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Synthesis and structural characterization of transition metal compound: New precursor for preparation of Zinc oxide nanoparticles

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Abstract

The Zn(II) complex Zn(L)(H2O)2, where L is the Schiff base ligand of N-(salicylidene)-N'-(o-hydroxyacetophenone) ethylenediamine, was synthesized and characterized by physico-chemical and spectroscopic methods. Nano-sized particles of ZnO were prepared by thermal method. ZnO nanoparticles were obtained by calcination of the nano-structure complexes at 260oC. The structures of the nano-sized compounds were characterized by X-ray powder diffraction and scanning electron microscopy. The thermal stabilities of the complex and nano-sized ZnO particles were studied by thermogravimetric analysis.

Keywords: Schiff base complexes, nanomaterials, Zinc oxide, Powder X-ray diffraction.

INTRODUCTION

The macroscopic properties of materials strongly depend on both the size and the morphologies of the microscopic particles they are made up from. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which is commonly called nanoscale materials, or simply nanomaterials. The synthesis of metal oxide nanoparticle has received considerable attention with their potential applications in various fields. Preparation of nanomaterials is important because physical and chemical properties depend on particle size. Self-assembly of molecular building blocks into targeted nanoscale architectures at interfaces represents a goal of supramolecular chemistry and materials science, with potential applications of these systems in nanotechnology.

Metal complexes of transition metals are of particular interest to inorganic chemists because of their structural, spectral and chemical properties are often strongly dependant on the nature of the ligand structure. Coordination complexes with substituted ketones have shown diverse structural and properties generating a variety of stereochemistry and a wide range of bonding interactions. The interest in the construction of unsymmetrical coordination complexes by reacting transition metal ions with tetra-dentate has been constantly growing over the past years [1–4]. Within this understanding lies an increased knowledge of molecular self-assembly [5, 6], metal–ligand complexation [7, 8] and disposition of metal binding sites [9]. By mastering these areas, new improved systems related to the fields of catalysis [10], supra-molecular chemistry [11, 12] and bioengineering [7] can be achieved and due to this application of coordination complexes [13]. Schiff bases and their complexes are versatile compounds synthesized from the condensation of an amino compound with carbonyl compounds and widely used for industrial purposes and also exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Many Schiff base complexes show excellent catalytic activity in various reactions [14- 23].

The synthesis and characterization of symmetrical tetra-dentate transition metal complexes have been thoroughly studied but comparatively fewer studies seem to have been done on complexes of unsymmetrical transition metal complexes derived form acetophenone. A search of the literature revealed that no work has been done on transition

metal complexes of the unsymmetrical ligand derived form acetophenones and ethylenediamine. Herein, I aimed to the synthesis, characterization of salen-type transition metal complexes and used it as new precursor for synthesis of metal oxides nano-sized material and its properties.

EXPERIMENTAL SECTION

2.1 Material and physical techniques

The ligand N-(salicylidene)-N'-(*o*-hydroxyacetophenone)ethylenediamine (LH_2) (Fig. 1) was prepared according to the literature procedure [24], all reagents and solvents for synthesis were commercially available and used as received. The metal content in the complex was analyzed by standard method. The analysis of carbon, hydrogen and nitrogen were performed on Carlo Erba 1108 elemental analyzer at Central Drug Research Institute (CDRI), Lucknow, India. The infrared spectra were obtained in KBr pellets on Shimadzu IRAFFINITY-1 at Government College of Pharmacy, Amravati, M.S. India. The room temperature magnetic susceptibility measurement of the resulting complex was measured by Gouy's method. The paramagnetic susceptibility was corrected for diamagnetism of ligand and metal ion. Thermograms of the complex was recorded in the temperature range room temperature to 700^{o}C, SEM image and XRD of synthesized compounds were recorded at VNIT, Nagpur, India.

