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Bis[2-(1,3-benzoxazol-2-yl)phenolato](1,10-phenanthroline)zinc(II)–2-(1,3-benzoxazol-2-yl)phenol (2/1)

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The title compound, $[Zn(C_{13}H_8NO_2)_2(C_{12}H_8N_2)]\cdot 0.5C_{13}H_9NO_2$, was prepared by the reaction of zinc acetate dihydrate, 2-(1,3-benzoxazol-2-yl)phenol and phenanthroline. It is a mononuclear mixed-ligand complex with an octahedral geometry. The co-crystallized free ligand, 2-(1,3-benzoxazol-2-yl)phenol, is disordered and located about a twofold axis.

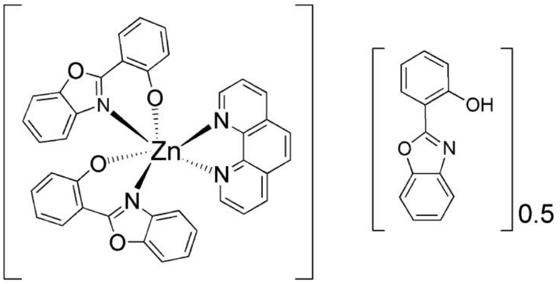
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.060
wR factor = 0.155
Data-to-parameter ratio = 16.1

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

Comment

In recent years, luminescent organic metal complexes, have been studied for their potential as photoluminescent or electroluminescent materials (Wang, 2001). For example, complexes with *N*,*O*-donor ligands have been used successfully as electroluminescent emitters (Cui *et al.*, 2005; Qiao *et al.*, 2004; Sapochak *et al.*, 2002; Li *et al.*, 2000). The emitting wavelengths are metal-tunable and/or ligand-tunable (Tong *et al.*, 2005; Zheng *et al.*, 2003). Introduction of a second ligand may also have important effects on the mechanism of emission (Qiao *et al.*, 2004), as well as significant variations in the emitting wavelength (Yam *et al.*, 2000). Zinc(II) complexes with 2-(1,3-benzoxazol-2-yl)phenol have been widely studied for their electroluminescent behavior and have already been accepted as excellent green–blue emitters in electroluminescent devices (Nakamura *et al.*, 1994; Hamada *et al.*, 1996). We have previously reported the structure of the mixed-ligand zinc(II) complex of 2-(1,3-benzoxazol-2-yl)phenol and 2-(1,3-benzothiazol-2-yl)phenol (Tong *et al.*, 2004), which shows excellent photoluminescence properties, and anticipated that the mixed-ligand zinc(II) complex of 2-(1,3-benzoxazol-2-yl)phenol and phenanthroline could exhibit similar properties. Accordingly, the title mixed-ligand zinc(II) complex, (I), was synthesized and its crystal structure determined (Fig. 1).



(I)

Complex (I) is a monomeric structure, in which the central Zn(II) ion is coordinated by two deprotonated 2-(1,3-benzoxazol-2-yl)phenol ligands and a phenanthroline ligand. The six-coordinate ZnN_4O_2 octahedral structure is distorted as indicated by the smaller bite angle of the phenanthroline

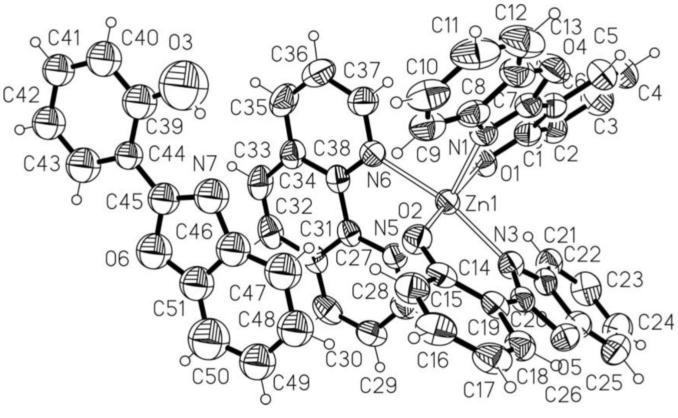


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level for the non-H atoms. H atoms are drawn as spheres of arbitrary radii.

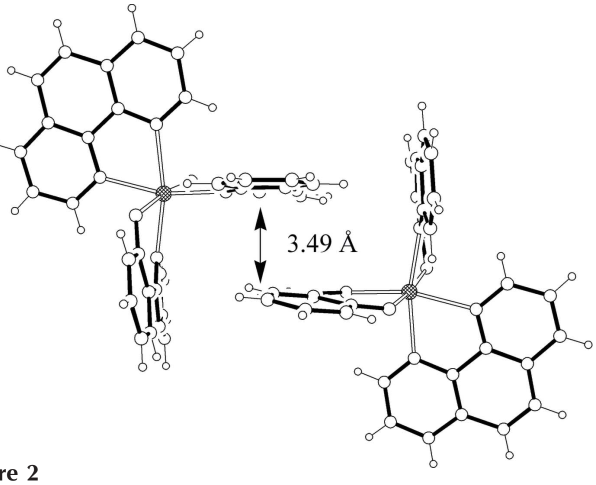


Figure 2
The π–π stacking interactions between deprotonated 2-(1,3-benzoxazol-2-yl)phenol ligands in the supramolecular structure.

