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Mn (II), Co(II), Cu(II) AND Zn(II) COMPLEXES OF ((E)-N'-(FURAN-2-YLMETHYLENE)NICOTINOHYDRAZIDE): SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITIES

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ABSTRACT

A bidentate ligand derived from furan-2-aldehyde and nicotinic acid hydrazide was characterized through analytical and spectral studies. Mn(II), Co(II), Cu(II) and Zn(II) complexes of nicotinic acid furan-2-ylmethylene-hydrazide have been synthesized and characterized by molar conductance, elemental analysis, UV-Vis, IR, ^{1}H NMR, ^{13}C NMR and ESR studies. The above studies confirm the electrolytical nature and octahedral geometry of the complexes. Further the antimicrobial studies have been carried out for the ligand and metal complexes.

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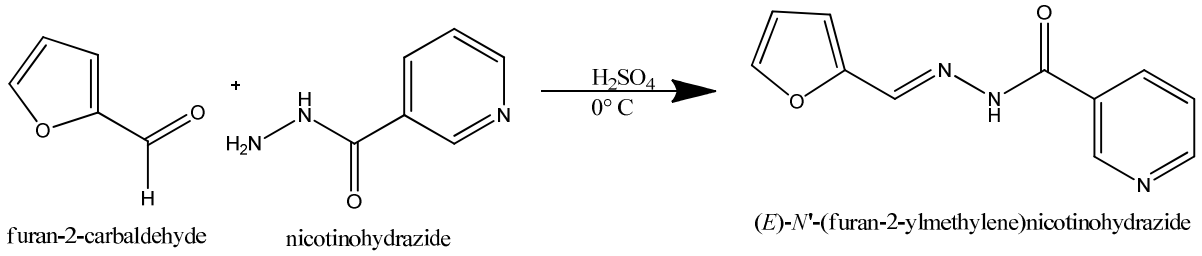
INTRODUCTION

Heterocyclic nuclei have received much attention due to their chemotherapeutic value in the development of novel antitubercular, antifungal, antibacterial, anticancer etc., Schiff base represents an important class of organic compounds and have often been used as chelating ligands in coordination chemistry. Metal complexes of Schiff base have more attention in the medicinal field than the parent Schiff base. Metal complexes of Schiff base have been well known for their easy synthesis, stability and wide applications[1-5]. The ligands containing N and O donor atoms posses a number of biological activities such as antimicrobial, antifungal, antiviral, anticonvulsant, anti-inflammatory, anti malarial etc. They are also used as powerful pesticides and insecticides apart from other biological applications[6,7]. These properties are enhanced when ligands form complexes with metals. The presence of donor atoms like N,O etc. play an important role in the formation of a stable chelate ring and this situation facilitates the complexation process[8-10]. A probe in the literature on some transition metal complexes of the Schiff bases clearly reveals that they act as neutral bidentate ligand and found to exhibit biological properties. (E)-N'-(furan-2-ylmethylene)nicotinohydrazide (FCNH) was prepared by treating furan-2-carboxaldehyde and nicotinic acid hydrazide. Using the synthesized compound as ligand, Manganese (II), cobalt (II), copper (II) and zinc (II) complexes were prepared. Both the ligand and complexes were characterized by elemental analyses, molar conductance, UV, IR, NMR, ESR, Cyclic Voltametry and Magnetic susceptibility and were screened for antimicrobial activities.

Experimental Methods

1.1. Synthesis of FCNH

To the ethanolic solution of Nicotinicacid hydrazide (3.4 g, 0.025 mol) taken in a round bottom flask, Furan-2-carboxaldehyde (2.2 mL, 0.025 mol) and a few drops of sulphuric acid (pH 3-4) were added. The reaction mixture was kept over a magnetic stirrer and stirred well in an ice cold condition for 3 h. The colourless solid formed was filtered and washed several times with petroleum ether (40-60%). The crude solid obtained was dried and recrystallized using absolute alcohol. The recrystallized product was dried over in vacuum.