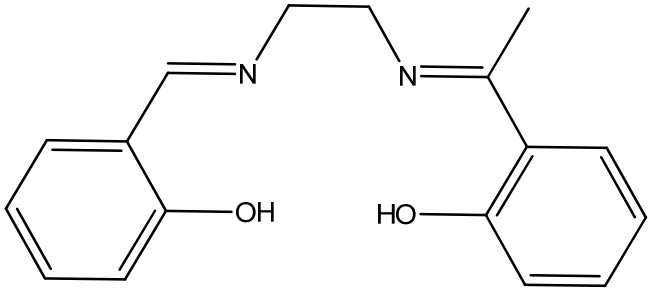

Fig 1 N-(salicylidene)-N'-(*o*-hydroxyacetophenone) ethylenediamine

2.2 Synthesis of $[ZnL(H_2O)_2]$

Ligand is highly soluble in hot DMF (90-100^{o}C) to increase solubility of ligand; minimum amount of DMF (10 mL) was used. To a hot stirred solution of 2 mmol of ligand in DMF, add a 2 mmol solution of $ZnCl_2$ and then reflux for 1h. Then pH of the solution was adjusted to 7.5-8 using alcoholic ammonia and resulting solution was further refluxed for about 4h. The colored solution was concentrated to Ca 15 ml and then cooled to room temperature to give precipitation of the complex. The complex thus separated out was filtered, washed with DMF and hot ethanol to give analytically pure product and dried in desiccator over $CaCl_2$. Color; white, Yield; 62%, Found; C, 53.28; H, 5.21; N, 7.30,Calculated for $C_{17}H_{20}N_2O_4Zn$; C, 53.49; H,5.24; N, 7.34%. IR(cm^{-1}); 1340 ν(C-O), 1598 ν (C=N).

2.3 Synthesis of ZnO nanoparticles

The precursor of Zn(II) complex (76.2 mg, 0.2 mmol) was dissolved in 1.4 mL of Oleic acid and formed a greenish black solution. This clear solution was heated to 260^{o}C for 2h under air atmosphere. At the end of the reaction, a black precipitate was formed. A small amount of toulene and a methyl alcohol (1: 2) were added to the reaction solution and ZnO nanoparticles were separated by centrifugation. The dark solid obtained was washed with EtOH and dried in vacuo.

RESULT AND DISCUSSION

Reaction between N_2O_2 donor Schiff base ligand and zinc(II)chloride yielded Zn(II) unsymmetrical Schiff base complex formulated as $[ZnL(H_2O)_2]$. The characteristic vibrational frequencies have been identified by comparing the spectra of complex with that of parent ligand and literature value of absorption of simple type of compound. The Schiff base exhibits a medium broad band at 3052 cm^{-1}, which may be due to the presence of intramolecular hydrogen bonding between phenolic hydrogen and azomethine nitrogen atom [24]. The absence of this band in the spectrum of complex (Fig. 1) indicates the deprotonation of the phenolic group and coordination of oxygen atom to metal ion. This is further supported by the shift or ν(C-O) (phenolic) band from 1283 cm^{-1} of the ligand to 1340 cm^{-1} in the spectrum of complex indicating the co-ordination of phenolic oxygen atom to the metal ion [25]. The strong band observe at 1635 cm^{-1} due to ν(C=N) stretch in ligand spectrum has been shifted to lower frequency 1598 cm^{-1}

upon co-ordination [26]. The Zn (II) complexes is diamagnetic and observe no d- d transition as expected for d^{10} system.

