

μ -4,4'-Bipyridine- $\kappa^2N:N'$ -bis[tri-aqua(4,4'-bipyridine- κN)cadmium(II)] bis(3-aminobenzoate) bis(perchlorate) dihydrate: a novel supramolecular system constructed by π - π and hydrogen-bonding interactions

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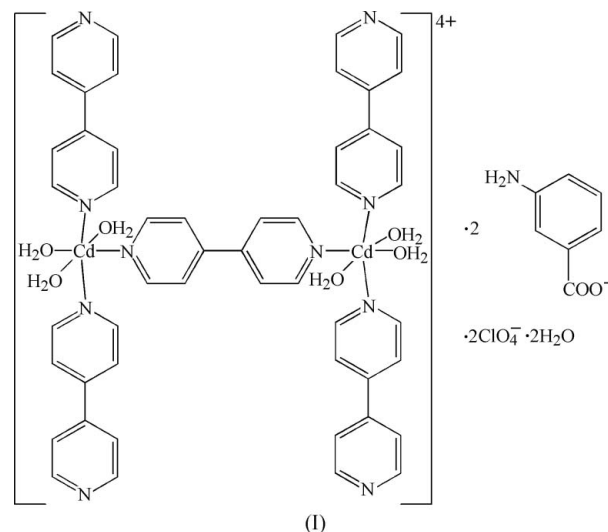
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The title dicadmium compound, $[\text{Cd}_2(\text{C}_{10}\text{H}_8\text{N}_2)_5(\text{H}_2\text{O})_6] \cdot (\text{C}_7\text{H}_6\text{NO}_2)_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, is located around an inversion centre. Each Cd^{II} centre is coordinated by three N atoms from three different 4,4'-bipyridine ligands and three O atoms from three coordinating water molecules in a distorted octahedral coordination environment. In the dicadmium cation unit, one 4,4'-bipyridine (4,4'-bipy) molecule acts as a bidentate bridging ligand between two Cd metal ions, while the other four 4,4'-bipy molecules act only as monodentate terminal ligands, resulting in a rare 'H-type' $[\text{Cd}_2(\text{C}_{10}\text{H}_8\text{N}_2)_5(\text{H}_2\text{O})_6]$ host unit. These host units are connected to each other *via* π - π stacking interactions, giving rise to a three-dimensional supramolecular grid network with large cavities. The 3-aminobenzoate anions, perchlorate anions and water molecules are encapsulated in the cavities by numerous hydrogen-bonding interactions. To the best of our knowledge, this is the first example of a coordination compound based on both 4,4'-bipyridine ligands together with discrete 3-aminobenzoate anions.

Comment

Over recent decades, the design and construction of supramolecular coordination polymers through coordination of metal ions with multifunctional organic ligands have received extensive attention due to their fascinating topologies, their electrostatic, optic and magnetic properties, and other potential applications (Li *et al.*, 1999; Moulton & Zaworotko, 2001; Lehn, 1990; Yaghi *et al.*, 2003; Eddaoudi *et al.*, 2001). To date, numerous examples of open metal-organic frameworks have been constructed *via* covalent interactions (Phan *et al.*, 2010; Yaghi *et al.*, 1998). Aside from covalent interactions, π - π and hydrogen-bonding contacts are also used to construct

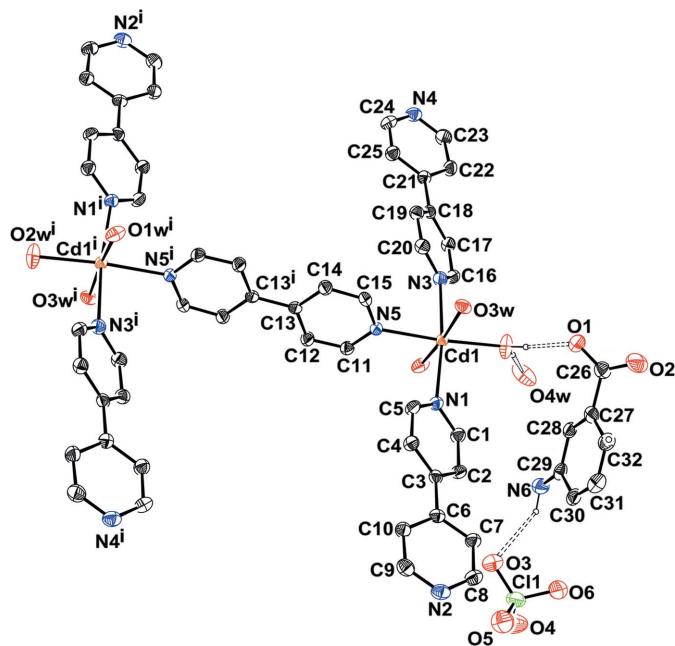
interesting coordination polymers with useful physico-chemical properties and intriguing structural topologies (Pan *et al.*, 2001; Jennieffer & Muthiah, 2011; Lipstman & Goldberg, 2009; Xu & Xie, 2010).



