Trade Science Inc.

April-June 2006 Volume 1 Issue 1-2

Inorganic CHEMISTRY

An Indian Journal

FULL PAPER

ICAIJ, 1(1-2), 2006 [24-31]

Synthesis And Structural Studies Of Transition Metal Complexes Derived From A Physiologically Active Monobasic Tridentate Ligand

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Received: 28th March, 2006
Accepted: 25th April, 2006

Web Publication Date : 15th May, 2006

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ABSTRACT

A new physiologically active tridentate ligand,2[1(2-hydroxy-1-naphthyl) methylideneamino]benzamide-H_2HNMAB has been synthesized. Oxovanadium(IV),Cr(III),Mn(II),Fe(III),Co(II),Ni(II),Cu(II)and Zn(II) complexes of the ligand have been prepared. The ligand is characterized by elemental analyses, infrared, UV, ^{1}H NMR and Mass spectral data and the metal chelates are characterized by elemental analyses,conductivity data, magnetic susceptibility measurements,infrared, ^{1}H NMR, UV-Vis-Near IR, ESR,AAS spectral data and TGA data. On the basis of the above data it is inferred that the ligand behaves as a monobasic tridentate ONO donor coordinating through the deprotonated phenolic oxygen ,oxygen of the amide carbonyl and nitrogen of the azomethine group. Oxovanadium(IV) complex is assigned a sulfate bridged dimeric square pyramidal geometry. Cr(III), Fe(III), Mn(II) and Co(II) complexes are proposed an octahedral geometry .Cu(II) and Ni(II) complexes are proposed with a square planar disposition. Zn(II) complex is proposed to a tetrahedral geometry.The ligand and the metal chelates were screened for their anti microbial activity against *S.aureus* and *E.Coli*, which are the gram +ve and gram –ve bacteria.

KEYWORDS

2[1(2-hydroxy-1-naphthyl) ethylideneamino]benzamide,
2-Hydroxy-1-naphthaldehyde;
2-Amino benzamide.

INTRODUCTION

Many transition metal complexes derived from various schiff base ligands were found to possess different physiological and biological activities such as antibacterial[1], antifungal[2], anticytotoxic[3], antitumor[4], anti insulin mimetic[5], chemotherapeutic[6], antituberculosis[7], antigastro intestinal infectious[8] and anti malarial[9]. 2-Hydroxy-1-naphthaldehyde[10,11] and 2-amino benzamide are potential chelating agents [12,13]. In view of the above applications, it is planned to synthesize the schiff base derived from 2-Hydroxy-1-naphthaldehyde and 2-amino benzamide and its various transition metal complexes.

EXPERIMENTAL

Materials and methods

2-Amino benzamide, 2-hydroxy-1-naphthaldehyde were purchased from Aldrich Chemical Company (USA). All the metal salts and other reagents used were of A R grade. Solvents like methanol, petroleum ether, ethanol, DMF, DMSO were purified before use.

Melting points of ligands and complexes were determined on Toshniwal hot stage melting point apparatus. C,H,N analysis was carried out using HERAEUS CHN rapid analyzer. Chloride was estimated by Mohr's method. Metal estimations were carried out by plasma emission spectrophotometer, Labtam Plasma scan-8410. Conductivity of the metal complexes were measured in DMSO and DMF solutions of 1x10^{-3} M solutions using Digisun digital conductivity meter model No:DL 909 having a dip type cell calibrated with KCl. Mass spectrum of the ligand was recorded on VG70-70H spectrophotometer. ^{1}H NMR spectra of the ligand and the Zn(II) complex were recorded on Jeol-GSX-440 MHz spectrophotometer. IR spectra of the ligand and metal complexes was recorded on Bruker IFS-66V FT IR spectrophotometer in the range 4000-400cm^{-1} as KBr pellet discs. UV-Vis-near IR spectra of the ligand and its metal complexes were recorded on a UV-Vis near IR Varian Cary 5E spectrophotometer. The EPR spectra were recorded at room temperature on EPR Vraian E-112 spectrophotometer in powder. The magnetic susceptibility measurements were carried out on a Faraday CAHN-7550-03 magnetic balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. The thermal analyses of the metal complexes were carried out on NETZSCH-TGA DTA-DSC instrument with a heating rate of 10^0C/min in dry air. The antimicrobial studies were done by disc diffusion method in a nutrient agar medium against two test organisms.

