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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$   
Disorder in main residue  
 $R$  factor = 0.056  
 $wR$  factor = 0.140  
Data-to-parameter ratio = 15.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**Bis[2-(benzimidazol-2-yl)phenolato- $\kappa^2N,O$ ]-  
zinc(II)–bis[5-amino-2-(benzimidazol-2-yl)-  
phenolato- $\kappa^2N,O$ ]zinc(II)–ethanol–water  
(0.56/0.44/2/0.5)**

Reacting zinc(II) with 2-(2-hydroxyphenyl)benzimidazole, H(hpb), and 2-(4-amino-2-hydroxyphenyl)benzimidazole, H(apb), yields a cocrystalline mixture of  $\text{Zn}(\text{hpb})_2$  and  $\text{Zn}(\text{apb})_2$ , complexes of the two deprotonated phenolate ligands. The ligands chelate to the  $\text{Zn}^{\text{II}}$  ions in a tetrahedral geometry and are statistically disordered with an occupancy ratio of 0.56 (1):0.44 (1). Ethanol and water molecules also cocrystallize in the crystal structure, with the O atom of the solvent water molecule located on a twofold axis, giving an overall formula  $[\text{Zn}(\text{C}_{13}\text{H}_{9.44}\text{N}_{2.44}\text{O})_2] \cdot 2\text{C}_2\text{H}_6\text{O} \cdot 0.5\text{H}_2\text{O}$ . The neutral complexes are connected to one another by intermolecular hydrogen bonding interactions that extend into three-dimensional arrays.

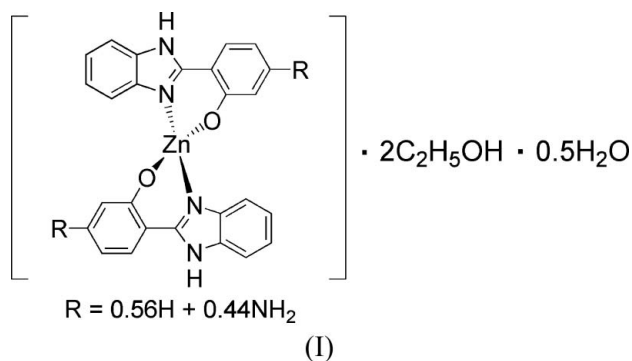
Received 28 June 2005

Accepted 11 July 2005

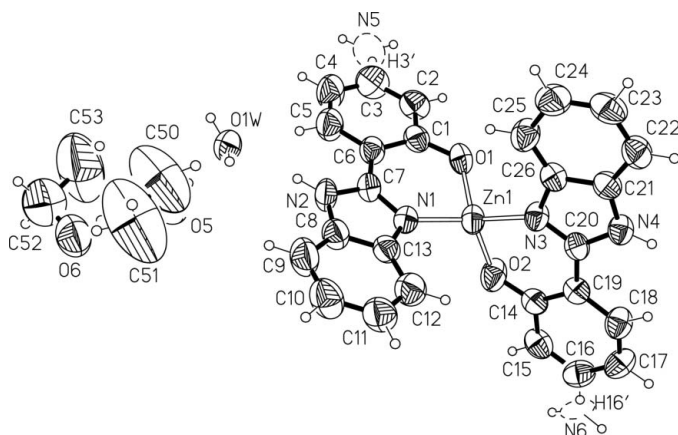
Online 20 July 2005

## Comment

Many  $d^{10}$ -metal complexes have shown excellent luminescent properties and have been used as emitters for electro-luminescent diodes (Nakamura *et al.*, 1994; Hamada *et al.*, 1996). Among them, some  $\text{Zn}^{\text{II}}$  complexes with  $N,O$ -donor ligands have shown improved electron transfer properties (Sapochak *et al.*, 2002; Yu *et al.*, 2003). Therefore, such  $\text{Zn}^{\text{II}}$  complexes have potential both as excellent emitters and as electron transfer materials in organic diodes.



