

# Hydrogen bond mediated open-frame networks in coordination polymers: supramolecular assemblies of Pr(III) and 3,5-dinitro-4-methylbenzoic acid with aza-donor compounds†

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Received (in Cambridge, UK) 23rd November 2004, Accepted 25th January 2005

First published as an Advance Article on the web 7th February 2005

DOI: 10.1039/b417754a

A coordination assembly of 3,5-dinitro-4-methylbenzoic acid and Pr(III), synthesized by hydrothermal methods forms a host structure, which is stable up to 300 °C, through C–H···O hydrogen bonds and accommodates different types of guest species varying from simple molecules like water to larger molecules like *trans*-1,2-bis(4-pyridyl)ethene.

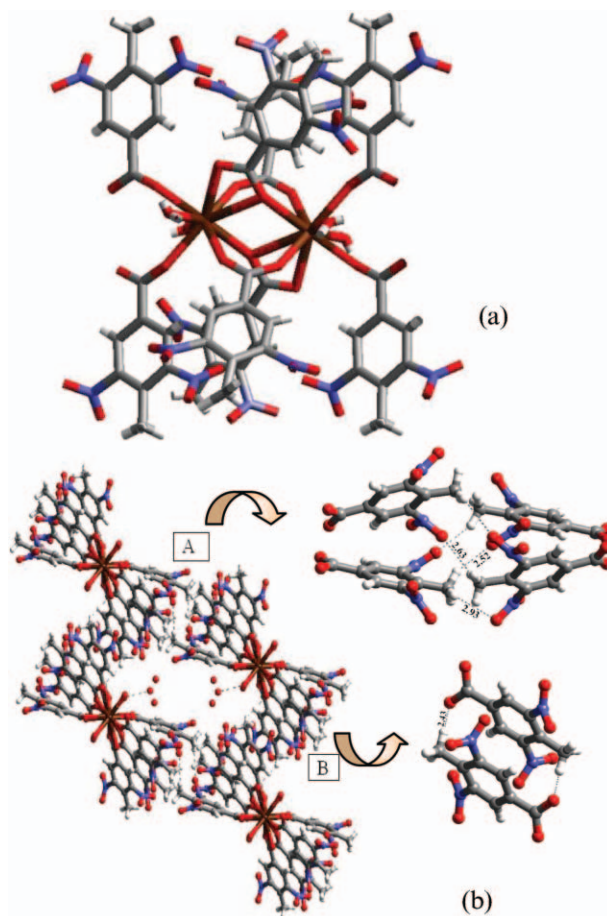
Naturally occurring inorganic minerals, like zeolites,<sup>1</sup> with well-defined open-frame networks, possessing different types of voids and channels, are the source of inspiration for current research activities in the design and synthesis of open-frame networks of varied architectures.<sup>2,3</sup> Metal–organic hybrids with distinctly strong bonding properties between metal and organic ligands are considered to be robust enough to mimic zeolite type structures.<sup>4</sup>

Several carboxylate mediated coordination polymers have proved to be quite successful in forming self-assembled open-frame networks that accommodate various guest species.<sup>5,6</sup> In most of these assemblies the host structures are designed to form exclusively through dative bonds. However, taking into account the nature of functional groups such as –NO<sub>2</sub> and –NH<sub>2</sub> to form well defined robust hydrogen bond networks,<sup>7</sup> but which have less affinity towards metal ions, we have focused on the syntheses of metal–organic supramolecular assemblies employing organic ligands having –NO<sub>2</sub> groups along with carboxylates in order to evaluate the role of both types of bonds in forming the requisite host structures, as only a few such structures are known in the literature.<sup>8</sup> For this purpose, syntheses of coordination assemblies of 3,5-dinitro-4-methylbenzoic acid (DNMB) with Pr(III), considering the growing interest of evaluation of lanthanide ions in the supramolecular studies,<sup>9</sup> have been carried out.

