

Diaquabis(2-oxidopyridinium-3-carboxylate- κ^2O^2,O^3)zinc(II)Huai-Yi Yan^a and Tai-Qiu Hu^{b*}^aDepartment of Chemistry, Xinzhou Teachers' University, Shanxi Xinzhou 034000, People's Republic of China, and ^bDepartment of Chemistry, Shandong Normal University, Jinan 250014, People's Republic of China

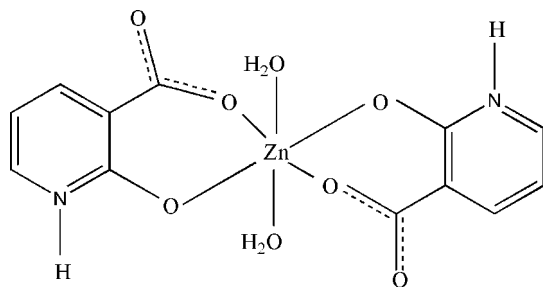
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Received 26 July 2007; accepted 1 August 2007

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.041; wR factor = 0.093; data-to-parameter ratio = 12.8.

In the title mononuclear complex, $[Zn(C_6H_4NO_3)_2(H_2O)_2]$, the six-coordinate Zn^{II} atom adopts an octahedral coordination geometry and is located on an inversion centre. There is a weak $\pi-\pi$ stacking interaction between adjacent pyridyl rings [the separation between the centroids of the pyridyl rings is 3.840 (2) Å and the perpendicular distance is 3.582 Å]. The crystal packing is stabilized by $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds.

Related literature

For a relevant crystal structure, see: Sakai *et al.* (2006).

Experimental

Crystal data

 $[Zn(C_6H_4NO_3)_2(H_2O)_2]$ $M_r = 377.61$ Monoclinic, $P2_1/c$ $a = 7.491$ (3) Å $b = 12.316$ (4) Å $c = 7.621$ (3) Å $\beta = 100.437$ (5)° $V = 691.5$ (4) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 1.82$ mm⁻¹ $T = 298$ (2) K $0.24 \times 0.18 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\min} = 0.669$, $T_{\max} = 0.839$

3479 measured reflections

1352 independent reflections

1069 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.048$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.042$ $wR(F^2) = 0.093$ $S = 1.04$

1352 reflections

106 parameters

3 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.56$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H4\cdots O3^i$	0.86	2.06	2.895 (4)	162
$O4-H5\cdots O1^{ii}$	0.84	1.88	2.711 (3)	170
$O4-H6\cdots O1^{iii}$	0.84	1.98	2.798 (3)	165

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

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2083).

References

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- Sakai, K. I., Imakubo, T., Ichikawa, M. & Taniguchi, Y. (2006). Dalton Trans. pp. 881–883.
- Sheldrick, G. M. (1996). SADABS (Version 2.10). University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E63, m2325 [doi:10.1107/S1600536807037750]

Diaquabis(2-oxidopyridinium-3-carboxylate- κ^2O^2,O^3)zinc(II)

H.-Y. Yan and T.-Q. Hu

Comment

Metal complexes containing N-heterocyclic ligands play a pivotal role in the area of modern coordination chemistry, and it has been reported that complexes containing 3-hydroxypicolinamide ligand display strong fluorescent emission (Sakai *et al.* 2006). The interest in this area prompted us to synthesize the title complex, (I), which crystal structure we report herein.

Fig. 1 shows the asymmetric unit and symmetry-related fragment of (I). The Zn^{II} atom lies at an inversion centre and adopts a slightly distorted octahedral geometry (Table 1). Between neighboring complexes there is a weak π - π stacking interaction, which links adjacent pyridyl rings; the relevant distances are $Cg1 \cdots Cg1^i = 3.840$ (2) Å and $Cg1 \cdots Cg1^i_{\text{perp}} = 3.582$ Å [symmetry codes: (i) $X, 1/2-Y, -1/2+Z$; $Cg1$ is the centroid of pyridyl ring; $Cg1 \cdots Cg1^i_{\text{perp}}$ is the perpendicular distance from ring $Cg1$ to ring $Cg1^i$]. Table 2 and Fig. 2 show the information of O—H \cdots O and N—H \cdots O hydrogen bonds, which consolidate the crystal structure.

