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Self-assembly of a coordination polymer $\{Zn(II)_3[(Btc)_2(Bzim)_3]\}_n$ and its properties

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Abstract : A coordination polymer $\{Zn(II)_3[(Btc)_2(Bzim)_3]\}_n$ (Btc = 1, 3, 5-benzene tricarboxylic acid, Bzim = benzimidazole) was successfully assembled in crystal state by hydrothermal method. Its molecular configuration was well defined by X-ray diffraction, element analysis and IR determination. Investigation re-

sults indicated that this coordination polymer possessed photoluminescence and thermal stability.

Keywords : Coordination polymer; Zinc complex; 1, 3, 5-benzene tricarboxylic acid; Benzimidazole.

INTRODUCTION

Carboxylic acid and nitrogen heterocyclic compounds have provided various coordination types in structural construction, and some of the new ordered molecular aggregations have already found their functionalities in practice applications^[1-4]. Therefore their preparation and property research become more important in coordination chemistry. In complexes with d10 configuration metals, either metal-ligand charge transfer (MLCT) or ligand-metal charge transfer (LMCT) resulted in strong fluorescence, and several zinc (II) complexes was previously reported^[5-6]. But till now the zinc (II) complex with 1, 3, 5-benzene tricar-

boxylic acid (Btc) and benzimidazole (Bzim) ligands has not yet been reported. In this work a supramolecular coordination polymer $\{Zn(II)3[(btc)2(bzim)3]\}_n$ was self-assembled by hydrothermal method. Its crystal structure was well defined by X-ray analysis, and some properties including photoluminescence and thermal stability were also investigated.

EXPERIMENTAL

Instrument and reagents

Elemental analysis was performed by a Perkin-Elmer 240 C element analyzer, Fourier transform infrared (FTIR) spectra were recorded on Nicolet IR 200

ORIGINAL ARTICLE

spectrophotometer (USA). Photoluminescence determinations were carried out on a FLS920 fluorescence spectrometer (Edinburgh Instruments, England). Thermal gravimetric analysis (TGA) data was taken on a TA Q-50TGA instrument (USA) under Ar atmosphere at a heating rate of 10°C/min. All reagents purchased with purity higher than 99.9% were used directly in this experiment.

Self-assembly of coordination polymer $\{Zn(II)_3[(Btc)_2(Bzim)_3]\}_n$

Under ambient conditions and with constant stirring, 1, 3, 5-benzene tricarboxylic acid (Btc, 0.023g, 0.1 mmol), benzimidazole (Bzim, 0.024 g, 0.2 mmol), Zn(Ac)₂·2H₂O (0.042g, 0.2mmol) and distilled water (8mL) were sufficiently mixed. The mixture was sealed in an autoclave which was heated at 160 °C for 72 h. After cooling down to room temperature at a rate of 5 °C/h, several yellow block crystals in 37% yield was separated by filtration. Calcd for C₁₃H₈N₂O₄Zn(%): C, 49.50; H, 3.04; N, 8.45. Found: C, 49.10; H, 3.09; N, 8.42. IR (KBr, cm⁻¹): 3428vs, 1614s, 1462s, 1401m, 1360m, 1071w, 1279w, 1238m, 1180w, 911w, 747s, 649w, 425w.

Crystal structure analysis

X-ray data collections and structure determination was performed on a Bruker SMART CCD (Germany). The data were collected using graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature (293 K). The crystal structure was solved by direct methods and refined by full-matrix least-square calculation on F2 with SHELX-97 program package^[7]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were placed in calculated positions. Crystal data for $\{Zn(II)_3[(Btc)_2(Bzim)_3]\}_n$: triclinic, $p+$, $a = 11.1892(6) \text{ \AA}$, $b = 11.3220(6) \text{ \AA}$, $c = 14.9436(8) \text{ \AA}$, $\alpha = 74.693(10)^\circ$, $\beta = 81.438(10)^\circ$, $\gamma = 80.031(10)^\circ$; $V = 1787.76(17) \text{ \AA}^3$, $Z = 6$, $T = 293(2) \text{ K}$, $D_c = 1.792 \text{ Mg/mm}^3$, $R1 = 0.0462$, $wR2 = 0.1220$.

