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

Dhananjay Dey^a, Gurpreet Kaur^b, Moumita Patra^c, Angshuman Roy Choudhury^b, Niranjan Kole^a, Bhaskar Biswas^{a,*}

^a Department of Chemistry, Raghunathpur College, Purulia 723133, India

^b Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali, Mohali 140 306, India

^c Department of Physics, Raghunathpur College, Purulia 723133, India

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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, (H₂L = *N*,*N'*-bis(salicyaldehydene)-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 H₂L 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 \sim 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 tion/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].

coagulation/flocculation [10,11], electrocoagulation [12], coagula-

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 \sim 98 nm and the







^{*} Corresponding author. Tel./fax: +91 3251 255235.

E-mail addresses: mr.bbiswas@rediffmail.com, bhaskarbiswas557@gmail.com (B. Biswas).

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, H₂L, *N,N*′-bis(salicyaldehydene)-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 CaCl₂ for subsequent use. Yield, 0.278 g (82.8%). Anal. Calc. for C₁₇H₁₈N₂O₃ (H₂L): C, 68.48; H, 6.08; N, 9.39. Found: C, 68.40; H, 6.02; N, 9.35%. ¹H NMR (CDCl₃) 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. ¹³C 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 (v_{C=N}), 3412 (v_{OH}), UV–Vis (λ_{max} , nm): ~221, 267, 316, 410 nm.

A methanolic solution of Zn(OAc)₂·2H₂O (0.657 g, 3 mmol) (10 cm³) was added dropwise to a solution of H₂L (0.596 g, 2 mmol) in the same solvent (15 cm³). 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 C₃₈H₃₈N₄O₁₀Zn₃ (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 (v_{OH}),1634, 1605 (v_{C=N}), 1497, 1460, 1420 (v_{OAc}), 1276 (v_{PhO}); UV–Vis (λ_{max} , nm): 266, 361.

2.2. Physical measurements

Infrared spectrum (KBr) was recorded with a FTIR-8400S SHI-MADZU spectrophotometer in the range 400–3600 cm⁻¹. ¹H NMR spectrum in DMSO-*d*₆ was obtained on a Bruker Avance 300 MHz spectrometer at 25 °C and was recorded at 299.948 MHz. Chemical shifts are reported with reference to SiMe₄. 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 °C in a static nitrogen atmosphere with a heating rate of 10 °C/min. Elemental analyses were performed on a Perkin Elmer 2400 CHN microanalyser. Electrospray ionization (ESI) mass spectrum was recorded using a Q-tof-micro quadruple 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 Merury CCD detector. The data were collected with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 295(2) 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 nanopartcle

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 α 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 = $[(A_o - A_t)/A_o] \times 100\%$, where, A_o 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 °C in a static nitrogen atmosphere with a heating rate of 10 °C per minute.

3. Results and discussion

3.1. Syntheses and formulation

The Schiff base ligand, H_2L , *N*,*N*-bis(salicyaldehydene)-1,3diaminopropan-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 and X-ray structural analysis of the zinc compound. The schematic presentation of syntheses is given below:

3.2. Description of crystal structure

The X-ray structural determination of compound 1 reveals a trinuclear neutral zinc(II) complex with the space group $P\bar{1}$. The compound 1 has been found to have a trinuclear molecule with a central Zn(II) ion lying on a center of inversion. An ORTEP view [21] of μ -acetato- μ -phenoxo-trizinc(II) complex of **1** with an atom labelling scheme is shown in Fig. 1. The trinuclear complex is built up of two mononuclear ZnL moieties linked through bridging acetate and μ_2 -phenolato groups to the central Zn atom. The coordination geometry around the terminal Zn centers (Zn1 and Zn1ⁱ) may be regarded as square pyramidal geometry where the equatorial plane of a terminal Zn1/Zn1ⁱ atom is formed by phenoxo-bridged oxygen (02/02ⁱ), phenoxo oxygen (01/01ⁱ), imine nitrogen (N3/ N3ⁱ), imine nitrogen (N4/N4ⁱ) and the axial positions are occupied by acetato bridged oxygen (03/03ⁱ). However, the coordination geometry of the central zinc ion (Zn2) may also be best described as distorted octahedral geometry, formed by six oxygen atoms from the same Schiff base ligands and bridging acetate ions which coordinate the terminal zinc ions. Thus four phenoxo-oxygen (O1/ $O1^{i}$, $O2/O2^{i}$) from two Schiff base ligands and two acetate ions act as bridges between the two terminal zinc ions (Zn1 and Zn1ⁱ) and the central zinc ion (Zn2). The four equatorial positions for terminal zinc ions (Zn1 and Zn1ⁱ) are occupied by two phenoxo oxygen atoms (02/02ⁱ, 01/01ⁱ) and two imine nitrogen atoms (N3/N4ⁱ, N4/ N4ⁱ) where as the central zinc ion is surrounded by four phenoxobridged oxygen atom (01, 01ⁱ, 02, 02ⁱ) from the two Schiff base ligands. Axial positions for all three zinc ions are coordinated by acetate bridged oxygen atom (O3, O4, O4ⁱ, O3ⁱ). The three zinc ions are in a perfect linear arrangement ($\angle Zn1-Zn2-Zn1^{i} = 180.0^{\circ}$). The distances between the central zinc ion (Zn2) and the two terminal zinc ions (Zn1/Zn1ⁱ) are 3.061(1) Å. In the crystalline state of **1**, neighbouring zinc complexes form one dimensional chain structure through parallel H-bonding interaction along b axis (Fig. S1). In fact, free aliphatic alcoholic oxygen atoms of one zinc complex act as hosts to form strong intermolecular H-bonds towards C-H bonds of another zinc complex (C11-H11...O5). The structural parameters are listed in Table 1. Selected bond lengths and angles are presented in Table S1, and the relevant hydrogen bonding parameters are summarized in Table S2.

3.3. Solution properties

The structural integrity in solution state for both the Schiff base ligand (H₂L) and trinuclear zinc(II) complex have been determined by proton NMR, UV–Vis spectroscopy and ESI mass spectral studies. Though the ligand is soluble in common organic solvents like methanol, acetonitrile, dichloromethane etc but the zinc complex is soluble in methanol–dimethyl sulphoxide (CH₃OH–DMSO; 95/5 (v/v)) and dimethyl formamide (DMF). The NMR spectra of Schiff base and its Zn(II) complex are recorded in chloroform (CDCl₃) and dimethylsulphoxide (DMSO-*d*6) solution respectively using tetramethylsilane (TMS) as an internal standard. Upon examinations it is found the phenolic-OH signals appeared in the spectrum of H₂L ligand at ~13.2 ppm (Fig. S2). The characteristic signals at 8.4 ppm indicate the proton of imine-CH and all aromatic-CH proton signals produce in the range of 7.3–6.8 ppm. The proton signal at 4.2 ppm assigns aliphatic alcoholic protons. There are no signals at ~13.2 ppm in the Zn(II) complex which assigns the deprotonated phenolic-OH groups during chelation with Zn(II) ion (Fig. S3). Slight shift of the signals ~8.3 ppm reflects the coordination of imine-N with zinc ions. The characteristic signals at 4.1 are assignable to non-involvement of the aliphatic alcoholic-OH group in chelation with Zn(II) ions.

The complex is stable in the solid state as well as in the solution phase. The UV–Vis spectra for ligand and trinuclear zinc(II) complex show high intensity transitions in the range of 200–470 nm. The Schiff base ligand H₂L shows the characteristic absorption bands at 221, 267, 316 and 411 nm in dimethyl sulphoxide (DMSO) solvent. The highly intense bands at 221 and 267 nm are assigned to π – π * transition of the C=N chromophore, whereas the band with low intensity at 316 nm is due to n– π * transition and a broad band ~411 nm is for intraligand charge transfer [22] (Fig. S4). On complexation with zinc metal ion, these bands were shifted to lower wavelength (bathochromic shift) region (361 and 266 nm) in DMSO, suggesting the coordination of imine nitrogen and phenolate oxygen with Zn(II) ion (Fig. S4).