Recently, a number of photoluminescent metal complexes with benzimidazole ligands have been reported. For example, bis[2-(2'-hydroxyphenyl)benzimidazolato]beryllium(II) (Tong *et al.*, 2005) exhibits a strong blue fluorescence emission. We anticipated that  $\text{Zn}^{\text{II}}$  complexes with ligands derived from benzimidazole should also have excellent photoluminescence; on the other hand, we were also interested in the synthesis and photoluminescence of mixed-ligand metal complexes of such ligands, and anticipated that the introduction of a second ligand may cause significant changes to the emission properties, including the emission wavelength.

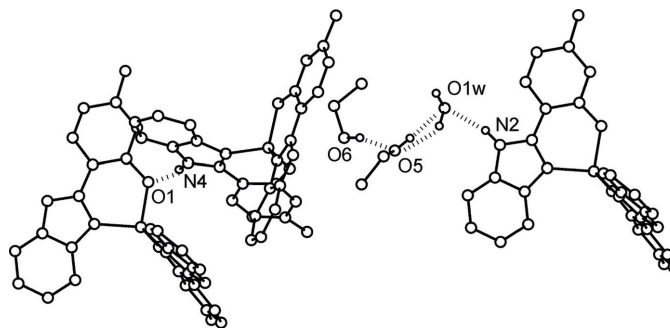

**Figure 1**

Plot of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The amine N atoms of the minor disorder component are shown as dotted ellipsoids.

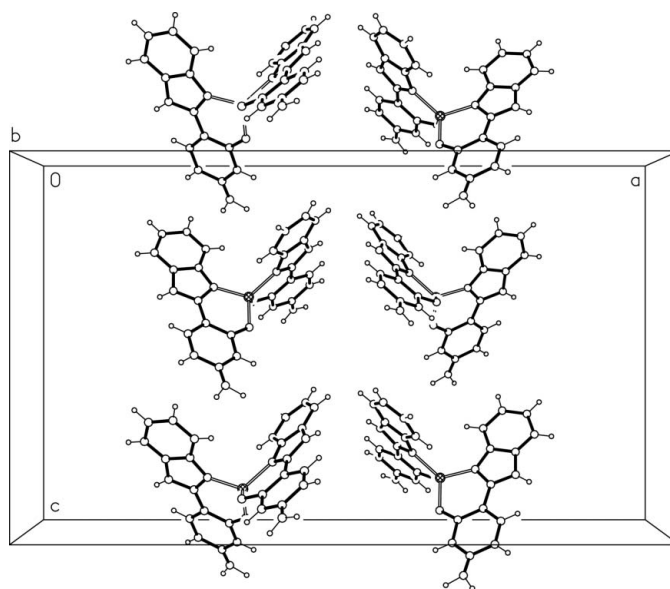
A mixed-ligand  $\text{Zn}^{\text{II}}$  complex with 2-(2'-hydroxyphenyl)benzoxazole and 2-(2'-hydroxyphenyl)benzothiazole has been reported from laboratory (Tong *et al.*, 2004) and is luminescent. 2-(4'-Amino-2'-hydroxyphenyl)benzimidazole, H(apb), and 2-(2'-hydroxyphenyl)benzimidazole, H(hpb), are similar ligands, but the introduction of an electron-donating amine group in the 4'-position will increase the negative charge density and result in the reduction of the energy gap; therefore the emitting wavelength will be red-shifted relative to those of H(hpb) or its  $\text{Zn}^{\text{II}}$  complexes.

