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Bis[2-(benzimidazol-2-yl)phenolato]zinc(II)–[2-(benzimidazol-2-yl)phenolato][2-(benzimidazol-2-yl)-4-bromophenolato]zinc(II)–ethanol–water (0.67/0.33/2/0.5)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.020 Å
Some non-H atoms missing
Disorder in main residue
R factor = 0.064
wR factor = 0.209
Data-to-parameter ratio = 15.6

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

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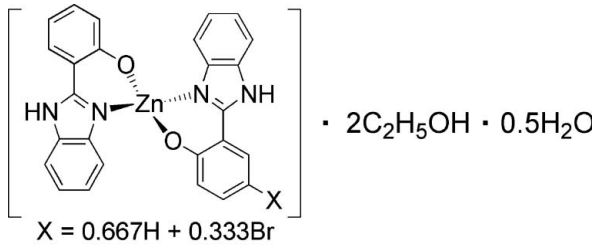
In the structure of the title compound, $[Zn(C_{13}H_9N_2O)(C_{13}H_{8.67}Br_{0.33}N_2O)]\cdot 2C_2H_6O\cdot 0.5H_2O$, the central zinc(II) ion is surrounded by an N_2O_2 environment with a tetrahedral geometry. One of the two deprotonated 2-(benzimidazol-2-yl)phenolate ligands is statistically disordered with 2-(benzimidazol-2-yl)-4-bromophenolate, with an occupancy ratio of 0.67 (2):0.33 (2). Ethanol and water molecules co-crystallize in the orthorhombic system, with the water O atom on a twofold axis. The complex molecules are linked to one another by intermolecular hydrogen bonds.

Comment

In recent years, zinc(II) complexes have become important owing to their potentials in luminescence (Yu *et al.*, 2003). We have been interested in the crystal structure and photoluminescence of organic–metal complexes with *N*,*O*-donor ligands, *e.g.* 2-(benzimidazol-2-yl)phenol, 5-amino-2-(benzimidazol-2-yl)phenol, 2-(benzoxazol-2-yl)phenol and 2-(benzothiazol-2-yl)phenol, and we have reported a number of mixed-ligand co-crystalline structures of Zn^{II} or Be^{II} complexes with them (Tong *et al.*, 2004; Tong, 2005*a*,b). 2-(Benzimidazol-2-yl)-4-bromophenol is a homologously substituted version of 5-amino-2-(benzimidazol-2-yl)phenol, but the structure of a mixed-ligand zinc(II) complex with 2-(benzimidazol-2-yl)-4-bromophenol and 2-(benzoimidazol-2-yl)phenol has not yet been reported. We report here the structure of this mixed-ligand zinc(II) complex, (I), containing ethanol and water solvent molecules.



(I)

In the crystal structure of (I) (Fig. 1), the central Zn^{II} ion is coordinated by two deprotonated ligands in a tetrahedral geometry. One of the 2-(benzimidazol-2-yl)phenolate anions is statistically disordered with the 2-(benzimidazol-2-yl)-4-bromophenolate anion, so that the single-crystal product can be regarded as a co-crystal of two complex species, *viz.* $[Zn(C_{13}H_9N_2O)_2]$ and $[Zn(C_{13}H_9N_2O)(C_{13}H_8BrN_2O)]$. The refinement generates a ratio of 0.67 (2):0.33 (2) of the former to the latter. The asymmetric unit also contains two solvent

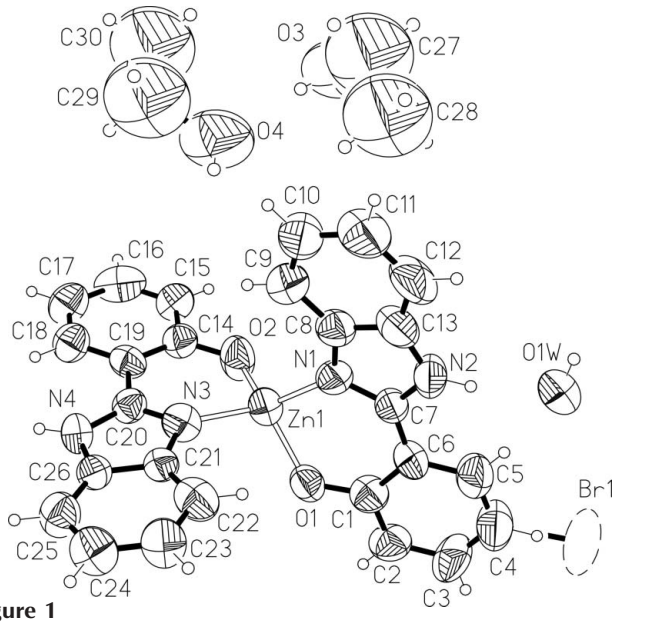


Figure 1
Plot of the asymmetric unit of (I) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The minor component Br atom is shown as a dotted ellipse.

