



Trade Science Inc.

ISSN : 0974 - 746X

Volume 7 Issue 5

# Inorganic CHEMISTRY

*An Indian Journal*

*Full Paper*

ICAJ, 7(5), 2012 [210-214]

## Antibacterial activity, synthesis and characterisation of complexes of Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Fe<sup>II</sup>, Mn<sup>II</sup>, Pd<sup>II</sup> and Cd<sup>II</sup> with thiosemicarbazone of 2-acetylbenzimidazole {(2E)-2-[1-(1H-benzimidazole-2-yl) ethylidene] hydrazinecarbothioamide}

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### ABSTRACT

Thiosemicarbazone of 2-acetylbenzimidazole {(2E)-2-[1-(1H-benzimidazole-2-yl) ethylidene] hydrazinecarbothioamide} (HActsc) is strong (N, S) donor complexing molecules and form chelates with Co<sup>II</sup>, Ni<sup>II</sup>, Fe<sup>II</sup>, Cu<sup>II</sup>, Mn<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Pd<sup>II</sup> of composition M (Actsc)<sub>2</sub> · nH<sub>2</sub>O (n = 0, 1 or 2) in neutral or basic medium. In anhydrous ethanol or methanol Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, and Cd<sup>II</sup> form dihalo complexes of composition [M(HActsc)X<sub>2</sub>] (X = Cl or Br).

The complexes have been analysed and characterised from the studies of electrical conductance value, magnetic susceptibility measurement, electronic absorption and infrared spectral data. The antibacterial activity of HActsc and its complexes have been evaluated against some gram positive and gram negative bacteria by disc diffusion method.

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### KEYWORDS

2-acetylbenzimidazole  
thiosemicarbazone;  
Bivalent metal complexes;  
Bacterial activity;  
Synthesis and  
characterization.

### INTRODUCTION

Benzimidazoles are remarkably effective compounds both with respect to their bacterial inhibitory activity and their favourable selectivity for drug design. Extensive biochemical and pharmacological studies have confirmed that substituted benzimidazole are effective against various strains of microorganism<sup>[1,2]</sup>. Some benzimidazole compounds inhibit the biosynthesis of ergosterol in the cell membrane of fungi. They have antibacterial, antifungal and antiviral activity<sup>[3-6]</sup>. Benzimidazole ring system is present in numerous antiparasitic and anti-tumoral drugs<sup>[7,8]</sup>. The

benzimidazole structure is present in nucleotides portion of vitamin B<sub>12</sub> and nucleus of some drugs act as proton pump inhibitors and anthelmintic agents. The antimicrobial activity of this class of compounds was investigated against helicobacter pillory and oral streptococci<sup>[10]</sup>. Certain 2-substituted benzimidazole derivatives are used as effective drugs of antihistaminic, cylostatic, oral analgesic, anti inflammatory and hypotensive activity<sup>[11]</sup>. It has been confirmed that benzimidazole has anti HIV effect<sup>[12]</sup>. The last decades have witnessed amazing research activity, towards the studies of coordination complexes of benzimidazole derivatives with a number of metal ions<sup>[13,14]</sup>. In

pursuance of our interest towards studies of metal complexes with benzimidazole derivatives<sup>[15-20]</sup> a new ligand 2-acetylbenzimidazole-thiosemicarbazone {(2E)-2-[1-(1H-benzimidazole-2-yl)ethylidene]hydrazinecarbothioamide} (HActtsc) has been synthesised and its some bivalent metal complexes have been prepared characterised and its antibacterial properties have been studied.

## EXPERIMENTAL

The ligand was prepared by condensing 2-acetylbenzimidazole with thiosemicarbazide in aqueous ethanol containing a few drops of acetic acid. The cream coloured precipitate obtained on refluxing, was filtered crystallised and dried over  $\text{CaCl}_2$  (M.P =  $248^\circ\text{C}$ ). The nitrogen found 29.71% required for  $\text{C}_{10}\text{H}_{11}\text{N}_5\text{S}$  (HActtsc), 30.04%. The metal salt and chemicals used were E Merck extra pure and BDH Anal R grade reagent. The magnetic susceptibility was determined at room temperature by Gouy method and i.r and u.v spectra were get recorded from IIT patna. The metal ions and halogens were estimated by standard method<sup>[16-20]</sup>.

