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Synthesis and Characterization of Cu(II), Co(II), Ni(II) and Zn(II) complexes of Schiff base Ligand Derived from 4-Nitrobenzohydrazide and 2-hydroxy Naphthaldehyde

K Ganga Rajam, Marri Pradeep Kumar and Shivaraj*

*Department of Chemistry, University College of Science, Osmania University, Hyderabad 500 007, **INDIA**

Email: gangaind781@gmail.com

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ABSTRACT

The synthesized semicarbazone Schiff base (HNNH) has been characterized and used for the preparation of Cu(II), Ni(II), Co(II) and Zn(II) binary complexes. These have been characterized using elemental analysis, molar conductivity, FT-IR, UV-Vis, TG-DTA, Mass and ESR spectral data. The melting points of the synthesized compounds were in the range of 280 ^{0}C to 360 ^{0}C while the conductivities measured in DMSO were in the range of 12.6 -32 µs indicates the compounds are non-ionic [1]. The SEM images of the ligand and Metal complexes imply the formation of metal complexes. The IR data of the ligand and its metal complexes showed that the ligand is mono negative tridentate which coordinated to the metal ions through the azomethine nitrogen atom, oxygen atom from hydroxyl group of naphthaldehyde ring and another oxygen atom from carbonyl group of the Schiff base. From the UV-Vis, magnetic susceptibility measurements and ESR data, the geometry has been assigned as square planar (for 1:1 complex) and Octahedral (for 1:2 complex). The ligand and its metal complexes have been screened for antibacterial and antifungal activity against the bacterial and fungal species. The Schiff base and its metal complexes showed the significant activity and further observed that the metal complexes showed more activity than Schiff base.

Keywords: SEM, metal complexes, tautomeric, 2-hydroxy naphthaldehyde.

INTRODUCTION

The chemistry of Schiff bases and metal complexes has been investigated extensively for last several decades leading new synthetic routes and variety of structures and their potential applications. Reactions of aldehydes and semicarbazide amines generally give semicarbazone Schiff bases or imines. The metals with *o*-hydroxy Schiff bases have been widely studied [2-4]. Furthermore, abilities of aryl hydrazones to coordinate to metals either in keto or enol tautomeric form [5] makes them attractive as ligands .The study of new kind of chemotherapeutic semicarbazones are now attracting the biochemist. Semicarbazone Schiff base derived from 4-Nitrobenzohydrazide and 2-hydroxynaphthaldehyde has already been reported [6] and investigated because of their wide applications in the field of Medicinal and clinical research. These semicarbazone Schiff base shows higher antibacterial and antifungal activity on chelation with metal ions. However a brief survey of the literature reveals that not much work has been carried out on semicarbazones and their metal complexes. The main aim of the present investigation is about synthesis, characterization and antimicrobial activity of binary complexes of transition metal ions with semicarbazone derived from 4-Nitrobenzohydrazide and 2-hydroxynaphthaldehyde.

MATERIALS AND METHODS

Metal salts, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, $Zn(CH_3COO)_2.6H_2O$, $NiCl_2.2H_2O$ and hydrazine hydrochloride were purchased from Merck, nitro benzoic acid and 2-hydroxynaphthaldehyde were purchased from Sigma Aldrich. Solvents such as water, methanol, acetone, petroleum ether and chloroform were purified by standard procedures. The metal ratio of the complexes was determined by Atomic Absorption Spectrophotometer (PerkinHelmer-300). IR spectra of the compounds were recorded on Schimadzu FTIR 8400S spectrometer in the range 4000–400 cm^{-1} using KBr pellet. The UV–Vis spectra were recorded on Schimadzu UV-Vis160 in DMSO in the wave length range 200–800 nm. The molar conductance was measured on Digital Conductivity Meter Lassco India using DMSO and DMF as the solvents at room temperature and magnetic moment measurements on Gouy Balance model No.7550.The melting points of the compounds were measured on Polmon instrument (Model No.MP-96).The percentage composition of C,H,N of the compounds were determined by Vario macro elemental analyzer (USA) and the ESR spectra of complexes were recorded by JES-FA200 ESR Spectrometer (JEOL-Japan).

Synthesis of Schiff base: 4-Nitrobenzohydrazide (1 m.mol) was dissolved in hot methanol which is added to dissolved methanol solution of 2-Hydroxynaphthaldehyde(1 m.mol) and stirred for 6 hrs at 60 ^{0}C. The dark yellow solid of (2-Hydroxynaphthalene-1yl)methylene-4-nitrobenzohydrazide was formed which was filtered and recrystallized in absolute ethanol and the purity of the compound was checked by TLC. Yield: 85%, M.P: 306 ^{0}C.

