Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Chloro[2-(1-ethyl-1*H*-benzimidazol-2-yl)phenol-κN^3][2-(1-ethyl-1*H*-benzimidazol-2-yl)phenolato-κ$^2N^3$,*O*]zinc(II)

Yi-Ping Tong[a,b] and Bao-Hui Ye[a]*

[a]School of Chemistry and Chemical Engineering, Sun Yat-Sen University, 510275 Guangzhou, People's Republic of China, and [b]Department of Chemistry, Hanshan Normal College, 521041 Chaozhou, People's Republic of China

Correspondence e-mail: cesybh@zsu.edu.cn

The title compound, [Zn($C_{15}H_{13}N_2O$)Cl($C_{15}H_{14}N_2O$)], has a mononuclear structure, in which the central zinc ion is coordinated by two benzimidazole N atoms, one phenolate O atom and a chloride ion in a distorted tetrahedral arrangement. In the crystal structure, there are intramolecular π–π stacking interactions between the phenol and benzimidazole ring systems; intermolecular π–π stacking interactions between the benzimidazole ring systems of adjacent molecules are also present. A strong intermolecular O—H···O hydrogen bond is also observed.

Received 17 September 2004
Accepted 8 November 2004
Online 27 November 2004

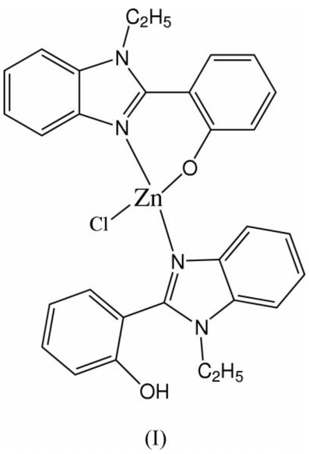
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.063
wR factor = 0.162
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, much attention has been paid to d^{10} metal complexes with aromatic *N,O*-donor ligands, because of their potential photoluminescent and electroluminescent properties (Wu *et al.*, 2000; White-Morris *et al.*, 2002; Felder *et al.*, 2001). For example, zinc complexes with 2,2′,2′′-tripyridylamine, 2,2′,3′′-tripyridylamine and 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate have exhibited excellent photoluminescent properties (Yang *et al.*, 2000; Zheng *et al.*, 2003). Among these, the neutral complexes have also shown excellent electroluminescence, due to better thermal stability and vacuum sublimation properties (Nakamura *et al.*, 1994; Hamada *et al.*, 1996, 1997). Some, such as bis[2-(2-hydroxyphenyl)benzothiazolate]zinc (Yu *et al.*, 2003), have even shown excellent electronic transport character. In our efforts to design and synthesize the neutral zinc complex with 2-(1-ethyl-1*H*-benzoimidazol-2-yl)phenol, to produce a highly photoluminescent and electroluminescent compound, we obtained instead a non-luminescent zinc complex, (I) (Fig. 1).



(I)

Compound (I) has a mononuclear structure, in which the central zinc ion is coordinated by two benzimidazole N atoms,

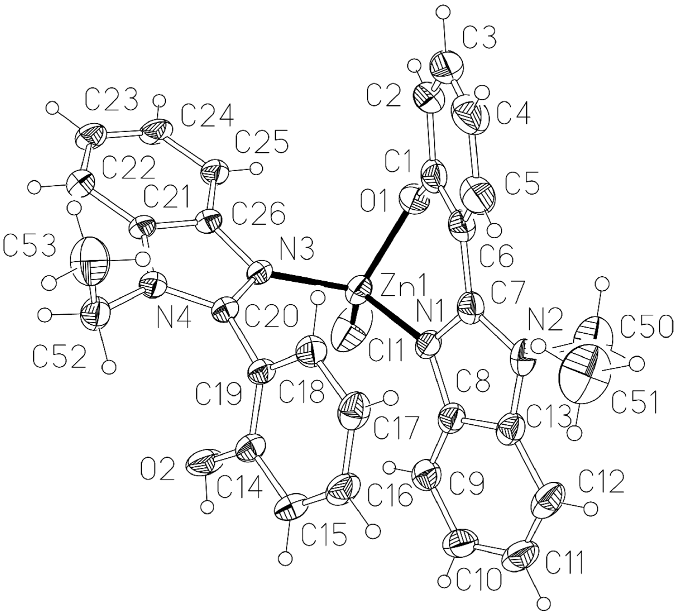


Figure 1
View of the molecule of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