Synthesis of the ligand

While continuously stirring, 2-hydroxy-1-naphthaldehyde(0.05mole,8.6g) in 10 ml of methanol was added to 2-amino benzamide (0.05mol,6.8g) in 10 ml of methanol. The mixture is stirred until an orange yellow compound separated out, which was filtered by suction,washed successively with methanol and pet.ether(60-80^0)(yield 80%) (m.p.199^0C). It was recrystallized from methanol-DMF (1:1) solvent.

Synthesis of metal complexes

To the methanolic solution (10ml) of metal chloride (1mmol) [Cr(III),0.266g;Mn(II),0.198g; Fe(III), 0.165g, Co(II),0.238g ;Ni(II),0.237g; Cu(II),0.172g; Zn(II).0.136g], hot methanolic(10ml)suspension of 2[1(2-hydroxy-1-naphthyl)methylidene amino] benzamide (H_2-HNMAB) was added in small proportions. The ligand dissolves completely in presence of the metal ion. A clear solution was formed. The pH of the mixture solution was adjusted to 5-6 using methanolic ammonia solution. The mixture solution was refluxed for 4hr., when the metal chelates separated. They were filtered in hot condition and washed successively with methanol and pet ether(60-80^0) and dried in vaccum. In case of Oxovanadium (IV) complex (1mmol,0.163g) vanadyl sulfate was dissolved in aqueous methanolic medium and the same procedure was adopted to isolate the complex. The purity of the complexes was tested by TLC using different mixtures of solvents. Oxovanadium(IV) yield, 70%;Cr(III)(60%), Mn(II), (68%), Fe(III), (50%), Co(II),(65%), Ni(II) (50%); Cu(II), (75%), Zn(II), (50%).

RESULTS AND DISCUSSION

The ligand and the complexes are soluble in 1,4 dioxane, DMF and DMSO. They are stable to air and moisture. The conductance measurements of $1x10^{-3}$ M solutions of complexes in DMSO reveal that all the complexes are non electrolytes. The chloride ion present in Cr(III), Fe(III) and Zn(II) complexes is non ionisable and occupy the inner coordination sphere. The elemental analyses show that the metal to ligand ratio is found to be 1:1 in all the metal chelates. The ligand H_2 HNMAB is orange red. The mass spectral data is in agreement with the analytical data, corresponding to the molecular formula $C_{18}H_{14}N_2O_2$. It shows prominent m/z peaks at 169,143,115,105 and 91 corresponding to the following fragmentation pattern(Figure 1).

The ^{1}H NMR spectrum of H_2HNMAB was recorded in DMSO-d_6. It shows a sharp signal at δ9.4(s) which is assignable (CH=N) to azomethine proton. The C_4-H of naphthalene moiety is identified at δ8.4(d). A multiplet observed at δ7.2-8.0 is due to the protons at C_3',C_4',C_5',C_6',C_7,C_8 and proton of amide. The doublet signal observed at δ6.85 is assigned to proton at C_3. The integral ratio of the protons is in agreement with the expected structure of the ligand[14].

