

APPLICATION OF SEMICARBAZON ZINC METAL COMPLEXE AS NANO PRECURSOR

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Abstract- Metal complexes, in addition to various applications, find use as nanoprecursors also. In the present study, a zinc semicarbazone complex was used to prepare ZnO nanoparticles, using polyol method. Synthesis and characterization of 2,4,5-trimethoxybenzaldehydesemicarbazone was carried out. Zinc complex of the ligand was prepared and a tetrahedral structure was proposed for it, based on various spectroscopic analysis. The application of the zinc complex, as nanoprecursor was checked. The prepared nanoparticles show spherical shape and were monodispersed. Particle size determination from band gap measurements using UV analysis, agreed with the SEM results.

Keywords : 2,4,5-trimethoxybenzaldehyde semicarbazone, Zn(II), Semicarbazide, IR, Mass, UV, TEM.

1. Introduction:

Coordination compounds possess a wide range of different structures depending on the metal ion, coordination number and denticity of the ligands involved. In the last few decades, many applications in Inorganic, Organic and Biological fields came up for them⁽¹⁻³⁾. Coordination Chemistry has always been a challenge to the Chemists as it has application in almost all branches of material science⁽⁴⁻⁸⁾.

Schiff bases can be directly prepared with easily-tunable electronic and steric effects. A variety of possible Schiff base metal complexes, with wide choice of ligands, and coordination environments, have been reported⁽⁹⁾. Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest recently. It is well known that N and O atoms play a key role in the coordination of metals at the active sites of numerous metal containing bio-molecules⁽¹⁰⁾.

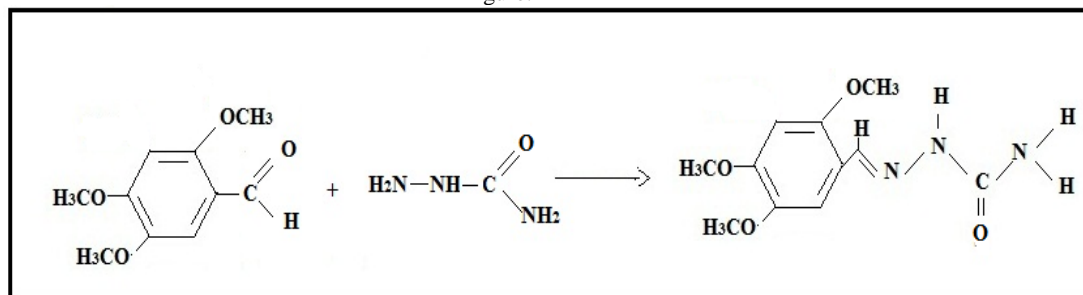
In recent years, new interesting applications are coming up in the field of medicine, and the metal complexes with Schiff base ligands of alternative structures, have attracted the attention of researchers⁽¹¹⁾. The Schiff base complexes of transition metal-metal ions have been extended enormously and embraced wide and diversified subjects comprising vast areas of organometallic compounds and influence various aspects of bio-coordination chemistry⁽¹²⁻¹⁷⁾. This inspires synthetic chemists to search for new metal complexes for bioactive compounds and zinc in particular.

2. EXPERIMENTAL METHOD

2.1. Synthesis of ligand

0.01 mol of acold ethanolic solution of 2,4,5-trimethoxy benzaldehyde was added to a 250ml RB flask containing 0.01 mol of semicarbazide in hot water. The mixture was refluxed for 4 to 5 hours at 80°C, with continuous stirring, and then allowed to cool overnight at room temperature. The isolated orange colored precipitate was filtered, washed with cold ethanol and dried under vacuum.

Figure: 1



2.2. Synthesis of complexes

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An aqueous solution of the corresponding metal salt (0.01 mol), (Zinc chloride hexahydrate), were mixed with hot ethanolic solution of the corresponding ligand (2,4,5-trimethoxy benzaldehyde semicarbazone) (0.02 mol). The mixture was refluxed for 4-5 hours at 70-80°C with continuous stirring, allowed to cool overnight at room temperature to get coloured metal complexes. The products were filtered, washed with 50% ethanol, and dried under vacuum.

