



Thermal and antibacterial studies of cobalt (II), nickel (II), copper (II) and zinc (II) complexes of hydrazone Schiff base

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ABSTRACT

Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base [LH₂] derived from 2-hydroxy-5-methyl-3-nitroacetophenone and isonicotinoyl hydrazide have been synthesized and characterized on the basis of molar conductance, magnetic susceptibilities, elemental analysis, infrared, ¹H NMR, electronic spectra and thermogravimetric analysis. The Schiff base acts as monobasic bidentate ligand commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. Which is confirmed by IR spectral data. Thermal analysis indicates the coordinated and lattice water molecules in the complexes which is also IR spectral data. The Schiff base and their metal complexes have been evaluated for their antibacterial activities.

Keywords: Schiff base, Magnetic susceptibility, Thermal, Antimicrobial studies

INTRODUCTION

Schiff bases are an important class of ligand in coordination chemistry. Schiff bases derived from hydrazones and aroyl hydrazines have been widely used as ligand for the synthesis of transition metal complexes¹. Schiff bases or their metal complexes have many applications in different fields² Hydrazones, heteroaroyl hydrazones ligands and their metal complexes are biologically active. Heteroaroyl hydrazones forms stable metal complexes with transition metal ions and inner transition metal ions due to complexing ability of ligand through keto-enol tautomerism and availability of other donor sites in the ligand i.e. isonicotinoyl hydrazide is one of the drug in chemotherapy of tuberculosis³. Due to its biological potency, pharmacological properties and synthetic flexibility of Schiff base derived from isonicotinic acid hydrazide^{4,5}. The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-methyl-3-nitroacetophenone and isonicotinoyl hydrazide.

EXPERIMENTAL SECTION

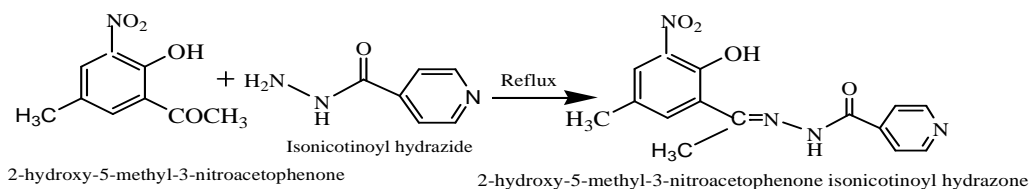
All the chemicals used were of AR grade and used as received isonicotinoyl hydrazide (IH) was obtained from E.Merck. 2-hydroxy-5-methyl-3-nitro acetophenone (HMNA) was prepared by known method.⁶ The solvents were purified by standard methods⁷.

Synthesis of 2-hydroxy-5-methyl-3-nitroacetophenone isonicotinoyl hydrazone [HMNAIH]:

A solution of isonicotinoyl hydrazide (0.02M) in 25ml of ethanol was added to an ethanolic solution (25ml) of 2-hydroxy-5-methyl-3-nitroacetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 3h. Then cooled to room temperature. The resulting pale yellow coloured solid was washed with ethanol, crystallized from

DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and melting point. It was also characterized by IR and ^1H NMR spectral studies.

Yield: 76% MP. 285 $^{\circ}\text{C}$



Scheme 1-Synthesis of the ligand (LH₂)

Table 1. Analytical data of the Ligand

Sr. No.	Ligand	Molecular Formula	Formula Weight	Colour and nature	Elemental Analysis		
					C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)
1.	HMNAIH	C ₁₅ H ₁₄ N ₄ O ₄	314.3	Yellow Crystalline	57.03 (57.32)	04.38 (04.49)	17.71 (17.83)

Preparation of complexes

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HMNAIH (0.02M) in 25ml of ethanol a suspension of respective metal salts [acetates of Co (II), Ni (II), Cu (II), and Zn (II)] was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6h. The precipitated complexes were filtered, washed with ethanol. Followed by ether and dried over fused calcium chloride. Yield: 55-60%

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods⁸. The ^1H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm^{-1} . Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[\text{HgCo}(\text{SCN})_4]$ as the calibrant. The thermo gravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0 min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

Table 2. Analytical data and molar conductance of the compounds

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)				μ_{eff} B.M.	Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
			M	C	H	N		
$[\text{Co}(\text{LH})_2 \cdot 2\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$	Black	739.5	7.80 (7.96)	48.15 (48.68)	4.36 (4.87)	14.98 (15.15)	4.60	5.5
$[\text{Ni}(\text{L})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$	Orange	407.0	14.31 (14.42)	44.35 (44.23)	4.51 (4.67)	13.80 (13.76)	Dia	9.19
$[\text{Cu}(\text{LH})_2] \cdot 3\text{H}_2\text{O}$	Brown	744.1	8.41 (8.53)	48.12 (48.38)	4.44 (4.84)	14.84 (15.05)	1.84	8.84
$[\text{Zn}(\text{LH})_2 \cdot 2\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$	Yellow	764.0	8.42 (8.56)	46.75 (47.12)	4.52 (4.97)	14.78 (14.66)	Dia	---

RESULTS AND DISCUSSION

The ligand HMNAIH and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, diffused reflectance spectra, molar conductance, magnetic susceptibility measurements and thermogravimetric analysis data.

