Syntheses and Characterization of Luminescent Materials of Compound $ZnO_6N_2C_{29}H_{28}$

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Keywords: Luminescent Materials; (4-hydroxyphenyl)acetate; 4,4'-trimethylenendipyridine

Abstract. One new luminescent materials of complex $C_{29}H_{28}N_2O_6Zn$ (**1**) was synthesized by evaporation methods using (4-hydroxyphenyl)acetate(4-HOBA), 4,4'-trimethylenendipyridine(TDP) and $Zn(NO_3)_2$. And the complex was characterized by elemental analysis, FT-IR, thermogravimetrie analysis(TGA), XRD, X-ray single-crystal structure analysis and fluorescence properties have been studied. As a result, complex **1** are one-dimensional(1-D) structure through TDP igands. Complex **1** emits the intensely luminescence with the fluorescence of 454 nm in a solid state at room temperature. CCDC: 1004211.

Introduction

Molecular self-assembly of luminescent materials is a rapidly developing indagate field of crystal engineering and coordination chemistry in recent years[1-6]. The self-assembly of luminescent materials of complex is effected by much factors, howbeit, policy synthesis or choice of the ligand are key factors for acquireing expected complexes[7,8]. The aromatic carboxylate ligand of hydroxyphenylaceticacid to build various complex may result in some tailorable structures[9-13]. Moreover, The pliable 4,4'-trimethylenendipyridine ligand is an outstanding candidate for to build novel structures as the accessorial ligands[14,15]. So far, work on the molecular assembly of luminescent materials involving (4-hydroxyphenyl)acetate (4-HOBA) ligand and N-containing auxiliary ligands is still scarce. In this study, we introduced 4-HOBA ligand together with the TDP ligand was prepared the zinc ions complex **1**. In addition, TGA, XRD and luminescent of complex **1** were discussed.

Physical Measurements

The chemicals were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. It shows the percentage of carbon, hydrogen and nitrogen of the complexes. The FT-IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer using KBr pellet at a resolution of 0.5 cm^{-1} (400 ~ 4000 cm^{-1}). Thermogravimetry analyses were performed on an automatic simultaneous thermal analyzer (PE TG/DTA 6300) under a flow of N_2 at a heating rate of 10 $^{\circ}C \cdot min^{-1}$ between ambient temperature and 800°C. Luminescence spectra for crystal solid samples were recorded at room temperature on a PERKIN ELMER LS 55 luminance meter. X-ray powdered diffraction pattern of the sample was recorded by an X-ray diffractometer (Rigaku D8) equipped with a graphite-monochromatic Cu*Ka* radiation.

Experimental

$C_{29}H_{28}N_2O_6Zn$ (**1**): To the solution of a zinc nitrate(0.145g, 0.5mmol), (4-hydroxyphenyl)acetate (0.076g, 0.5mmol) and 4,4'-trimethylenendipyridine (0.0991g, 0.5mmol) were dissolved in 3:1 water/methanol solution and the pH was adjusted to 7 with 0.14mol/L potassium hydroxide solution. The mixture was stirred for 35 min, the precipitate was dissolved an aqueous NH_3 solution(25%) was added drop by dropp dropped into the mixture to give a clear solution. After three weeks, colorless crystals were obtained by evaporation at room temperature in 45.2% yield (based on Zn). Anal. Calcd for $C_{29}H_{28}N_2O_6Zn$: C 61.55, H 4.99, N 4.95%; found: C 61.39, H 4.80, N 4.91 %.

X-ray structure determination

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART APEXII CCD diffractometer. The diffraction data were collected with Mo *K*α radiation(λ=0.71073Å). Empirical absorption corrections were carried out by using the SADABS program. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL crystallographic software package. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. The crystal structure data of complex **1** were listed in Table 1, the selected bond lengths and bond angles in Table 2 and hydrogen bond lengths and bond angles in Table 3.

Table 1 Crystal data and structure refinements of complex 1

Empirical formula	$C_{29}H_{28}N_2O_6Zn$	V /Å^3	2679.5(15)
Formula weight	565.90	Z	4
Temperature / K	296(2)	μ/ mm^{-1}	0.962
Size / mm	0.30 x 0.20 x 0.18	D_c / (g·cm^{-3})	1.403
θ range for data collection / (°)	2.21 to 25.00	F(000)	1176
Crystal system	Monoclinic	Reflections collected	16539
Space group	$P2_1/c$	Independent reflections (R_{int})	4697 (0.0537)
a / Å	12.125(5)	Goodness of fit on F^2	1.085
b / Å	21.791(6)	R_1, wR^2 ($I>2\sigma(I)$)	0.0811, 0.2325
c / Å	11.415(3)	R_1, wR_2 (all data)	0.1075, 0.2534
β/ (°)	117.322(3)	$(\Delta\rho)_{max}$,$(\Delta\rho)_{min}$ / e.Å^3	1.286, -0.583

