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(Acetonitrile-κN){2-[bis(2-pyridylethyl)amino]ethanol-$\kappa^4 N,N',N'',O$}zinc(II) bis(perchlorate) monohydrate

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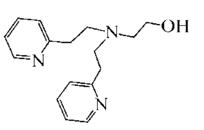
In the title compound, $[Zn(C_2H_3N)(C_{16}H_{21}N_3O)](ClO_4)_2\cdot H_2O$, the Zn^{II} ion is coordinated by two pyridyl N atoms, one amine N atom, and an ethanol O atom from the *N*,*N*′,*N*″,*O*-tetradentate 2-[bis(2-pyridylethyl)amino]ethanol donor ligand. The fifth coordination site is filled by an acetonitrile N atom, and there is one solvent water molecule in the asymmetric unit. The 2+ charge of the cationic portion of the complex is balanced by two perchlorate counter-anions.

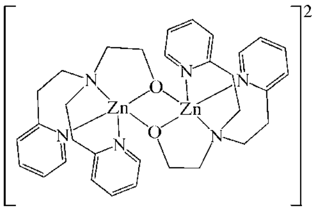
Comment

Zinc complexes of multidentate N-donor ligands with pendant alcohol or alkoxide O-donors have been useful for modelling alkaline phosphatase, a Zn^{II}-containing phosphomonoesterase that catalyzes the hydrolysis of phosphate monoesters at high pH (Kimura *et al.*, 1994). Recently, we reported the crystal structure of a new Zn^{II} complex containing the 2-[bis(2-pyridylethyl)amino]ethanol ligand, (I), in which the ethanol group was deprotonated upon coordinating to a Zn^{II} centre to form a bridging alkoxide ligand in a dimeric Zn^{II} structure, (II), in the solid state (Zhang & Liang, 2004). The previous crystal structure was obtained by crystallizing the complex in an aqueous solution. We report here on a crystal structure of a similar complex, (III), crystallized from acetonitrile, in which the monomeric Zn^{II} complex of the ligand 2-[bis(2-pyridylethyl)amino]ethanol is obtained and the ethanol H atom remains bound to the O atom of the ethanol unit.

As shown in Fig. 1, complex (III) has five donor atoms coordinated to the Zn^{II} centre. The calculated τ value for the Zn^{II} centre in (III) is 0.23, which shows that it is closer to square-pyramidal geometry [N2—Zn1—N4 = 159.35 (6)° and N1—Zn1—O1 = 145.36 (6)°; $\tau = 0$ correlates to perfect square-pyramidal geometry and $\tau = 1$ correlates to perfect trigonal–bipyramidal geometry (Addison *et al.*, 1984)]. The structure of (III) can be viewed as having atoms N1, N2, N4, O1 and Zn1 as the basal atoms and N3 in the apical position of a pseudo-square-pyramidal complex.



(I)



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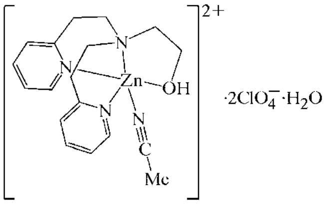

(III)

The Zn–ligand bond lengths in (III) (Table 1) are similar to those found in analogous Zn^{II} complexes. For example, the $Zn—N_{py}$ bond lengths (py is pyridine) of 2.0418 (15) Å (Zn1—N1) and 2.0498 (14) Å (Zn1—N3) are similar to the analogous $Zn—N_{py}$ bond lengths in (II) [2.049 (4) and 2.068 (4) Å; Zhang & Liang (2004)]. However, the amine N2—Zn1 bond of 2.1336 (14) Å in (III) is shorter than that found in the dimeric complex [2.231 (4) Å]. The longer $Zn—N_{amine}$ bond in (II) can be explained by the fact that the Zn^{II} centre in (II) adopts a more trigonal–pyramidal shape than in (III), with a τ value of 0.46. Because the amine atom N3 of (II) can be considered as more of an axial ligand in a trigonal–bipyramidal geometry than the analogous amine atom N2 in (III), the $Zn—N_{amine}$ bond in (II) is expected to be longer. Comparison of the Zn—O bonds in complexes (II) and (III) also reveals differences in bond lengths [1.959 (3) Å in (II) and 2.0552 (14) Å in (III)]. This observed lengthening of the

