



Synthesis, Crystal Structure and Photoluminescence of Cocrystal of Bis(2-(2-hydroxyphenyl)benzimidazole)zinc and DMF Solvate

YI-PING TONG¹, YAN-WEN LIN^{2,*} AND YAN CHEN³

¹Department of Chemical Engineering, Huizhou University, Huizhou 516007, P.R. China

²Department of Life Science, Huizhou University, Huizhou 516007, P.R. China

³Department of Chemistry, Hanshan Normal University, Chaozhou 521041, P.R. China

*Corresponding author: Fax: + 86 752 2527229; Tel: + 86 752 2527229; E-mail: linyw@hzu.edu.cn

(Received: 6 November 2010;

Accepted: 18 August 2011)

AJC-10281

The Zn(II) complex with 2-(2-hydroxyphenyl)benzimidazole, namely [Zn(2-(2-hydroxyphenyl)benzimidazole)₂]-2DMF (1·2DMF) has been synthesized and characterized using X-ray crystallography and photoluminescence. The crystal data for this complex is as follows: orthorhombic, space group *pbcn*, *M_r* = 630.01, *Z* = 4, *a* = 15.405(4) Å, *b* = 8.818(3) Å, *c* = 22.068(6) Å, *V* = 2997.5(15) Å³, *D_c* = 1.396 g/cm³, *μ* = 0.867 mm⁻¹, *F*(000) = 1312, the final *R₁* and *wR₂* are 0.0468 and 0.1093 for 2394 unique reflections (*I* ≥ 2σ(*I*)) and *R₁* and *wR₂* are 0.0755 and 0.1225 for all 14163 reflections. The steady-state and time-resolved photoluminescent spectra for this compound have also been studied. The emission property can be ascribed to π→π* ligand-centered charge transfer transition (LCCT).

Key Words: Crystal structure, Photoluminescence, Zinc complex, 2-(2-Hydroxyphenyl)benzimidazole.

INTRODUCTION

The Zn(II) complexes with *N,O*-donor chelate ligands have been widely studied owing to their potential applications in electroluminescence field in recent decades¹⁻⁶. These neutral compounds have important behaviours such as improved vacuum-film-forming and thermally deposited properties, which are very important for their performance in organic light-emitting diodes⁷⁻¹⁰.

The *N,O*-donor phenolic ligands are very important for the construction of luminescent neutral complexes with excellent electroluminescence property. The deprotonated species for these organic ligands are suitable for the formation of different organic metal complexes with different coordination modes and/or coordination geometries as the O atoms of deprotonated hydroxy group could act as terminal ligand or as bridging ligands. Thus, different complexes with monomeric to oligomeric structures have been synthesized and applied as emitters in organic diodes with blue or greenish blue light.

We have been interested in the syntheses, structures and photoluminescence of organic metal complexes with *N,O*-donor phenolic ligands¹¹, and reported a crystal structure of **1** without solvate¹². Herein, we report another structure of **1** co-crystallized with DMF solvate, *i.e.* 1·2 DMF, which is quite different from **1** in structure,¹² together with steady-state and time-resolved fluorescence analyses and thermogravimetric analysis (TG).

EXPERIMENTAL

All the reagents were of analytical grade and used without further purification, unless otherwise stated. Elemental analysis was performed with a Vario E1 elemental analyzer; the steady-state and time-resolved fluorescence spectra were carried with an Edinburgh instrument FLS920 fluorescence spectrophotometer using Xe light and hydrogen gas light resource; TG data were collected with a Perkin-Elmer TGS-2 analyzer.

Synthesis: A solution of zinc acetate dihydrate (0.11 g, 0.5 mmol) in DMF (20 mL) was mixed with a solution of 2-(2-hydroxyphenyl)benzimidazole (0.21 g, 1 mmol) in DMF (20 mL), the resulting solution was allowed to stand unperturbedly for a few weeks. Colourless plate crystals were found with a yield of *ca.* 70%. Anal. calcd. for C₃₂H₃₂N₆O₄Zn, C, 61.0; H, 5.12; N, 13.34, found C, 61.05; H, 5.15; N, 13.38. FTIR (in KBr pellet/cm⁻¹): 3331 s, 1568 s, 1484 m, 1442 m, 1408 s, 1308 m, 1248 m, 1140 m, 871 w, 745 m, 654 m, 560 w, 501 w.

