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STUDY ON SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF BIDENDATE SCHIFF BASE TRANSITION METAL COMPLEXES

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ABSTRACT

In this study, four new transition metal complexes were synthesized using Schiff base ligand HL which was acquired by the condensation of Indole-3-carboxaldehyde and 2-(methylthio)aniline. Various Physico-chemical techniques, molar conductance, Proton nuclear magnetic resonance (1H NMR) spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and Ultraviolet-visible spectroscopy (UV) have characterized these complexes. The conductivity values suggest that these complexes are inherently non-electrolytes. The structural geometry of the prepared complexes was determined. The ligand HL and its metal complexes were screened for antimicrobial activity using the disc agar diffusion process. The result reveals that the complexes of Cu (II) have been shown to have higher antimicrobial activity.

Keywords: Schiff Base, Indole-3-Carboxaldehyde, 2-(methylthio)aniline, 1HNMR, FT-IR, Antimicrobial Activity.
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INTRODUCTION

Schiff base is a significant class of ligands derived from amino and carbonyl compounds that coordinate with metal ions through azomethine nitrogen. The C=N linkage is an azomethine derivative that is important for biological activity and has been reported to have remarkable antibacterial, antifungal, anticancer and antimalarial activities.[1-2] Compare to aliphatic aldehyde, aromatic aldehyde forms a stable Schiff base since aliphatic aldehyde forms unstable which readily polymerizes. Schiff bases are usually chelate ligands of bi, tri (or) tetradentate and form very stable complexes with metal ions. In recent years, due to their significanceas catalysts in many reactions, there has been increased interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands.[3-6] The Schiff base complexes with metals like Co (II), Cu (II) and Zn (II) ions have played a major role in the growth of coordination chemistry. These complexes are more curious under physiological circumstances because of DNA binding and cleavage. [7-9] It was reported that Schiff base derivatives of indole-3-carboxaldehyde with various L-amino acids and as well as with aminophenol were found to be more stable when labeled with 99m technecium andit also becomes radioactive, which was further used for visualizing the tumors and also for the rapid clearance of the tumor. Also, Schiff base derivatives of Indole -3-carboxaldehyde helps in the circulation of blood by clearing the blocks in the blood vessels.[10] Cobalt and nickel complexes were foundto have wide application in disease management programs which increased the number of attempts to synthesis these complexes with superior potency and lesser toxicity than the existing medicinal drugs.[11] The present study was therefore aimed at ensuring the antimicrobial activity of newly synthesized Schiff base complexes, as stated in many works, and also at assessing the biological activity of indole-3- carboxaldehyde related Schiff base complexes. The synthesis, characterization and antimicrobial activity of the Cu (II), Ni (II), Co (II) and Zn (II) complexes with Schiff base ligand (HL) derived from Indole-3- carboxaldehyde and 2-(methylthio)aniline were recorded here. The results were concise in the light of observed physiological activity and scope of future growth.

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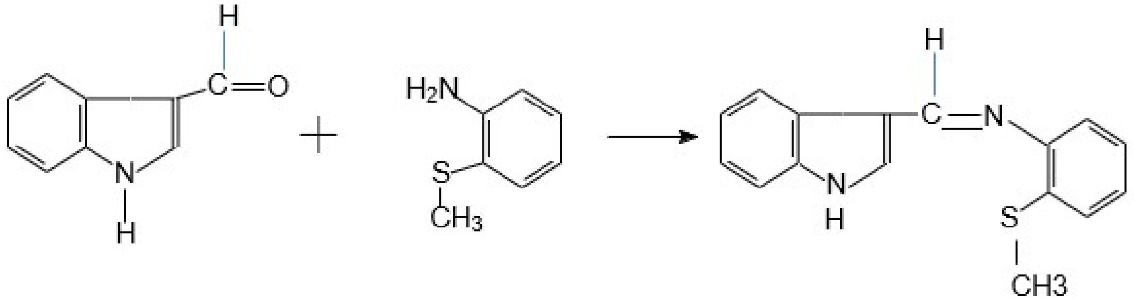
EXPERIMENTAL

Materials and Methods

In the present work, all chemicals used were of analytical grade and were used without purification. Thin-layer chromatography has confirmed the purity of compounds. Elemental analysis of the compounds was performed on vario micro cubes elemental analyzer. Conductance measurements were done by using WTW conductivity meter. Infra-red spectrum were recorded using Schimadzu on FTIR 470 IR spectrophotometer using KBr pellet. The ^1H NMR spectrum was obtained by the 111,400 MHz Brucker Advance spectrometer.Using a Schimadzu UV-Vis.160A- UV-Visible spectrophotometer in the 200-800 nm range, the electronic spectra of the ligand and its metal complexes were obtained.