Scheme 1
Synthesis of FCNH

1.1.1. Synthesis of metal complexes

Synthesis of copper (II) complex : To the methanolic solution of FCNH (2.15 g, 0.01 M),copper (II) chloride (0.85 g, 0.005 M) was added. The reaction mixture was taken in a round bottom flask and kept over a magnetic stirrer cum hot plate and stirred under hot condition. After 2 h the product separated as a pale green solid was washed, filtered and dried over in vacuum.

RESULTS AND DISCUSSION

A number of furan derivatives have been shown to possess strong bactericidal and fungal properties. Nicotinic acid hydrazide and its derivatives as ligands with potential nitrogen

bands are interesting and have gained special attention not only the structural chemistry of their multifunctional coordination modes but also of their importance in medicinal and pharmaceutical field. Owing these consideration an attempt has been made to synthesis a Schiff base, (E)-N'-(furan-2-ylmethylene)nicotinohydrazide (FCNH) using furan-2-carboxaldehyde and nicotinic acid hydrazide. Metal complexes have been synthesized using Mn(II), Co (II), Cu(II) and Zn(II) chlorides with. The synthesized ligand was characterized through IR, ^{1}H-NMR, ^{13}C- NMR and Mass. The structure of FCNH was derived from its infrared spectrum which showed v NH amide at 3230 cm^{-1}, v CH-Ar at 2831 cm^{-1}, v C=O amide at 1680 cm^{-1} and v C=N at 1649 cm^{-1}. The ^{1}H- NMR (300 MHz, DMSO-d6) was showed δ 11.9 (s, 1H, OH (enolic)), δ 9.0(s, 1H, NH), δ 8.7-7.5 (m, 7H, Ar-H) and δ 6.9 (s, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d6) showed δ 163, 149, 145, 138, 133, 132, 128, 113, 112 and the mass spectra show (M+) m/z = 215.8 (Figure 1).

