

## Tris(1,10-phenanthroline- $\kappa^2N,N'$ )-cadmium(II) bis(perchlorate) 3.5-hydrate: a water chain stabilized by perchlorate anions

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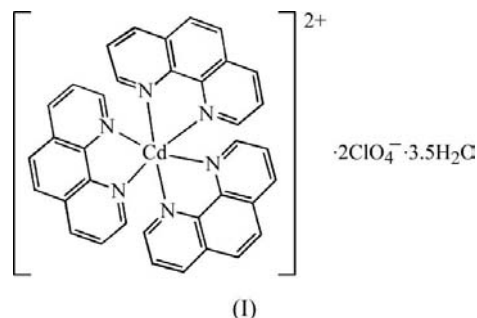
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The title compound,  $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ , contains a cross-shaped one-dimensional channel along the  $c$  axis which encapsulates an ordered water chain. This water chain features a centrosymmetric cyclic water hexamer unit with a chair-like conformation. Neighbouring hexamers are linked by bridging water molecules. The host perchlorate anions recognize and stabilize the guest water chain *via* three kinds of hydrogen-bond patterns, leading to the formation of a complex one-dimensional  $\{[(\text{H}_2\text{O})_7(\text{ClO}_4)_4]^{4-}\}_n$  anionic chain. One perchlorate acts as a single hydrogen-bond acceptor dangling on the chain, the second perchlorate on the chain serves as a double hydrogen-bond acceptor for only one water molecule to form an  $R_2^2(6)$  ring, where both entities lie on a twofold axis, while the third perchlorate, which also lies on a twofold axis, accepts two hydrogen bonds from two equivalent water molecules and is involved in the construction of an  $R_6^5(14)$  ring.

### Comment

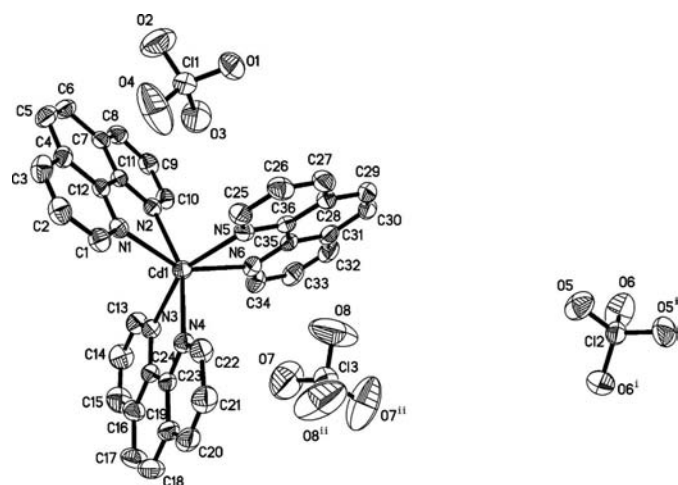
The study of water clusters and water chains in confined environments such as organic and inorganic host matrices is of much interest, in consideration of the essential role of hydrogen-bonded water aggregates in many biological, chemical and physical processes (Ludwig, 2001). Metal-organic supramolecular structures with suitable organic ligands may provide void spaces where water clusters or chains can exist (Cheruzel *et al.*, 2003; Liu & Xu, 2005; Biswas *et al.*, 2008). However, the water arrays of particular shapes in crystal hosts are still not well understood and much work is required to rationalize the influence of the overall structures on such water aggregations. Previously, we described a cyclic water tetramer stabilized by host  $[3\text{-O}_3\text{S-C}_6\text{H}_4\text{-PO}_3\text{H}]^{2-}$  anions (Du *et al.*, 2008). In the present work, (I), we report a

novel water chain stabilized by three types of perchlorate anions.



