

A planar cyclic hexamer of water molecules in dichlorido(2,4,6-tri-2-pyridyl-1,3,5-triazine)cadmium(II) trihydrate

Hong-Zhen Xie* and Wei-Juan Pan

State Key Laboratory Base of Novel Functional Materials and Preparation Science, Faculty of Materials Science and Chemical Engineering, Ningbo University, Zhejiang 315211, People's Republic of China
Correspondence e-mail: zhengyueqing@nbu.edu.cn

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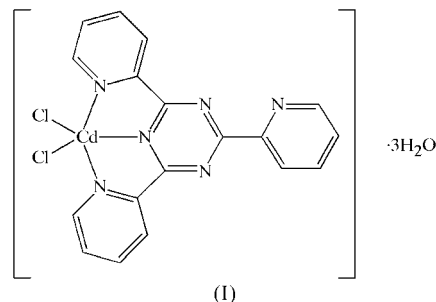
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In the title compound, $[\text{CdCl}_2(\text{C}_{18}\text{H}_{12}\text{N}_6)] \cdot 3\text{H}_2\text{O}$, the Cd atom has a distorted square-pyramidal coordination geometry. The solvent water molecules are hydrogen bonded to each other to form planar cyclic water hexamers, which, together with other hydrogen bonds, interlink the Cd complex molecules to give one-dimensional supramolecular ribbons that extend along the [111] direction. The chains are assembled into two-dimensional layers parallel to (111) by π - π stacking interactions. Furthermore, interlayer π - π stacking interactions and weak $\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonds complete the formation of a three-dimensional framework.

Comment

In recent years, there has been growing interest in theoretical and experimental research directed at unravelling the structural details of a variety of water clusters in different environments (Atwood *et al.*, 2001; Moorthy *et al.*, 2002; Ghosh & Bharadwaj, 2004). Moreover, it is widely accepted that both water-MOF (metal-organic framework) and water-water interactions are important for the stability of the overall structure (Michaelides *et al.*, 2003). A number of studies of small water clusters have concentrated on the hexamer that exists in the bulk water found in some molecular solids (Custelcean *et al.*, 2000). To date, three types of cyclic water hexamers have been detected in host lattices characterized using X-ray crystallographic analysis, and they are denoted as 'chair', 'boat' and 'planar' cyclic water hexamers. In the structure of the title compound, (I), cyclic water hexamers with the 'planar' conformation are present. A similar cyclic planar water hexamer was observed in the structure of bimesityl-3,3-dicarboxylic acid monohydrate (Moorthy *et al.*, 2002). The title compound was obtained during attempts to prepare the Cd analogue of $[\text{Co}(\text{C}_2\text{O}_4)(\text{TPTZ})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ (TPTZ is 2,4,6-tri-2-pyridyl-1,3,5-triazine; Cheng *et al.*, 2006).

The asymmetric unit of (I) contains one $[\text{CdCl}_2(\text{TPTZ})]$ complex molecule and three symmetry-independent water molecules. The central Cd^{II} ion is five-coordinated by three N



atoms from a TPTZ ligand and two chloride ions, which results in a distorted square-pyramidal coordination geometry; a similar coordination geometry is found in the structure of the dichloridocadmium(II) complex of the tridentate *N,N*-dimethyl-*N'*-(pyridin-2-ylmethylene)ethane-1,2-diamine ligand (Bian *et al.*, 2003). Atom Cl2 is located at the apex of the pyramid, and atoms N1, N2, N3 and Cl1 lie at the four corners of the base of the square pyramid. Atom Cd1 is displaced by 0.542 (1) Å from the base toward Cl2 (Fig. 1). Selected bond lengths and angles involving atom Cd1 are presented in Table 1. As far as is known, five-coordinated Cd^{II} complexes only represent about 5% of all known cadmium complexes (Sigel & Martin, 1994; Wang *et al.*, 2003).

