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New Complex of Zn(II) with 3,4,5-Trimethoxybenzoate and 2-Methylimidazolyl: Synthesis, Structure, and Luminescence Properties[1]

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Abstract—A new zinc(II) complex Zn(TMB)$_2$(2-MIM)(H$_2$O)$_2$ (**I**), where HTMB is 3,4,5-trimethoxybenzoic acid, 2-MIM is 2-methylimidazole, was synthesized and characterized by Powder X-ray diffraction, FT-IR and photoluminescence spectrum. The complex crystallizes in the monoclinic crystal system (space group $C2/c$) with the unit cell parameters: $a = 18.104(9)$, $b = 8.509(4)$, $c = 17.688(9)$ Å, $\beta = 103.185(9)°$, $Z = 4$, $R_1 = 0.0740$ and $wR_2 = 0.1790$. At room temperature the photoluminescence spectrum of complex **I** in the solid state exhibits maximum excitation at 314 nm and maximum emission at 337 nm.

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INTRODUCTION

With the center ions of zinc, more and more coordination compounds have attracted considerable attention to researchers because of their absorbing architectures and potential applications in magnetism, nonlinear optics, molecular recognition, and catalysis [1–8]. Zinc, whose coordination number could be four [9–11], five [12], and six [13], shows various coordination behaviors. In view of this, we have obtained unexpectedly a novel septocoordination compound Zn(TMB)$_2$(2-MIM)(H$_2$O)$_2$ (**I**) and particularly concerned its unique crystal structure and fluorescence properties.

EXPERIMENTAL

Materials and methods. All reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were performed on a Perkin-Elmer 240C automated analyzer. Fourier transform infrared spectroscopy (**FT-IR**) was recorded from KBr pellets in a range of 4000–400 cm^{-1} on a Nicolet FT-IR 360 spectrometer. Powder X-ray diffraction (**XRD**) measurements were performed using an X'Pert PRO diffractometer (Spectris Pte Ltd.) with monochromatized CuK_α radiation ($\lambda = 1.5418$ Å). Photoluminescence (**PL**) excitation and emission spectra were recorded at room temperature by F-4500 FL Spectrophotometer with a spectral resolution of 1 nm.

Synthesis of complex I. As a selected ligand, 3,4,5-trimethoxybenzoic acid (2.0 mmol, 0.425 g), 2-methylimidazole (0.082 g, 1.0 mmol), and zinc nitrate (0.290 g, 1 mmol) were added to 15 ml of a ethanol–water (1 : 2 (v/v)) solution with stirring at room temperature. After 1 h, the pH value of the mixture was adjusted to about 5.5 with a NaOH solution (6 mol/l), and then the cloudy solution was continually stirred for 0.5 h. After the insoluble solis were filtered off, the colorless filtrate was kept at room temperature and colorless block single crystals of the title complex were harvested after 5 days.

For $C_{24}H_{30}N_2O_{12}Zn$

anal. calcd., %:	C, 47.74;	H, 5.00;	N, 4.64.
Found, %:	C, 47.13;	H, 4.88;	N, 4.36.

IR (KBr; ν, cm^{-1}): 3474 (H$_2$O), 1558 ν_{as}(COO$^-$), 1394 ν_s(COO$^-$), 1542 (C=N), 1217 (C–N).

X-ray crystallography. Diffraction intensities for the crystals were collected at 298 K on a Bruker SMART 1000 CCD diffractometer employing graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) in ω and φ scan modes. The structure was solved by direct methods [14] and refined by full-matrix least-squares method on F^2 using the SHELXS-97 and SHELXL-97 programs, respectively [15, 16]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. 2-Methylimidazolyl was found to be symmetrically disordered, which could only be characterized by split positions being equally occupied. The crystallographic data and experimental refinement parameters of the

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Table 1. Crystalloraphic data and experimental details for complex **I**

Parameter	Value
Formula weight	603.87
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions:	
a, Å	18.104(9)
b, Å	8.509(4)
c, Å	17.688(9)
β, deg	103.185(9)
V, Å^3	2653(2)
Z	4
ρ_{calcd}, mg/m^3	1.542
Absorption coefficient, mm^{-1}	0.993
F(000)	1256
Crystal size, mm	$0.12 \times 0.10 \times 0.06$
θ range for data collection, deg	2.31–25.02
Index ranges	$-21 \le h \le 21$ $-10 \le k \le 10$ $-21 \le l \le 21$
Reflections collected	12024
Independent reflections	2313
Completeness to $\theta = 25.02$, %	99.1
Absorption correction	None
Data/restraints/parameters	2316/4/200
Goodness-of-fit on F^2	1.123
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0740$, $wR_2 = 0.1790$
R indices (all data)	$R_1 = 0.0914$, $wR_2 = 0.1896$
Largest diff. peak and hole, e Å^{-3}	0.840 and –0.699

title complex are given in Table 1. Selected bond lengths and angles are listed in Table 2. The atomic coordinates and other parameters of the structure **I** have been deposited with the Cambridge Crystallographic Data Centre (no. 787602); see deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html.