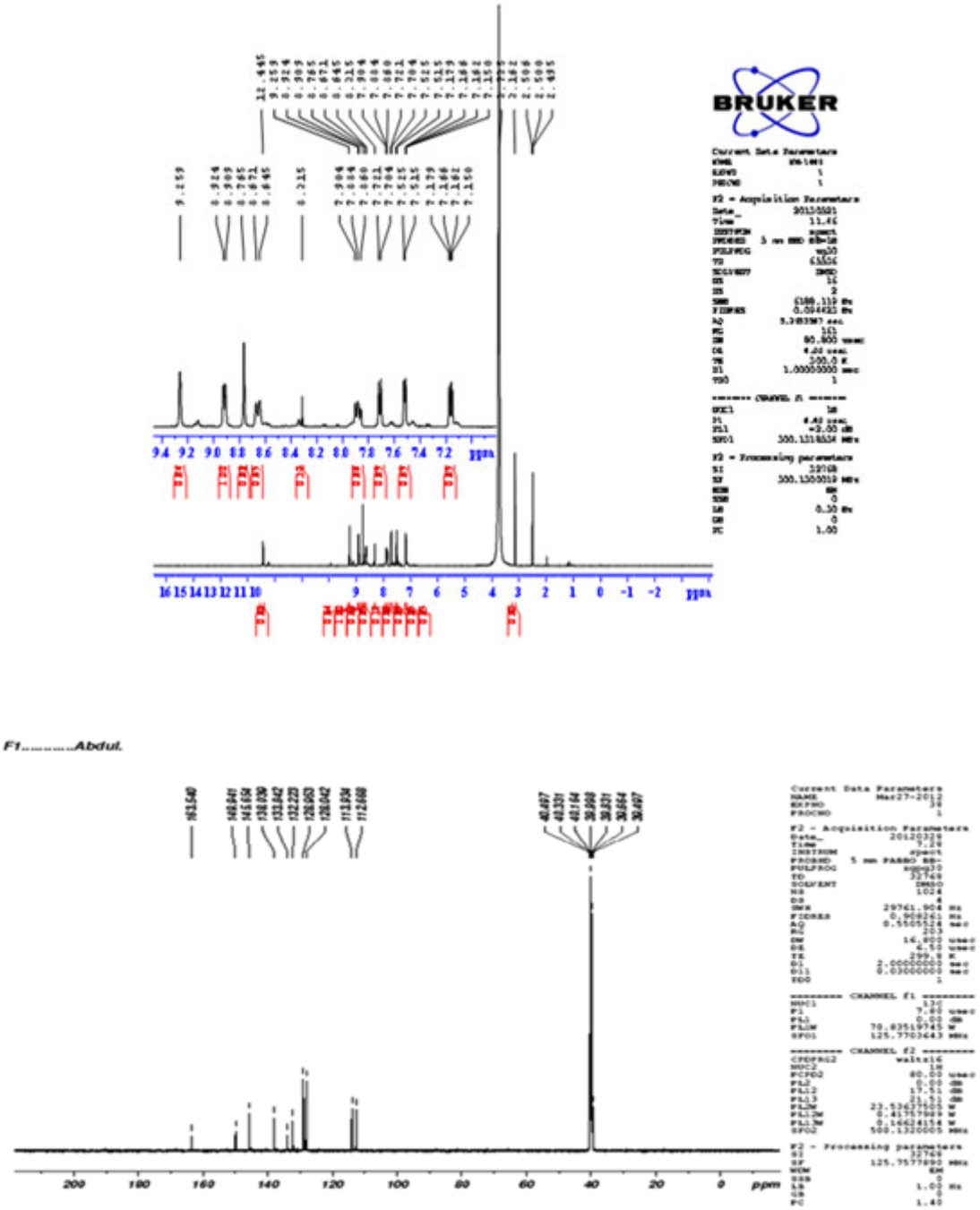


Figure 1
^{1}H and ^{13}C NMR Spectra of FCNH

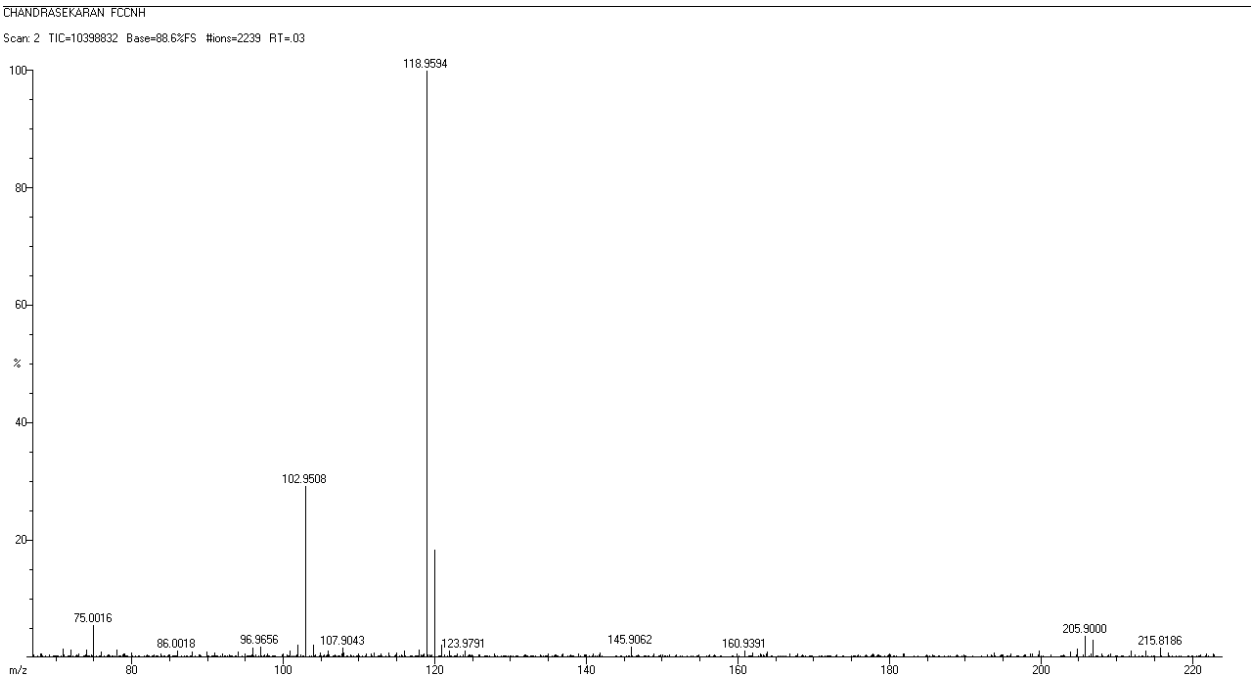
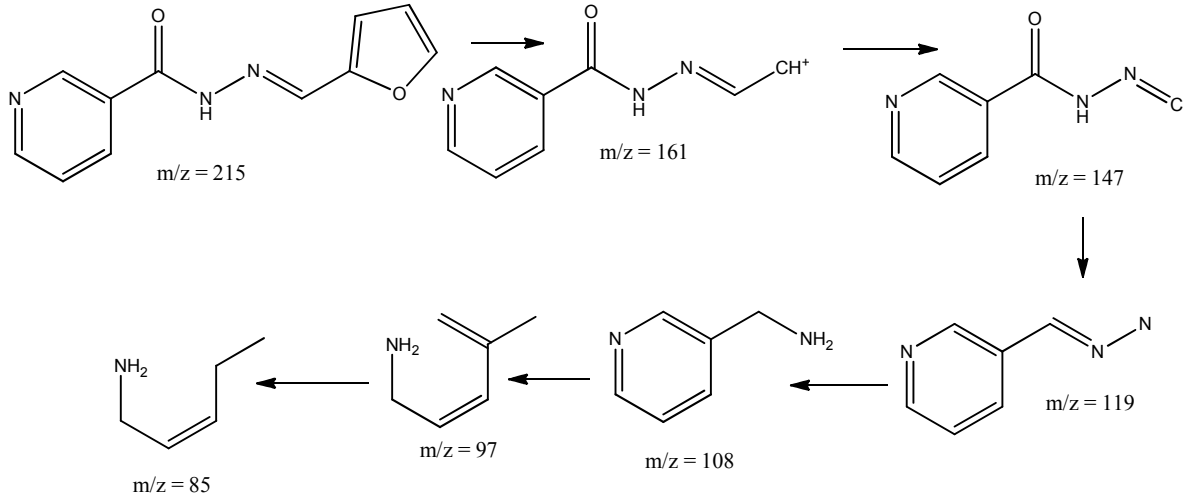


Figure 2
MASS Spectrum of FCNH



Scheme 2
Mass fragmentation of FCNH

The synthesized metal complexes were characterized by elemental analysis, UV, FT-IR and ESR spectral studies. The results of elemental analysis of the ligand and its complexes ,shown in Table 1, are in good agreement with those required by the proposed formulae. The complexes are freely soluble in DMF and DMSO. The molar conductance of the soluble complexes are lie in the range λ = 95-125 10^{-3} Ω^{-1} mol^{-1} cm^{2}, in 10^{-3} DMSO, indicating their electrolytic nature, while the geometry of the complexes was confirmed from elemental analysis, molar conductance, IR, electronic spectra, ESR, Cyclic Voltametry. The ligand and

its complexes have been screened for the in vitro antimicrobial analysis.

