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Bis(3-hydroxypyridine-κN)bis(3-nitrobenzoato-κO)zinc(II)

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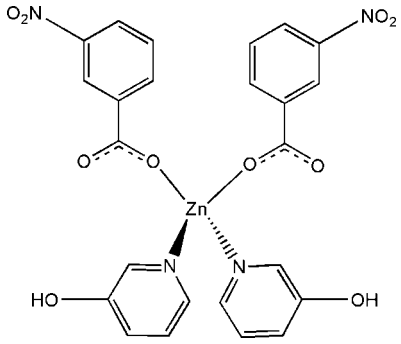
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.080; data-to-parameter ratio = 12.3.

The title complex, $[Zn(C_7H_4NO_4)_2(C_5H_5NO)_2]$, has site symmetry 2. The Zn^{II} ion is located on a crystallographic twofold rotation axis and assumes a distorted tetrahedral ZnN_2O_2 coordination geometry. Molecules are linked by an intermolecular O—H···O hydrogen bond and π–π stacking interactions between pyridine rings [centroid–centroid speparation 3.594 (1) Å].

Related literature

For general background, see: Su & Xu (2004); Xu *et al.* (2007). For a related structure, see: Yan *et al.* (2008).



Experimental

Crystal data

$[Zn(C_7H_4NO_4)_2(C_5H_5NO)_2]$
M_r = 587.79
Monoclinic, $C2/c$
a = 22.992 (4) Å
b = 7.2412 (12) Å
c = 15.797 (3) Å
β = 111.584 (5)°
V = 2445.6 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 294 K
0.33 × 0.30 × 0.24 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.655, T_{max} = 0.770
10172 measured reflections
2179 independent reflections
2038 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.080
S = 1.18
2179 reflections
177 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn—N1	2.0486 (16)	Zn—O2	1.9527 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O3^{i}	0.91	1.73	2.642 (2)	174

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The work was supported by the ZIJIN project of Zhejiang University, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2223).

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supporting information

Acta Cryst. (2009). E**65**, m927 [doi:10.1107/S1600536809027147]

Bis(3-hydroxypyridine-κN)bis(3-nitrobenzoato-κO)zinc(II)

Jun-Hua Li, Jing-Jing Nie and Duan-Jun Xu

S1. Comment

As part of our ongoing investigation on the nature of π–π stacking (Su & Xu, 2004; Xu *et al.*, 2007), the title complex with pyridine ligand has recently been prepared in the laboratory, and its crystal structure is reported here.

The molecule has site symmetry 2, the Zn^{II} cation located on a twofold axis is coordinated by two hydroxypyridine ligands and two nitrobenzoate anions with a distorted tetrahedral geometry (Fig. 1 and Table 1). The O—Zn—O bond angle of 120.90 (9)° is much larger than the N—Zn—N bond angle of 101.72 (6)°. The partially overlapped arrangement of parallel pyridine rings is observed in the crystal structure (Fig. 2), the face-to-face separation of 3.594 (1) Å between N1-pyridine and $N1^{ii}$-pyridine rings [symmetry code: (ii) 1 - *x*, 1 - *y*, -*z*] suggests the existence of π–π stacking between the parallel pyridine rings, similar to the situation found in *catena*-[(μ_2-3,5-dinitro-2-oxybenzoato)(μ_2-3-hydroxy-pyridine)- copper(II)] (Yan *et al.*, 2008). Intermolecular O—H···O hydrogen bond between hydroxyl and carboxyl groups is also present in the crystal structure (Table 2).

S2. Experimental

A water–ethanol solution (20 ml, 1:1) of 3-nitrobenzoic acid (0.17 g, 1 mmol), sodium carbonate (0.075 g, 0.7 mmol), 3-hydroxypyridine (0.19 g, 2 mmol) and zinc chloride (0.067 g, 0.5 mmol) was refluxed for 6 h. After cooling to room temperature the solution was filtered. The single crystals of the title compound were obtained from the filtrate after 4 d.

