Syntheses, Structures and Properties of a New Zn(II) Complex Based on the 2-(Benzoimidazol-2-yl-methyl)-1*H*-tetrazole Ligand

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A new Zn(II) complex $[Zn_2(bimt)_2(Ac)(OH)]_n$ (**1**) has been synthesized by the reaction of the flexible ligand 2-(benzoimidazol-2-yl-methyl)-1*H*-tetrazole (Hbimt) with $Zn(Ac)_2 \cdot 2H_2O$ and characterized by single-crystal X-ray diffraction and IR spectra. In complex **1**, Zn1 and Zn2 ions are connected by μ_2-bridging acetate and hydroxide groups to form a 6-membered ring. The bimt units coordinate to Zn1 and Zn2 ions in a bidentate bridging mode with two nitrogen atoms from the same benzoimidazole ring and connect the 6-membered rings resulting in the formation of a 2D network structure. Adjacent layers are further packed to a three-dimensional network through van der Waals bonds. A thermogravimetric analysis was carried out, and the photoluminescent behavior of the complex was investigated.

Key words: Zinc Complex, 2-(Benzoimidazol-2-yl-methyl)-1*H*-tetrazole, Crystal Structure, Fluorescence, Thermostability

Introduction

Recently, considerable effort has been concentrated not only on the synthetic strategy to obtain complexes with an intriguing variety of structures and topologies but also on their potential applications in ion exchange, molecular recognition and separation, heterogeneous catalysis or catalyst supports, gas sorption and storage, drug delivery and medical imaging, and optical, magnetic, and porous materials [1 – 11]. However, it is still a challenge to predict the structures of the complexes. The self-assembly processes of the complexes are influenced by many factors, such as the geometry and flexibility of the ligands, the coordination characteristics of the central metal ions, the ratio of ligand to metal ion, the counterions, the solvent system, the temperature, the crystallization method, and so on. Among them, the choice of the organic ligand is a key step in the construction of specific architectures of the complexes because these are the organic units that serve to coordinate to the metal centers and pass on the structural information expressed in metal coordination preferences throughout the extended structure. Systematic studies of diverse ligands, leading to different structures in the formation of complexes, are thus important and of intense interest [12 – 14].

It is well known that multidentate *N*-heterocyclic ligands have been widely used in the preparation of new complexes, and a number of complexes based on imidazole, triazole, tetrazole, benzimidazole, benzotriazole, pyridine, pyrazine, and piperazine and their derivatives have been reported [15 – 22]. As an *N*-heterocyclic ligand, 2-(benzoimidazol-2-yl-methyl)-1*H*-tetrazole (Hbimt) possesses several interesting structural features. First, there are five potential donors in the free ligand. Second, Hbimt can be used as a neutral ligand or as an anionic ligand since one hydrogen atom can be removed forming a bimt unit. Third, Hbimt can offer a greater tunability of structural frameworks due to the presence of the methylene spacer. Fourth, Hbimt can act as both a hydrogen bond acceptor and donor due to the presence of the imino group of the benzoimidazole ring and the nitrogen atoms of the benzoimidazole and tetrazole rings to construct a supramolecular framework. Recently, we focused our attention on the synthesis, structure, and properties of complexes with Hbimt, and a number of complexes containing this ligand have been prepared [19, 23 – 27]. In this study, through the reaction of Hbimt with $Zn(Ac)_2 \cdot 2H_2O$, we obtained a new complex with the formula $[Zn_2(bimt)_2(Ac)(OH)]_n$ (**1**). The IR spectrum, the photoluminescent behavior and thermogravimetric features have also been investigated.

Experimental Section

The ligand 2-(benzoimidazol-2-yl-methyl)-1*H*-tetrazole (Hbimt) was synthesized according to the literature

method [19]. All chemicals were commercially available and used without further purification. IR data were recorded on a Nexus-470 FTIR spectrometer with KBr pellets in the 400 – 4000 cm^{-1} region. Elemental analyses (C, H, and N) were carried out on a Flash EA 1112 elemental analyzer. Solid-state luminescence spectra were recorded with a Fluoro Max-P fluorescence spectrophotometer. TG measurements were performed by heating the sample from 30 to 750 °C at a rate of 10 °C min^{-1} in air on a Netzsch STA 409 PC/PG differential thermal analyzer.