Table 1
Elemental analysis, molecular weight and melting point of the FCNH and its complexes

Compounds	Mol. Formula	Mol. Weight	Melt. Point	Elemental Analysis % Found (% Calc.)			
				C	H	N	O
FCNH	$C_{11}H_9N_3O$	215	158	61.18 (61.39)	3.96 (4.22)	19.45 (19.53)	14.78 (14.87)
Mn-FCNH	$C_{22}H_{22}Cl_2MnN_6O_4$	591	178	44.30 (44.61)	3.58 (3.74)	14.26 (14.19)	16.65 (16.81)
Co-FCNH	$C_{22}H_{22}Cl_2CoN_6O_4$	595	268	44.08 (44.31)	3.62 (3.72)	14.12 (14.09)	16.15 (16.10)
Cu-FCNH	$C_{22}H_{22}Cl_2CuN_6O_4$	599	294	43.70 (43.97)	3.55 (3.69)	13.70 (13.99)	15.68 (15.98)
Zn-FCNH	$C_{22}H_{22}Cl_2ZnN_6O_4$	602	226	43.56 (43.84)	3.44 (3.68)	14.01 (13.94)	15.68 (15.85)

3.2.2. IR – Spectra

The IR spectral data of the ligand (FCNH) and its metal complexes are presented in Table 2. The IR spectrum of ligand was compared with the IR spectra of the complexes to indentify the coordination sites of the ligand. The IR spectrum of ligand showed a characteristic sharp band at 3230, 1680 and 1157 cm^{-1} can be attributed to the v (NH), v (C=O) stretching and bending v (C=N) observed. The v (C=N) mode of the ligand appeared at 1157 cm^{-1} in the spectrum of the ligand has been found shifted to lower frequency in the spectra of the complexes indicate the involvement of nitrogen atom of the azomethine in binding with the metal ions. The band appeared at 1680 cm^{-1} due to v(C=O) carbonyl group of amide moiety of the ligand has been shifted to lower frequency by 14 – 62 cm^{-1} in the spectrum of each complex corroborating the coordination of oxygen atom of amide with the metal ions. Hence it is concluded that the compound FCNH act as a neutral bidentate ligand. Further all the complexes exhibits band around 651 – 588 and 596 – 460 cm^{-1} are assignable to v (M – O) and v (M – N) respectively[12-14].

Table 2
Characteristic IR bands of the FCNH and its metal complexes

Compounds	*v (NH) cm^{-1}*	*v(CH) cm^{-1}*	*v(C=O) cm^{-1}*	*v(C=N) cm^{-1}*	*v(M-O) cm^{-1}*	*v(M-N) cm^{-1}*
FCNH	3230	2831	1680	1157	-	-
Mn-FCNH	3205	3072	1666	1126	640	596
Co-FCNH	3211	2870	1618	1132	594	460
Cu-FCNH	3402	2852	1654	1112	588	470
Zn-FCNH	3219	2846	1653	1128	651	594