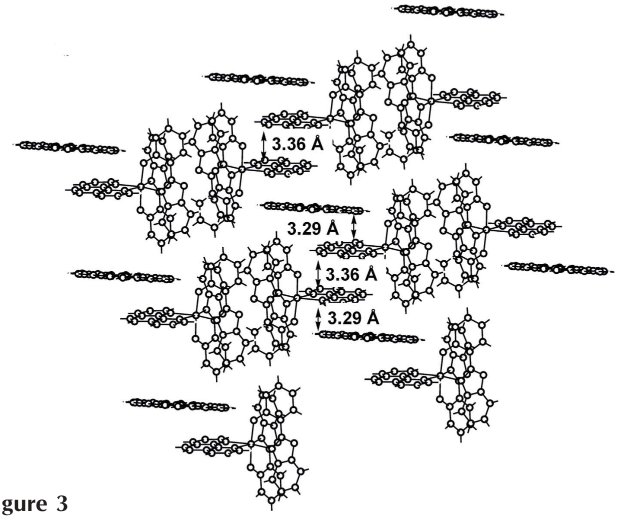


Figure 3
The stacking pattern formed by intermolecular π–π stacking interactions in the supramolecular structure.

ligand [74.1 (1)°]. The Zn—N(benzoxazole) lengths are 2.147 (3) and 2.190 (3) Å; the Zn—O lengths are 2.013 (2) and 2.039 (2) Å. The Zn—N and Zn—O lengths are both slightly greater than in similar structures reported in the literature (Decken & Gossage, 2005 Wu *et al.*, 2000; Yam *et al.*, 2000), while the Zn—N(phenanthroline) bond lengths are 2.222 (3) and 2.245 (3) Å, which are also slightly larger than reported previously (Viossat *et al.*, 2005; Chen *et al.*, 2004). The dihedral angles between phenolate and benzoxazole rings of deprotonated 2-(1,3-benzoxazol-2-yl)phenol are 10.0 (2) and 13.2 (3)°, indicating a slightly distorted structure of the deprotonated 2-(1,3-benzoxazol-2-yl)phenol ligands upon ligation to Zn(II) ions. The interplanar distances between deprotonated 2-(1,3-benzoxazol-2-yl)phenol ring systems (Fig. 2) and phenanthroline ring systems (Fig. 3) between adjacent molecules are 3.49 and 3.36 Å, respectively, indicative of intermolecular π–π stacking interactions. Such interactions can also be observed between phenanthroline and adjacent free 2-(1,3-benzoxazol-2-yl)phenol ring systems, with an interplanar distance of 3.29 Å (Fig. 3). These intermolecular π–π stacking interactions connect adjacent molecules and extend to form three-dimensional arrays (Fig. 3). Intramolecular hydrogen bonds between the phenol OH group and benzoxazole N atoms [O—H$\cdots$N 2.706 (13) Å] in the free 2-(1,3-benzoxazol-2-yl)phenol molecules are also observed in the supramolecular arrays.

Experimental

To a solution of zinc acetate dihydrate (0.1 mmol, 0.022 g) in water (2 ml), was added a mixed solution of 2-(1,3-benzoxazol-2-yl)phenol (0.2 mmol, 0.042 g) and phenanthroline (0.1 mmol, 0.016 g) in ethanol (5 ml); the resulting solution was allowed to stand unperturbed for several days to give colorless crystals of (I)in *ca* 50% yield. Analysis found: C 69.41, H 3.83, N 10.27%; calculated for $C_{44.5}H_{28.5}N_{4.5}O_5Zn$: C 69.27, H 3.72, N 10.37%.

Crystal data

$[Zn(C_{13}H_8NO_2)_2(C_{12}H_8N_2)]\cdot 0.5C_{13}H_9NO_2$
$M_r = 771.59$
Triclinic, $P\overline{1}$
$a = 9.5062$ (6) Å
$b = 11.4587$ (7) Å
$c = 16.5322$ (11) Å
$\alpha = 92.931$ (1)°
$\beta = 101.219$ (1)°
$\gamma = 90.509$ (1)°
$V = 1763.78$ (19) Å^3
$Z = 2$
$D_x = 1.453$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4173 reflections
$\theta = 2.2$–$25.3°$
$\mu = 0.75$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.36 × 0.16 × 0.13 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.773$, $T_{\max} = 0.909$
14563 measured reflections
7498 independent reflections
5775 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.0°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.156$
$S = 1.05$
7498 reflections
465 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 0.7982P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$A\cdots$N7	0.82	2.01	2.706 (13)	142

The free 2-(1,3-benzoxazol-2-yl)phenol ligand is twofold disordered about a center of symmetry. The occupancy factors for this molecule should thus be 0.5 and the refinement generated reasonable geometrical parameters and displacement parameters for these atoms when compared with those of coordinated 2-(1,3-benzoxazol-2-yl)phenolate, suggesting strongly the reasonability of the assumption of the occupancy factors for the disordered free ligand. The refinement formula was also in good agreement with that of the elemental analysis. The H atoms were placed at calculated positions (C—H = 0.93 Å for all aromatic ring H atoms and 0.82 Å for hydroxy H atoms) and refined using the riding-model approximation, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) for all aromatic ring H atoms and $1.5U_{\rm eq}$(C) for all hydroxy H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL97*.

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