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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.028

wR factor = 0.077

Data-to-parameter ratio = 13.4

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Triaqua(pyridine-2,5-dicarboxylato- $\kappa^2\text{N},\text{O}^2$)-
[4,4,5,5-tetramethyl-2-(4-pyridyl)imidazoline-
1-oxyl- κN^2]zinc(II)

The title compound, $[\text{Zn}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_{12}\text{H}_{16}\text{N}_3\text{O})(\text{H}_2\text{O})_3]$, was prepared from the imino nitroxide radical ligand 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, zinc(II) perchlorate and potassium pyridine-2,5-dicarboxylate. The Zn^{II} ion exists in a distorted octahedral coordination geometry with one pyridyl N atom from a radical ligand, one N and one O atom from a bidentate pyridine-2,5-dicarboxylate ligand and three O atoms from water molecules. A two-dimensional network is formed through $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions.

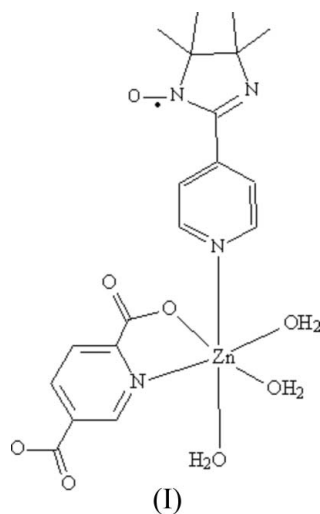
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Comment

In the preparation of molecular magnetic materials, transition metal complexes with organic nitroxide radical ligands have attracted widespread interest in recent years (Caneschi *et al.*, 1991, 1989). Nitroxide radicals are especially attractive due to their coordination ability and their ability to build crystal structures in the form of one-dimensional chains, or two- and three-dimensional networks. The pyridine-2,5-dicarboxylic acid ligand, which possesses diverse functional groups and can give various possibilities to form bridging coordination and hydrogen bonds, is very interesting and has good potential for self-assembly (Liang *et al.*, 2001; Zarracino *et al.*, 2004).



In the title complex, (I), the Zn^{II} ion adopts a distorted octahedral coordination geometry with one radical ligand *via* the pyridyl N atom, one bidentate pyridine-2,5-dicarboxylate anion and three water molecules (Fig. 1). The equatorial plane is formed by atoms N4 and O4 of the pyridine-2,5-dicarboxylate ligand in a bidentate chelating mode, and two O atoms (O6 and O7) of two water molecules. The pyridyl ring of the pyridine-2,5-dicarboxylate ligand makes an angle of

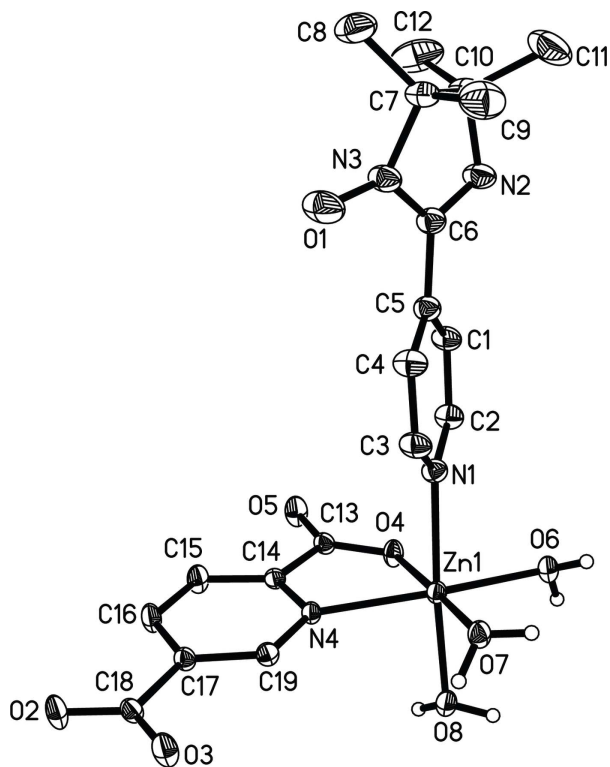


Figure 1
A view of (I), showing displacement ellipsoids drawn at the 30% probability level. H atoms bonded to C atoms have been omitted.

11.7 (5)° with the equatorial plane. The axial sites are occupied by one pyridyl N atom (N1) from the radical ligand and one O atom (O8) of the third water molecule (see Table 1 for selected geometric parameters).

The radical ligand is coordinated as a monodentate ligand through the pyridyl N atom, while the O atom of the oxide group remains uncoordinated. The nitroxide group (O1/N3/C6/N2), as expected, is essentially planar, indicating the easy delocalization of the free electron within this group. However, it forms a dihedral angle of 33.3 (4)° with the pyridyl ring plane. The shortest intermolecular contact between nitroxide groups is 3.825 (8) Å.

