

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURES AND LUMINESCENCE OF TWO ZINC(II) COMPLEXES WITH BENZIMIDAZOLE LIGANDS

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Two new zinc(II) complexes have been synthesized and studied by single crystal X-ray diffraction method: $[\text{Zn}(\text{L1})\text{Cl}_2] \cdot 2\text{DMF}$ (**1**) and $[\text{Zn}(\text{L2})\text{Cl}_2] \cdot \text{DMF}$ (**2**) (L1 = 3,3'-bis(2-benzimidazolyl)-2,2'-dipyridine, L2 = 3,3'-bis[2-bis(2-ethylbenzimidazolyl)]-2,2'-dipyridine). Compound **1** is monoclinic, $C2/c$, $a = 23.142(3)$, $b = 11.845(1)$, $c = 14.735(3)$ Å; compound **2** is orthorhombic, $C222_1$, $a = 12.140(7)$, $b = 16.283(9)$, $c = 16.51(1)$ Å. In both compounds, Zn(II) cations are coordinated by two chlorine atoms and two benzimidazole nitrogen atoms in a slightly distorted tetrahedron fashion. Structural features responsible for fluorescent properties of the complexes are discussed.

Keywords: crystal structure, fluorescence, dimethylformamide.

Luminescent metal complexes have potential applications in light emitting devices (LEDs) because of their high luminescence efficiency, high thermal stability and ease of fabrication [1–3]. The properties of the complexes, including the emission color, thermal stability and carrier mobility, strongly depend on the nature of the ligands utilized, and can be tuned by the modification of the ligands. It has been well understood that rigid and sterically hindered molecular structures are essential to obtain high fluorescence efficiency [4].

Benzimidazole derivatives and their transition metal complexes providing insight concerning coordination chemistry [5, 6] and biochemistry [7, 8] have extensively spurred current research interest. Several studies on transition metal benzimidazole complexes with luminescent properties have been reported [9, 10]. In this regard, luminescent zinc complexes with benzimidazole ligands have been considerably investigated as potential luminescent materials [11, 12]. We have previously reported such a complex of 3,3'-bis(2-benzimidazolyl)-2,2'-dipyridine (L1) with hydrated zinc(II) perchlorate [13]. As an extension of our previous investigation, we synthesized L2 as an alkylated derivative of L1. In this paper we use L1, L2 and ZnCl_2 as the study system to explore coordination modes of the ligands and their relation to fluorescence properties.

Experimental. Physical measurements. L1 and L2 were prepared according to a literature method [9, 13]. All other chemicals were obtained from commercial sources and used as received. The C, H and N micro-analyses were carried out on a Flash 1112 elemental analyzer. The FT-IR spectrum (KBr pellets) were recorded in the range of 400–4000 cm^{-1} on a Nicolet Avatar-360 spectrometer. The UV-vis spectra were recorded on a UV-3010 spectrometer. Corrected luminescence spectra were obtained with a F-4500 spectrofluorimeter.

Preparation of $[\text{Zn}(\text{L1})\text{Cl}_2] \cdot 2\text{DMF}$ (1**).** A mixture of L1 (0.388 g, 1 mmol) and ZnCl_2 (0.136 g, 1 mmol) in DMF (30 ml) was reacted at 70 °C for 2 hours. After cooling to room temperature the solution was filtered. On slow evaporation of the filtrate (within 10 days) at room temperature colorless block-shaped single crystals suitable for X-ray diffraction were obtained. Yield: 71 %. Anal. Calcd.

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(%) for $C_{30}H_{30}Cl_2N_8O_2Zn$: C, 53.71; H, 4.51; N, 16.70. Found (%): C, 53.48; H, 4.65; N, 16.89. IR (KBr, cm^{-1}): 3088 (*m*, $\nu(-N-H)$), 3060 (*w*, $\nu(-C-H)$), 1654 (*s*, $\nu(-C=O)$), 1618 (*w*, benzimidazole and pyridine rings), 1592 (*w*, benzimidazole and pyridine rings), 1564 (*w*, benzimidazole and pyridine rings), 1432 (*m*), 771 (*m*, $\delta(-Ar-H)$).