Synthesis of metal complexes:

The complexes of Zn (II), Co (II), Ni (II) and Cu (II) were prepared by refluxing and continue stirring 1:2 and 1:1 molar mixtures of the respective metal salts with the ligand for 4-6 hrs. The contents were cooled and allowed to crystallization. The complexes were collected by filtration and then washed several times with absolute ethanol solution.

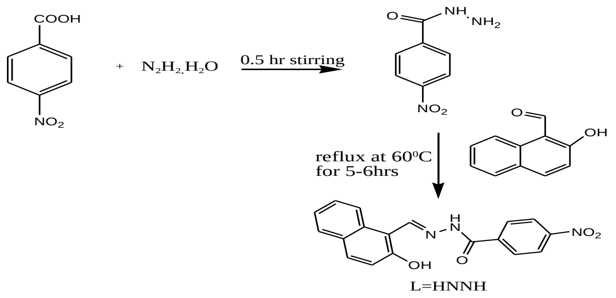
RESULTS AND DISCUSSION

The synthesized Schiff base, (2-Hydroxynaphthalene-1yl) methylene-4-nitrobenzohydrazide (**Scheme-1**) forms stable complexes with Co(II), Ni(II), Cu (II) and Zn(II) metal ions. The analytical data of the complexes, together with their physical properties are given in **Table-1**. The analytical data of the complexes corresponds to the general stoichiometry M(L)Cl and $M(L)_2$, where M = Co(II), Ni(II), Zn(II) and Cu(II), L = (HNNH). The value of molar conductance of complexes in DMSO indicates that the $[M(L)_2]$ and M(L)Cl complexes are non-electrolytes [7]. Magnetic moments of the complexes are 4.46 & 4.48 B.M [Co(II)] , 2.94 & 3.18 B.M [Ni(II)] and 1.73 & 1.93 B.M [Cu(II)] respectively.

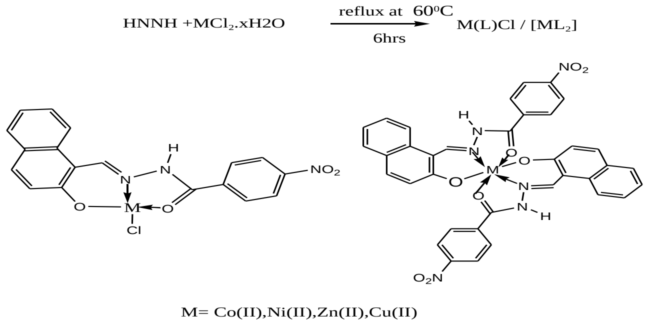
Table-1: Elemental analysis, Melting points, Molar conductance and Magnetic Susceptibility data

Compound	M.wt	Melting point (^{0}C)	Yield (%)	Elemental analysis data				Molar Conductance Ω^{-1} Cm^{2} Mol^{-1}	Magnetic Susceptibility B.M
				M%	C%	H%	N%		
HNNH	335.3	306	90.2	-	63.91(64.47)	3.82(3.91)	12.51(12.53)	12.1	-
[Cu(HNNH)Cl]	432.3	305	81	13.41(14.67)	49.54(49.89)	2.52(2.79)	9.34(9.70)	32	1.73
[Co(HNNH)Cl]	428.7	335	76	13.55(13.75)	49.98(50.43)	2.84(2.82)	9.79(9.80)	24.2	4.46
[Ni(HNNH)Cl]	428.5	330	68.2	13.71(13.70)	50.36(50.46)	2.21(2.82)	9.71(9.81)	21.6	2.94
[Zn(HNNH)Cl]	435.1	340	84.6	15.01(15.03)	49.49(49.68)	2.64(2.78)	9.10(9.66)	15.8	-

[Cu(HNNH)2]	**732.2**	**315**	**72.2**	**8.50(8.68)**	**58.98(59.06)**	**3.10(3.30)**	**11.12(11.48)**	**13.1**	**1.93**
[Co(HNNH)2]	**727.1**	**342**	**64.4**	**7.94(8.10)**	**58.91(59.43)**	**3.01(3.32)**	**10.99(11.55)**	**29.8**	**4.48**
[Ni(HNNH)2]	**727.3**	**>350**	**88.4**	**7.88(8.07)**	**59.26(59.45)**	**3.21(3.33)**	**11.59(11.56)**	**24.7**	**3.18**
[Zn(HNNH)2]	**734.0**	**>350**	**76.4**	**8.59(8.91)**	**59.24(58.91)**	**3.12(3.3)**	**11.25(11.45)**	**18.4**	**-**