3.2.1. UV- Spectra

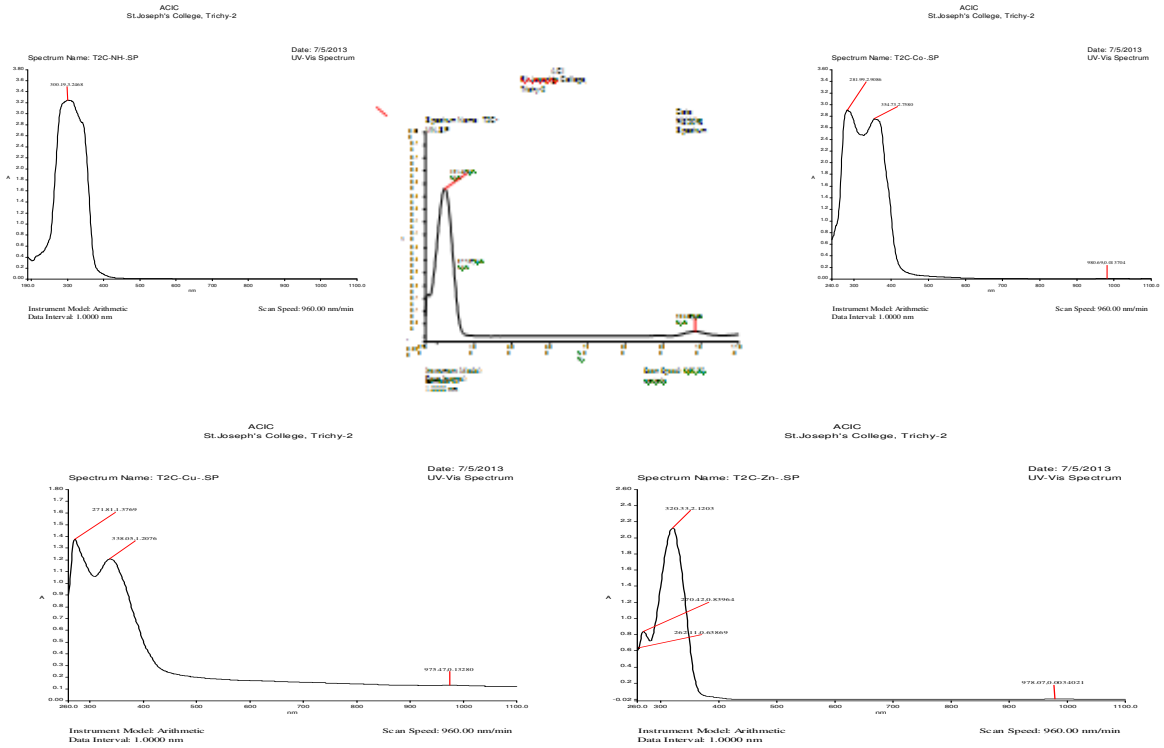


Figure 3
UV spectrum of FCNH

The electronic spectra of the ligand and its complexes were recorded in DMSO solution, the results are shown in Table 3 and the spectra are shown in the fig 3. The electronic spectrum of Mn (II) complex gives a distinct transition at 32362 cm^{-1} which are assignable to π →π* transition, which are typical of Mn(II) complexes with an octahedral coordination geometry. For Co (II) complex, two distinct bands appeared at 16447 and 14858 cm^{-1} are assignable to $^2Eg \rightarrow 2T_1g$ and $^4A_2g(F) \rightarrow ^4T_1g(F)$ transitions respectively. These absorptions favor octahedral geometry. The electronic spectrum of Cu (II) complex exhibit two bands in the region 31847 and 10197cm-1 corresponding to π →π* $^2B_1g \rightarrow ^2A_1g$ respectively, which are in good agreement with the distorted octahedral geometry. The Zn (II) complex is diamagnetic and the electronic spectrum of the complex is dominated only by ligand bands. The UV spectrum of zinc complex exhibit in the region of 31948 cm^{-1} which are assignable to n →π* transition, which are typical of Mn(II) complexes with an octahedral coordination geometry[15-19].

Table 3
Magnetic Susceptibility and electronic transition of FCNH and its metal complexes

Compounds	Magnetic Moment B.M	Absorption Maxima		Transition Assignment	Geometry
		nm	cm-^{1}		
FCNH	-	311	32154	n→π*	---
Mn-FCNH	5.90	309	32362	π →π*	Octahedral
Co-FCNH	3.89	608 673	16447 14858	$^{2}Eg \rightarrow 2T_1g$ $^{4}A_2g(F) \rightarrow {}^{4}T_1g(F)$	Octahedral
Cu-FCNH	2.84	314 981	31847 10197	π →π* $^{2}B_1g \rightarrow {}^{2}A_1g$	Octahedral
Zn-FCNH	0	313	31948	n →π*	Octahedral

