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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 ware examined. ZnO nanoparticles with diameter between 15 and 20 nm were simply synthesized by solid-state transformation of compound 1 at 700 °C.

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#### 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 anticancer 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].

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http://dx.doi.org/10.1016/j.materresbull.2016.02.010 0025-5408/© 2016 Published by Elsevier Ltd. 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<sub>3</sub>]<sub>2</sub> (**1**), (H<sub>2</sub>L=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

 $Zn(NO_3)_2$ ·6H<sub>2</sub>O 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<sup>-1</sup> 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<sub>3</sub> 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-K $\alpha$  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<sub>2</sub>L)

The asymmetric tridentate Schiff base H<sub>2</sub>L 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<sub>3</sub> (5 ml) was then added and the yellow precipitate was filtered off and subsequently dried in air. The crude product was recrystallized from CHCl<sub>3</sub>–hexane (1/4 v/v). Yield: 90%. m.p.:46–48 °C.

#### 2.3. Preparation of zinc complex [Zn(HL)NO<sub>3</sub>]<sub>2</sub> as single crystal (1)

0.01 mol H<sub>2</sub>L 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

 $Zn(NO_3)_2$ ·6H<sub>2</sub>O (0.5 mmol) and ligand (H<sub>2</sub>L) (5 mmol) were dissolved in 15 ml EtOH. The solution was charged into a Teflonlined 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.

 $10 \,^{\circ}$ C/min in air. Nanoparticles of zinc oxide were synthesized at 700  $^{\circ}$ C after 4 h. The synthesized nanoparticles were characterized by FT-IR, XRD and SEM techniques. The IR spectrum and powder XRD diffraction showed that calcination was completed and the entire organic compound was decomposed.

#### 2.6. Crystallographic data collection and structural refinement

X-ray data for the complex was collected on a STOE IPDS-II diffractometer with graphite monochromated Mo-K $\alpha$  radiation. The crystal of Zn complex was gold-yellow. A high-quality piece of crystal was chosen using a polarizing microscope; they were mounted on a glass fiber and then used for data collection. Cell constants and an orientation matrix for data collection were obtained from the least-squares refinement of diffraction data. Data was collected at a temperature of 298(2) K in a series of  $\omega$ scans in 1° oscillations and integrated using the Stöe XAREA software package [22]. A numerical absorption correction was applied using the X-RED [23] and X-SHAPE [24] software packages. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods using SIR2004 [25]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on  $F^2$  using SHELXL [26]. All hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms.

#### 3. Results and discussion

The pure ligand, 2-[(2-hvdroxy-propylimino) methyl] phenol (H<sub>2</sub>L), was obtained and isolated during the condensation reaction of the 1-amino-2- propanol with 2-hydroxybenzaldehyde in ethanol and the obtained ligand being stable in air was characterized by the FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra. The FT-IR spectrum of the ligand exhibits bands at 3377, 1635 and 1581 cm<sup>-1</sup> assigned to v(O-H), v(C=N) and v(C=C) vibrations respectively. The <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ (ppm)) spectrum of the ligand exhibits a resonance at  $\delta$ = 13–10 due to benzyl –OH, at  $\delta$ =8.35 due to —HC=N proton, at  $\delta$ =4.11 due to CH proton, at  $\delta$ =3.68 due to  $CH_2$  protons, at  $\delta$ =3-1.5 due to aliphatic –OH and at  $\delta$ =1.28 due to -CH<sub>3</sub> protons, respectively. All the aromatic protons of ligand are clearly observed in the expected region  $\delta$  = 7.32–6.88. The <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of the ligand exhibits resonances at  $\delta(ppm)$  = 20.86, 66.98, 67.27, 117.08, 118.65, 131.49, 132.50, 161.25, 166.80 and 166.83. There are 10 distinct signals in the <sup>13</sup>C NMR spectrum of the ligand, in agreement with the proposed structure.

Single crystal of zinc organic coordination complex  $[Zn(HL) NO_3]_2$  (1) was prepared by the reaction of  $H_2L$  with hexa hydrate zinc(II) nitrate. The formation of the ligand and its complex is shown in Fig. 1.

