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Key indicators

Single-crystal X-ray study
 $T = 110\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.058
 wR factor = 0.152
Data-to-parameter ratio = 17.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Tetraaquabis(1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene)zinc(II) bis(perchlorate) and its supramolecular assembly

The structure of the title compound, $[\text{Zn}(\text{C}_{12}\text{H}_{10}\text{N}_4)_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$, determined at 110 K, reveals a unique layered supramolecular aggregation stabilized by a combination of coordination, hydrogen-bonding and π - π forces. Disordered molecules of solvent (methanol or a mixture of methanol and water) occupy the channel-like voids formed between the layers. The zinc cations have $\bar{1}$ site symmetry.

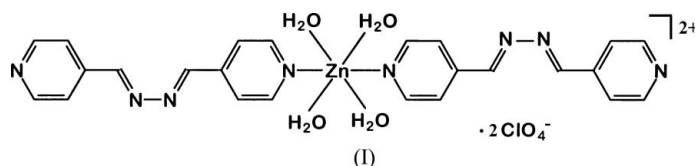
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Comment

We have recently studied the coordination chemistry of a series of bipyridyl-type ligands with zinc ions (among other transition metals) and with metalloporphyrins (Patra & Goldberg, 2002; Diskin-Posner *et al.*, 2002, 2001). In this context we report here the molecular structure of the title compound, (I) (Fig. 1), and its unique supramolecular assembly in crystals. The 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (*L*) ligand bears two terminal pyridyl groups, which can function as effective ligation sites for transition metal ions as well as excellent proton acceptors in hydrogen bonding in the presence of strong proton-donating agents. Additionally, *L* has an aromatic nature with delocalized π electrons, preserving a nearly planar geometry both in its coordination complexes with metal ions and as a free non-coordinated species in its protonated or base forms (Kennedy & Waterson, 2003; Ciurtin *et al.*, 2001).



Compound (I) consists of octahedral $[\text{Zn}(\text{H}_2\text{O})_4(\text{L})_2]^{2+}$ dications and two perchlorate anions, with the zinc cations occupying inversion centres. Selected geometric data are given in Table 1). The crystal structure appears to be a solvate,

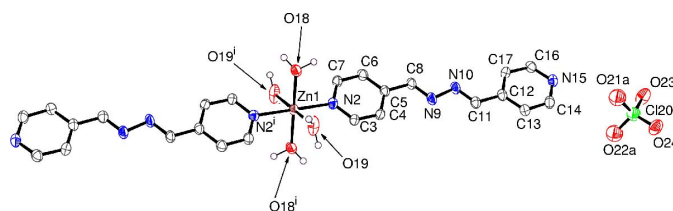


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids. C-bound H atoms have been omitted and only the major orientation of the perchlorate anion is shown. [Symmetry code: (i) $2 - x$, $1 - y$, $2 - z$.]

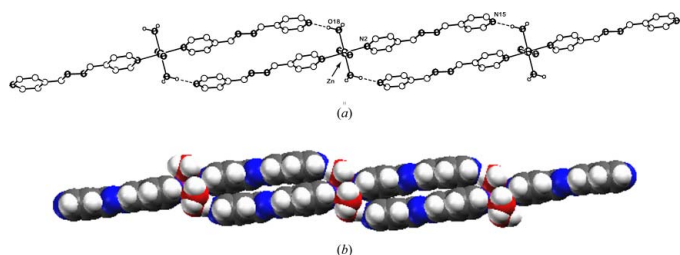


Figure 2
Illustration of the double chains that form by hydrogen bonding between three adjacent $[Zn(L)_2(H_2O)_4]^{2+}$ species. Along the chain, centers of inversion are located at the zinc ions and between the overlapping ligands. (a) Ball-and-stick diagram (only H atoms of H_2O_{18} are shown; hydrogen bonds are indicated by broken lines). (b) Space-filling illustration.