Pale yellow single crystals obtained from the hydrothermal reaction of an aqueous solution of DNMB and praseodymium acetate (PA) gave a coordination complex, **1**, [Pr<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>O<sub>6</sub>)<sub>6</sub>·(H<sub>2</sub>O)<sub>4</sub>]·6H<sub>2</sub>O, as characterized by X-ray diffraction techniques.‡

Analysis of the coordination geometry reveals that **1** is a dinuclear metal complex with two Pr(III) ions being bridged by the carboxylate groups of two DNMB molecules with an average Pr–O distance of 2.400 Å (Fig. 1(a)). Unique metal–ligand bond distances are given in Table 1. In addition, each Pr(III) shows a nine coordination environment with further bonding to three more DNMB molecules and two water molecules in such a manner that

one of the DNMB molecules forms chelated Pr–O bonds, through carboxylate groups. The average Pr–O distance is 2.665 Å. The remaining two DNMB molecules, however, act as bis-monodentate ligands towards Pr(III), giving rise to one-dimensional polymers, with Pr–O distances of 2.418 and 2.495 Å. The water molecules are coordinated to Pr(III) at distances of 2.563 and 2.610 Å. The three-dimensional arrangement of these species, however, is quite intriguing in the formation of an open-frame network through the anticipated hydrogen bonding networks



**Fig. 1** (a) Coordination of DNMB and water around Pr(III) forming a dinuclear unit in the crystal structure of complex, **1**. (b) Formation of channels, occupied by six water molecules. C–H···O hydrogen bonds between the units denoted A and B are shown in expansion.

† Electronic supplementary information (ESI) available: Experimental details, ORTEP diagrams and thermogravimetric data. See <http://www.rsc.org/suppdata/cc/b4/b417754a/>

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**Table 1** Bond distances around the coordination sphere of Pr(III)

Compound	Pr–O <sub>(carboxylate)</sub>			
	Pr–O <sub>(water)</sub>	Bridging	Chelating	$\mu$ -oxo bridging
1	2.563(7)	2.391(6) <sup>a</sup>	2.559(6)	2.460(6)
	2.610(6)	2.408(6) <sup>a</sup>	2.772(6)	
2	2.563(2)	2.418(6) <sup>b</sup>	2.567(2)	2.483(2)
		2.495(6) <sup>b</sup>		
	2.563(2)	2.420(2) <sup>a</sup>	2.828(2)	
	2.421(2) <sup>a</sup>			
	2.422(2) <sup>b</sup>	2.467(2) <sup>b</sup>		
3	2.567(4)	2.393(4) <sup>a</sup>	2.572(4)	2.486(4)
	2.628(4)	2.406(4) <sup>a</sup>	2.708(4)	
	2.428(4) <sup>b</sup>	2.472(4) <sup>b</sup>		
	2.472(4) <sup>b</sup>			
4	2.552(3)	2.405(3) <sup>a</sup>	2.577(3)	2.488(2)
	2.617(3)	2.414(2) <sup>a</sup>	2.730(2)	
	2.424(3) <sup>b</sup>	2.468(2) <sup>b</sup>		

<sup>a</sup> Bridging within the bimetallic unit. <sup>b</sup> Bridging between bimetallic species.

between the –CH<sub>3</sub> and –NO<sub>2</sub> groups. A typical arrangement is shown in Fig. 1(b).

Two different types of hydrogen bonding networks, as represented by A and B in Fig. 1(b), connect four neighboring units with the formation of C–H $\cdots$ O hydrogen bonds with H $\cdots$ O distances in the range 2.43–2.95 Å. Thus, the aggregation of the coordination units through C–H $\cdots$ O hydrogen bonds, results in the formation of channels (6  $\times$  15 Å<sup>2</sup>), which are occupied by six water molecules (see Fig. 1(b)).

It is apparent from the thermogravimetric analysis that water molecules in the channels are being evacuated at around 130 °C and the complex is found to be crystalline and stable as confirmed by X-ray powder diffraction methods. We wished to insert hydrocarbons like naphthalene and anthracene in such channels as these hydrocarbons are well known to act as guests.<sup>7</sup> But, our experiments revealed that the components crystallized separately, perhaps due to incompatibility between the dimensions of the channels and the guests.