This new Zn(II) complex containing the tridentate Schiff base ligand bridged Zn centers was characterized by FT-IR, UV-vis spectroscopies and single-crystal X-ray analysis. The complex is quite air stable as solid and also in solution. Nanostructures of compound **1** were obtained by solvothermal process. Fig. 2 gives an overview of the methods used for the synthesis of [Zn(HL)NO<sub>3</sub>]<sub>2</sub> using the two different routes. Calcination of compound **1** as nanostructure in air at 700 °C for 4 h results in ZnO nanoparticles.

#### 3.1. FT-IR spectral studies

The FT-IR spectra of the nanostructure products prepared by the solvothermal method and of the bulk material produced by the slow evaporation are distinguishable but the most important peaks



**Fig. 3.** IR spectra of (a) nano-particles of compound 1 produced by solvothermethod, (b) bulk materials as synthesized of **1**.



Fig. 2. Materials produced and synthetic methods.

are similar in the two spectra (Fig. 3). The spectra in KBr matrix confirm that the strong absorption band at about 1650 cm<sup>-1</sup> which is assigned to the C=N stretch of the coordinated Schiff base ligands [27] whereas for the free ligand the same band is observed at 1635 cm<sup>-1</sup>. From the FT-IR spectrum of the complex we can observe some new absorption bands at 490 and 436 cm<sup>-1</sup> with weak intensity, which are absent in the spectrum of the free ligand. so it is concluded that these bands were presumably ascribed to vibrations of the Zn-O bond and Zn-N bond, respectively [28,29]. The mode of the coordination of the nitrate group can be determined by infrared spectroscopy; in compound 1 the single absorption band at 1763  $cm^{-1}$ , is associated with the monodentate nitrate in agreement with the structural data [30]. The broad band in the region 3400-3500 is attributed to coordinated aliphatic OH [31].

#### 3.2. Crystal structure description of copper complex $[Zn(HL)NO_3]_2(1)$

Crystallographic data for the complex are listed in Table 1. Selected bond distances and angles are summarized in Table 2. As seen from Table 1 the [Zn(HL)NO<sub>3</sub>]<sub>2</sub> complex crystallizes as gold single crystals in the space group P-1. The unit cell contains two distinct entities of [Zn(HL)NO<sub>3</sub>]. The structure of the nitrato complex is depicted in Fig. 2 and important bond lengths and angles are compiled in Table 2.

The structure consists of a centrosymmetric dimer (Fig. 4), comprising two zinc(II) ions, two monodentate nitrate anions and two tridentate Schiff base (H<sub>2</sub>L) ligands bonded by the aliphatic oxygen, the imine nitrogen and the deprotonated phenolate oxygen (O,N,O) atoms of H<sub>2</sub>L. The deprotonated phenoxy bridges the two zinc atoms and links the two halves of the dimer together. The geometry about the five-coordinate zinc atom is between a trigonal bipyramidal (TBP) and square pyramidal (SP) with equatorial angles in the range 102-131° and an axial angle (O

#### Table 1

Crystal data and structure refinement for zinc coordination complex [Zn(HL)NO<sub>3</sub>]<sub>2</sub>.

Empirical formula	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>10</sub> Zn <sub>2</sub>
Formula weight	611.17
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	8.7918(18)
b (Å)	8.8762(17)
c (Å)	9.1799(18)
α (°)	104.20(3)
β (°)	117.09(3)
γ (°)	94.49(3)
V, Å <sup>3</sup>	603.1(2)
Z	1
$D_{cal}$ (Mg/m <sup>3</sup> )	1.683
Absorption coefficient $(mm^{-1})$	2.051
F (000)	312
$\theta$ range for data collection (°)	2.63-25
Index ranges	-10 < = h < = 10, -10 < = k < = 10,
-	-10 < = 1 < = 10
Reflections collected	4469
Independent reflections [R <sub>int</sub> ]	2116 [0.0400]
Completeness to $\theta = 25^{\circ}$ (%)	99.7
Absorption correction	Multi-scan
Refinement method	full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	2116/0/168
Goodness-of-fit on F2	0.844
Final R indices $[I > 2\sigma(I)]$	$R_1^a = 0.0298$ , $wR_2^b = 0.0561$
R indices (all data)	$R_1 = 0.0480$ , $wR_2 = 0.0588$
Largest difference in peak and hole(e, $Å^{-3}$ )	0.390 and -0.236

