

## Concerted coordination and hydrogen-bonding network of the 1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene $[\text{Zn}(\text{MeOH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ 3:1 complex

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Received 10 February 2005

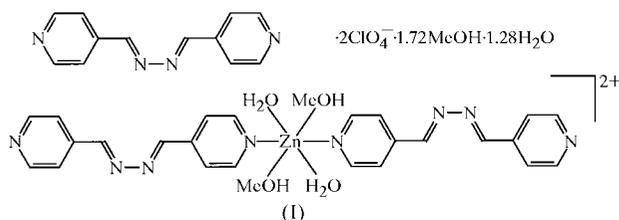
Accepted 17 February 2005

Online 11 March 2005

In the title compound, diaquabis(1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene)dimethanolzinc(II) bis(perchlorate) 1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene methanol 1.72-solvate 1.28-hydrate,  $[\text{Zn}(\text{C}_{12}\text{H}_{10}\text{N}_4)_2(\text{CH}_4\text{O})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{C}_{12}\text{H}_{10}\text{N}_4 \cdot 1.72\text{CH}_4\text{O} \cdot 1.28\text{H}_2\text{O}$ , determined at *ca* 110 K, the Zn cation and the extended dipyridyl ligand both lie across inversion centres in space group  $P\bar{1}$ . The structure consists of a network arrangement of the constituent species stabilized by a combination of coordination, hydrogen bonding and  $\pi$ - $\pi$  forces. Uncoordinated methanol and water solvent molecules occupy the otherwise void spaces within and between the networks.

### Comment

We have been exploring the coordination chemistry of a large series of polyimine ligands with transition metal ions (Patra & Goldberg, 2002, 2003*a,b*) and with metalloporphyrins (Diskin-Posner *et al.*, 2001, 2002). Tailored derivatives of 4,4'-bipyridyl ligands with various spacers between the bipyridyl functions are very effective in the formation of diverse architectures *via* coordination through metal ion connectors (*e.g.* Co, Ni, Mn, Zn, Ag and Pb). Such ligands are also excellent proton acceptors in hydrogen bonding (through their N-atom sites) in the presence of strong proton-donating agents.



We refer here to the 1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene ligand (*L*), and its hydrogen bonding and coordination

to  $[\text{Zn}(\text{MeOH})_2(\text{H}_2\text{O})_2]^{2+}$  cations, affording self-assembled two-dimensional networks. Another important feature of *L* is its aromatic nature, with delocalized  $\pi$  electrons, preserving the planar geometry of the ligand both in its coordination polymers or oligomers with various transition metals and as a free non-coordinated species in its protonated or base forms (Kennedy & Waterson, 2003; Ciurtin *et al.*, 2001).

The title compound, (I) (Fig. 1), consists of the octahedral  $[\text{Zn}(\text{L})_2(\text{MeOH})_2(\text{H}_2\text{O})_2]^{2+}$  dication, two perchlorate anions and another ligand species hydrogen bonded to the water ligands. The dication and the extended bipyridyl moieties reside on crystallographic inversion centres. The crystal structure is a solvate incorporating additional molecules of methanol and water, not bound to the metal centre, in the unit cell.

The solvated zinc ion [labelled hereafter as Zn(*s*)] coordinates at *trans*-related sites to two molecules of the ligand [ $\text{Zn}-\text{N} = 2.120$  (2) Å; Table 1], forming a linear  $L-\text{Zn}(s)-L$  oligomer. Adjacent units of the latter are aligned parallel to one another in an offset manner along the long molecular axis, in such a way that the pyridyl ends of one trimer hydrogen bond to the Zn-bound water ligands of two adjacent  $L-\text{Zn}(s)-L$  trimers [ $\text{O} \cdots \text{N} = 2.798$  (3) Å; Fig. 2]. The double chains thus formed propagate along the  $[11\bar{1}]$  axis through the crystal. The overlapping planar ligand segments of neighbouring oligomers in these double chains further interact with one another through  $\pi$ - $\pi$  interactions, as indicated by the very close interligand spacing. The mean interplanar distance between the parallel stacked pyridyl rings N2/C3-C7 and C12-C14/N15/C16/C17 at  $(1-x, 2-y, 1-z)$  is 3.369 (7) Å, the shortest atom-to-atom distance between these two rings being 3.252 (3) Å (Fig. 3). The overlapping pyridyl rings are nearly parallel to each other, the angle between their normals being 5.6 (2)°. The third ligand moiety provides a bridging unit

