

Synthesis, Characterisation and Antimicrobial Activity of Schiff Base Derived From Dehydroacetic Acid And Isonicotinic Acid Hydrazide And Its Fe(III), Co(III), Ni(II), Cu(II), Zn(II) Metal Complexes

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Abstract- A Schiff's base of dehydroacetic acid designed to develop novel antimicrobial and antifungal agent having broad spectrum of activity and potency. The new Schiff base hydrazone (9E)-N'-(1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)ethylidene)isonicotinohydrazide (DHA-INH) prepared by condensation of isonicotinic acid hydrazide with dehydroacetic acid in ethanolic medium. The nitrates of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) were treated with tridentate DHA-INH to develop novel mononuclear metal complexes having 1:2 metal to ligand proportion with octahedral geometry. The structure of ligand was established by elemental analysis, UV-Visible, FTIR, ¹H NMR, ¹³C NMR and mass spectral studies. The metal complexes were characterised by UV-visible spectroscopy, FTIR, elemental analysis, molar conductance, powder x-ray diffraction and magnetic susceptibility. Ligand and metal complexes were tested *in vitro* against Gram positive *B. subtilis*, *Staphylococcus aureus*; and Gram negative *Escherichia coli*, *Pseudomonas aeruginosa* as antibacterial and *Candida glabrata*, *Candida tropicalis* as antifungal activity. Metal complexes shows enhanced activity than free ligands.

Keywords- Dehydroacetic acid, Isonicotinic acid hydrazide, Schiff base hydrazone, metal complexes, antimicrobial activity.

I. INTRODUCTION

Schiff bases generally synthesised by condensation of primary amines with compounds having active carbonyl groups. In medicinal and pharmaceuticals Schiff bases play an important role [1,2] such as anti-inflammatory [3], antifungal [4], antibacterial [5], antioxidant [6], antitubercular [7], antitumor [8] etc. The excellent reactivity and biological activity of acid hydrazides R-CO-NH-NH₂ [9] and its Schiff bases with active pharmacophore (-CONH-N=CH/R-R) shows good chelating property towards transition metals to form complexes and such types of complexes prominently

used as fungicides, herbicides and insecticides. [10] Dehydroacetic acid is an important biologically active compound used as precursor to prepare number of heterocyclic derivatives with remarkable antifungal and antibacterial activity. [11] The INH-derivatives show significant coordination ability with transition metal ions. [12] As a continuation of our interest in the coordination behaviour of Schiff bases derived from DHA, we are reporting here the transition metal complexes of novel Schiff base derived by the condensation of DHA and INH. The Schiff base act as a tridentate ligand coordinating through ONO donor atoms.

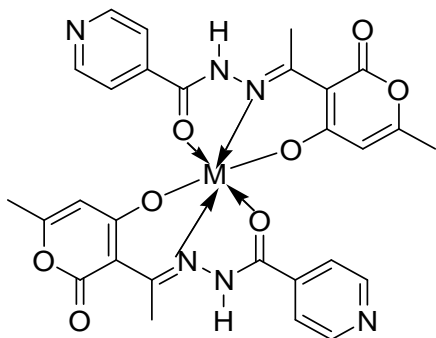
II. RESULT AND DISCUSSION

The Schiff's base ligand were prepared from DHA and INH in 1:1 molar ratio and found correct from elemental, mass and other spectral analysis. Ligand and its metal complexes were all coloured except Zn(II) complex, stable at room temperature, insoluble in common organic solvents but soluble in DMSO, non-hygroscopic in nature. Powder x-ray data indicate that all metal complexes have orthorhombic crystal system with cell parameter $a \neq b \neq c$ and inter axial angle $\alpha \neq \beta \neq \gamma$ condition. From physicochemical and spectral analysis, the structure of synthesized compound were found in good agreement with proposed structures.

