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# A novel three-dimensional Cd$^{II}$ coordination polymer: poly[[aquabis(2,2′-bipyridine)($\mu_5$-pyrazol-1-ide-3,5-dicarboxylato)($\mu_4$-pyrazol-1-ide-3,5-dicarboxylato)($\mu_3$-pyrazole-3,5-dicarboxylato)tetracadmium(II)] dihydrate]

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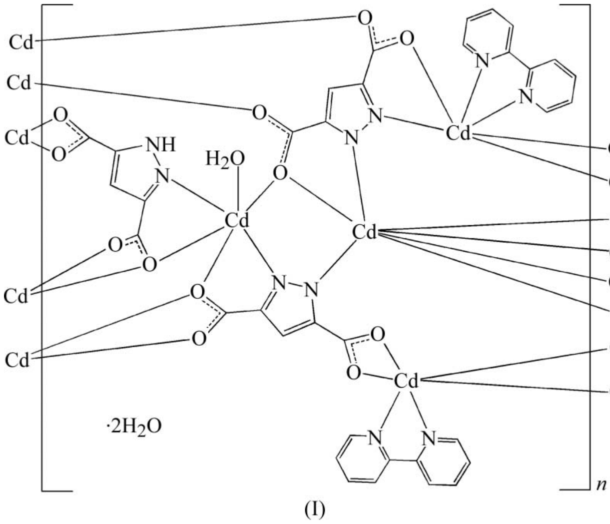
The title compound, $\{[Cd_4(C_5H_2N_2O_4)(C_5HN_2O_4)_2(C_{10}H_8N_2)_2(H_2O)]\cdot2H_2O\}_n$, crystallized in the monoclinic space group $P2_1/n$ and displays a three-dimensional architecture. The asymmetric unit is composed of four crystallographically independent Cd$^{II}$ centres, two triply deprotonated pyrazole-3,5-dicarboxylic acid molecules, one doubly deprotonated pyrazole-3,5-dicarboxylic acid molecule, two 2,2′-bipyridine ligands, one coordinated water molecule and two interstitial water molecules. Interestingly, the Cd$^{II}$ centers exhibit two different coordination numbers. Two Cd$^{II}$ centres adopt a distorted octahedral arrangement and a third a trigonal–prismatic geometry, though they are all hexacoordinated. However, the fourth Cd$^{II}$ center is heptacoordinated and displays a pentagonal–bipyramidal geometry. The three anionic ligands adopt $\mu_3$-, $\mu_4$- and $\mu_5$-bridging modes, first linking Cd$^{II}$ centers into a one-dimensional wave-like band, then into a wave-like layer and finally into a three-dimensional coordination framework, which is stabilized by hydrogen bonds.

## Comment

The assembly of metal–organic frameworks (MOFs) has attracted much attention due not only to their potential applications in gas adsorption, photochemistry, magnetism and catalysis, but also to their intriguing topologies (Ferey *et al.*, 2005). However, one of the biggest challenges is how to rationally design new materials and construct the related frameworks with desired structures and properties. In this regard, the self-assembly of organic ligands containing N- and/or O-donor atoms as building blocks, especially polycarboxylic acids and transition metal ions under hydrothermal conditions, has been documented to be one of the most efficient and fruitful methods (Zhao *et al.*, 2011). Up to now, a variety of MOFs with one-, two- and three-dimensional structures have been constructed by assembling transition metals and polycarboxylic acids such as benzene-1,3,5-tricarboxylic acid, benzene-1,4-dicarboxylic acid, and so on, this being due to their rigidity as building blocks and the variety of their coordination modes (Dincă & Long, 2008; Tong *et al.*, 2011; Li *et al.*, 1998). Recently, pyrazole-3,5-dicarboxylic acid has been employed to assemble MOFs because it is an intriguing multidentate ligand with two N-atom donors from the pyrazole ring and two carboxylate groups (Pan, Huang, Li, Wu *et al.*, 2000). The participation of the N atoms of the pyrazole ring together or individually may lead to unusual multidimensional architectures because of their flexible coordination modes, which may be tuned by the pH value of the reaction mixture removing the N-bound H atom (Pan, Huang & Li, 2000). To date, coordination polymers containing pyrazole-3,5-dicarboxylic acid and Cd$^{II}$ centres have rarely been investigated (Pan *et al.*, 2001). In contrast to other transition metals, interestingly, the Cd$^{II}$ centres may exhibit different coordination numbers in one compound, which could determine the magnitude of the channel of the desired MOFs (Xia *et al.*, 2004). We report here the synthesis and structural characterization of a three-dimensional Cd coordination polymer, namely poly[[aquadi(2,2′-bipyridine)($\mu_5$-pyrazol-1-ide-3,5-dicarboxylato)($\mu_4$-pyrazol-1-ide-3,5-dicarboxylato)($\mu_3$-pyrazole-3,5-dicarboxylato)tetracadmium(II)] dihydrate], (I), which demonstrates a variety of coordination modes of pyrazole-3,5-dicarboxylic acid and two different coordination numbers of the Cd$^{II}$ centres.