Hence, we carried out hydrothermal synthesis of DNMB and PA in the presence of 4,4'-bipyridyl (bpy) with a hope that bpy will facilitate the creation of larger channels as it is well known to act as a spacer in many other assemblies to accommodate large guest molecules. To our surprise, crystal structure determination,

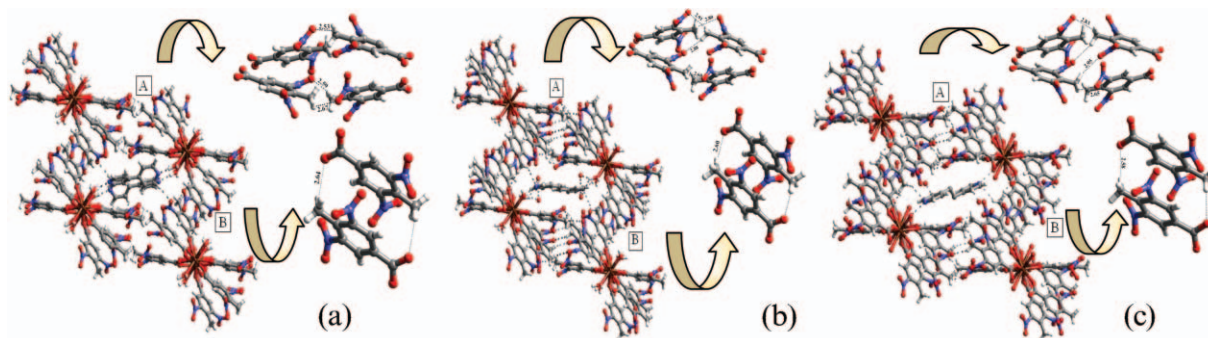
however, discloses that a complex, [Pr<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>O<sub>6</sub>)<sub>6</sub>·(H<sub>2</sub>O)<sub>4</sub>]·2C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>, **2**, was formed, in which bpy exists as a free ligand in the asymmetric unit without coordinating to Pr(III).<sup>‡</sup> Nevertheless, complexes **1** and **2** are isostructural, with similar aggregation patterns and channels due to the association of the neighboring coordination units through C–H $\cdots$ O hydrogen bonds, except for the guest molecules. The C–H $\cdots$ O hydrogen bonds observed in **2** are acyclic with H $\cdots$ O distances in the range 2.53–2.92 Å as shown in Fig. 2(a). Such an arrangement ultimately constituted channels (7  $\times$  14 Å<sup>2</sup>), in a three-dimensional arrangement as shown in Fig. 3, which are occupied by two molecules of bpy, replacing all six water molecules observed in complex, **1**.

The bpy molecules in the channels interact with the host through the formation of O–H $\cdots$ N hydrogen bonds (N $\cdots$ O, 2.77 and 2.80 Å). Furthermore, the open-frame network observed in complexes **1** and **2** is quite stable even to perform guest-exchange reactions, as we noted that a reaction between complex **1** (possessing water in the channels) and bpy gave exclusively complex, **2** (channels filled with bpy) in 100% yield.

Similar observations were also noted for the guest-exchange reaction between complex **1** and *trans*-1,2-bis(4-pyridyl)ethene (bpyee), forming a complex, [Pr<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>O<sub>6</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>](C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>)·(4H<sub>2</sub>O), **3**,<sup>‡</sup> except that four water molecules still remain in the channels along with bpyee. The open-frame network, positions of bpyee and water molecules within the channels (6  $\times$  16 Å<sup>2</sup>) are shown in Fig. 2(b). In fact, complex **3** could not be synthesized by a direct reaction between DNMB and PA in the presence of bpyee.

