

**Diaquabis[2'-(4,5-diazafluoren-9-ylidene)picolinohydrazidato- $\kappa^2 N,O$ ]-zinc(II) tetrahydrate: a metal–water chain complex containing cyclic water hexamers**

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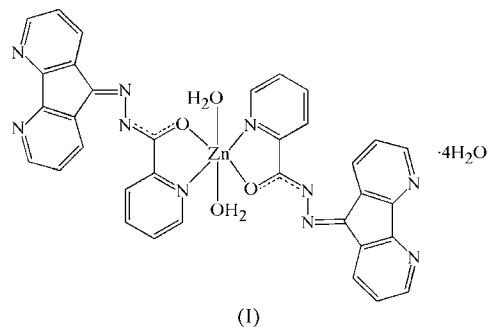
In the title compound,  $[Zn(C_{17}H_{10}N_5O)_2(H_2O)_2] \cdot 4H_2O$ , cyclic water hexamers forming one-dimensional metal–water chains are observed. The water clusters are trapped by the co-operative association of coordination interactions and hydrogen bonds. The  $Zn^{II}$  ion resides on a centre of symmetry and is in an octahedral coordination environment comprising two O atoms and two N atoms from two 2'-(4,5-diazafluoren-9-ylidene)picolinohydrazidate ligands and two water molecules.

**Comment**

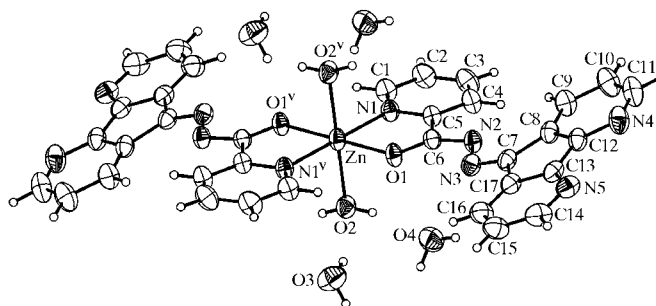
Over recent decades, considerable attention has been paid to theoretical (Xantheas, 1994; Kim *et al.*, 1999) and experimental (Neogi *et al.*, 2004) studies of small water clusters because of their importance in understanding the structures and characteristics of liquid water and ice (Ma *et al.*, 2004). So far, small water clusters,  $(H_2O)_n$  ( $n = 2-8, 10, 12, 14, 16, 18, 45$ ), have been obtained in organic or metal–organic crystal hosts (Li *et al.*, 2006). Of all water clusters, the water hexamer is particularly interesting as it is the building block of ice  $I_h$  and appears to be relevant to liquid water as well (Speedy *et al.*, 1987). Theoretical calculations have found that several different isomers for the water hexamer, such as ring, block, bag, cage and prism topologies, are almost isoenergetic (Kim & Kim, 1998). To date, chair (Zhao *et al.*, 2004), boat (Park *et al.*, 1993) and planar (Moorthy *et al.*, 2002) cyclic hexamers trapped by hydrogen bonding in host lattices have been reported. We report here the title metal–water chain complex,  $[Zn(L)_2(H_2O)_2] \cdot 4H_2O$  ( $L = 4,5$ -diazafluoren-9-ylidene)picolinohydrazidato), (I), containing the cyclic water hexamer, in which the water cluster is trapped not only by hydrogen bonds but also by coordination interactions.

As shown in Fig. 1, the structure of complex (I) consists of one  $[Zn(L)_2(H_2O)_2]$  complex molecule and four solvent water

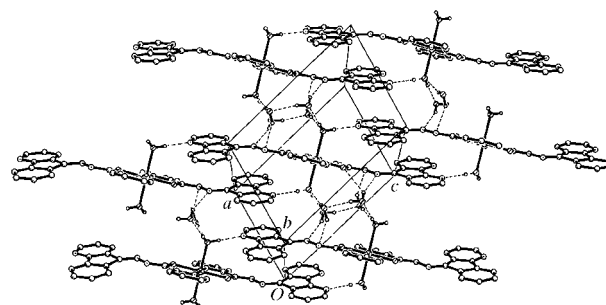
molecules. The  $Zn^{II}$  ion resides on a centre of symmetry and is coordinated by two O atoms and two N atoms from two  $L$  ligands arranged *trans* to each other in the equatorial plane,



and two aqua ligands occupying the apical coordination sites to furnish an octahedral geometry. The ligand  $L$  coordinates to the  $Zn^{II}$  ion as a mono-deprotonated bidentate ligand *via* the enolic O atom of the amide group and the N atom of the pyridyl group. Within the hydrazine component, both N atoms (N2 and N3) have effectively planar coordination and the N–N bond distance (Table 1) is typical of the value in hydrazine for both N atoms having planar coordination [mean value 1.401 (3) Å; Allen *et al.*, 1987]. The dihedral angle between the diazafluorene plane and the pyridyl plane is small [22.1 (2)°]. This is due to the small N3–N2–C6–O1 torsion angle