X-ray structure determination: A colourless single crystal for the present Zn(II) complex with a dimension of *ca.* 0.57 mm × 0.48 mm × 0.23 mm was selected and mounted on a glass fiber for X-ray diffraction analysis. The determination and data collection were performed with MoK α radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD diffractometer equipped with a graphite monochromator situated in the incident beam. A total of 14163 reflections were collected in

the range of $1.85^\circ \leq \theta \leq 28^\circ$ by using a ω - 2θ scan mode at 293(2) K, in which 3476 independent reflections with $R_{\text{int}} = 0.0374$ and 2394 observed reflections with $I > 2\sigma(I)$ were used in the structure determination and refinements. The structure was solved by direct method and refined on F^2 by a full-matrix least-squares method using SHELXTL program package¹³. The absorption correction was performed by using SADABS¹⁴. All the non-hydrogen atoms were refined anisotropically and the organic hydrogen atoms were placed at calculated positions with isotropic refinement. The final refinement gave $R = 0.0468$, $wR = 0.1225$ ($w = 1/[\sigma^2(F_o^2) + (0.0578 P)^2 + 0.9188 P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 2394 observed reflections with $I > 2\sigma(I)$, goodness-of-fit on $F^2 = 1.030$ and $(\Delta/\sigma)_{\text{max}} = 0.000$. The maximum peak in the final difference Fourier map is $0.374 \text{ e}/\text{\AA}^3$ and the minimum one $-0.34 \text{ e}/\text{\AA}^3$. Details of crystal data collection and refinement parameters for the title compound is listed in Table-1. All non-hydrogen fractional atomic coordinates and equivalent isotropic temperature factors of the present Zn(II) complex are listed in Table-2. The main bond parameters around central Zn atom are given in Table-3.

Thermal stability determination: Thermogravimetric analysis (TG) was performed to investigate thermal stability of the Zn(II) complex under flow dinitrogen atmosphere at a heating rate $10^\circ\text{C}/\text{min}$ by heating the microcrystals.

RESULTS AND DISCUSSION

Structural description: As shown in Fig. 1, the present compound is a co-crystal consisting of a Zn(II) complex, **1** and DMF solvate with a formula $1 \cdot 2\text{DMF}$, in which the complex consists of a Zn(II) cation and two deprotonated 2-(2-hydroxyphenyl)benzimidazolate anions, with a tetrahedral geometry. The central Zn(II) cation is surrounded by two N and two O atoms from two deprotonated 2-(2-hydroxyphenyl)benzimidazolate ligands with a ZnO_2N_2 environment being similar to that of **1** without solvate found previously¹². The dihedral angles between the two ligand ring systems are *ca.* 77° , indicating significant distortion from ideal tetrahedral structure, which is quite different from the case of **1** without solvate, where the tetrahedral geometry is only slightly distorted (the corresponding dihedral angle is 89°)¹². The N-Zn-N and O-Zn-O angles ($122.62(12)^\circ$ and $125.28(13)^\circ$, respectively) are ideal for tetrahedral geometry, but the O-Zn-O angle is 15.2° larger than that found in **1** without solvate.¹² As shown in Table-3, the Zn-N bond length [$1.9727(19) \text{ \AA}$] is obviously

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT
OF THE TITLE COMPOUND

Empirical formula	$\text{C}_{33}\text{H}_{32}\text{N}_6\text{O}_4\text{Zn}$
Formula weight	630.01
Temperature	293 (2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	
a (\AA)	15.405 (4)
b (\AA)	8.818 (3)
c (\AA)	22.068 (6)
Volume (\AA^3)	2997.5 (15)
Z	4
Calculated density (g cm^{-3})	1.396
Absorption coefficient (mm^{-1})	0.867
F (000)	1312
Crystal size (mm^3)	$0.57 \times 0.48 \times 0.23$
θ Range for data collection ($^\circ$)	$1.85\text{--}28.0$
Index ranges	$-19 \leq h \leq 19, -7 \leq k \leq 11, -29 \leq l \leq 23$
Reflections collected	14163
Independent reflections	3476 [$R_{\text{int}} = 0.0374$]
Completeness to θ_{max} (%)	95.8
Max. and min. transmission	0.8255 and 0.6379
Data / restraints / parameters	3476 / 0 / 199
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0468, wR_2 = 0.1093$
R indices (all data)	$R_1 = 0.0755, wR_2 = 0.1225$
Largest difference peak and hole ($\text{e}/\text{\AA}^3$)	0.374 and -0.340
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2

larger and the Zn-O bond length [$1.9185(18) \text{ \AA}$] is obviously smaller than those in **1** without solvate.¹² The dihedral angles between the benzimidazole and phenolate moieties are only *ca.* 3° , indicating more planar in the ligand rings in $1 \cdot 2 \text{ DMF}$ than in **1** without solvate,¹² where they are *ca.* 7.2° and 7.3° .

