Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

Shakoya Paulin,[a] Pierre Kelly,[a] Kenneth B. Williams,[a] Andrea M. Goforth,[b] Mark D. Smith,[b] LeRoy Peterson Jr[a]* and Hans-Conrad zur Loye[b]

[a]Chemistry Department, Francis Marion University, Florence, South Carolina 29501, USA, and [b]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA

Correspondence e-mail: lpeterson@fmarion.edu

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.082
Data-to-parameter ratio = 13.8

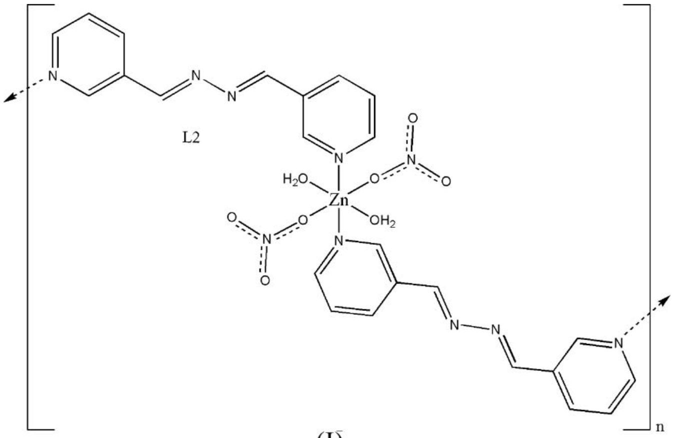
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 November 2006
Accepted 3 January 2007

The polymeric title complex, $[Zn(NO_3)_2(C_{24}H_{20}N_8)(H_2O)_2]_n$, 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.

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 (*L*2) is used to link Zn^{II} centers into one-dimensional chains.



(I)

The crystal structure of (I) is built upon neutral $Zn(L2)_2(OH_2)_2(NO_3)_2$ 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 *L*2 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 *L*2, the two pyridyl rings N1/C1–C5 and N4/C8–C12 are twisted at a dihedral angle of 34.6 (1)°. 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

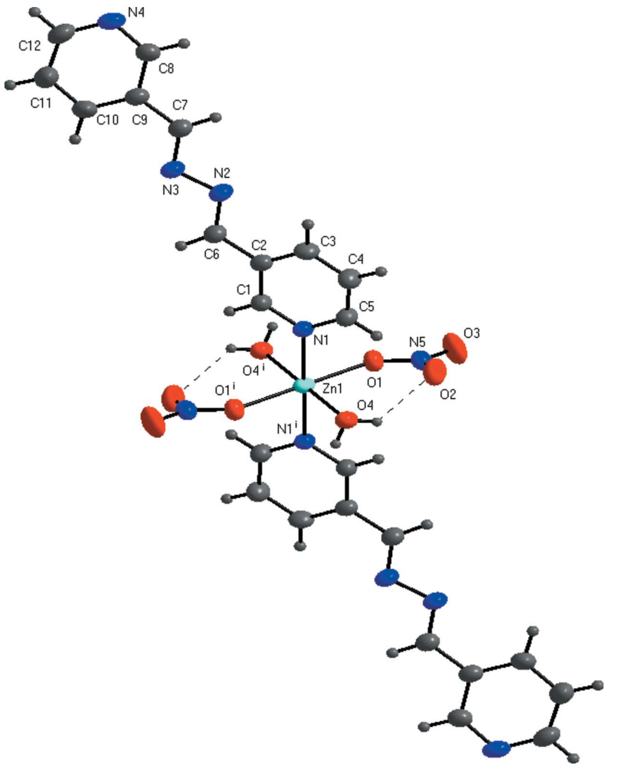


Figure 1
The structure of (I), with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines. [Symmetry code: (i) $1 - x, 1 - y, -z$]

