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Bis(1*H*-benzimidazole-κN^3)(oxydiacetato-$\kappa^3 O,O',O''$)zinc(II)

Lei Cao, Ning Li and Duan-Jun Xu*

Department of Chemistry, Zhejiang University, Hangzhou, 310027, People's Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

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Key indicators

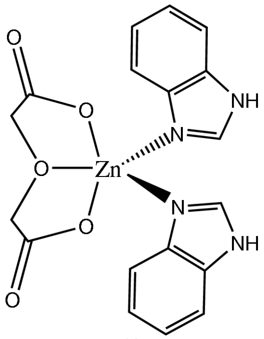
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.027
wR factor = 0.070
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Zn(C_7H_6N_2)_2(C_4H_4O_5)]$, one oxydiacetate dianion and two benzimidazole molecules coordinate to the Zn^{II} atom in distorted trigonal-bipyramidal coordination geometry. The interplanar distance of 3.422 (4) Å between parallel benzimidazole rings of neighbouring molecules indicates the existence of π–π stacking.

Comment

The X-ray crystal structures of benzimidazole (BZIM) complexes of first-row transition metals such as Mn^{II} (Chen *et al.*, 2003), Co^{II} (Liu *et al.*, 2003), Ni^{II} (Liu & Xu, 2004) and Cu^{II} Bukowska-Strzyzewska & Tosik, 1983) have shown that π–π stacking of the BZIM rings commonly occurs. As a part of our ongoing investigations into π–π stacking in metal complexes, the title BZIM complex of Zn^{II}, (I), (Fig. 1) has been prepared.



(I)

The oxydiacetate (ODA) dianion in (I) is disordered over two positions in a 0.42:0.58 ratio; in both ODA conformations the Zn atom assumes distorted trigonal-bipyramidal coordination geometry, formed by two BZIM molecules and one tridentate ODA dianion. The ODA chelates to the Zn atom in a meridional configuration, with both carboxy groups of ODA coordinating to the Zn atom in monodentate mode. Except for the ether atom O3, the ODA is close to planar, with a maximum atomic deviation from the least-squares plane of 0.096 (2) Å for C3. The ether O3 atoms (O3*a* and O3*b*) are randomly disordered on both sides of the mean plane formed by the other atoms of ODA, with displacements of 0.277 (6) and −0.325 (5) Å, respectively. Thus, the five-membered chelate rings display envelope conformations, with the atoms O3*a* and O3*b* occupying the flap positions. This meridional envelope conformation of ODA agrees with that found in most other ODA complexes of transition metals (Allen, 2002).

The ether O atom of ODA and two BZIM N atoms form an equatorial coordination plane around the Zn atom; the Zn—N bond distances in (I) (Table 1) are comparable to the values of

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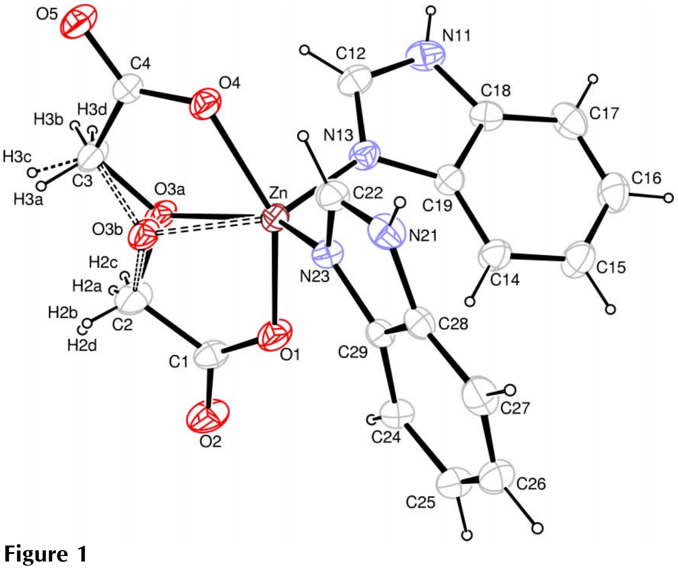

Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. The O3*b*-containing disorder component is represented with dashed lines.

2.039 (2) and 2.044 (2) Å found in the (benzyl)benzimidazole complex of Zn^{II} (Bei *et al.*, 2001). Two coordinated carboxy O atoms occupy the axial sites of the trigonal bipyramid, with a bond angle of 149.84 (6)°, which is very similar to the value of 149.13 (19)° found in another ODA complex of Zn^{II} (Li *et al.*, 2003).

The uncoordinated carboxyl O atoms (O2 and O5) are hydrogen bonded to BZIM ligands of neighbouring complexes (Table 2) to form the supramolecular structure shown in Fig. 2.

An overlapped arrangement of BZIM rings of neighbouring complex molecules is observed in the crystal structure (Fig. 3). The interplanar distance of 3.422 (4) Å between neighbouring parallel BZIM rings indicates the existence of significant π–π stacking.

