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# Phenoxo bridged dinuclear Zn(II) Schiff base complex as new precursor for preparation zinc oxide nanoparticles: Synthesis, characterization, crystal structures and photoluminescence studies

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ABSTRACT

Nanoparticles of a novel Zn(II) Schiff base complex, $[Zn(HL)NO_3]_2$ (**1**), ($H_2L$ = 2-[(2-hydroxy-propylimino) methyl] phenol), was synthesized by using solvothermal method. Shape, morphology and chemical structure of the synthesized nanoparticles were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier Transform Infrared Spectoscopy (FT-IR) and UV–vis spectroscopy. Structural determination of compound **1** was determined by single-crystal X-ray diffraction. The results were revealed that the zinc complex is a centrosymmetric dimer in which deprotonated phenolates bridge the two five-coordinate metal atoms and link the two halves of the dimer. The thermal stability of compound **1** was analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effect of the initial substrates concentration and reaction time on size and morphology of compound **1** nanostructure was investigated as well. Furthermore, the luminescent properties of the complex **1** were examined. ZnO nanoparticles with diameter between 15 and 20 nm were simply synthesized by solid-state transformation of compound **1** at 700 °C.



## 1. Introduction

Recently zinc complexes of tridentate Schiff-base ligands have received continual and considerable attention in many fields of research because of their potential usage in various applications such as biomolecules, catalysts, optoelectronic etc. [1–4].

Dinuclear group 12 metal ions complexes of Schiff base ligands are well-studied area of research in coordination chemistry because of their key roles in many applications [5]. Among them dinuclear Zn(II) complexes have attracted great attention due to their potential use in many applications such as biomedical as anti-cancer drug [6] biology as antibacterial and antifungal agent [7], as functional model complexes of enzymes [8] and chemical industries as catalyst [9]. Moreover zinc Schiff base complexes have founded to show the luminescence properties [10] which makes them suitable to generate OLED devices with various frameworks and improved properties [11,12].

Nano coordination complex can be synthesized using various methods and conditions including microwave, sonochemistry [13–15], coordination modulation, hydrothermal, solvothermal etc. [16,17]. Normally decreasing the size of coordination complexes from bulk powder crystalline to nano-size improve their properties and applications [18].

Zinc oxide is a well-known semiconductor. It has used in many applications such as surface acoustic wave devices, gas sensor devices, laser and optoelectronic devices [19]. Zinc oxide nanoparticles can be prepared by different methods. From these methods, the use of zinc coordination complex as precursors for the preparation of zinc(II) oxide is one of the most commonly used methods because of its simplicity, low cost reaction, fairly low temperature method, and no necessity for use of surfactant or capping molecules [18,20].

In this study we were used a simple solvothermal method to synthesize nanostructured zinc(II) supramolecular compound, $[Zn(HL)NO_3]_2$ (**1**), ($H_2L$ = 2-[(2-hydroxy-propylimino) methyl] phenol) and its use as a precursor for preparation of ZnO nanoparticles without any surfactant or capping agents. In comparison with the reported methods for preparing ZnO nanoparticles [18–20], the advantage of thermal decomposition route lies in its simplicity, including simple synthesis, relatively low temperature and high

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yield of nano-size ZnO product. The photoluminescence properties of $H_2L$ ligand and the zinc complex (**1**) in solutions of methanol were examined.

## 2. Experimental

### 2.1. Materials and methods

$Zn(NO_3)_2{\cdot}6H_2O$ was purchased from Merck India Ltd., 1-amino-2-propanol and 2-hydroxybenzaldehyde from Sigma–Aldrich, USA. All the chemicals and solvents employed for the synthesis were of analytical grade and used as received without further purification.

FT-IR spectra of the ligand and the complex were recorded in the 4000–400 $cm^{-1}$ wavenumber region by using KBr disks as standard on a Thermo SCIENTIFIC model NICOLET iS10 spectrophotometer. The UV-vis absorption spectra were obtained by using a PG instruments Ltd., T70/T80 series (UV–vis) spectrometer in the range of 800–200 nm wavelength with HPLC grade methanol as solvent. A Brucker Avance DPX 400 MHz instrument was used to record the NMR spectra with TMS and $CDCl_3$ as the internal standard and the solvent, respectively. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [21]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromatic Cu-Kα radiation to investigate the crystalline structure and phase identification. The nano samples were characterized by a scanning electron microscopy (SEM) (Philips XL 30). HRTEM analysis was performed using HRTEM microscope (Philips CM30). Thermogravimetric analysis (TG) and Differential scanning calorimetry (DSC) of the title compound was performed on a computer-controlled NETZSCH model PC Luxx 409 apparatus. A single-phased powder sample of 1 was loaded into alumina crucible and heated with a heat rate of 10 °C/min from room temperature to 800 °C under an argon atmosphere.