The incorporation of transition metal ions into one-, two- and three-dimensional coordination frameworks is currently of great interest in supramolecular chemistry (Ma *et al.*, 2004; Granifo *et al.*, 2004; Cheng *et al.*, 2011; Hazra *et al.*, 2011). Notably, the selection of multifunctional organic ligands, such as carboxylates, bipyridine (bipy) or its derivatives, and mixtures of both carboxylate and bipy ligands, is a key step in the design and assembly of expected compounds (Tong & Chen, 2000; Liao *et al.*, 2004; Prior *et al.*, 2003; Ayyappan *et al.*, 2002). In general, 4,4'-bipy ligands may act in bidentate bridging or monodentate terminal coordination modes to transition metal ions, leading to the formation of one-dimensional linear, zigzag, ladder, molecular antenna railroads and chains, two-dimensional square and rectangular grid networks, or three-dimensional non-interpenetrated and interpenetrated networks (Biradha *et al.*, 2006).

Recently, 4-aminobenzoate anions and 4,4'-bipy ligands have been chosen to construct transition metal coordination compounds (Li *et al.*, 2003; Qiu *et al.*, 2008); however, a careful investigation of the Cambridge Structural Database (CSD; Allen, 2002) revealed that no examples of coordination polymers or other compounds incorporating a mixture of 4,4'-bipy ligands and 3-aminobenzoate anions have been reported. In our continuing efforts to prepare new coordination frameworks (Fang & Wang, 2010; Wang & Fang, 2010; Wang *et al.*, 2010), we have isolated a new cadmium metal-organic framework, μ -4,4'-bipyridine-bis[triaqua(4,4'-bipyridine)cadmium(II)] bis(3-aminobenzoate) bis(perchlorate) dihydrate, (I), which is constructed from 3-aminobenzoate anions and 4,4'-bipy ligands. The 4,4'-bipy ligands in (I) exhibit a rare 'H-type' mode to cadmium metal ions, resulting in the formation of a rectangular grid network hosting the organic ligands, anions and water molecules *via* weak noncovalent interactions.

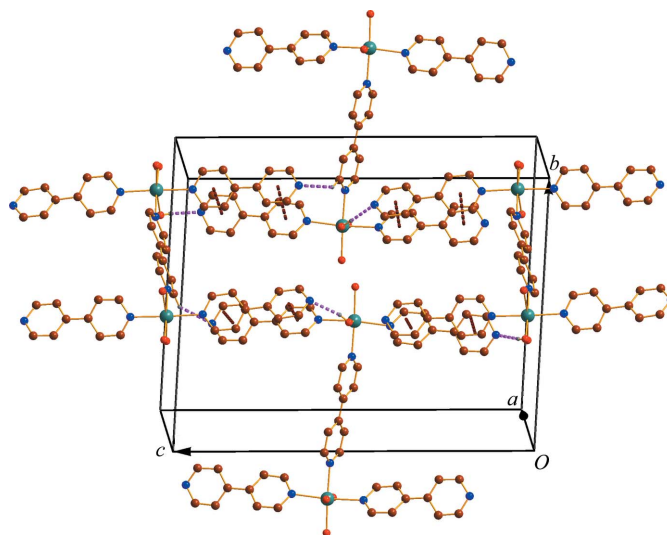
Compound (I) (Fig. 1) is built up of a dicadmium unit which is located around an inversion centre. The asymmetric unit


Figure 1

View of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only H atoms engaged in hydrogen bonding are shown (small spheres of arbitrary radii). Hydrogen bonds are shown as dashed lines. Only the major component of the disordered 3-aminobenzoate anion is shown. [Symmetry code: (i) $-x, -y, -z + 1$.]