### Preparation of complexes $\text{M}(\text{Acttsc})_2 \cdot n\text{H}_2\text{O}$

( $\text{M} = \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Pd}^{\text{II}}, \text{Cd}^{\text{II}}, \text{and Zn}^{\text{II}}$ )

An aqueous ethanolic solution of metal acetate (sulphate in case of Fe and chloride in case of  $\text{Pd}^{\text{II}}$ ) 0.01 mol of 30 ml (50% ethanol) was treated with hot ethanolic solution on ligand and refluxed for 0.5 hour with stirring on a steam bath. The product obtained immediately in most of the cases. When the pH of the resulting mixture was raised to 5–6 by adding aqueous solution of sodium acetate and diluted with water. The complexes separated were filtered, washed with aqueous ethanol and dried over  $\text{CaCl}_2$ . The dried samples were analysed and results are given in TABLE 4.

### Preparation of $[\text{M}(\text{HActtsc})\text{X}_2]$

( $\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cd}^{\text{II}} \text{ or } \text{Zn}^{\text{II}}$ )

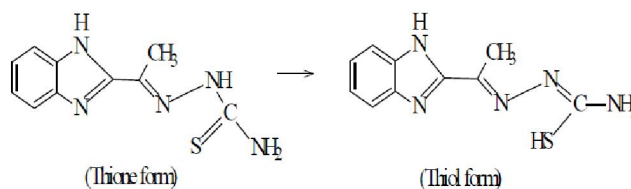
Ehanolic solution of 0.01 mole of metal halide (in 20–25 ml) was treated with 0.01 mol of ligand in hot dry ethanol (20–25 ml). The resulting solution was refluxed for 0.5 hour and concentrated in a open basin when crystalline precipitate separated. The products were

collected on a filter, washed with cold ethanol and dried over  $\text{CaCl}_2$  in a desiccator. Result of elemental analysis of complexes are given in TABLE 4.

The thermal studied was performed with heating rate  $10^\circ\text{C}$  per minutes in static air.

## RESULTS AND DISCUSSION

The condensation products of 2-acetylbenzimidazole and thiosemicarbazide (HActtsc) potent (S.N.N) donor and act as tridentate mono-anionic coordinating ligand in neutral medium.



In weakly acid, medium (pH- 3-4), the methanol solution of metal halide coordinates with neutral ligand and form dihalo complexes  $[\text{M}(\text{HActtsc})\text{X}_2]$  ( $\text{M} = \text{Cu}^{\text{II}}, \text{Co}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Ni}^{\text{II}} \text{ or } \text{Zn}^{\text{II}}$  and  $\text{X} = \text{Cl}^- \text{ or } \text{Br}^-$ ). In neutral or basic medium HActtsc form neutral bis chelates,  $\text{M}(\text{Acttsc})_2 \cdot n\text{H}_2\text{O}$ . ( $\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}} \text{ and } \text{Pd}^{\text{II}}$ ). The neutral bis chelates are insoluble in organic solvents as well as in water. The dihalo complexes are slightly soluble in ethanol; methanol and dioxane but both neutral and dihalo complexes are fairly soluble in DMF and DMSO. The freshly prepared solution of both series of complexes in DMF show negligible molar electrical conductance value ( $8\text{--}13 \text{ ohm}^{-1}, \text{mol}^{-1}, \text{cm}^2$ ) suggesting non-ionic nature of the complexes and halogens are coordinated in dihalo complexes<sup>[21]</sup>. The neutral complexes  $[\text{M}(\text{Acttsc})_2]2\text{H}_2\text{O}$  ( $\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}} \text{ and } \text{Ni}^{\text{II}}$ ) gradually loss water molecules and become anhydrous below  $90^\circ\text{C}$  suggesting the presence of  $\text{H}_2\text{O}$  as hydrate or lattice water in hydrated complexes. As usual  $\text{Cd}^{\text{II}}, \text{Zn}^{\text{II}} \text{ and } \text{Pd}^{\text{II}}$  complexes  $[\text{M}(\text{Acttsc})_2], [\text{M}(\text{HActtsc})\text{X}_2]$  ( $\text{M} = \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Pd}^{\text{II}} \text{ and } \text{X} = \text{Cl} \text{ or } \text{Br}$ ) are diamagnetic. Both bis chelates of  $\text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}} \text{ and } \text{Cu}^{\text{II}}$  and dihalo complexes  $[\text{M}(\text{HActtsc})\text{X}_2]$  ( $\text{M} = \text{Cu}^{\text{II}} \text{ or } \text{Ni}^{\text{II}}$ ) are paramagnetic and their magnetic moment values occur in the range of octahedral field<sup>[22,23]</sup> (TABLE 1). The electronic absorption spectra of complexes show very strong absorptions below 400 to 430 nm. The