Table 2

|--|

Bond lengths (Å)			
$Zn(1)-O(5)^{*}$	1.982(2)	$Zn(1)-Zn(1)^{*}$	3.0955(12)
Zn(1)-N(1) Zn(1)-O(2)	2.009(2) 2.054(2)	Zn(1)-O(5) Zn(1)-O(1)	2.066(2) 2.227(3)
Angles (°)			
$O(5)^{*}1-Zn(1)-N(1)$	125.81(10)	N(1)-Zn(1)-O(5)	88.76(9)
$O(5)^{*}1-Zn(1)-O(2)$	102.06(10)	O(2)-Zn(1)-O(5)	105.36(10)
N(1)-Zn(1)-O(2)	131.88(11)	$O(5)^{\circ}$ -Zn(1)-O(1)	101.94(10)
$O(5)^{-2}Zn(1)-O(5)$	80.24(9)	N(1)-Zn(1)-O(1)	77.21(10)
O(2)-Zn(1)-O(1)	89.61(11)	O(5)-Zn(1)-O(1)	164.18(8)

(1)-Zn(1)-O(5)) of 164.18°. The O(5) bridge forms an asymmetric linkage to the zinc atoms with markedly different zinc-oxygen distances (Zn(1)-O(5) 2.066 Å and O(5)\*-Zn(1) 1.982 Å). The Zn(1)- $Zn(1)^*$  separation of 3.096 Å is almost equal to that observed in the analogous zinc(II) complex of the reduced Schiff base ligand [32].

The nitrate group, acts as a monodentate ligand with a Zn-O distance (Zn(1)-O(2)) of 2.054 Å, typical for monodentate nitrate. The zinc-nitrogen and zinc-oxygen bond distances of Zn(1)-N (1) = 2.009, Zn(1)-O(1) = 2.227, Zn(1)-O(5) = 2.066 and Zn(1)-O(5) = 2.066 $(5)^*$  = 1.982 Å are considered normal, but significantly different from those observed for the analogous zinc(II) complexes with reduced ligands [33].

The zinc atom is displaced in the basal  $O(2) N(1) O(5)^*$  donor atom plane. The stereochemistry adopted by the zinc atom in the complex is between trigonal bipyramidal and square pyramidal geometries. Addison et al. [34] have used an angular structural parameter  $\tau$  (index of trigonality) for distinguishing between a trigonal bipyramidal (TBP) and square pyramidal (SP) geometry in five-coordinate complexes;  $\tau = [\beta - \alpha/60^{\circ}]$  where  $\alpha$  and  $\beta$  are the two largest angles.  $\tau = 0$  for an ideal square pyramid ( $\alpha$ ,  $\beta = 180$ ) and  $\tau = 1$  for an ideal trigonal bipyramid ( $\alpha = 120^{\circ}$  and  $\beta = 180^{\circ}$ ). Using this criterion, the  $\tau$  value is found to be 0.538 indicating that Zn is between trigonal bipyramidal ( $\tau$  = 1) and square pyramidal



<sup>a</sup> R =  $\sum(|Fo-Fc|)/\sum|Fo|$ . <sup>b</sup> wR = { $\sum [w(|Fo-Fc|)^2]/\sum [w|Fo|^2]$ }<sup>1</sup>/<sub>2</sub>.

 $(\tau = 0)$  geometries. The crystal packing of complexes **1** are stabilized by means of hydrogen bonding and  $\pi - \pi$  stacking interactions. The aliphatic hydroxyl group shows hydrogen bonds with oxygen of nitrate ion of adjacent molecule  $(O(1)-H\cdots O(4))$  which makes two neighboring molecules close together in 1.968 Å and form a 3D network as depicted in Fig. 5. As shown in the figure, the hydrogen bonded supramolecular network is further supported by  $\pi - \pi$  stacking interactions, in which the centroid-tocentroid separation of two phenyl rings is found to be 4.125 Å.