*Synthesis of $[Zn_2(bimt)_2(Ac)(OH)]_n$ (**1**)*

A mixture of $Zn(Ac)_2 \cdot 2H_2O$ (0.2 mmol), Hbimt (0.2 mmol), water (5 mL), and DMF (1 mL) was placed in a 25 mL Teflon-lined stainless-steel vessel and heated at 373 K for 3 d. After the mixture had been cooled to room temperature at a rate of 10 °C h^{-1}, pale-yellow crystals of **1** suitable for X-ray diffraction were obtained. Yield: 55 %. – Anal. for $C_{20}H_{18}N_{12}O_3Zn_2$ (605.24): calcd. C 39.87, H 3.01, N 27.91; found C 40.25, H 2.96, N 27.31. – FT-IR (KBr, cm^{-1}): ν = 3452 (s), 3130 (s), 3003 (s), 1588 (s), 1531 (m), 1497 (s), 1452 (s), 1427 (s), 1312 (s), 1158 (m), 1099 (s), 742 (s), 644 (m), 475 (m).

Crystal structure determination

A single crystal of complex **1** was selected and attached to a thin glass fiber. X-Ray diffraction was performed on a Rigaku Saturn 724 CCD area detector with a graphite monochromator at the X-ray source (Mo K_α radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. The data were collected by an ω scan mode at a temperature of 293(2) K, the crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by Direct Methods, completed by difference Fourier techniques and refined by full-matrix least-squares based on F^2 using the SHELX-97 program package [28]. The hydrogen atoms were assigned with common isotropic displacement parameters and included in the final refinement by using geometrical restraints. Crystallographic parameters and structure refinement data are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC 896853 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

*IR spectroscopy of $[Zn_2(bimt)_2(Ac)(OH)]_n$ (**1**)*

In the IR spectra the absorption band at 3452 cm^{-1} can be attributed to the O–H stretching vibrations.

Table 1. Crystal data and structure refinement data of complex **1**.

Complex	**1**
Empirical formula	$C_{20}H_{18}N_{12}O_3Zn_2$
Formula weight	605.24
Temperature, K	293(2)
Crystal size, mm^3	0.16 × 0.14 × 0.10
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	18.841(4)
b, Å	10.611(2)
c, Å	12.404(3)
β, deg	107.55(3)
Volume, $Å^3$	2364.4(9)
Z	4
Calculated density, g cm^{-3}	1.70
Absorption coefficient, mm^{-1}	2.1
$F(000)$, e	1224
2θ range data collection, deg	2.23 – 25.50
hkl range	$-18 \rightarrow 22, \pm 12, \pm 15$
Refls. collected / unique	19 115 / 4397
Ref. parameters	335
Final indices $R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0724 / 0.1521
Final indices $R1$ / $wR2$ (all data)	0.0906 / 0.1621
Goodness-of-fit on F^2	1.190
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	0.61 / −0.68

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1**[a].

Zn1–O3	1.948(4)	Zn1–O2	1.956(4)
Zn1–N7	1.995(4)	Zn1–N1	2.008(4)
Zn2–O1	1.947(5)	Zn2–O3	1.955(4)
Zn2–N2A	1.986(5)	Zn2–N8B	2.000(5)
O3–Zn1–O2	107.42(18)	O3–Zn1–N7	104.43(18)
O2–Zn1–N7	111.71(19)	O3–Zn1–N1	115.40(18)
O(2)–Zn1–N1	103.61(18)	N7–Zn1–N1	114.26(18)
O1–Zn2–O3	108.19(19)	O1–Zn2–N2A	106.5(2)
O3–Zn2–N2A	109.57(18)	O1–Zn2–N8B	113.6(2)
O3–Zn2–N8B	101.77(18)	N2A–Zn2–N8B	116.9(2)

[a] Symmetry transformations used to generate equivalent atoms: A: $x, -y+2.5, z-0.5$; B: $x, -y+1.5, z-0.5$.

The absorption band at 3130 cm^{-1} originates from stretching vibrations of Ar–H. The sharp bands observed at 1588, 1497 and 1452 cm^{-1} are due to stretching vibrations of C=C, C=N, and N=N. The band at 1312 cm^{-1} is the result of C–N stretching vibrations. The band at 742 cm^{-1} belongs to *o*-phenylene vibrations. Separations (Δ) between ν_a(COO) and ν_s(COO) are different for the unidentate, chelating (bidentate) and bridging carboxylate groups. In **1**, Δ is 161 cm^{-1} (1588 and 1427 cm^{-1}), and the carboxylate groups are thus coordinated to Zn(II) ions in a bridging mode. The above findings are consistent with the results of the X-ray diffraction study.