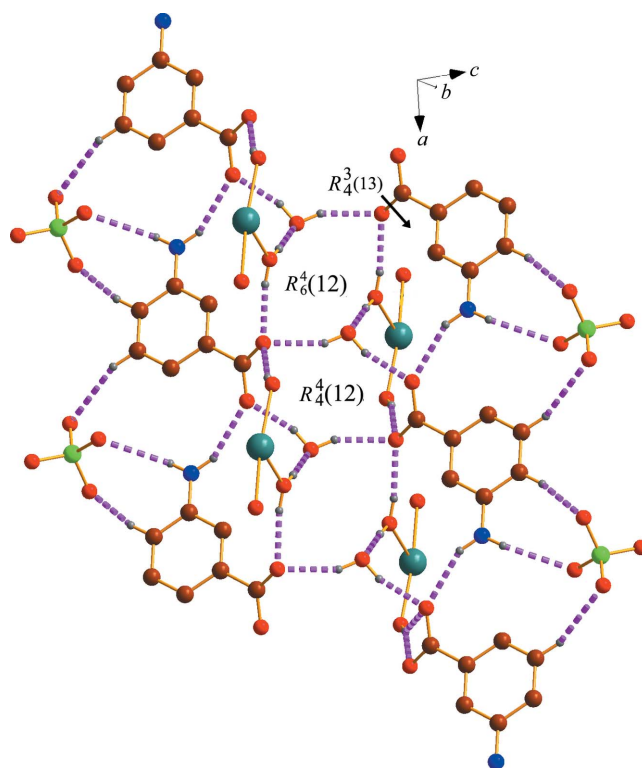
contains an isolated $[\text{Cd}(4,4'\text{-bipy})_{2.5}(\text{H}_2\text{O})_3]^{2+}$ cation, one 3-aminobenzoate anion, one perchlorate anion and one water molecule. The interstitial 3-aminobenzoate anion is independently disordered over two positions with an occupancy ratio of 64:36 (see *Refinement* section). The Cd^{II} centre is six-coordinated by three N atoms from three different 4,4'-bipy ligands and three aqua ligands, displaying a distorted octahedral coordination environment. The Cd–O and Cd–N bond distances and their relevant bond angles (Table 1) range from 2.2275 (16) to 2.3699 (19) Å and 86.35 (6) to 174.51 (7)°, respectively, values that are within the range of those observed for other Cd^{II} complexes with oxygen or nitrogen donors (Qiu *et al.*, 2007). Interestingly, only one 4,4'-bipy molecule in three crystallographically independent bipy ligands acts as a bidentate bridging ligand between two Cd metal ions, while the other two function only as monodentate terminal ligands. This leads to the formation of an 'H-type' host unit. There are numerous examples of metal coordination compounds derived from 4,4'-bipy ligands, but only two cases with an 'H-type' host unit, namely $[\text{Cd}_2(\text{NO}_3)_2(4,4'\text{-bipy})_5(\text{H}_2\text{O})_4](\text{PF}_6)_2$ (Dong *et al.*, 2000) and $[\text{Cd}_2(\text{NO}_3)_2(4,4'\text{-bipy})_5(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Aoyagi *et al.*, 2000).

The most striking feature of the structure is that the rare 'H-type' host units are connected to each other *via* face-to-face π – π interactions among the pyridine rings of the 4,4'-bipy ligands to form a rectangular grid network (Fig. 2). Each rectangular grid is constructed from closely stacking 4,4'-bipy ligands of four 'H-type' units with a large cavity of ca 11.7×23.8 Å, based on the distances between the Cd atoms at the


Figure 2

A ball-and-stick perspective view of the rectangular grid formed *via* the π – π overlap of adjacent 4,4'-bipy ligands of the four 'H-type' host units. Hydrogen bonds and π – π interactions are shown as dashed lines and non-interacting H atoms have been omitted for clarity.

corners of the described box. The centroid–centroid distances between neighbouring 4,4'-bipy ligands are in the range ca 3.6–4.0 Å (Table 2), indicating normal π – π stacking interactions (Lee *et al.*, 2007); it may be noted that one of these interactions displays a much greater slippage of 1.737 Å, which


Figure 3

A ball-and-stick perspective view of the three independent components (3-aminobenzoate and perchlorate anions, and water molecules) in (I) running along the a axis assembled by hydrogen bonds (dashed lines). Non-interacting H atoms have been omitted for clarity.