The ^1H NMR spectra of ligand HMNAIH shows signals⁹⁻¹² at δ 12.63, (1H, s, phenolic OH); 11.18, (1H, s, imino); 8.98 and 7.95 (4H, d, isonicotinic); 8.07 and 7.25, (2H, m, phenyl) and 3.24 ppm, (3H, s, methyl) and 2.46 ppm (3H, s, Ar-methyl)

All these values and analytical data is consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. All the compounds are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF (10^{-3} M) solution at room temperature (Table.2) shows all the complexes are non electrolytes.

IR spectra of ligand shows¹³⁻¹⁷ $\nu(\text{C}=\text{N})$ peaks at 1612 cm^{-1} and absence of $\text{C}=\text{O}$ peak at around $1700 - 1750\text{ cm}^{-1}$ indicates the Schiff base formation. Other reported peaks are $\nu(\text{N}-\text{H})$ at 3211 cm^{-1} , $\nu(\text{OH})$ at 2803 cm^{-1} , $\nu(\text{C}=\text{O})$ phenolic at 1526 cm^{-1} , pyridyl ring breathing peak at 1066 cm^{-1} , $\nu(\text{N}-\text{N})$ peak at 998 cm^{-1} and $\nu(\text{C}=\text{N})$ peak at 1612 cm^{-1} , The $\nu(\text{C}=\text{N})$ peak of ligand is found to be shifted to lower frequencies by $38-48\text{ cm}^{-1}$ in the spectra of complexes indicating the coordination via the azomethine nitrogen, which is also confirmed by appearance of bands in the range of $340 - 348\text{ cm}^{-1}$ which have been assigned to $\nu(\text{M}-\text{N})$ band.

Thermogravimetric studies:

All the complexes are stable up to $60-70^\circ\text{C}$. All the complexes except Cu (II) show two stage decomposition pattern and Cu (II) show three stage decomposition pattern. The percentage weight loss data (Table 3) up to 140°C indicates the loss of one water molecule from Co (II) and Ni (II) complexes each, loss of two water molecule from Zn (II) complexes and loss of three water molecules (lattice) from Cu (II) complexes each. Further loss in weight up to $220-240^\circ\text{C}$ was observed. The percentage weight loss data indicates loss of one coordinated water molecule from Ni (II), complexe each, loss of two coordinated water molecule from Co (II) and Zn (II) complexes each. There is no weight loss at $220-240^\circ\text{C}$ in Cu(II) complexe indicates the absence of coordinated water molecule in this complex.¹⁸⁻²²

Table 3. The percentage weight loss data of complexes of HMNAIH

Complexes	The percentage weight loss at		Half decomposition Temperature ($^\circ\text{C}$)
	110-140 $^\circ\text{C}$ Observed (Calc.)	220-240 $^\circ\text{C}$ Observed (Calc.)	
Co(II)	2.48 (2.40)	4.87 (4.8)	435.0
Ni(II)	4.46 (4.4)	4.88 (4.4)	460.0
Cu(II)	7.4 (7.2)	---	470.0
Zn(II)	4.4 (4.7)	4.8 (4.7)	450.0

Antimicrobial activity:

The compounds are found to show low bacteriocidal behavior against most of the bacterial culture and resistance towards the other. In general the results reveal that the activity of the ligand was found to enhance on complexation with metal. The inhibition effect of the ligand and its metal complexes on the growth of various bacteria²³⁻³⁴ is summarized in Table 4.

Table 4. Antimicrobial activity

Ligand and its Complexes	Zone of inhibition (in mm)						
	<i>B.subtilis</i> (mm)	<i>P.vulgaris</i> (mm)	<i>S.aureus</i> (mm)	<i>E.coli</i> (mm)	<i>P.fluorescen</i> (mm)	<i>A.aerogenes</i> (mm)	<i>B.megatherium</i> (mm)
HMNAIH	R	R	S ₁₇	R	S ₇	R	R
Co- HMNAIH	S ₁₃	S ₁₄	R	S ₁₁	R	S ₁₂	R
Ni- HMNAIH	R	R	S ₁₀	R	R	R	R
Cu- HMNAIH	S ₁₅	S ₇	R	S ₁₂	R	S ₁₁	S ₈
Zn- HMNAIH	S ₁₄	R	R	S ₁₂	S ₁₂	S ₁₁	S ₁₄

S-Sensitive
R-Resistant

CONCLUSION

All the complexes contain lattice water and shows weight loss up to 320°C indicates decomposition of ligand molecule. Further a horizontal curve was observed beyond 640°C suggest the formation of final decomposition products i.e. stable metal oxides of respective metals. On the basis of half decomposition temperature the order of thermal stability is found to be Ni (II) > Cu (II) > Zn (II) > Co (II). The analysis of magnetic moment, thermal analysis and electronic spectral data shows structural changes. The structural changes of all complexes have marked effect on the sensitivity and sensitivity varies with organisms.

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