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### Synthesis, characterization and spectral studies of metal (II) complexes derived from benzofuran-2-carbohydrazide and 2-acetylthiophene Schiff's base

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#### ABSTRACT

The complexes of the type  $MLCl_2$ , where  $M = Cu(II)$ ,  $ML_2 \cdot 2H_2O$ , where  $M = Co(II)$ ,  $Ni(II)$  and  $ML_2$ , where  $M = Zn(II)$ ,  $Cd(II)$  and  $Hg(II)$ ,  $L = [BCAT]$  Schiff's base derived from reaction between benzofuran-2-carbohydrazide with 2-acetylthiophene. The ligand acts as bidentate by coordinating through carbonyl oxygen and azomethine nitrogen atoms. Structures have been elucidated on the basis of elemental analysis, conductivity measurement, magnetic properties, spectral studies like IR,  $^1H$  NMR, ESR and electronic spectral studies. On the basis of spectral characterization we proposed tentative structures for all these complexes. The antibacterial and antifungal activities of the ligand and their metal complexes have been screened by MIC method.

**Keywords:** Benzofuran Schiff's base, Spectral studies, Metal complexes and Antimicrobial studies.

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#### INTRODUCTION

Benzofuran compounds are largely present in nature particularly among plant kingdom, often such natural products, possessing useful pharmacological properties and biological properties [1-2]. Some of the benzofuran derivatives such as 2-acetylbenzofuran, 2-nitrobenzofuran etc, are well known biodynamic agents possessing various Pharmacological properties [3-4]. The chemistry of Schiff's bases have wide applications in food industries, dye industries, analytical chemistry, catalysis fungicidal, agrochemical and biological activity [5-7]. Most of the benzofuran compounds are know to be potential antimicrobial [8], analgesic [9], antiviral [10] and antiinflametry [11] agents. Some of natural compounds with benzofuran nucleus are used as effective medicines in the treatment of heart diseases, whooping cough and as a pesticide [12].

Many hydrazones and their complexes with metals have provoked wide interest in their diverse spectra of biological and pharmaceutical activities such as anticancer, antitumor and antioxidative activities as well as the inhibition of lipid peroxidation etc [13-15]. The enhanced biological activities of the Schiff's bases have been seen when complexed with metal ions [16]. In the present investigation, we report the synthesis of Schiff's base derived from reaction between benzofuran-2-carbohydrazide and 2-acetylthiophene and synthesis of metal complexes with Co(II), Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) metal ions. All the complexes were characterized on the basis of elemental analysis, molar conductance, IR, <sup>1</sup>H NMR, ESR, electronic spectral studies and magnetic susceptibility measurement. Schiff's base and its metal complexes are screened for their biological activity against *E. coli* and *S. aureus* and *A. niger* and *A. flavus*.

## MATERIALS AND METHODS

### Experimental

All the chemicals used were of analytical grade. The benzofuran-2-carbohydrazide was prepared by the literature method [17]. The metal and chloride contents are determined as per Vogel's procedure [18]. The magnetic susceptibility measurement was made on Gouy balance using Hg[Co(NCS)<sub>4</sub>] as the calibrant at room temperature. Conductance measurement was made on Elico CM-180 conductivity bridge in DMF (10<sup>-3</sup>M) solution using a dip-type conductivity cell fitted with a platinum electrode having cell constant 0.1 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>. The ESR spectra of Cu(II) complex in polycrystalline state was recorded on Varian E-4X band spectrophotometer using (TCNE) as a 'g' marker (g = 2.00277) at room temperature. The IR spectra of ligand and their complexes were recorded in KBr disc in the range of 4000-350 cm<sup>-1</sup> on Perkin-Elmer FT IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded in DMSO-d<sub>6</sub> on Bruker 400 MHz spectrophotometer, using TMS as an internal standard. The electronic spectra were recorded on Elico SL-159 double beam UV-Vis spectrophotometer in the range of 200-1100 nm in DMF (10<sup>-3</sup>M) solution. The FAB Mass spectra were recorded on a Jeol SX 102/Da-600 Mass spectrophotometer at the central drug research institute (CDRI), Lucknow.

### Synthesis of Schiff's base (BCAT)

A solution of benzofuran-2-carbohydrazide (1.76g, 0.01mol) was added to 2-acetylthiophene (1.08 mL, 0.01mol) in methanol (25 mL). The reaction mixture was refluxed on a water bath for about 4-5 hrs. The Schiff's base was separated on removal of 50% of the solvent and cooling to the room temperature. It was filtered, washed with ethanol and recrystallised from ethanol. The Schiff's base was dried in vacuum over the anhydrous CaCl<sub>2</sub>. The purity of the Schiff's base was checked by TLC.