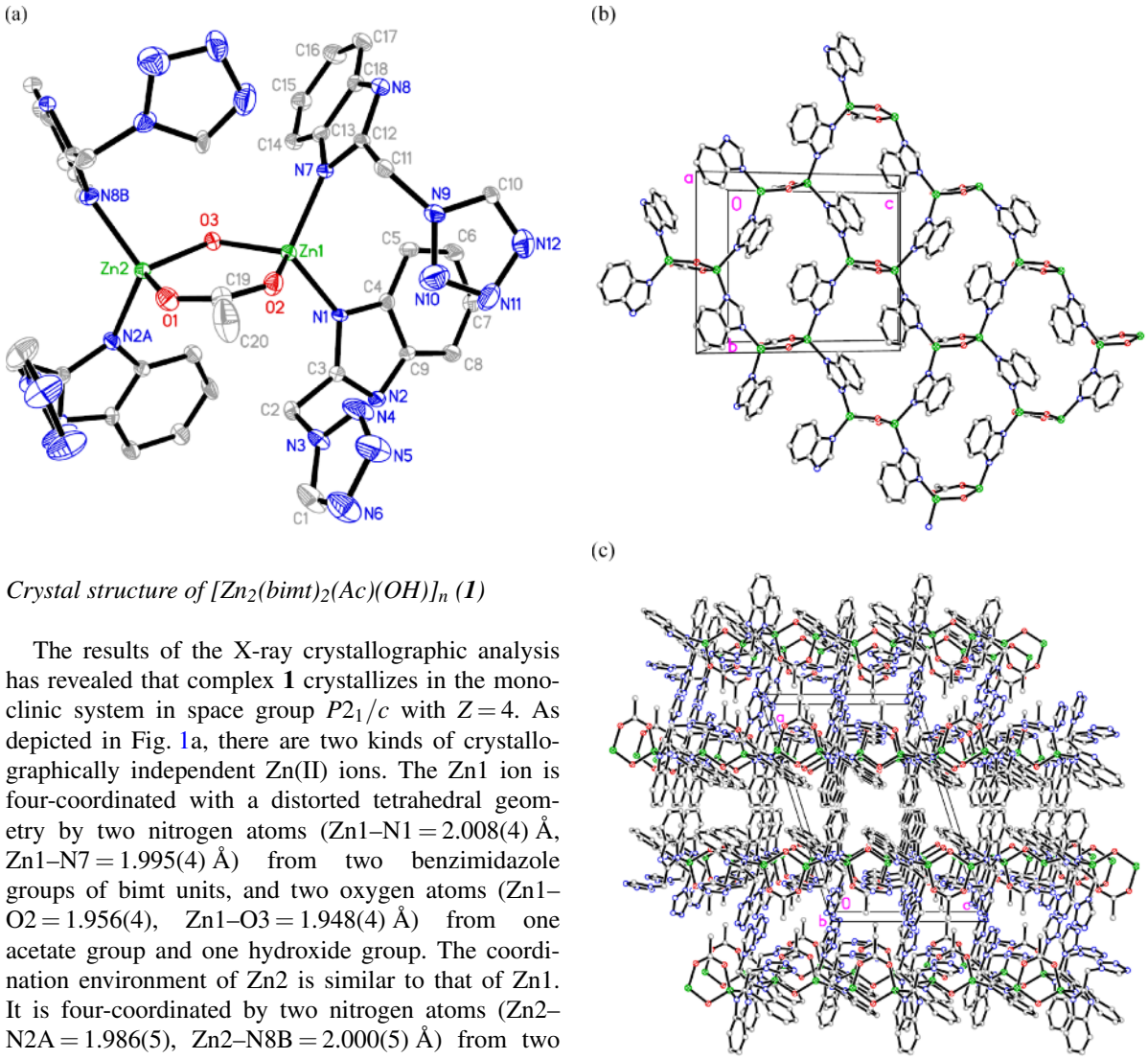

Fig. 1 (color online). (a) Coordination environment of the Zn(II) ions in complex **1** with the atom numbering scheme. Hydrogen atoms are omitted for clarity (symmetry codes: A: x, $-y+2.5$, $z-0.5$; B: x, $-y+1.5$, $z-0.5$); (b) view of the 2-D structure of complex **1**. Hydrogen atoms, methylene groups and tetrazole rings are omitted for clarity; (c) view of the 3D structure of complex **1**.