might correspond to an edge-to-edge interaction. This arrangement is similar to that of $[\text{Cd}_2(4,4'\text{-bipy})_4(\text{H}_2\text{O})_6](\text{ClO}_4)_2(\text{paba})_2 \cdot 4,4'\text{-bipy} \cdot 5\text{H}_2\text{O}$ (paba is 4-aminobenzoate), whose structure is constructed from infinite stacking 'H-type' chains (Qiu *et al.*, 2008). Obviously, to form suitable π - π interactions and reduce electrostatic forces from the short 2,2'/H...H contacts, the pyridine rings within the two monodentate terminal 4,4'-bipy ligands are not coplanar, with dihedral angles between them of 31.17 (11) and 30.22 (11)°. Furthermore, the terminal 4,4'-bipy ligands are connected to the $\text{Cd}(\text{OH}_2)_3$ units of adjacent cations by water-pyridine O-H...N and pyridine-pyridine C-H...N hydrogen bonds (Table 3 and Fig. 2).

In the structure of (I), three independent components (3-aminobenzoate, perchlorate anions and lattice water molecules) are encapsulated in the cavities by multiple hydrogen bonds (Table 3). The $\text{Cd}(\text{OH}_2)_3$ units are surrounded by the lattice water molecules and the carboxylate O atoms of the 3-aminobenzoate anions, and all of these are connected to each other *via* strong O-H...O hydrogen bonds in a cyclic $R_6^4(12)$ motif (Etter *et al.*, 1990; Bernstein *et al.*, 1995). Meanwhile, the 3-aminobenzoate anions are arranged in a chain running along the *a* axis through amine-carboxylate N-H...O hydrogen bonds, which are further linked to the $R_6^4(12)$ rings, giving rise to $R_4^3(13)$ and $R_4^4(12)$ rings (Fig. 3). In addition, a C-H... π contact (Table 3) also enhances the stability of the component. The remaining voids are occupied by numerous perchlorate anions that are linked to cations and 3-aminobenzoate anions by N-H...O and C-H...O hydrogen bonds (Table 3).

Experimental

A mixture of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.419 g, 1 mmol), 4,4'-bipy (0.390 g, 2.5 mmol) and 75% ethanol solution (20 ml) was stirred for 30 min at 353 K and then added to 3-aminobenzoic acid (0.137 g, 1 mmol); the pH of the resulting solution was adjusted to 7.0 with an aqueous solution of sodium hydroxide (0.1 mol l⁻¹). The mixture was stirred continuously for 30 min and then filtered. Colourless single crystals were obtained at room temperature by slow evaporation of the filtrate over a period of several days (yield 78%, based on Cd). **Caution:** cadmium and its compounds are toxic and perchlorate salts are potentially explosive.

Crystal data

$[\text{Cd}_2(\text{C}_{10}\text{H}_8\text{N}_2)_5(\text{H}_2\text{O})_6](\text{C}_7\text{H}_6\text{NO}_2)_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\beta = 91.686 (1)^\circ$
$M_r = 1621.00$	$V = 3357.98 (11) \text{ \AA}^3$
Monoclinic, $P2_1/n$	$Z = 2$
$a = 7.4436 (1) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 19.0015 (4) \text{ \AA}$	$\mu = 0.80 \text{ mm}^{-1}$
$c = 23.7517 (5) \text{ \AA}$	$T = 123 \text{ K}$
	$0.25 \times 0.19 \times 0.16 \text{ mm}$

Data collection

Bruker APEXII area-detector diffractometer	29403 measured reflections
Absorption correction: multi-scan (SADABS; Shelldrick, 2003)	6746 independent reflections
$T_{\min} = 0.826$, $T_{\max} = 0.883$	5834 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cd1—O2W	2.2275 (16)	Cd1—O1W	2.3499 (16)
Cd1—N5	2.3269 (17)	Cd1—N1	2.3509 (18)
Cd1—O3W	2.3336 (15)	Cd1—N3	2.3699 (19)
O2W—Cd1—N5	174.51 (7)	O3W—Cd1—N1	94.23 (6)
O2W—Cd1—O3W	87.63 (6)	O1W—Cd1—N1	92.38 (6)
N5—Cd1—O3W	87.24 (6)	O2W—Cd1—N3	89.89 (7)
O2W—Cd1—O1W	93.56 (6)	N5—Cd1—N3	88.04 (6)
N5—Cd1—O1W	91.30 (6)	O3W—Cd1—N3	88.68 (6)
O3W—Cd1—O1W	173.12 (5)	O1W—Cd1—N3	84.55 (6)
O2W—Cd1—N1	95.99 (7)	N1—Cd1—N3	173.54 (6)
N5—Cd1—N1	86.35 (6)		

Table 2

π - π stacking interactions (\AA , $^\circ$).