S3. Refinement

Hydroxy H atom was located in a difference Fourier map and was refined as riding in as-found relative position, U_{iso}(H) = 1.5U_{eq}(O). Aromatic H atoms were placed in calculated positions with C—H = 0.93 Å and were refined in riding mode with U_{iso}(H) = 1.2U_{eq}(C).

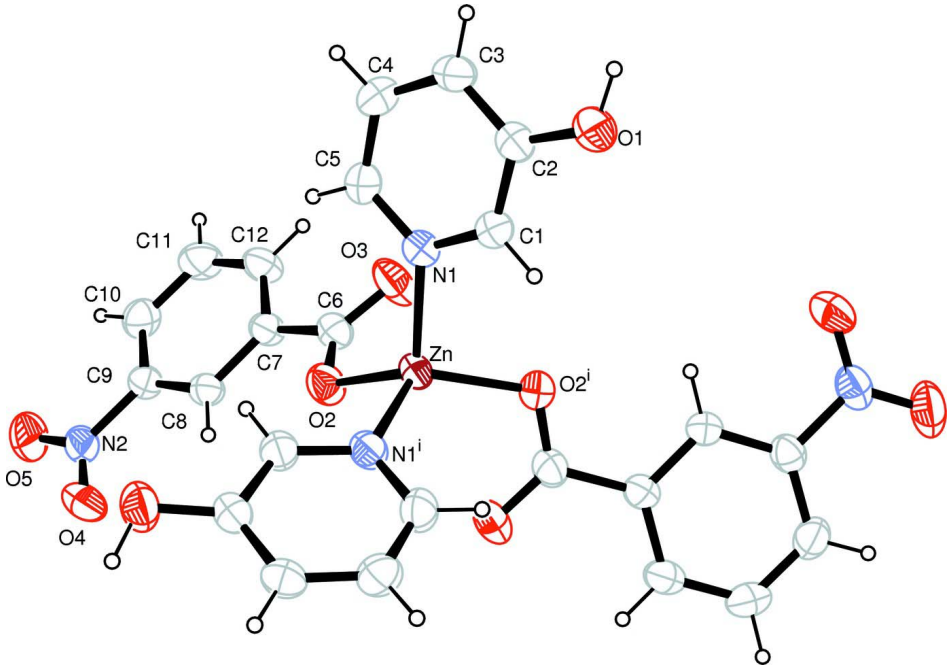

Figure 1

The molecular structure of the title compound with 40% probability displacement (arbitrary spheres for H atoms) [symmetry code: (i) 1 - *x*, *y*, -*z* + 1/2].

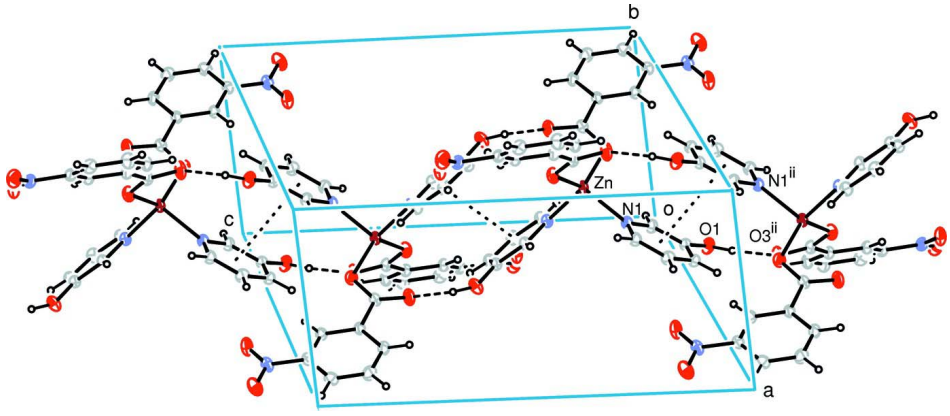

Figure 2

The unit cell packing diagram of the title compound showing π–π stacking between pyridine rings. Dashed and dotted lines indicate hydrogen bonding and π–π stacking, respectively [symmetry code: (ii) 1 - *x*, 1 - *y*, -*z*].