Interestingly, the water solvent molecules hydrogen bond to each other to form a cyclic water hexamer, which is centrosymmetric. The main hydrogen bonds are listed in Table 2. The environment of the water hexamer is shown in Fig. 2. Within the cluster, the six water molecules are coplanar and each water molecule acts as both a single hydrogen-bond donor and an acceptor. The average $\text{O} \cdots \text{O}$ distance of 2.84 Å is close to the corresponding distance in liquid water (2.85 Å; Narten *et al.*, 1982). In addition, atoms O1, O2 and O3 donate hydrogen

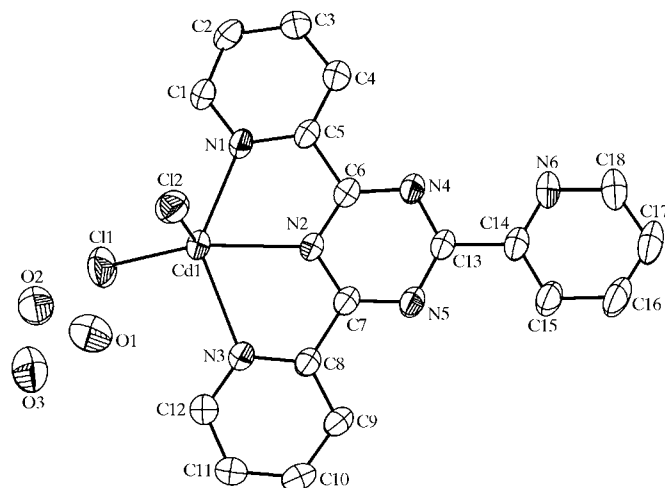


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 45% probability level. H atoms have been omitted.

bonds to atoms Cl2, N6(1 - x, 2 - y, 1 - z) and Cl1, respectively, of neighbouring Cd complex molecules. As a consequence of these hydrogen bonds, the water hexamers and Cd complex molecules are assembled into one-dimensional supramolecular ribbons, which extend along the [111] direction (Fig. 2). Adjacent parallel ribbons are stacked into two-dimensional layers parallel to (111) by intermolecular π - π stacking interactions between the pyridyl ring containing atom N1 and the pyridyl ring containing atom N6 in the centrosymmetrically related molecule at (1 - x, 1 - y, 1 - z). The mean interplanar distance is 3.34 (3) Å and the distance between the respective ring centroids is 3.561 (2) Å. Another strong π - π stacking interaction links adjacent layers; the pyridyl ring containing atom N1 stacks over the pyridyl ring containing atom N3 in the molecule at (x - 1, y, z). The mean interplanar distance is 3.42 (3) Å and the distance between the respective ring centroids is 3.703 (2) Å. The interlayer π - π stacking interactions, together with a weak C1-H1...Cl1 hydrogen bond, lead to the formation of a three-dimensional framework.

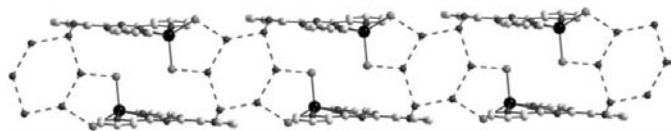


Figure 2
The one-dimensional supramolecular chain assembled by hydrogen bonds in (I). Hydrogen bonds are indicated by dashed lines.

Experimental

TPTZ (0.312 g, 1.0 mmol) and oxalic acid were dissolved with stirring in aqueous methanol (30 ml, 1:1 v/v). CdCl₂·2.5H₂O (0.228 g, 1.0 mmol) was added to the above solution to obtain a yellow solution (pH = 0.74), which was filtered. The resulting yellow filtrate was maintained at room temperature and afforded pale-yellow crystals one week later by slow evaporation (yield 5% based on the initial CdCl₂·2.5H₂O input).

Crystal data

[CdCl ₂ (C ₁₈ H ₁₂ N ₆)]·3H ₂ O	$\gamma = 99.21$ (3)°
$M_r = 549.68$	$V = 1065.3$ (4) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.9567$ (18) Å	Mo $K\alpha$ radiation
$b = 11.118$ (2) Å	$\mu = 1.31$ mm ⁻¹
$c = 11.568$ (2) Å	$T = 298$ (2) K
$\alpha = 106.71$ (3)°	$0.29 \times 0.25 \times 0.22$ mm
$\beta = 98.67$ (3)°	

Table 1

Selected geometric parameters (Å, °).