Synthesis of Schiff Base Ligand

Indole-3-carboxaldehyde (1.45g 10mmol) dissolved in absolute ethanol (20mL) was added slowly to a constant stirring solution of 2-(methylthio)aniline (1.24g 10mmol) in 20ml of ethanol and this content was refluxed for 2 hours and then transferred into a beaker containing ice. Pale yellow crystals separated which was filtered, washed with ethanol, dried in a vacuum over anhydrous $CaCl_2$.The reaction behind this is shown in Scheme -1. Yield: 80%, melting point: 249^0 C.



Scheme-1: Synthesis Route of Schiff Base Ligand HL

Synthesis of Complexes 1-4 with Schiff Base Ligand

[Dichlorobis(*Z)-N-(*1*H*-indol-3-yl)methylene-2-(methylthio)anilinecopper(II)]:[Cu(HL)$_2$Cl$_2$]

An ethanolic solution of the $CuCl_2.2H_2O$ (10mmol) was added to ethanolic solution of HL ligand (20mmol), (*Z)-N-(*1*H*-indol-3-yl)methylene-2-(methylthio)aniline in 1:2 (Metal: ligand) ratio. Then the content was refluxed for 3 hours and cooled. The dark green colored solid separated which was filtered, washed with distilled water and dried in a desiccator.Yield:65%.

[Dinitratobis(*Z)-N-(*1*H*-indol-3-yl)methylene-2-(methylthio)anilinecobalt(II)]: [Co(HL)$_2$(NO$_3$)$_2$]

An ethanolic solution of the $Co(NO_3)_2.6H_2O$ (10mmol) was added to an ethanolic solution of HL ligand, (20mmol) (*Z)-N-(*1*H*-indol-3-yl)methylene-2-(methylthio)aniline in 1:2 (Metal: ligand) ratio. Then the content was refluxed for 3 hours and cooled. The brown colored solid separated which was filtered, washed with distilled water and dried in a desiccator.Yield:70%.

[bis*(Z)-N-(1H*-indol-3-yl)methylene-2-)(methylthio)anilinenickel(II)]sulphate:[Ni(HL)$_2$]SO$_4$

An ethanolic solution of the $NiSO_4.6H_2O$ (10mmol) was added to an ethanolic solution of HL ligand, (20mmol) (*Z)-N-(*1*H*-indol-3-yl)methylene-2-(methylthio)aniline in 1:2 (Metal: ligand) ratio. Then the content was refluxed for 3 hours and cooled. The brown-colored solid separated which was filtered, washed with distilled water and dried in a desiccator. Yield:65%.

[bis(*Z*)-*N*-(1*H*-indol-3-yl)methylene-2-(methylthio)anilinezinc(II)]sulphate:[Zn(HL)$_2$]SO$_4$

An ethanolic solution of the $ZnSO_4.H_2O$ (10mmol) was added to an ethanolic solution of HL Ligand, (20mmol) *(Z)-N-(*1*H*-indol-3-yl)methylene-2-(methylthio) aniline in 1:2 (Metal: ligand) ratio. Then the content was refluxed for 3 hours and cooled. The pale yellow colored solid separated which was filtered, washed with distilled water and dried in a desiccator. Yield: 60%.

RESULT AND DISCUSSION

Physical Properties of the Ligand and Complexes 1-4

Some physical data like molecular formula, molecular mass and analytical data of the ligand HL and complexes 1-4 were given in Table-1. These complexes 1-4 were found to be colored solid and were decomposed above 300^0C.

Table-1: Some Physical Data of Ligand and Complexes 1-4

Ligand and Complexes	Molecular Formula	Molecular Mass	Elemental Analysis Found (Calculated) in %			
			C	H	N	S
Ligand	$C_{16}H_{13}N_2S_1$	265	72.45 (72.42)	4.90 (4.86)	10.56 (10.52)	6.04 (6.01)
$[Cu(HL)_2Cl_2]$	$C_{32}H_{26}N_4S_2Cl_2Cu$	664.44	57.79 (57.75)	3.91 (3.89)	8.42 (8.39)	4.82 (4.78)
$[Co(HL)_2(NO_3)_2]$	$C_{32}H_{26}N_6S_2O_6Co$	712.93	53.86 (53.81)	3.64 (3.61)	11.78 (11.74)	4.49 (4.43)
$[Ni(HL)_2]SO_4$	$C_{32}H_{26}N_4S_2Ni$	588.69	65.23 (65.21)	4.42 (4.39)	9.51 (9.49)	5.44 (5.40)
$[Zn(HL)_2]SO_4$	$C_{32}H_{26}N_4S_2Zn$	595.38	64.50 (64.48)	4.37 (4.35)	9.41 (9.38)	5.37 (5.34)

Molar Conductivity

The molar conductivity measurements for these complexes were carried out by dissolving in DMF (10^{-3} M). The observed molar conductance value given in Table-2 claims that these complexes 1-4 were non-electrolytes in nature. Their conductance lies in the range (12-18 $ohm^{-1}cm^2mol^{-1}$). But these values were slightly greater than that of non-electrolytes which indicated that there would be partial solvolysis of the complexes in DMF medium[4].