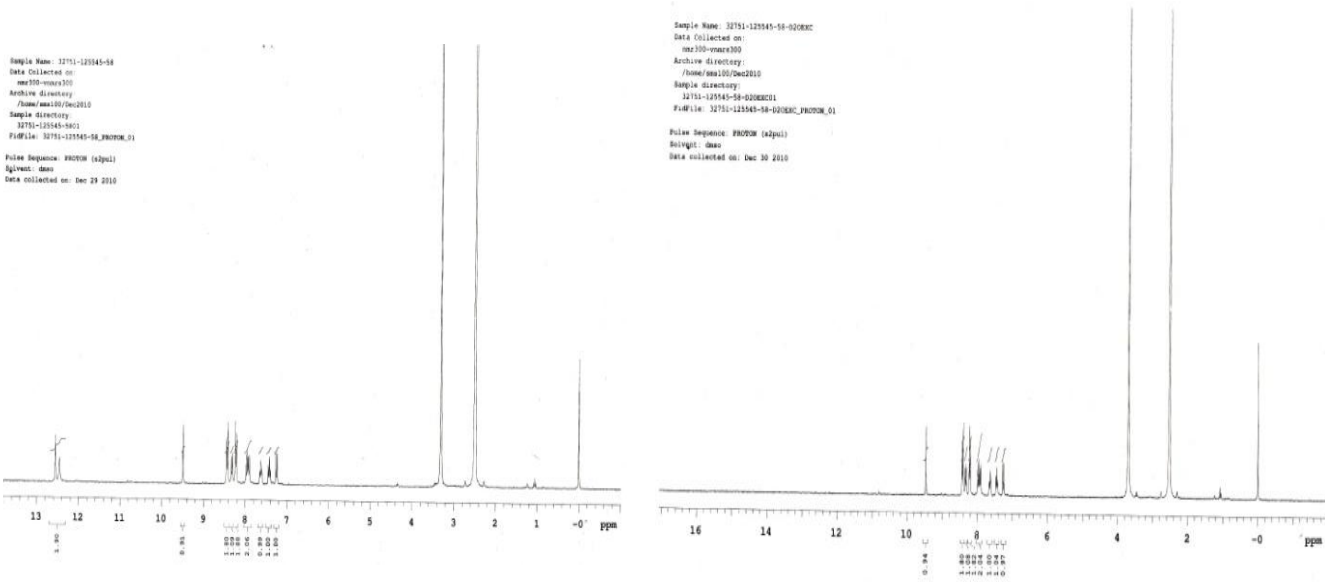


Scheme-1



Scheme-2

^{1}H-NMR: The ^{1}HNMR spectrum of Schiff base (HNNH) is recorded in DMSO-d$_6$ solvent using Tetramethylsilane (TMS) as internal standard. In the ^{1}HNMR spectrum of ligand, two signals appeared between 12- 13 δ are due to the O-H protons which conformed the keto and enolic form of N=C-OH and C-OH proton of C$_{(Phenolic)}$ –OH (**Fig-1a**). The chemical shifts of the different types of protons found in the ^{1}HNMR spectrum of the Schiff base is compared with its diamagnetic Zn(II) complex. It is found that OH(phenolic) and enolic(O-H) proton signals are disappeared In Zn(II)complexes, which are present in the ligand ^{1}HNMR spectrum confirms the complexation. Hydrazones can exist in the keto or in the enol tautomeric form in the solid state as O=C-N-H and C-O-H protons, respectively [8]. These hydrogen resonances are seen in the high delta values because they are attached to highly electronegative atoms like oxygen and nitrogen, hence in a low electron density environment. This assignment can be confirmed by the deuterium exchange proton spectrum in which the proton signals are disappeared (**Fig-1b**).



(a) (b)

Fig-1: (**a**) ^{1}HNMR Spectrum of HNNH and (**b**) D_2 Exchange NMR Spectrum of HNNH

^{13}C-NMR: The ^{13}C NMR Spectrum of Schiff base is recorded in $CDCl_3$ solvent. The azomethine carbon gives a peak at 139 δ, C=O at 158 δ, C-OH at 150 δ, C-N (nitro) at 148 δ, Nitrobenzene C=C at 121,123 δ and C=C (naphtha) at 128, 132 δ, N^*=C-O at 109 δ and remaining all the carbons appeared in aromatic region 119-132δ.

ESR: The complex $[Cu(HNNH)_2]$ may have tetragonal geometry. EPR spectrum of Cu(II) complex was recorded at room temperature in DMSO solution, on the x-band at 9.4 GHz under the magnetic field strength 3400 G. EPR spectrum shows a well–resolved anisotropic broad signal. The analysis of spectrum gives, $g\|$ = 2.25 and $g\perp$ = 2.01. The trend $g\| > g\perp > 2.0023$, observed for the complex, under study, indicates that the unpaired electron is localized in $dx^2{-}y^2$ orbital of the Cu(II) ion and the spectral features are characteristic for axial symmetry. Tetragonal elongated geometry is thus confirmed for the aforesaid complex [9].