Preparation of $[Zn(L2)Cl_2] \cdot DMF$ (2**).** The synthetic procedure was similar to **1**; pale-red or yellow block-shaped crystals suitable for X-ray diffraction were obtained in 65 % yield. Anal. Calcd. (%) for $C_{31}H_{31}Cl_2N_7OZn$: C, 56.94; H, 4.78; N, 14.99. Found (%): C, 56.87; H, 4.73; N, 15.03. IR (KBr, cm^{-1}): 3060 (*w*, $\nu(-C-H)$), 1668 (*s*, $\nu(-C=O)$), 1614 (*w*, benzimidazole and pyridine rings), 1587 (*w*, benzimidazole and pyridine rings), 1561 (*m*, benzimidazole and pyridine rings), 1476 (*m*), 1437 (*s*), 758 (*m*, $\delta(-Ar-H)$).

X-Ray structural analyses. The single crystals of **1** and **2** were studied on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_{α} radiation source ($\lambda = 0.71073 \text{ \AA}$). The intensity data were collected at room temperature using ω -2 θ scan technique. The data were corrected for Lorentz polarization factor and absorption. The structures were solved by direct methods with SHELXS-97 and expanded using Fourier techniques [14]. Non-hydrogen atoms were refined in anisotropic approximation with some restrictions on atomic thermal parameters for DMF molecule in structure **2**; most hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. A summary of the crystal structure parameters, data collection, structure determination and refinement is provided in Table 1. Selected bond lengths and angles are listed in Table 2. CIF files containing complete information on the structures **1** and **2** were deposited with CCDC, deposition numbers 725701 and 725702, respectively; the files are freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystal data, data collection and refinement details for **1** and **2**

Compound	1	2
Formula	$C_{30}H_{30}Cl_2N_8O_2Zn$	$C_{31}H_{31}Cl_2N_7OZn$
<i>M</i>	670.89	653.90
Crystal size, mm	0.49 × 0.45 × 0.43	0.46 × 0.34 × 0.30
Color	Colourless	Yellow
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>C222₁</i>
<i>a</i> , <i>b</i> , <i>c</i> , \AA	23.142(3), 11.845(1), 14.735(3)	12.140(7), 16.283(9), 16.51(1)
α , β , γ , deg.	90, 128.759(1), 90	90, 90, 90
<i>V</i> , \AA^3	3149.8(9)	3263(3)
<i>Z</i>	4	4
<i>D</i> _{calc} , $g \cdot cm^{-3}$	1.415	1.331
μ , mm^{-1}	0.991	0.951
θ , deg.	2.26–25.50	2.43–25.49
Reflection collected	10112	12153
Independent reflections (<i>R</i> _{int})	2924 (0.0248)	3050 (0.0618)
Reflections observed	2474	2634
GOOF on <i>F</i> ²	1.052	1.093
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0318	0.0702
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0783	0.0814
Residual extrema, $e \cdot \text{\AA}^{-3}$	0.362/−0.333	0.660/−0.746
CCDC deposition number	725701	725702

Table 2

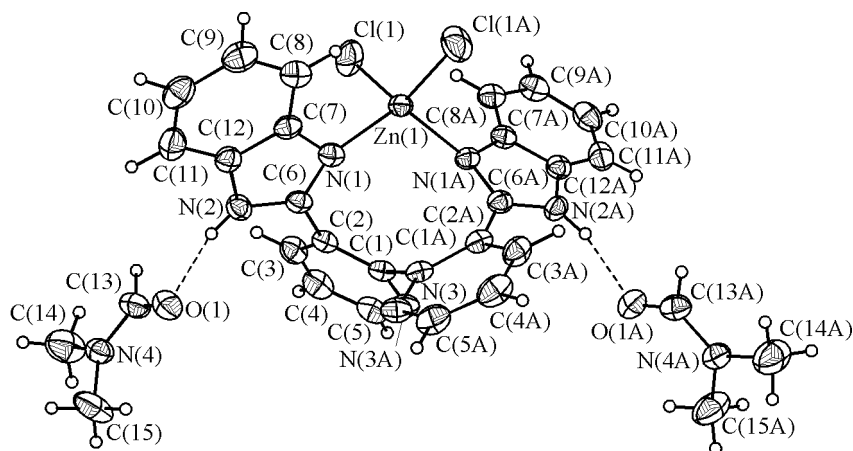
Selected bond lengths d , Å and angles ω , deg. for complexes **1** and **2**