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Crystal data

$[Zn(C_7H_4NO_4)_2(C_5H_5NO)_2]$
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Hall symbol: -C 2yc
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$b = 7.2412$ (12) Å
$c = 15.797$ (3) Å
$\beta = 111.584$ (5)°
$V = 2445.6$ (8) Å^3
$Z = 4$
$F(000) = 1200$
$D_x = 1.596$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2092 reflections

θ = 2.0–25.0°
μ = 1.07 mm^{-1}
T = 294 K

Block, colourless
0.33 × 0.30 × 0.24 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.655, T_{max} = 0.770

10172 measured reflections
2179 independent reflections
2038 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25.2°, θ_{min} = 1.9°
h = −27→27
k = −7→8
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.080
S = 1.18
2179 reflections
177 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 1.01P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Zn	0.5000	0.60825 (4)	0.2500	0.03308 (13)
N1	0.51519 (7)	0.4295 (2)	0.15973 (11)	0.0353 (4)
N2	0.76573 (8)	0.9962 (2)	0.57621 (11)	0.0428 (4)
O1	0.41195 (6)	0.2005 (2)	−0.04113 (10)	0.0502 (4)
H1A	0.4151	0.1741	−0.0959	0.075*
O2	0.57415 (6)	0.7413 (2)	0.32834 (9)	0.0430 (3)
O3	0.57500 (8)	0.8529 (3)	0.19867 (10)	0.0582 (4)
O4	0.73267 (8)	0.9305 (3)	0.61402 (11)	0.0597 (4)
O5	0.81810 (8)	1.0587 (3)	0.61763 (12)	0.0639 (5)
C1	0.46440 (9)	0.3618 (3)	0.09435 (13)	0.0376 (4)
H1	0.4256	0.3830	0.0983	0.045*
C2	0.46675 (9)	0.2612 (3)	0.02073 (12)	0.0360 (4)
C3	0.52475 (9)	0.2297 (3)	0.01547 (13)	0.0386 (4)