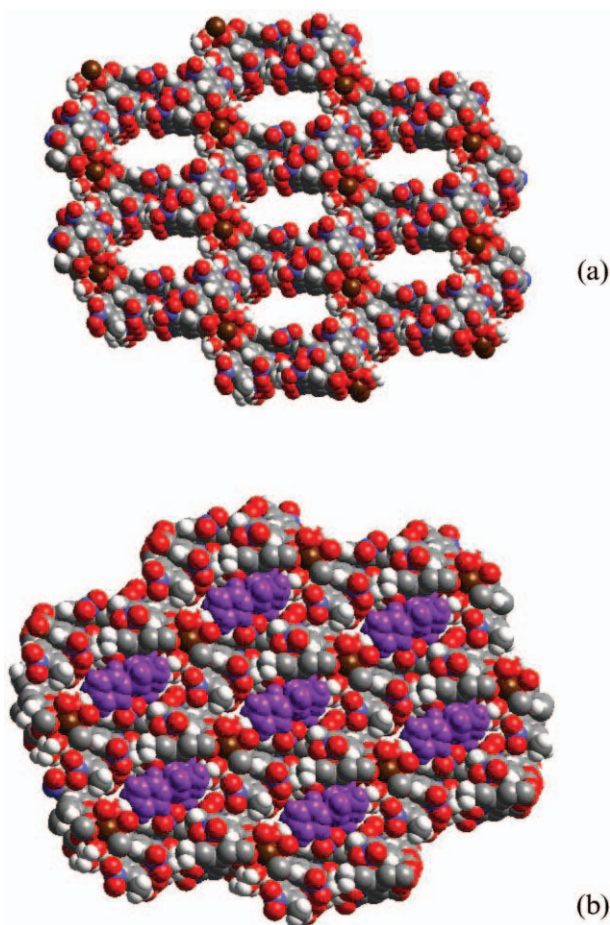
In contrast, 1,2-bis(4-pyridyl)ethane (bpyea), an analogue of bpyee, forms the complex [Pr<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>O<sub>6</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>](C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>)·(4H<sub>2</sub>O), **4**, directly from a reaction between DNMB and PA along with bpyea.<sup>‡</sup> The molecular arrangement in complex **4** is shown in Fig. 2(c). This complex also is isostructural to those of **1–3** but bpyea molecules occupy the channels (5  $\times$  16 Å<sup>2</sup>) as guest molecules. Thus, in addition to the robustness, the open-frame network formed by DNMB and Pr(III) also shows the flexibility to accommodate additional molecules. Perhaps interaction between the coordination units through weak bonds (C–H $\cdots$ O hydrogen bonds), which would reorganize with ease, rather than strong bonds, facilitated the expansion of the channels.

In conclusion, we have demonstrated the utilization of both coordinate bonds as well as hydrogen bonds to form host–guest complexes. Further, the robustness of the host network formed by DNMB and Pr(III) is comparable to those of similar structures



**Fig. 2** Channels observed in the complexes, **2**, **3** and **4** which are occupied by (a) 4,4'-bipyridine, (b) *trans*-1,2-bis(4-pyridyl)ethene and (c) 1,2-bis(4-pyridyl)ethane, respectively. Arrows indicate the vivid description of C–H $\cdots$ O hydrogen bonding pattern between the adjacent units.





**Fig. 3** Representation of channels ( $7 \times 14 \text{ \AA}^2$ ) observed in the three-dimensional arrangement of complex, 2, (a) without guest molecules and (b) with guest molecules 4,4'-bipyridine.

formed by purely dative bonds. We believe that the complexes presented in this communication will emerge as leading examples to explore numerous systems employing different types of organic ligands and we are currently exploring many of these systems.

We thank Dr. S. Sivaram, Director, NCL, and Dr. K. N. Ganesh, Head of the Division, NCL for their encouragement. One of us (SV) thanks CSIR, New Delhi for the award of JRF.