#### 3.3. UV-vis spectra

The absorption spectra of ligand and its complex were recorded in EtOH solutions in the range 200–800 nm and depicted in Fig. 6. The observed bands at 252 nm, 318 nm and 401 nm for H<sub>2</sub>L Schiff base ligand are related to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions and the band in 401 nm is related to C=N chromophore. In the complex a band in the range 358 nm was observed after interaction of metal ions with ligands. This band is assigned to  $\pi \rightarrow \pi^*$  transition with more extended conjugated system after deprotonation of phenolic hydrogens, and formation of phenoxides in complexes [35]. The d– d transitions were not observed in the visible region for zinc(II) complex consistent with the d<sup>10</sup> configuration of the Zn(II) ion [36].



Fig. 6. UV-vis spectra of H<sub>2</sub>L and Zn(II) complex in methanol.



Fig. 5. Molecular packing of complex 1 (a) showing hydrogen bonding and (b)  $\pi$ - $\pi$  stacking interactions. Hydrogen atoms of least interest are omitted for clarity in (b).



**Fig. 7.** The PL spectrum of the  $[Zn(HL)NO_3]_2$  and the H<sub>2</sub>L ligand.

#### 3.4. Luminescence property

The photoluminescence emission of the Schiff base ligand and Zn(II) complex **1** were studied at room temperature (298 K) in methanolic solution with the same concentration (see Fig. 7). It can be seen that the emission spectral of the zinc complex do not resemble that of ligand. The ligand is not emissive while the corresponding Zn(II) complex emits enhanced blue bond through complexation.

The fluorescence of the ligand is probably quenched by photoinduced electron transition of metal ion during complexation due to the presence of a lone pair of electron of donor atoms in ligand [37,38]. The origin of the strong fluorescence efficiency of complex is attributed to the coordination of Zn(II). The chelation of the ligand to Zinc ion plays an important role and greatly increases the rigidity of ligand and reduces the loss of energy by thermal vibration [39–41]. So, the emission of the complex is assigned to the fluorescence from the intraligand emission excited states, while no emission from metalcentered excited state (MLCT/LMCT) are not expected because of the difficulty of the oxidation or reduction due to d<sup>10</sup> configuration [42–44]. Thus, complex **1** may have potential application as a luminescent material in blue lightemitting materials.

#### 3.5. XRD and SEM studies

The reaction between 2-[(2-hydroxy-propylimino) methyl] phenol ( $H_2L$ ) and hexa hydrate zinc(II) nitrate provided a crystalline material of the general formula [Zn(HL)NO<sub>3</sub>]<sub>2</sub> (**1**). The effect of the initial substrates concentration and reaction time on size and morphology of compound 1 nanostructure was

Table 3 Experimental condition to prepare  $[Zn(HL)NO_3]_2$  nanostructures by solvothermal method in methanol.

Sample no	H <sub>2</sub> L (mmol)	$Zn(NO_3)_2 \cdot 6H_2O \ (mmol)$	Time (h)	Section
1 2	5 5	5 5	24 12	Fig. 9a Fig. 9b
3	2.5	2.5	24	Fig. 9c

investigated. The conditions are summarized in Table 3. The morphology and grain (crystalline) size of compound **1** prepared by the solvothermal process were studied by X-ray



Fig. 8. Thermal behavior of compound 1.

diffraction (XRD) techniques and scanning electron microscopy (SEM). Fig. 8 shows the simulated XRD pattern from single crystal X-ray data of compound **1** (Fig. 8a) in comparison with the XRD pattern of the typical sample of compound **1** prepared by solvothermal method (Fig. 8b).

Acceptable matches, with slight differences in  $2\theta$ , were observed between the simulated and experimental powder X-ray diffraction patterns. This indicates that the compound obtained



0 KV 20.0 KA TUIII KTKT-EIW3200 SN.000





Fig. 9. XRD patterns; (a) simulated pattern based on single crystal data of compound 1 and (b) nano-size of compound 1.



**Fig. 10.** SEM images of nanostructure of compound **1** obtained from solvothermal method in different concentrations and reaction's time. Samples (a) 0.005 mol, 24 h, (b) 0.005, 12 h and (c) 0.0025 mol, 24 h.

by the solvothermal process as nanostructures are identical to that obtained by single crystal diffraction. The significant broadening of the peaks indicates that the particles are of nanometer dimensions.

In solvothermal method two parameters were investigated as effective parameter on size and morphology of obtained structures; the initial substrates concentration and reaction time (Table 3). As it has been seen in Fig. 9 in 5 mmol concentration of initial material and 12 h reaction time some nanostructures with uniform morphology and average diameter of 70 nm were obtained.