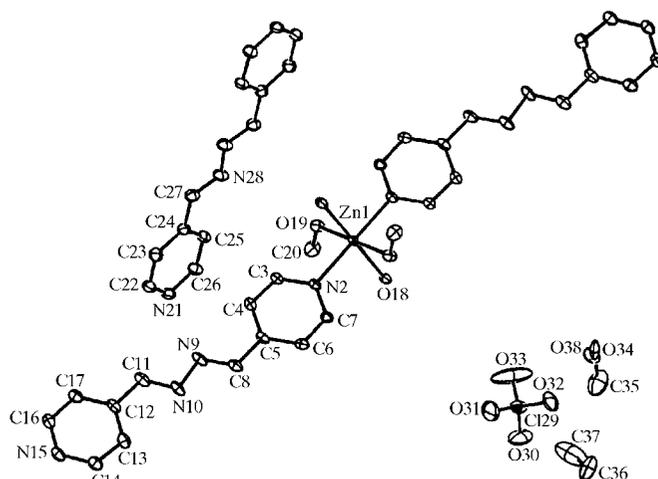
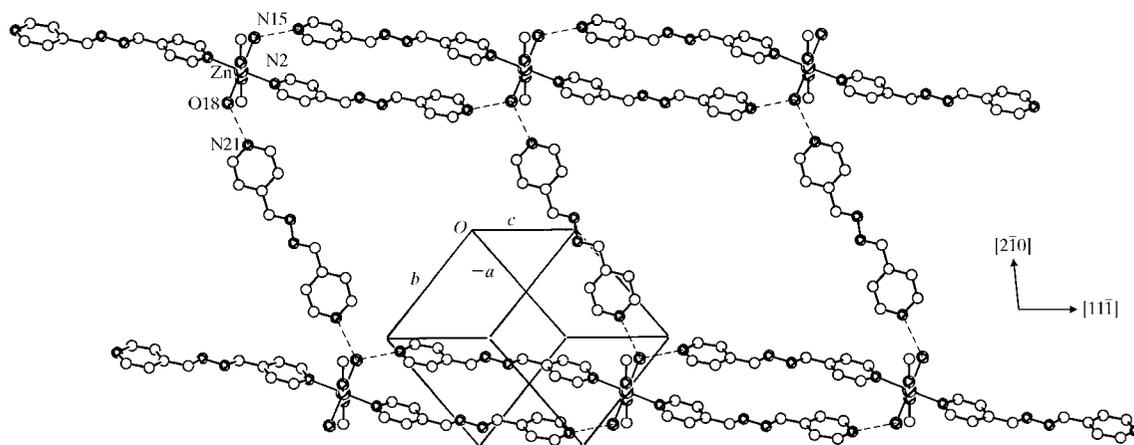


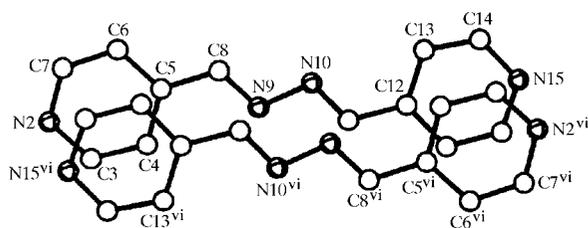
Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level at *ca* 110 K. The large displacement parameters of the perchlorate and solvent species indicate unresolved disorder.



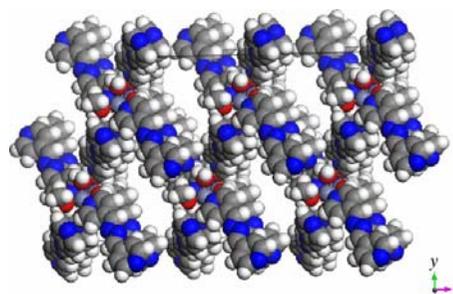
**Figure 2**

An illustration of the intermolecular network arrangement. Hydrogen bonds are indicated by thin broken lines. Double chains with  $\pi$ - $\pi$  stacked ligand species extend horizontally along the  $[11\bar{1}]$  axis of the crystal. Adjacent double chains in this network are displaced with respect to one another along the  $[2\bar{1}0]$  axis. The perchlorate and solvent species have been omitted for clarity. All non-C atoms are denoted by darkened circles.