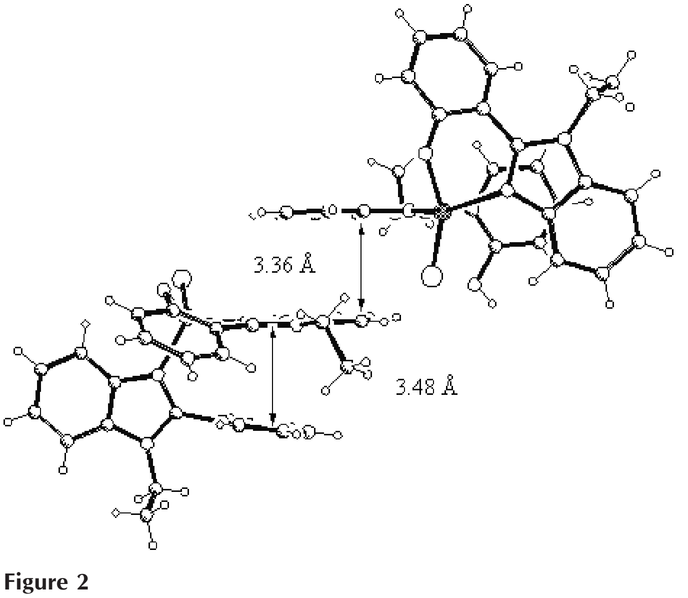


Figure 2
The π–π stacking interactions in the crystal structure.

one phenolate O atom and a chloride ion in a distorted tetrahedral arrangement. The two Zn—N bonds are slightly different, with distances of 2.021 (3) and 1.989 (3) Å, and the Zn—O distance is 1.974 (3) Å; these are all similar to literature values (Yu *et al.*, 2003; Zhang *et al.*, 2004). The Zn—Cl distance is 2.188 (2) Å, which is slightly shorter than documented values of 2.258 and 2.280 Å (Darensbourg *et al.*, 1998; Quiroz-Castro *et al.*, 2000). Steric hindrance caused by the ethyl groups forces the ligands to be highly distorted, with torsion angles of −28.8 (7) and −98.9 (5)° for C1—C6—C7—N1 and C14—C19—C20—N3, respectively. This non-coplanarity between phenol(ate) and benzimidazole ring systems is quite different from other similar mononuclear complexes (Crane *et al.*, 1995), where the benzimidazole and phenol(ate) moieties are almost coplanar.

In the crystal structure there are intramolecular π–π stacking interactions between the phenol and benzimidazole ring systems, with a distance of *ca* 3.48 Å (Fig. 2). Intermolecular π–π stacking interactions between the benzimidazole ring systems of adjacent molecules are also present; the stacking distance is *ca* 3.36 Å. A strong intermolecular O—H···O hydrogen bond is also observed (Table 2). Both the π–π stacking and the hydrogen-bond interactions contribute to the stability of the supramolecular arrays.

The non-luminescent behavior of (I) is probably due to structural changes and the presence of the heavier coordinated Cl atom. The non-coplanarity of the ligands can directly reduce the photoluminescent properties. Generally speaking, the heavy-atom effect will cause the enforcement of intersystem crossing (ISC), *e.g.* from the S_1 excited state to the T_1 excited state. Therefore, the fluorescent emission efficiency will certainly reduce. Both these effects are harmful to photoluminescence. This is in agreement with the observed behavior of (I).

Experimental

The title compound, (I), was synthesized by a multi-step reaction based on literature methods (Anthony & Philip, 1981). Firstly, the ligand 2-(1-ethyl-1*H*-benzoimidazol-2-yl)phenol was synthesized *via* a two-step reaction from a mixture of salicylic acid (0.138 g, 1 mmol) and *o*-phenylenediamine (0.108 g, 1 mmol) in syrupy phosphoric acid at *ca* 520 K for over 5 h (yield *ca* 10%). The crude product was then further reacted with bromoethane under reflux conditions to give 2-(1-ethyl-1*H*-benzimidazol-2-yl)phenol in *ca* 70% yield. Secondly, (I) was synthesized under hydrothermal conditions. A mixture of zinc acetate dihydrate (0.1 mmol, 0.022 g), the synthesized ligand (0.2 mmol, 0.055 g) and water (10 ml) with a pH value of *ca* 10 controlled by the addition of small amounts of KOH and hydrochloric acid solutions, was sealed in a Teflon-lined 23 ml stainless steel container, heated at a temperature of 433 K for 4 d, and then cooled to room temperature at a rate of 5 K h^{-1}. Analysis found: C 62.46, H 4.58, and N 9.69%; calculated for $C_{30}H_{27}ClN_4O_2Zn$: C 62.51, H 4.72, and N 9.72%.

