Dibenzoato(1,10-phenanthroline)zinc(II)

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Key indicators

Single-crystal X-ray study
$T = 292$ K
Mean σ(C–C) = 0.007 Å
R factor = 0.054
wR factor = 0.146
Data-to-parameter ratio = 16.3

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

In the molecule of the title compound, [Zn($C_7H_5O_2$)$_2$-($C_{12}H_8N_2$)], the coordination about the Zn^{II} center is best described as distorted octahedral. The crystal structure is stabilized by π–π stacking of neighboring phenyl groups.

Comment

There has been considerable interest in the design and synthesis of Zn^{II} complexes with carboxylate ligands in coordination chemistry due to their essential roles in the regulation and catalytic activity of biological systems (Fraústo da Silva & Williams, 1991).

(I)
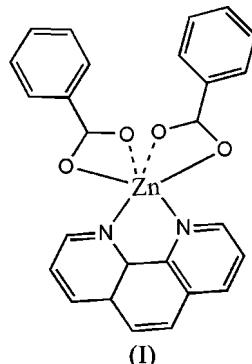
In the literature, there are several reports of the structures of Zn^{II} complexes with the benzoate ligand, e.g. [Zn(C_7H_5-O_2)$_2$($C_5H_6N_2$)$_2$] (Shanmuga Sundara Raj et al., 2000), [Zn$_2$($C_5H_6N_2$)$_3$(OH)]$_n$ (Yang et al., 2005) and [Zn$_2$($C_5H_6N_2$)$_4$-($C_{10}H_{14}N_2O$)$_2$] (Necefoğlu, Clegg & Scott, 2002). In these structures, the benzoate anions act as monodentate or bidentate bridging ligands. To the best of our knowledge, there are fewer reports on chelating mononuclear Zn^{II}–benzoate complexes. We report here the crystal structure of such a complex, namely dibenzoato(1,10-phenanthroline)zinc(II), (I), with a chelating benzoate ligand.

Although the Zn atom has primary four-coordination, close contacts of atoms O2 and O3 (Table 1) may be considered to give six-coordination; these distances are much greater than the sum of the corresponding ionic radii (2.14 Å; Day & Selbin, 1969). Similar reported Zn···O contacts are 2.687 (6) Å in [Zn($C_7H_5O_3$)(H$_2$O)$_3$($C_6H_6N_2O$)]·$C_7O_3H_5$ (Hökelek & Necefoğlu, 2001), 2.50 (1) Å in [Zn(n-HOC$_6$H$_4$COO)$_2$(C_5H_5N)$_2$]·-2C_5H_5N (Nadzhafov et al., 1981), 2.494 (8) Å in {[Zn(p-H$_2$NC$_6$H$_4$COO)$_2$]·1.5H$_2$O}$_n$ (Amiraslanov et al., 1980) and 2.404 (2) Å in [Zn($C_6H_6N_2O$)$_2$($C_7H_5O_3$)$_2$] (Necefoğlu, Hökelek et al., 2002). The six-coordination around Zn^{II} can be described as distorted octahedral, formed by two benzoate anions and one phenanthroline ligand (Table 1 and Fig. 1).
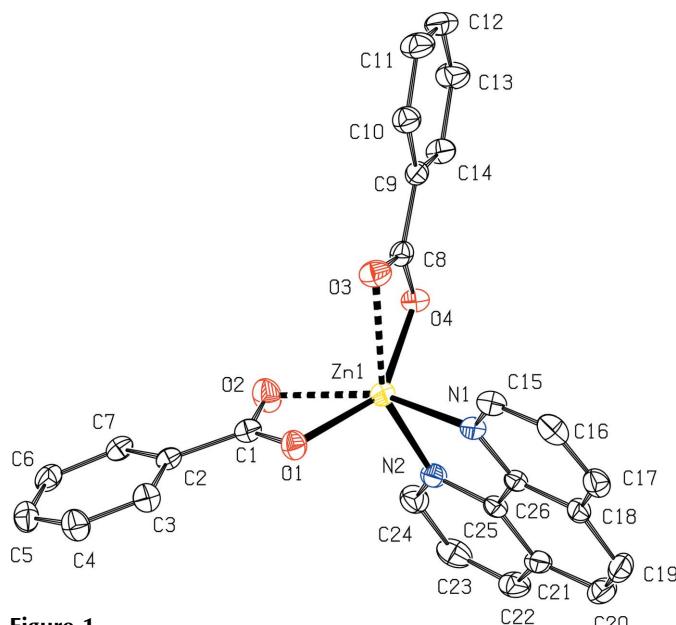
Figure 1
A drawing of the title molecular structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.
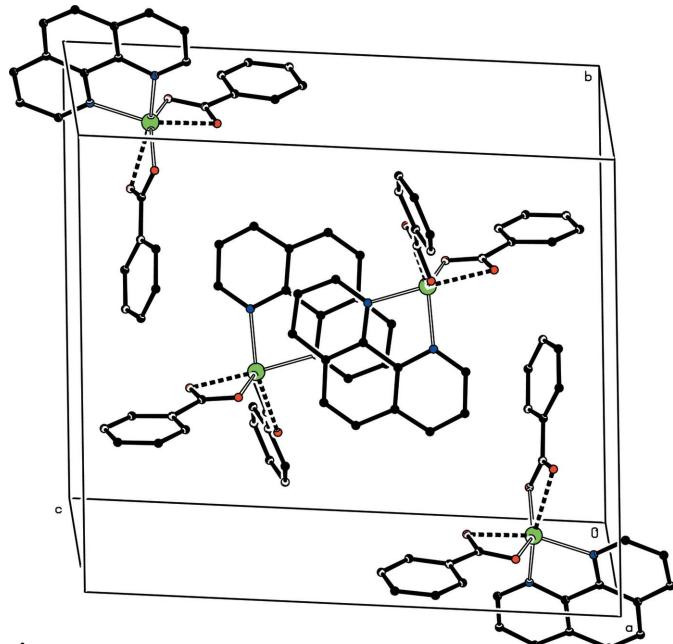