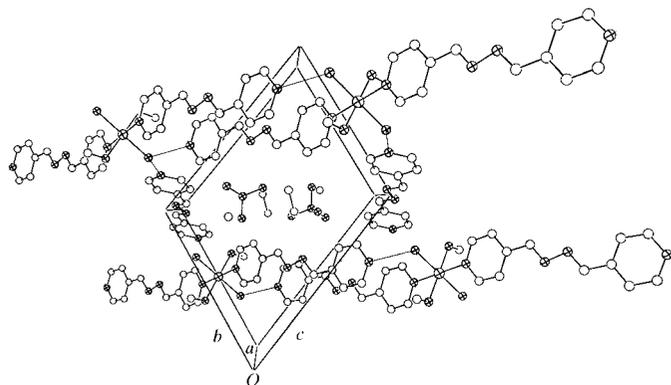
**Figure 3**

The overlap between two ligands related by inversion at  $(\frac{1}{2}, 1, \frac{1}{2})$ , with a mean interplanar distance of 3.369 (7) Å between the pyridyl rings. Atom N2 of each ligand coordinates directly to the Zn atom, while atom N15 of each ligand hydrogen bonds to the zinc-bound water ligand O18 (Fig. 2). [Symmetry code: (vi)  $1 - x, 2 - y, 1 - z$ ].



**Figure 5**

Space-filling perspective of the channel structure formed by the stacked network arrays (excluding the perchlorate ions and the disordered solvent molecules, which occupy the channel voids), viewed approximately down the  $a$  axis.



**Figure 4**

The crystal packing viewed down the  $a$  axis of the crystal, showing the anion and disordered solvent moieties accommodated in channel voids propagating through the supramolecular networks. Atoms of the perchlorate anions are denoted by crossed circles; those of the O36/C37 methanol and O38 water groups are represented by open circles (methanol group O34/C35, which nearly coincides with O38, has been omitted for clarity). All non-C atoms in the cation are denoted by crossed circles. The contents of more than one unit cell are shown.

between different double chains by hydrogen bonding through its N-atom sites on both sides, accepting the second H atom of the zinc-bound water ligands [ $O \cdots N = 2.773(3)$  Å].

The binding pattern described above results in a supramolecularly assembled network in the form of a nearly square grid (Fig. 2). The van der Waals width of the void space in the grid is about 8 Å, sizeable enough to accommodate the perchlorate anions and additional methanol and water solvent molecules. The zinc-bound methanol ligands hydrogen bond to the lattice-occluded solvent [represented by O34, O36 (methanol) and O38 (water) in Table 2], the latter lying also within hydrogen-bonding distance of the perchlorate anions. The network arrays stack in the crystal along the  $[111]$  axis. The crystal packing of (I) viewed down the  $a$  axis is shown in Fig. 4, illustrating the inclusion of the perchlorate anions and disordered solvent molecules in channel voids propagating through the crystal. A space-filling illustration of the channel structure down  $a$ , excluding these species, is presented in Fig. 5. This structure illustrates nicely the high versatility of bipyridyl ligands in the construction of hybrid organic-inorganic supramolecular assemblies.

## Experimental

The title compound was synthesized by reacting stoichiometric amounts of zinc perchlorate hexahydrate with *L* dissolved in hot methanol, followed by crystallization by slow cooling.