*Crystal structure of $[Zn_2(bimt)_2(Ac)(OH)]_n$ (**1**)*

The results of the X-ray crystallographic analysis has revealed that complex **1** crystallizes in the monoclinic system in space group $P2_1/c$ with $Z=4$. As depicted in Fig. 1a, there are two kinds of crystallographically independent Zn(II) ions. The Zn1 ion is four-coordinated with a distorted tetrahedral geometry by two nitrogen atoms (Zn1–N1 = 2.008(4) Å, Zn1–N7 = 1.995(4) Å) from two benzimidazole groups of bimt units, and two oxygen atoms (Zn1–O2 = 1.956(4), Zn1–O3 = 1.948(4) Å) from one acetate group and one hydroxide group. The coordination environment of Zn2 is similar to that of Zn1. It is four-coordinated by two nitrogen atoms (Zn2–N2A = 1.986(5), Zn2–N8B = 2.000(5) Å) from two benzimidazole groups of bimt units, and two oxygen atoms (Zn2–O1 = 1.947(5), Zn2–O3 = 1.955(4) Å) from one acetate group and one hydroxide group in a distorted tetrahedral coordination environment. The nitrogen atoms coordinating to Zn1 and Zn2 ions originate from two crystallographically independent deprotonated 2-(benzoimidazol-2-yl-methyl)-1*H*-tetrazole ligands. In one kind of bimt units, the dihedral angle between the benzoimidazole (C3, C4, C5, C6, C7, C8, C9, N1, N2) and tetrazolate (C1, N3, N4, N5, N6) rings is 83.2°. In the other kind of bimt units, the dihedral angle between the benzoimidazole (C12 C13, C14, C15, C16, C17, C18, N7, N8) and tetrazolate (C10, N9, N10, N11, N12) rings is 97.9°. The Zn–N and Zn–O bond lengths are close to those in complexes $\{[Zn(bdic)(bmt)H_2O]\cdot 0.5H_2O\}_n$ (H_2bdic = 1,3-benzenedicarboxylic acid, bmt = 1-((benzotriazol-1-yl)methyl)-1*H*-1,2,4-triazole) [29] and $[Zn_3(L)(btc)_2(H_2O)_2]\cdot 3H_2O$ (L = 1,2,4,5-tetrakis(imidazol-1-ylmethyl)benzene; btc = 1,3,5-ben-

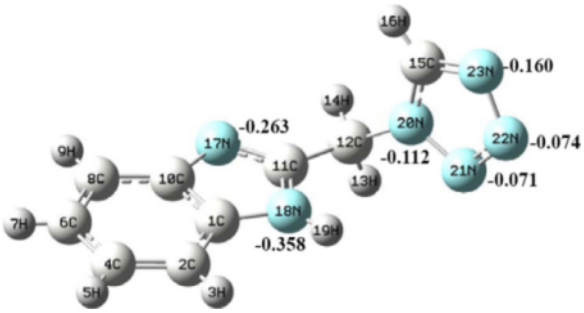

Fig. 2 (color online). The Mulliken atomic charge distributions of the N atoms in the free Hbimt ligand.

zenetricarboxylate) [30]. The Zn1 and Zn2 ions are connected by μ_2-bridging acetate groups and μ_2-bridging hydroxide groups to give a 6-membered ring with the Zn1–Zn2 distance at 3.2717(12) Å. Atoms Zn1, Zn2, O1, O2, O3, and C19 are nearly coplanar (the mean deviation from the least-squares plane is 0.0384 Å).

As shown in Fig. 1b, bimt units coordinate to Zn1 and Zn2 ions in the bidentate bridging mode with two nitrogen atoms from the same benzoimidazole ring connecting the 6-membered rings resulting in a 2D network structure containing hexagons of zinc atoms. Six vertices of the net are occupied by three Zn1 and three Zn2 ions, and four bimt units and two 6-membered rings act as the six edges. The Zn1–Zn2 distances are 6.081 and 6.101 Å. In addition, in each hexagonal net, three Zn1 ions and three Zn2 ions lie nearly in the same plane (the mean deviation from the least-squares plane is 0.0459 Å). As depicted in Fig. 1c, adjacent layers are further packed into a three-dimensional network through van der Waals forces. In the crystal, intramolecular O–H···N hydrogen bonds (the bond length and bond angle are 3.116(6) Å and 112.7°, respectively) between hydroxide groups and the benzoimidazole rings consolidate the packing of the molecules.