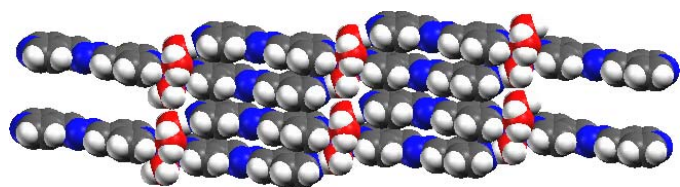


Figure 3
Space-filling diagram of the π - π stacking of the double chains along the a axis of (I) that yields tightly packed two-dimensional layers. Two double chains are shown.

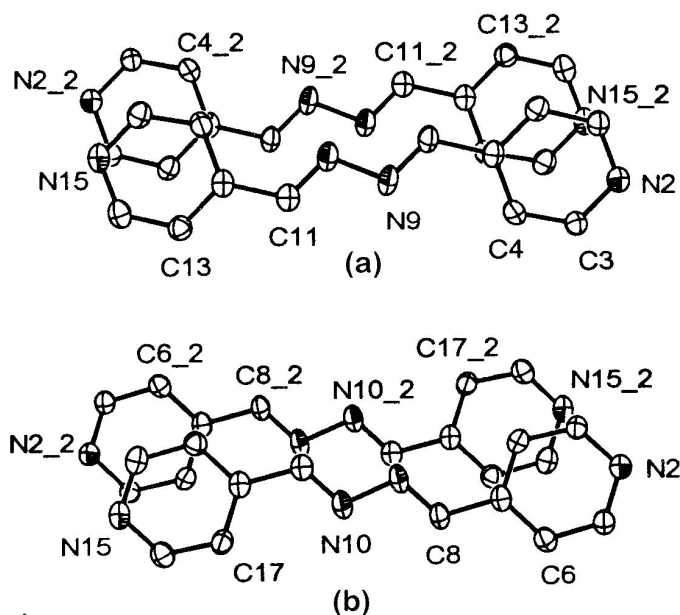


Figure 4
Detail of (I) showing the stacking and overlapping modes between π - π -interacting ligands. (a) Within the double chains. (b) Between the molecular surfaces of the double chains. Atomic labels $_2$ refer to ligands related by inversion, at $(\frac{1}{2}, 0, \frac{1}{2})$ in (a) and $(1, 0, \frac{1}{2})$ in (b), to the parent segment.

incorporating disordered molecules of methanol or a mixture of methanol and water, which are not coordinated to the metal centre. The tetraaqua zinc ion is coordinated at *trans*-related sites by two molecules of the ligand, forming a linear $(L)-Zn(H_2O)_4-(L)$ unit. Adjacent units are aligned parallel to

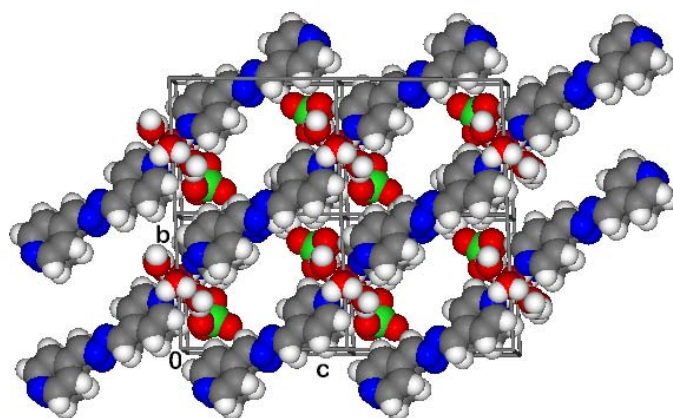


Figure 5
Space-filling view of the crystal structure of (I) viewed down the a axis, showing edge-on the supramolecular layers parallel to the $(0, 2, -2)$ lattice plane, and their perchlorate-bridged packing in the crystal which creates large channel-voids at $(x, \frac{1}{2}, \frac{1}{2})$.