Crystal structure

Each the zinc ions is covalently bound by two N-atoms of two TDP ligands and two oxygen atoms from different two 4-HOBA ligands in the asymmetric unit of complex **1**, displaying a distorted tetrahedron geometry.The Zn(1)-N and Zn(1)-O distances fall in the range of 1.916(5) ~ 2.060(5) Å.The carboxyl group of 4-HOBA coordinates to the zinc ions in a monodentate fashion. The carboxyl group of 4-HOBA and a hydrogen atom of TDP form intramolecular hydrogen bond(C(27)-H(27)···O(4)), with the C···O bond length of 3.197(10)Å and the C–H···O bond angle of 141.3°(Fig.1(a)). Every TDP ligands bridges two neighbouring zinc ions to form a one-dimensional(1-D) chain along, and the TDP ligand has *TT* conformation. The Zn···Zn distance is 12.125Å by the bridging TDP in complex **1**. The reverse arrangement of 4-HOBA ligand one-dimensional chain on both sides, with the help of hydrogen-bonded interactions between adjacent 1-D sheet[O(5)-H(5O5)···O(2)^{iii} , Symmetry codes: ^{iii} x-1,-y+3/2,z-1/2], the polymeric sheet are assembled to form a two-dimensional structure(Fig.1(b) and Table.3). With the help of stacking interactions between adjacent the polymeric sheet are assembled to form a supramolecular 3-D network structure.

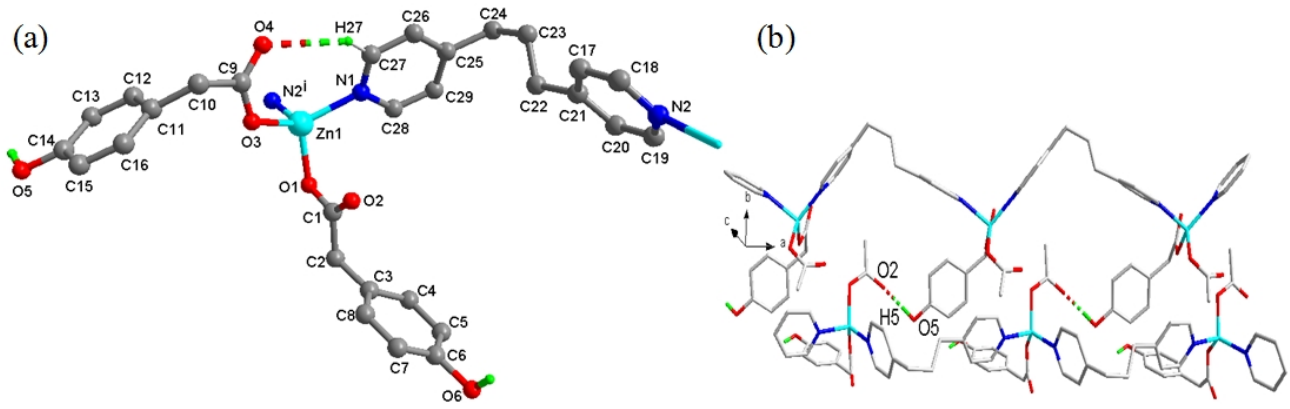

Fig.1 (a) Molecular structure (Symmetry codes: [i] x-1,y,z) and (b) 2-*D* structure of complex **1**

Tabulation 2 Concernment bond lengths (Å) and bond angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)-O(3)	1.916(5)	Zn(1)-O(1)	1.945(5)	Zn(1)-N(1)	2.013(6)
Zn(1)-N(2)^{i}	2.060(5)	O(5)-C(2)	1.373(8)	O(6)-C(6)	1.410(4)
O(3)-Zn(1)-O(1)	108.5(2)	O(3)-Zn(1)-N(1)	124.1(2)	O(1)-Zn(1)-N(1)	110.4(2)
O(3)-Zn(1)-N(2)^{i}	105.6(2)	O(1)-Zn(1)-N(2)^{i}	98.4(2)	N(1)-Zn(1)-N(2)^{i}	106.7(2)

Symmetry code: [i] x-1,y,z

Tabulation 3 Hydrogen bond (H···A)/Å) and bond angles (°)

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(27)-H(27)···O(4)	0.93	2.42	3.197(5)	141.3
O(5)-H(5O5)···O(2) [iii]	0.82	1.90	2.718(8)	178.6
C(10)-H(10A)···O(6) [iv]	0.97	2.56	3.323(6)	135.6

Symmetry code: [iii] x-1,-y+3/2,z-1/2 [iv] -x+1,y-1/2,-z+1/2

IR spectrum and Thermal analysis

The IR spectra of the complex **1** exhibit the typical antisymmetric 1601 cm^{-1} and symmetric 1383 cm^{-1} stretching bands of carboxy groups, the values $\Delta\nu(\nu_{as}(COO^{-})$-$\nu_{s}(COO^{-}))$ of 218cm^{-1}, indicate that 4-HOBA is monodentate. Meanwhile, characteristic bands 1516 and 1436 cm^{-1} in 1 belong to the stretching vibration of -N=C- of TDP.