In order to probe the solution stability of the complex, we have performed UV–Vis spectral measurements for the zinc complex in CH₃OH–DMSO solution (95/5; v/v) at room temperature at various time intervals. The LF band for the complex at 361 nm remained unaffected over a period of at least 5 days revealing that the complex is stable in solution at room temperature. The ESI mass spectral study of **1** further consolidates the solution stability. $[Zn_3L_2(\mu-O_2CCH_3)_2]$ (**1**) exhibits the molecular ion peak, at *m*/*z* 929.9327 in methanol medium (Fig. S5). ESI-MS (MeOH) *m*/*z* 929.93 [**1** + Na⁺] (calc. 929.03).

3.4. Fluorescence properties

It is well known that, d¹⁰ transition metal (such as Zn(II), Cd(II) and Hg(II)) complexes usually exhibit diverse luminescent properties [23]. Here, steady-state fluorescence studies have been employed as independent evidence of complexation between the ligand and zinc ion. The solution state luminescent spectra of H₂L and **1** in CH₃OH–DMSO (95/5; v/v) at room temperature are depicted in Fig. 2. The Schiff base ligand exhibits luminescent emission band at 352 and 441 nm upon excitation at 267 nm. The zinc complex displays luminescent emission bands at 455 nm. (λ_{ex} = 266 nm). Compared to the emission peak of the H₂L ligand, the luminescent behaviour of zinc complex **1** is red shift which tentatively ascribed to ligand-to-metal charge transfer (LMCT) [23]. Fluorescence properties of the ligand and complex (Fig. S2) indicate that it can exhibit strong fluorescence property.

Quenching of fluorescence of a ligand by transition metal ions during complexation is a rather common phenomenon which is explained by processes such as magnetic perturbation, redoxactivity, electronic energy transfer, etc. [24]. Enhancement of fluorescence through complexation is, however, of much interest as it opens up the window for photochemical applications of the metal complexes [25,26]. Factors like a simple binding of ligand



Scheme 1. Preparative procedure of the ligand and zinc complex (1).



Fig. 1. ORTEP Plot of $[Zn_3L_2(\mu-O_2CCH_3)_2]$ (1) (30% ellipsoid probability) with atom numbering scheme.

Crystal parameters	1
Empirical formula	C ₃₈ H ₃₈ N ₄ O ₁₀ Zn ₃
Formula weight	906.83
T (K)	293(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	ΡĪ
Unit cell dimensions	
a (Å)	9.5022(12)
b (Å)	10.5453(15)
c (Å)	13.0143(8)
α (°)	66.820(18)
β(°)	78.47(3)
γ(°)	89.67(3)
$V(Å^3)$	1170.8(3)
Ζ	1
D_{calc} (Mg/m ³)	1.286
Absorption coefficient (mm ⁻¹)	1.575
F(000)	464
Theta range for data collection (°)	1.7-27.50
Index ranges	$-12\leqslant h\leqslant 12$,
	$-13\leqslant k\leqslant 13$,
	$-16 \leqslant l \leqslant 16$
Reflections collected	10199
Independent reflections	5285
R _{int}	0.120
Goodness-of-fit GooF on F ²	0.91
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0894, wR_2 = 0.2812$
Largest diff. peak and hole ($e \dot{A}^{-3}$)	0.94 and -0.63

to the d¹⁰ metal ions [26], an increased rigidity in structure of the complexes [27], a restriction in the photoinduced electron transfer (PET) [25,28], etc. are assigned to the increase in the photoluminescence. In the present case, the enhancement of the fluorescence of **1** [λ_{abs} (nm), 266; λ_{em} (nm); 455] compared to the ligand [λ_{abs} (nm), 267; λ_{em} (1) nm; 352, 436] seem to be responsible for the first two factors.



Fig. 2. Luminescence spectra of H₂L and 1, recorded in CH₃OH–DMF solutions.

3.5. Thermogravimetric analysis

The thermal behaviour of the trinuclear zinc-Schiff base complex (1) was followed up to 800 °C in a static nitrogen atmosphere with a heating rate of 10 °C per minute. Thermal analysis of **1** shows that it decomposes in three steps. In the first step, release of two bridging acetate molecules in the temperature range 100–275 °C is occurred with a mass loss 13.18% (calc. 13.08%) (Fig. S6). In the second and third step, the mass corresponding to ligand part is lost. The residual part of zinc complex remains as zinc oxide powder which is further consolidated by the observation of straight line at 405 °C.

