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Benzoato[hydridotris(3,5-methylphenylpyrazolyl)borato-κ^3N,N',N'']zinc(II)

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Key indicators

Single-crystal X-ray study
T = 571 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.104
Data-to-parameter ratio = 16.2

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

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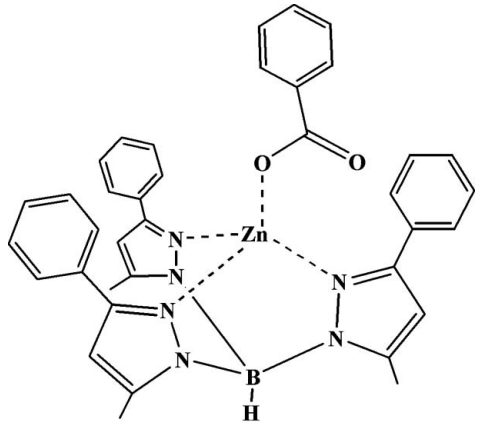
In the title compound, $[Zn(C_7H_5O_2)(C_{30}H_{28}BN_6)]$, the Zn atom is coordinated by three N atoms of the tridentate pyrazolyl groups and the carboxylate O atoms of the benzoate ligand in an isobidentate manner due to a short-range interaction between the Zn atom and the carbonyl O atom [2.593 (2) Å], giving a distorted trigonal–bipyrimidal environment.

Comment

Matrix metalloproteinases (MMPs) are a class of structurally related zinc-containing endopeptidases comprising more than 20 mammalian MMPs. The MMP catalytic domains exhibit high sequence homology and structural similarity. Each includes two structurally and mechanistically distinct Zn^{II} centers. One is thought to stabilize the protein structure whereas the other is crucial for catalysis (Whittaker *et al.*, 1999). Single-crystal X-ray structure and solution NMR studies show that this zinc ion is coordinated by three imidazolyl groups from histidine (His) residues and one hydroxide in the activated enzymes (Parkin, 2004; He *et al.*, 2004). One of the most important model complexes of MMPs is hydridotris(3,5-methylphenylpyrazoly)borate zinc hydroxide (TpZn-OH), (II), since this compound exhibits high structural similarity to the catalytic center of this class of enzymes (Parkin, 2004; Jacobsen & Cohen, 2004; Puerta & Cohen, 2003). The zinc ion adopts a tetrahedral geometry with bond distances and angles very close to the corresponding parameters in the enzymes. To shed light on the mechanism of enzyme interaction with biorelevant molecules, much effort has been devoted to the spectroscopic and structural studies of this class of model complexes with different small molecules.



(I)

The title complex, (I), is analogous to (II) except that it has a benzoate ligand coordinated to the Zn atom, through