### Synthesis of Metal (II) complexes

Metal complexes were prepared by adding (0.1 mol, 20 mL) of aqueous solution of metal (II) chlorides to the Schiff's base (0.1mol, 20 mL) in methanol. The complexes did not separate immediately, the reaction mixture was refluxed on a water bath for about 2-3 hours, on partial removal of the solvent (50%) and cooled to room temperature. The precipitated light colored complexes were filtered out washed with water and ethanol to remove the unreacted salts and ligand. All the complexes were dried in open air and kept in vacuum desiccators.

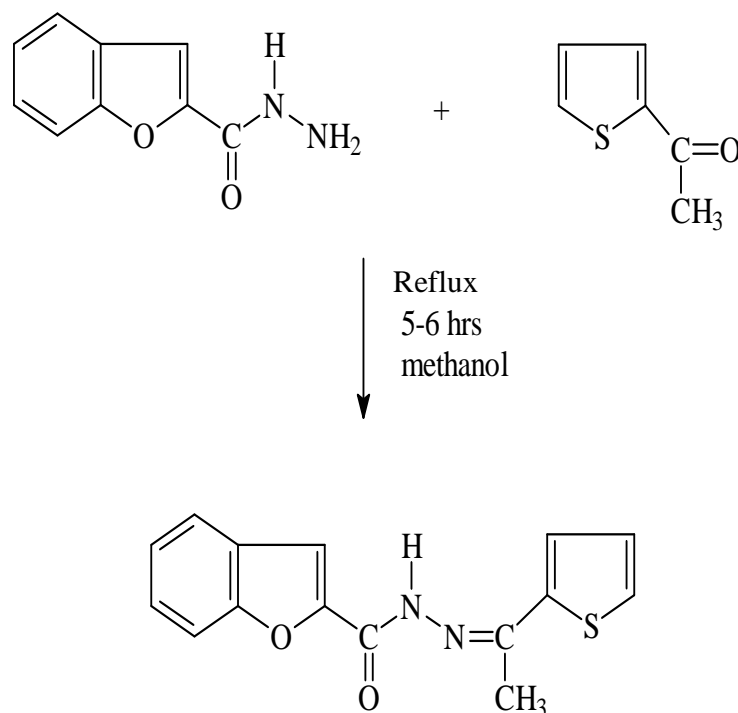


Fig-1 Synthesis of Schiff's base

$C_{15}H_{12}O_2N_2S$ : Mol. Wt = 284, m. p = 154<sup>0</sup>C, Yield = 75%

#### Antibacterial and antifungal assays

The ligand and complexes were screened for their antibacterial and antifungal activity by agar cup plate zone of inhibition technique [19] against two bacteria *E.coli*, and *S. aureus* and two fungal species *A. niger* and *A. flavus* by MIC method.

#### Antibacterial screening using agar-cup plate method

Peptone 10g, NaCl 10g, Yeast extract 5g, Agar 20g in 1000mL of distilled water were used as the medium.

Initially, the stock cultures of bacteria were revived by inoculating in broth media and grown at 37°C for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 hrs old culture (100  $\mu$ l, 10<sup>-4</sup> cfu) and spread evenly on the plates. After 20 min, the wells were filled with the compound at different concentration. Gentamycine was used as standard. All the plates were incubated at 37°C for 24 hrs and the diameter of inhibition zone were recorded.

### Antifungal screening using cup-plate method

Methodology: Potato Dextrose Agar (PDA) 250g of peeled potato were boiled for 20 min and squeezed and filtered. To this filtrate, 20g of dextrose was added and the volume was made up to 1000mL by distilled water.

Initially the stock cultures were revived by inoculating in broth media and grown at 37°C for 48hrs. The agar plates of the above media were prepared and wells were made in the plate, each plate was inoculated with 48 hrs, old culture (100µL, 10<sup>4</sup> cfu) and spread evenly on the plate. After 20 min, the wells were filled with a compound at different concentration. Amphotericin was used as standard. All the plates were incubated at 37°C for 48 hrs and the diameter of inhibition zone were noted.

## RESULTS AND DISCUSSION

The physical appearance and analytical data indicates 1:1 stoichiometry for Cu(II) complex and 1:2 for Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) complexes (Table-1). The molar conductance of the complexes falls in the range of 16.30 - 6.50 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> in DMF (10<sup>-3</sup>M) solution. These values suggest non - electrolytic nature of the complexes [20]. All the complexes possess high melting point and are stable in air and are partially or insoluble in common organic solvents and soluble in DMF, DMSO and pyridine.