3.2.3. ESR Spectrum

ESR spectral studies of FCNH-Cu was recorded at room temperature (300 K) (Fig 4). The ESR spectral analysis of spectra showed that $g_{\parallel}$ = 2.21 and $g_{\perp}$ = 2.01. Thus $g_{\parallel} > g_{\perp} > 2.0023$. These observations

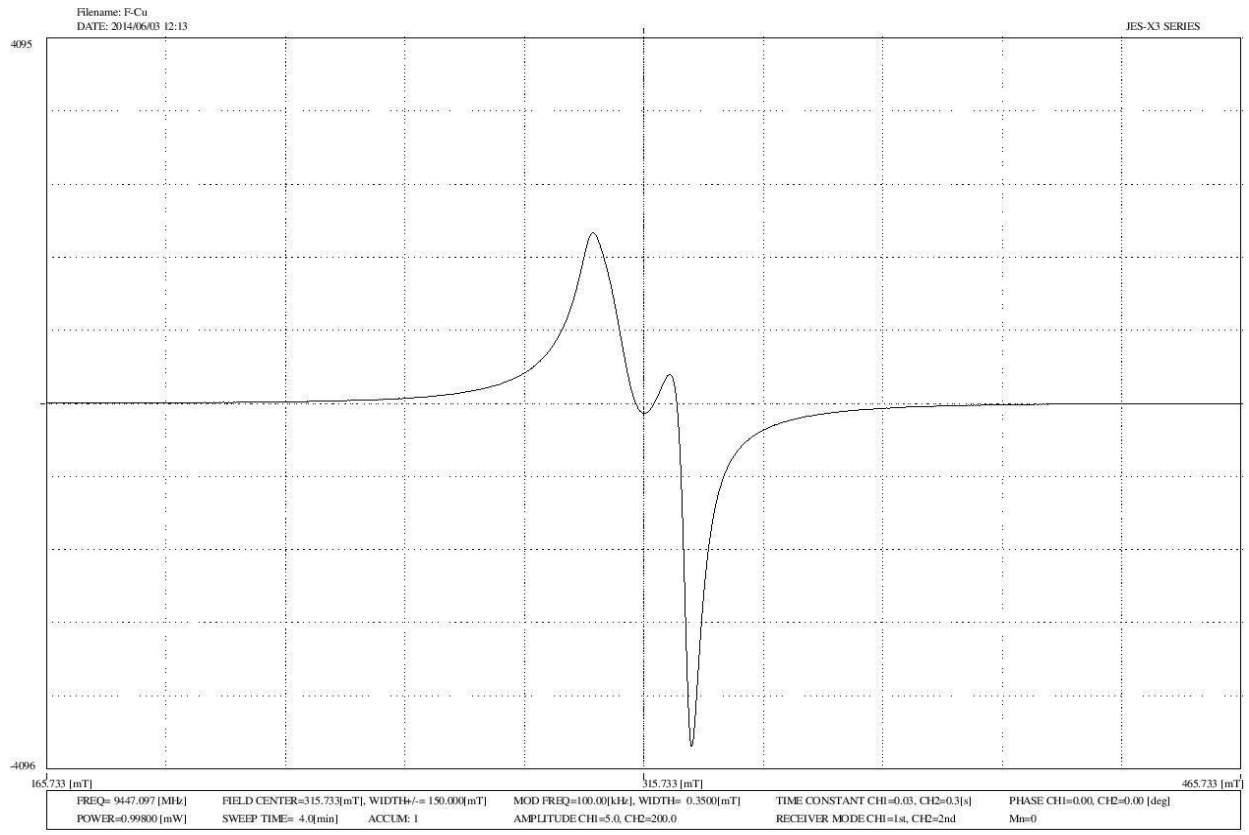


Figure 4
ESR spectrum of FCNH

indicates that the unpaired electron is localized in d_x^2-d_y^2 orbital of the Cu(II) ion and hence the system is axially symmetric[19-21]. Thus the octahedral elongated geometry is confirmed for the aforesaid complex (Fig 5).