The intermolecular hydrogen bond interactions between the NH group of complex molecules and the carbonyl O atom of adjacent DMF solvate (N-H...O $2.745(3) \text{ \AA}$) are present (Table-4, Fig. 2), rendering them into three-dimensional network. No other supramolecular interactions are found in

TABLE-2
NON-HYDROGEN FRACTIONAL COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC
TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^5$) (U_{eq}) FOR Zn(II) COMPOUND

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Zn(1)	5000	143(1)	7500	41(1)	C(6)	4188(2)	231(3)	6102(1)	39(1)
O(1)	4044(1)	-857(2)	7112(1)	56(1)	C(7)	4958(2)	1136(3)	6232(1)	37(1)
O(70)	-163(2)	1934(3)	5312(1)	87(1)	C(8)	6087(2)	2676(3)	6082(1)	41(1)
N(1)	5374(1)	1217(2)	6761(1)	38(1)	C(9)	6735(2)	3628(3)	5864(1)	55(1)
N(2)	5366(1)	2010(2)	5799(1)	43(1)	C(10)	7364(2)	4059(4)	6270(1)	62(1)
N(60)	96(2)	1046(3)	6249(1)	57(1)	C(11)	7362(2)	3576(3)	6870(1)	56(1)
C(1)	3784(2)	-691(3)	6549(1)	44(1)	C(12)	6723(2)	2619(3)	7085(1)	48(1)
C(2)	3045(2)	-1538(4)	6365(1)	59(1)	C(13)	6083(2)	2171(3)	6679(1)	38(1)
C(3)	2744(2)	-1498(4)	5783(1)	63(1)	C(30)	660(3)	207(4)	6655(2)	90(1)
C(4)	3146(2)	-620(4)	5350(1)	59(1)	C(40)	-642(2)	1778(5)	6513(2)	82(1)

the lattice, which is different from the cases in **1** without DMF solvate found previously¹², where both intermolecular hydrogen bond and π - π stacking interactions are present¹². It is probable that the co-crystallized DMF solvate blocks the formation of π - π stacking interactions between the ligand ring systems of adjacent molecules. Moreover the intermolecular N-H...O hydrogen bond between benzimidazole NH group and carbonyl O atom of adjacent DMF solvate in **1**·2DMF is substituted for the intermolecular N-H...O hydrogen bond between benzimidazole NH group and phenolate O atom of adjacent complex in **1** without DMF solvate¹².

TABLE-3
BOND DISTANCES (Å) AND BOND ANGLES (°)
FOR Zn(II) COMPOUND

Bond distances		Bond angles	
Zn(1)-O(1)	1.9185(18)	O(1) # 1-Zn(1)-O(1)	125.28(13)
Zn(1)-N(1)	1.9727(19)	O(1) # 1-Zn(1)-N(1) # 1	94.38(8)
N(2)-C(8)	1.403(3)	O(1)-Zn(1)-N(1) # 1	111.40(8)
O(1)-C(1)	1.314(3)	O(1) # 1-Zn(1)-N(1)	111.40(8)
N(1)-C(7)	1.334(3)	O(1)-Zn(1)-N(1)	94.38(8)
N(1)-C(13)	1.390(3)	N(1) # 1-Zn(1)-N(1)	122.62(12)
N(2)-C(7)	1.379(3)		