Table-2: Molar Conductivity of the Complexes

Complexes	Conductance in DMF($ohm^{-1}cm^2mol^{-1}$)
$[Cu(HL)_2Cl_2]$	12
$[Co(HL)_2(NO_3)_2]$	14
$[Ni(HL)_2]SO_4$	15
$[Zn(HL)_2]SO_4$	18

^{1}H NMR Spectra of the Ligand

In the ^{1}H NMR spectra of the Schiff base ligand HL given in Fig.-1**,** the singlet peak that occurred in the range 7.22ppm was due to the azomethine group. The peak at 6.17ppm showed the presence of aromatic ring protons. The peak at 1.87-1.12 ppm was due to proton at Indole ring.[12]

Infra-Red Spectra of the Ligand and Complexes 1-4

The sharp peak at 1634.32 cm^{-1} was the characteristics band for azomethine ύ(CH=N) group of the ligand HL (Table-3).[13] The formation of CH=N linkage was also supported by the absence of bands at 1735cm^{-1} and 3420cm^{-1} which were characteristics stretching frequencies of the free carbonyl group of aldehyde and amino group of amine present in the starting material respectively.

This band of the ligand HL was now shifted to lower frequencies range from 1633 cm^{-1} - 1604 cm^{-1} indicating complexation with metals. The peaks in the region 1383 cm^{-1} - 1333 cm^{-1} were due to the stretching vibration of C-N. The peaks in the region 427 cm^{-1} - 422 cm^{-1} were due to stretching vibrations of M-N [14]. The band in the frequency region 1500 cm^{-1} was due to C=C of the aromatic skeleton.

UV- Visible Spectra of the Ligand and Complexes 1-4

The electronic spectral data of the ligand HL and the complexes 1-4 in DMF (10^{-3}mol^{-1}) were given in Table-4. The ligand HL exhibited two bands at 38,470cm^{-1} and 27,843cm^{-1} attributed to $\pi - \pi^*$ and n- π^* electronic transition respectively. In the spectra of the complexes 1-4, these bands were shifted to a lower wavelength indicating the coordination of the ligand to the metal ion and it also showed d-d transition ofthe metal d-orbitals in the visible region.[15]

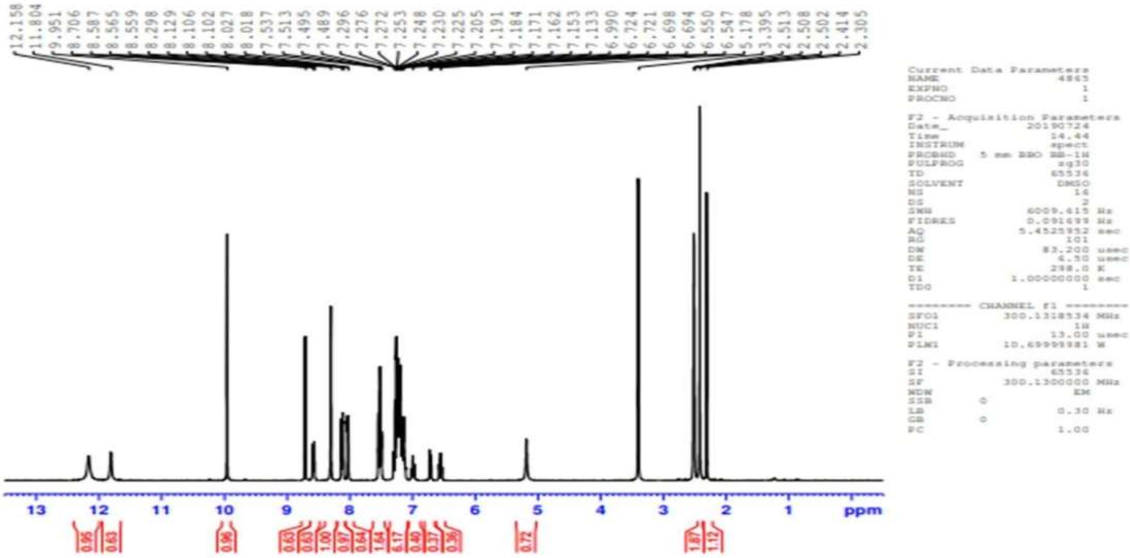


Fig.-1 ^{1}H NMR Spectra of Schiff Base Ligand HL

Table-3: Selected FT-IR Frequencies (cm^{-1}) of the Ligand and Complexes 1-4

Compound	ὺ C=N	ὺ C-N	ὺ M-N	ὺ M-S
Ligand	1634	1333	--	--
[Cu(HL)$_2$Cl$_2$]	1633	1338	427	410
[Co(HL)$_2$(NO$_3$)$_2$]	1607	1383	423	395
[Ni(HL)$_2$]SO$_4$	1604	1360	422	398
[Zn(HL)$_2$]SO$_4$	1604	1359	423	405