3.6. XRD patterns of ZnO nanoparticle

XRD patterns of ZnO compound reflect that all the diffraction peaks of ZnO match the standard data for a ZnO nanoparticle. All the diffraction peaks (Fig. 3) can be well indexed to the hexagonal ZnO wurtzite structure (JCPDS No. 36–1451). The sharp and intense peaks in Fig. 3 indicate that the samples are highly crystal-line. The lattice parameters obtained by CELSIZ programme are



Fig. 3. PXRD plot of ZnO nanoparticle.



Fig. 4. SEM image of ZnO nanoparticle.

a = 3.25191 and c = 5.21034 which gives the ratio c/a = 1.6 (almost an ideal wurtzite structure). No other diffraction peaks corresponding to impurity is found confirming the high purity of the synthesized products. The mean crystalline sizes of ZnO nanostructures were calculated using the Scherrar's formula:

$$D = 0.9\lambda/\beta \cos \emptyset$$

where, λ is the wavelength of X-rays (1.540 for Cu K α), \emptyset is the Bragg's angle, β is the full width at half maximum. The calculated mean crystalline size of ZnO nanoparticles synthesized by pyrolytic method is 98 nm.

3.7. Scanning electron microscopy image (SEM)

To obtain detailed information about the microstructure and morphology of the synthesized ZnO nanoparticle, scanning electron microscopy (SEM) was carried out. Fig. 4 represents the image of pure ZnO nanoparticle powders. It can be seen clearly that the powders are rods and bulks which have a diameter of about 98 nm. As shown in the inset of the figure, the shape of the grain is almost cylindrical with average grain size ~98 nm.

3.8. UV-Vis spectrum of ZnONp

It is well known that the optical absorption behaviour of photocatalyst could significantly affect the photocatalytic activity. For the characterization of the fabricated ZnONPs, in the present study, an UV–Vis spectrophotometer was employed to record the absorbance spectra in the wavelength range of 220–500 nm for dispersed ZnONPs in distilled water. The absorbance spectrum of ZnONPs is shown in Fig. 5. A strong absorption band ranging from 200 to 450 nm was observed for ZnONPs due to the metal ion [29]. The $n \rightarrow \sigma^*$ absorption bands appeared at approximately 269 nm and the $n \rightarrow \pi^*$ absorption band was observed at 335 nm. This UV–Vis spectrum is consisted with previously reported data [29].

The band gap energy of ZnO nanoparticles was calculated based on the absorption spectrum of the ZnONp according to the equation, $E_{bg} = 1240/\lambda$ (eV), where, E_{bg} is the band gap energy of the photocatalyst, λ is the wavelength in nm. The calculated band gap of the ZnONp is 3.7 eV. This indicates that synthesized ZnO has a suitable band gap for photocatalytic degradation of dyes.

3.9. Photoluminescence (PL) spectrum of ZnONp

The PL spectra are useful to disclose the efficiency of charge carrier trapping, immigration, and transfer and to understand the fate



Fig. 5. UV-Vis spectrum (left) and steady-state fluorescence spectrum (right) of ZnO nanoparticle in water at room temperature.

of electron hole pairs in semiconductor particles since PL emission results from the recombination of free carriers [30]. The PL spectra of ZnO photocatalyst was examined using 269 nm excitation wavelength and are depicted in Fig. 5. ZnONp showed a strong emission peak 367 nm which can be attributed to the defect-related emissions and is in accordance with the reported values for ZnO, which possesses an exciton-related violet emission [31].

4. Photocatalytic activity of ZnONp under visible light

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. The spectrum of the MB solution (Fig. 6) in aqueous medium shows characteristics peaks at 246, 292, 600 and 664 nm (Scheme 2).

The decrease in absorbance of the aqueous solution at 664 nm with visible light illumination in the ZnONP suspension is due to the breakdown of the chromophore. The photodegradation of methylene blue was employed to evaluate the photocatalytic activities of the ZnO nanoparticles. The photocatalytic properties of ZnONP are known to depend on several factors like size, morphology, surface area and electronic state. The self degradation of MB in visible light was negligible in the absence of photocatalyst. It is proved that when the particle sizes of nanostructures increase beyond the optimum size, the photocatalytic activity decreases due to decrease in surface area. The ZnONP synthesized by pyrolytic method took 60 min, for maximum MB degradation.