Table-1 Analytical, molar conductance and magnetic susceptibility data for Schiff's base and their Metal (II) complexes

Compound	Yield (%)	Mol wt	m.p (°C)	% found (calcd)						Λ <sup>*</sup> M	μ <sub>eff.</sub> (BM)
				C	H	N	S	M	Cl		
[C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S]	75	284	154	62.73 (63.38)	4.47 (4.22)	9.89 (9.85)	10.48 (11.26)	--	--	--	--
[Cu(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S)Cl <sub>2</sub> ] <sub>n</sub>	60	417	>300	44.21 (43.16)	3.05 (2.87)	6.92 (6.71)	7.35 (7.67)	15.86 (15.23)	17.11 (17.02)	16.30	1.72
[Co(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> .2H <sub>2</sub> O]	65	661	297 d	54.15 (54.46)	3.10 (3.32)	8.23 (8.47)	9.42 (9.68)	8.45 (8.91)	--	15.20	4.89
[Ni(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> .2H <sub>2</sub> O]	62	660	290 d	54.31 (54.54)	3.16 (3.33)	8.29 (8.48)	9.37 (9.69)	8.40 (8.89)	--	12.50	2.95
[Zn (C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> ]	60	631	274 d	56.96 (57.05)	3.15 (3.48)	8.41 (8.87)	9.85 (10.14)	10.28 (10.36)	--	9.30	--
[Cd (C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> ]	65	678	>290	52.88 (53.09)	3.14 (3.24)	8.15 (8.25)	9.15 (9.43)	16.10 (16.51)	--	--	--
[Hg (C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> ]	60	766	>295	46.48 (46.99)	2.66 (2.87)	7.22 (7.31)	8.16 (8.35)	(26.10)	--	6.50	--

\* Molar conductance values in ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>.

### Magnetic moment's studies

The observed magnetic moment for Co(II) complex (4.89 BM) has been used as criteria to determine the type of geometry around the Co(II). The values suggest an octahedral geometry for this complex [21]. The magnetic moment values for Ni(II) complex (2.95 BM) slightly higher than the spin only value (2.83 BM) indicating an octahedral environment around Ni(II) complex [22] The observed magnetic moment for the Cu(II) complex is (1.72 BM) suggesting a distorted octahedral geometry around the Cu(II) complex.

### Electronic spectral studies

The electronic spectra of Co(II) complex show two bands at 16129 and 20833 cm<sup>-1</sup>. These two bands are assigned to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) (v_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) (v_3)$  transitions, respectively, in an octahedral environment [23]. The band  $v_1$  has been calculated using band-fitting procedure [24]. The octahedral geometry is further supported by the values of ligand field parameters like Dq, B',  $\beta$ ,  $\beta\%$  and LFSE. All these values are given in Table-2. The reduction in Racah parameter values from free ion value (971) suggests measure of covalent character of the M-L bond. The six coordinated Ni(II) complex exhibit two bands at 15151 and 25906 cm<sup>-1</sup>, are assignable to  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F) (v_2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P) (v_3)$  transitions, respectively, in an octahedral environment. The lowest band  $v_1$  (10Dq) could not be observed due to limited range of the instrument used. However, it was calculated by using an equation suggested by Underhill and Billing [24]. The  $\beta$  value for Ni(II) complex is less than the Co(II) complex indicating more covalency of M-L bond. The Cu(II) complex show broad asymmetric band in the region 12820-18552 cm<sup>-1</sup>. The broadness of the band may be due to dynamic Jahn-Teller distortion [25]. These observations suggest the distorted octahedral structure around Cu(II) ion.

**Table-2 Electronics spectral data and ligand field parameters of the Co (II), Ni(II) and Cu(II) complexes in DMF (10<sup>-3</sup>M) solution**

Complexes	Transitions in cm <sup>-1</sup>			Dq cm <sup>-1</sup>	B'cm <sup>-1</sup>	$\beta$	$\beta\%$	$v_2/v_1$	LFSE kcal/mole
	$v_1^*$	$v_2$	$v_3$						
[Co(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> .2H <sub>2</sub> O]	7499	16129	20833	863	964	0.992	0.720	2.15	14.79
[Ni(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> S) <sub>2</sub> .2H <sub>2</sub> O]	9230	15151	25906	923	890	0.855	14.42	2.5	31.64
[Cu(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S)Cl <sub>2</sub> ] <sub>n</sub>	12820-18552			1568	-	-	-	-	26.88

