2004) 1374.
[17] S. Supriya, S. Manikumari, P. Raghavaiah, S.K. Das, New J. Chem. 27 (2003) 218.
[18] K.V. Katti, P.K. Bharadwaj, J.J. Vittal, R. Kannan, Synth. React. Inorg. Met.-Org. Nano-Met. 38 (1) (2008).
[19] L. Infantes, S. Motherwell, CrystEngComm 4 (2002) 454.
[20] P. Misra, M. Nayek, P. Lemoine, R. Koner, S. Mohanta, J. Coord. Chem. 61 (7) (2008) 1088.
[21] C.-B. Liu, G.-B. Che, C.-B. Li, Y.C. Cui, Acta Crystallogr. Sect. C Cryst. Struct. Commun. 62 (4) (2006) 153.
[22] A.X.S. Bruker, SAINT Software Reference Manual, Madison, WI, 1998.
[23] G.M. Sheldrick, SADABS, Siemens Area Detector Absorption Corrected Software, University of Göttingen, Germany, 1996.
[24] G.M. Sheldrick, SHELXTL NT, Version 5.1; Program for Solution Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[25] M.J. Frisch et al., Gaussian 03, Revision C.02; Gaussian, Inc., Wallingford, CT, 2004 (See supplementary for complete reference).
[26] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, J. Verschoor, J. Chem. Soc. Dalton Trans. 7 (1984) 1349.
[27] M.C. Etter, Acc. Chem. Res. 23 (1990) 120.
[28] S. Manikumari, V. Shivaiah, S.K. Das, Inorg. Chem. 41 (2002) 6953.
[29] J.N. Moorthy, R. Natarajan, P. Venugopalan, Angew. Chem. Int. Ed. 41 (2002) 3417.
[30] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, CrystEngComm 4 (2002) 121.
[31] S.R. Choudhury, A.D. Jana, E. Colacio, H.M. Lee, G. Mostafa, S. Mukhopadhyay, Cryst. Growth Des. 7 (2007) 212.
[32] D. Ghoshal, T.K. Maji, T. Mallah, T.H. Lu, G. Mostafa, N.R. Chaudhuri, Inorg. Chim. Acta 358 (2005) 1027.
[33] I.G.D. Muro, F.A. Mautner, M. Insausti, L. Lezama, M.I. Arriortua, T. Rojo, Inorg. Chem. 37 (1998) 3243.