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Solvent-free Synthesis, Characterization and Biological Activity of Transition Metal Complexes of Schiff Base Ligand Derived (E)-N'-((1H-indol-3-yl) methylene)-4-chlorobenzohydrazide

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ABSTRACT

The present study explores the microwave-assisted synthesis, characterization, and biologicalactivity of transition metal complexes of a Schiff base ligand derived from (E)-N'-((1H-indol-3-yl)methylene)-4-chlorobenzohydrazide. The ligand and its metal complexes were synthesized using an eco-friendly microwave irradiation method to enhance reaction efficiency and yield. Metal complexes were derived from nitrate of Co(II), Ni(II), Cu(II), Zn(II), salts with novel ligand at the end of the reaction all metal complexes show fine colour. By TLC and melting point of each complex was confirming the formation of metal complex. The synthesized compounds were characterized by various spectroscopic techniques, including FT-IR, UV-Vis, NMR, and elemental analysis. The metal complexes were further analyzed using Infrared spectroscopy, UV-visible spectroscopy and thermogravimetric analysis. The antibacterial activities of the Schiff base ligand and its metal complexes were tested against Escherichia coli, Staphylococcus aurous and Salmonella Typhi.

Keywords: Microwave irradiation, Benzohydrazide, Thermal Study, Novel Schiff Base Ligand, Antibacterial Activity.

I. INTRODUCTION

Schiff bases have been extensively studied due to their important biological and pharmacological properties. The coordination of Schiff base ligands with transition metals frequently results in greater biological activity [1]. Microwave-assisted synthesis provides an efficient and green approach for obtaining these complexes with better yields and reduced reaction time. This study focus on the synthesis and characterization of transition metal complexes derived from (E)-N'-((1H-indol-3-yl)methylene)-4-chlorobenzohydrazide and evaluates their biological potential. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions [2].The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been predictable that many of these complexes may serve as models for biologically important species [3,4]. Microwave-

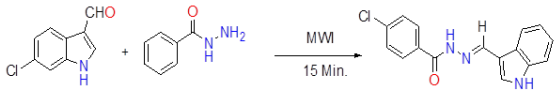
assisted method is generally characterized by higher yields, higher selectivity, milder reaction conditions, and shorter reaction times compared to conventional method [5, 6].It is an actual approach to green and sustainable chemistry due to its environmental friendly features [7]. The use of microwave as an alternative energy source allows less time-consuming synthesis because of rapid heating and transfer of energy to the reaction medium, permits the employment of eco-friendly solvents or solvent-free conditions, and favours catalytic transformations [8, 9]. Now a day, use of scientific microwave for synthesis is becoming popular. Microwave method is the solvent free, green and eco-friendly synthesis. It helps to reduce pollution, gives better yield and reduces cost. Simple reaction conditions and important is time saving [10-12]. Synthesis using microwave irradiation technique is environmentally very safe and effective [13-14]. The Schiff base ligand containing azomethine (C=N) group [15]. The products of ketone or aldehyde with primary amine are generally known as Schiff base [16]. Schiff bases have remarkable property of forming binuclear complexes and serve as excellent chelating ligands [17-18]. Schiff base metal complexes have broad applications and have been used as analytical reagents [19], catalysts [20], and showed anti-tumor [21], anti-viral [22], anti-fungal [23] and anti-bacterial [24] activities. They are biologically very active compounds, having biological activities like antibacterial [25], antimicrobial [26], anticancer [27], plant growth inhibitors [28] and so on.

II. METHODS AND MATERIAL

All the synthetic grade, analytical grade reagents as well as chemicals were purchased from Sigma Aldrich, Loba Chem., Merck chemicals. Newly synthesized compounds melting point was found using an electro thermal digital apparatus and uncorrected. ^{1}H-NMR, spectral data were recorded on a Bruker (400 MHz, 100 MHz) spectrometer. Chemical shift (ppm) was referred to as the internal standard Tetramethyl silane (TMS). The synthesized compound was monitored by thin-layer chromatography and find out the molecular weight using LC-MS.