In the crystal structure, there are extensive intermolecular hydrogen-bond interactions between pyridine-2,5-dicarboxylate ligands and coordinated water molecules (Table 2), from which a two-dimensional double-layered network parallel to (011) is formed (Fig. 2).

Experimental

The title compound was prepared by adding an aqueous solution (5 ml) of potassium pyridine-2,5-dicarboxylate (0.1 mmol) to a methanol solution (15 ml) of zinc(II) perchlorate (0.1 mmol) and 2-(4'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (0.1 mmol). The mixture was stirred for 2 h and then filtered. The filtrate was evaporated slowly at room temperature, and red block-shaped crystals suitable for X-ray analysis were obtained. Analysis, calculated for $C_{19}H_{25}N_4O_8Zn$: C 45.35, H 4.97, N 11.14%; found: C 45.66, H 4.06, N 11.37%.

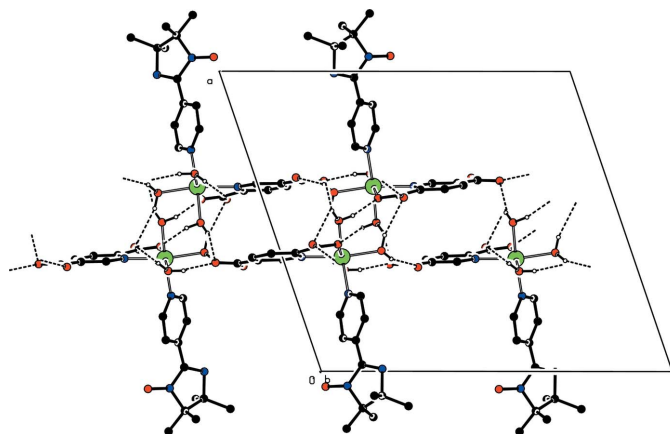


Figure 2
A partial packing diagram of (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines. Colour code: green Zn, red O, blue N and black C.

Crystal data

$[Zn(C_7H_3NO_4)(C_{12}H_{16}N_3O)(H_2O)_3]$
 $M_r = 502.80$
 Monoclinic, $P2_1/c$
 $a = 16.978$ (6) Å
 $b = 7.355$ (3) Å
 $c = 18.812$ (7) Å
 $\beta = 108.867$ (5)°
 $V = 2222.9$ (14) Å³
 $Z = 4$

$D_x = 1.502$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3163 reflections
 $\theta = 2.3$ – 25.2 °
 $\mu = 1.16$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 0.26 × 0.24 × 0.18 mm

Data collection

Bruker APEX-II CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.651$, $T_{max} = 0.810$
 11537 measured reflections

3931 independent reflections
 3205 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$
 $\theta_{max} = 25.0$ °
 $h = -18 \rightarrow 20$
 $k = -8 \rightarrow 7$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.077$
 $S = 1.06$
 3931 reflections
 293 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.57P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.43$ e Å⁻³
 $\Delta\rho_{min} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—O7	2.0634 (16)	Zn1—N1	2.1699 (19)
Zn1—O4	2.0765 (16)	Zn1—N4	2.1904 (18)
Zn1—O8	2.0782 (16)	O1—N3	1.268 (2)
Zn1—O6	2.1440 (16)		
O7—Zn1—O4	177.63 (5)	O8—Zn1—N1	175.44 (6)
O7—Zn1—O8	89.04 (6)	O6—Zn1—N1	87.12 (6)
O4—Zn1—O8	91.74 (7)	O7—Zn1—N4	100.89 (6)
O7—Zn1—O6	94.23 (5)	O4—Zn1—N4	76.91 (6)
O4—Zn1—O6	88.03 (5)	O8—Zn1—N4	87.89 (6)
O8—Zn1—O6	88.40 (6)	O6—Zn1—N4	164.36 (6)
O7—Zn1—N1	92.16 (7)	N1—Zn1—N4	96.20 (6)
O4—Zn1—N1	87.23 (7)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6A \cdots O3 ⁱ	0.85	1.88	2.697 (3)	160
O6—H6B \cdots O5 ⁱⁱ	0.85	2.28	3.097 (3)	161
O7—H7A \cdots O2 ⁱ	0.85	1.87	2.700 (2)	167
O7—H7B \cdots O5 ⁱⁱⁱ	0.85	1.94	2.790 (3)	178
O8—H8A \cdots O4 ⁱⁱ	0.85	1.79	2.629 (2)	167
O8—H8B \cdots O2 ^{iv}	0.85	1.92	2.728 (3)	159

Symmetry codes: (i) $x, -y - \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z$.

H atoms were placed in calculated positions, with C—H = 0.93–0.96 Å and O—H = 0.85 Å, and were allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ or $1.5U_{\text{eq}}(\text{O or methyl C atoms})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); 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, 1998) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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