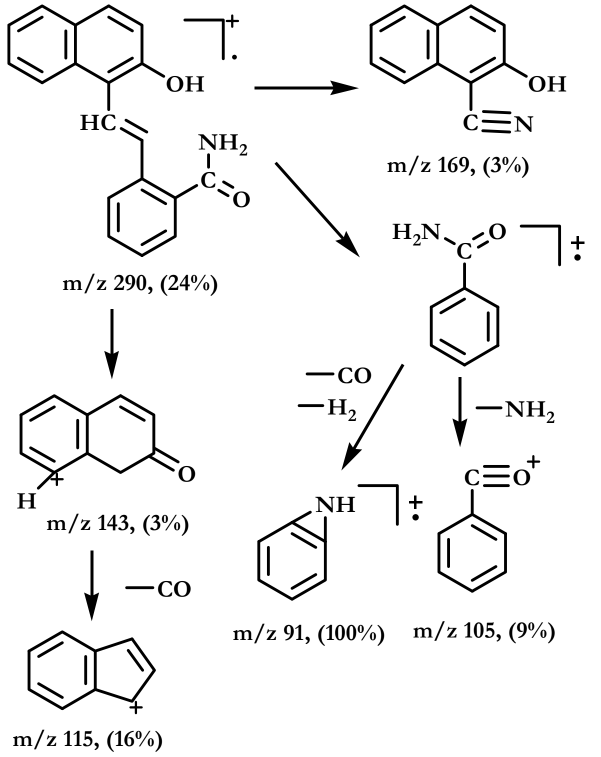

Figure 1: Mass fragmentation of H_2–HNMAB

The electronic spectrum shows a band at 386nm (25,906 cm^{-1}), which is assignable to O=C-NH_2 chromophore of the ligand. A broad multiple band of high intensity observed at 442-480nm (22624-20830 cm^{-1}) is attributed to azomethine chromophore. These bands indicate n→π and π* transitions of azomethine and amide chromophores. A band which appears at 318nm (31446 cm^{-1}) may contain characteristic π→π* transition of benzonoid moiety[15].

The infrared spectrum of the ligand was recorded in KBr discs. It shows medium intensity bands at 3385 and 3170 cm^{-1} which are attributed respectively to νNH_2 and νOH IR bands. The strong intense band observed at 1665 $cm^{-1}$is assignable to ν C=O(amide) carbonyl. The sharp band observed at 1618 $cm^{-1}$is attributable to νC=N(azomethine). The band at 1350cm^{-1}corresponds to νC-O(phenolic). In the IR spectra of all the complexes the IR spectral band due to νNH_2 which was at 3385 cm^{-1} undergoes an upward shift to an extent of 25 cm^{-1} and appears at 3410 cm^{-1} and the ν C=O(amide) band at 1665 cm^{-1} undergo a negative shift and appears at 1540 cm^{-1}. These transformations show that the ν C=O(amide) coordinates through the carbonyl oxygen and as a result the νNH_2 at 3385 cm^{-1} undergoes an upward shift. If the nitrogen of νNH_2 of amide coordinates the νNH_2 would have undergone a downward shift and ν C=O(amide) would have undergone an upward shift. νC=N(azomethine) undergoes a negative shift to the extent of 60cm^{-1}, in the IR spectra of all the complexes which supports the coordination of

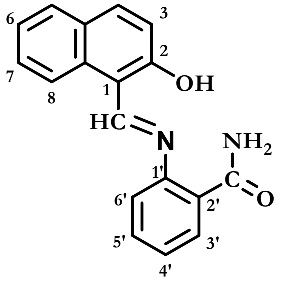

Figure 2: Structure of H_2–HNMAB

nitrogen of azomethine group in complexation[16]. In the spectra of all the complexes, the νC-O(phenolic) which was at 1350cm^{-1} in the free ligand undergoes an upward shift by 20-30cm^{-1}. This is supported by the disappearance of free ligand band at 3170cm^{-1}, which is due to νOH. This band is absent in the spectra of all the complexes. This shows that the phenolic OH undergoes deprotonation with subsequent coordination of phenolic oxygen in complexation[17]. The ligand is behaving as a mono basic tridentate ligand with O:N:O donor sequence. In the oxovanadium (IV) complex the band observed at 973cm^{-1} is due to ν V=O and the new non ligand bands observed at 1160,1120,1110 and 1000 cm^{-1} are due to bidentate coordination of oxygens of sulfate, proving that the complex is a sulfate bridged dimeric complex[18]. New non ligand bands observed at 400-600 cm^{-1} are due to ν M-N and ν M-O bonds. The IR spectra of Cr(III) and Fe(III) complexes show a broad trough at 3400-3000cm^{-1} which is due to νOH[19]. This indicates the presence of coordinated water molecules in these complexes. The presence of the coordinated water is further supported by the new non ligand bands in the region 950-980 cm^{-1} and 645-570 cm^{-1} which are due to rocking and wagging modes of water respectively[20]. In the spectra of Cr(III), Fe(III) and Zn(II) complexes new non ligand bands observed at 330, 278 and 260 cm^{-1} are ascribed to ν M-Cl bands respectively to these complexes[21].