Calculated values

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of ligand and its Cd(II), Zn(II) and Hg(II) complexes are taken in DMSO-D<sub>6</sub>. The signal at  $\delta$  9.36 (s, 1H) is assigned to amide proton (-CONH) of ligand. The signal of this -CONH proton is disappeared in the spectra of Cd(II), Zn(II) and Hg(II) complexes and this shows that the ligand loses the proton after enolisation. Thus confirming bonding through oxygen atom. The aromatic protons at  $\delta$  8.10 - 6.76 (m, Ar H) shift down field in the complexes. The signal at  $\delta$  2.54 (s, 3H) is assigned to protons of methyl group of 2-acetylthiophene. Thus <sup>1</sup>H NMR spectral observations supplements the assigned geometry.

### Mass spectra

The FAB mass spectra (Fig-4) of Schiff's base (BCAT) were performed to determine their molecular weight and fragmentation pattern. The mass spectra of the ligand showed molecular ion peak, M<sup>+</sup> at m/z 284 corresponding to its molecular weight. The ligand gave a fragment ion peak at m/z 160 by expulsion of C<sub>6</sub>H<sub>6</sub>NS species. This fragment ion underwent fragmentation with loss of NH<sub>2</sub> and gives a fragment ion at m/z 145, further fragmentation with loss of CO gave a peak at m/z 117. This supports the structure of the ligand.