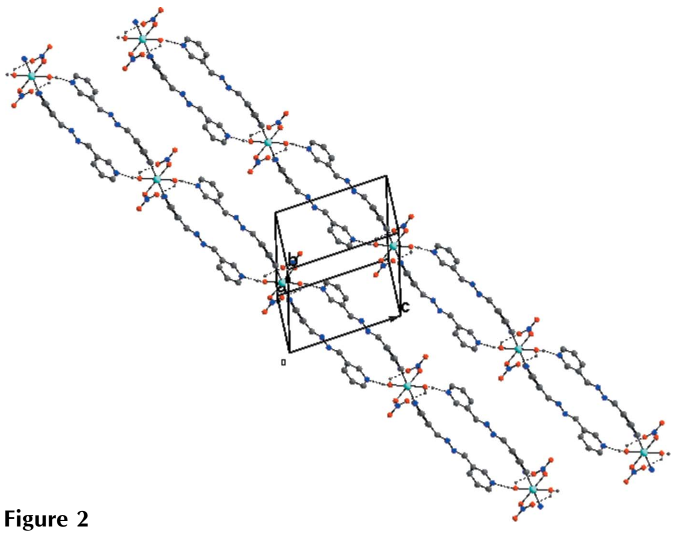


Figure 2
View of the crystal packing in (I) showing the one-dimensional chains. All H atoms except for those of water have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

involved in an intramolecular O4—H4*B*···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 *L*2 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—H4*A*···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 *L*2 ligands. The chains run along the [$11\overline{1}$] 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 *L*2 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 *L*2 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 *L*2 (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 $[Zn^{II}(4,4'\text{-bipyridine})_2(NO_3)_2\cdot CH_2Cl_2]_n$ were obtained at the interface of the two solutions after several weeks.

Crystal data

$[Zn(NO_3)_2(C_{24}H_{20}N_8)(H_2O)_2]$
$M_r = 645.90$
Triclinic, $P\overline{1}$
$a = 7.8267$ (11) Å
$b = 8.5320$ (11) Å
$c = 11.7409$ (16) Å
$\alpha = 81.113$ (2)°
$\beta = 73.696$ (2)°
$\gamma = 66.468$ (2)°
$V = 689.12$ (16) Å^3
$Z = 1$
$D_x = 1.556$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.96$ mm^{-1}
$T = 150$ (1) K
Irregular fragment, yellow
0.40 × 0.26 × 0.14 mm

Data collection

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

Refinement

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

Acta Cryst. (2007). E**63**, m420–m422 Paulin *et al.* • $[Zn(NO_3)_2(C_{24}H_{20}N_8)(H_2O)_2]$ **m421**

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O4—H4A\cdots N4^{ii}$	0.79 (3)	1.97 (3)	2.750 (2)	170 (2)
$O4—H4B\cdots O2$	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 $U_{iso}(H) = 1.2U_{eq}(C)$.

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*.

Financial support from the National Science Foundation, awards CHE-0314164 and CHE-0315152, is gratefully acknowledged.

References

Brandenburg, K. (2005). *Diamond.* Version 3.0e. Crystal Impact GbR, Bonn, Germany.

Bruker (2001). *SMART* (Version 5.625), *SAINT-Plus* (Version 6.22) and *SADABS* (Version 2.05). Bruker AXS Inc., Madison, Wisconsin, USA.

Chin, C., Suslick, K. S. & Kenneth, S. (1993). *Coord. Chem. Rev.* **128**, 293–322.

Davis, H., Peterson, L. Jr, Goforth, A. M., Smith, M. D., Zhang, P. & zur Loye, H.-C. (2004). *J. Chem. Crystallogr.* **34**, 299–306.

Dong, Y.-B., Smith, M. D., Layland, R. C. & zur Loye, H.-C. (2000). *Chem. Mater.* **12**, 1156–1161.

Dong, Y.-B., Smith, M. D. & zur Loye, H.-C. (2000*a*). *Inorg. Chem.* **39**, 4927–4935.

Dong, Y.-B., Smith, M. D. & zur Loye, H.-C. (2000*b*). *J. Solid State Chem.* **155**, 143–153.

Janiak, C. (2003). *Dalton Trans.* pp. 2781–2804.

Khalil, S., Peterson, L. Jr, Goforth, A. M., Hansen, T. J., Smith, M. D. & zur Loye, H.-C. (2005). *J. Chem. Crystallogr.* **35**, 405–411.

Kitagawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.

Perkins, W. J., Maxwell, T., Goforth, A. M., Smith, M. D., Peterson, L. R. Jr & zur Loye, H.-C. (2005). *Acta Cryst.* E**61**, m2047–m2049.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.

m422 Paulin *et al.* • $[Zn(NO_3)_2(C_{24}H_{20}N_8)(H_2O)_2]$ *Acta Cryst.* (2007). E**63**, m420–m422