#### 3.6. Thermal studies

The thermogravimetry (TG) and differential thermal analysis (DSC) were carried out in flowing dry argon at the heating rate of  $10 \,^{\circ}$ C/min on approximately 10 mg sample. The result of TG and DSC measurements of the nano Zn-complex is shown in Fig. 10.

The thermogram of the zinc complex indicates that the complex is thermally stable up to nearly  $280 \,^{\circ}$ C. It can be seen from Fig. 10 that the DSC curve shows an exothermic peak at  $280 \,^{\circ}$ C



Fig. 11. XRD pattern of ZnO nanoparticles prepared by calcination at 700  $^\circ C$  of compound  $[Zn(HL)NO_3]_2$  (1).



Fig. 12. FT-IR absorption spectra of zinc oxide.



**Fig. 13.** Scanning electron microscopy (SEM) images of ZnO nanoparticles prepared by direct calcination of compound **1** obtained by solvothermal method.

corresponding to a sharp weight loss in the TG curve; it shows that the complex undergoes decomposition. As shown in this figure there is no endothermic behavior in the DSC curve. The result suggests that there is neither lattice nor coordination water in the complex. Decomposition of nanostructures of compound **1** occurs between 280 and 700 °C with a mass loss of 77.5% (calc. 73.4%) then the decomposition of the compound ultimately results in a solid that appears to be ZnO.

#### 3.7. Nano zinc oxide

Zinc(II) oxide was obtained from calcination of nanocompound **1**; in air atmosphere at 700 °C. Fig. 11 shows the XRD pattern of the residue obtained from direct calcination at 700 °C of compound **1**. The obtained pattern matches with the standard pattern of hexagonal zinc(II) oxide with the lattice parameters (a = 3.24982 Å, C = 5.20661 Å and z = 2) which are same to the reported values, (JCPDS Card Number 36–1451).

The formation of ZnO powders was further supported by FT-IR spectra as shown in Fig. 12. The FT-IR spectra show main absorption band at about  $3500 \text{ cm}^{-1}$  which correspond to the O—H mode. The absorption band at about  $480 \text{ cm}^{-1}$  is the stretching mode of ZnO [45–47].

Fig. 13 and Fig. 14 show the SEM and HRTEM images of the obtained residue from calcination of the nanostructure of title compound at 700 °C. The SEM image of products shows uniform morphology, but for a better resolution, the zinc oxide products were seen under a transmission electron microscope. As can be seen, the products are formed with mean diameter of 15–20 nm. The histogram of images indicates that the diameter of ZnO nanoparticles is varying between 15 and 20 nm with the average size of 17 nm (Fig. 15).

#### 4. Conclusion

In this work, a new dinuclear Zn(II) Schiff base complex, [Zn(HL)  $NO_3]_2$  (1), (H<sub>2</sub>L = 2-[(2-hydroxy-propylimino) methyl] phenol) has been synthesized using a thermal gradient approach and by solvothermal method. The structure of compound 1 was characterized by single crystal X-ray diffraction. Based on the characterization results the crystal structure of compound 1 consisted of a centrosymmetric dimer, comprising two zinc(II) ions, two



Fig. 14. TEM images of ZnO nanoparticles obtained from compound 1.



Fig. 15. The particle size distribution of ZnO nanoparticles.

monodentate nitrate anions and two tridentate Schiff base (H<sub>2</sub>L). Coordination number of the Zn(II) ions was found to be five. The photoluminescent studies suggest that the emission spectrum is originated from ligand to metal charge transition, and it may have potential applications in relevant chemistry and physics fields. Furthermore, nanostructures of compound **1** were prepared using different conditions based on the initial reagents concentration and reaction time. The result showed the morphology and particle sizes of the nanostructures do not depend on the concentrations of the initial reagents but lowering the time of reaction was decreased size of nanostructures and preventing agglomerated particles. Nanostructure of compound **1** was characterized by X-ray powder diffraction (XRD), FT-IR spectroscopy, thermal gravimetric (TG) and differential scanning calorimetry (DSC). Calcination of nano compound **1** at 700 °C produces ZnO nanoparticles.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. materresbull.2016.02.010.

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