1		2	
Bond	d	Bond	d
Zn(1)—N(1)	2.052(2)	Zn(1)—N(1)	2.073(7)
Zn(1)—Cl(1)	2.2344(7)	Zn(1)—Cl(1)	2.257(2)
Angle	ω	Angle	ω
N(1)—Zn(1)—N(1)	115.89(9)	N(1)—Zn(1)—N(1)	116.3(4)
N(1)—Zn(1)—Cl(1)A	108.72(5)	N(1)—Zn(1)—Cl(1)	109.8(2)
N(1)—Zn(1)—Cl(1)	102.97(5)	N(1)—Zn(1)—Cl(1)A	103.0(2)
Cl(1)—Zn(1)—Cl(1)	118.17(5)	Cl(1)—Zn(1)—Cl(1)	115.5(2)

Results and discussion. Infrared spectra. In the IR spectrum, both **1** and **2** show main vibrational frequencies for the benzimidazolic ring such as the $\nu(\text{N—H})$, $\nu(\text{C—H})$, $\nu(\text{C=C}) + \nu(\text{C=N})$ vibrations and $\delta(\text{N—H})$ and $\delta(\text{C—H})$ benzimidazolic ring out of plane vibrations [15]. All these bands are shifted towards higher energy in relation to the free ligand, indicating coordination through the benzimidazole nitrogen atom. The intense absorption bands of C=O appear at 1654 cm^{-1} for **1** and 1668 cm^{-1} for **2** indicating the presence of DMF molecules in both crystal structures.

Crystal structure descriptions. The molecular structure of **1** is shown in Fig. 1. The Zn(II) center is in a slightly distorted tetrahedral coordination geometry with two N-donor atoms from L1 and two Cl[−] anions. The bond angles around the Zn(II) ion are in the range $103.0\text{—}118.2^\circ$, and the Cl—Zn—Cl bond angle of $118.17(5)^\circ$ is large probably due to the Cl...Cl repulsion. The Zn—Cl and Zn—N bond lengths, $2.2343(7)\text{ Å}$ and $2.052(2)\text{ Å}$, respectively, are comparable to those observed in previously reported complexes $[\text{ZnCl}_2(\text{BzTz})_2]$ (Zn—Cl 2.234 , 2.255 Å and Zn—N 2.039 , 2.021 Å), (BzTz = N-(5,6-dihydro-4H-1,3-thiazin-2-yl)-2-aminobenzimidazole) [16]. In the crystal structure, the benzimidazole rings make dihedral angles of 48.6° with pyridine planes, and the dihedral angles between the two pyridine planes are 73.3° .

As shown in Fig. 1, each $[\text{Zn}(\text{L1})\text{Cl}_2]$ unit links two DMF molecules through intermolecular hydrogen bonds: N(2)...O(1) $2.703(2)\text{ Å}$. There are intramolecular hydrogen bonds in $[\text{Zn}(\text{L1})\text{Cl}_2]$ unit: C(8)...Cl(1) $3.594(2)\text{ Å}$ and C(15)...O(1) $2.763(5)\text{ Å}$ and in DMF molecule: C(15)...O(1) $2.763(5)\text{ Å}$. It is interesting to note that there are weak intermolecular C—H... π interactions in the crystal structure of **1**. The donor atom H4 of pyridine ring aims at the π -cloud of the neighboring imidazole ring Cg(1).

Fig. 1. Molecular structure of complex **1** and attached DMF

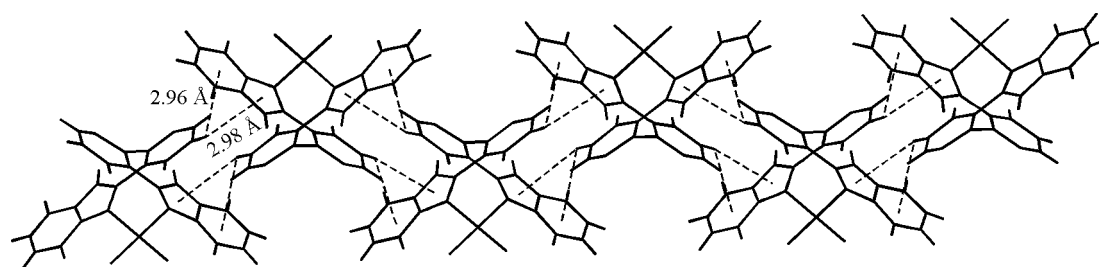


Fig. 2. 1D Packing of molecules in complex **1**. The intermolecular C—H... π interactions are shown by dashed lines

(N1/C6/N2/C12/C7) and benzene ring Cg(2) (C7/C8/C9/C10/C11/C12). The H(4)...Cg(1) distance is 2.980 Å with C...Cg(1) of 3.752(3) Å and C(4)—H(4)...Cg(1) angle of 141.0°. The H(4)...Cg(2) distance is 2.960 Å with C...Cg(2) of 3.539(3) Å and C(4)—H(4)...Cg(2) angle of 122.0°. The nearest mononuclear units are interlinked by these weak intermolecular C—H... π interactions into a one-dimensional chain (Fig. 2).