RESULTS AND DISCUSSION

Complex's crystal structure

X-ray diffraction results indicated that in crystal of

the coordination polymer $\{Zn(II)_3[(Btc)_2(Bzim)_3]\}_n$, an independently asymmetric unit was constructed by three zinc atoms (Zn1-Zn3), two Btc and three Bzim molecules (Figure 1A). The coordinating situation around zinc atoms was shown in Figure 1B. The first Btc molecule ligated three zinc atoms with two coordinating types, including $\mu_2-\eta^2:\eta^1$ -bridge model and $\mu_1-\eta^1:\eta^0$ -monodentate model^[8] to form coordination bonds in different lengths: Zn(1)-O(1), 2.026(3) Å; Zn(2)-O(2), 2.020(3) Å, Zn(3)-O(1), 2.167(3) Å; and Zn(1)-O(6A), 1.907(3) Å, Zn(3)-O(4A), 1.922(3) Å. The second Btc molecule provided three coordination types, including $\mu_2-\eta^1:\eta^1$ -bridge model (Zn(1)-O(8), 1.946(3) Å and Zn(3)-O(7), 1.975(3) Å); $\mu_1-\eta^1:\eta^0$ -monodentate model (Zn(1)-O(9A), 1.924(3) Å); and $\mu_1-\eta^1:\eta^1$ -chelating model (Zn(2)-O(11A), 2.370(4) Å and Zn(2)-O(12A), 1.999(3) Å). Beside ligations from Btc molecules, Zn(2) and Zn(3) atoms were also coordinated by N atoms from three Bzim molecules to form N-Zn bonds with lengths of Zn(2)-N(3), 2.018(4) Å; Zn(2)-N(5), 1.986(4) Å and Zn(3)-N(1), 1.963(4) Å. The conjugated N(2) and N(5) atoms with high charge density and strong electron donating effect enhanced coordination bonds, and then both Zn(2)-N(3) and Zn(2)-N(5) were shorter in bond lengths^[9]. Btc molecules provided abundantly coordination models, and therefore crystal architecture for the title coordination polymer displayed a 3D networks. Meanwhile Bzim molecules filling in crystal voids enlarged and sustained this 3D networks. If the Bzim molecules were removed, the 3D networks would present in a honeycombed structure stretching along in both a and b axes (Figure 2)^[10] with porosity at 50.4%.

Thermal stability of the title complex

Thermal stability of the title complex was determined by thermogravimetric analysis (TGA) in range of 25 - 650 °C with at rate 10 °C/min, and the TGA's curve was shown as Figure 3. The Bzim molecules began to lose at $t > 350 \text{ }^\circ\text{C}$, and the finally losing ratio was 21.1 %, which was near the theoretical value (20.6%). The Btc framework molecules began to lose at $t > 420 \text{ }^\circ\text{C}$, and the crystal architecture was destroyed. Two Bzim molecules were lost at different temperatures according to their different coordination situations.

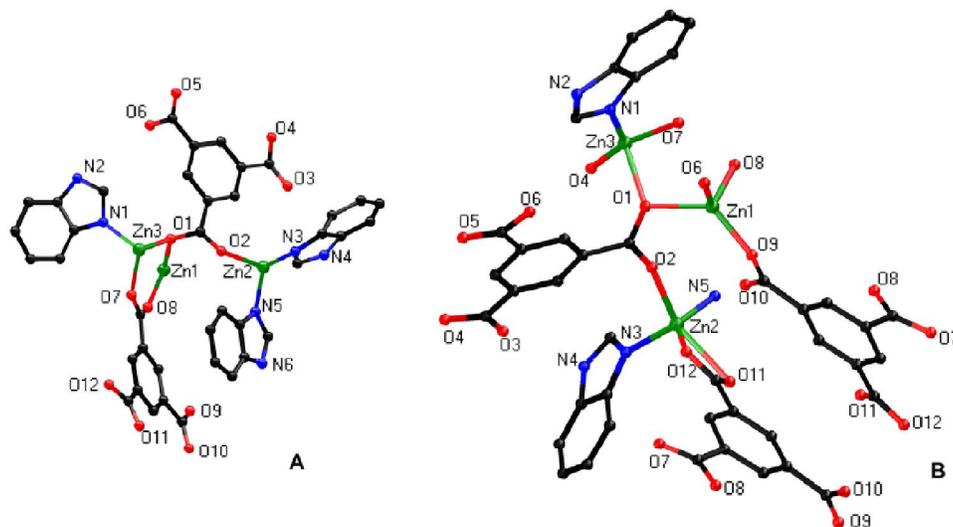


Figure 1 : (A) The single core of $Zn(II)_3[(Btc)_2(Bzim)_3]$ in an independently asymmetric unit. (B) Coordinating situation around zinc (II) ions in crystal architecture of the prepared complex (all H atoms were omitted for clarity).