In the spectrum of Cu (II) complex, the broadband appeared at 15,336cm^{-1}was attributed to d-d transition and the other two bands at 22,680cm^{-1}and 37,914cm^{-1} were attributed to ^{2}B1g$\rightarrow$^{2}B2g and ^{2}B1g $\rightarrow$^{2}Eg transition respectively. These bands confirmed the geometry around Cu (II) ion was octahedral[16-17].The electronic spectra of Co(II) complex has three bands at 14,637cm^{-1},29,686cm^{-1} and 37,914cm^{-1} which were attributed to ^{4}T1g(F) -->^{4}T2g(F), ^{4}T1g(F) -->^{4}A2g(F), ^{4}T1g(F)--> ^{4}T2g(p) transitions respectively, a characteristic of octahedral geometry[18]. In the electronic spectra of Ni (II) complex, the band that appeared at 24,691cm^{-1} was attributedto the transition ^{1}A1-->^{1}B1 or ^{1}A1-->^{1}E which was consistent with square planar geometry[19]. The electronic spectra of the Zn (II) complex do not possess an adsorption band for d-d transition due to the non- availability of d-electrons. The bands observed at 37,828cm^{-1} and 29,797cm^{-1} confirmed tetrahedral geometry.[20-21]

Antimicrobial Activity of the Ligand and the Complexes 1-4

Transition metal complexes play a major role in biological studies since they possess antimicrobial and anticancer properties. The present work suggests that transition metals with Schiff base ligand containing heterocyclic components, benzene ring and –N=CH group have more biological activity. So the prepared ligand HL and complexes 1-4 were screened for antibacterial activity against S. aureus and E.coli. The antifungal activity against Candida albicans and A.niger by using disc-agar diffusion method[22]. It was seen from Table-5 that the inhibition zone shown by metal complexes was greater than that of ligand HL and copper complex was found to be more active towards antimicrobial activity than other complexes.

Table-4: Electronic Spectra of the Ligand and their Complexes 1-4

Compound	Λ max cm^{-1}	Assignment	Geometry
Ligand	38,470	$\pi - \pi^{*}$	
	27,843	$n - \pi^{*}$	
[Cu(HL)2Cl2]	15,336	d-d transition	Octahedral
	22,680	$^{2}B_{1g}$-->$^{2}B_{2g}$	
	37,914	$^{2}B_{1g}$ -->$^{2}E_{g}$	
[Co(HL)2(NO3)2]	14,637	$^{4}T_{1g(F)}$ -->$^{4}T_{2g(F)}$	Octahedral
	29,686	$^{4}T_{1g(F)}$ -->$^{4}A_{2g(F)}$	
	37,914	$^{4}T_{1g(F)}$--> $^{4}T_{2g(p)}$	
[Ni(HL)2]SO4	24,691	$^{1}A1$-->$^{1}B1$ or $^{1}A1$-->^{1}E	Square planar
[Zn(HL)2]SO4	37,828	$\pi - \pi^{*}$	Tetrahedral
	29,797	$n - \pi^{*}$	

Table-5: Antimicrobial Activity Data of Ligand and their Complexes 1-4

Ligand and Complexes	Zone of Inhibition in mm			
	S.aureus	E.coli.	Candida albicans	A.niger
Ligand	10	13	10	14
$[Cu(HL)_2Cl_2]$	16	20	18	20
$[Co(HL)_2(NO_3)_2]$	14	18	16	18
$[Ni(HL)_2]SO_4$	12	15	13	16
$[Zn(HL)_2]SO_4$	12	16	18	15

CONCLUSION

From the above discussion, we conclude that ligand HL is bidentate. The ligand HL was coordinated to four dissimilar metals ions through nitrogen and sulphur atom to form the corresponding complexes. Conductivity measurements indicated that all the complexes were non-electrolytes. Cu (II) and Co (II) complexes were found to possess octahedral geometry whereas Ni (II) was Square planar and Zn (II) complexes were tetrahedral. These complexes are biologically active and possess enhanced antimicrobial activity.

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