RESULTS AND DISCUSSION

In complex I, as shown in Fig. 1, the asymmetry unit consists one Zn^{2+} cation, one TMB ligand, one 2-MIM ligand, and one aqua molecule.

The zinc ion is seven-coordinate with six oxygen atoms and one nitrogen atom, of which four oxygen atoms are from two TMB ligands, two O are from water molecules, and one nitrogen atom is from the 2-MIM ligand. This $[ZnO_6N]$ coordination sphere [17] can be described as a distorted pentagonal bipyramid with twofold axis geometry. The Zn–O bond distances vary in the range of 2.324(7) from 2.478(7) Å. The dihedral angle O(1)–O(2)–O(2A)–O(1) is 29.60°, which indicates large twist in the equatorial plane.

All of coordination water and 2-MIM molecules in the title complex are involved in intermolecular hydrogen bonding interactions. N(2) forms an intermolecular H-bonding interaction with the carbonyl O atom of the TMB ligand; the distance of $N(2)\cdots O(2)^{\#1}$ ($^{\#1}$ $x, -1 + y, z$) is 2.804(13) Å and angle $N(2){-}H(2A)\cdots O(2)$ is 167°. The independent water molecule is involved in two kinds of hydrogen bonds: $O(6){-}H(6A)\cdots O(3)^{\#2}$ and $O(6){-}H(6A)\cdots O(5)^{\#3}$ ($^{\#2}$ $3/2 - x, 3/2 - y, -z$; $^{\#3}$ $x, 2 - y, 1/2 + z$). The distances of $O(6)\cdots O(3)$ and $O(6)\cdots O(5)$ are 2.974(9) and 2.952(10) Å, respectively. The extension of these hydrogen bonds stabilizes a 3D structure in the title com-

Table 2. Selected bond lengths and bond angles for complex **I***

Bond	d, Å	Bond	d, Å
Zn(1)–N(1)	2.198(9)	Zn(1)–O(2)	2.324(7)
Zn(1)–O(1)	2.478(7)	Zn(1)–O(6)	2.404(8)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Zn(1)O(1)$^{\#1}$	89.9(4)	N(1)Zn(1)O(2)$^{\#1}$	143.7(4)
N(1)Zn(1)O(6)$^{\#1}$	85.3(4)	O(1)Zn(1)O(2)$^{\#1}$	53.8(2)
O(1)Zn(1)O(6)$^{\#1}$	83.9(2)	O(2)Zn(1)O(6)$^{\#1}$	91.4(3)
O(2)Zn(1)O(2A)$^{\#2}$	86.4(3)	O(6)Zn(1)O(6A)$^{\#2}$	173.73(2)

* Symmetry codes: $^{\#1}$ x, y, z; $^{\#2}$ $2 - x, y, 1/2 - z$.