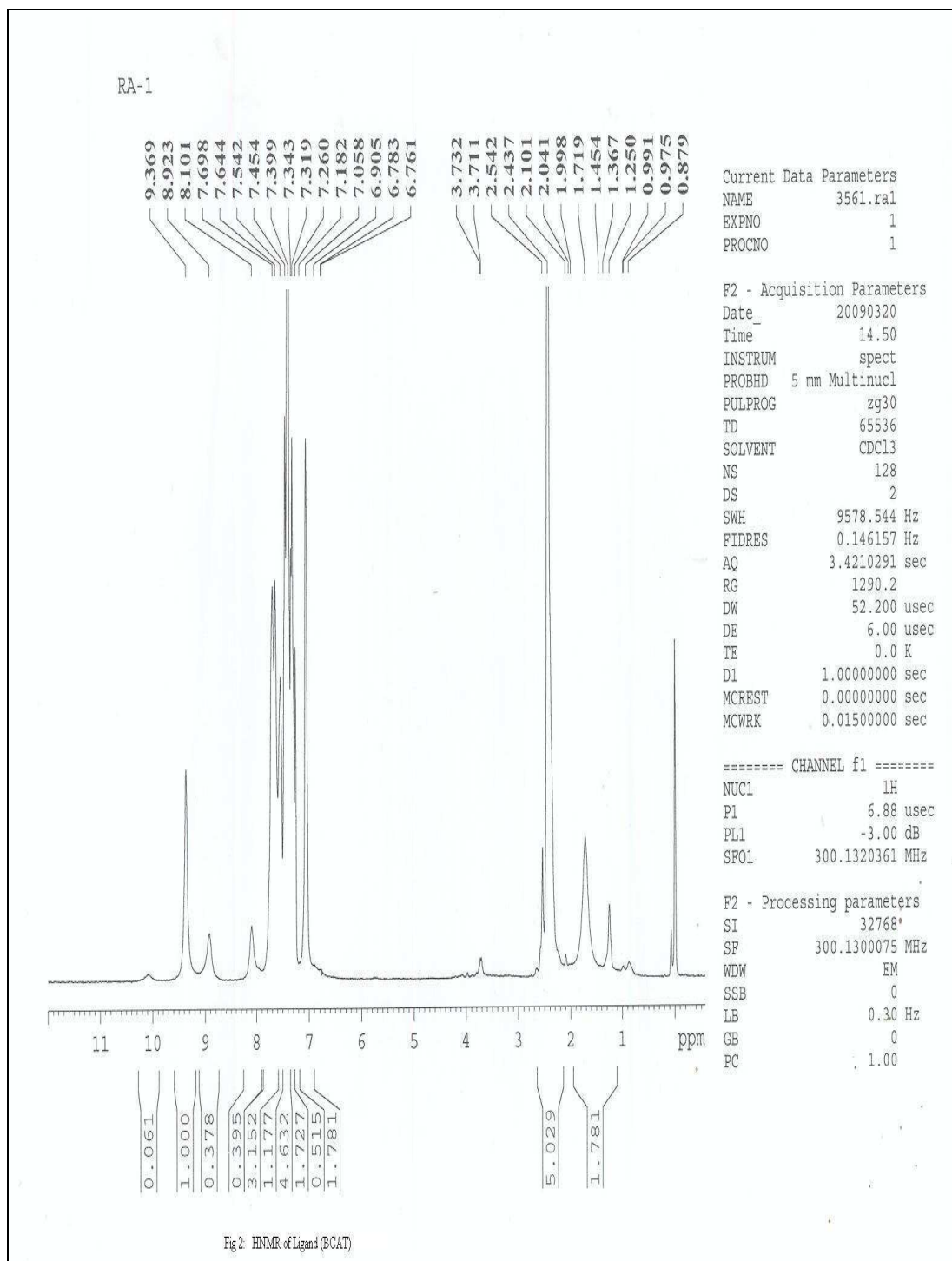


Fig-2 <sup>1</sup>H NMR of Ligand [BCAT]