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complexes form deep colouration in DMF and these are due to strong charge transfer transitions with L → M or M → L absorption. The electronic absorption spectra of Cu (II) complexes [Cu(Acttsc)<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O shows strong absorption below 420 nm and electronic shoulder at 640-700 nm assignable to combination of <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub> and <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>2g</sub> transition in tetragonal field<sup>[24]</sup>. Both neutral Pd (Acttsc)<sub>2</sub> and Pd (Acttsc)Cl<sub>2</sub> display strong absorption below 420 nm and a shoulder near 440-460 nm. This shoulder in complexes is suggested to originate from <sup>1</sup>A<sub>1g</sub> = <sup>1</sup>A<sub>2g</sub> transition of planar Pd (II) complexes<sup>[24]</sup>. No distinct electronic absorption band was observed for Mn (II) complex due to extremely weak nature of spin forbidden transition<sup>[23]</sup>. A medium shoulder at 450 – 470 nm at strong charge transfer absorption below 420 nm observed for Fe (Acttsc)<sub>2</sub>H<sub>2</sub>O can be attributed to <sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub> transition in octahedral field<sup>[23]</sup>. The electronic absorption spectra of both [Ni(Acttsc)<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O and [Ni(HActtsc)Cl<sub>2</sub>] are similar in DMF solution and display a medium band at 460 – 480 and strong absorption below 410 nm. The strong absorption below 410 nm is attributed to charge transfer transition and weak medium band is assigned to <sup>1</sup>B<sub>1g</sub> → <sup>1</sup>B<sub>2g</sub> transition in distorted tetragonal field.

TABLE 1 : Analytical and physical data of complexes.

Compound	Colour	Electrical Conductance ohm <sup>-1</sup> mol <sup>-1</sup> cm <sup>2</sup>	μ <sub>eff</sub> (BM) at 302 ± 1 <sup>0</sup> K
Mn(HL) <sub>2</sub>	Dirty yellow	6	5.86
Fe(HL) <sub>2</sub> .2H <sub>2</sub> O	Reddish brown	8	4.92
Co(HL) <sub>2</sub> .2H <sub>2</sub> O	Brown	7	3.41
Ni(HL) <sub>2</sub> .2H <sub>2</sub> O	Orange brown	8	3.21
Cu(HL) <sub>2</sub>	Brown	6	1.86
Zn(HL) <sub>2</sub>	Orange	6	Dia
Cd(HL) <sub>2</sub>	Yellow	7	Dia
Cu(H <sub>2</sub> L) <sub>2</sub> Cl <sub>2</sub>	Grey	18	1.79
Cu(H <sub>2</sub> L) <sub>2</sub> Br <sub>2</sub>	Dark grey	20	1.86
Zn(H <sub>2</sub> L) <sub>2</sub> Cl <sub>2</sub>	White	21	Dia
Cd(H <sub>2</sub> L) <sub>2</sub> Cl <sub>2</sub>	White	22	Dia
Cd(H <sub>2</sub> L) <sub>2</sub> Br <sub>2</sub>	White	15	Dia
Ni(H <sub>2</sub> L) <sub>2</sub> Cl <sub>2</sub>	Greenish yellow	20	3.02