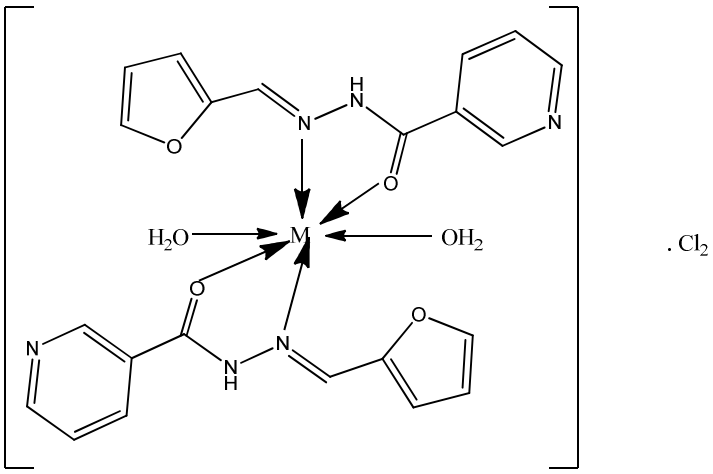


Figure 5
General Structure of metal complex of FCNH

1.2. Antimicrobial Studies

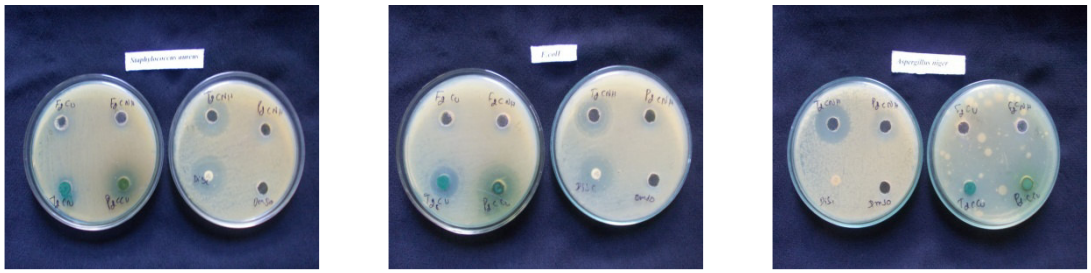


Figure 6
Antimicrobial activities of FCNH and its metal complexes.

Table 4
Disc diffusion method results of FCNH, metal complexes and standard drugs (diameter of the zone of inhibition (mm)) at 100 µl mm/ml.

	Concentration of DMSO extract added and Zone of inhibition (100 µl mm/ml)		
Organism	*Staphylococcus aureus*	*E.coli*	*A.niger*
FCNH	30	30	27
Mn-FCNH	22	24	28
Co-FCNH	30	32	31
Cu-FCNH	22	31	15
Zn-FCNH	24	28	26
DMSO	-	-	-
STANDRED	27	30	10

The potency of the synthesized compounds as antimicrobial was tested against pathogenic strains by disc diffusion method[22] and the results are shown in Table 4 and Fig 6. The synthesized compounds were dissolved in DMSO at a concentration of 100 µl mm/ml. The respective microbial culture was swabbed into the nutrient agar plates for uniform distribution of colonies. All synthesized compounds were poured into each well using a sterile micro pipette and streptomycin was used as standard. The plates were incubated for 72 hr. The zone of inhibition was measured after the incubation. It is observed that the FCNH and metal chelates possess higher activity than the standard.

CONCLUSION

The ligand, FCNH and its metal complexes have been synthesized and characterized by elemental analysis, UV, IR, NMR, mass, ESR and magnetic moment measurements. It is revealed from the IR studies that the ligand coordinated to metal as a neutral bidentate ligand. The results of UV spectral studies and magnetic susceptibility studies confirm the octahedral geometry of the complexes. Antimicrobial screening of ligand and its metal complexes showed their excellent activity. The zone of inhibition of metal complexes is comparably higher than the free ligand.

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