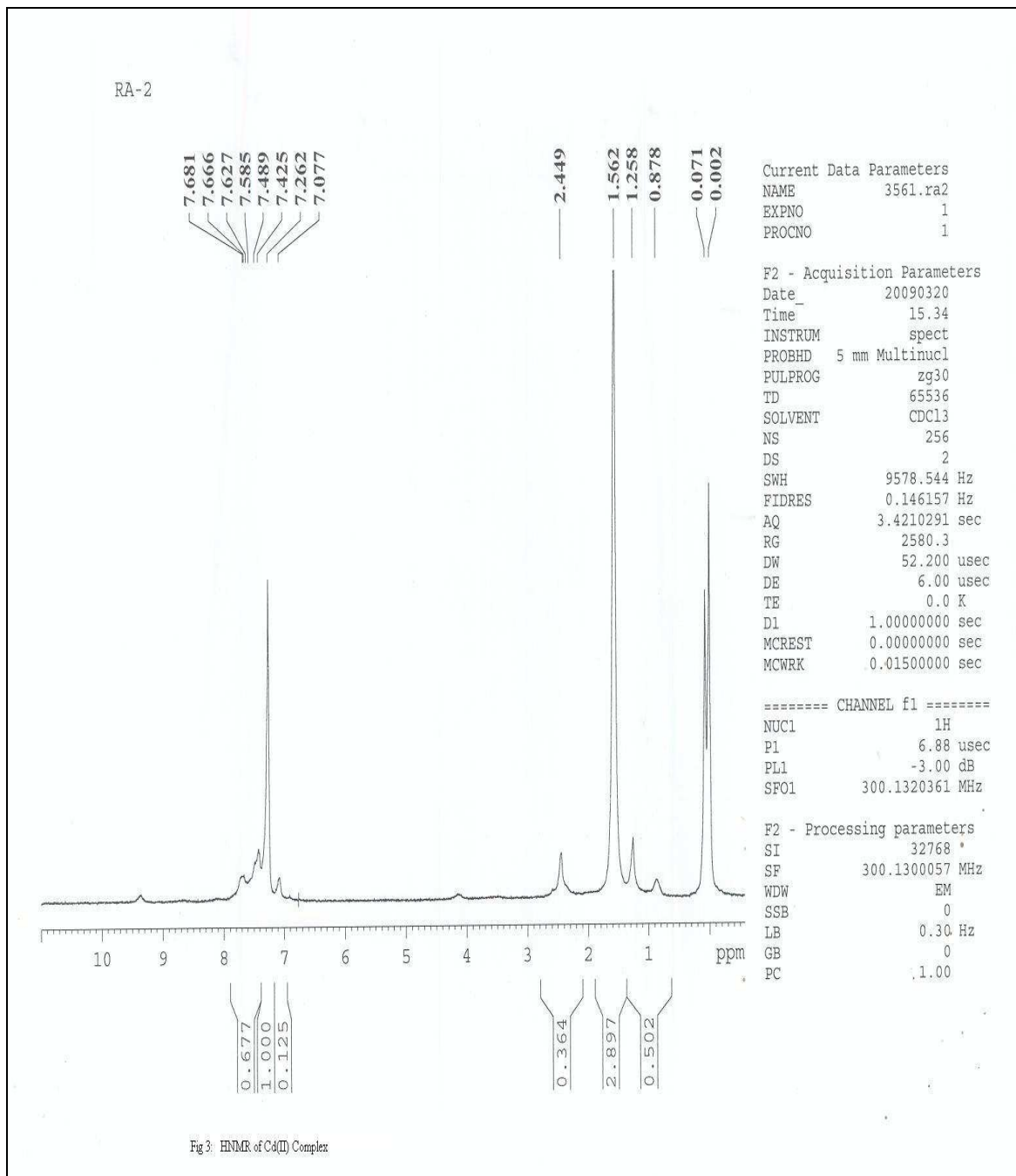
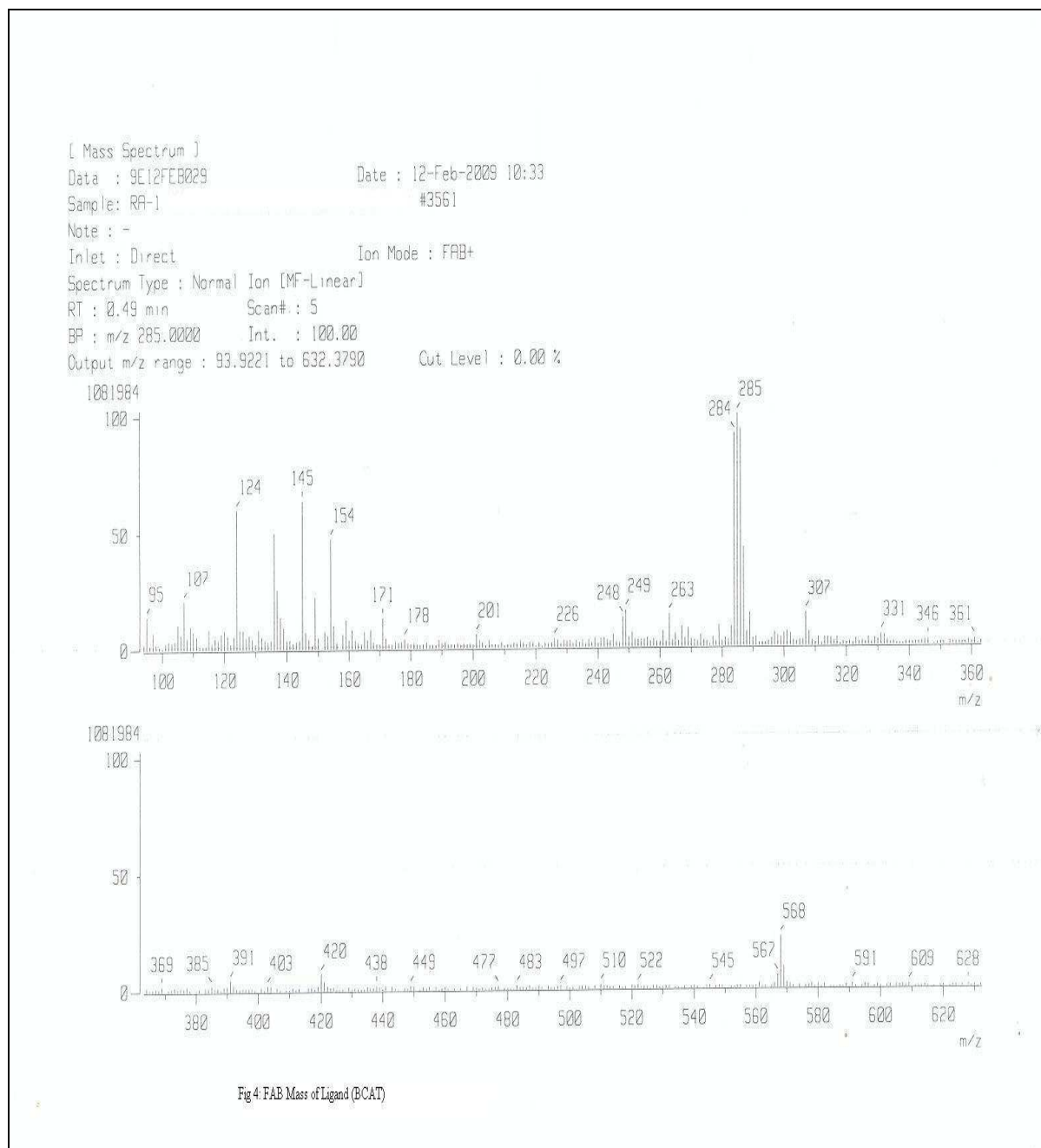


Fig-3 <sup>1</sup>H NMR of Cd(II) complex.