Infrared spectra and mode of binding:

Infrared spectroscopy can be used as a good analytical tool to follow the complexation of the transition metal ions by the organic ligands [10, 11]. The diagnostic IR frequencies of the ligand and its Complexes are compiled in **Table- 2**.The infrared spectrum of the free ligand is compared with that of the complexes to determine the coordination sites that may have involved in the chelation. Theoritically, the characteristic *v*(C= N) absorptions of Schiff bases come in the region 1600–1471 cm^{-1}. In the present case, it appears as a shoulder to the amide II band nearly at 1580 cm^{-1} in the spectrum of the free hydrazone shifts the frequencies in the range 1587 -1528 cm^{-1} in the spectra of the metal complexes, indicating coordination of the azomethine nitrogen [12, 13, 8]. The *v*(C=O) absorption in the spectrum of free hydrazone is observed at 1648 cm^{-1}, while in the complexes it is shifted to 1663– 1642 cm^{-1} in accordance with coordination through the carbonyl oxygen [14]. Hydrazones can exist in the keto or in the enol tautomeric form in the solid state [8]. And, the absorption due to *v*(C= O) observed at 1648cm^{-1} confirms that the compound is in the keto form in the solid state. There are two well-defined infrared absorptions at 1648 and 1625cm^{-1}, which were assigned to the amide I and amide II bands, respectively. These bands are shifted to the low frequency region than the theoretical values due to the conjugation of the amide groups with the aromatic group. Because of conjugation, the double bond nature of C =O decreases and hence the bond order decreases, which causes a shift to the lower frequency region. Amide II band seen at 1625cm^{-1} points out to the secondary amide exists in the *Trans* conformation [8]. A very broad band observed in the region

3000–3500 cm^{-1} comprising of both the –OH and –NH– stretching absorptions. These O-H/N-H broad band at 3000–3500 cm^{-1} for the ligand disappears in some of the complex and some of the complexes it is not disappeared may be because of non ionized N-H band , suggesting coordination through deprotonated phenolic oxygen and keto/enolic form of carbonyl. It is very difficult to differentiate the bands in the fingerprint region, but a well-defined band at 1245cm^{-1} may be due to phenolic C–O stretching vibration [7]. The IR spectrum of the complex was compared with that of the ligand and remarkable differences are noticed between them. The shifting of strong band at 1648cm−1 due to (C =O) (amide I) in the ligand spectrum to lower frequency region/absence in the metal spectrum conformed the coordination of C=O with metal ion [5, 15, 16]. The band due to (C= N) (amide II) at 1625cm^{-1} appeared in the ligand spectrum is shifted to lower frequency region of complex spectrum indicates coordination of the enolic oxygen atom to the metal atom. The extra bands appeared in the lower frequency region of 531–469cm-^{1} confirmed the M-O bonding [17, 18].

Table-2: Characteristic infrared absorption frequencies of ligand and its metal complexes

S.No.	Compound	$\upsilon_{O\text{-}H}$ cm^{-1}	$\upsilon_{N\text{-}H}$ cm^{-1}	$\upsilon_{C\text{-}O}$ (Phenolic) cm^{-1}	$\upsilon_{C=O}$ (Amide-I) cm^{-1}	$\upsilon_{N\text{-}C/N=C}$ (Amide-II) cm^{-1}	$\upsilon_{C=N}$ cm^{-1}	$\upsilon_{M\text{-}O}$ cm^{-1}
1	**HNNH**	**3418**	**3214**	**1245**	**1648**	**1625**	**1580**	**-**
2	**[Cu(HNNH)Cl]**	**-**	**3423**	**1239**	**1642**	**1616**	**1561**	**526**
3	**[Co(HNNH)Cl]**	**-**	**3385**	**1248**	**1658**	**1616**	**1528**	**491**
4	**[Ni(HNNH)Cl]**	**-**	**3442**	**1243**	**1649**	**1621**	**1576**	**531**
5	**[Zn(HNNH)Cl2]**	**-**	**3424**	**1242**	**1663**	**1619**	**1587**	**529**
6	**[Cu(HNNH)2]**	**-**	**3442**	**1242**	**1645**	**1621**	**1579**	**528**
7	**[Co(HNNH)2]**	**-**	**-**	**1246**	**-**	**1617**	**1575**	**469**
8	**[Ni(HNNH)2]**	**-**	**-**	**1249**	**-**	**1617**	**1574**	**531**
9	**[Zn(HNNH)2]**	**-**	**3421**	**1242**	**1655**	**1619**	**1576**	**526**

Electronic spectra and magnetic moment measurements:

The magnetic moments (μ_{eff} B.M) of the complexes are presented in **Table-1**. The electronic absorption spectra of ligand and metal complexes were recorded in DMSO solvent, in the range of 200-800 nm (**Fig-3**). The electronic spectrum of free Schiff base shows three bands in that, two high energy bands at 261 & 323 nm are due to π-π * and n- π* transitions respectively [19] and the low energy band at 377 nm due to the π-π* transition of azomethine chromophore. Cu(II) 1:1 complex shows four bands at 257 nm, 272 nm, 335 nm and 479 nm as well as Cu(II) 1:2 complex also shows four bands at 264 nm, 330 nm, 411 nm and 536 nm. The electronic spectrum of Ni(II) 1:1 complex displays four bands at 259 nm, 323 nm, 378 nm and 632 nm as well as Ni(II) 1:2 complex also shows four bands at 265 nm, 323 nm, 380 nm and 444 nm. The electronic spectrum of Co(II) 1:1 complex shows four bands at 274 nm, 327 nm, 471 nm and 596 nm, while in the Co(II) 1:2 complex shows five bands at 271 nm, 316 nm, 394 nm, 521 nm and 591nm. The electronic spectrum of Zn(II) 1:1 complex shows three bands at 261 nm, 323 nm and 411nm as well as Zn(II)1:2 complex also shows three bands at 261 nm, 326 nm and 431 nm [20]. Zn complexes itself are dia magnetic, no d-d transitions possible [21]. For Co(II) and Ni(II) complexes theoretically three allowed transitions are expected in the visible region, but often these expectations are overlooked in practice and these bands usually appear overlapped due to the very small energy difference between the d levels.

The magnetic moment of Cu(II) 1:1 was seen at 1.73 B.M , Cu(II) (1:2) at 1.93 B.M, Ni((II)1:1 at 2.94 B.M, Ni(II)1:2 at 3.18 B.M,Co(II)1:1 at 4.46 B.M,Co(II)1:2 at 4.48 B.M and Zn(II) complexes have been found to be diamagnetic in nature [21] . On the basis of electronic spectra and magnetic susceptibility measurements, a distorted octahedral geometry for M(II) (1:2) and square planar for M(II) 1:1 complexes are suggested [21, 22].

Thermal Analysis:

The thermal properties of the complexes were investigated by thermo grams (TGA and DTA). **Fig-2** shows TGA and DTA curves for [$Co(HNNH)_2$] complex. In the temperature range from 400-600°C, 51.8% weight reduction was found, which was related to the loss of some part of compound. In the temperature range from 600-800°C, 27.37% weight reduction was found, which was related to the loss of another part of compound and the final weight loss found in the range of 800-1000°C temperature is that 11.5% of the sample weight decreased that is related to lose of other part of the compound and the remaining percentage is in the form of metal oxide. In this method, phase changes or chemical reactions can be tailored to the study of heat absorbed or released. This method for assessing Phase changes in solids at high temperatures is suitable. In this observation exothermic processes occur during the heating of the sample that indicates the phase change [13], i.e. solid to liquid during the thermal reaction at higher temperature at 400-490^{0}C and also implies that the positive peak at 412^{0}C -490^{0}C the signal of DTA 28.84µv/mg ,4.3µv/mg and 61.1µv/mg in [$Co(HNNH)_2$] complex indicates the crystalline melting of solid that Concludes the complexes are in crystalline nature.

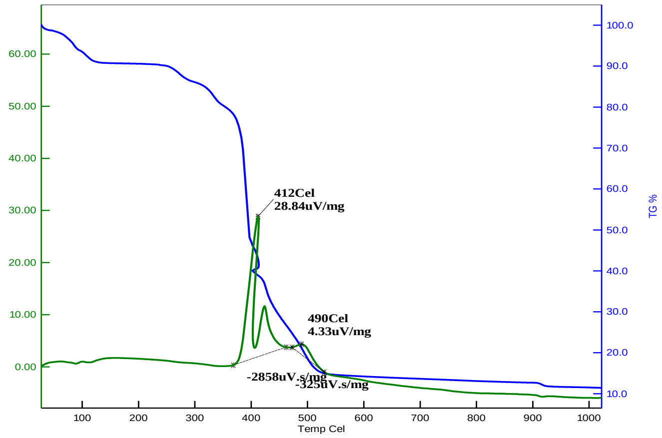


Fig-2: TGA –DTA Curve of [$Co(HNNH)_2$]