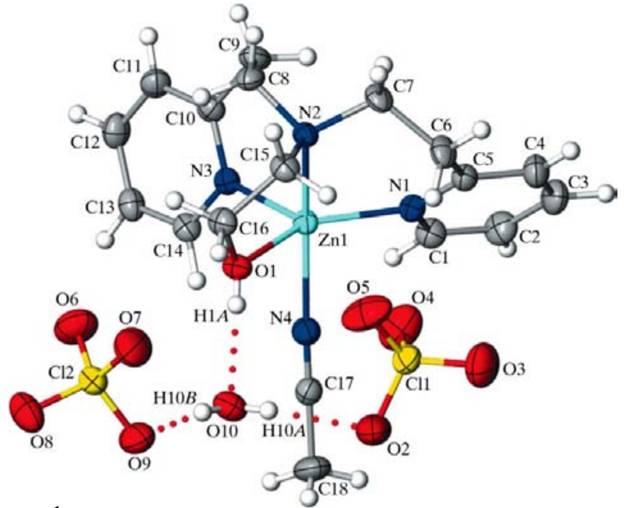

Figure 1
The molecular structure of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dotted lines denote possible hydrogen-bond interactions.

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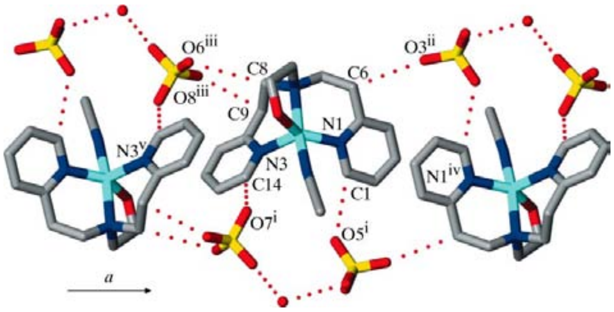

Figure 2
A view of the molecular packing of (III), projected perpendicular to the *a* axis, showing the hydrogen-bond network (dotted lines denote possible hydrogen-bond interactions). H atoms have been omitted for clarity. [Symmetry codes: (i) $x, y - 1, z$; (ii) $2 - x, 2 - y, 2 - z$; (iii) $1 - x, 2 - y, 2 - z$; (iv) $2 - x, 1 - y, 2 - z$; (v) $1 - x, 1 - y, 2 - z$.]

Zn—O bond in (III) is consistent with a Zn^{II} metal centre bonded to a neutral ethanol O-atom donor, whereas the intramolecular Zn—O bond in (II) involves a monoanionic alkoxide O-atom donor. Several previous studies have shown that Zn^{II}–alcohol complexes with neutral coordinating O-atom donors have Zn—O bonds longer than 2 Å (Follner, 1972; Lutz & Bakker, 2003; Iranzo *et al.*, 2003), while Zn^{II}–alkoxide compounds typically exhibit Zn—O bonds shorter than 2 Å (Kimura *et al.*, 1994; Hahn *et al.*, 2003; Davies *et al.*, 1998).

Inspection of the asymmetric unit of (III) (Fig. 1) reveals one complex cation, one uncoordinated water molecule and two perchlorate anions. The ethanol OH group of (III) forms an intermolecular O1—H1*A*···O10 hydrogen bond with a water molecule, which further links two adjacent perchlorate anions *via* O10—H10*A*(H10*B*)···O2(O9) close contacts (Table 2). As can be seen in Fig. 2, the organization of this motif is influenced by a complex blend of weak C—H···perchlorate interactions that extend along the *a* axis. Although a structural feature of this organization is inversion-related face-to-face stacking of pyridyl fragments, only the pyridyl (N3) moiety adopts a favourable geometry for π–π stacking [interplanar distance = 3.434 (3) Å and centroid–centroid distance = 3.862 (3) Å].

Experimental

Caution! Although no problems were encountered in this work, metal perchlorate complexes are potentially explosive and should be handled with proper precautions and in small amounts.