(I)

Single-crystal structure analysis reveals that (I) exhibits a three-dimensional architecture. The asymmetric unit of (I) consists of four crystallographically independent Cd$^{II}$ centres, two triply deprotonated pyrazole-3,5-dicarboxylic acid ligands, one doubly deprotonated pyrazole-3,5-dicarboxylic acid ligand, two 2,2′-bipyridine ligands, one coordinated water molecule and two interstitial water molecules (Fig. 1). The Cd1

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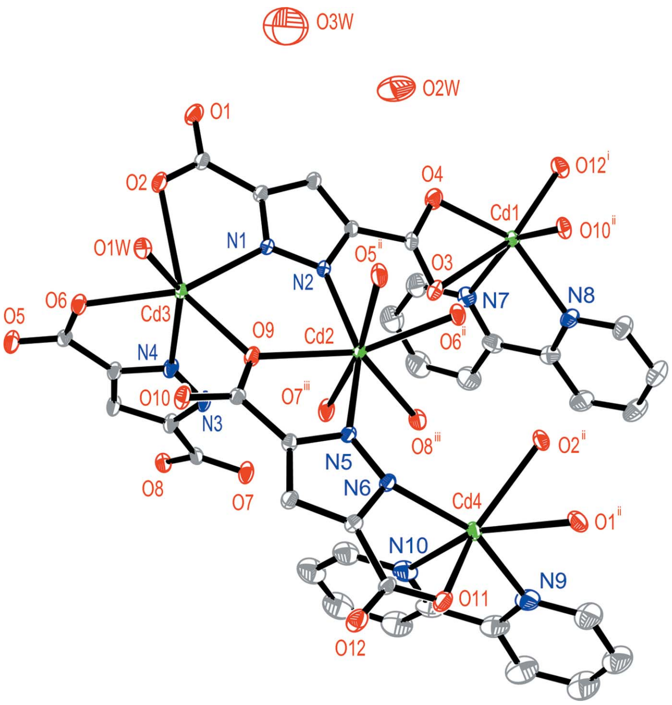

**Figure 1**

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and all H atoms have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 2, -y + 2, -z + 1$.]