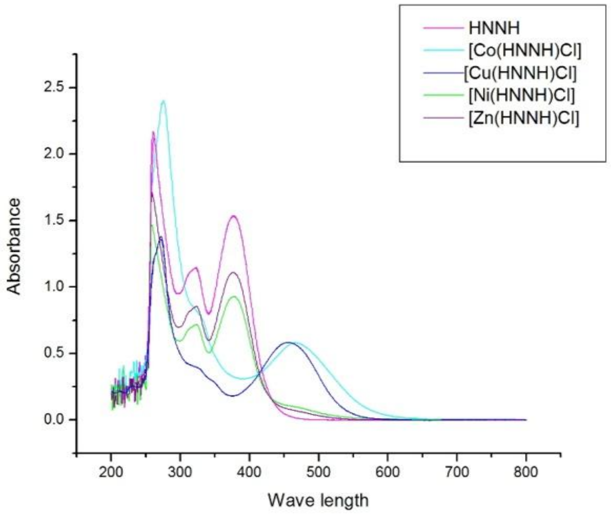
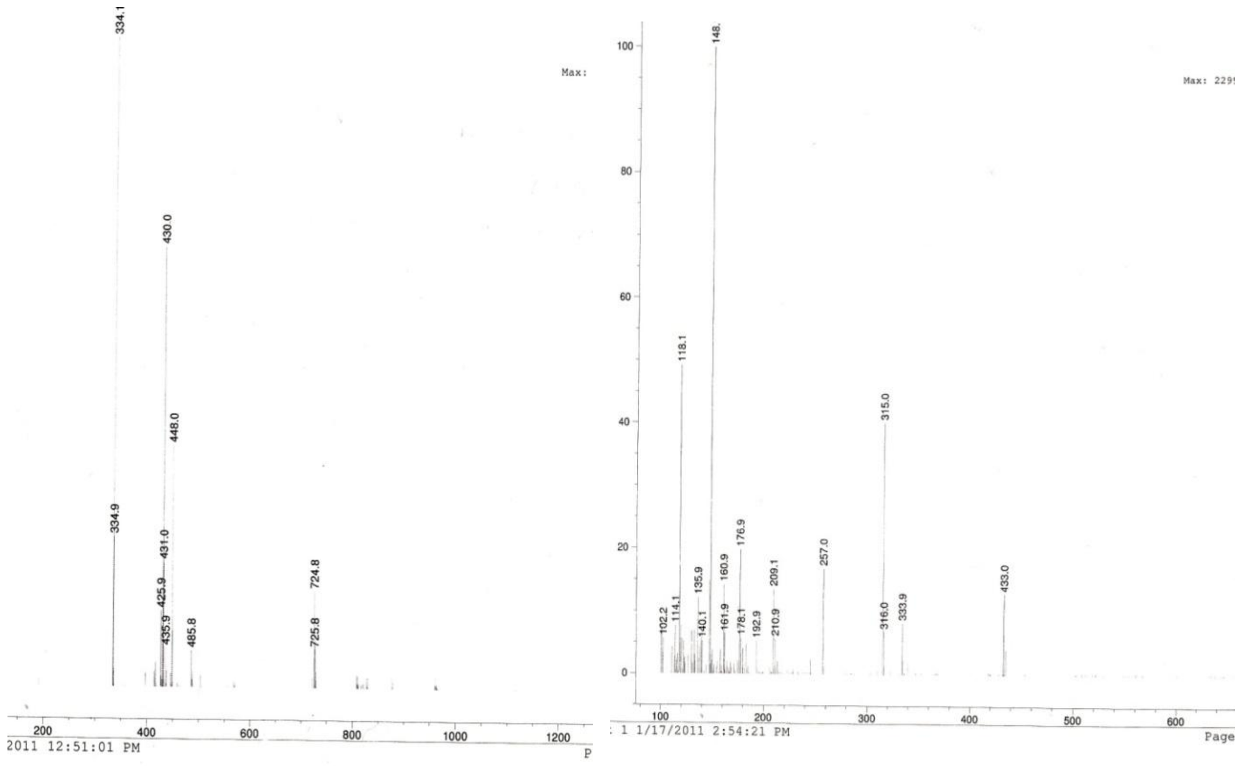


Fig-3: Electronic absorption spectra of ligand and its metal complexes.

MASS Spectra:

The mass spectrum of [Ni(HNNH)$_2$] complex (**Fig- 4a**) shows peak attributed to the molecular ion m/z value at, 725.8 (M-1) and [Cu (HNNH)Cl] complex (**Fig- 4b**) shows molecular ion peak m/z value at 433 (M+1) and remaining all the metal complexes show m/z peaks at (M+1). This data is in good agreement with the proposed molecular formula of these complexes. The mass spectral data support the structures of mononuclear transition metal complexes [23, 24].