III. CONCLUSION

In this paper we report synthesis of novel DHA-INH Schiff base ligand and its transition metal complexes. The molecular structures of the synthesized compounds was evaluated by physicochemical as well as spectral analysis. Infrared spectra reveals that the ligand behaves as monobasic tridentate ligand coordinate through nitrogen of azomethine group, enolic oxygen atom and carbonyl oxygen atom. The magnetic moment measurement shows that all complexes are paramagnetic except Co(III) and Zn(II) which was diamagnetic. From conductance value of all complexes

indicate nonelectrolytic nature. They show 1:2 metal to ligand stoichiometry with octahedral geometry and orthorhombic crystal system. The ligands and metal complexes were tested *in vitro* for their antibacterial and antifungal activities. As expected, Cu(II) complex possesses prominent antibacterial activity against the tested strains of pathogenic bacteria.



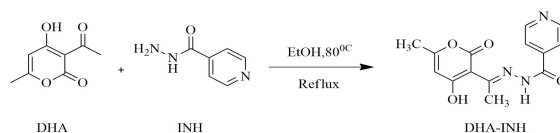
IV. EXPERIMENTAL

Isonicotinic acid and dehydroacetic acid of pure analytical grade were purchased from Sigma Aldrich and used as supplied for synthesis of ligand DHA-INH. A R grade transition metal nitrates of S. D. Fine chemicals were used for the preparation of metal complexes. Elemental analysis was performed by Thermo Scientific (Flash 2000) CHN elemental analyzer, FT-IR were taken on Perkin Elmer version-1 from 450 cm^{-1} to 4000 cm^{-1} . The UV-Vis spectra were recorded on Shimadzu UV 1800 Spectrophotometer for complexes in DMSO. Magnetic moments were measured by Guoy's method at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant and were corrected for diamagnetism of the components using Pascal's constants. Conductance were measured on Elico Cm-180 Conductometer using 10^{-3} M solution in DMSO. ^1H and ^{13}C NMR of were taken in $\text{DMSO}-d_6$ on 400MHz JEOL JNM ECS400.

Synthesis of ligand DHA-INH:

Dehydroacetic acid (DHA) (0.06mole, 10.08g) was dissolved in 40ml of redistilled ethanol in round bottomed flask. After complete dissolution of DHA, 40ml of isonicotinic acid hydrazide (INH) (0.06mole, 8.23gm) solution was added in it. After heating at 80°C for half an hour, orange coloured precipitate was obtained. It was filtered and washed with hot ethanol, dried and recrystallised from DMSO. (87% yield, m.p. 220°C)

Reaction-



Scheme 1. Synthesis of ligand DHA-INH

Formation of the Schiff base ligand of hydrazide and its proposed structure

Synthesis of metal complexes:

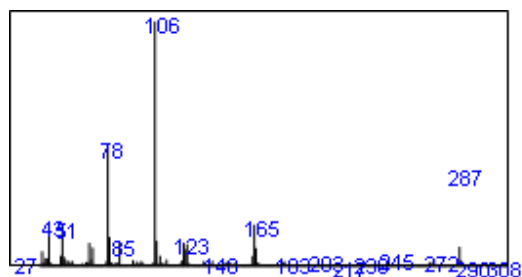
Metal nitrates we chosen grinding method for preparation of complexes. Metal:Ligand was taken in 1:2 proportion (0.001mole:0.002mole) grinded well for half an hour with addition of few ml of methanol, after some time colour changes from orange to, black for Fe(III), brown Co(III), green Ni(II), green Cu(II), Zn(II) colourless. All metal complexes were digested for half an hour in the alcoholic solution filtered and dried in oven at 80°C . In case of cobalt complex, Co(II) nitrate was used as a salt but due to air oxidation cobalt complex exists in Co(III) state.[13-14] Let required it is proved by taking magnetic moment and that is diamagnetic in nature.

^1H and ^{13}C NMR of DHA-INH:

^1H and ^{13}C NMR of DHA-INH was taken in DMSO. Ligand shows signal at 2.10 ppm (s, 3H, CH_3); 2.60 ppm (s, 3H, $\text{N}=\text{C}-\text{CH}_3$); 5.85 ppm (s, 1H, olefinic); 7.82 ppm (s, 2H, β -H of pyridine ring); 8.77 ppm (s, 2H, α -H of pyridine ring); 12.00 ppm (s, 1H, CONH peak); ^{13}C NMR shows signal at 163.80 ppm (C-1); 107.63 ppm (C-2); 182.31 ppm (C-3); 95.35 ppm (C-4); 170.75 ppm (C-5); 19.80 ppm (C-6); 150.40 ppm (C-7); 17.57 ppm (C-8); 162.45 ppm (C-9); 122.33 ppm (C-10); 134.34 ppm (C-11); 161.41 ppm (C-12) in agreement with the proposed ligand structure. Analytical Calculated for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4$: C 58.46, H 4.51, N 14.60; found C 58.53, H 4.56, N 14.63.