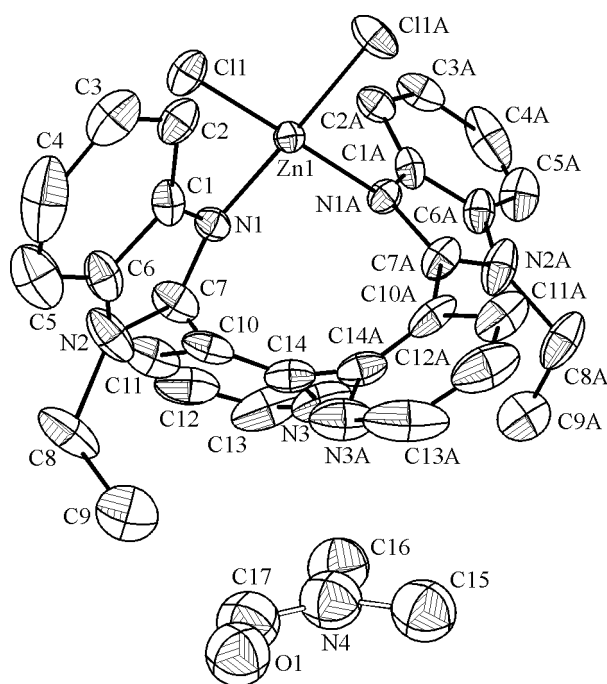


Fig. 3. Molecular structure of the complex **2** and solvated DMF

and C(9)—H(9B)...Cg(1) angle of 161.0°. The adjacent molecules are linked by these weak intermolecular C—H... π interactions into a one-dimensional chain (Fig. 4).

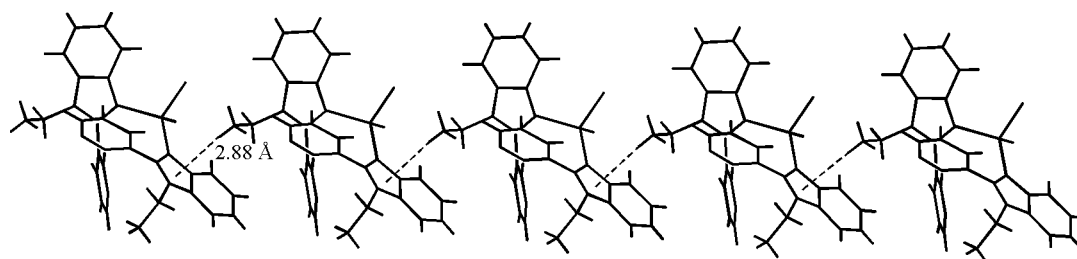
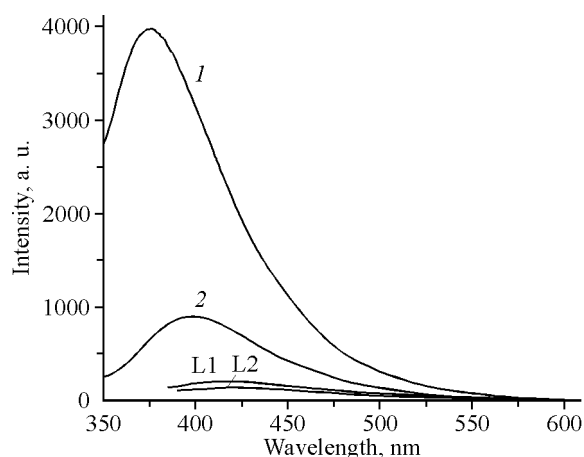


Fig. 4. 1D Packing of molecules in complex **2**. The intermolecular C—H... π interactions are shown by dashed lines