(a) (b)

Fig-4: (**a**) Mass spectrum of [Ni(HNNH)$_2$] and (**b**) Mass spectrum of [Cu(HNNH)Cl]

Molecular Modeling:

The possible geometries of metal complexes were evaluated using the molecular calculations with Argus lab 4.0.1version software. The metal complexes were built and geometry optimization was done using this software. The molecular modeling pictures are shown in **Fig-5**. Important details of bond lengths as per the 3D structures of the Cu (II) complex and ligand obtained as a result of energy minimization. The obtained bond lengths of ligand are C=N-1.29 A^0, C=O-1.26 A^0, C-O (naphtha) -1.40 A^0 and N-N-1.38 A^0. Where as in the Cu(II) Complex bond lengths are C=O-1.329 A^0, N=C-1.419 A^0, C –O(naphtha)-1.51 A^0 ,O$_{(Naphtha)}$-Cu-2.022, O$_{(Carbonyl)}$-Cu-1.997 A^0 and N$_{(Azo)}$-Cu-2.01 A^0. Based on the values, it is observed that when the ligand (HNNH) is coordinated with the copper (II) ion there is an increase in the bond lengths in between the above mentioned atoms, which confirms the coordination of azomethine group through nitrogen atom, oxygen atom of C-O$_{(Naphtha)}$ group. When the atoms are coordinated with the metal ions by donating the lone pair of electrons there is decrease in electron density on the coordinating atoms, hence bond lengths increases in metal complexes. This supports the proposed structure of the complex.

The HOMO and LUMO energy values are calculated by using Software and given below [25].

Ligand	HOMO (eV)	LUMO (eV)	Total Energy	Heat of formation (K.cal/mole)
HNNH	-5.924	-2.91	-4359	-142.077$_{\text{(Jaback fragmentation method)}}$

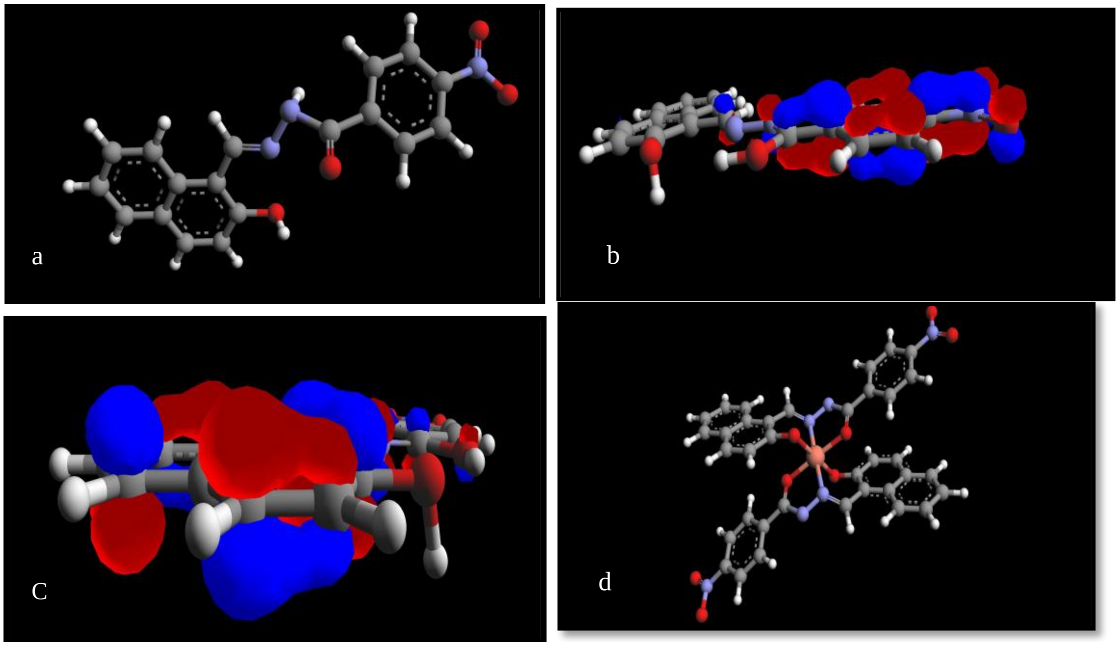
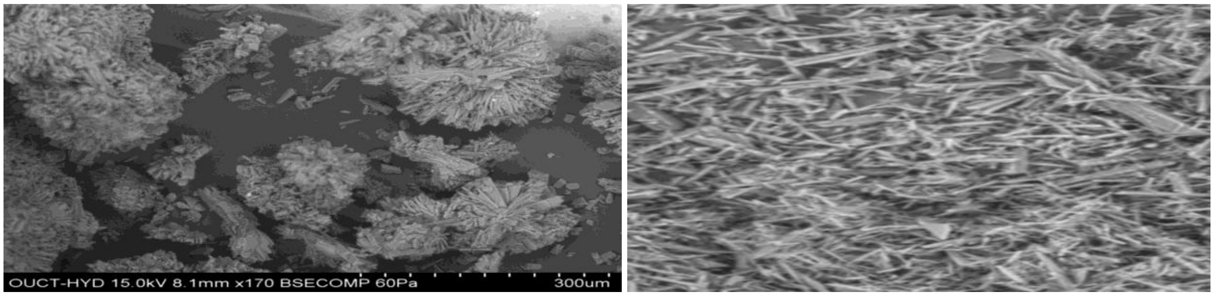