atom is hexacoordinated and adopts a distorted octahedral arrangement defined by two 2,2′-bipyridine (2,2′-bpy) N atoms in a chelating mode and four carboxylate O atoms from two different anionic ligands, *viz.* pyrazol-1-ide-3,5-dicarboxylate (PDC) and pyrazole-3,5-dicarboxylate (HPDC). The equatorial plane of the Cd1 geometry is composed of atoms N7, N8, O4 and O10; two apical positions are occupied by O3 and O12 from two different PDC ligands. The small chelating angles of 70.70 (16) (N7—Cd1—N8 from 2,2-bpy) and 52.01 (11)° (O3—Cd1—O4 from the same carboxylate group) reflect the distortion of the Cd1 geometry, as do the Cd1—N/O bond lengths [2.206 (3)–2.719 (4) Å; Table 1], which are typical for such coordination geometries reported in the literature (Fang & Zhang, 2006). In contrast, the Cd2 center is heptacoordinated and lies in a pentagonal–bipyramidal geometry constructed by five carboxylate O atoms (O5, O6, O7, O8 and O9) from two different PDC and one HPDC unit, and two N atoms (N2 and N5) from two separate pyrazole rings. Atoms N2 and N5 occupy two axial positions and the other atoms (O5, O6, O7, O8 and O9) form the equatorial pentagonal planes. The Cd—O bond lengths involving Cd2 range from 2.324 (3) to 2.619 (3) Å and the angles vary from 52.88 (10) to 115.78 (12)°. It is worth noting that the Cd2—O5 and Cd2—O7 bond lengths are much longer than the others, probably due to stereochemical requirements (O5 and O7 sit on axial sites). Similar to Cd1, both Cd3 and Cd4 are hexacoordinated, but the coordination geometries are different. Atom Cd3 displays a trigonal–prismatic geometry by two sets of chelated N and O atoms from $\mu_3$-HPDC and $\mu_4$-PDC, respectively, a bridging carboxylate O atom of $\mu_5$-PDC and a terminal water molecule. However, atom Cd4, like Cd1, is located in a very distorted octahedral geometry, the equatorial plane of which is composed of N6, O1 and two 2,2′-bpy N atoms, with the axial positions occupied by two carboxylate O atoms from $\mu_4$-PDC and $\mu_5$-PDC. Apparently, the Cd3 polyhedron shares one vertex with that of Cd4 through O2 and those of two separate adjacent Cd2 through O6 and O9, respectively. It should be noted that the Cd3—O1*W* bond length [2.275 (3) Å] is

