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# Bis(1H-benzimidazole-κN^3)bis(4-hydroxy-benzoato-κO)zinc(II) 0.25-hydrate

In the title compound, $[Zn(C_7H_5O_3)_2(C_7H_6N_2)_2]\cdot 0.25H_2O$, the Zn^{II} atom is coordinated by two 4-hydroxybenzoate anions and two benzimidazole (bzim) molecules, resulting in a distorted ZnO_2N_2 tetrahedral geometry. The short face-to-face distance of 3.28 (4) Å between parallel partially overlapped bzim ligands of neighboring molecules indicates the existence of π–π stacking in the crystal structure.

Comment

As part of our ongoing investigation into the nature of π–π stacking in metal complexes, we have prepared a series of phases incorporating aromatic ligands such as quinoline (Pan & Xu, 2004) and benzimidazole (bzim) (Li *et al.*, 2005; Zheng *et al.*, 2005). We present here the title mixed-ligand Zn^{II} complex, (I) (Fig. 1), for comparison with the structures reported previously.
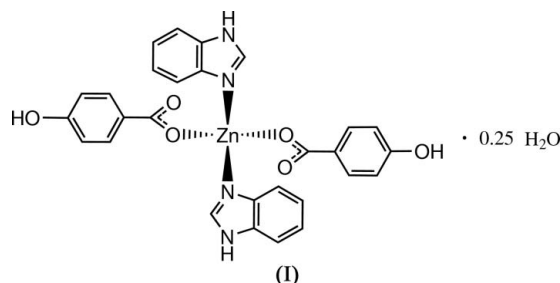
Compound (I) is isostructural with a Co^{II} complex (Zheng *et al.*, 2005), in which a compressed Co—O—C angle [103.5 (2)°] suggested a long but genuine Co—O bonding interaction of 2.561 (3) Å (*i.e.* a highly asymmetric bidentate coordination by the carboxylate group of the 4-hydroxybenzoate anion in question). As shown in Table 1, the Zn—O and Zn—N bond distances in (I) are comparable with the corresponding normal Co—O bond distances [1.970 (2) and 1.993 (2) Å] and Co—N bond distances [2.026 (3) and 2.013 (3) Å], but the Zn···O5 separation of 2.693 (2) Å is significantly longer than the corresponding Co—O bond in the Co^{II} complex. The Zn—O4—C41 angle of 108.2 (2)° is also larger than the compressed Co—O—C angle.

These findings suggest there is no significant bonding interaction between atoms Zn and O5 in (I). Thus, the metal coordination polyhedron for (I) is a somewhat distorted ZnO_2N_2 tetrahedron, compared to distorted trigonal bipyramidal for the Co^{II} complex. The difference in coordination number and coordination geometry between the two compounds might arise from the different electronic configurations of the two metal ions.
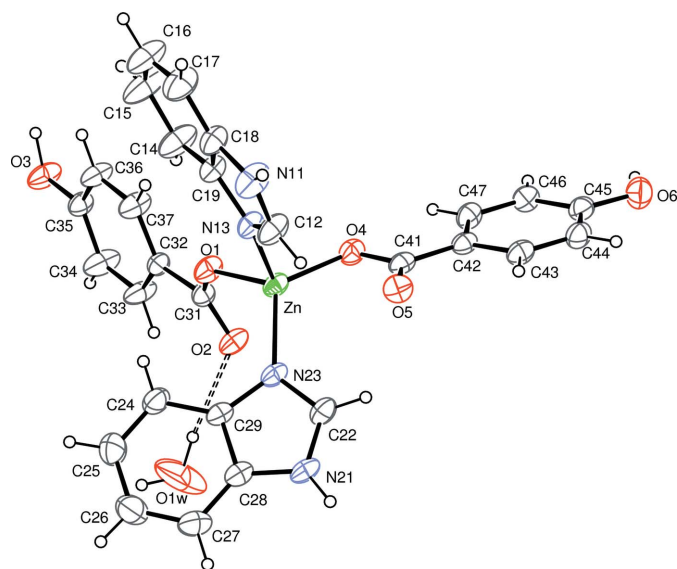
metal-organic papers

Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). The dashed line indicates a hydrogen bond.
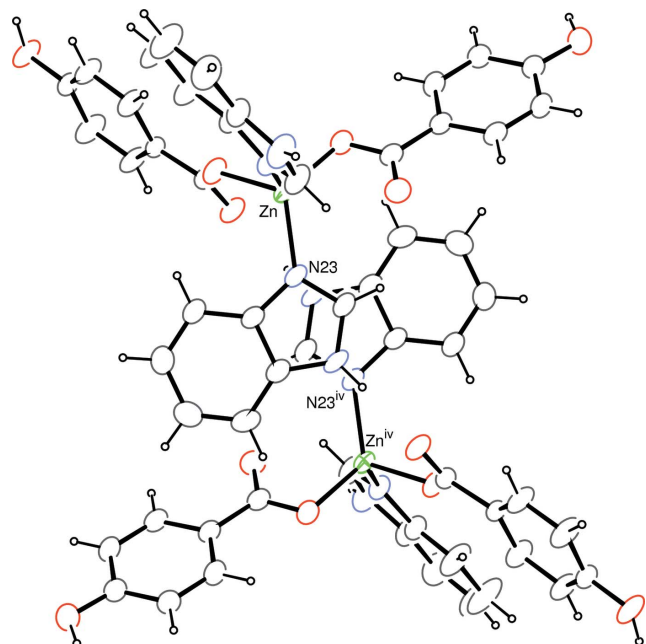

Figure 2
The π–π stacking between parallel N23-imidazole and N23^{iv}-imidazole rings in (I) [symmetry code: (iv) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$].

A partially overlapped arrangement is observed between parallel N23-imidazole and N23^{iv}-imidazole rings (see Fig. 2 for symmetry code). The face-to-face separation of 3.28 (4) Å indicates the existence of π–π stacking. The disordered non-coordinated water molecule, situated close to a twofold axis, is hydrogen bonded to the uncoordinated carboxyl O2 atom. Further O—H···O and N—H···O interactions (Table 2) involving the ligands help to stabilize the crystal structure of (I).

Experimental

Commercial analytical grade reagents were used. $ZnCl_2$ (1 mmol), 4-hydroxybenzoic acid (2 mmol), bzim (2 mmol) and Na_2CO_3 (1 mmol) were dissolved in a mixture of water (15 ml) and ethanol (5 ml). The solution was refluxed for 4 h and filtered after cooling to room temperature. Single crystals of (I) were obtained from the filtrate after 3 d.

Crystal data

$[Zn(C_7H_5O_3)_2(C_7H_6N_2)_2]\cdot 0.25H_2O$	$D_x = 1.479$ Mg m^{-3}
$M_r = 580.37$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 5766
$a = 13.064$ (3) Å	reflections
$b = 27.434$ (6) Å	$\theta = 3.0$–$23.0°$
$c = 15.069$ (4) Å	$\mu = 0.99$ mm^{-1}
$\beta = 105.138$ (4)°	$T = 295$ (2) K
$V = 5213$ (2) Å^3	Block, colorless
$Z = 8$	$0.29 \times 0.20 \times 0.11$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	3148 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.035$
Absorption correction: multi-scan	$\theta_{max} = 25.2°$
(*ABSCOR*; Higashi, 1995)	$h = -15 \rightarrow 15$
$T_{min} = 0.745$, $T_{max} = 0.902$	$k = -32 \rightarrow 25$
13925 measured reflections	$l = -16 \rightarrow 18$
4714 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 5.4788P]$
$wR(F^2) = 0.098$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4714 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
361 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Zn—O1	1.957 (2)	Zn—N13	2.010 (2)
Zn—O4	1.982 (2)	Zn—N23	1.991 (3)
O1—Zn—O4	102.03 (10)	O4—Zn—N13	110.52 (10)
O1—Zn—N13	102.08 (10)	O4—Zn—N23	120.39 (10)
O1—Zn—N23	112.11 (10)	N13—Zn—N23	108.15 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···O2	0.97	2.39	3.358 (13)	174
O3—H3A···O4^i	0.98	1.77	2.701 (3)	157
O6—H6A···O2^{ii}	0.95	1.75	2.698 (4)	174
N11—H11···O3^{iii}	0.86	2.04	2.895 (4)	174
N21—H21···O2^{iv}	0.86	1.95	2.804 (4)	172

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y, -z+\frac{3}{2}$; (iii) $x+1, -y+1, z+\frac{1}{2}$; (iv) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1$.

The non-coordinated water molecule is situated close to a twofold axis such that O1W···O1W^i [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] = 1.79 Å. Its site-occupancy factor was refined and converged to

0.258 (9), and was fixed as 0.25 in the final cycles of refinement; this water molecule is thus disordered. The H atoms attached to O1W were placed in theoretical positions (Nardelli, 1999). The H atoms of the hydroxy groups were located in a difference map. The O-bound H atoms were refined as riding in their as-found relative positions, with $U_{iso}(H) = 1.5U_{eq}(O)$. Other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and refined as riding with $U_{iso}(H) = 1.2U_{eq}(carrier)$.

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, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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