Fig-5: (**a**) Energy optimization diagram of ligand (**b**) LUMO plot of ligand (**c**) HOMO Plot of ligand (**d**) Energy optimization diagram of [Cu(HNNH)$_2$]

SEM Analysis: The scanning electron micrographs revealed the morphology of Schiff base and Cu(II) complexes. The scanning electron micrographs are taken at 20 kV accelerating voltage and magnification is fixed according to need from 150x to 1000x. In SEM image macroscopic phase separation in dense layer is noticed. The void spaces are certainly due to the result of macroscopic phase separation [26]. In scanning electron micrograph of HNNS (**Fig-6b**), the morphology showed that the surface was powdery and soft with large macroscopic phase separation. This phase separation was minimized after formation of metal complexes [27]. Also the powdery and softness is reduced and appears crystals like structure due to introduction of metal ion that indicates the formation of metal complexes (**Fig-6a**). The similar observations were reported for the reduction in phase separation and softness of the surface indicates the crystalline nature of metal complex. The scanning electron micrograph figures clear that there is a strong change in morphology of Schiff base on complexation [19].



(a) (b)

Fig-6: (**a**) SEM image of [Cu(HNNH)$_2$] and (**b**) SEM image of HNNH

APPLICATIONS

Antimicrobial activity: The ligand and its metal complexes were screened against bacterial and fungal species with reference to the standard drugs as Zentamycine and Ketoconazole respectively, presented in **Table-3**. Pseudomonas aeruginosa (P. aeruginosa), Escherichia coli (E. colli) (Bacteria) and Aspergillus niger (A. niger), Rhizopus oryzae (R. oryze (Fungi) are used for activity test. The antimicrobial action is studied by paper disc method (Kirby-Bauer method) [11].The compounds are dissolved in DMSO and acetone mixture. Filter paper disc (4 mm) were prepared and placed on nutrient agar medium. These Petri dishes were incubated at 35 ^{0}C for 48 hrs.The growths of the microbes have been measured by recording the diameter of the inhibition zone. Comparative study of the ligand and its complexes indicate that the complexes exhibit higher antimicrobial activity than free ligand (**Table-3**). The increase in antimicrobial activity of the complexes can be explained on the basis of Overtone's concept and Tweed's Chelation theory [28-31]. The (1:2) binary metal complexes show the more activity than the (1:1) binary metal complexes.

Table-3: Antimicrobial Screening of ligand and its metal complexes

Compound	***P. aeruginosa***	***E. colli***	***A. niger***	***R. oryzea***
HNNH	+	+	+	-
[Cu(HNNH)$_2$]	++	+++	++	-
[Co(HNNH)$_2$]	+++	++	+++	+++
[Ni(HNNH)$_2$]	+	++	+	++
[Zn(HNNH)$_2$]	+++	++	+++	++
[Cu(HNNH)Cl]	+	++	+	-
[Co(HNNH)Cl]	++	+	++	++
[Ni(HNNH)Cl]	-	+	+	++
[Zn(HNNH)Cl]	++	+	+	+
Zentamycine	+++	+++	-	-
Ketoconazole	-	-	+++	+++

highly active :+++(inhibition zone 10-12 mm): meditatively active :++(inhibition zone 7-10 mm); slightly active :+(inhibition zone 5-7 mm; inactive: - (inhibition zone < 5 mm).

CONCLUSIONS

Co(II), Ni(II), Zn(II) and Cu(II) complexes of Schiff base which was derived from 4-Nitrobenzohydrazide and 2-hydroxynaphthaldehyde were synthesized and characterized. Conductance measurements indicate that the complexes are non-electrolytes in solution and the thermal analysis reveals that there is a phase change from Solid to liquid at higher temperatures and the SEM image confirms that ligand gets crystelinity on binding to the metal. The spectral data reveal that the Schiff base acts as a mono negative tridentate ligand and the Co(II), Ni(II), Zn(II) and Cu(II) complexes have square planar geometry for 1:1 complexes and an octahedral geometry for 1:2 complexes. The antimicrobial activity of the ligand and its complexes against microbes such as R. oryzea, E. coli, A. niger and P. aeruginosa reveals that the1:2 complexes possess higher antimicrobial activity than 1: 1 complexes and the activity of ligand is increased upon complexation.

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AUTHORS' ADDRESSES

1. **Dr. Shivaraj**
Professor,
Department of chemistry,
Osmania University, Hyderabad, Telangana-500007
Email: Shivaraj_sunny@yahoo.com.
2. **K.Ganga Rajam**
Research Scholar,
Department of chemistry,
Osmania University, Hyderabad, Telangana-500007
Email: gangaind781@gmail.com
3. **Marri. Pradeep Kumar**
Department of chemistry,
Osmania University, Hyderabad, Telangana-500007
Email: pradeepchemm@gmail.com