Experimental

A diluted sodium hydroxide H₂O solution was added dropwise into 30 ml of a, aqueous solution containing Zn(ClO₄)₂·6H₂O (0.1862 g, 0.500 mmol) and 2-hydroxyl-3-carboxylpyridine (0.1232 g, 1.00 mmol) until the pH value reached 4, and the solution was stirred for another a few minutes. Colorless single crystals were obtained after the mixed solutions were allowed to stand at room temperature for one week.

Refinement

H atoms of water molecule and N—H bond were located in a difference Fourier map and refined as riding in their as-found positions, with O—H = 0.842–0.844 Å, $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$, N—H = 0.86 Å, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$. other H atoms were placed in calculated positions, and refined as riding, with C—H = 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

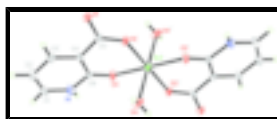


Fig. 1. The coordination structure of (I) showing the atom numbering scheme with thermal ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z$].

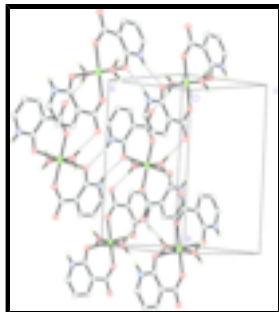


Fig. 2. Unit cell and hydrogen bonds (in broken lines).

Diaquabis(2-oxidopyridinium-3-carboxylate- $\kappa^2 O^2, O^3$)zinc(II)

Crystal data

[Zn(C₆H₄NO₃)₂(H₂O)₂]

$M_r = 377.61$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.491 (3) \text{ \AA}$

$b = 12.316 (4) \text{ \AA}$

$c = 7.621 (3) \text{ \AA}$

$\beta = 100.437 (5)^\circ$

$V = 691.5 (4) \text{ \AA}^3$

$Z = 2$

$F_{000} = 384$

$D_x = 1.814 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 899 reflections

$\theta = 2.8\text{--}23.7^\circ$

$\mu = 1.82 \text{ mm}^{-1}$

$T = 298 (2) \text{ K}$

Block, colourless

$0.24 \times 0.18 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298(2) \text{ K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.669$, $T_{\max} = 0.839$

3479 measured reflections

1352 independent reflections

1069 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 2.8^\circ$

$h = -9 \rightarrow 7$

$k = -15 \rightarrow 15$

$l = -9 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.093$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.1015P]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.04$	$(\Delta/\sigma)_{\max} < 0.001$
1352 reflections	$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$
106 parameters	$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.5000	0.0000	0.02360 (19)
O3	0.7719 (3)	0.45670 (17)	-0.0125 (3)	0.0286 (6)
O2	0.4399 (3)	0.34197 (17)	-0.0143 (3)	0.0292 (6)
N1	1.0205 (4)	0.3608 (2)	0.1060 (4)	0.0311 (7)
H4	1.0815	0.4196	0.1018	0.037*
O1	0.4702 (3)	0.16478 (17)	-0.0133 (3)	0.0311 (6)
O4	0.5772 (4)	0.49450 (16)	0.2831 (3)	0.0380 (7)
H6	0.5680	0.5530	0.3379	0.057*
H5	0.5382	0.4413	0.3350	0.057*
C5	0.5381 (4)	0.2586 (3)	0.0077 (4)	0.0228 (8)
C4	0.7405 (5)	0.2668 (2)	0.0606 (4)	0.0223 (7)
C3	0.8381 (5)	0.1755 (3)	0.1208 (5)	0.0314 (8)
H1	0.7760	0.1103	0.1241	0.038*
C6	0.8375 (4)	0.3666 (2)	0.0498 (4)	0.0227 (7)
C1	1.1143 (5)	0.2713 (3)	0.1673 (5)	0.0364 (9)
H3	1.2396	0.2746	0.2030	0.044*
C2	1.0253 (5)	0.1758 (3)	0.1770 (5)	0.0394 (10)
H2	1.0874	0.1130	0.2197	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0219 (3)	0.0139 (3)	0.0354 (4)	-0.0001 (2)	0.0063 (2)	0.0005 (2)
O3	0.0201 (12)	0.0185 (12)	0.0485 (16)	0.0002 (10)	0.0099 (11)	0.0047 (11)
O2	0.0235 (13)	0.0132 (12)	0.0500 (17)	-0.0005 (9)	0.0040 (11)	-0.0004 (10)
N1	0.0239 (17)	0.0284 (16)	0.041 (2)	-0.0038 (12)	0.0047 (13)	0.0047 (13)