**Figure 1**  
 The structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (v)  $1 - x, 1 - y, 1 - z$ .]

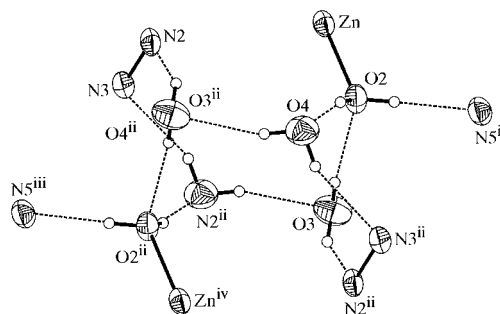


**Figure 2**  
 The two-dimensional structure of (I). Dashed lines indicate hydrogen bonds. H atoms attached to C atoms have been omitted for clarity. [Symmetry codes: (i)  $1 + x, y, z - 1$ ; (ii)  $-x, 1 - y, 1 - z$ ; (iii)  $-1 - x, 1 - y, 2 - z$ ; (iv)  $x - 1, y, z$ .]

[1.5 (5)°] and the  $sp^2$  hybridization of the C6 (amide) and C7 (diazfluorene) atoms.

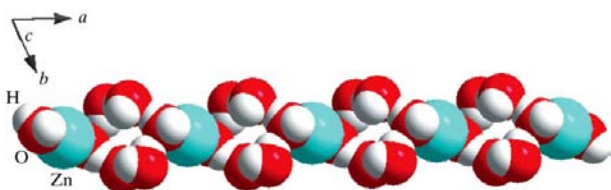
The  $[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_2]$  complex molecules are linked into one-dimensional chains along the [101] direction *via*  $\text{O}2-\text{H}2\text{B}\cdots\text{N}5^i$  hydrogen-bond interactions [symmetry code: (i)  $1+x, y, z-1$ ]. Within these chains, the separation between two diazafluorene rings is 3.351 (5) Å, indicating significant  $\pi-\pi$  stacking interactions. Along the [100] direction, the one-dimensional chains are stacked *via*  $\pi-\pi$  interactions between two diazafluorene rings of adjacent chains to generate two-dimensional layers parallel to the *ac* plane [mean interplanar distance = 3.428 (5) Å] (Fig. 2). The layers are stabilized by five independent hydrogen bonds of  $\text{O}-\text{H}\cdots\text{N}$  and  $\text{O}-\text{H}\cdots\text{O}$  types (Table 2).

Interestingly, a cyclic centrosymmetric water hexamer [ $R_6^6(12)$ ; Bernstein *et al.*, 1995] that adopts a chair conformation (Fig. 3) is observed in the solid state. The hydrogen-bonding parameters are reported in Table 2. The average  $\text{O}\cdots\text{O}$  distance is 2.864 (4) Å, which is nearly identical to the value of 2.854 (6) Å observed in liquid water (Speedy *et al.*, 1987). However, it is longer than the corresponding values in ice  $I_h$  [2.759 (3) Å; Benson & Siebert, 1992], and in water trapped in the organic compound  $\text{DMNY}\cdot 2.5\text{H}_2\text{O}$  [2.783 (3) Å; DMNY is 2,4-dimethyl-5-aminobenzo[*b*][1,8]-naphthyridine; Custelcean *et al.*, 2000] and in the metal-organic framework of  $[\text{Pr}(\text{pbc})(\text{Hpbc})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$  [2.783 (3) Å;  $\text{H}_2\text{pbc}$  is pyridine-2,6-dicarboxylic acid; Ghosh & Bharadwaj, 2003], as well as the calculated value of 2.718 (9) Å for the cyclic water hexamer (Stephens & Vagg, 1982). The average of the widely different  $\text{O}\cdots\text{O}\cdots\text{O}$  angles is 102 (12)°, which is smaller than that observed in  $\text{DMNY}\cdot 2.5\text{H}_2\text{O}$  [116.5 (2)°] and larger than that in  $[\text{Pr}$



**Figure 3**

A molecular drawing showing the cyclic water hexamer and its coordination environment. [Symmetry codes: (i)  $1+x, y, z-1$ ; (ii)  $-x, 1-y, 1-z$ ; (iii)  $-1-x, 1-y, 2-z$ ; (iv)  $x-1, y, z$ .]