Mass Spectra of the Ligand:

In the mass spectrum, the molecular ion peak of the ligand is observed at m/z 287(M^+) corresponds to its molecular formula $[\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4]^+$ which confirms the formation of desired ligand of DHA-INH which is exactly equal to that calculated and theoretically from the given structure (287).

Mass spectrum of Ligand ($C_{14}H_{13}N_3O_4$)

IR spectra:

The comparison of FTIR spectrum of metal complexes with that of parent ligand to find out mode of bonding (Table 1). The IR spectra of free ligand shows some characteristic bands at 3451 cm^{-1} , 3062 cm^{-1} , 1687 cm^{-1} , 1583 cm^{-1} , 1360 cm^{-1} . These bands corresponds to ν_{OH} (intermolecular hydrogen bonding) and decreased by $10\text{--}20\text{ cm}^{-1}$ due to involvement in complexation, $\nu_{\text{N-H}}$ (N-H stretch), $\nu_{\text{C=O}}$ (carbonyl stretch), $\nu_{\text{C=N}}$ (azomethine stretch) and $\nu_{\text{C-O}}$ (enolic stretch) respectively.[15,16] In the metal complexes shift of $\nu_{\text{C-O}}$ stretch bands appear upwards which suggested the participation of enolic oxygen in coordination with metal ions. The increased value of N-H frequency in case of metal complexes due to involvement of adjacent azomethine N atom in coordination.[17] There was a change in the C=O frequency which shows the involvement in coordination.[18] The presence of non ligand frequencies at $504\text{--}552\text{ cm}^{-1}$ and $626\text{--}657\text{ cm}^{-1}$ can be assigned to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ respectively.[19]

Electronic Spectra and Magnetic Measurements :

The electronic absorption spectra of metal complexes and free ligand were observed in DMSO at $200\text{--}800\text{ nm}$. Free ligand shows three electronic absorption bands 39215 cm^{-1} , 29411 cm^{-1} , 24570 cm^{-1}

characteristics of $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions of carbonyl and azomethine moiety.[20] The Fe(III) complex show low intensity bands in the range $22225\text{--}24096\text{ cm}^{-1}$ and 28129 cm^{-1} . In high spin complexes ${}^6A_{1g}$ is ground term therefore, the transition are assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ with 5.26 BM suggesting octahedral geometry. Transitions are weak and obscured by charge transfer bands tailing into visible region of spectra.[21] The Co(III) showed bands at 29673 cm^{-1} and Ni(II), Cu(II) complexes at $25974\text{--}26954\text{ cm}^{-1}$, $28635\text{--}39062\text{ cm}^{-1}$ assigned to the L to M charge transfers and magnetic moments 2.97 B.M. , 1.86 B.M. for Ni(II) and Cu(II) complexes. Suggesting octahedral arrangement around metal ions. Co(III) and Zn(II) complex is diamagnetic as expected its geometry is most probably octahedral.

X-ray diffraction study:

The x-ray diffractogram of Fe(III), Co(III), Ni(II), Cu(II) and Zn(II) complexes were scanned in the range $5\text{--}60^\circ$ at wavelength 1.540598 \AA . The x-ray diffraction data of metal complexes with respect to major peaks having relative intensity greater than 10% have been indexed by using computer program.[22] The diffractogram of metal complexes and associated data depict the 2θ value as each peak relative intensity and inter planer spacing i.e. (d-value) and lattice constants a,b, and c for each unit cell parameter and miller indices (h ,k ,l) (Table 3). The unit cell volume is calculated by using standard formula. The Fe(III) complex shows fifteen reflections with maxima at $2\theta(23.99)$ corresponding to d-value 3.77 \AA . The Co(III)(Figure 1), Ni(II), Cu(II) and Zn(II) complexes show eight, twelve, ten, twelve reflections as $2\theta(26.69)$, $2\theta(12.31)$, $2\theta(26.93)$, $2\theta(26.28)$ with d-value 3.33 \AA , 7.18 \AA , 3.30 \AA , 3.34 \AA . The 'd' values of reflections were obtained using Bragg's equation, $n\lambda=2d\sin\theta$. To calculate the unit cell volume of complexes for orthorhombic crystal system $V=abc$ equation was used.