We report here the structure, (I), of the single crystalline product, containing two different complex species, obtained by reacting  $\text{Zn}^{\text{II}}$  with H(hpb) and H(apb). In each case, the central  $\text{Zn}^{\text{II}}$  cation is chelated by two ligands through the benzimidazole N atoms and the phenolate O atoms of the deprotonated ligands. The coordination geometry at the Zn atom is approximately tetrahedral in both compounds. The anionic ligands are statistically disordered with respect to the 4-substituents on the phenolate rings. Refinement converged with the occupancies of the disordered H and  $\text{NH}_2$  substituents at 0.56 (1):0.44 (1). Hence, the products are best described as the cocrystalline complexes  $[\text{Zn}(\text{C}_{13}\text{H}_9\text{N}_2\text{O})_2]_{0.56}$ ,  $[\text{Zn}(\text{hpb})_2]_{0.56}$ , and  $[\text{Zn}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O})_2]_{0.44}$ ,  $[\text{Zn}(\text{apb})_2]_{0.44}$ . The asymmetric unit also contains two ethanol solvent molecules in general positions and a solvent water molecule with its O atom located on a twofold axis.

The bond dimensions [ $\text{Zn}-\text{N} = 1.950$  (4) and  $1.966$  (4) Å, and  $\text{Zn}-\text{O} = 1.918$  (4) and  $1.927$  (4) Å] around the central  $\text{Zn}^{\text{II}}$  ion are slightly shorter than those found in other  $\text{Zn}^{\text{II}}$  complexes with *N,O*-donor ligands (Yu *et al.*, 2003; Sapochak *et al.*, 2002). The dihedral angles between the phenolate and benzimidazole rings are *ca* 7.7 and 8.0°, indicating a reasonable degree of planarity in the ligand systems. This is similar to the situation in the  $\text{Be}^{\text{II}}$  complex with H(hbp) (Tong *et al.*, 2005). Intermolecular  $\text{N4}-\text{H}\cdots\text{O1}$  hydrogen bonds link the complex molecules, while  $\text{N2}-\text{H}\cdots\text{O1W}$  bonds link the complexes to uncoordinated water molecules (Table 1). Additional  $\text{O5}-\text{H}\cdots\text{O1W}$ ,  $\text{O1W}-\text{H}\cdots\text{O5}$  and  $\text{O6}-\text{H}\cdots\text{O5}$


**Figure 2**

Intermolecular hydrogen bonds in the crystal structure, drawn as dashed lines. With the exception of those involved in hydrogen-bond interactions, H atoms have been omitted for clarity.


**Figure 3**

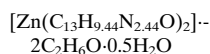
Perspective view of the stacking pattern. The solvent water and ethanol molecules have been omitted for clarity.

hydrogen bonds link the solvent residues and also connect adjacent molecules into three-dimensional arrays (Fig. 3).

## Experimental

A solution of 2-(4'-amino-2'-hydroxyphenyl)benzimidazole (0.1 mmol, 0.023 g) and 2-(2'-hydroxyphenyl)benzimidazole (0.1 mmol, 0.021 g) in ethanol (10 ml) was diffused very slowly into a solution of zinc acetate dihydrate (0.1 mmol, 0.022 g) in water (5 ml). The product separated into the ethanol layer, and colorless plate-like crystals were isolated after two weeks in approximately 70% yield. Analysis found: C 60.45, H 5.48, N 11.37%; calculated for  $\text{C}_{30}\text{H}_{51.88}\text{N}_{4.88}\text{O}_{4.5}\text{Zn}$ : C 60.23, H 5.37, N 11.43%. Measurements performed on several specimens all gave the same cocrystalline structure. It was not possible to find discrete samples of either bis[2-(2'-hydroxyphenyl)benzimidazolato]zinc(II) or bis[2-(4'-amino-2'-hydroxyphenyl)benzimidazolato]zinc(II) among the crystalline products.