H<sub>2</sub>L = H<sub>2</sub>ActtSc

The i.r spectra of ligand and complexes were recorded in KBr disc in the range 400 – 4000 cm<sup>-1</sup> on FTIR spectrophotometer. The ligand display medium bands between 2940–3280 cm<sup>-1</sup> due to ν(C—H) of CH<sub>3</sub> plus ν(NH) of imidazole ring and thiohydrazone part of NH<sub>2</sub> group. The NH of imidazole ring and

δ(C—H) of methyl group are retained in complexes. It is found that no major change in i.r stretch was observed in 3μ region. The ν(C=N) imidazole and ν(C=N) of ketoimine part of thiohydrazone was assigned to i.r bands located at 1632 and 1595 cm<sup>-1</sup> in free ligand. The ν(C=N) of ligand shift to lower wave number by 10-25 cm<sup>-1</sup> in complexes supporting the involvement of both (C=N) nitrogen to metal atom. In case of bis chelate of Zn<sup>II</sup>, Cd<sup>II</sup> and Pd<sup>II</sup> the ν(C=N) was observed near 1628±3 cm<sup>-1</sup> suggesting that imidazole ring (C=N) is not involved in coordination. The δ(NH) of ligand was localised at 1565 cm<sup>-1</sup> and it is not affected appreciably in its complexes. The ligand displays a number of medium and strong i.r bands in finger print region. The band near 982 cm<sup>-1</sup> in free ligand is assigned to ν(C=S) of ligand and strong band at 746 cm<sup>-1</sup> to phenyl ring (C—H) out of plane bending band. The ν(C=N) was shifted to lower frequency by 25 – 30 cm<sup>-1</sup> in dihalo complexes [M(HActtsc)X<sub>2</sub>] (TABLE 2) suggesting coordination of HActtsc also with sulphur in thione form. The ν(C=S) of ligand disappear near 982 and a new band appears near 760 – 780 wave number attributed from ν(C—S) of deprotonated thiol sulphur in bis ligated neutral complexes. The large shift of ν(C—S) neutral complexes M (Acttsc)<sub>2</sub>nH<sub>2</sub>O suggested the coordination of deprotonated thiol sulphur of thiosemicarbazone. The hydrated complexes display a broad medium band near 670-690 cm<sup>-1</sup> attributed to rocking band ρ(H<sub>2</sub>O). The ligand displays three prominent i.r bands in far i.r region at 616, 567 and 521 cm<sup>-1</sup>. These i.r bands are affected slightly on coordination. The new i.r bands at 470 ± 5 and 425 ± 10 cm<sup>-1</sup> in some complexes are attributed to (M—N) and (M—S) stretching vibration<sup>[24,25]</sup>.

TABLE 2 : Diagnostics IR bands of ligand and its complex as Cm<sup>-1</sup>.

Compound	ν(CH) + ν(NH) + ν(H <sub>2</sub> O)	ν (CN)	ν (C=S)	ν(M—N) + ν(M—S)
H <sub>2</sub> ActtSc = H <sub>2</sub> L	3280, 3040, 2940	1632 1595	982	
Ni(HL) <sub>2</sub> .2H <sub>2</sub> O	3400 br 2950	1612 1590	735	460 423
Co(HL) <sub>2</sub> .2H <sub>2</sub> O	3350–3130, 2940	1610 1585	746	465 418
Cu(HL) <sub>2</sub>	3270, 3030, 2960	1608 1580	736	462 421
Zn(HL) <sub>2</sub>	3245, 3060, 2950	1613 1590	728	455 420
[Cu(H <sub>2</sub> L)Cl <sub>2</sub> ]	3240, 3050, 2940	1615 1585	956	470 418
[Cd(H <sub>2</sub> L)Br <sub>2</sub> ]	3245, 3040, 2960	1618 1583	962	472 420

TABLE 3 : Result of antibacterial activity (1000 ppm).