In complex **1**, the weight-loss step occurred from 30 to 396 ˚C(Obsd. 53.83%, Calcd.53.44%) which corresponds to the decomposition of framework structure on two 4-HOBA ligand. Complex **1** starts slowto decompose after 431˚C, this structure is similarly adopted by $[Co(bpp)(H_2O)(nip)]_n$[16].

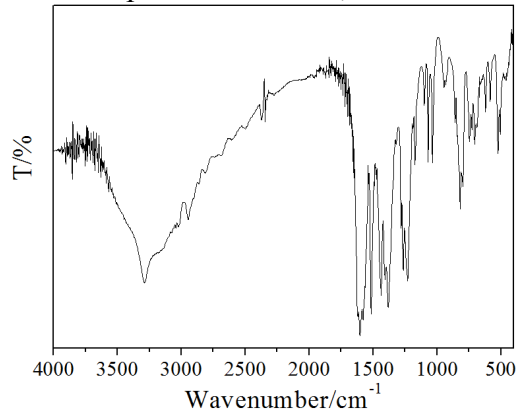

Fig.2 IR for complex **1**

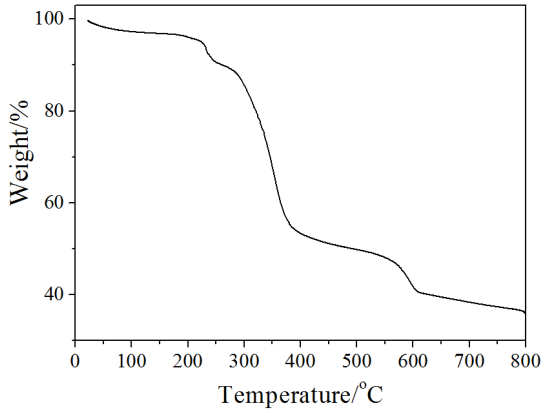

Fig.3 TG for complex **1**

X-ray powder diffraction and Luminescent Property

Although the experimental patterns show several slightly broadened diffraction peaks in comparison to those simulated from the single-crystal data, it can still be regarded that the bulk as-synthesized aterials represent the pure phases of complex **1** (in Fig.4, black: simulation of single crystal; red: solid samples).

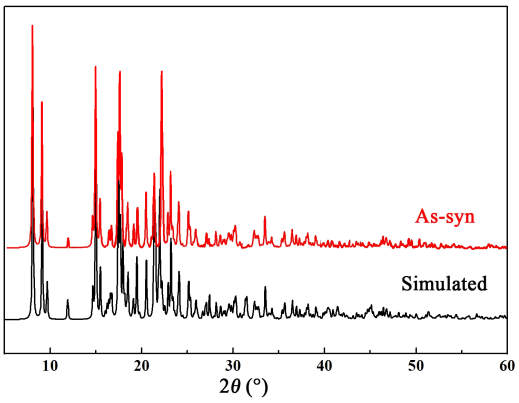

Fig.4 XRD for complex **1**

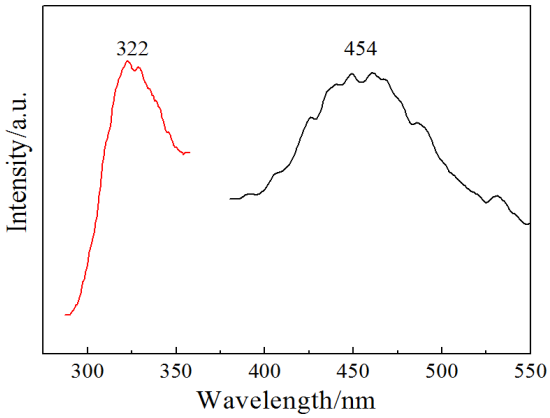

Fig.5 Photoluminescent spectrum for complex **1**

In complex **1**, fluorescent property of compound has been investigated in the solid state. Two emission peaks at about 368 nm (l_{ex} = 307 nm) and 455 nm (l_{ex} = 372 nm) were observed for free 4-HOBA and TDP ligands, respectively. On complexation of these ligands with Zn(II) atoms, strong fluorescence with emission broad peak centered at 454 nm (λ_{ex}=322 nm) for compound **1** was observed at room temperature(Fig.5), which may originate from the π-π* transition emission of ligand-to-ligand charge transfer(LLCT) in aromatic rings of the two ligands .

Summary

A new 1-D zinc(II) complex based on 4-HOBA and TDP ligands are reported. This successful preparation of the title compound indicates that the TDP can be an outstanding proposer for the construction of coordination polymers. Complex **1** emits the intensely luminescence with the fluorescence of 454 nm.

Acknowledgment

This work was supported by the Guangdong Science and Technology Department (No. S2012020011054 and 2011B090400415) and the Zhanjiang Municipality (No. 2011C3108001) projects

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