H3	0.5283	0.1659	−0.0335	0.046*
C4	0.57718 (9)	0.2956 (3)	0.08477 (14)	0.0442 (5)
H4	0.6166	0.2729	0.0834	0.053*
C5	0.57162 (9)	0.3943 (3)	0.15562 (14)	0.0402 (5)
H5	0.6075	0.4377	0.2016	0.048*
C6	0.59870 (9)	0.8367 (3)	0.28242 (13)	0.0376 (4)
C7	0.66049 (9)	0.9261 (3)	0.33534 (13)	0.0341 (4)
C8	0.68297 (9)	0.9269 (3)	0.43004 (13)	0.0341 (4)
H8	0.6590	0.8799	0.4613	0.041*
C9	0.74167 (9)	0.9988 (3)	0.47648 (12)	0.0355 (4)
C10	0.77887 (9)	1.0701 (3)	0.43250 (15)	0.0434 (5)
H10	0.8185	1.1168	0.4654	0.052*
C11	0.75552 (11)	1.0701 (3)	0.33837 (16)	0.0491 (5)
H11	0.7795	1.1182	0.3073	0.059*
C12	0.69704 (10)	0.9994 (3)	0.29032 (14)	0.0426 (5)
H12	0.6818	1.0006	0.2270	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.03108 (18)	0.0418 (2)	0.02401 (18)	0.000	0.00732 (12)	0.000
N1	0.0354 (8)	0.0405 (9)	0.0294 (8)	0.0019 (7)	0.0112 (7)	−0.0008 (6)
N2	0.0417 (9)	0.0484 (11)	0.0331 (9)	0.0088 (8)	0.0074 (8)	−0.0057 (7)
O1	0.0417 (8)	0.0636 (10)	0.0403 (8)	−0.0044 (7)	0.0091 (6)	−0.0163 (7)
O2	0.0361 (7)	0.0557 (9)	0.0345 (7)	−0.0105 (6)	0.0097 (6)	−0.0003 (6)
O3	0.0593 (10)	0.0789 (11)	0.0279 (8)	−0.0163 (8)	0.0061 (7)	−0.0030 (7)
O4	0.0613 (10)	0.0864 (13)	0.0321 (8)	0.0003 (9)	0.0181 (8)	−0.0025 (8)
O5	0.0444 (9)	0.0838 (12)	0.0466 (9)	−0.0016 (8)	−0.0031 (7)	−0.0135 (9)
C1	0.0326 (9)	0.0459 (11)	0.0346 (10)	0.0012 (8)	0.0128 (8)	−0.0037 (8)
C2	0.0387 (10)	0.0363 (10)	0.0311 (9)	−0.0001 (8)	0.0107 (8)	−0.0001 (8)
C3	0.0471 (11)	0.0372 (10)	0.0358 (10)	0.0031 (8)	0.0201 (9)	−0.0017 (8)
C4	0.0369 (10)	0.0519 (13)	0.0477 (12)	0.0064 (9)	0.0203 (9)	−0.0001 (10)
C5	0.0323 (9)	0.0470 (12)	0.0376 (11)	0.0017 (8)	0.0086 (8)	−0.0014 (8)
C6	0.0374 (10)	0.0423 (11)	0.0313 (10)	−0.0018 (8)	0.0106 (8)	−0.0048 (8)
C7	0.0366 (10)	0.0374 (10)	0.0292 (9)	−0.0012 (8)	0.0131 (8)	−0.0014 (7)
C8	0.0339 (9)	0.0399 (10)	0.0310 (10)	−0.0013 (8)	0.0148 (8)	−0.0011 (7)
C9	0.0359 (9)	0.0382 (10)	0.0310 (10)	0.0033 (8)	0.0106 (8)	−0.0036 (8)
C10	0.0329 (10)	0.0482 (12)	0.0478 (12)	−0.0067 (9)	0.0133 (9)	−0.0054 (9)
C11	0.0477 (12)	0.0589 (14)	0.0498 (13)	−0.0082 (10)	0.0287 (10)	0.0030 (10)
C12	0.0491 (11)	0.0501 (12)	0.0322 (10)	−0.0043 (9)	0.0193 (9)	0.0011 (9)

Geometric parameters (Å, º)

Zn—N1	2.0486 (16)	C3—C4	1.381 (3)
Zn—N1^{i}	2.0486 (16)	C3—H3	0.9300
Zn—O2	1.9527 (13)	C4—C5	1.373 (3)
Zn—O2^{i}	1.9527 (13)	C4—H4	0.9300
N1—C1	1.335 (2)	C5—H5	0.9300

N1—C5	1.347 (3)	C6—C7	1.504 (3)
N2—O4	1.223 (2)	C7—C12	1.390 (3)
N2—O5	1.226 (2)	C7—C8	1.392 (3)
N2—C9	1.465 (3)	C8—C9	1.379 (3)
O1—C2	1.353 (2)	C8—H8	0.9300
O1—H1A	0.9147	C9—C10	1.385 (3)
O2—C6	1.274 (2)	C10—C11	1.383 (3)
O3—C6	1.237 (2)	C10—H10	0.9300
C1—C2	1.390 (3)	C11—C12	1.377 (3)
C1—H1	0.9300	C11—H11	0.9300
C2—C3	1.385 (3)	C12—H12	0.9300