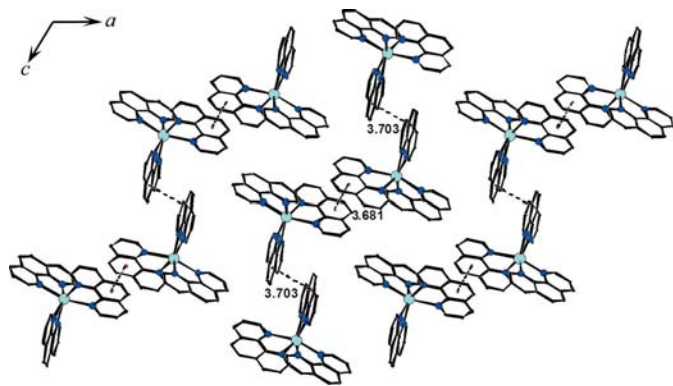
Compound (I) crystallizes in the monoclinic  $C2/c$  space group. The asymmetric unit contains an isolated  $[\text{Cd}(\text{phen})_3]^{2+}$  cation (phen is 1,10-phenanthroline), one full and two half perchlorate anions, and three and a half lattice water molecules where the latter resides on a twofold axis (Fig. 1). The Cd1 ion exhibits a slightly distorted octahedral geometry in which the Cd<sup>II</sup> ion is coordinated to six N atoms from three phen ligands. The Cd–N bond lengths (Table 1) are in the expected range (Harvey *et al.*, 2000). The positive charges of the  $[\text{Cd}(\text{phen})_3]^{2+}$  cation are compensated by one full and two half perchlorate anions, among which the Cl1 atom occupies a general position while the Cl2 and Cl3 atoms lie on a twofold axis. The discrete  $[\text{Cd}(\text{phen})_3]^{2+}$  ions are assembled into a two-dimensional layer *via*  $\pi$ - $\pi$  packing interactions as well as van der Waals forces (Fig. 2). The overall three-dimensional arrangement of the bulky  $[\text{Cd}(\text{phen})_3]^{2+}$  ions and the somewhat smaller perchlorate counter-ions results in cross-shaped channels down the  $c$  axis, which accommodate a large number of solvent water molecules (Fig. 3).

A closer analysis reveals that an ordered one-dimensional water chain running along the channel is formed *via* the

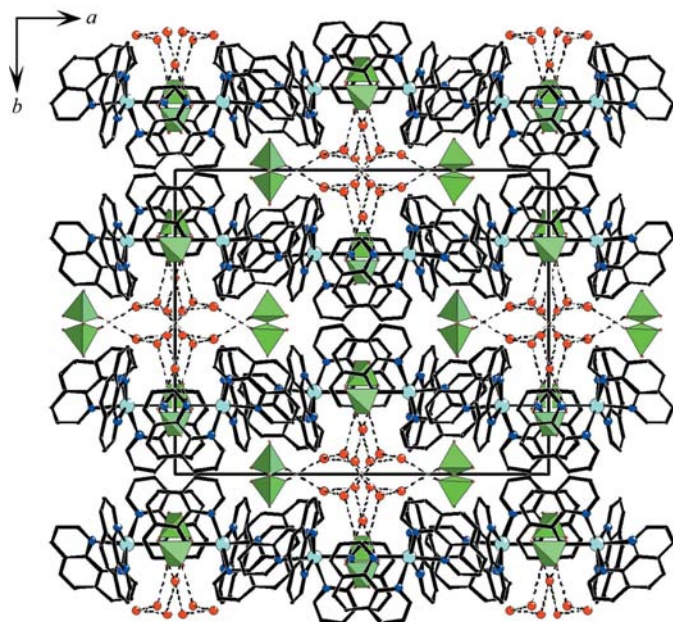


**Figure 1**

View of the selected unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Lattice water molecules have been omitted for clarity. [Symmetry codes: (i)  $-x, y, -z + \frac{3}{2}$ ; (ii)  $-x, y, -z + \frac{1}{2}$ .]