Table : 1: Physical parameters of the ligand and its zinc complex

Sl.No	Compound	Molecular weight	Melting point (°C)	Colour	Molecular Formula
1	L ₁	253.29	260	Orange	C ₁₁ H ₁₅ N ₃ O ₄
2	[Zn(L ₁) ₂]	571.97	260	Yellow	[Zn(C ₁₁ H ₁₅ N ₃ O ₄) ₂]

3. Spectral Characterization Data

IR spectra analysis

The IR spectra of 2,4,5-trimethoxy benzaldehyde and its Zn(II) metal complexes are provided below:-

Figure : 2

IR spectra of L₁

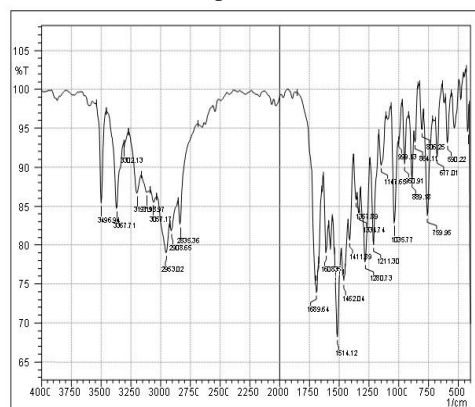
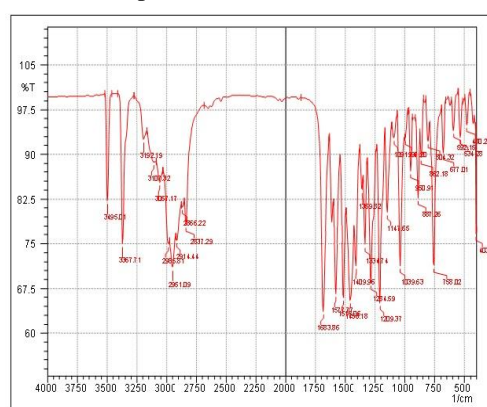


Figure : 3

IR spectra of [Zn(L₁)₂]



IR Spectra of band 1689.64cm⁻¹ can be assigned to the C=O stretching vibration in the ligand (L₁) while its transition metal show absorption shifted to values 1683.86cm⁻¹ in ZnCl₂. The azomethine nitrogen of the free ligand due to ν(C=N) show a strong absorption at 1608.73cm⁻¹. This is seen to suffer lower shift to values of 1577.77 cm⁻¹ in the complexes of ZnCl₂ correspondingly. In the metal complexes, (M-N) bands appear in the region of 534.28cm⁻¹ and (M-O) bands at 403.12 cm⁻¹. The IR absorption band values are summarized in table 2.

Table : 2: IR spectral values of L₁ and its metal complexes

Compounds	ν (C=N)	ν (N-H)	ν (C=O)	ν (M-O)	ν (M-N)
L ₁	1608.73	3367.71	1689.64	-	-
[Zn(L ₁) ₂]	1577.77	3367.71	1683.86	403.12	534.28

UV spectral analysis

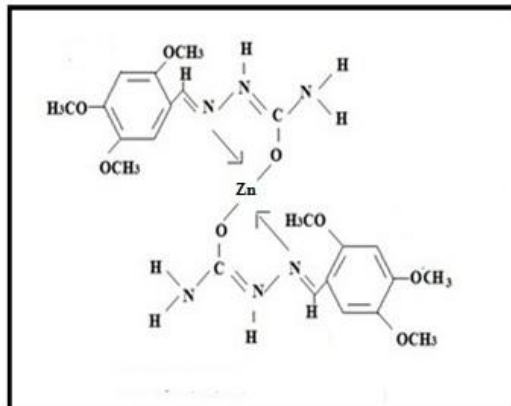
The electronic spectra of the complexes were recorded in DMSO as solvent. The Zn(II) complexes exhibited bands in the range 200–700 nm, corresponding to π-π* and/or n π* transitions. The absorption spectrum of [Zn(L₁)₂] band at 286.28 nm, are attributed to π-π* transitions. Ground state Zn (II) showed bands corresponding to ³T_{1g}(P) → ³A_{2g}(P) suggesting tetrahedral geometries, for the complexes.