each other in an offset manner along the long molecular axis, in such a way that the N15-pyridyl sites of one unit hydrogen bond (Table 2) on both sides to the zinc-bound water ligands O18 of two neighboring units, forming ‘double chains’ (Fig. 2). The overlapping planar ligand segments of neighboring moieties in these double chains [the angle between the normals to these planes is $1.2 (1^\circ)$] further interact with one another through π - π interactions. The mean interplanar distance between the parallel stacked ligands $[N2 \cdots C17^{ii}]$, symmetry code: (ii) $1 - x, -y, 1 - z$ is $3.36 (6) \text{ \AA}$, indicative of strong attraction between them. Along the chain, each $ZnL_2(H_2O)_4$ entity is engaged in four hydrogen bonds through the two N15 (as proton acceptors) and two H_2O_{18} (as proton donors) sites. A similar mode of supramolecular aggregation has been observed recently for the diaquadimethanzinc complex with the same ligand (Shoshnik *et al.*, 2005). Owing to the aromatic nature of L in (I), the hydrogen-bonded chains π - π stack tightly on top of one another along the a axis of the unit cell, forming flat layered zones in the crystal structure (Fig. 3). The mean spacing between overlapping ligands of consecutive hydrogen-bonded chains in such layers is $3.32 (6) \text{ \AA}$ (Fig. 4). The layers thus formed are parallel to the $(02\bar{2})$ plane. Association of these layers in the normal direction is assisted by the perchlorate anions, which accept hydrogen bonds from the zinc-bound water ligands of neighboring layers and bridge between them (Table 2). Fig. 5 illustrates the resulting crystal structure, characterized by *ca* 6 \AA -wide channel voids, which propagate along the a axis of the crystal structure and accommodate the disordered crystallization solvent. These results, along with earlier observations in a closely related compound (Shoshnik *et al.*, 2005), illustrate nicely the considerable versatility of bipyridyl-type ligands in the construction of hybrid organic-inorganic supramolecular assemblies by utilizing diverse combinations of the molecular recognition features of such ligands, including coordination, hydrogen bonding and π - π interactions. Relating to the previous report, it appears that, on changing the stoichiometry of the zinc bis(perchlorate) hexahydrate

reaction with *L* from 1:2 in (I) to 1:3 (Shoshnik *et al.*, 2005), a different supramolecular architecture is formed. In the latter, the additional ligand inserts between, and nearly perpendicular to, the double-chain aggregates by hydrogen bonding through its N atoms on both sides to the hydrated zinc nodes. This configuration affords an open supramolecular network (Fig. 6), as opposed to the more tightly packed array in the present structure (Fig. 3).

Experimental

Compound (I) was synthesized by reacting zinc perchlorate hexahydrate with *L* in a 1:2 ratio, dissolved in hot methanol, followed by crystallization by slow cooling.

Crystal data

$[\text{Zn}(\text{C}_{12}\text{H}_{10}\text{N}_4)_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$	$Z = 1$
$M_r = 756.81$	$D_x = 1.290 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.2316 (3) \text{ \AA}$	Cell parameters from 2237 reflections
$b = 10.5151 (4) \text{ \AA}$	$\theta = 2.0\text{--}27.0^\circ$
$c = 13.4031 (5) \text{ \AA}$	$\mu = 0.83 \text{ mm}^{-1}$
$\alpha = 90.500 (2)^\circ$	$T = 110 (2) \text{ K}$
$\beta = 103.127 (3)^\circ$	Prism, yellow
$\gamma = 100.5940 (18)^\circ$	$0.35 \times 0.30 \times 0.20 \text{ mm}$
$V = 974.28 (7) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	3171 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.035$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 27.0^\circ$
$T_{\text{min}} = 0.758, T_{\text{max}} = 0.851$	$h = 0 \rightarrow 9$
7657 measured reflections	$k = -13 \rightarrow 13$
4113 independent reflections	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.407P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.152$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.83 \text{ e \AA}^{-3}$
4113 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
236 parameters	
H-atom parameters constrained	

Table 1

Selected interatomic distances (\AA).