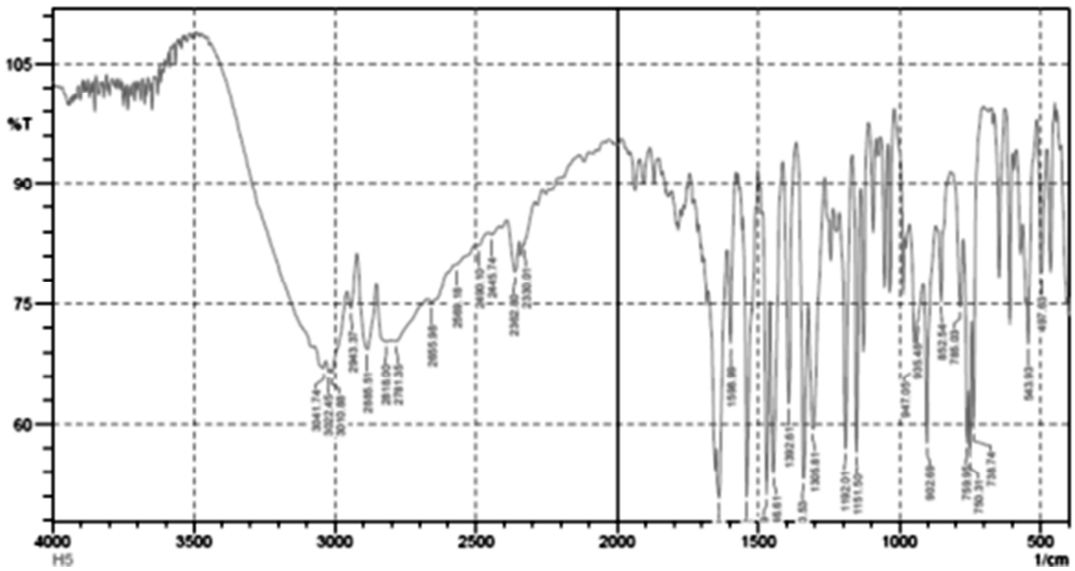

Fig. 1: IR Spectrum of Zn(II) Complex

The powder X-ray diffraction indicates crystalline nature of Zn (II) complex (Fig. 2) [27]. The Zn(II) ion in octahedral environment with the ligand and two neutral water ligand also confirmed by TG analysis.

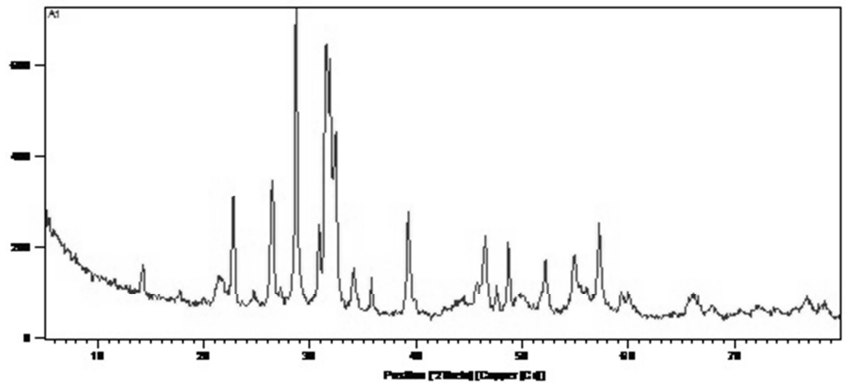

Fig. 2: Powder X-ray diffraction of Zn(II) Complex

The TG curve of Zn(II) Complex (Fig. 3) indicates that the compound is stable up to 140^{O}C. Removal of two co-coordinated water takes place in the range 140-280^{O}C. (The weight loss observed 9.46 Calculated 9.44%). Rapid weight loss has been observed around 300^{O}C presumably due to decomposition of organic constituent of the complex molecule. The decomposition continues up to 650^{O}C as indicated by the consistency in weight in the plateau of thermogram.