Compound	P. aeruginosa	B. Cereus	S. aureus	E. Coli
HActtsc	+	++	++	++
Zn(Acttsc) <sub>2</sub>	++	++	+++	+++
Cu(Acttsc) <sub>2</sub>	++	++	++++	++
Co(Acttsc) <sub>2</sub> .2H <sub>2</sub> O	+++	+++	++++	+++
Pd(Acttsc) <sub>2</sub>	+++	++++	++++	+++
Mn(Acttsc) <sub>2</sub>	++	++	+++	++
Ni(Acttsc) <sub>2</sub> .2H <sub>2</sub> O	+++	+++	++	+++
Fe(Acttsc) <sub>2</sub> .2H <sub>2</sub> O	++	+++	+++	++
[Cu(HActtsc)Cl <sub>2</sub> ]	+++	+++	++++	++
[Cd(HActtsc)Cl <sub>2</sub> ]	++	+++	+++	++
Ciprofloxine	++++	++++	++++	++++

Most active +++++, highly active +++, moderately active ++, slightly active +

TABLE 4 : Analytical and physical data of complexes.

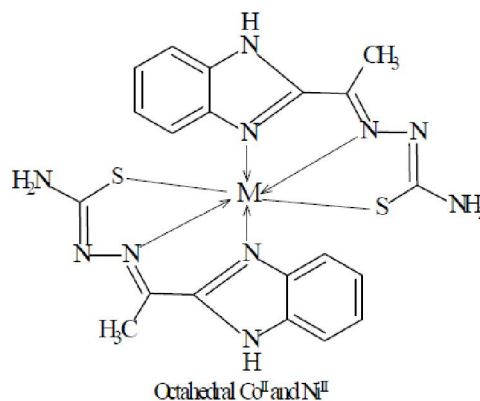
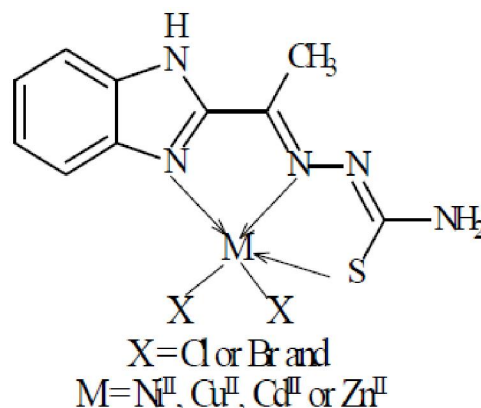
Compound		% Found (Cal)				
Colour		Metal	Nitrogen	Carbon	Hydrogen	Sulphur
[Cu(LH) <sub>2</sub> ]2H <sub>2</sub> O	Brownish Grey	11.41 (11.26)	24.68 (24.84)	42.31 (42.57)	4.41 (4.28)	11.11 (11.34)
[Ni(LH) <sub>2</sub> ] 2H <sub>2</sub> O	Brownish Yellow	10.61 (10.49)	24.92 (25.07)	42.66 (42.14)	4.38 (4.29)	11.33 (11.44)
[Co(LH) <sub>2</sub> ]	Reddish Brown	10.93 (11.27)	26.51 (26.77)	45.69 (45.93)	4.41 (4.22)	12.01 (12.26)
[Fe(LH) <sub>2</sub> ] 2H <sub>2</sub> O	Brown	9.88 (10.06)	25.31 (25.18)	43.41 (43.15)	4.52 (4.31)	11.11 (11.41)
[Mn(LH) <sub>2</sub> ]	Cream	10.37 (10.58)	27.01 (27.18)	46.01 (46.30)	4.41 (4.24)	11.92 (12.33)
[Zn(LH) <sub>2</sub> ]	Yellow	12.01 (12.33)	26.41 (26.61)	45.69 (45.37)	4.12 (3.87)	11.81 (12.09)
[Cd(LH) <sub>2</sub> ]	Yellow	19.41 (19.67)	24.01 (24.16)	41.71 (41.83)	3.86 (3.65)	11.47 (11.32)
PdL <sub>2</sub>	Orange	18.51 (18.66)	42.32 (42.11)	24.32 (24.55)	5.81 (3.57)	17.31 (17.21)
Pd(LH)Cl	Orange brown	28.31 (28.25)	32.32 (32.18)	18.66 (18.59)	2.73 (2.65)	8.36 (8.50)
Cu(LH)Cl <sub>2</sub>	Grey	17.17 (17.27)	32.38 (32.63)	19.11 (19.04)	2.83 (2.72)	8.73 (8.70)
Cd(LH)Cl <sub>2</sub>	Cream	26.63 (26.96)	28.71 (28.85)	16.93 (16.80)	2.61 (2.41)	7.76 (7.69)
Zn(LH)Cl <sub>2</sub>	White	17.48 (17.74)	32.33 (32.44)	18.72 (18.97)	2.91 (2.70)	8.76 (8.68)
Ni(LH)Cl <sub>2</sub>	Greenish-yellow	16.13 (16.23)	33.23 (33.07)	19.28 (19.29)	2.88 (2.77)	8.89 (8.81)
Cu(LH)Br <sub>2</sub>		13.72 (13.81)	26.33 (26.29)	15.41 (15.32)	2.33 (2.18)	7.00 (7.00)