Zn1—O18	2.087 (2)	Zn1—N2	2.131 (3)
Zn1—O19	2.130 (2)		

Table 2

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O18—H18A \cdots N15 ⁱⁱ	0.95	1.80	2.748 (3)	179
O18—H18B \cdots O23 ⁱⁱⁱ	0.90	2.01	2.911 (3)	179
O19—H19A \cdots O22A ⁱⁱⁱ	0.94	1.96	2.903 (5)	180
O19—H19B \cdots O22B ^{iv}	0.97	1.84	2.690 (14)	144
O19—H19B \cdots O21A ^{iv}	0.97	2.43	3.246 (7)	141

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

The perchlorate anion exhibits partial positional disorder between two possible sites with relative occupancies of 0.75 and 0.25. The

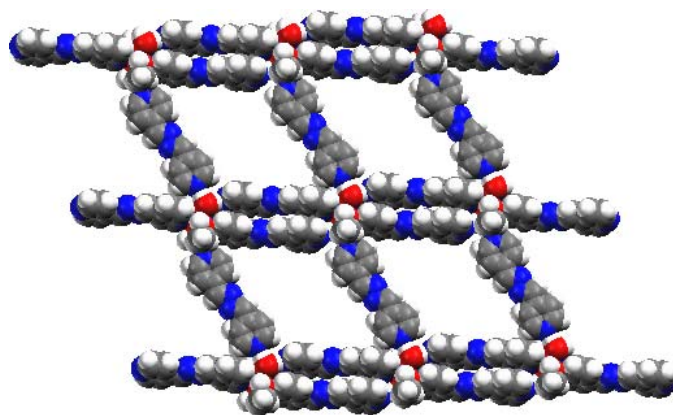


Figure 6

Network formation in a related compound (Shoshnik, *et al.*, 2005) of 1:3 zinc:*L* composition by tessellating the double chains to one another *via* additional ligands, which hydrogen bond on both sides to the double-chain arrays.

latter relates to atoms Cl20 and two oxygen sites, O21 and O22. Atoms O23 and O24 have an occupancy of 1, as they are part of both perchlorate fragments. The nature of the crystallization solvent could not be determined/modelled reliably from diffraction data, because of severe positional disorder and fractional occupancies at each site. Conventional refinement excluding the solvent species converged at $R(F) = 0.13$. The residual peak distribution, residual electron-density count (38 e \AA^{-3}) and void volume (199.0 \AA^3) as calculated by *PLATON* (Spek, 2003) are consistent with the presence of about two molecules of methanol or a mixture of 1–2 methanol molecules and one water molecule per unit cell. The *PLATON/SQUEEZE* software was then applied to subtract the contribution of the disordered solvent from the diffraction data, which were subsequently used in the final refinement. The exclusion of the solvent seems to have a negligible effect on the characterization of the supramolecular structure. C-bound H atoms were located in idealized positions and refined as riding on their carrier atoms with fixed U_{iso} values. O-bound H atoms were positioned geometrically ($\text{O—H} = 0.90\text{--}0.97 \text{ \AA}$) on the basis of reasonable hydrogen-bonding contacts and refined as riding on their carrier atoms with fixed U_{iso} values (0.080 \AA^2).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DS ViewerPro* (Accelrys, 2002), *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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References

- Accelrys (2002). *DS ViewerPro*. Version 5.0. Accelrys Inc., San Diego, CA, USA.
- Altomare, A., Burla, M. C., Camalli, M., Casciarano, M., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

- Ciurtin, D. M., Dong, Y.-B., Smith, M. D., Barklay, T. & zur Loye, H.-C. (2001). *Inorg. Chem.* **40**, 2825–2834.
- Diskin-Posner, Y., Patra, G. K. & Goldberg, I. (2001). *Dalton Trans.* pp. 2775–2782.
- Diskin-Posner, Y., Patra, G. K. & Goldberg, I. (2002). *Chem. Commun.* pp. 1420–1421.
- Kennedy, A. R. & Waterson, F. R. N. (2003). *Acta Cryst.* **C59**, o613–o615.
- Nonius (1999). *COLLECT*. Nonius, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Patra, G. K. & Goldberg I. (2002). *Dalton Trans.* pp. 1051–1057.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shoshnik, R., Elengoz, H. & Goldberg, I. (2005). *Acta Cryst.* **C61**, m187–m189.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.