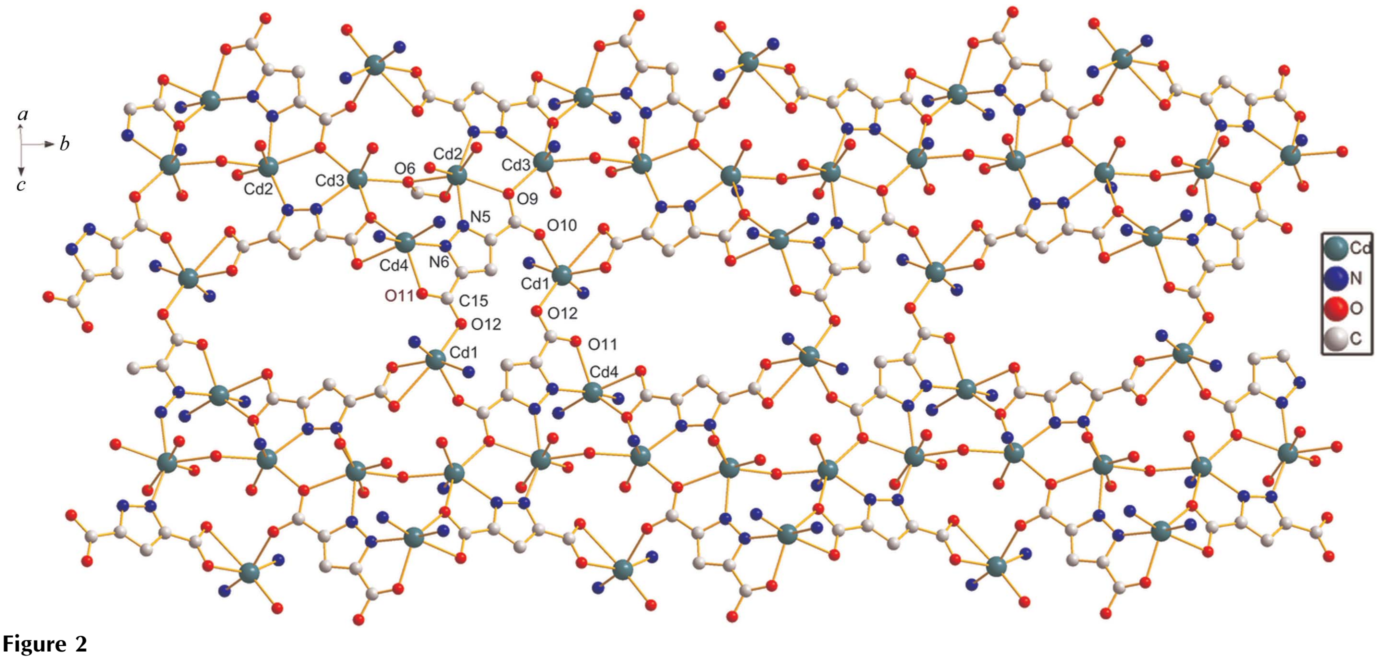

**Figure 2**

A perspective view of the two-dimensional layered structure of (I). All 2,2′-bipyridine C atoms and all H atoms have been omitted for clarity, as have the uncoordinated water molecules.

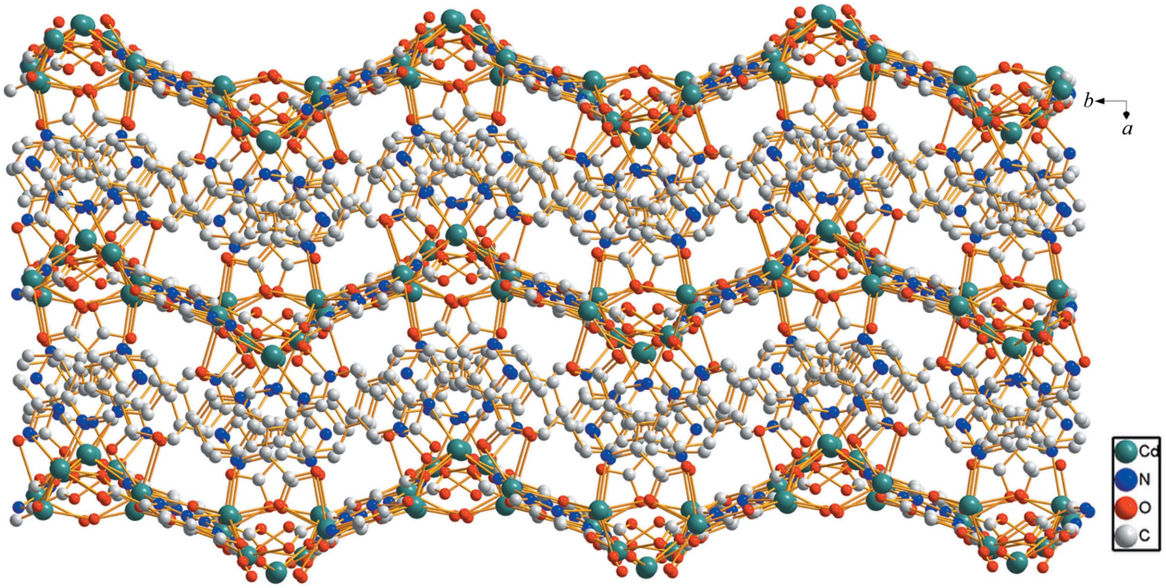

**Figure 3**
Packing diagram showing the wave-like layers of (I). All H atoms and the uncoordinated water molecules have been omitted for clarity.

significantly longer than those of coordinated hydroxy groups, excluding the possibility that O1*W* could be a hydroxy group (Bruno *et al.*, 2002).

Interestingly, the three crystallographically independent anionic ligands show different coordination modes in this complex, *viz.* $\mu_5$, $\mu_4$ and $\mu_3$. $\mu_5$-PDC chelates two Cd atoms (Cd2 and Cd4) through O9 and N5, and O11 and N6, respectively, and bridges two adjacent atoms (Cd1) from different units with O10 and O12, respectively. The polyhedra of the Cd2 and Cd3 centers share apex atom O9 from $\mu_5$-PDC and O6 from $\mu_3$-PDC together alternatively to form a wave-like nano-band along the *b* axis (Figs. 2 and 3). The adjacent wave-like bands are bridged to form a two-dimensional wave-like layer through carboxylate groups (O12 and O11) of $\mu_5$-PDC. $\mu_3$-HPDC bridges one Cd$^{II}$ centre (Cd2) with one carboxylate group and two Cd$^{II}$ centres (Cd2 and Cd3) from an adjacent layer through the other carboxylate group and an N atom (N1) of the pyrazole ring to form a three-dimensional framework, but leaves atom N3 free with one H atom, which was confirmed by the observation of an N—H stretching vibration at 3424 cm$^{-1}$ (Pan, Huang & Li, 2000). The other point to note is that each carboxylate group is almost in the plane of the attached pyrazole rings [the dihedral angles between them range from 3.264 (5) to 11.887 (5)°].