### Crystal data

$[\text{Zn}(\text{C}_{12}\text{H}_{10}\text{N}_4)_2(\text{CH}_3\text{O})_2(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_2 \cdot \text{C}_{12}\text{H}_{10}\text{N}_4 \cdot 1.72\text{CH}_3\text{O} \cdot 1.28\text{H}_2\text{O}$	$V = 1211.56(4) \text{ \AA}^3$
$M_r = 1073.28$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.471 \text{ Mg m}^{-3}$
$a = 9.4168(2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.8321(2) \text{ \AA}$	Cell parameters from 4290 reflections
$c = 13.1414(3) \text{ \AA}$	$\theta = 2.7\text{--}27.0^\circ$
$\alpha = 67.8394(8)^\circ$	$\mu = 0.70 \text{ mm}^{-1}$
$\beta = 81.3045(9)^\circ$	$T = 110(2) \text{ K}$
$\gamma = 78.3162(9)^\circ$	Prism, yellow
	$0.30 \times 0.20 \times 0.15 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer	4492 reflections with $I > 2\sigma(I)$
$1^\circ \varphi$ and $\omega$ scans	$R_{\text{int}} = 0.029$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 27.0^\circ$
$T_{\text{min}} = 0.818, T_{\text{max}} = 0.903$	$h = 0 \rightarrow 12$
10 055 measured reflections	$k = -13 \rightarrow 13$
5216 independent reflections	$l = -16 \rightarrow 16$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 2.505P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{\text{max}} = 0.028$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.92 \text{ e \AA}^{-3}$
5216 reflections	$\Delta\rho_{\text{min}} = -1.17 \text{ e \AA}^{-3}$
347 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Zn1—O18	2.0977 (18)	Zn1—O19	2.1642 (19)
Zn1—N2	2.120 (2)		
O18—Zn1—N2	90.15 (8)	O18 <sup>i</sup> —Zn1—O19	88.77 (7)
O18 <sup>i</sup> —Zn1—N2	89.85 (8)	N2 <sup>i</sup> —Zn1—O19	91.20 (8)
O18—Zn1—O19	91.23 (7)	N2—Zn1—O19	88.80 (8)

Symmetry code: (i)  $-x, -y + 1, -z + 2$ .

**Table 2**

Hydrogen-bond and short-contact 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 <sup>i</sup> ···N21 <sup>ii</sup>	0.97	1.80	2.773 (3)	180
O18—H18B <sup>i</sup> ···N15 <sup>iii</sup>	0.97	1.83	2.798 (3)	180
O19—H19···O34 <sup>iv</sup>	0.98	1.69	2.653 (7)	167
O19···O38 <sup>iv</sup>	—	—	2.752 (7)	—
O36···O30	—	—	2.904 (7)	—
O36···O34 <sup>v</sup>	—	—	2.937 (8)	—
O36···O38 <sup>v</sup>	—	—	2.937 (7)	—

Symmetry codes: (ii)  $-x + 1, -y + 1, -z + 2$ ; (iii)  $x - 1, y - 1, z + 1$ ; (iv)  $x, y, z + 1$ ; (v)  $-x, -y + 1, -z + 1$ .

The perchlorate anion exhibits very wide amplitude displacement parameters, indicative of partial rotational disorder that could not be resolved. The content and structure of the crystallization solvent

could not be determined precisely from the diffraction data, owing to severe positional disorder and fractional occupancies at each site. The approximate unit-cell content that best fits the diffraction data was assessed as 1.72 molecules of methanol and 1.28 molecules of water distributed randomly in the crystal within and between the self-assembled networks. The O34/C35 and O36/C37 fragments represent methanol species with 36 and 50% occupancy, respectively. Atom O38 (nearly coinciding with the position of O34) represents a water molecule with 64% occupancy. These solvent species are located near and disordered about inversion centres. According to this model, the O34/C35 (methanol) and O38 (water) groups are distributed randomly in the crystal at the same site in different unit cells. The coinciding position of these two species results from the hydrogen bonding of either one to the Zn-bound methanol ligand O19. The apparent disorder of the solvent species seems to have a negligible effect on the precise characterization of the network structure. H atoms were placed at idealized positions ( $\text{C—H} = 0.95$  and  $0.98 \text{ \AA}$ ); those attached to C atoms were refined using a riding model with fixed displacement parameters. The displacement parameters of the H atoms of the Zn-coordinated methanol and aqua groups were allowed to refine freely. H atoms of the water solvent molecules could not be located. The relatively high residual density should be attributed to the unresolved solvent.

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: *ORTEPIII* (Burnett & Johnson, 1996) and *DS ViewerPro* (Accelrys, 2002); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Goutam Kumar Patra for the synthesis of the organic ligand.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1374). Services for accessing these data are described at the back of the journal.

## References

- Accelrys (2002). *DS ViewerPro*. Version 5.0. Accelrys Inc., San Diego, CA, USA.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- 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). *J. Chem. Soc. 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 BV, 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). *J. Chem. Soc. Dalton Trans.* pp. 1051–1057.
- Patra, G. K. & Goldberg, I. (2003a). *Cryst. Growth Des.* **3**, 321–329.
- Patra, G. K. & Goldberg, I. (2003b). *Eur. J. Inorg. Chem.* pp. 969–977.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.