The coordination geometry of Zn(II) in complex **2** (Fig. 3) is similar to that of complex **1**. As in complex **1**, bipyridyl in **2** is not bonded to Zn(II) cations as a bidentate ligand, apparently due to great torsion angle between the two pyridine rings of 61.5°. The bond angles around Zn(II) ions are in the range 103.0—116.3°. The Zn—Cl and Zn—N bond lengths are similar to the corresponding values in complex **1**. The DMF molecule is disordered over two overlapping positions due to a double axis. The dihedral angle between benzimidazole ring and pyridine plane is 64.4°, which is larger than that observed in complex **1**. There are C—H... π interactions in the crystal structure of **2**. The donor atom H9B of pyridine ring aims at the π -cloud of the neighboring imidazole ring Cg(1) (N1/C1/N2/C6/C7). The H(9B)...Cg(1) distance is 2.880 Å with C...Cg(1) of 3.81(2) Å

Fig. 5. The solid-state fluorescence spectra of L1, L2, complexes **1** and **2**



UV-vis and fluorescence spectra. The solid-state fluorescence spectra of **1** and **2** with L1 and L2 at room temperature are depicted in Fig. 5. Complexes **1** and **2** both exhibit stronger blue fluorescence compared to that of the free ligands with the emission maxima at 375 and 399 nm upon excitation for **1** and **2**, and 329 and 336 nm for L1 and L2, respectively. The maxima could be assigned to the intra-ligand $\pi-\pi^*$ transition emission. The enhanced luminescence efficiency is therefore attributed to the coordination of the ligands to Zn(II) ions that effectively increase the rigidity of the ligands and reduce the loss of energy via radiationless decay of the intra-ligand emission excited state. Meanwhile, the blue shift (46 and 63 nm) in the complexes may be owing to the reduced conjugation of the ligand upon coordination.

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REFERENCES

1. Wang S. // *Coord. Chem. Rev.* – 2001. – **215**, N 1. – P. 79 – 98.
2. Li J., Zhou J.H., Li Y.Z. et al. // *Inorg. Chem. Commun.* – 2004. – **7**, N 4. – P. 538 – 541.
3. Che C.M., Wan C.W., Ho K.Y. et al. // *New. J. Chem.* – 2001. – **25**. – P. 63 – 65.
4. Tong Y.P., Zheng S.L., Chen X.M. // *J. Mol. Struct.* – 2007. – **826**, N 2. – P. 104 – 112.
5. Mothilal K.K., Karunakaran C., Rajendran A. et al. // *J. Inorg. Biochem.* – 2004. – **98**, N 2. – P. 322 – 332.
6. Sun W.H., Shao C.X., Chen Y. et al. // *Organometallics.* – 2002. – **21**, N 21. – P. 4350 – 4355.
7. Ayhan-Kilcigil G., Tuncbilek M., Altanlar N., Goker. H. // *IL Farmaco.* – 1999. – **54**, N 8. – P. 562 – 565.
8. Aghatabay N.M., Neshat A., Karabiyik T. et al. // *Eur. J. Med. Chem.* – 2007. – **42**, N 2. – P. 205 – 213.
9. Liu Q.D., Jia W.L., Wang S. // *Inorg. Chem.* – 2005. – **44**, N 5. – P. 1332 – 1343.
10. Liu S.G., Zuo J.L., Li Y.Z. et al. // *J. Mol. Struct.* – 2004. – **705**, N 3. – P. 153 – 157.
11. Xiao B., Hou H.W., Fan Y. T. et al. // *Inorg. Chem. Commun.* – 2007. – **10**, N 3. – P. 376 – 380.
12. Yue S.M., Xu H.B., Ma J.F. et al. // *Polyhedron.* – 2006. – **25**, N 3. – P. 635 – 644.
13. Miao S.B., Ji B.M., Du C.X. // *Chin. J. Struct. Chem.* – 2007. – **26**, N 4. – P. 439 – 444.
14. Sheldrick G.M. SHELXS-97 and SHELXL-97. Programs for Crystal Structure Refinement. – Germany, University of Göttingen, 1997.
15. Ceniceros-Gomez A.E., Barba-Behrens N., Quirioz-Castro M.E. et al. // *Polyhedron.* – 2000. – **19**, N 15. – P. 1821 – 1827.
16. Maldonado-Rogado M.A., Vinuezas-Zahinos E., Luna-Giles F. et al. // *Ibid.* – 2007. – **26**, N 13. – P. 3112 – 3120.