supplementary materials

O1	0.0294 (15)	0.0143 (12)	0.0481 (17)	-0.0043 (9)	0.0030 (12)	-0.0012 (10)
O4	0.0605 (19)	0.0224 (13)	0.0321 (15)	-0.0024 (12)	0.0107 (13)	-0.0018 (11)
C5	0.025 (2)	0.0215 (18)	0.0217 (18)	0.0005 (13)	0.0047 (15)	0.0018 (13)
C4	0.0251 (18)	0.0194 (16)	0.0229 (18)	0.0008 (14)	0.0057 (14)	0.0011 (13)
C3	0.034 (2)	0.0257 (19)	0.035 (2)	0.0005 (15)	0.0062 (16)	0.0052 (15)
C6	0.0184 (17)	0.0271 (18)	0.0235 (18)	0.0024 (13)	0.0059 (14)	-0.0004 (14)
C1	0.0199 (19)	0.047 (2)	0.042 (2)	0.0052 (16)	0.0042 (16)	0.0102 (18)
C2	0.032 (2)	0.036 (2)	0.049 (3)	0.0134 (17)	0.0055 (18)	0.0166 (17)

Geometric parameters (Å, °)

Zn1—O2	1.996 (2)	O1—C5	1.261 (4)
Zn1—O2 ⁱ	1.996 (2)	O4—H6	0.8415
Zn1—O3 ⁱ	2.124 (2)	O4—H5	0.8440
Zn1—O3	2.124 (2)	C5—C4	1.500 (4)
Zn1—O4	2.131 (3)	C4—C3	1.374 (4)
Zn1—O4 ⁱ	2.131 (3)	C4—C6	1.438 (4)
O3—C6	1.270 (4)	C3—C2	1.390 (5)
O2—C5	1.256 (4)	C3—H1	0.9300
N1—C1	1.345 (4)	C1—C2	1.361 (5)
N1—C6	1.362 (4)	C1—H3	0.9300
N1—H4	0.8600	C2—H2	0.9300
O2—Zn1—O2 ⁱ	180.0	Zn1—O4—H5	116.4
O2—Zn1—O3 ⁱ	92.22 (9)	H6—O4—H5	111.5
O2 ⁱ —Zn1—O3 ⁱ	87.78 (9)	O2—C5—O1	121.3 (3)
O2—Zn1—O3	87.78 (9)	O2—C5—C4	121.3 (3)
O2 ⁱ —Zn1—O3	92.22 (9)	O1—C5—C4	117.4 (3)
O3 ⁱ —Zn1—O3	180.00 (13)	C3—C4—C6	118.4 (3)
O2—Zn1—O4	92.38 (8)	C3—C4—C5	119.1 (3)
O2 ⁱ —Zn1—O4	87.62 (8)	C6—C4—C5	122.6 (3)
O3 ⁱ —Zn1—O4	92.82 (9)	C4—C3—C2	123.1 (3)
O3—Zn1—O4	87.18 (9)	C4—C3—H1	118.4
O2—Zn1—O4 ⁱ	87.62 (8)	C2—C3—H1	118.4
O2 ⁱ —Zn1—O4 ⁱ	92.38 (8)	O3—C6—N1	117.6 (3)
O3 ⁱ —Zn1—O4 ⁱ	87.18 (9)	O3—C6—C4	127.1 (3)
O3—Zn1—O4 ⁱ	92.82 (9)	N1—C6—C4	115.3 (3)
O4—Zn1—O4 ⁱ	180.0	N1—C1—C2	119.8 (3)
C6—O3—Zn1	120.79 (19)	N1—C1—H3	120.1
C5—O2—Zn1	132.0 (2)	C2—C1—H3	120.1
C1—N1—C6	125.8 (3)	C1—C2—C3	117.6 (3)
C1—N1—H4	117.1	C1—C2—H2	121.2
C6—N1—H4	117.1	C3—C2—H2	121.2
Zn1—O4—H6	116.3		
O2—Zn1—O3—C6	-30.0 (2)	C6—C4—C3—C2	2.1 (5)
O2 ⁱ —Zn1—O3—C6	150.0 (2)	C5—C4—C3—C2	-178.3 (3)