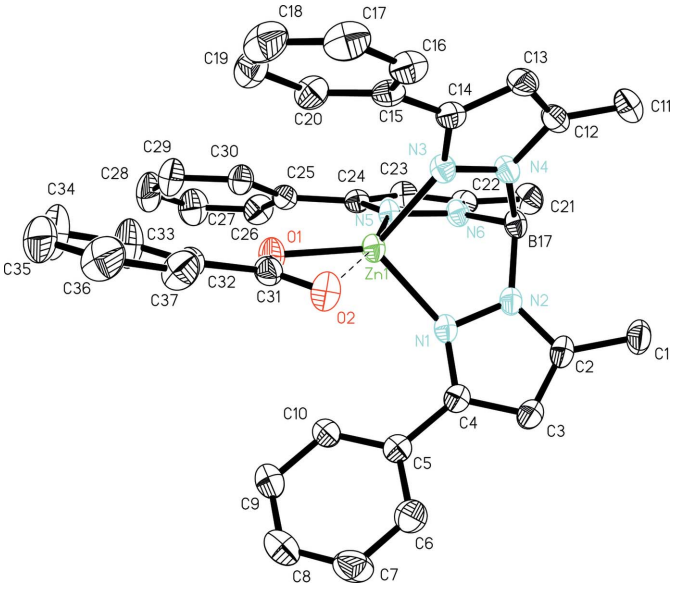


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

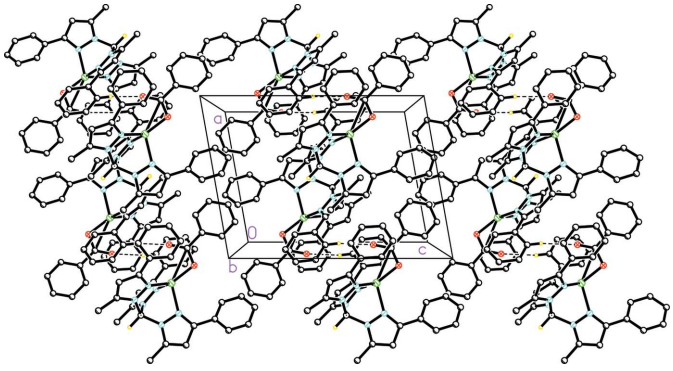


Figure 2
Packing diagram of the title compound, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

carboxylate atom O1, in a monodentate mode (Fig. 1). The tridentate hydridotris(3,5-methylphenylpyrazoly) ligand is coordinated to zinc *via* N1, N3 and N5 of the pyrazolyl ligands. The geometry of the Zn atom is distorted trigonal bipyrimidal because of the presence of a short-range interaction between atoms Zn and O2 [2.593 (2) Å]. Atoms O2 and N5 occupy axial positions, with an angle of 169.81 (9)° at the Zn atom. Atoms O1, N1 and N3 occupy equatorial positions, with the angles at the Zn atom between 98.85 (10) and 128.63 (10)°. The Zn—N and Zn—O bond distances and other bond lengths and angles are in normal ranges (Allen *et al.*, 1987; Orpen *et al.*, 1989).

C—H···O intra- and intermolecular interactions (Table 2) link the molecules into dimers which are arranged parallel to the *ac* face (Fig. 2). In addition, there are π–π interactions between the (C25–C30)^{ii} and N1/N2/C2–C4 rings [symmetry code: (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$], with a distance between the centroids of 3.831 Å, and there are C—H···π interactions, [shortest H···centroid distance of 2.790 Å, angle about H of 165°] between C17—H17 and the ring centroid of (C25–C30)^{ii}.

Experimental

Equimolar quantities of hydridotris(3,5-methylphenylpyrazolyl)borate zinc hydroxide (69.2 g, 0.12 mmol; Puerta & Cohen, 2002) and benzoic acid (14.9 g, 0.12 mmol) were separately dissolved in 10 and 2 ml methanol, respectively. The solutions were mixed, and stirred magnetically for 30 min. The resulting solid was collected and dried under vacuum. The solid was redissolved in dichloromethane and crystals were obtained by diffusion of hexane into the solution (yield 54.8 mg, 81.6%).

Crystal data

$[Zn(C_7H_5O_2)(C_{30}H_{28}BN_6)]$
M_r = 669.87
Monoclinic, $P2_1/c$
a = 10.147 (2) Å
b = 23.561 (5) Å
c = 13.776 (3) Å
β = 100.09 (3)°
V = 3242.4 (11) Å^3
Z = 4
D_x = 1.372 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 571 (2) K
Prism, green
0.20 × 0.20 × 0.20 mm

Data collection

Bruker 1K CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.856, T_{max} = 0.856
69871 measured reflections
7014 independent reflections
3841 reflections with $I > 2\sigma(I)$
R_{int} = 0.110
θ_{max} = 27.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.00
7014 reflections
432 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 2.4383P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0020 (2)

Table 1
Selected geometric parameters (Å, °).

Zn—O1	1.920 (2)	N2—B	1.548 (4)
Zn—N1	2.029 (3)	N4—B	1.535 (4)
Zn—N3	2.038 (3)	N6—B	1.552 (4)
Zn—N5	2.081 (2)		
O1—Zn—N1	128.63 (10)	N3—Zn—N5	90.64 (10)
O1—Zn—N3	123.21 (10)	O2—Zn—O1	56.04 (9)
N1—Zn—N3	98.85 (10)	O2—Zn—N3	94.53 (9)
O1—Zn—N5	113.83 (10)	O2—Zn—N1	96.33 (9)
N1—Zn—N5	91.52 (10)	O2—Zn—N5	169.81 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
C30—H30···O1	0.93	2.47	3.111 (4)	126
C16—H16···O2^{i}	0.93	2.55	3.438 (5)	160

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

H atoms were positioned geometrically, with N—H = 0.86 Å, and C—H = 0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*N*), where x = 1.5 for methyl and x = 1.2 for all other H atoms. The H atom attached to boron was refined isotropically; B—H = 1.11 (2) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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