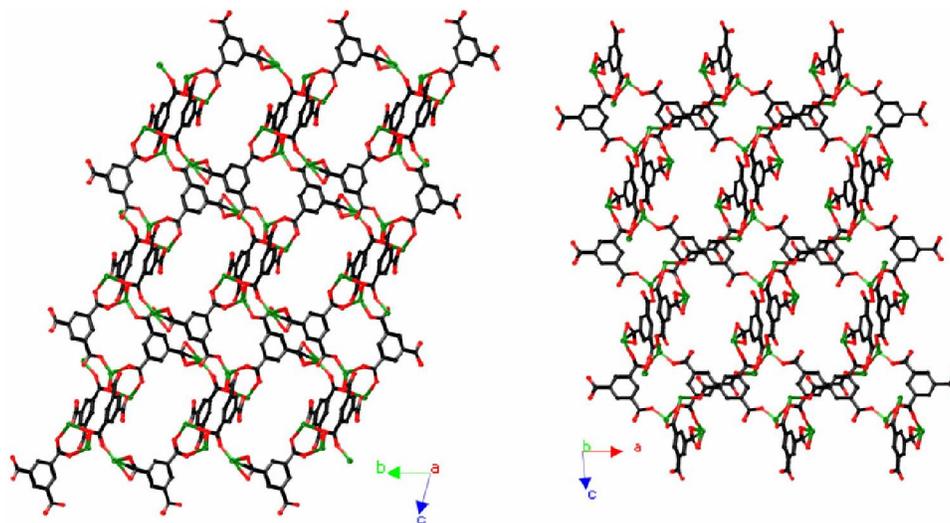


Figure 2 : The honeycombed frames for titled complex along with *a*- (left) and *b*- (right) axis orientations (Bzim molecules were omitted).

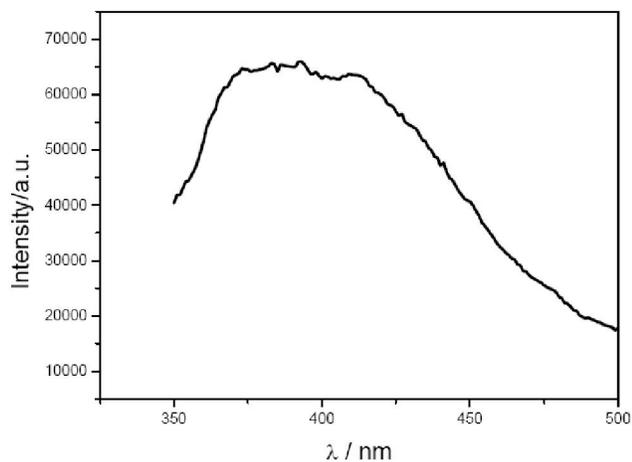


Figure 3 : Fluorescent emission spectrum of the title complex ($\lambda_{Ex} = 330\text{nm}$)

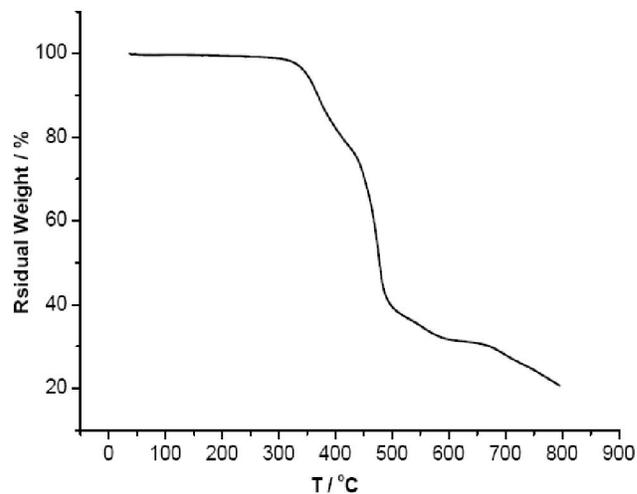


Figure 4 : Thermogravimetric analysis of the title complex

ORIGINAL ARTICLE

Photoluminescence of the title complex

In solid state, when the coordination polymer was excited in UV (330 nm), it exhibited a strong and broad emission spectrum in range of 370-410 nm (Figure 4). This photoluminescence was different from those for both Btc and Bzim appeared around 330 nm^[11]. Therefore the ligand-metal charge transfer (LMCT) mechanism for the photoluminescence of the title complex was concluded, and this photoactivity was also enhanced by π - π stacking between Btc and Bzim molecules in the crystal architecture^[12].

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