



A perfectly linear trinuclear zinc–Schiff base complex: Synthesis, luminescence property and photocatalytic activity of zinc oxide nanoparticle



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ABSTRACT

A perfectly linear trinuclear zinc(II) complex $[Zn_3L_2(\mu-O_2CCH_3)_2]$ (**1**) containing a (N,O)-donor Schiff base ligand, ($H_2L = N,N'$ -bis(salicylaldehyde)-1,3-diaminopropan-2-ol) has been synthesized and characterized by single crystal X-ray diffraction study. The X-ray crystal structure of **1** contains three zinc(II) centers which are inter-connected through μ_2 -phenolato and μ -acetato bridges. The terminal zinc centers are in square pyramid geometry and central zinc ion is in distorted octahedral coordination geometry. Both H_2L and **1** exhibit good fluorescence properties in solution. **1** has been used as a precursor to fabricate zinc oxide nanoparticles (ZnONPs) by pyrolytic method. ZnONP has been characterized by powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), FT-IR spectroscopy and UV–Vis spectroscopy techniques. ZnONP has been employed as photocatalytic agent to degrade the organic dye, viz. Methylene blue under visible light and by exposing to visible light for 1 h, ZnONP degraded methylene blue dye nearly 80%.

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1. Introduction

Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their unusual configurations, structural lability and sensitivity to molecular environments as functional materials [1–3]. Schiff bases can accommodate different metal centres involving various coordination modes allowing successful synthesis of homo- and heterometallic complexes with varied stereochemistry. Zinc being an essential and one of the most bio-relevant transition metal ions; next to iron (human beings contain an average of ~2–3 g of zinc). It is no surprise that di- and trinuclear Zn^{II}–Schiff base complexes have attracted particular interest as synthetic structural mimics of the active site of a range of metalloenzymes [4,5], new cancer therapeutic agents and their photochemical materials [6–9].

Excess apply of various dyes in the textile industry has led to the severe surface water and groundwater contamination by releasing the toxic and coloured effluents, which are usually disposed by various physical and chemical methods, such as

coagulation/flocculation [10,11], electrocoagulation [12], coagulation/carbon adsorption process [13] and so on. However, these methods barely transfer the pollutants from one phase to another without destruction or have the other limitations. In recent years, as a promising tool to substitute the traditional wastewater treatment, semiconductor-assisted photocatalysis among the advanced oxide processes (AOP) has attracted the public concern for its ability to convert the pollutants into the harmless substances directly in the waste water. Till now, many kinds of semiconductors have been studied as photocatalysts including TiO₂, ZnO, CdS, WO₃ and so on [14–17]. TiO₂ is the most widely used effective photocatalyst for its high efficiency, photochemical stability, non-toxic nature and low cost. As a contrast, ZnO, a kind of semiconductor that has the similar band gap as TiO₂, is not thoroughly investigated. However, the greatest advantage of ZnO is that it absorbs large fraction of the solar spectrum and more light quanta than TiO₂ [18].

In this present work, we have synthesized and crystallographically characterized a perfectly linear trinuclear Zn(II)–Schiff base complex (**1**). Fluorescence studies for both the Schiff base ligand and complex exhibits strong emission at room temperature. We have also prepared zinc oxide nanoparticle from this trinuclear complex as a precursor in the dimension of ~98 nm and the

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nanoparticles have been characterized by powder X-ray diffraction study and scanning electron microscope imaging. The visible light driven photocatalytic activity of synthesized ZnO nanoparticle was demonstrated using methylene blue (MB) as a representative dye and the catalytic efficiency is optimized with respect to pH of the solution.

2. Experimental

2.1. Preparation of the complex

2.1.1. Chemicals, solvents and starting materials

High purity Salisaldehyde (E. Merck, India), 1,3-diaminopropan-2-ol (Lancaster, UK), methylene blue (Aldrich, UK), zinc(II) acetate dihydrate (E. Merck, India) were purchased from respective concerns and used as received. All the other reagents and solvents are of Analytical grade (A.R. grade) and were purchased from commercial sources and used as received.

2.1.2. General synthesis of the Schiff base ligand (H_2L) and zinc compound (**1**)

The Schiff base ligand, H_2L , *N,N'*-bis(salicylaldehyde)-1,3-diaminopropan-2-ol was synthesized in a reported literature [19]. Salisaldehyde (0.244 g, 2 mmol) was heated under reflux with 1,3-diaminopropan-2-ol (0.089 g, 1 mmol) in 30 ml dehydrated alcohol. After 10 h the reaction solution was evaporated under reduced pressure to yield a gummy mass, which was dried under vacuum and stored over $CaCl_2$ for subsequent use. Yield, 0.278 g (82.8%). *Anal. Calc.* for $C_{17}H_{18}N_2O_3$ (H_2L): C, 68.48; H, 6.08; N, 9.39. Found: C, 68.40; H, 6.02; N, 9.35%. 1H NMR ($CDCl_3$) δ = 3.68 (dd, J = 12.4, 6.8 Hz, 2H), 3.84 (dd, J = 12.4, 4.0 Hz, 2H), 4.23–4.25 (m, 1H), 6.88 (t, J = 7.2 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 7.25 (dd, J = 7.6, 1.6 Hz, 2H), 7.32 (td, J = 8.8, 1.6 Hz, 2H), 8.36 (s, 2H) ppm. ^{13}C NMR δ , 62.9, 70.2, 117.0, 118.5, 118.6, 131.5, 132.5, 161.1, 167.3 ppm. IR (KBr, cm^{-1}): 1634, 1611 ($\nu_{C=N}$), 3412 (ν_{OH}), UV–Vis (λ_{max} , nm): ~221, 267, 316, 410 nm.

A methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.657 g, 3 mmol) (10 cm^3) was added dropwise to a solution of H_2L (0.596 g, 2 mmol) in the same solvent (15 cm^3). The yellow solution of the ligand immediately became colourless with quick precipitation of white crystalline compound. It was filtered and recrystallized from methanol–dimethyl formamide solvent mixture. The solvent mixture produced colourless crystals. Yield: 0.453 g (69% based on metal salt). *Anal. Calc.* for $C_{38}H_{38}N_4O_{10}Zn_3$ (**1**): C, 50.32; H, 4.22; N, 6.18. Found: C, 50.40; H, 4.27; N, 6.27%. IR (KBr, cm^{-1}): 3436 (ν_{OH}), 1634, 1605 ($\nu_{C=N}$), 1497, 1460, 1420 (ν_{OAc}), 1276 (ν_{PHO}); UV–Vis (λ_{max} , nm): 266, 361.

2.2. Physical measurements

Infrared spectrum (KBr) was recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range $400\text{--}3600\text{ cm}^{-1}$. 1H NMR spectrum in $DMSO-d_6$ was obtained on a Bruker Avance 300 MHz spectrometer at $25\text{ }^\circ\text{C}$ and was recorded at 299.948 MHz. Chemical shifts are reported with reference to $SiMe_4$. Ground state absorption was measured with a JASCO V-530 UV–vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Thermal analysis was carried out on a PerkinElmer Diamond TG/DTA system up to $800\text{ }^\circ\text{C}$ in a static nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Elemental analyses were performed on a Perkin Elmer 2400 CHN microanalyser. Electrospray ionization (ESI) mass spectrum was recorded using a Q-tof-micro quadrupole mass spectrometer. The pH value of the solutions was measured by Systronics pH meter at room temperature.

2.3. X-ray diffraction study

Single crystal X-ray diffraction data were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury CCD detector. The data were collected with graphite monochromated $Mo\ K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at $295(2)\text{ K}$ using ω scans. The data were reduced using Crystal Clear suite and the space group determination was done using Olex2. The structure was solved by direct method and refined by full-matrix least-squares procedures using the SHELXL-97 software package using Olex2 suite [20,21].

2.4. Physicochemical characterization of ZnO nanoparticle

Size and morphology of the 98 nm ZnO nanoparticle was characterized by powder X-ray diffraction (PXRD) pattern and Scanning Electron Microscopy (SEM) to examine their structure, shape and surface morphology. The XRD pattern was measured by X-ray diffractometer (Bruker D8 advance) in the range from 25° to 80° using $Cu\ K\alpha$ radiation. The SEM image has been obtained using a microscope (FESEM, JEOL, and JSM-6700F).

2.5. Photocatalytic experiments

The photocatalytic activity of ZnO nanoparticles was evaluated by degradation of methylene blue (MB) dye solution. All the experiments were carried out in presence of visible light. A 250 ml Borosil beaker with outside water circulation was placed on a magnetic stirrer, above which a high pressure mercury vapour lamp (125 W, Philips) emitting visible light was placed. ZnO nanoparticle at a dose of 100 mg (solid) was added to 100 ml MB dye solution ($1.2 \times 10^{-4}\text{ M}$) in the beaker. The distance of the light source from the upper level of dye solution is 18 cm for maximum utilization of light. The solution was stirred in dark for 10 min to establish the adsorption equilibrium. The zero time reading was taken and the solution was then irradiated with visible light. Aliquots of 5 ml samples were taken at regular time interval (10 min) and centrifuged to analyse the percent degradation of the MB dye. The percentage dye degradation was calculated using formula:

Degradation = $[(A_0 - A_t)/A_0] \times 100\%$, where, A_0 is the initial dye absorbance; A_t is the dye absorbance at time (t).

To study the effect of pH on degradation efficiency, the pH of the MB dye solution was systematically adjusted by adding 0.1 (M) HCl or NaOH.

2.6. Thermogravimetric analysis of **1**

The thermal behaviour of the trinuclear zinc complex (**1**) was followed up to $700\text{ }^\circ\text{C}$ in a static nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C}$ per minute.

3. Results and discussion

3.1. Syntheses and formulation

The Schiff base ligand, H_2L , *N,N'*-bis(salicylaldehyde)-1,3-diaminopropan-2-ol was synthesized by condensing 1,3-diaminopropan-2-ol with 2-salisaldehyde in 1:2 M ratio in dry ethanol. The trinuclear zinc(II) complex **1** was prepared by mixing zinc(II) acetate and the ligand in methanol–dimethyl formamide medium. The coordination geometry of **1** was determined by mainly single crystal X-ray diffraction study along with different spectroscopic and analytical techniques. The colourless crystals suitable for X-ray data collection were obtained by slow evaporation of resultant reaction mixture (Scheme 1). The formulation was confirmed by elemental analysis, IR, UV–Vis, 1H NMR, mass spectral analysis

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