The Cd$^{II}$ centres show two different coordination numbers (six and seven) in (I), another example of which is also found in the literature (Wang *et al.*, 2007). The water molecules fill the molecular cavities, which leads to a lack of a solvent-accessible void due to the coordinated 2,2′-bpy ligand (77 Å$^3$, 1.9% of the whole unit-cell volume solvent-accessible void calculated using the SQUEEZE method in *PLATON*; Spek, 2009). Furthermore, hydrogen bonds (Table 2) between water molecules (O1*W*, O2*W* and O3*W*) and the carboxylate O atoms (O1, O3, O4, O8 and O10) of the framework, and between a pyrazole N atom (N3) and the carboxylate O7 atom, enhance the stability of the three-dimensional structure.

## Experimental

$Cd(NO_3)_2\cdot4H_2O$ (0.154 g, 0.5 mmol), pyrazole-3,5-dicarboxylic acid (0.156 g, 1.0 mmol) and 2,2′-bipyridine (0.156 g, 1.0 mmol) were mixed with deionized water (8 ml) in a 25 ml Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated to 433 K. The temperature was maintained for 3 d and then the mixture was allowed to cool naturally to obtain colorless crystals of (I) [yield 42%, based on $Cd(NO_3)_2\cdot4H_2O$]. Elemental analysis calculated for $C_{35}H_{26}Cd_4N_{10}O_{15}$: C 32.93, H 2.05, N 10.97%; found: C 33.34, H 1.96, N 11.13%. IR (KBr pellet, $\nu$/cm$^{-1}$): 3424, 3140, 1623, 1555, 1508, 1439, 1365, 1018, 846, 762, 651, 579.

### *Crystal data*

$[Cd_4(C_5H_2N_2O_4)(C_5HN_2O_4)_2(C_{10}H_8N_2)_2(H_2O)]\cdot2H_2O$
$M_r$ = 1276.26
Monoclinic, $P2_1/n$
$a$ = 15.574 (3) Å
$b$ = 16.197 (3) Å
$c$ = 16.928 (3) Å
$\beta$ = 109.21 (3)°
$V$ = 4032.3 (14) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.17 mm$^{-1}$
$T$ = 293 K
0.16 × 0.13 × 0.13 mm

### *Data collection*

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.72, $T_{max}$ = 0.76
38399 measured reflections
9211 independent reflections
8760 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.113
$S$ = 1.08
9211 reflections
578 parameters
656 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.99 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.24 e Å$^{-3}$

H atoms bonded to C atoms were placed in calculated positions and treated using a riding-model approximation, with C—H = 0.96 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C). We investigated a split-occupancy model for O3*W* but it did not offer any overall advantage over the model chosen. Initially, the aqua H atoms were located in a difference