Complex (III) was synthesized by treating the ligand (I) (0.030 g, 0.11 mmol) with 1 equivalent of $Zn(ClO_4)_2·6H_2O$ (0.041 g, 0.11 mmol) in CH_3CN (10 ml) with stirring for 1 h at room temperature. Diethyl ether (25 ml) was then layered on the light-yellow acetonitrile solution and the mixture was set aside for crystallization. After 4 d, colourless crystals of (III) had formed (0.037 g, 0.058 mmol, 53% yield). A single crystal from this procedure was used for X-ray analysis. ^{1}H NMR (500 MHz, CD_3CN): δ 8.55 (*d*, py-6H), 8.19 (*t*, py-4H), 7.71 (*d*, py-5H), 7.60 (*t*, py-3H), 3.86 (*t*, NCH_2CH_2OZn), 3.28–3.04 (py-CH_2CH_2N), 2.97 (*t*, NCH_2CH_2OZn); ^{13}C NMR (CD_3CN): δ 162.1 (py-2), 149.9 (py-6), 142.1 (py-4), 127.1 (py-3), 124.7 (py-5), 60.7 (NCH_2CH_2OZn), 58.5 (NCH_2CH_2OZn), 54.5 (py-CH_2CH_2N), 33.5 (py-CH_2CH_2N); FT–IR (KBr, ν, cm^{-1}): 3448 (O—H, *str*, *br*), 3073, 2948, 2926, 2871, 2809 (C–H, *str*), 1608, 1571, 1486, 1445 (pyridine ring), 1085, 622 (ClO_4^-). Elemental analysis calculated for $C_{18}H_{26}Cl_2N_4O_{10}Zn$: C 36.35, H 4.41, N 9.42%; found: C 35.98, H 4.67, N 9.05%. MS (ESI): *m/z* 334 ([L^1—H + *M* — CH_3CN]$^+$).

Crystal data

$[Zn(C_2H_3N)(C_{16}H_{21}N_3O)](ClO_4)_2·H_2O$
$M_r = 594.72$
Monoclinic, $P2_1/c$
$a = 17.3792$ (13) Å
$b = 7.8924$ (6) Å
$c = 18.6583$ (14) Å
$\beta = 109.487$ (1)°
$V = 2412.6$ (3) Å^3
$Z = 4$
$D_x = 1.637$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.30$ mm^{-1}
$T = 193$ (2) K
Block, colourless
0.35 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.659$, $T_{max} = 0.881$
16837 measured reflections
5502 independent reflections
4695 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.05$
5502 reflections
409 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 1.2239P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.91$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.0418 (15)	Zn1—N4	2.1273 (16)
Zn1—N3	2.0498 (14)	Zn1—N2	2.1336 (14)
Zn1—O1	2.0552 (14)		
N1—Zn1—N3	115.63 (6)	N1—Zn1—N2	95.93 (6)
N1—Zn1—O1	145.36 (6)	N3—Zn1—N2	98.17 (6)
N3—Zn1—O1	98.96 (6)	O1—Zn1—N2	80.23 (6)
N1—Zn1—N4	90.27 (6)	N4—Zn1—N2	159.35 (6)
N3—Zn1—N4	96.83 (6)	N4—C17—C18	179.7 (3)
O1—Zn1—N4	83.49 (6)		
O1—Zn1—N2—C15	22.41 (11)	N1—Zn1—N2—C7	−3.19 (12)
N3—Zn1—N2—C8	1.24 (13)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O10	0.73 (3)	1.88 (3)	2.602 (2)	170 (3)
O10—H10*A*···O2	0.76 (3)	2.07 (3)	2.836 (3)	175 (3)
O10—H10*B*···O9	0.76 (3)	2.06 (3)	2.809 (3)	172 (3)
C1—H1···O5^{i}	0.94 (2)	2.57 (2)	3.318 (3)	136 (2)
C6—H6*A*···O3^{ii}	0.88 (3)	2.58 (2)	3.293 (3)	139 (2)
C8—H8*A*···O6^{iii}	0.97 (2)	2.79 (2)	3.432 (3)	124 (1)
C9—H9*B*···O8^{iii}	0.87 (2)	2.67 (2)	3.402 (3)	143 (2)
C14—H14···O7^{i}	0.99 (2)	2.42 (2)	3.303 (3)	149 (2)

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

Methyl H atoms were treated as riding, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, and were allowed to rotate freely during refinement using the AFIX 137 command of *SHELXTL* (Bruker, 2000). All other H atoms were located in a difference density map and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2002) and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *X-SEED*; software used to prepare material for publication: *X-SEED* (Barbour, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3036). Services for accessing these data are described at the back of the journal.

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