4.1. Mechanistic pathway for photocatalytic degradation by nanoparticle

The photocatalytic degradation of a dye in the presence of metal oxide nanoparticle is initiated by photoexcitation of the nanoparticle which leads to the formation of electron–hole pair [32]. Part of



Fig. 6. Adsorption changes of MB aqueous solution at room temperature in the presence of ZnO nanoparticles obtained under sunlight irradiation.



Scheme 2. Structure of methylene blue dye.

these photogenerated carriers recombine in the bulk of the nanoparticle, while the rest migrate to the surface of the catalyst, where the holes act as powerful oxidants and electrons as powerful reluctant. The high oxidative potential of the hole causes the direct oxidation of the dye to reactive intermediates [32]. In the other hand hydroxyl radicals are formed by the decomposition of water or by the reaction of hole with OH⁻, behave as reactive intermediate for degradation. The hydroxyl radical is an extremely non-selective oxidant which leads to partial or complete mineralization of the dye.

(i)
$$\text{ZnO} + h\gamma \rightarrow e^- + h^+$$
; (ii) $O_2 + e^- \rightarrow O_2^-$;
(iii) $h^+ + H_2O \rightarrow OH^- + H^+$; (iv) $h^+ + OH^- \rightarrow OH^-$;

(v) Dye + OH[•]
$$\rightarrow$$
 RCOO[•] \rightarrow CO₂ + H₂O + Inorganic ions

Alternatively, the electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of the dye radical anion which is subsequently degraded.

In such photocatalytic process, the separation and recombination of photogenerated charge carriers are competitive pathways and photocatalytic activity is effective when recombination between them is prevented.

4.2. Effect of pH

The effect of pH on the photocatalytic activity was studied by varying the pH of the dye solution. It can be seen from Fig. 7 that pH has a significant effect on the photodegradation rate. From the figure it is seen that the rate of degradation is directly proportional to solution pH. At normal condition ZnONp degraded 78% MB dye at pH \sim 7.2 under visible light. When we increased the pH up to 12 for MB in aqueous solution, the% degradation increases up to 99%, but with decrease in pH of the MB, degradation percentage decreased in a greater extent (\sim 60%). It can be rationalised with the fact that there exists an electrostatic interaction between the catalyst surface and the dye molecules which consequently enhances or inhibits the photodegradation rate [33]. The effect of pH value on photocatalysis is generally due to surface charge of the catalyst and the charge on dye molecules [34]. The change in pH shifts the redox potentials of the valence and conduction bands, which might affect the interfacial charge transfer [35]. The surface of ZnO is positively charged at low pH whereas with rise in pH the surface becomes negatively charged. As MB is a cationic dye, high pH favours the adsorption of dye molecule on the catalyst surface



Fig. 7. Change of % degradation of MB in aqueous solution at different pH in the presence of ZnO nanoparticles under visible light irradiation at room temperature.

which results in high degradation efficiency. The degradation rate was found to be enhanced in alkaline conditions and maximum activity was obtained at pH 12. At pH 12, 99% dye degradation is observed for ZnONP (Fig. 7).

5. Conclusions

Herein we report the synthesis and single crystal isolation of a new acetato- and phenoxo-bridged trinuclear zinc(II) complex of the type $[Zn_3L_2(\mu-O_2CCH_3)_2]$, where H_2L is (NO)-donor compartmental Schiff base ligand. Both ligand and zinc complex exhibits strong fluorescence property in MeOH-DMSO solvent mixture and fluorescence intensity enhances for trinuclear zinc(II)-Schiff base complex compared to ligand. In the presence of visible light, ZnONP can efficiently catalyze the decolorization and degradation of MB in the aqueous suspension. Photodegradation of MB is accelerated by the increase of pH of its solution in the range of 5-12. The prepared ZnONP has been found to be quite stable under visible light illumination at a pH of approximately 7.2, and there is some activation of the surfaces of ZnO particles by this light.

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Appendix A. Supplementary material

CCDC 996174 contains the supplementary crystallographic data for this complex 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.ica.2014.06.014.

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