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## Notes and references

‡ Crystal data for complex, 1:  $[\text{Pr}(\text{C}_8\text{H}_5\text{N}_2\text{O}_6)_3(\text{H}_2\text{O})_2] \cdot 3(\text{H}_2\text{O})$ ,  $M_r = 906.41$ , yellow needles,  $0.35 \times 0.27 \times 0.19 \text{ mm}$ , triclinic,  $P\bar{1}$ ,  $a = 9.483(3)$ ,  $b = 12.593(3)$ ,  $c = 15.517(4) \text{ \AA}$ ,  $\alpha = 76.89(9)$ ,  $\beta = 78.10(9)$ ,  $\gamma = 81.33(9)^\circ$ ,  $V = 1755.4(12) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.715 \text{ g cm}^{-3}$ ,  $\mu = 1.488 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 46.50$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $T = 298(2) \text{ K}$ , 14587 total reflections,  $R_1 = 0.0598$  and  $wR2 = 0.1884$  for 4903 reflections ( $I > 2\sigma(I)$ ). CCDC 233738.

Crystal data for complex, 2:  $[\text{Pr}(\text{C}_8\text{H}_5\text{N}_2\text{O}_6)_3(\text{H}_2\text{O})_2] \cdot (\text{C}_{10}\text{H}_8\text{N}_2)$ ,  $M_r = 1008.55$ , yellow needles,  $0.37 \times 0.23 \times 0.18 \text{ mm}$ , triclinic,  $P\bar{1}$ ,  $a = 9.774(4)$ ,  $b = 12.721(6)$ ,  $c = 16.355(7) \text{ \AA}$ ,  $\alpha = 72.01(9)$ ,  $\beta = 82.90(9)$ ,  $\gamma = 83.15(9)^\circ$ ,

$V = 1912.2(18) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.752 \text{ g cm}^{-3}$ ,  $\mu = 1.372 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 46.60$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $T = 298(2) \text{ K}$ , 16061 total reflections,  $R_1 = 0.0255$  and  $wR2 = 0.0661$  for 5183 reflections ( $I > 2\sigma(I)$ ). CCDC 233739.

Crystal data for complex, 3:  $[\text{Pr}(\text{C}_8\text{H}_5\text{N}_2\text{O}_6)_3(\text{H}_2\text{O})_2] \cdot 0.5 \cdot (\text{C}_{12}\text{H}_{10}\text{N}_2) \cdot 2(\text{H}_2\text{O})$ ,  $M_r = 979.50$ , yellow needles,  $0.41 \times 0.29 \times 0.22 \text{ mm}$ , triclinic,  $P\bar{1}$ ,  $a = 9.510(9)$ ,  $b = 12.669(9)$ ,  $c = 16.430(2) \text{ \AA}$ ,  $\alpha = 72.28(2)$ ,  $\beta = 79.06(2)$ ,  $\gamma = 79.72(2)^\circ$ ,  $V = 1836(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.772 \text{ g cm}^{-3}$ ,  $\mu = 1.429 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 46.70$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $T = 298(2) \text{ K}$ , 15345 total reflections,  $R_1 = 0.0345$  and  $wR2 = 0.0711$  for 4253 reflections ( $I > 2\sigma(I)$ ). CCDC 233740.

Crystal data for complex, 4:  $[\text{Pr}(\text{C}_8\text{H}_5\text{N}_2\text{O}_6)_3(\text{H}_2\text{O})_2] \cdot 0.5 \cdot (\text{C}_{12}\text{H}_{12}\text{N}_2) \cdot 2(\text{H}_2\text{O})$ ,  $M_r = 980.51$ , yellow needles,  $0.39 \times 0.26 \times 0.20 \text{ mm}$ , triclinic,  $P\bar{1}$ ,  $a = 9.517(2)$ ,  $b = 12.747(2)$ ,  $c = 16.366(3) \text{ \AA}$ ,  $\alpha = 72.21(2)$ ,  $\beta = 78.98(3)$ ,  $\gamma = 79.84(2)^\circ$ ,  $V = 1840.8(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.769 \text{ g cm}^{-3}$ ,  $\mu = 1.425 \text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 46.54$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $T = 298(2) \text{ K}$ , 11563 total reflections,  $R_1 = 0.0283$  and  $wR2 = 0.0768$  for 5016 reflections ( $I > 2\sigma(I)$ ). CCDC 233741. See <http://www.rsc.org/suppdata/cc/b4/b417754a/> for crystallographic data in .cif or other electronic format.