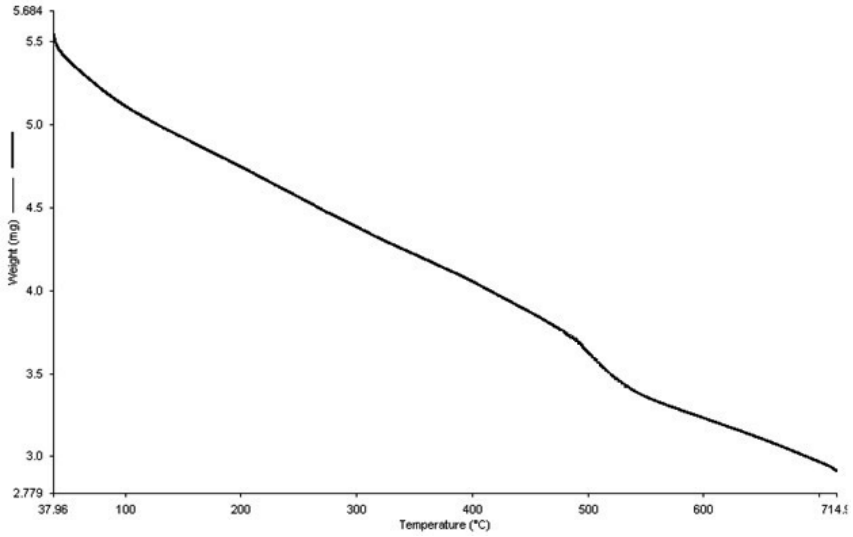

Fig. 3: TGA graph of Zn(II) complex

ZnO nanoparticles can be synthesized from the decomposition of the Zn(II) complex precursor in oleic acid under air atmosphere. The IR spectrum of ZnO nanoparticle (Fig. 4) exhibits band at about 557 cm^{-1} that can be assigned to the stretching mode of ZnO. The nanoparticle size of metal oxides measured by XRD and SEM indicate that the size of Metal oxide nanoparticles was about 300-500 nm (Fig.5 and 6).