2.1 Synthesis of Novel Ligand

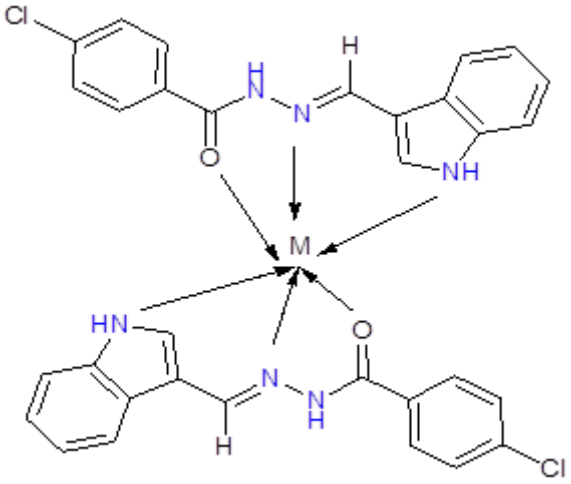
The novel Schiff base ligand was prepared by the reaction between 6-chloro-1H-indole-3-carbaldehyde (0.294 gm., 0.02 mmol) and Benzohydrazide (0.212 gm., 0.01mmol) under solvent free condition in scientific microwave oven about 15 minutes. The microwave irradiated product was washed with pet ether and filtered. The final product was recrystallized from ethanol to give light yellow crystals. The purity of the product was monitored by the use of TLC, using n-hexane and ethylacetate (7:3). Yield84%, M.P.198°C.



6-chloro-1*H*-indole-3-carbaldehyde Benzohydrazide (*E*)-*N*′-((1*H*-indol-3-yl)methylene)-4-chlorobenzohydrazide

2.2 Synthesis of Metal Complexes

The metal salt and Schiff base ligand were mixed in a 1:2 (metal: ligand) grinder ratio. The reaction mixture was irradiated in a microwave oven. The precipitated complexes were collected by filtration, washed, and dried under vacuum. The metal salts used were $Co(NO_3)_2.6H_2O$, Ni $(NO_3)_2.6H_2O$, Cu $(NO_3)_2.3H_2O$, and Zn $(NO_3)_2.6H_2O$



M(II)= Co,Ni,Cu,Zn

III.RESULTS AND DISCUSSION

All metal complexes and novel Schiff base ligand are coloured, solid and stable at room temperature. They possess sharp melting point. The transition metal complexes are insoluble in common organic solvents but soluble in DMF and DMSO.

3.1 Elemental Analysis

The elemental analysis of Schiff base ligand (Found: C = 64.45); H = 4.03; N= 14.03; O= 5.02; Cl= 11.83%); Calcd: C = 64.54; H = 4.06; N =14.11; O=5.37; Cl= 11.91 %) indicated that the ligand has the molecular formula i.e. $C_{16}H_{12}ClN_3O$.

3.2 Physical Properties

Physical properties of the novel Schiff base ligand and metal complexes summarized in Table No. 1.

Sr. No	Molecular formula	Color	Melting point (ºc)	Time Sec./Min	Yield %
1	$C_{16}H_{12}ClN_3O$	Light Yellow	293	15 min.	84
2	$[C_{16}H_{12}ClN_3O]Co$	Dark Yellow	276	230	83
3	$[C_{16}H_{12}ClN_3O]Ni$	Pale Yellow	287	143	89
4	$[C_{16}H_{12}ClN_3O]Cu$	Light Green	263	190	88
5	$[C_{16}H_{12}ClN_3O]Zn$	Green	256	110	87

3.3 Mass Spectral Studies

The mass spectrum study of novel Schiff base ligand showed a peak at m/z. 297.7(M+1) that corresponds to the molecular weight of the Schiff base ligand 297.7.

3.4 ^{1}HNMR Spectral Studies

Observed ^{1}H NMR peaks (ppm) of novel Schiff base ligand shows different peaks. The characteristic peak observed at 8.56pm is due to H from azomethine group at 11.41 ppm is due to H-from NH of Indole ring. The peaks observed at 7.55-7.40 ppm are due to H-from aromatic rings.

3.5 Infrared Spectra Analysis

The IR spectrum of novel ligand show characteristics band at 1614cm^{-1} which indicates (C=N) stretching vibration of azomethine group. The vibrational band at 3300 cm^{-1} assigned N-H stretching in the ligand. Band observed at 1452 cm^{-1} corresponds to C=C stretching. The band observed at 3191 cm^{-1} indicates aromatic C-H stretching in the ligand.

IR spectral study of Ni metal complex: The band appeared at 1725cm^{-1} corresponds to azomethine (C=N) stretching, whereas same azomethine band is observed at 1630 cm^{-1} in spectrum of ligand. Which indicate coordination of ligand with metal ion.The band appeared at 3200cm^{-1} indicates the aromatic (C-H) stretching in complex, whereas same aromatic (C-H) stretching is observed at 3280 cm^{-1} in spectrum of ligand. The band observed at 3400 cm^{-1} assign to (N-H) stretching, whereas in spectrum of ligand it is observed at 3415 cm^{-1}.The vibration observed at 1483 cm^{-1} due to aromatic (C=C) stretching. The characteristics band appeared at 572 cm^{-1} assign to (M-N) vibration, which confirms coordination of azomethine and metal ion [29].