- W. H. Meier, D. H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types*, Elsevier, Boston, 1996; R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982.
- B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022–2043; H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, *Nature*, 1999, **402**, 276–279; C. L. Bowes and G. A. Ozin, *Adv. Mater.*, 1996, **8**, 13; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Whithersby and M. Schroder, *Coord. Chem. Rev.*, 1999, **183**, 117.
- K.-L. Lu, J.-C. Wang, H.-C. Wu, Y.-L. Lu and Y.-H. Liu, *Inorg. Chem.*, 2002, **41**, 2592–2597; M. Hong, Q. Shi, K. Tatsumi, Y. Liang, D. Sun and R. Cao, *Inorg. Chem.*, 2002, **41**, 2087–2094; R. Kitaura, K. Fujimoto, S. Noro, M. Kondo and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2002, **41**, 133–135; H. Wiczman and Y. Tor, *J. Am. Chem. Soc.*, 2001, **123**, 3375–3376; J.-M. Lehn, *Comprehensive Supramolecular Chemistry*, Pergamon, New York, 1996; M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2000, **112**, 3180–3182; S. Ijima and T. Ichihashi, *Nature*, 1993, **363**, 603–605.
- W. Mori and S. Takamizawa, *J. Solid State Chem.*, 2000, **152**, 120–129; M. D. Hollingsworth, *Science*, 2002, **295**, 2410–2413; H. Bourahma, B. Moulton, V. Kravtsov and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2002, **124**, 9990–9991; D. L. Reger, R. F. Semeniuc and M. D. Smith, *Eur. J. Inorg. Chem.*, 2002, 543–546.
- C. Janiak, *Angew. Chem., Int. Ed.*, 1997, **36**, 1431–1434; Y. Cui, H. L. Ngo and W. B. Lin, *Inorg. Chem.*, 2002, **41**, 1033–1035; B. Schmaltz, A. Jouaiti, M. W. Hosseini and A. De Cian, *Chem. Commun.*, 2001, 1242–1243; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1659; D. M. L. Goodgame, S. Menzer, A. T. Ross and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 2605–2606; T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, New York, 1994; S. Noro, S. Kitagawa, M. Kondo and K. Seiki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081–2084.
- H. Li, M. Eddaoudi, M. O'Keefe, B. Chen, D. B. Moler, T. M. Reinecke and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **35**, 319–330; B. L. Chen, M. Eddaoudi, M. O'Keefe, S. T. Hyde and O. M. Yaghi, *Science*, 2001, **291**, 1021–1023; G. D. Enright, K. A. Udachin, I. L. Moudrakovski and J. A. Ripmeester, *J. Am. Chem. Soc.*, 2003, **125**, 9896–9897.
- V. R. Pedireddi, W. Jones, A. P. Charlton and R. Docherty, *Chem. Commun.*, 1996, 997–998; V. R. Pedireddi and J. PrakashaReddy, *Tetrahedron Lett.*, 2002, **43**, 4927–4930; V. R. Pedireddi and J. PrakashaReddy, *Tetrahedron Lett.*, 2003, **44**, 6679–6683; V. R. Pedireddi, J. PrakashaReddy and K. K. Arora, *Tetrahedron Lett.*, 2003, **44**, 4857–4860.
- V. R. Pedireddi and S. Varughese, *Inorg. Chem.*, 2004, **43**, 450–457; K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward and M. J. Zaworotko, *Chem. Commun.*, 1999, 1327–1328.
- L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori and K. Kaneko, *J. Am. Chem. Soc.*, 2003, **125**, 3062–3067; Y. Fukuda, A. Nakao and K. Hayashi, *J. Chem. Soc., Dalton Trans.*, 2002, 527–533; R. Gheorghe, M. Andruh, A. Muller and M. Schmidtman, *Inorg. Chem.*, 2002, **41**, 5314–5316.