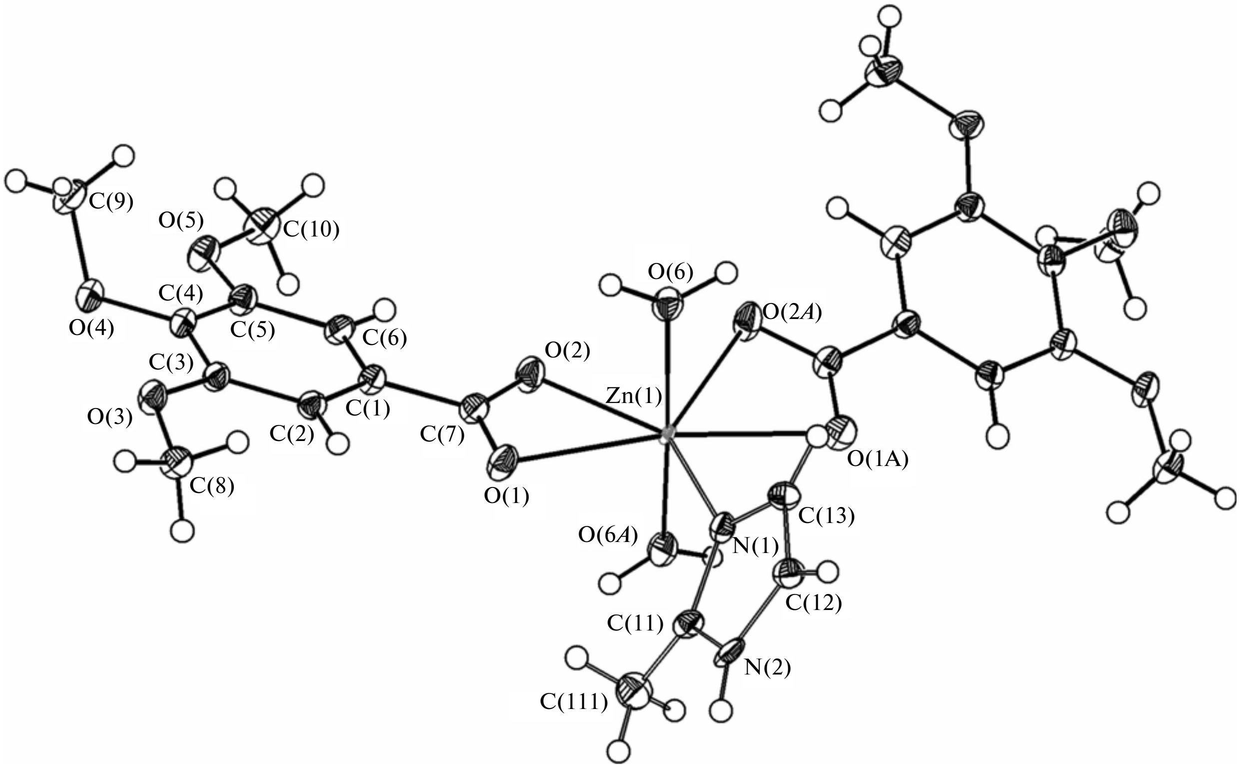

Fig. 1. Coordination environment of the Zn ion in complex **I**.

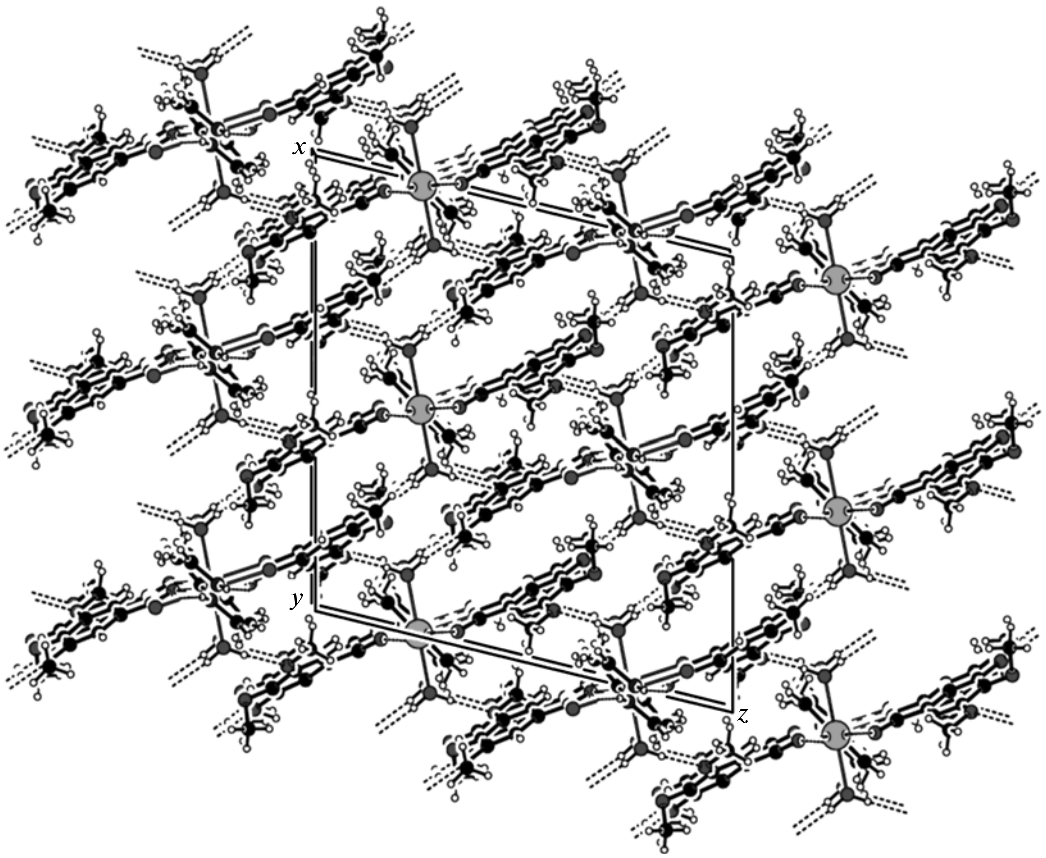

Fig. 2. Molecular fragments linked by hydrogen bonds.