Symmetry code for # 1: $-x + 1, y, -z + 3/2$

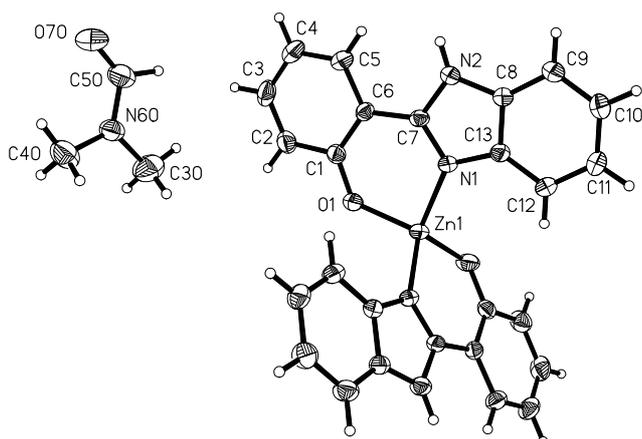


Fig. 1. Ortep diagram for the Zn(II) compound at 30 % probability level

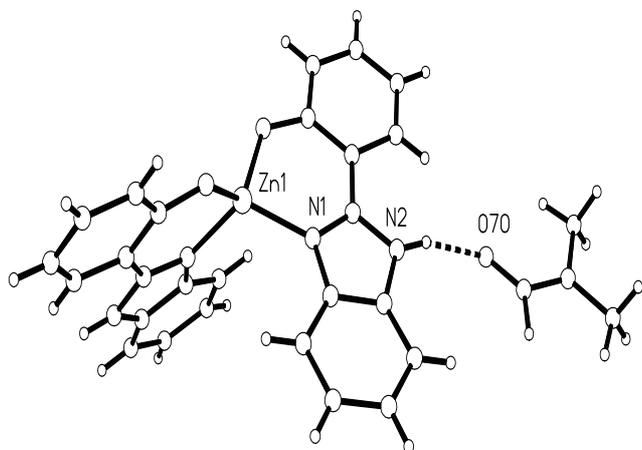


Fig. 2. The N-H...O hydrogen bond interactions between the Zn(II) complex molecule and adjacent DMF solvate

It is interesting that the DMF solvate has much a large effect on the coordination geometry, causing **1** much further

distorted with respect to the case without DMF solvate. This can be ascribed to the observed fact that the supramolecular interactions in **1**·2DMF are markedly different from those in **1** without DMF solvate¹².

TABLE-4
HYDROGEN BOND GEOMETRIES (Å AND °)
FOR Zn(II) COMPOUND

D-H...A	d(D-H)	d(H...A)	d(D...A)
N(2) - H(2A)...O(70) # 2	0.86	1.92	2.745(3)

Symmetry code for # 2: $x + 1/2, -y + 1/2, -z + 1$

Photoluminescent properties: The photoluminescent property of the present Zn(II) complex has been investigated. It emits strong blue light in solid state with maximal emission wavelength at 441 nm (excitation wavelength 325 nm, Fig. 3). The emission nature can be attributed to the ligand-centered charge transfer transition (LCCT) with $\pi \rightarrow \pi^*$ transition property based on molecular orbital calculation (Fig. 4) and previous literatures^{12,15,16}.

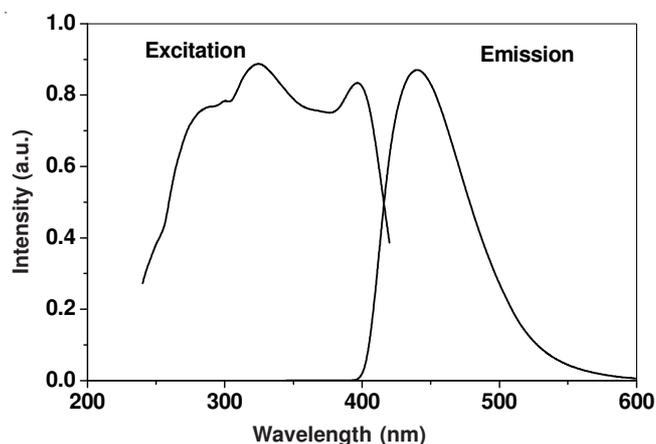


Fig. 3. The excitation (left) and emission (right) spectra of the Zn(II) compound at room temperature in solid state (excitation wavelength 325 nm)

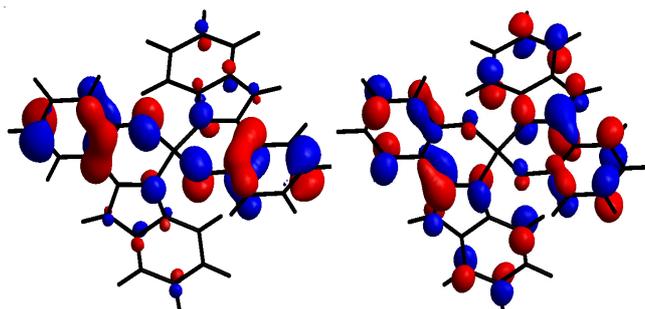


Fig. 4. Contour plots of relevant molecular orbitals of HOMO (left) and LUMO (right) for **1**

The time-resolved emission spectrum has also been carried out. The emission profile can be well fitted using a single exponential decay mode, which gives a lifetime of *ca.* 4.55 ns at room temperature, strongly indicating fluorescent property for the emission process. The lifetime is similar to other Zn(II) complex found previously^{6,12,15}.

Thermal stability analysis: TG curve shows two decomposition temperature of *ca.* 195 and 385 °C for the present

Zn(II) complex, in which the first weight loss of *ca.* 23.2 % corresponds to the weight loss of DMF solvate and the latter the weight loss of decomposition of **1** (Fig. 5).