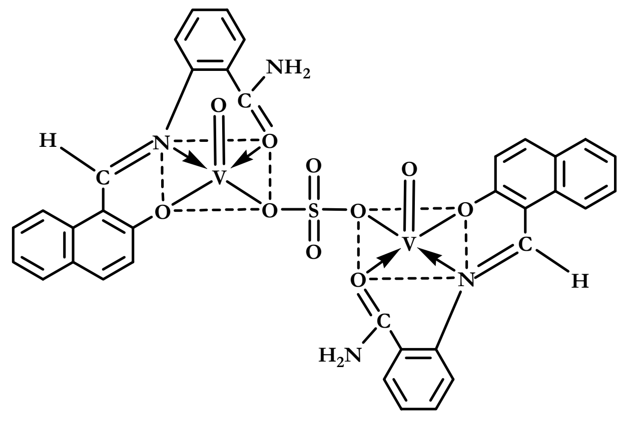

Figure 3: VO(II) complex

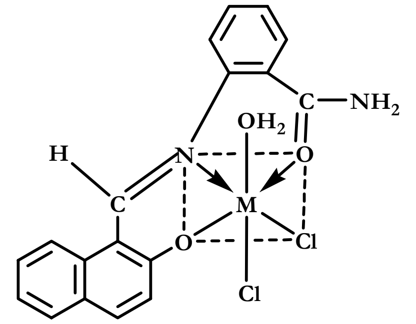

Figure 4: Structure of complexes M=Cr(III) and Fe(III)

Magnetic susceptibility measurements

The oxovanadium(IV) complex shows a magnetic moment value of 1.9 B.M., which is in conformity with the single unpaired electron in this complex[22]. The magnetic moment of Cr(III) complex is 3.95 B.M., which is in agreement with the spin only magnetic moment of the complex in an octahedral geometry[23]. The Mn(II) complex exhibits a magnetic moment value of 5.98 B.M.It is in good agreement with the proposed high spin octahedral geometry for this complex[24]. The Fe(III) complex shows a magnetic moment value of 6.0B.M., which is well within the range that is expected for a high spin octahedral Fe(III) complex[25]. The Co(II) complex shows a magnetic moment value of 4.26 B.M.This is in conformity with the proposed high spin octahedral complex[26]. The Ni(II) complex exhibits diamagnetism. This shows its square planar disposition[27]. The Cu(II) complex shows a magnetic moment value of 1.9 B.M., which is in agreement with its spin only magnetic moment with one unpaired electron[28].

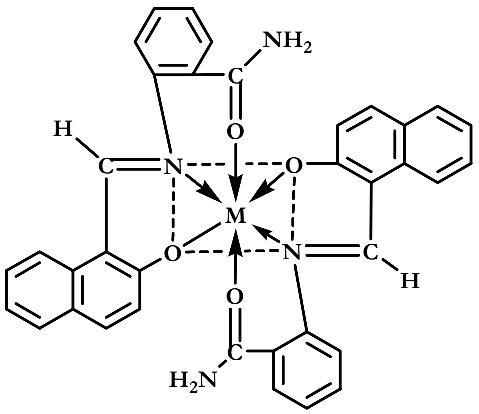

Figure 5: Structure of complexes M=Mn(II) and Co(II)

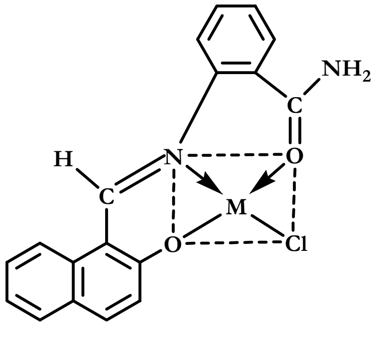

Figure 6: Structure of complexes M=Cu(II) and Ni(II)

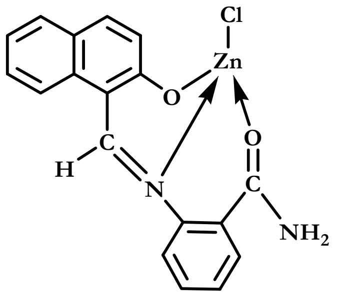

Figure 7: Zn (II) Complex

Electronic spectra

The UV-Vis spectra of the free ligand (H_2 HNMAB) undergoes modification and transformation in its band structure in the range 386-480 nm. The intensities of the bands increase upon complexation. This reveals the involvement of amide and azomethine chromophore in metal binding process. In addition the complexes show characteristic d-d transitions, which are assignable to various electronic transitions. These are consistent with proposed geometries.