IR spectral study of Cu metal complex: A stretching observed at 1620 cm^{-1}, which corresponds to azomethine (C=N) stretching vibrations, whereas same stretching is observed at 1660 cm^{-1} in spectrum of ligand. The band appeared at 3190 cm^{-1} assign to aromatic (C-H) stretching, whereas same stretching is observed at 3281 cm^{-1} in spectrum of ligand. The vibration observed at 1574 cm^{-1} due to aromatic (C=C) stretching. The coordination of metal to nitrogen was justified by stretching observed at 492 cm^{-1} [30].

3.6 Electronic Spectra

UV-Vis spectrum of both metal complexes Ni(II), Cu(II) recorded in the wavelength region 200nm to 400nm in DMSO solution.

UV-Vis spectral data of Ni: Electronic spectrum of Ni(II) complex shows absorption maxima at 43478 (230), 44247 (226) and 47169 (212) assign to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively indicating that complex possess octahedral geometry [31].

UV-Vis spectral data of Cu: Electronic spectrum of Cu (II) complex shows absorption maxima at 45454 (220) and 47619 (210) assign to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions showing that complex possess octahedral geometry [32].

3.7 Thermo gravimetric Analysis

To determine the thermal stability and chemical composition of Ni(II), and Cu (II) complexes, thermo gravimetric analysis has been performed in a temperature range of 30-600 °C in nitrogen atmosphere at a heating rate of 10°C/min. Thermal analysis was used mainly for the confirmation of the water molecule or solvent associated with being in the sphere of coordination or in the outer sphere of the complex and the information about its properties, the nature of the intermediate products and final thermal decomposition. From the TGA curves, the weight loss was calculated for the different steps and compared with the theoretically calculated weight for the suggested formulas based on the results obtained from the elemental analyzes.

The TGA curve of Ni (II) was carried out in the temperature range from 30^{0}C to 600^{0}C. The heating was carried out in the nitrogen atmosphere, with heating rate 10^{0}C min^{-1}.

In the range of 30^{0}C to 145^{0}C water of crystallization lost with 10% weight loss is observed. Then loss up to organic moiety total weight loss of 85.14% at 500^{0}C. Stable curve indicates formation of metal oxide of nickel.

The TGA curve of Cu (II) was carried out in the temperature range from 28^{0}C to 600^{0}C. The heating was carried out in the nitrogen atmosphere, with heating rate 10^{0}C min^{-1}. The thermogram of Cu (II) shows total weight loss of 69.51%. Firstly loss water of crystallization in the range of 29.74^{0}C to 93.52^{0}C. Lastly loss of organic moiety with total weight loss at 500^{0}C was 84.832%. A stable curve shows the formation of metal oxide of copper.

3.8 Biological Activity

Antibacterial activity of novel Schiff base ligand and its metal complexes were summarized in Table 2.

Sr. No	Compound	Minimum inhabitation concentration (ug/ml)		
		E. Coli	S. Aureus	S. Typhi
1	$C_{16}H_{12}ClN_3O$	100	125	250
2	$[C_{16}H_{12}ClN_3O]$ Co	62.5	125	50
3	$[C_{16}H_{12}ClN_3O]$ Ni	125	250	100
4	$[C_{16}H_{12}ClN_3O]$ Cu	100	125	100
5	$[C_{16}H_{12}ClN_3O]$ Zn	125	62.5	50

Antibacterial activity of synthesized novel ligand and its metal complexes were performing against Escherichia Coli, Staphylococcus Aureus and Salmonella Typhi. Which were grown overnight at 37^{0}C temperature. The minimum inhibitory concentration (MIC) was evaluated against test bacteria. Concentration ranging is in between 0.4 ug/ml to10 ug/ml.

Co(II) shows better and Ni(II), Cu(II), Zn(II) good antibacterial activity on E.coli as compared to rest of metal complexes and parent ligand. Zn (II) complex shows excellent antibacterial activity on S.Aureus as compared to rest of metal complexes and parent ligand. Zn (II) and Ni (II) show excellent antibacterial activity on S.Typhi as compared to rest of metal complexes and parent ligand.

The reason for the better antimicrobial activity of the complexes as compared to the ligands may be because the chelation reduces the polarity of the metal ion by partial sharing of its positive charge with the donor

groups and possibly π-electron delocalization within the whole chelate ring. This process thus increases the lipophilicity of the complexes, which subsequently enhances the penetration through the lipid layer of cell membrane and restricts further multiplicity of the microorganism. Among the metal complexes [33].

IV. CONCLUSION

This study successfully synthesized and characterized transition metal complexes of a Schiff base ligand using a microwave-assisted method. The obtained complexes exhibited significant antibacterial properties, highlighting their potential applications in medicinal chemistry.

The microwave method declares the principle of green chemistry. The novel ligand was synthesized from between 6-chloro-1H-indole-3-carbaldehyde and Benzohydrazide. It forms stable complexes with transition metal ions such as Co (II), Ni (II), Cu (II) and Zn (II). The novel ligand and its four metal complexes show good antibacterial activity.

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