**Figure 4**

A view of a metal-water chain along the *a* axis, containing cyclic water hexamers.

(pbc)(Hpbc)( $\text{H}_2\text{O}$ ) $_2$ ] $\cdot 4\text{H}_2\text{O}$  [98.36 (5)°]. The coordinated water molecule (O2) has a tetrahedral geometry, with two  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, one  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bond and one water-metal coordination bond. Meanwhile, each of the other water molecules (O3 and O4) involves three hydrogen bonds, *viz.* two water-water hydrogen bonds and one water-hydrazine hydrogen bond. Therefore, each water molecule acts as both hydrogen donor and acceptor to form a cyclic water hexamer. Two water molecules in the cyclic hexamers bind to the  $\text{Zn}^{\text{II}}$  ions, resulting in an infinite metal-water chain along the *a* axis (Fig. 4). To the best of our knowledge, such cyclic water clusters containing metal-water chains are very rare (Ghosh & Bharadwaj, 2003; Turner *et al.*, 2004).

## Experimental

An ethanol-dimethylformamide (2:1 *v/v*) solution (40 ml) of the ligand HL (0.5 mmol, 0.15 g) and an aqueous solution (10 ml) of  $\text{Zn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (0.25 mmol, 0.26 g) were mixed together, and then five drops of pyridine were added. Red single crystals of (I) suitable for X-ray structure analysis were obtained after two months by slow evaporation of the solvents at room temperature.

### Crystal data

$[\text{Zn}(\text{C}_{17}\text{H}_{10}\text{N}_5\text{O}_2)(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$	$V = 849.4 (3) \text{ \AA}^3$
$M_r = 774.09$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.513 \text{ Mg m}^{-3}$
$a = 7.9310 (16) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.340 (2) \text{ \AA}$	$\mu = 0.79 \text{ mm}^{-1}$
$c = 11.734 (2) \text{ \AA}$	$T = 291 (2) \text{ K}$
$\alpha = 74.87 (3)^\circ$	Block, red
$\beta = 75.64 (3)^\circ$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$\gamma = 68.06 (3)^\circ$	

### Data collection

Bruker SMART APEXII CCD	5042 measured reflections
area-detector diffractometer	3915 independent reflections
$\varphi$ and $\omega$ scans	2724 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.002$
(SADABS; Sheldrick, 2003)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.797, T_{\text{max}} = 0.858$	

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1019P)^2 + 0.1755P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
3915 reflections	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
242 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0010 (2)

**Table 1**

Selected geometric parameters (Å, °).

Zn—O1	2.069 (2)	N2—C6	1.318 (4)
Zn—N1	2.087 (3)	N2—N3	1.391 (4)
Zn—O2	2.202 (3)	N3—C7	1.296 (4)
N3—N2—C6—O1	1.5 (5)	N2—N3—C7—C17	−178.1 (3)
N3—N2—C6—C5	−178.4 (3)	N2—N3—C7—C8	3.9 (6)

H atoms attached to C atoms were included in calculated positions and treated as riding atoms, with  $\text{C}-\text{H} = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Water H atoms were found in a difference map, relocated

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A $\cdots$ O4	0.85	1.97	2.799 (4)	166
O2—H2B $\cdots$ N5 <sup>i</sup>	0.85	1.92	2.771 (4)	177
O3—H3A $\cdots$ N2 <sup>ii</sup>	0.85	2.26	2.988 (5)	143
O3—H3B $\cdots$ O2	0.85	2.05	2.847 (5)	157
O4—H4A $\cdots$ N3 <sup>ii</sup>	0.85	2.19	2.993 (4)	159
O4—H4B $\cdots$ O3 <sup>ii</sup>	0.85	2.12	2.947 (5)	164

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

in idealized positions with O—H = 0.85 Å, and refined as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); 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: GZ3031). Services for accessing these data are described at the back of the journal.

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