The electronic spectrum of oxovanadium(IV) complex shows three bands at 13,300;16,000 and 24,666 cm^{-1} which are assignable to $^2B_2 \rightarrow {}^2E$; $^2B_2 \rightarrow {}^2B_1$; $^2B_2 \rightarrow {}^2A_1$ transitions respectively in a square pyramidal geometry[29]. The UV-Vis spectrum of Cr(III) complex shows three electronic transitions at 17851, 23980 and 26363 cm^{-1} which are ascribed to $^4A_{2g} \rightarrow {}^4T_{2g}$; $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) transitions respectively[30]. These transitions reveal that the Cr(III) complex is in a high spin octahedral geometry. The electronic spectra of Mn(II) and Fe(III) complexes show respectively low intensity bands in the range 9100-30600 $cm^{-1}$and high intensity bands in the range 33000-31200 cm^{-1}. The low intensity bands are assigned to several doubly forbidden transitions from $^6A_{1g} \rightarrow {}^4E_g$; $^6A_{1g} \rightarrow {}^4A_{1g}$ and $^6A_{1g} \rightarrow {}^4G$. On the basis of various physico chemical data the Mn(II) complex is assigned an octahedral geometry with a 1:2 metal to ligand ratio. This is very well supported by the conductance measurements and elemental analyses. The Fe(III) comlpex is proposed a high spin octahedral geometry with a 1:1 metal to ligand ratio[31]. This is also supported by the other data such as IR spectral data, elemental analyses, conductance measurements, magnetic moment and metal estimations by AAS. The appearance of ν M-Cl in the far IR spectra also support its geometry. The UV-Vis near IR spectrum of the Co(II) complex shows spectral bands at 9180, 16890 and 23640 cm^{-1} which are interpreted respectively to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$. The ratio of ν_2/ν_1 is 1.83 and this supports the octahedral geometry[32] proposed. Various physico chemical studies also reveal that the metal to ligand ratio in this complex is 1:2. The electronic spectrum of Ni(II) complex exhibit distinct peaks at 22600 and 31150 cm^{-1} which are assigned respectively to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ in a square planar geometry[33]. The Cu(II) complex shows three transitions in the range 13210,15440 and 21739 cm^{-1} which are assignable to $^2B_1 \rightarrow {}^2B_2$; $^2B_1 \rightarrow {}^2A_2$ and $^2B_1 \rightarrow {}^2E$ transitions in a square planar geometry[34]. The Zn(II) complex shows no electronic transitions and it is proposed a tetrahedral geometry[35].

^1H NMR spectrum of Zn(II) complex was recorded in DMSO-d_6. The spectrum clearly indicates the complexation of the ligand with Zn((II). The azomethine protons shifts to down field to δ10.10 compared to its position in the free ligand at δ9.4.This confirms the coordination of nitrogen of azomethine group in complexation. The doublet due to C_4-H in the free ligand at δ 8.4 shifts to down field at δ 8.8 .The multiplet of free ligand observed at δ 7.2-8.0 shifts to upfield to δ 6.6-8.0 with the merger of the signal at δ 6.85 of C_3-H.This shows that the extended conjugation in the chelated ring is resulting in metal ligand coordination. On the basis of IR, analytical, conductance, ^{1}H NMR data it was proposed a tetrahedral geometry[34] along with a Cl^- coordinating in the fourth position.

ESR Spectra

The ESR spectrum of oxovanadium(IV) complex was recorded at room temperature as powder. It shows a single intense signal with a g_{av} value of 2.057. It is consistent with the proposed square pyramidal geometry for this complex[29].

The ESR spectrum of Cu(II) complex shows a single broad signal. It indicates that the proposed square planar geometry is valid[34]. The g_{av} value is 2.135.