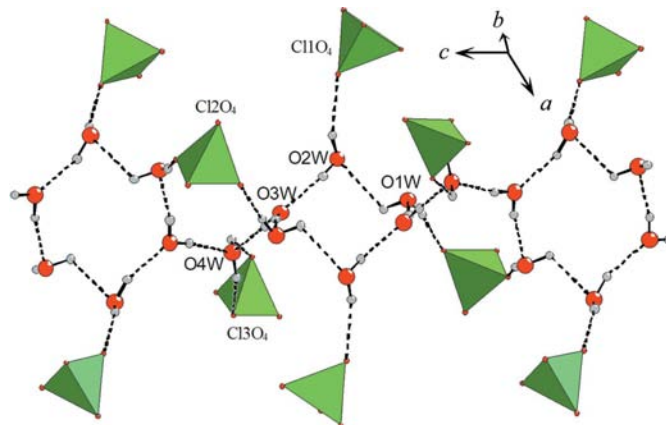
**Figure 2**

The  $\pi$ - $\pi$  packing interactions (represented by dashed lines) of the bulky  $[\text{Cd}(\text{phen})_3]^{2+}$  ions in (I).  $\pi$ - $\pi$  distances are given in Å. (Cd and N atoms are drawn as cyan and blue circles, respectively, in the electronic version of the paper.)

**Figure 3**

View of the three-dimensional crystal packing of (I) down the  $c$  axis. Hydrogen bonds are represented by dashed lines. (The perchlorate tetrahedra are green, and the Cd, O and N atoms are drawn as cyan, red and blue circles, respectively, in the electronic version of the paper.)

hydrogen-bonding associations among these water molecules. The geometric parameters of the water morphology are summarized in Table 2. The water chain features a centrosymmetric cyclic water hexameric unit with a chair-like conformation and with neighbouring hexamers linked together by a bridging water molecule (Fig. 4). Characterization of such water hexamers has been theoretically and experimentally documented in the literature (Kim *et al.*, 1998, 1999; Custelcean *et al.*, 2000; Zhao *et al.*, 2004). A striking feature of (I) is that the host perchlorate anions recognize and stabilize the guest water chain *via* three kinds of hydrogen-bond patterns, *i.e.* the  $\text{ClO}_4$  group acts as a single hydrogen-bond acceptor for one  $\text{H}_2\text{O}$ , the  $\text{Cl}_2\text{O}_4$  group serves as a double

**Figure 4**

View of the one-dimensional  $[(\text{H}_2\text{O})_7(\text{ClO}_4)_4]^{4-}$  anion chain in (I). Hydrogen bonds are represented by dashed lines. (The perchlorate tetrahedra are green, and the O and H atoms are drawn as red and grey circles, respectively, in the electronic version of the paper.)

hydrogen-bond acceptor for two  $\text{H}_2\text{O}$ , while the  $\text{Cl}_3\text{O}_4$  group serves as a double hydrogen-bond acceptor for only one  $\text{H}_2\text{O}$ . The hydrogen-bonding associations of the one-dimensional water chain and these three types of perchlorate anions lead to the formation of a complex one-dimensional  $[(\text{H}_2\text{O})_7(\text{ClO}_4)_4]^{4-}$  anionic chain. Such an anionic chain features three kinds of rings discussed here according to graph-set analysis nomenclature (Bernstein *et al.*, 1995). The cyclic water hexamer can be specified as having an  $R_6^6(12)$  pattern. The second ring, including five water molecules and one perchlorate anion, can be specified as having an  $R_6^5(14)$  pattern, whereas the third ring, including one water molecule and one perchlorate anion, can be specified as having an  $R_2^2(6)$  pattern. Overall, the alternate arrangement of the edge-shared  $R_6^6(12)$  and  $R_6^5(14)$  rings constitutes the extended one-dimensional structure, and the  $R_2^2(6)$  rings are located on one side of the  $R_6^5(14)$  rings in a corner-shared fashion, whereas the perchlorate anions not involved in the ring patterns dangle from both sides of the  $R_6^6(12)$  rings.

In summary, a novel one-dimensional water chain stabilized by three types of perchlorate anions is observed in (I), which provides a good example of how the water aggregations are influenced by the overall structure of their surroundings.