**Fig-4 FAB Mass of Ligand[BCAT]**

### IR spectra

The main stretching frequency of IR spectra of the ligand and their complexes are presented in Table-3. These bands will give valuable information regarding bonding modes of ligand to metal ions in the complexes. The IR spectra of the ligand give a broad band at  $3161\text{ cm}^{-1}$  assignable to  $\nu(\text{NH})$  stretching vibration.. These bands shift to higher wave number side in the complexes indicating non-involvement of 'N' of the amide group in coordination with Co(II), Ni(II) and Cu(II)



complexes [26]. The strong band observed at  $1680\text{ cm}^{-1}$  in free ligand is assigned to  $\nu(\text{C}=\text{O})$  stretch of  $-\text{CONH}$  group [27]. This band shift to lower wave number side in Cu(II) complex by about  $30\text{-}17\text{ cm}^{-1}$  indicating participation of the carboxyl oxygen atom in coordination [28]. In the case of Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) complexes this band disappears indicating enolisation and deprotonation of  $-\text{OH}$  group confirming coordination through oxygen atom of carbonyl group. Medium to strong intensity band at  $1612\text{ cm}^{-1}$  in the free ligand is assigned to  $\nu(\text{C}=\text{N})$  stretch of the azomethine group [29]. This  $\nu(\text{C}=\text{N})$  stretch shift to lower wave number side in all the complexes by about  $46\text{-}12\text{ cm}^{-1}$  indicating involvement of the azomethine nitrogen in bonding with all the metal ions [30]. Many worker's [31,32] have reported  $\nu(\text{C}-\text{O}-\text{C})$  stretching vibrations of furan ring in the region  $1020\text{-}1250\text{ cm}^{-1}$ , in the present case the  $\nu(\text{C}-\text{O}-\text{C})$  stretch at  $1225\text{ cm}^{-1}$  remain unaltered in the metal complexes indicating non-participation of the furan ring oxygen atom in bonding with metal.

Metal ligand vibrations are generally observed in the far-IR region and usually give valuable information regarding the bonding of ligand to the metal-ions. The weak intensity non-ligand bands observed in the complexes in the region  $538\text{-}515\text{ cm}^{-1}$  and  $446\text{-}430\text{ cm}^{-1}$  are assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  stretching vibration respectively [33]. In the case of Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes deprotonation takes place after enolisation. In these complexes we found the new band appearing around  $1380\text{ cm}^{-1}$  due to  $\nu(\text{C}-\text{O})$  stretching vibration. In the case of Cu(II) complex where both bridging and terminal halogens are present we assign terminal  $\nu(\text{M}-\text{Cl})$  at  $390\text{ cm}^{-1}$  and bridging at  $360\text{ cm}^{-1}$  in view of earlier report [34]. We assign the broad and weak intensity non-ligand bands in the region  $380\text{-}360\text{ cm}^{-1}$  to  $\nu(\text{M}-\text{Cl})$  stretching vibrations.

**Table- 3 Important IR spectral bands ( $\text{cm}^{-1}$ ) for ligand and its metal complexes**

Complexes	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
BCAT [ $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ ]	3161	1680	1612	--	--
$[\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]_n$	3445/3342	1650	1600	515	439
$\text{Co}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2 \cdot 2\text{H}_2\text{O}$	3163	--	1593	538	446
$[\text{Ni}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2 \cdot 2\text{H}_2\text{O}]$	3263	--	1596	524	430
$[\text{Zn}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2]$	--	--	1595	523	432
$[\text{Cd}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2]$	--	--	1566	520	442
$[\text{Hg}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2]$	--	--	1592	518	436

### ESR spectra

The ESR spectra of powdered sample of  $[\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]_n$  was recorded at room temperature. The spectra have asymmetric bands with  $g_{11} (2.42) > g_{\perp} (2.23) > \text{TCNE} (2.00277)$ , indicating the unpaired electron lie predominately in the  $dx^2-y^2$  orbital with possibly mixing of  $dz^2$  because of the low symmetry [35,36]. The exchange interaction parameter 'G' is calculated using  $G = (g_{11}-2) / (g_{\perp}-2)$ . The value of 'G' is less than 4 indicate exchange interaction between the metal ions.

