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catena-Poly[[diaquadinitratozinc(II)]-bis(μ -1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene)]

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Key indicators

Single-crystal X-ray study

$T = 150\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.029

wR factor = 0.082

Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

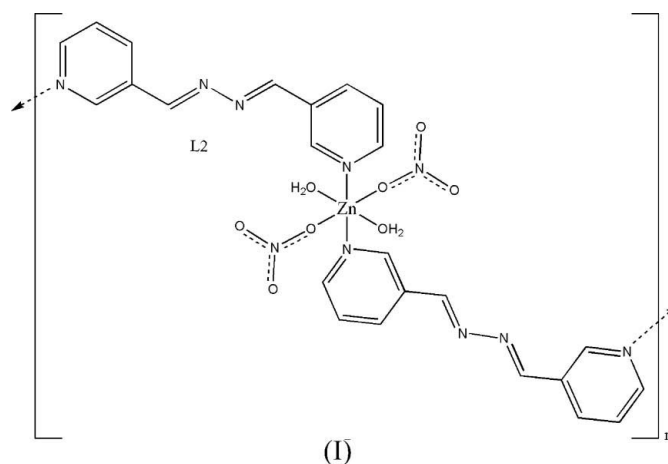
The polymeric title complex, $[\text{Zn}(\text{NO}_3)_2(\text{C}_{24}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]_n$, features distorted ZnN_2O_4 octahedra with each Zn^{II} atom being located on an inversion center. Adjacent Zn ions are doubly bridged by two equivalent 1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene ligands to form linear chains.

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Comment

There has been much effort directed at the construction of new coordination polymers due to their potentially interesting and useful properties (Chin *et al.*, 1993; Kitagawa *et al.*, 2004; Janiak, 2003). In this context, we have been highly successful in utilizing N,N' -bipyridyl-type ligands to link metal centers to form such polymeric materials (Perkins *et al.*, 2005; Khalil *et al.*, 2005; Davis *et al.*, 2004; Dong *et al.*, 2000*a,b*). As a continuation of this work, we report the details of the crystal structure of the title complex, (I), in which 1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene ($L2$) is used to link Zn^{II} centers into one-dimensional chains.



The crystal structure of (I) is built upon neutral $\text{Zn}(L2)_2(\text{OH}_2)_2(\text{NO}_3)_2$ units (Fig. 1). The Zn^{II} ion is located on an inversion center and is situated in a distorted N_2O_4 octahedral coordination environment. The axial positions are occupied by two N atoms from pairs of equivalent $L2$ ligands. The equatorial positions are occupied by four O atoms, two from equivalent pairs of water molecules and two O atoms from equivalent pairs of monodentate nitrates (Table 1). For $L2$, the two pyridyl rings N1/C1–C5 and N4/C8–C12 are twisted at a dihedral angle of $34.6(1)^\circ$. As expected for the nitrate, the N–O bond corresponding to the coordinated O atom is slightly longer than the other two N–O bonds (Table 1). One of the uncoordinated nitrate O atoms is

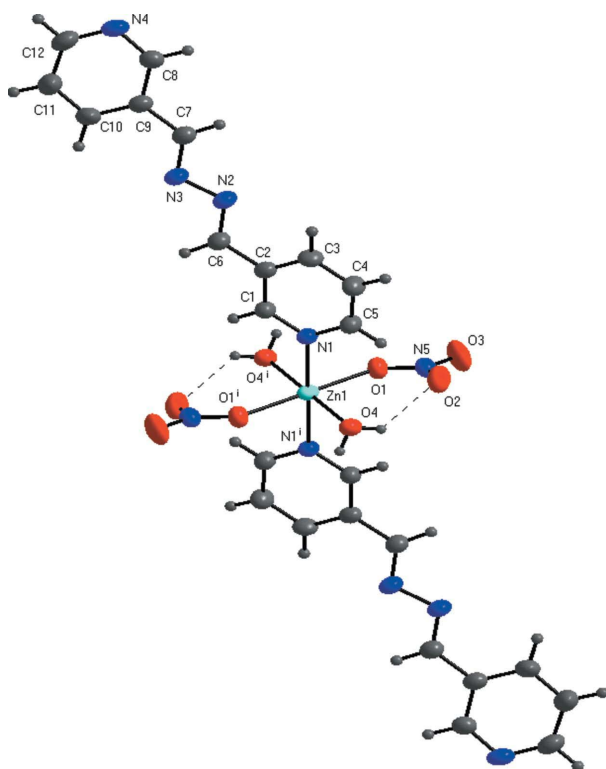


Figure 1

The structure of (I), with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines. [Symmetry code: (i) $1 - x, 1 - y, -z$]