## Experimental

For the preparation of (I), a mixture of  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (134 mg, 0.32 mmol) and 1,10-phenanthroline (54 mg, 0.30 mmol) in distilled water (12 ml) with two drops of 10% HCl was placed in a Parr Teflon-lined autoclave (23 ml) and heated at 423 K for 3 d. Yellow block-shaped crystals were collected in *ca* 76% yield based on 1,10-phenanthroline. Analysis calculated for  $\text{C}_{36}\text{H}_{31}\text{CdCl}_2\text{N}_6\text{O}_{11.5}$ : C 47.26, H 3.41, N 9.18%; found: C 47.32, H 3.51, N 9.23%. IR data (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3535 (*m*), 3364 (*m*), 3064 (*m*), 2925 (*m*), 1625 (*s*), 1594 (*m*), 1579 (*m*), 1519 (*s*), 1497 (*m*), 1429 (*s*), 1344 (*m*), 1225 (*m*), 1147 (*s*), 1098 (*vs*), 929 (*m*), 865 (*m*), 844 (*s*), 772 (*m*), 724 (*s*), 642 (*m*), 622 (*s*), 514 (*m*), 419 (*m*).

## Crystal data

$[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3.5\text{H}_2\text{O}$	$V = 7441.5 (7) \text{ \AA}^3$
$M_r = 914.97$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 28.1954 (15) \text{ \AA}$	$\mu = 0.80 \text{ mm}^{-1}$
$b = 19.6534 (11) \text{ \AA}$	$T = 296 \text{ K}$
$c = 15.7245 (9) \text{ \AA}$	$0.32 \times 0.12 \times 0.06 \text{ mm}$
$\beta = 121.348 (1)^\circ$	

## Data collection

Bruker SMART CCD area-detector diffractometer	23241 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	6960 independent reflections
$T_{\min} = 0.642$ , $T_{\max} = 0.745$	5256 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
6960 reflections	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
532 parameters	
11 restraints	

**Table 1**

Selected bond lengths ( $\text{\AA}$ ).

Cd1—N4	2.329 (3)	Cd1—N6	2.347 (3)
Cd1—N1	2.336 (3)	Cd1—N5	2.390 (3)
Cd1—N3	2.338 (3)	Cd1—N2	2.420 (3)

**Table 2**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA $\cdots$ O2W	0.85 (3)	2.30 (9)	2.718 (9)	111 (7)
O1W—H1WB $\cdots$ O5 <sup>i</sup>	0.85 (6)	2.03 (6)	2.868 (6)	167 (8)
O2W—H2WA $\cdots$ O3W <sup>ii</sup>	0.86 (6)	1.85 (4)	2.667 (7)	158 (10)
O2W—H2WB $\cdots$ O4	0.85 (7)	2.02 (7)	2.808 (6)	155 (7)
O3W—H3WA $\cdots$ O4W	0.85 (6)	1.99 (7)	2.831 (7)	170 (9)
O3W—H3WB $\cdots$ O1W	0.85 (8)	1.89 (7)	2.728 (8)	168 (10)
O4W—H4WA $\cdots$ O8	0.85 (5)	2.38 (3)	3.006 (11)	131 (2)

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

H atoms bonded to C atoms were positioned geometrically (C—H = 0.93  $\text{\AA}$ ) and included in the refinement in the riding-model

approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Water H atoms were located in a difference map and refined with  $U_{\text{iso}}(\text{H})$  values set at  $1.5U_{\text{eq}}(\text{O})$ . The O—H and H $\cdots$ H distances in each water molecule were restrained to be 0.85 (1) and 1.38 (1)  $\text{\AA}$ , respectively. The final difference electron-density Fourier map shows some minor perchlorate disorder.

Data collection: SMART (Bruker, 2008); cell refinement: SMART; data reduction: SAINT (Bruker, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); 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: SK3355). Services for accessing these data are described at the back of the journal.

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