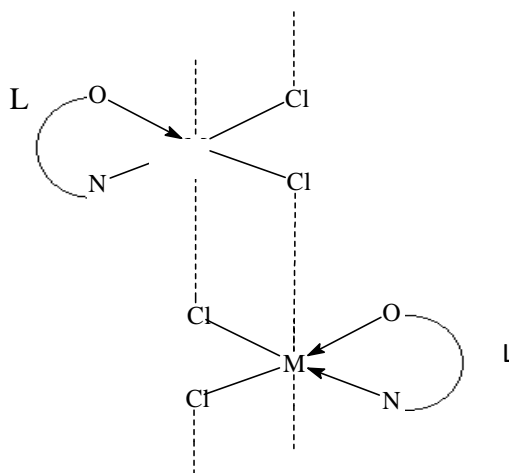
### Antibacterial and antifungal activity

All the metal complexes and ligand were for tested antimicrobial activity against bacteria *E.colli* and *S aureus* and antifungal activity against *A.niger* and *A flavus* by MIC method. The MIC values indicate that the Schiff's base was found to be biological inactive against any bacteria. The Hg (II) complex showed significantly enhanced both antibacteria *E.colli* and *S aureus* and ani

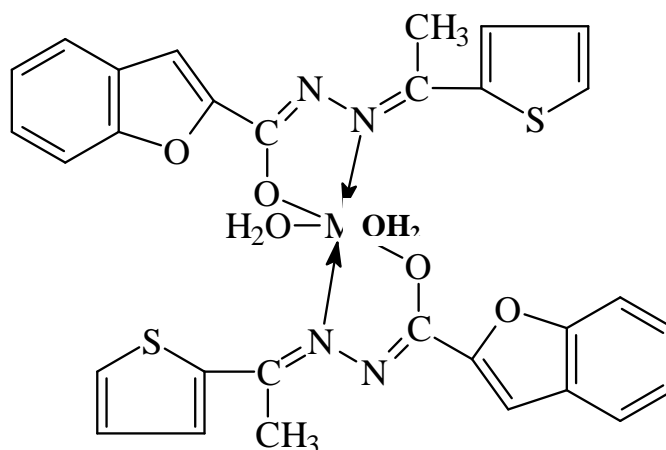
fungal *A.niger* and *A.flavus* all other complexes have shown less inhibition against all bacteria tested (Table-4).

**Table- 4** The MIC values of Antibacterial and Antifungal activity results of ligand and its metal complexes.

Ligand/Complexes	MIC ( $\mu\text{g/mL}$ ) values of Antibacterial		MIC ( $\mu\text{g/mL}$ ) values of Antifungal	
	<i>E.coli</i>	<i>S.aureus</i>	<i>A.niger</i>	<i>A.flavus</i>
BCAT [ $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ ]	800	>800	>800	>800
$[\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]_n$	800	200	>800	>800
$\text{Co}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2 \cdot 2\text{H}_2\text{O}$	800	400	>800	>800
$[\text{Ni}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2 \cdot 2\text{H}_2\text{O}]$	800	800	>800	400
$[\text{Zn}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2]$	800	400	>800	800
$[\text{Cd}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2]$	80	400	>800	800
$[\text{Hg}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{S})_2]$	25	25	25	25
Gentamycin	25	25	--	--
Amphotericin	--	--	100	400

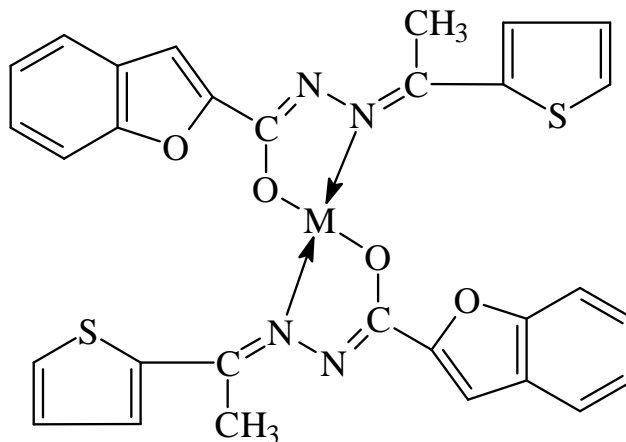


**Fig -5** Suggested structure of Cu (II) complex



Where  $M = \text{Ni}(\text{II})$  or  $\text{Co}(\text{II})$

**Fig- 6** Suggested structures of Ni (II) & Co (II) complexes



Where M = Zn (II), Cd (II) or Hg (II)

Fig- 7 Suggested structures of Zn (II), Cd (II) & Hg (II) complexes

### CONCLUSION

Based on the Spectral studies, magnetic moment and conductance studies we suggest the probable structure to all the complexes as ligand bridged octahedral polymeric to Cu(II) complex, dimeric octahedral to Co(II) and Ni(II) complexes and Tetra hedral structures to Zn(II), Cd(II) and Hg(II) complexes.

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