### 2.2. Synthesis of 2-[(2-hydroxy-propylimino) methyl] phenol ($H_2L$)

The asymmetric tridentate Schiff base $H_2L$ was obtained by addition of a solution of 0.01 mol 1-amino-2-propanol (0.75 g) in ethanol (10 ml) to a solution of 0.01 mol 2-hydroxybenzaldehyde (1.22 g) in 10 ml ethanol and the reaction mixture was stirred and heated to reflux for 1 h. After evaporation of ethanol, a yellow viscous oil was obtained, which was allowed to stand overnight in a refrigerator. $CHCl_3$ (5 ml) was then added and the yellow precipitate was filtered off and subsequently dried in air. The crude product was recrystallized from $CHCl_3$–hexane (1/4 v/v). Yield: 90%. m.p.:46–48 °C.

### 2.3. Preparation of zinc complex $[Zn(HL)NO_3]_2$ as single crystal (1)

0.01 mol $H_2L$ ligand was added into 0.01 mol hexa hydrate zinc (II) nitrate in 10 ml ethanol. The reaction mixture was stirred under reflux condition for 4 h and then a light yellow precipitate was removed by filtration. The resulting yellow solution was then left undisturbed. After several days, gold block-shaped X-ray diffraction quality single crystals appeared. The product was secured in 72% yield. m.p.: >250 °C.

### 2.4. Synthesis of $[Zn(HL)NO_3]_2$ (1) nanostructure by solvothermal method

$Zn(NO_3)_2{\cdot}6H_2O$ (0.5 mmol) and ligand ($H_2L$) (5 mmol) were dissolved in 15 ml EtOH. The solution was charged into a Teflon-lined stainless steel autoclave and heated at 150 °C for 24 h. After the autoclave was cooled immediately to room temperature, the product was filtered, dried and characterized. m.p: >250 °C

### 2.5. Preparation of ZnO nanoparticles

The Schiff base zinc(II) complex $[Zn(HL)NO_3]_2$ (**1**), was loaded into a crucible and then was placed in oven and heated at a rate of

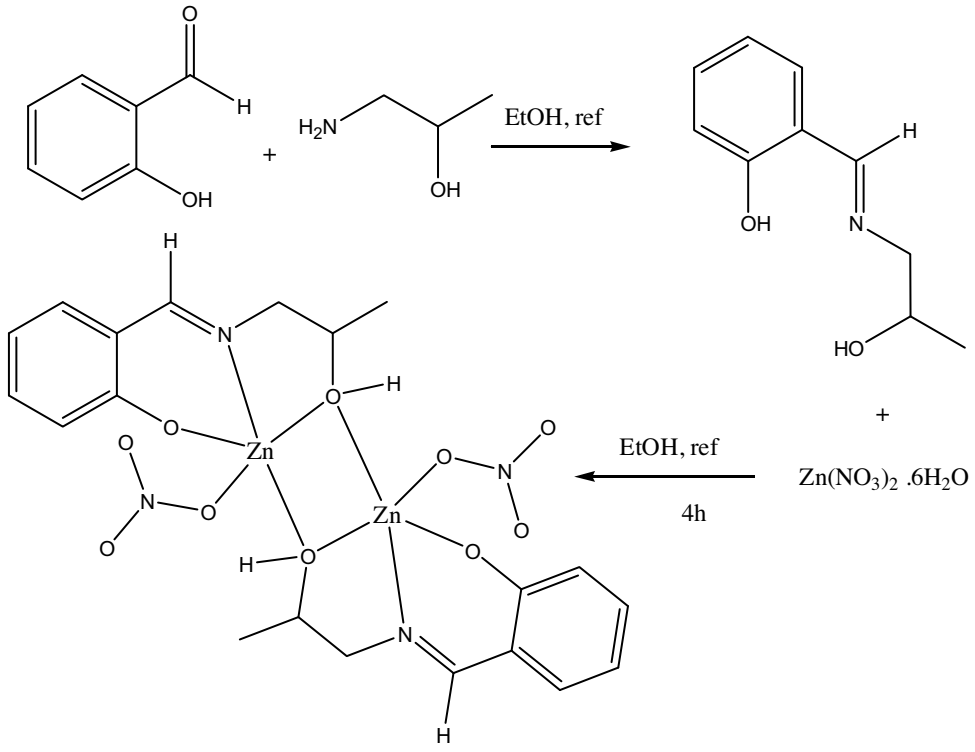


**Fig. 1.** Schematic representation of the synthesis of title compound.