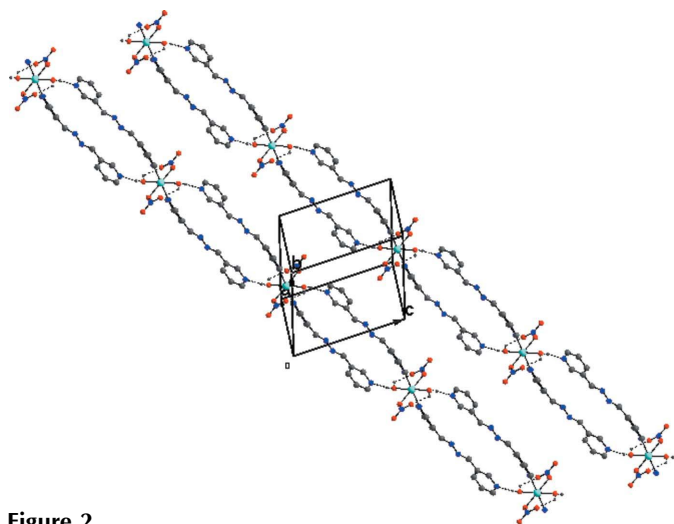


Figure 2

View of the crystal packing in (I) showing the one-dimensional chains. All H atoms except for those of water have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

involved in an intramolecular O4—H4B...O2 hydrogen bond (Table 2) to a coordinated water molecule located on the same Zn^{II} center.

It is noteworthy that only one of the two pyridyl N atoms of L2 directly coordinates a Zn^{II} ion. The other pyridyl N atom interacts indirectly with an adjacent Zn^{II} ion by forming an outer-sphere O4—H4A...N4 hydrogen bond (Table 2) with a coordinated water molecule located on the adjacent Zn^{II} center. This interaction, along with the inner-sphere Zn^{II}—N2

coordination bond noted previously, generates a double chain structure (Fig. 2) involving two equivalent L2 ligands. The chains run along the $[11\bar{1}]$ direction with a non-bonded Zn^{II}...Zn^{II} distance of 15.578 (1) Å. To our knowledge, the generation of such a double chain structure involving both inner- and outer-sphere coordination by L2 is the first of its kind for this ligand.

Experimental

All chemicals and solvents were purchased from commercial sources and used without further purification. The L2 ligand (Dong *et al.*, 2000) was prepared as previously described. Complex (I) was obtained by slow diffusion of an ethanol solution containing zinc nitrate hexahydrate (0.50 mmol) into a dichloromethane solution (8 ml) containing a mixture of L2 (1.0 mmol) and of 4,4'-bipyridine (1.0 mmol). A mixture of yellow, irregularly shaped crystals of (I) and colorless bar-shaped crystals of formula $[\text{Zn}^{\text{II}}(4,4'\text{-bipyridine})_2(\text{NO}_3)_2 \cdot \text{CH}_2\text{Cl}_2]_n$ were obtained at the interface of the two solutions after several weeks.

Crystal data

| | |
|--|---|
| $[\text{Zn}(\text{NO}_3)_2(\text{C}_{24}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]$ | $V = 689.12 (16) \text{ \AA}^3$ |
| $M_r = 645.90$ | $Z = 1$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.556 \text{ Mg m}^{-3}$ |
| $a = 7.8267 (11) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 8.5320 (11) \text{ \AA}$ | $\mu = 0.96 \text{ mm}^{-1}$ |
| $c = 11.7409 (16) \text{ \AA}$ | $T = 150 (1) \text{ K}$ |
| $\alpha = 81.113 (2)^\circ$ | Irregular fragment, yellow |
| $\beta = 73.696 (2)^\circ$ | $0.40 \times 0.26 \times 0.14 \text{ mm}$ |
| $\gamma = 66.468 (2)^\circ$ | |

Data collection

| | |
|--|--|
| Bruker SMART APEX CCD diffractometer | 6421 measured reflections |
| ω scans | 2831 independent reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | 2720 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.670, T_{\max} = 0.870$ | $R_{\text{int}} = 0.027$ |
| | $\theta_{\max} = 26.4^\circ$ |

Refinement

| | |
|--|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.1395P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.029$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.082$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| $S = 1.07$ | $\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$ |
| 2831 reflections | $\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$ |
| 205 parameters | Extinction correction: SHELXL97 |
| H atoms treated by a mixture of independent and constrained refinement | Extinction coefficient: 0.026 (4) |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------------------|-------------|-------------------------|-------------|
| Zn1—O1 | 2.1839 (12) | N5—O3 | 1.236 (2) |
| Zn1—O4 | 2.0795 (12) | N5—O2 | 1.239 (2) |
| Zn1—N1 | 2.1487 (13) | N5—O1 | 1.2653 (18) |
| O1—Zn1—O1 ⁱ | 180 | O4—Zn1—N1 | 89.21 (5) |
| O4—Zn1—O1 | 95.05 (5) | N1—Zn1—O1 ⁱ | 87.98 (5) |
| O4 ⁱ —Zn1—O1 | 84.95 (5) | N1 ⁱ —Zn1—N1 | 180 |
| O4—Zn1—O4 ⁱ | 180 | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O4—H4A...N4 ⁱⁱ | 0.79 (3) | 1.97 (3) | 2.750 (2) | 170 (2) |
| O4—H4B...O2 | 0.78 (3) | 2.29 (3) | 2.856 (2) | 130 (2) |

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

The water-bound H atoms were refined without constraint; see Table 2. The remaining H atoms were included in the riding-model approximation, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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