The antibacterial activity of HActtsc and some of its complexes were screened by the agar disc diffusion method<sup>[26,27]</sup> against gram positive and gram negative bacteria. The results are summarized in TABLE 3.

As can be seen from data (TABLE 3) that in vitro antibacterial activity are persistent against microorganisms. The activity of complexes at 1000 ppm concentration are much larger compared to free ligand. The Pd<sup>II</sup>, Cu<sup>II</sup> and Co<sup>II</sup> complexes show higher activity than other complexes.

It has been found that antibacterial activity of ligand was insignificant (50 ppm) still the complexes display slight activity. The larger activity of coordinated ligand may be due to chelation effect as well as the decrease in polarization of the metal ion that can change the lipophilicity of complex, increasing the interacting capacity of bacteria. The activity was compared with ciprofloxine. The activity in each case for ligand and HActtsc complexes with metal was lower than ciprofloxine taken as reference.

The probable structure of bis chelates and dihalo complexes are shown in Figure 1, 2 and 3.

Figure 1 : Structure of [M(ActtSc)<sub>2</sub>] (Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup>).Figure 2 : Structure of five coordinated [M(HActtSc)X<sub>2</sub>].



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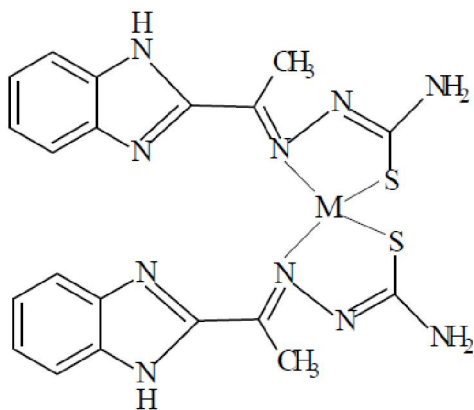


Figure 3 : Structure of four coordinated Zn<sup>II</sup>, Cd<sup>II</sup> and Pd<sup>II</sup> complexes [M(ActtSc)<sub>2</sub>].nH<sub>2</sub>O.

## CONCLUSION

Depending on the nature of metal and p<sup>H</sup> of medium, the HActtsc coordinate as both tridentate neutral or monobasic acidic ligand forming bond through N,N and S atom. In some cases of Zn (II) and Cd (II) bis chelate the ligand is probably bidentated and forms bond with N and deprotonated thiol 'S' only. The antibacterial activities of metal complexes were found higher than free ligand molecules.

## ACKNOWLEDGEMENT

Thanks are due to Head Chemistry Department of chemistry IIT Patna for recording i.r and electronic absorption spectra. Help rendered by biotechnology department of science college Patna is thankfully acknowledged for providing laboratory facility for screening of antibacterial activity.

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