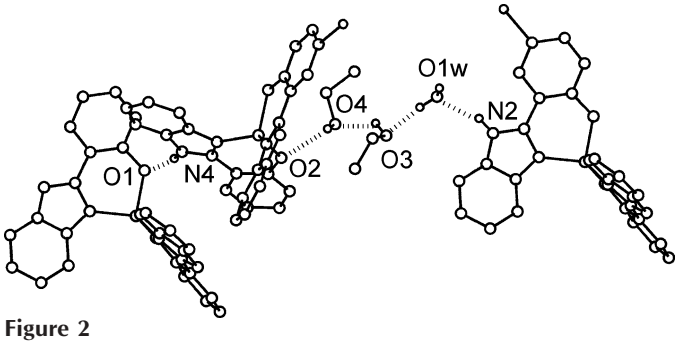


Figure 2
The intermolecular hydrogen-bond (dashed lines) systems in the supramolecular array. With the exception of those involved in hydrogen-bond interactions, H atoms have been omitted for clarity.

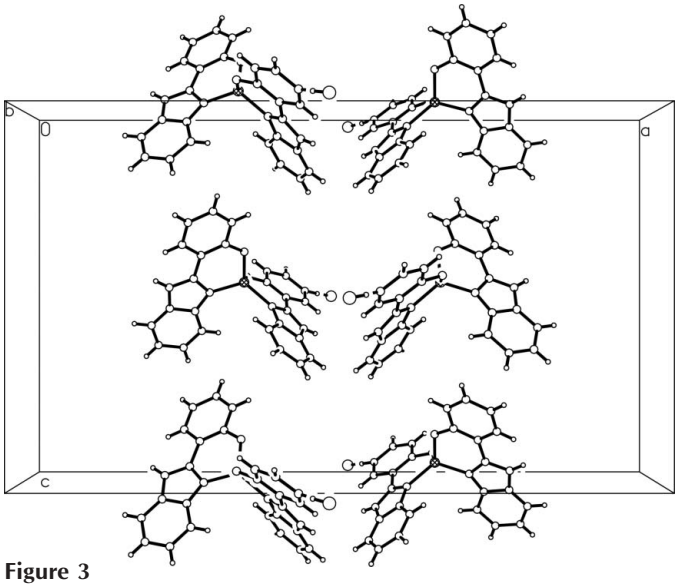


Figure 3
Perspective view of the stacking pattern. The solvent water and ethanol molecules have been omitted for clarity.

ethanol molecules in general positions and a water molecule with the O atom located on a twofold axis.

The geometrical parameters involving the central Zn^{II} ion (Table 1) are similar to those found in a similar co-crystalline zinc(II) complex (Tong, 2005*b*), while the C—Br bond dimension [1.901 (6) Å] is comparable to that found in the literature (Li *et al.*, 2002). The dihedral angles between the phenolate and benzimidazole rings are *ca* 9.4 and 11.5°, similar to cases in the literature (Tong, 2005*a*), indicating a reasonable degree of coplanarity in the ligand systems. An intermolecular hydrogen bond (N4—H···O1) connects directly adjacent complex molecules, while N2—H···O1*W* and O4—H···O2 hydrogen bonds connect complexes with solvent water and ethanol molecules, respectively, and these solvent residues are also connected to one another by O1*W*—H···O3 and O3—H···O4 hydrogen bonds (Fig. 2). These hydrogen bonds connect adjacent molecules into three-dimensional arrays (Fig. 3).