## Crystal data


 $M_r = 598.21$ 
Orthorhombic, *Iba2*
 $a = 32.131$  (4) Å

 $b = 9.7172$  (13) Å

 $c = 18.918$  (2) Å

 $V = 5906.7$  (13) Å<sup>3</sup>
 $Z = 8$ 
 $D_x = 1.345$  Mg m<sup>-3</sup>
Mo  $K\alpha$  radiation

Cell parameters from 2666

reflections

 $\theta = 2.5$ – $20.7^\circ$ 
 $\mu = 0.88$  mm<sup>-1</sup>
 $T = 293$  (2) K

Plate, colorless

 $0.35 \times 0.27 \times 0.04$  mm

## Data collection

Bruker APEX area-detector diffractometer

 $\varphi$  and  $\omega$  scansAbsorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.749$ ,  $T_{\max} = 0.966$ 

15485 measured reflections

5974 independent reflections

3932 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.047$ 
 $\theta_{\text{max}} = 27.0^\circ$ 
 $h = -41 \rightarrow 27$ 
 $k = -12 \rightarrow 11$ 
 $l = -18 \rightarrow 24$ 

## Refinement

Refinement on  $F^2$ 
 $R[F^2 > 2\sigma(F^2)] = 0.056$ 
 $wR(F^2) = 0.140$ 
 $S = 1.04$ 

5974 reflections

378 parameters

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.063P)^2]$ 
where  $P = (F_o^2 + 2F_c^2)/3$ 
 $(\Delta/\sigma)_{\text{max}} = 0.001$ 
 $\Delta\rho_{\text{max}} = 0.51$  e Å<sup>-3</sup>
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

Absolute structure: Flack (1983),

2640 Friedel pairs

Flack parameter: 0.026 (16)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N2}-\text{H2A} \cdots \text{O1W}$	0.86	2.02	2.839 (5)	160
$\text{O1W}-\text{H1W} \cdots \text{O5}$	0.84 (1)	2.12 (5)	2.755 (6)	132 (6)
$\text{N4}-\text{H4A} \cdots \text{O1}^i$	0.86	1.98	2.816 (5)	165
$\text{O5}-\text{H5C} \cdots \text{O1W}$	0.82	1.95	2.755 (6)	169
$\text{O6}-\text{H6C} \cdots \text{O5}^{ii}$	0.82	1.90	2.695 (8)	163

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

For the ligands, the 2-(2'-hydroxyphenyl)benzimidazolone ion is disordered with respect to the 2-(4'-amino-2'-hydroxyphenyl)benzimidazolone ion. The C–N (amino group) dimensions were restrained to be equal to each other, and the resulting values of 1.354 (8) and 1.355 (8) Å were regarded as reasonable when compared with those found in the literature (Czugler *et al.*, 1976; Lin *et al.*, 1978). The solvent water and ethanol molecules are disordered. The O–H dimensions of the water molecule were restrained to *ca* 0.85 (1) Å, which is typical for refinement of disordered water molecules; the short non-bonding intermolecular  $\text{O1W}-\text{H1W} \cdots \text{H5A}$  contacts may be related to the disorder in the water and ethanol

molecules. For the ethanol molecules, the C–C and C–O dimensions were restrained to typical values of *ca* 1.500 (5) and 1.420 (5) Å, respectively, and the refinement of other geometrical parameters around the ethanol molecules can be considered to be reasonable. The occupancy factor for the amine groups in both ligands refined to 0.44 (1), with that for both disordered H atoms 0.56 (1). The empirical formula from the refinement is consistent with that from elemental analysis. Non-water H atoms were placed in calculated positions using the riding-model approximation (C–H = 0.93 Å for aromatic ring, 0.96 Å for methyl, 0.97 Å for methylene H atoms; N–H = 0.86 Å for amino and imidazole H atoms; O–H = 0.82 Å for the ethanol OH group), with their displacement parameters tied to those of the parent atoms [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic, amine, methylene and water H atoms;  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl and ethanol OH group 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*.

The author thanks Professor Xiao-Ming Chen, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, People's Republic of China, for his generous help and support of this work, and also thanks Hanshan Normal College, People's Republic of China, for support of this work.

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