Table 1. FTIR frequencies of ligand and metal complexes

Compounds	MolFormula	IR Bands (various stretchings in cm^{-1})					
		$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C=O amide})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
DHA-INH	$C_{14}H_{13}N_3O_4$	30 62	158 3	168 7	136 0	---	---
Fe(DHA-INH) ₂	$C_{28}H_{26}N_6O_8Fe$	30 72	155 9	168 0	138 4	501	617
Co(DHA-INH) ₂	$C_{28}H_{26}N_6O_8Co$	30 75	156 7	166 3	138 4	547	629
Ni(DHA-INH) ₂	$C_{28}H_{26}N_6O_8Ni$	30 63	154 3	165 9	136 3	542	643
Cu(DHA-INH) ₂	$C_{28}H_{26}N_6O_8Cu$	30 58	156 2	168 0	138 4	547	646
Zn(DHA-INH) ₂	$C_{28}H_{26}N_6O_8Zn$	30 75	156 5	166 8	138 4	532	628

Table 2 : Physicochemical and analytical data of ligand and complexes

Compounds	Coulor	Molecular Weight	M.P. (°C)	Found (Calculated)%				Magnetic moment (BM) (at 298K)	Conductance (Mho cm ⁻¹ mol ⁻¹)
				C	H	N	M		
DHA-INH	Orange	287	200	58.58 (58.46)	4.56 (4.51)	14.63 (14.60)	-	1.1	
Fe(III)-DHA-INH ₂	Brown	628	300	53.52 (53.48)	3.85 (3.81)	13.37 (13.34)	5.26	4.8	
Cu(II)-DHA-INH ₂	Brown	631	300	53.26 (53.20)	3.83 (3.80)	13.31 (13.29)	Diamagnetic	11.0	
Ni(II)-DHA-INH ₂	Green	630	300	53.28 (53.22)	3.83 (3.81)	13.31 (13.30)	2.97	6.5	
Zn(II)-DHA-INH ₂	Green	635	300	52.87 (52.77)	3.80 (3.78)	13.21 (13.20)	1.86	3.8	
Zn(II)-DHA-INH ₂	Colorless	636	300	52.72 (52.68)	3.79 (3.76)	13.17 (13.15)	Diamagnetic	2.4	

The 'd' values of reflections were obtained using Bragg's equation, $n\lambda = 2d \sin\theta$. To calculate the unit cell volume of complexes for orthorhombic crystal system $V = abc$ equation was used.

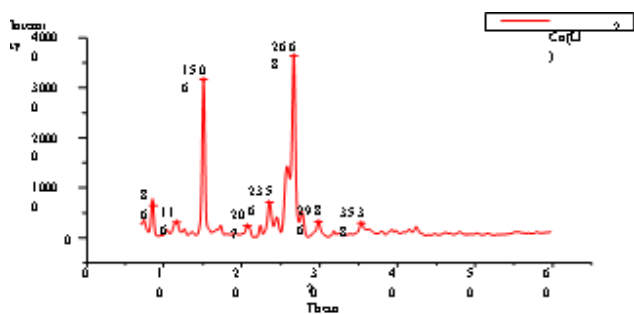


Figure 1. Powder xrd of Co(L1)₂ showing Intensity vs 2θ value

Table 3: Lattice constant, Unit cell Volume, Crystal system, Inter-planar spacing of complexes