Experimental

Into a solution of 2-(benzimidazol-2-yl)phenol (0.021 g, 0.1 mmol) and 2-(benzimidazol-2-yl)-4-bromophenol (0.029 g, 0.1 mmol) in ethanol (4 ml), was diffused a solution of zinc acetate dihydrate (0.022 g, 0.1 mmol) in water (2 ml) very slowly over a period of about three weeks. Colorless X-ray quality single crystals were isolated with a yield of *ca* 80%. Analysis found: C 58.78, H 4.87, N 9.15%; calculated for $C_{30}H_{30.67}Br_{0.33}N_4O_{4.5}Zn$: C 58.97, H 5.06, N 9.17%. Measurements performed on several specimen all gave the same results, *i.e.* the co-crystal, neither bis[2-(benzimidazol-2-yl)phenolato]zinc(II) nor bis[2-(benzimidazol-2-yl)-4-bromo-phenolato]zinc(II) could be found among the crystal samples.

Crystal data

$[Zn(C_{13}H_9N_2O)(C_{13}H_{8.67}Br_{0.33}N_2O)]\cdot 2C_2H_6O\cdot 0.5H_2O$
M_r = 611.26
Orthorhombic, *Iba*2
a = 32.459 (3) Å
b = 9.408 (1) Å
c = 19.053 (2) Å
V = 5818.5 (10) Å^3
Z = 8
D_x = 1.396 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1648 reflections
θ = 2.3–26.1°
μ = 1.35 mm^{-1}
T = 293 (2) K
Plate, colorless
0.36 × 0.26 × 0.05 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.643, T_{max} = 0.936
12802 measured reflections
4727 independent reflections
2387 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 26.0°
$h = -40 \rightarrow 31$
$k = -11 \rightarrow 10$
$l = -18 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.209
S = 0.95
4727 reflections
303 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1164P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Absolute structure: Flack (1983), 1772 Friedel pairs
Flack parameter: 0.01 (3)

Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.901 (6)	Zn1—N1	1.953 (8)
Zn1—O2	1.917 (7)	Zn1—O1	1.954 (6)
Zn1—N3	1.942 (8)		
O2—Zn1—N3	95.2 (3)	O2—Zn1—O1	116.3 (3)
O2—Zn1—N1	121.1 (3)	N3—Zn1—O1	111.1 (3)
N3—Zn1—N1	120.3 (3)	N1—Zn1—O1	94.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O3^{i}	0.84 (2)	1.91 (3)	2.733 (11)	165 (8)
O4—H4*O*···O2^{ii}	0.82	1.98	2.797 (12)	171
O3—H3*O*···O4	0.82	1.92	2.738 (16)	173
N2—H2*A*···O1*W*	0.86	2.02	2.833 (9)	157
N4—H4*A*···O1^{iii}	0.86	1.97	2.799 (8)	163

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

One of the two 2-(benzimidazol-2-yl)phenolate anion ligands is statistically disordered with respect to 2-(benzimidazol-2-yl)-4-bromophenolate. The refinement results in a ratio of 0.67 (2):0.33 (2) of H to Br substituents on the statistically disordered 4-position of the phenolate ring. The C—C and C—O bond dimensions of the two heavily disordered solvent ethanol molecules were restrained to be respectively identical to each other, and the same isotropic or anistropic displacement parameters were used for these C atoms; the resulting bond dimensions were considered to be acceptable. The O—H bond dimensions for the disordered solvent water molecule were restrained to a typical value [0.85 (2) Å]. The short intermolecular Br1···C28 contact is related to the disorder of the relevant ethanol molecule. The final empirical formula from the refinement for the title compound is in agreement with that from the elemental analysis. Non-water H atoms were placed in calculated positions using the riding-model approximation (C—H = 0.93 Å for the aromatic ring, 0.96 Å for methyl and 0.97 Å for methylene H atoms; N—H = 0.86 Å for imidazole H atoms; O—H = 0.82 Å for the ethanol OH group H atoms), with their displacement parameters tied to those of the parent atoms [U_{iso}(H) = 1.2U_{eq}(C,O) for aromatic, methylene and water H atoms; U_{iso}(H) = 1.5U_{eq}(C,O) for methyl and ethanol OH 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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References

Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Li, J., Zhang, F.-X. & Shi Q.-Z. (2002). *Chin. J. Inorg. Chem.* **18**, 643–645.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Tong, Y.-P. (2005*a*). *Acta Cryst.* E**61**, m1472–m1474.
Tong, Y.-P. (2005*b*). *Acta Cryst.* E**61**, m1595–m1597.
Tong, Y.-P., Chen, X.-M. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m166–m168.
Yu, G., Yin, S., Liu, Y., Shuai, Z. & Zhu, D. (2003). *J. Am. Chem. Soc.* **125**, 14816–14824.