Although there are five potential nitrogen donors in the free Hbimt ligand, the Mulliken atomic charge distributions of the N atoms are significantly different (Fig. 2). In the Hbimt ligand, the Mulliken charges are −0.263 for N17, −0.358 for N18, −0.160 for N23, −0.071 for N21, and −0.074 for N22. So N17 and N18 have comparative advantage in coordinating to metal ions. Therefore, the deprotonated 2-(benzoimidazol-2-yl-methyl)-1*H*-tetrazole can easily coordinate to Zn(II) ions in a bidentate bridging mode leading to complex **1**. If the reaction conditions are appropriate, the Hbimt ligand can act as a bridging ligand or as a tridentate ligand forming high-dimensional structures [19, 23].

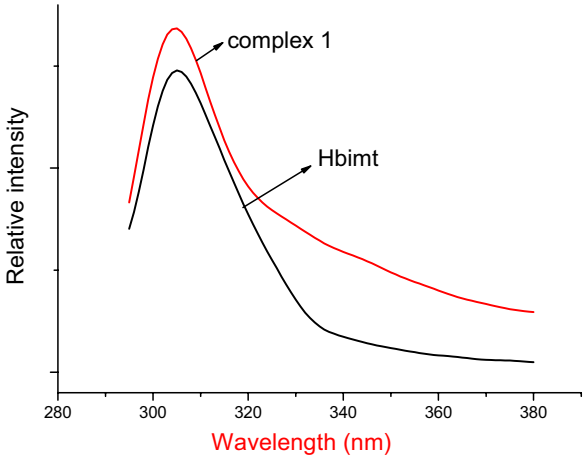

Fig. 3 (color online). Solid-state emission spectra of the Hbimt ligand and complex **1** at room temperature.

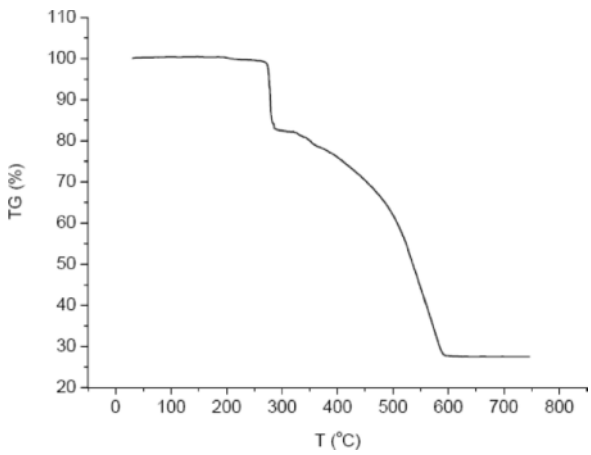

Fig. 4. The TG curve of complex **1**.

Fluorescence spectra

A number of d^{10} transition metal complexes with Zn(II) and Cd(II) atoms have been investigated regarding their fluorescence properties because of their potential applications in chemical sensors, photochemistry, and light-emitting diodes (LEDs) [30–32]. The solid-state luminescence properties of complex **1** were investigated at room temperature. As shown in Fig. 3, the main emission peak of the complex was observed at 304 nm when excited at 283 nm. At the same

time, a photoluminescence spectrum of the free ligand Hbimt was also measured in the solid state to understand the nature of the emission band. The free ligand Hbimt also displays an emission band at 304 nm ($\lambda_{ex} = 283$ nm). So we can assume that the emission spectrum of complex **1** can be tentatively assigned to the intraligand charge transfer because a similar emission is observed for free ligand Hbimt [33].

Thermogravimetric analysis

Thermogravimetric (TG) analyses of complex **1** have been conducted in air between 30 and 750 °C (Fig. 4). The TG curve shows that **1** is stable up to 252 °C. Then there is decomposition above 252 °C to leave ZnO (observed 27.4 %, calculated 26.9 %). Finally a plateau region is observed above 604 °C.

Conclusion

Through the assembly of the ligand 2-(benzoimidazol-2-yl-methyl)-1*H*-tetrazole with $Zn(Ac)_2 \cdot 2H_2O$, a new 2D complex $[Zn_2(bimt)_2(Ac)(OH)]_n$ (**1**) was obtained. In this complex, the Hbimt ligands are deprotonated and coordinated to the metal ions in a bidentate bridging mode with two nitrogen atoms from the same benzoimidazole ring although there are five potential nitrogen donors in the free Hbimt ligand. A similar coordination mode is also observed in the complex $[Cd(bimt)(Hbimt)Br]_n$ [19]. The origin of this behavior can be traced back to the differences of the Mulliken atomic charge distributions of the N atoms in the same ligand. If we change the reaction conditions, the Hbimt ligands can coordinate in different ways [19, 23]. As a promising type of a flexible *N*-heterocyclic ligand, Hbimt can be potentially utilized in constructing more complexes with charming structures under different conditions.

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