O2—Zn—O2^{i}	120.90 (9)	C3—C4—H4	119.7
O2—Zn—N1	114.84 (6)	N1—C5—C4	121.20 (18)
O2^{i}—Zn—N1	101.72 (6)	N1—C5—H5	119.4
O2—Zn—N1^{i}	101.72 (6)	C4—C5—H5	119.4
O2^{i}—Zn—N1^{i}	114.84 (6)	O3—C6—O2	123.17 (18)
N1—Zn—N1^{i}	101.64 (9)	O3—C6—C7	120.52 (18)
C1—N1—C5	118.48 (16)	O2—C6—C7	116.28 (16)
C1—N1—Zn	116.48 (12)	C12—C7—C8	119.53 (18)
C5—N1—Zn	124.53 (13)	C12—C7—C6	120.34 (17)
O4—N2—O5	123.22 (18)	C8—C7—C6	120.03 (17)
O4—N2—C9	118.26 (17)	C9—C8—C7	118.50 (17)
O5—N2—C9	118.52 (18)	C9—C8—H8	120.8
C2—O1—H1A	112.0	C7—C8—H8	120.8
C6—O2—Zn	111.90 (12)	C8—C9—C10	122.55 (18)
N1—C1—C2	123.20 (17)	C8—C9—N2	118.40 (17)
N1—C1—H1	118.4	C10—C9—N2	119.04 (17)
C2—C1—H1	118.4	C11—C10—C9	118.19 (19)
O1—C2—C3	124.38 (17)	C11—C10—H10	120.9
O1—C2—C1	117.54 (17)	C9—C10—H10	120.9
C3—C2—C1	118.08 (17)	C12—C11—C10	120.46 (19)
C4—C3—C2	118.33 (17)	C12—C11—H11	119.8
C4—C3—H3	120.8	C10—C11—H11	119.8
C2—C3—H3	120.8	C11—C12—C7	120.76 (19)
C5—C4—C3	120.66 (18)	C11—C12—H12	119.6
C5—C4—H4	119.7	C7—C12—H12	119.6

O2—Zn—N1—C1	−168.19 (13)	Zn—O2—C6—C7	−172.72 (13)
O2^{i}—Zn—N1—C1	−35.82 (15)	O3—C6—C7—C12	−11.6 (3)
N1^{i}—Zn—N1—C1	82.92 (14)	O2—C6—C7—C12	166.42 (19)
O2—Zn—N1—C5	3.54 (18)	O3—C6—C7—C8	171.9 (2)
O2^{i}—Zn—N1—C5	135.91 (16)	O2—C6—C7—C8	−10.1 (3)
N1^{i}—Zn—N1—C5	−105.36 (17)	C12—C7—C8—C9	−0.9 (3)
O2^{i}—Zn—O2—C6	−63.65 (13)	C6—C7—C8—C9	175.64 (17)
N1—Zn—O2—C6	58.89 (15)	C7—C8—C9—C10	0.1 (3)
N1^{i}—Zn—O2—C6	167.73 (14)	C7—C8—C9—N2	−178.86 (17)
C5—N1—C1—C2	−1.9 (3)	O4—N2—C9—C8	0.0 (3)

Zn—N1—C1—C2	170.31 (15)	O5—N2—C9—C8	179.42 (18)
N1—C1—C2—O1	−179.81 (18)	O4—N2—C9—C10	−179.00 (19)
N1—C1—C2—C3	0.2 (3)	O5—N2—C9—C10	0.4 (3)
O1—C2—C3—C4	−178.31 (19)	C8—C9—C10—C11	0.6 (3)
C1—C2—C3—C4	1.7 (3)	N2—C9—C10—C11	179.55 (19)
C2—C3—C4—C5	−1.9 (3)	C9—C10—C11—C12	−0.5 (3)
C1—N1—C5—C4	1.8 (3)	C10—C11—C12—C7	−0.3 (3)
Zn—N1—C5—C4	−169.79 (15)	C8—C7—C12—C11	1.0 (3)
C3—C4—C5—N1	0.1 (3)	C6—C7—C12—C11	−175.53 (19)
Zn—O2—C6—O3	5.2 (3)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O3^{ii}	0.91	1.73	2.642 (2)	174

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