Mass spectral analysis

The Electron impact mass spectrum of the ligand L_1 shows a molecular ion (M^+) peak at $m/z = 253.29$ amu corresponding to species $C_{11}H_{15}N_3O_4$ which confirms the proposed formula. The intensities of these peaks give the idea of the strength of the fragments. The mass spectrum of the Zn(II) complex showed a molecular ion peak at $m/z = 571.97$.

Proposed structure of metal complex

Figure : 4



4. Biological studies of zinc metal complexes as nano precursors:

The normal cell process may be affected by the formation of hydrogen bond through the azomethine nitrogen atom with the active centers of cell constituents leading to interference with the cell wall synthesis^(18,19). The variation in antimicrobial activity is owing to the character of metal ions and moreover the cell membrane of the microorganisms.

Zinc oxide nanoparticles have many applications. Zinc oxide nanoparticles are conventionally used as catalysts and initiator in various chemical reactions. They also find uses in gas sensor materials, as UV absorbers and as pigment in cosmetics and paints. They are also used in various electronic applications like varistors. Zinc oxide has an optical band gap in the UV region and this makes it an extremely efficient UV absorber.

There are many different methods for the preparation of Zinc oxide nanoparticles. One of the best methods used to prepare monodisperse oxide nanoparticles is the so called polyol method.

4.1. Synthesis of Zinc oxide nanoparticles

The complexes of Zinc as prepared were used for preparing Zinc oxide nanoparticles. The polyol used was ethylene glycol. From TG analysis, it was found that the complexes were stable around 160 degree Celsius and hence this temperature was used as the injecting temperature. A common method was used for the preparations as detailed below.

Ethylene glycol was heated to 165 degree Celsius in a two necked RB flask. The complexes were individually dispersed in ethylene glycol and injected in a stretch to the hot ethylene glycol solution to yield immediate precipitation of oxide nanoparticles respectively. The precipitates were centrifuged and washed several times with distilled water and absolute ethanol. They were then dried in air at 60 °C for one day, under controlled environment. The products were characterized by TEM and UV.

4.2. Characterisation using UV visible studies

The UV-Vis absorption spectra of ZnO nanoparticles prepared with the complexes in the case of ZnO nanoparticles prepared using semicarbazones derivatives, the band edge is observed around 375 nm.

4.3.Characterisation using TEM

The samples had an irregular shape and were mostly non-spherical. The cardinal steps involved in the formation of crystallites from solutions are the nucleation and growth, but the rapid aggregation process prevents the individual nanoparticles growing into larger particles.

Table : 3: Absorption edges, band edges and particle sizes for ZnO samples isolated

Precursor - Zn(II) complex of :	Band edge (nm)	Particle Size (nm)
L_1	330	4.71

The blue shift in band gaps from that of bulk in the case of the prepared nano particles enables us to calculate the particle size indirectly using the Bruz equation. The Bruz equation is

$$\Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r}$$

A lower temperature favoured the formation of particles of irregular morphology while at higher temperature nearly spherical aggregates of the nanoparticles were obtained.

The data shows that the Zinc complexes are efficient nanoprecursors and when applied in polyol method can yield monodisperse nanoparticles.

CONCLUSION:

Characterization was done by the aid of IR, UV, Magnetic moment studies, Mass, and NMR studies. Structures of the complexes were proposed using available resources. Zinc complexes were assigned tetrahedral geometries. The zinc complexes were also investigated to check for their suitability as nano precursors. It was found that semicarbazones derivatives were suitable candidates for use as nano precursors. Almost monodisperse nanoparticles were obtained by using polyol method. Ethylene glycol was used as the high boiling solvent in the study. The nano nature of the materials synthesized was checked using UV band gap measurement and the resultant size was confirmed using TEM.

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