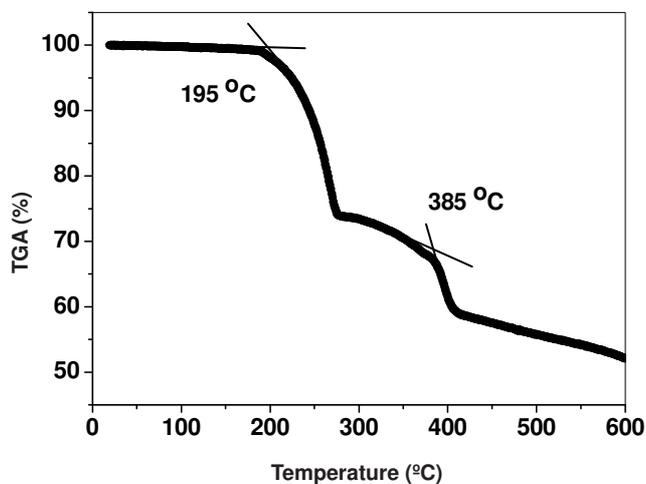


Fig. 5. TGA plot for Zn(II) complex

Conclusion

Zn(II) complexes with 2-(2-hydroxyphenyl)benzimidazole ligand has been prepared. Single-crystal X-ray diffraction analysis and elemental analysis show that its composition is [Zn(2-(2-hydroxyphenyl)benzimidazolates)2]·2DMF, namely (**1**·2DMF). In **1**, the ZnN₂O₂ core has a four-coordinate configuration with distorted tetrahedral geometry. Molecular orbital analyses and photoluminescent studies indicate that its light-emitting property is $\pi \rightarrow \pi^*$ ligand-centered charge transfer transition (LCCT).

Supplementary materials: CCDC-603058 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/

deposit [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

ACKNOWLEDGEMENTS

This work was supported by the Natural Science Foundation of Department of Education of Guangdong Province (05z016) and the Natural Science Foundation of Guangdong Province (No. 06301028), China.

REFERENCES

1. N. Nakamura, S. Wakabayashi, K. Miyairi and T. Fujii, *Chem. Lett.*, 1741 (1994).
2. Y. Hamada, T. Sano, H. Fujii and Y. Nishio, *Japan. J. Appl. Phys.*, **35**, L1339 (1996).
3. L.S. Sapochak, F.E. Benincasa, R.S. Schofield, J.L. Baker, K.K.C. Riccio, D. Fogarty, H. Kohlmann, K.F. Ferris and P.E. Burrows, *J. Am. Chem. Soc.*, **124**, 6119 (2002).
4. W. Yang, H. Schmider, Q. Wu, Y.-S. Zhang and S. Wang, *Inorg. Chem.*, **39**, 2397 (2000).
5. Y.-P. Tong, X.-M. Chen and S.W. Ng, *Acta Crystallogr.*, **E60**, m166 (2004).
6. S.-L. Zheng, J.-P. Zhang, X.-M. Chen, Z.-L. Huang, Z.-Y. Lin and W.-T. Wong, *Chem. Eur. J.*, **9**, 3888 (2003).
7. G. Yu, S. Yin, Y. Liu, Z. Shuai and D. Zhu, *J. Am. Chem. Soc.*, **125**, 14816 (2003).
8. T.S. Kim, T. Okubo and T. Mitani, *Chem. Mater.*, **15**, 4949 (2003).
9. S. Wang, *Coord. Chem. Rev.*, **215**, 79 (2001).
10. P. Wang, Z. Hong, Z. Xie, S. Tong, O. Wong, C.-S. Lee, N. Wong, L. Hung and S. Lee, *Chem. Comm.*, 1664 (2003).
11. Y.-P. Tong, S.-L. Zheng and X.-M. Chen, *Inorg. Chem.*, **44**, 4270 (2005).
12. Y.-P. Tong, S.-L. Zheng and X.-M. Chen, *Eur. J. Inorg. Chem.*, 3734 (2005).
13. G.M. Sheldrick, SHELXTL 6.10. Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.
14. R. Blessing, *Acta Crystallogr. A*, **51**, 33 (1995).
15. S.-L. Zheng and X.-M. Chen, *Aust. J. Chem.*, **57**, 703 (2004).
16. S.-L. Zheng, J.-H. Yang, X.-L. Yu, X.-M. Chen and W.-T. Wong, *Inorg. Chem.*, **43**, 830 (2004).