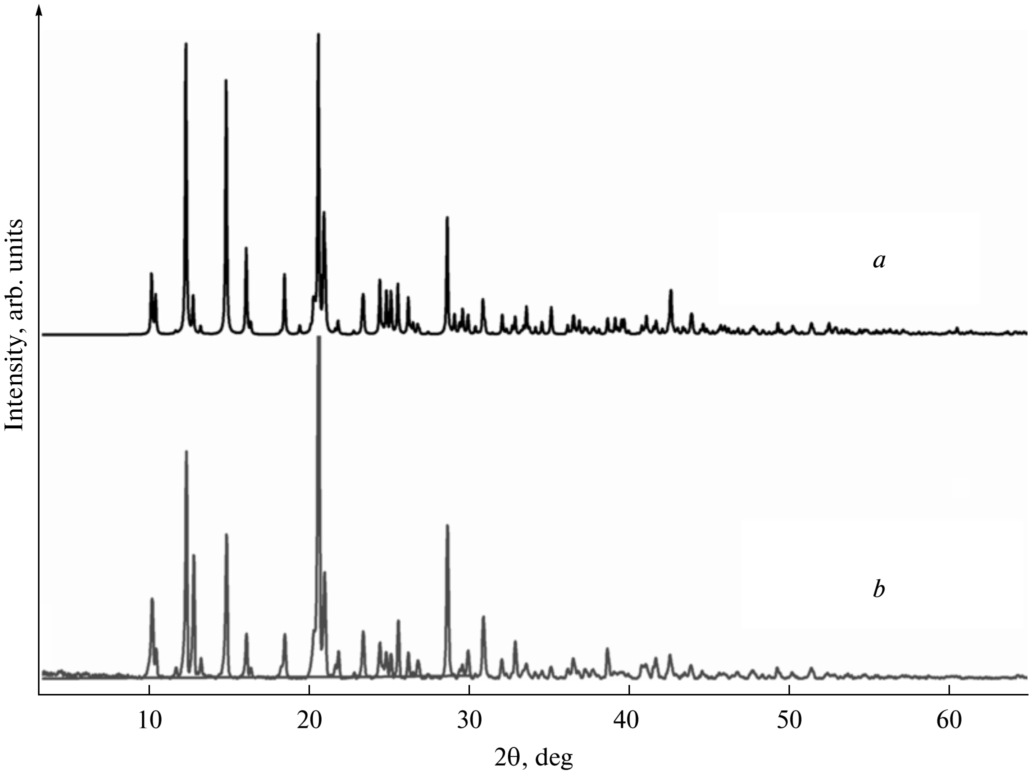

Fig. 3. Powder XRD patterns: simulated (*a*), experimental (*b*).

plex. Figure 2 presents a fragment of packing arrangement in the title complex.

The purity of complex **I** is confirmed by powder XRD analysis (Fig. 3). The experimental XRD patterns is in good agreement with those obtained from the simulated based on the single-crystal XRD at room temperature, indicating the phase purity of the samples. The subtle differences in intensity may be due to the preferred orientation of the powder samples.

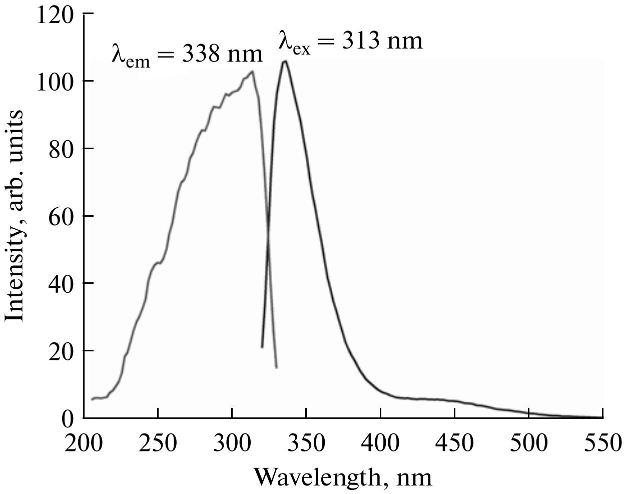

Fig. 4. Photoluminescence spectrum of complex **I** in the solid state at room temperature.

The photoluminescence measurement result of complex **I** in the solid state at room temperature is shown in Fig. 4. When detected at 337 nm, complex **I** shows broad excitation with the maximum peak at 314 nm. However, if complex **I** is excited at 313 nm, the strong luminescence is observed with the maximum wavelength centered at 338 nm, since the Zn^{2+} ion in the complex has saturated *d*-layer electrons. This emission band would likely originate from the ligand-to-ligand π_L–π_L^* charge-transfer (LLCT) transition emission.

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