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Cd1—O3 | 2.719 (4) | Cd3—O1$W$ | 2.275 (3) |
| Cd1—O4 | 2.216 (3) | Cd3—O2 | 2.482 (3) |
| Cd1—O10$^{\mathrm{i}}$ | 2.362 (3) | Cd3—O6 | 2.265 (3) |
| Cd1—O12$^{\mathrm{ii}}$ | 2.206 (3) | Cd3—O9 | 2.227 (3) |
| Cd1—N7 | 2.335 (4) | Cd3—N1 | 2.251 (3) |
| Cd1—N8 | 2.324 (4) | Cd3—N4 | 2.425 (4) |
| Cd2—O5$^{\mathrm{i}}$ | 2.575 (3) | Cd4—O1$^{\mathrm{i}}$ | 2.408 (4) |
| Cd2—O6$^{\mathrm{i}}$ | 2.341 (3) | Cd4—O2$^{\mathrm{i}}$ | 2.365 (3) |
| Cd2—O7$^{\mathrm{iii}}$ | 2.619 (3) | Cd4—O11 | 2.332 (3) |
| Cd2—O8$^{\mathrm{iii}}$ | 2.324 (3) | Cd4—N6 | 2.245 (3) |
| Cd2—O9 | 2.423 (3) | Cd4—N9 | 2.329 (4) |
| Cd2—N2 | 2.271 (3) | Cd4—N10 | 2.353 (4) |
| Cd2—N5 | 2.310 (3) | | |

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+2, -y+2, -z+1$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N3—H3$A\cdots$O7$^{\mathrm{iii}}$ | 0.86 | 1.94 | 2.786 (5) | 169 |
| O1$W$—H1$A\cdots$O8$^{\mathrm{iv}}$ | 0.85 | 1.88 | 2.721 (4) | 168 |
| O1$W$—H1$B\cdots$O3$^{\mathrm{v}}$ | 0.85 | 2.03 | 2.762 (4) | 143 |
| O2$W$—H2$C\cdots$O4 | 0.85 | 2.01 | 2.849 (7) | 171 |
| O2$W$—H2$D\cdots$O1$^{\mathrm{vi}}$ | 0.85 | 2.10 | 2.951 (8) | 178 |
| O3$W$—H3$E\cdots$O1 | 0.85 | 2.16 | 3.010 (12) | 177 |
| O3$W$—H3$F\cdots$O2$W$ | 0.85 | 2.23 | 3.079 (14) | 178 |

Symmetry codes: (iii) $-x+2, -y+2, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{5}{2}, z-\frac{1}{2}$; (v) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+1, -y+2, -z+1$.

Fourier map and their positions were adjusted, using the HIMP command in *XP* (*SHELXTL*; Bruker, 2000), to O—H = 0.85 Å. In the final cycles, these H atoms were constrained to ride on their parent O atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$.

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: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DT3011). Services for accessing these data are described at the back of the journal.

## References

Bruker (2000). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Dincă, M. & Long, J. R. (2008). *Angew. Chem. Int. Ed.* **47**, 6766–6779.

Fang, R.-Q. & Zhang, X.-M. (2006). *Inorg. Chem.* **45**, 4801–4810.

Ferey, G., Mellot-Draznieks, C., Serre, C. & Millange, F. (2005). *Acc. Chem. Res.* **38**, 217–225.

Li, H. L., Eddaoudi, M., Groy, T. L. & Yaghi, O. M. (1998). *J. Am. Chem. Soc.* **120**, 8571–8572.

Pan, L., Frydel, T., Sander, M. B., Huang, X. & Li, J. (2001). *Inorg. Chem.* **40**, 1271–1283.

Pan, L., Huang, X. Y. & Li, J. (2000). *J. Solid State Chem.* **152**, 236–246.

Pan, L., Huang, X. Y., Li, J., Wu, Y. & Zheng, N. (2000). *Angew. Chem. Int. Ed.* **39**, 527–530.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Tong, F., Sun, Z.-G., Chen, K., Zhu, Y.-Y., Wang, W.-N., Jiao, C.-Q., Wang, C.-L. & Li, C. (2011). *Dalton Trans.* **40**, 5059–5065.

Wang, H.-S., Shi, W., Xia, J., Song, H.-B., Wang, H.-G. & Cheng, P. (2007). *Inorg. Chem. Commun.* **10**, 856–859.

Xia, S. Q., Hu, S. M., Dai, J. C., Wu, X. T., Zhang, J. J., Fu, Z. Y. & Du, W. X. (2004). *Inorg. Chem. Commun.* **7**, 51–53.

Zhao, D., Daren, J., Timmons, D. J., Yuan, D. Q. & Zhou, H.-C. (2011). *Acc. Chem. Res.* **44**, 123–133.