Experimental

An aqueous solution (15 ml) of $ZnCl_2$ (1 mmol), H_2ODA (1 mmol) and Na_2CO_3 (1 mmol) was mixed with an ethanol solution (5 ml) of BZIM (2 mmol). The solution was refluxed for 5 h and then filtered. Colourless single crystals were obtained after 5 d.

Crystal data

$[Zn(C_7H_6N_2)_2(C_4H_4O_5)]$
$M_r = 433.72$
Monoclinic, $C2/c$
$a = 25.049$ (6) Å
$b = 7.0568$ (18) Å
$c = 21.420$ (5) Å
$\beta = 107.783$ (3)°
$V = 3605.4$ (15) Å^3
$Z = 8$
$D_x = 1.598$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6382 reflections
$\theta = 2.4$–25.5°
$\mu = 1.40$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.32 × 0.28 × 0.22 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.648$, $T_{max} = 0.737$
7413 measured reflections
3258 independent reflections
2883 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.2°$
$h = -30 \rightarrow 17$
$k = -8 \rightarrow 8$
$l = -25 \rightarrow 25$

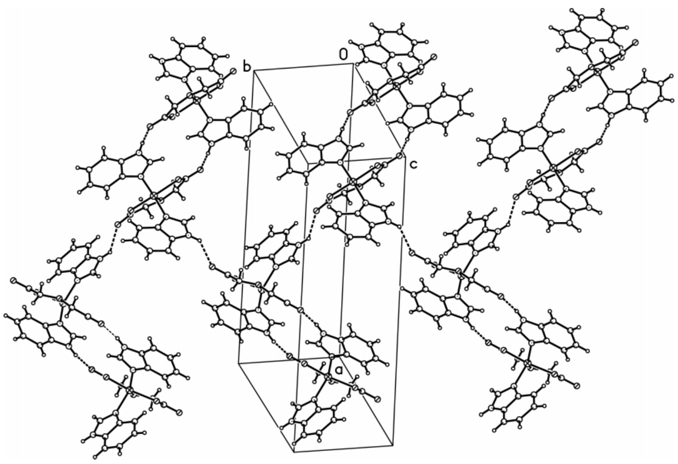

Figure 2
Unit-cell packing diagram for (I). Dashed lines indicate the intermolecular hydrogen bonding.

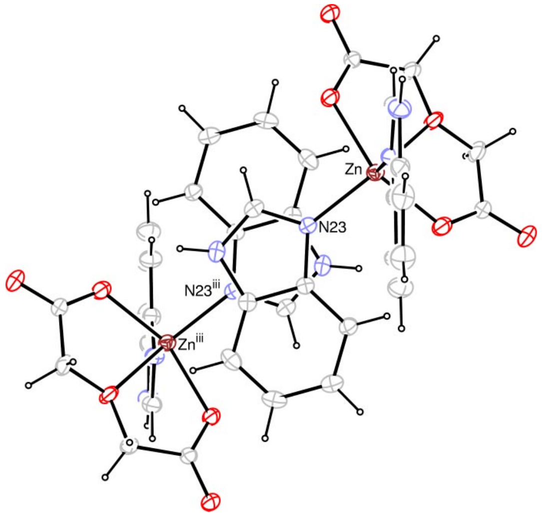

Figure 3
π–π stacking of BIZM rings in neighbouring molecules of (I). [Symmetry code: (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.]

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.070$
$S = 1.04$
3258 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 2.2003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N13	2.0205 (18)	Zn—O3*a*	2.098 (9)
Zn—N23	2.0181 (16)	Zn—O3*b*	2.105 (6)
Zn—O1	2.0406 (15)	Zn—O4	2.0807 (14)
N23—Zn—N13	110.87 (7)	N13—Zn—O3*a*	105.79 (18)
N23—Zn—O1	101.26 (6)	O1—Zn—O3*a*	76.2 (2)
N13—Zn—O1	99.80 (7)	O4—Zn—O3*a*	75.4 (2)
N23—Zn—O4	95.40 (6)	N23—Zn—O3*b*	125.90 (12)
N13—Zn—O4	97.45 (7)	N13—Zn—O3*b*	123.00 (12)
O1—Zn—O4	149.84 (6)	O1—Zn—O3*b*	75.59 (18)
N23—Zn—O3*a*	143.09 (18)	O4—Zn—O3*b*	74.27 (18)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N11—H11⋯O2^{i}	0.86	2.04	2.750 (3)	139
N21—H21⋯O5^{ii}	0.86	1.88	2.722 (2)	165

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

The occupancies of the disordered atoms O3*a* and O3*b* were initially refined and converged to 0.424 (8) and 0.576 (8), respectively. In the final cycles of refinement, the occupancies of O3*a* and O3*b* were fixed at 0.42 and 0.58, respectively. Methylene H atoms were placed in calculated positions, with C—H = 0.97 Å, and included in the final cycles of refinement in riding mode, with appropriate fractional site occupancies. The other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and were included in the final cycles of refinement in a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ of the carrier atoms. Trial refinements in space group *Cc* did not resolve the O3 disorder and were unstable.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku Corporation, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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