Crystal data

$[Zn(C_{15}H_{13}N_2O)Cl(C_{15}H_{14}N_2O)]$
$M_r = 576.38$
Monoclinic, $P2_1/c$
$a = 11.6509$ (10) Å
$b = 18.0743$ (17) Å
$c = 16.5092$ (16) Å
$\beta = 128.360$ (2)°
$V = 2726.0$ (4) Å^3
$Z = 4$
$D_x = 1.404$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1612 reflections
$\theta = 2.2$–25.9°
$\mu = 1.03$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.17 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.844$, $T_{max} = 0.904$
15264 measured reflections
5582 independent reflections
3103 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 26.5°$
$h = -11 \rightarrow 14$
$k = -21 \rightarrow 22$
$l = -20 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.163$
$S = 1.01$
5582 reflections
346 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.62$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.974 (3)	Zn1—N3	2.021 (3)
Zn1—N1	1.989 (3)	Zn1—Cl1	2.1876 (16)
O1—Zn1—N1	91.60 (14)	N1—Zn1—Cl1	116.60 (11)
O1—Zn1—N3	106.26 (13)	N3—Zn1—Cl1	113.81 (11)
N1—Zn1—N3	112.01 (14)	C1—O1—Zn1	116.3 (3)
O1—Zn1—Cl1	114.14 (12)		
C1—C6—C7—N1	−28.8 (7)	C14—C19—C20—N3	−98.9 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.82	1.86	2.679 (4)	179

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

The H atoms were placed in calculated positions (C—H = 0.93 Å for all aromatic ring H atoms, 0.96 Å for all methyl H atoms, 0.97 Å for all methylene H atoms, and 0.82 Å for the hydroxyl H atom). They were refined using the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for all aromatic ring H atoms and methylene H atoms, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for all methyl H atoms and the hydroxyl H atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL*97.

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

References

Anthony, W. A. & Philip, J. B. (1981). *J. Heterocycl. Chem.* **18**, 803–805.

Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Crane, J. D., Hughes, R. & Sinn, E. (1995). *Inorg. Chim. Acta*, **237**, 181–185.

Darensbourg, D. J., Yoder, J. C., Struck, G. E., Holtcamp, M. W., Draper, J. D. & Reibenspies, J. H. (1998). *Inorg. Chim. Acta*, **274**, 115–121.

Felder, D., Nierengarten J. & Barigelletti, F. (2001). *J. Am. Chem. Soc.* **123**, 6291–6299.

Hamada, Y., Sano, T., Fujii, H. & Nishio, Y. (1996). *Jpn. J. Appl. Phys.* **35**, L1339—L1341.

Hamada, Y., Sano, T., Fujii, H., Nishio, Y., Takahashi, H. & Shibata, K. (1997). *Appl. Phys. Lett.* **71**, 3338–3340.

Nakamura, N., Wakabayashi, S., Miyairi, K. & Fujii, T. (1994). *Chem. Lett.* pp. 1741–1742.

Quiroz-Castro, E., Bernes, S., Barba-Behrens, N., Tapia-Benavides, R., Contreras, R. & Noth, H. (2000). *Polyhedron*, **19**, 1479–1484.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

White-Morris, R. L., Olmstead, M. M., Jiang, F., Tinti, D. S. & Balch, A. L. (2002). *J. Am. Chem. Soc.* **124**, 2327–2336.

Wu, Q., Lavigne, J. A., Tao, Y., D'Iorio, M. & Wang, S. (2000). *Inorg. Chem.* **39**, 5248–5254.

Yang, W., Schmider, H., Wu, Q., Zhang, Y. & Wang, S. (2000). *Inorg. Chem.* **39**, 2397–2404.

Yu, G., Yin, S., Liu, Y., Shuai, Z. & Zhu, D. (2003). *J. Am. Chem. Soc.* **125**, 14816–14824.

Zhang, J., Gao, S. & Che, C. (2004). *Eur. J. Inorg. Chem.* pp. 956–959.

Zheng, S. L., Zhang, J. P., Chen, X. M., Huang, Z. L., Lin, Z. Y. & Wong, W. T. (2003). *Chem. Eur. J.* **9**, 3888–3896.