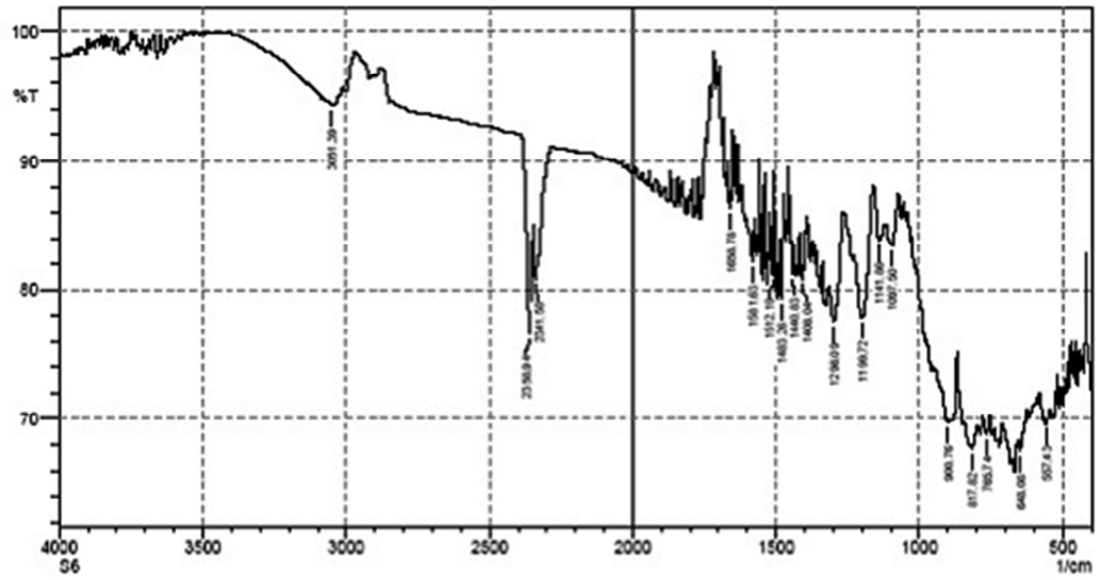

Fig. 4: IR Spectrum of ZnO nanomaterial

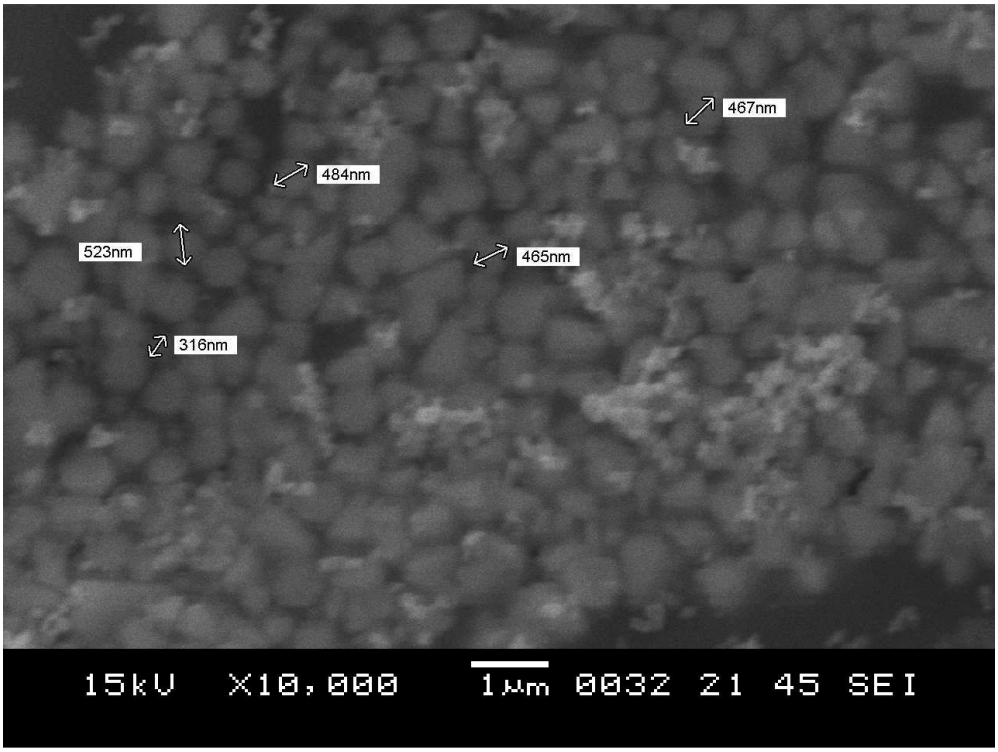

Fig. 5: SEM image of ZnO nanomaterial

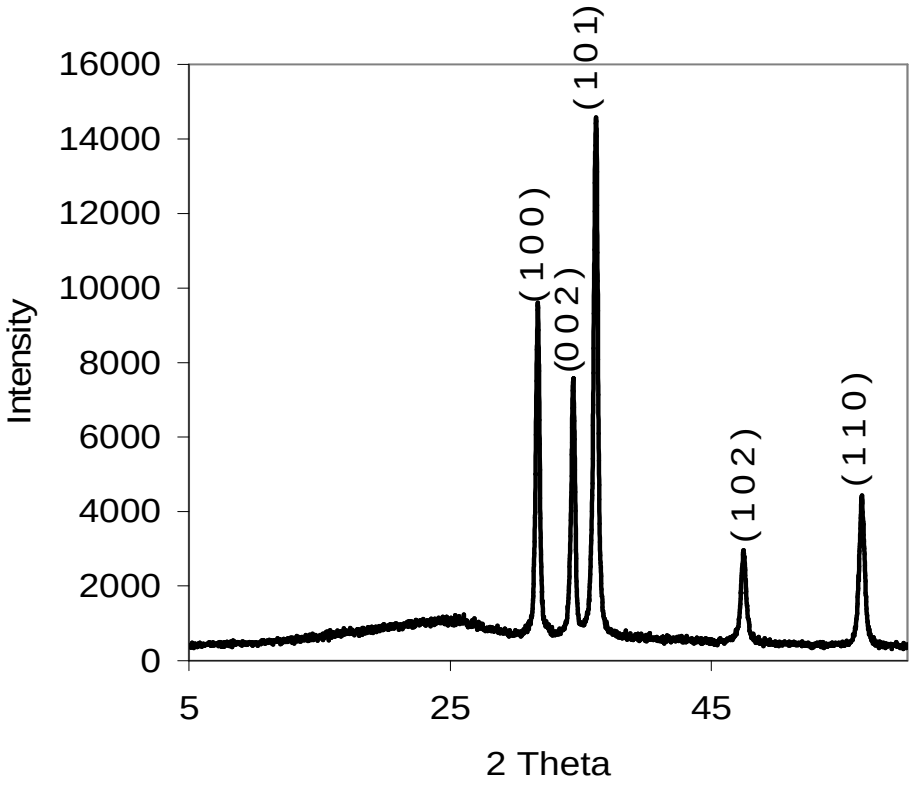

Fig. 6: Powder X-ray diffraction of ZnO nanomaterial

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