O4—Zn1—O3—C6	62.5 (2)	Zn1—O3—C6—N1	-153.4 (2)
O4 ⁱ —Zn1—O3—C6	-117.5 (2)	Zn1—O3—C6—C4	29.8 (4)
O3 ⁱ —Zn1—O2—C5	-164.5 (3)	C1—N1—C6—O3	-176.6 (3)
O3—Zn1—O2—C5	15.5 (3)	C1—N1—C6—C4	0.6 (5)
O4—Zn1—O2—C5	-71.6 (3)	C3—C4—C6—O3	175.3 (3)
O4 ⁱ —Zn1—O2—C5	108.4 (3)	C5—C4—C6—O3	-4.3 (5)
Zn1—O2—C5—O1	-177.9 (2)	C3—C4—C6—N1	-1.6 (4)
Zn1—O2—C5—C4	2.3 (4)	C5—C4—C6—N1	178.8 (3)
O2—C5—C4—C3	165.9 (3)	C6—N1—C1—C2	0.0 (6)
O1—C5—C4—C3	-13.9 (4)	N1—C1—C2—C3	0.4 (6)
O2—C5—C4—C6	-14.5 (5)	C4—C3—C2—C1	-1.5 (6)
O1—C5—C4—C6	165.6 (3)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H4 \cdots O3 ⁱⁱ	0.86	2.06	2.895 (4)	162
O4—H5 \cdots O1 ⁱⁱⁱ	0.84	1.88	2.711 (3)	170
O4—H6 \cdots O1 ^{iv}	0.84	1.98	2.798 (3)	165

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

Fig. 1

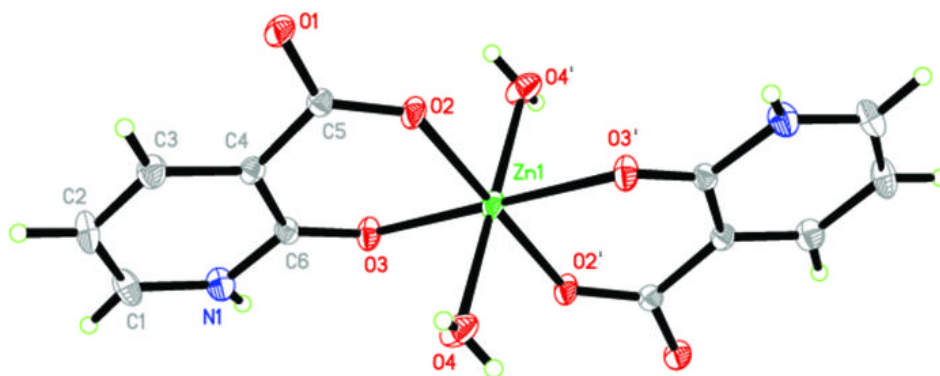


Fig. 2