$Cg1$ is the centroid of the N1/C1—C5 ring, $Cg2$ is the centroid of the N2/C6—C10 ring, $Cg3$ is the centroid of the N3/C16—C20 ring and $Cg4$ is the centroid of the N4/C21—C24 ring.

CgI	CgJ	$CgI \cdots CgJ^a$	$CgI \cdots P(J)^b$	$CgJ \cdots P(I)^c$	Slippage
$Cg1$	$Cg4^{vii}$	3.9576 (13)	3.935	3.956	0.466
$Cg1$	$Cg4^{iii}$	3.6423 (13)	3.367	3.385	1.388
$Cg2$	$Cg3^{viii}$	3.7461 (13)	3.319	3.388	1.737
$Cg3$	$Cg2^{ii}$	3.7245 (13)	3.528	3.494	1.192

Symmetry codes: (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (vii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$. Notes: (a) distance between centroids; (b) perpendicular distance of CgI on ring plane J ; (c) perpendicular distance of CgJ on ring plane I ; slippage = vertical displacement between ring centroids.

Table 3

Hydrogen-bond geometry (\AA , $^\circ$).

$Cg5$ is the centroid of the C27—C32 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C30—H30...O6	0.95	2.31	3.228 (6)	163
C11—H11...N4 ⁱ	0.95	2.61	3.406 (3)	142
C14—H14...O4 ⁱⁱ	0.95	2.50	3.262 (3)	137
C23—H23...O4 ⁱⁱⁱ	0.95	2.58	3.336 (3)	137
C31—H31...O3 ^{iv}	0.95	2.48	3.166 (6)	129
O1W—H1W...O1 ^v	0.83	2.00	2.791 (2)	160
O1W—H2W...N2 ^{vi}	0.83	2.10	2.924 (3)	177
O2W—H3W...O4W	0.83	1.81	2.641 (3)	176
O2W—H4W...O1	0.83	1.94	2.765 (2)	171
O3W—H6W...N4 ^{vii}	0.84	1.92	2.750 (3)	170
N6—H6A...O3	0.88 (1)	2.37 (2)	3.196 (4)	157 (4)
N6—H6B...O2 ^v	0.88 (1)	2.23 (2)	3.090 (4)	166 (4)
N6'—H6'1...O6	0.88 (1)	2.41 (2)	3.275 (7)	167 (8)
N6'—H6'2...O3 ^{iv}	0.88 (1)	2.63 (3)	3.481 (8)	162 (8)
O4W—H7W...O1 ^{viii}	0.79 (4)	2.04 (4)	2.801 (3)	163 (4)
O4W—H8W...O2 ^v	0.79 (4)	1.93 (4)	2.695 (3)	165 (4)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x, -y + 1, -z + 1$; (iv) $x + 1, y, z$; (v) $x - 1, y, z$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (viii) $-x + 1, -y + 1, -z + 1$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.066$
 $S = 1.06$
 6746 reflections
 526 parameters
 26 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$