Cd1-N2	2.298 (3)	Cd1-N3	2.418 (3)
Cd1-N1	2.392 (3)	Cd1-Cl2	2.4650 (11)
Cd1-Cl1	2.4049 (12)		
N2-Cd1-N1	68.19 (10)	Cl1-Cd1-N3	101.59 (7)
N2-Cd1-Cl1	139.44 (7)	N2-Cd1-Cl2	106.25 (7)
N1-Cd1-Cl1	103.21 (8)	N1-Cd1-Cl2	99.85 (7)
N2-Cd1-N3	68.61 (10)	Cl1-Cd1-Cl2	114.31 (5)
N1-Cd1-N3	135.15 (9)	N3-Cd1-Cl2	103.11 (7)

Table 2

Hydrogen-bond geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
O1-H1A...O2	0.85	2.02	2.854 (4)	166
O1-H1B...Cl2	0.86	2.34	3.183 (4)	167
O2-H2A...N6 ⁱ	0.87	2.09	2.908 (4)	159
O2-H2B...O3 ⁱⁱ	0.86	2.02	2.794 (4)	149
O3-H3A...Cl1	0.87	2.60	3.325 (4)	142
O3-H3B...O1	0.88	2.00	2.864 (6)	168

Symmetry codes: (i) -x + 1, -y + 2, -z + 1; (ii) -x + 2, -y + 3, -z + 2.

Data collection

Rigaku R-Axis RAPID diffractometer	10540 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	4829 independent reflections
$T_{\min} = 0.506$, $T_{\max} = 1.000$	4035 reflections with $I > 2\sigma(I)$
(expected range = 0.379–0.750)	$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	271 parameters
$wR(F^2) = 0.114$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\max} = 1.17$ e Å ⁻³
4829 reflections	$\Delta\rho_{\min} = -0.83$ e Å ⁻³

H atoms bonded to C atoms were placed in geometrically calculated positions and were refined using a riding model, with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{C})$. H atoms attached to O atoms were found in a difference Fourier synthesis and were refined using a riding model, with the O-H distances fixed as initially found and with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{O})$. The highest peak in the final residual electron-density map is located 0.85 Å from atom Cd1 and the deepest hole is located 0.65 Å from the same atom.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); 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: LN3046). Services for accessing these data are described at the back of the journal.

References

- Atwood, J. L., Barbour, L. J., Ness, T. J., Raston, C. J. & Raston, P. L. (2001). *J. Am. Chem. Soc.* **123**, 7192–7193.
- Bian, H. D., Xu, J. Y., Gu, W., Yan, S.-P., Liao, D.-Z., Jiang, Z.-H. & Cheng, P. (2003). *Chin. J. Struct. Chem.* **22**, 710–712.
- Cheng, D.-Y., Xu, W. & Zheng, Y.-Q. (2006). *Acta Cryst.* **E62**, m2561–m2563.
- Custelcean, R., Afloroaei, C., Vlassa, M. & Polverjean, M. (2000). *Angew. Chem. Int. Ed.* **39**, 3094–3096.
- Ghosh, S. K. & Bharadwaj, P. K. (2004). *Inorg. Chem.* **43**, 5180–5182.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

metal-organic compounds

- Michaelides, A., Skoulika, S., Bakalbassis, E. G. & Mrozinski, J. (2003). *Cryst. Growth Des.* **3**, 487–492.
- Moorthy, J. N., Natarajan, R. & Venugopalan, P. (2002). *Angew. Chem. Int. Ed.* **41**, 3417–3420.
- Narten, A. H. A., Thiessen, W. E. & Blum, L. (1982). *Science*, **217**, 1033–1034.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSO (2002). *CrystalStructure*. Rigaku/MSO Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sigel, H. & Martin, R. B. (1994). *Chem. Soc. Rev.* **23**, 83–88.
- Wang, D.-Q., Dou, J.-M. & Niu, M.-J. (2003). *Acta Chim. Sin.* **61**, 551–555.