Figure 2
A packing diagram for (I). H atoms have been omitted.

The average Zn—O bond length (2.193 Å) is longer than the corresponding value [1.953 (2) Å] in [Zn₂(C₇H₅O₃)₄(C₁₀H₁₄N₂O)₂]·2H₂O (Hökelek & Necefoğlu, 1996), where Zn is four-coordinate. The average Zn—N bond length [2.115 (3) Å] in (I) is a little shorter than the corresponding value in the octahedrally coordinated zinc complex [Zn(DENA)₂(NCS)₂]·2H₂O [2.171 (4) Å; DENA is diethylnicotinamide; Bigoli et al., 1973].

The crystal packing of (I) is stabilized by extended π–π stacking of the phenyl ring systems (Fig. 2), characterized by interplanar distances in the range 3.414 (3)–3.620 (3) Å.

Experimental

The title compound, (I), was prepared from Zn(OAc)₂·2H₂O (0.219 g, 1.0 mmol) and benzoic acid (0.260 g, 2.0 mmol) in MeOH (20 ml). The mixture was stirred for 2 h and then poured into phenanthroline (0.198 g, 1.0 mmol) and stirred to obtain a clear solution. Well shaped colorless prisms were obtained by allowing the solution to stand at room temperature for two months (yield 0.0613 g, 28%; m.p. 485 K).

Crystal data
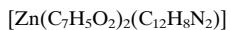
[Zn(C₇H₅O₂)₂(C₁₂H₈N₂)]
$M_r = 487.79$
Monoclinic, $P2_1/n$
$a = 7.5698 (9)$ Å
$b = 16.7052 (19)$ Å
$c = 18.017 (2)$ Å
$\beta = 101.813 (2)°$
$V = 2230.1 (4)$ Å³
$Z = 4$

$D_x = 1.453$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2907 reflections
$\theta = 2.3–23.5°$
$\mu = 1.14$ mm⁻¹
$T = 292 (2)$ K
Needle, colorless
$0.60 \times 0.14 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
$T_{min} = 0.549$, $T_{max} = 0.935$
12837 measured reflections
4855 independent reflections

3389 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.0°$
$h = -9 \rightarrow 9$
$k = -21 \rightarrow 13$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.146$
$S = 1.12$
4855 reflections
298 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 2.2799P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.33$ e Å⁻³
$\Delta\rho_{min} = -0.26$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Zn1—O4	1.996 (3)	Zn1—N2	2.120 (3)
Zn1—O1	2.044 (3)	Zn1—O2	2.302 (3)
Zn1—N1	2.109 (3)	Zn1—O3	2.431 (3)
O4—Zn1—O1	143.73 (12)	N1—Zn1—O2	159.83 (12)
O4—Zn1—N1	105.95 (12)	N2—Zn1—O2	97.23 (13)
O1—Zn1—N1	102.28 (12)	O4—Zn1—O3	58.39 (11)
O4—Zn1—N2	100.70 (12)	O1—Zn1—O3	98.67 (11)
O1—Zn1—N2	106.87 (12)	N1—Zn1—O3	92.08 (12)
N1—Zn1—N2	78.57 (13)	N2—Zn1—O3	154.10 (12)
O4—Zn1—O2	94.20 (11)	O2—Zn1—O3	99.31 (12)
O1—Zn1—O2	59.72 (11)		

H atoms were positioned geometrically, with C—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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