Unit cell of compound	Lattice constant			Unit cell volume (Å ³)	Edge length	Inter axial angle	Crystal system	Z	d-value (Å)
	a(Å)	b(Å)	c(Å)						
Fe(III)	19.2655	20.8652	13.0450	5243.80	a = b = c	α = β = γ	Orthorhombic	23	3.70
Co(II)	20.1254	20.8465	13.0450	5472.95	a = b = c	α = β = γ	Orthorhombic	26	3.33
Ni(II)	11.8600	23.890	16.627	4711.01	a = b = c	α = β = γ	Orthorhombic	12	7.18
Cu(II)	14.0250	19.6320	19.2658	5304.62	a = b = c	α = β = γ	Orthorhombic	26	3.30
Zn(II)	21.0540	22.0050	13.112	6074.14	a = b = c	α = β = γ	Orthorhombic	26	3.34

Antimicrobial activity of the complexes :

The ligand and metal complexes were evaluated by screening of the compounds by standard method i.e. agar cup plate method [24] against a panel of human pathogenic microorganisms: Gram positive, *Staphylococcus aureus*, *B. subtilis*, Gram negative, *Escherichia coli* and *Pseudomonas aeruginosa*, were used for the antibacterial assay, while for the antifungal assay *Candida glabrata* and *Candida tropicalis* were used for the studies. The compounds were diluted in dimethylsulfoxide (DMSO) with 1 mg/ml concentrations for bioassay. NA (Nutrient agar) was used as the culture media for antibacterial activity and PDA (Potato Dextrose agar) and YPD (yeast peptone dextrose) agar were used as the culture media for antifungal activity. The standard compounds used for comparison of antibacterial and antifungal growth were Chloramphenicol and Griseofulvin (250 ug/ml) respectively. All metal complexes derived from DHA-INH shows increased inhibition effects on growth of the tested antimicrobial species (Table 4, Figure 2). The activity of ligand significantly increased after coordination with metal ions. In the present study, the order of bioactivity of ligand and its complexes for antibacterial study was Cu(II) > Zn(II) > Co(III) > Ni(II) > DHA-INH > Fe(III), and for antifungal activity order was DHA-INH > Co(III) > Fe(III) and Cu(II), Ni(II), Zn(II) did not show any activity. Cu(II) shows higher activity because it easily adsorbed on the surface of the cell wall of microorganisms.[25]

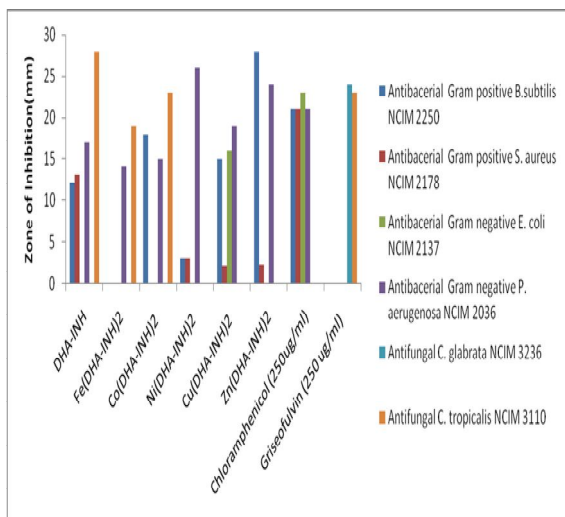


Figure 2. Graphical presentation of antimicrobial activity of synthesized compounds

Table 4 : Report for Antimicrobial Testing of ligand and its metal complexes

Test Compounds	Inhibition Zone (in mm)					
	Antibacterial				Antifungal	
	Gram positive		Gram negative		C. glabrata	C. tropicalis
	<i>S. aureus</i> NCIM 2178	<i>S. aureus</i> NCIM 2178	<i>E. coli</i> NCIM 2137	<i>P. aeruginosa</i> NCIM 2036	NCIM 2036	NCIM 3110
DHA-INH	12	13	00	17	00	28
Fe(DHA-INH) ₂	00	00	00	14	00	19
Co(DHA-INH) ₂	18	00	00	15	00	23
Ni(DHA-INH) ₂	03	03	00	26	00	00
Cu(DHA-INH) ₂	15	21	16	19	00	00
Zn(DHA-INH) ₂	28	23	00	24	00	00
Chloramphenicol (250ug/ml)	21	21	23	21	00	00
Griseofulvin (250 ug/ml)	00	00	00	00	24	23

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