The 3-aminobenzoate anion showed significantly elongated displacement ellipsoids indicating disorder over two positions. The occupancy factor was initially obtained from refinement with a free variable, and then fixed to define the occupancy for each disordered group. Thus, it was refined as being disordered over two sites, with an occupancy ratio of 64:36. The corresponding bond lengths and angles within the two orientations were restrained to be similar with a tolerance of 0.02 Å and the anisotropic displacement parameters of the two *ipso* C atoms (C27 and C27') were constrained to be identical. All water H atoms were tentatively located in difference density Fourier maps and were refined with O–H distance restraints of 0.83 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. In the last stage of refinement, they were treated as riding on their parent O atoms. All H atoms attached to C atoms were fixed geometrically and treated as riding, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The positions of the amine H atoms were refined with N–H distance restraints of 0.88 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-III* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *XP in SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3162). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Aoyagi, M., Biradha, K. & Fujita, M. (2000). *Bull. Chem. Soc. Jpn.*, **73**, 1369–1373.
- Ayyappan, P., Evans, O. R. & Li, W. (2002). *Inorg. Chem.* **41**, 3328–3330.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed.* **34**, 1555–1573.
- Biradha, K., Sarkar, M. & Rajput, L. (2006). *Chem. Commun.* pp. 4169–4179.
- Bruker (2004). *APEX2* (Version 7.23A) and *SAINT* (Version 7.23A). Bruker AXS Inc., Madison, Wisconsin, USA.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP-III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Cheng, A. L., Ma, Y., Sun, Q. A. & Gao, E. Q. (2011). *CrystEngComm*, **13**, 2721–2726.
- Dong, Y. B., Smith, M. D., Layland, R. C. & zur Loye, H. C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 775–780.
- Eddaoudi, M., Moler, D. B., Li, H. L., Chen, B. L., Reinecke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Fang, Z. & Wang, J. (2010). *Acta Cryst.* **E66**, o2912.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Granifo, J., Garland, M. T. & Baggio, R. (2004). *Acta Cryst.* **C60**, m97–m100.
- Hazra, A., Kanoo, P. & Maji, T. K. (2011). *Chem. Commun.* **47**, 538–540.
- Jennifer, S. J. & Muthiah, P. T. (2011). *Acta Cryst.* **C67**, m69–m72.
- Lee, E. C., Kim, D., Jurecka, P., Tarakeswar, P., Hobza, P. & Kim, K. S. (2007). *J. Phys. Chem. A*, **111**, 3446–3457.
- Lehn, J. (1990). *Angew. Chem. Int. Ed.* **29**, 1304–1319.
- Li, H., Eddaoudi, M., O'Keeffe, M. & Yaghi, O. M. (1999). *Nature*, **402**, 276–279.
- Li, X. J., Sun, D. F., Cao, R., Sun, Y. Q., Wang, Y. Q., Bi, W. H., Gao, S. Y. & Hong, M. C. (2003). *Inorg. Chem. Commun.* **6**, 908–911.
- Liao, Y.-C., Liao, F.-L., Chang, W.-K. & Wang, S.-L. (2004). *J. Am. Chem. Soc.* **126**, 1320–1321.
- Lipstman, S. & Goldberg, I. (2009). *Acta Cryst.* **C65**, m371–m373.
- Ma, C.-B., Hu, M.-Q., Zhang, C.-X., Chen, F., Chen, C.-N. & Liu, Q.-T. (2004). *Acta Cryst.* **C60**, m288–m290.
- Moulton, B. & Zaworotko, M. (2001). *J. Chem. Res.* **101**, 1629–1658.
- Pan, L., Frydel, T., Sander, M. B., Huang, X. Y. & Li, J. (2001). *Inorg. Chem.* **40**, 1271–1283.
- Phan, A., Doonan, C. J., Uribe-Romo, F. J., Knobler, C. B., O'Keeffe, M. & Yaghi, O. M. (2010). *Acc. Chem. Res.* **43**, 58–67.
- Prior, T. J., Bradshaw, D., Teat, S. J. & Rosseinsky, M. J. (2003). *Chem. Commun.* pp. 500–501.
- Qiu, Y., Liu, Z., Li, Y., Deng, H., Zeng, R. & Zeller, M. (2008). *Inorg. Chem.* **47**, 5122–5128.
- Qiu, Y. C., Wang, K. N., Liu, Y., Deng, H., Sun, F. & Cai, Y. P. (2007). *Inorg. Chim. Acta*, **360**, 1819–1824.
- Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tong, M. L. & Chen, X. M. (2000). *CrystEngComm*, **2**, 1–5.
- Wang, J., Fan, J., Guo, L. Y., Yin, X., Wang, Z. H. & Zhang, W. G. (2010). *Inorg. Chem. Commun.* **13**, 322–325.
- Wang, J. & Fang, Z.-L. (2010). *Acta Cryst.* **E66**, m1230–m1231.
- Xu, G. & Xie, Y. (2010). *Acta Cryst.* **C66**, m201–m203.
- Yaghi, O. M., Li, H. L., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.
- Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim, J. (2003). *Nature*, **423**, 705–714.