CONCLUSION

The ligand H_2-HNMAB acts as a monobasic tridentate ONO donor coordinating through the deprotonated phenolic oxygen, oxygen of νC=O (amide) and nitrogen of azomethine group. On the basis of analytical, conductance,thermal,spectral and magnetic data, the oxovanadium(IV) complex is assigned a geometry of sulfate bridged square pyramidal, Cr(III), Fe(III) complexes possess an octahedral geometry with a metal to ligand ratio of 1:1.In addition they also possess two water molecules and one Cl^- coordinated to the metal ion.Mn(II) and Co(II) complexes possess an octahedral geometry with each metal ion coordinating with 2 moles of the ligand. The Ni(II) and Cu(II) complexes possess a 1:1 metal to ligand ratio with a Cl^- ion occupying the fourth coordination position.

ANTI MICROBIAL STUDIES

The anti microbial studies were carried out by Disc diffusion Method[36]. The medium used was Nutrient Agar. Peptone 10g, Meat extract 10g, NaCl 5g and distilled water 1 lit were used.

Procedure

The various constituents required for preparing nutrient agar broth were sterilized at 15 lbs for 15min. Before neutralizing to pH 7.2, the nutrient agar was added with 1.5% agar agar and it was sterilized later. The medium was sterilized at 121^{0}C by autoclaving it for 15min. It was cooled to 55^{0}C and 20 ml of it was poured into each of the 4” sterile petri plates. The plates were kept on a flat surface and were allowed to solidify. 18hr old culture colonies were taken

TABLE 1: Analytical and conductivity data of the ligand and complexes

Ligand/Complex	Found (Calcd) %						Λ_M
	Metal	Carbon	Hydrogen	Nitrogen	Sulphur	Chloride	mhos cm^2 mol^{-1}
H_2HNMAB [$C_{18}H_{14}N_2O_2$]	--	74.48 (74.45)	4.83 (4.81)	9.65 (9.68)	--	--	--
[$VOC_{18}H_{13}N_2O_2]_2SO_4$	12.46 (12.44)	52.71 (52.68)	3.21 (3.22)	10.27 (10.30)	3.88 (3.90)	--	6.0
[$CrC_{18}H_{15}N_2O_3Cl_2$]	12.64 (12.60)	52.22 (52.36)	4.22 (4.12)	6.89 (6.80)	--	8.66 (8.60)	17.0
[$MnC_{36}H_{26}N_4O_4$]	8.71 (8.68)	68.26 (68.24)	4.15 (4.40)	8.88 (8.84)	--	--	7.0
[$FeC_{18}H_{15}N_2O_3Cl_2$]	13.44 (13.41)	51.94 (51.88)	4.12 (4.08)	6.77 (6.72)	--	8.55 (8.52)	17.0
[$CoC_{36}H_{26}N_4O_4$]	935 (9.25)	67.88 (67.81)	4.10 (4.08)	8.82 (8.79)	--	--	5.0
[$NiC_{18}H_{13}N_2O_2Cl$]	15.36 (15.32)	56.51 (56.40)	3.43 (3.40)	7.33 (7.31)	--	9.28 (9.26)	5.0
[$CuC_{18}H_{13}N_2O_2Cl$]	16.63 (16.59)	55.71 (55.67)	3.39 (3.35)	7.26 (7.21)	--	9.30 (9.14)	6.0
[$ZnC_{18}H_{13}N_2O_2Cl$]	16.87 (16.77)	55.45 (55.40)	3.36 (3.33)	7.21 (7.18)	--	9.11 (9.09)	18.0

and were spread over the nutrient agar plates.1ml of the culture was placed on to each of the nutrient agar plates by a sterile forceps and it was spreaded. Filter paper discs of 6mm diameter were prepared and were autoclaved for 15 min at 121^{0}C.The ligand and metal complexes were dissolved in DMSO in concentrations of 200, 100 and 50 μg /ml.The sterile paper discs were soaked. The paper discs were allowed to dried. The discs were placed at a distance of 2.5 cm from each other on the surface of the inoculated media. The plates were kept in the refrigerator for 1hr. to allow the diffusion of the compound into the medium and they were later on placed in the incubator at 37^{0}C for 24hrs.The results of incubation of the bacterial growth with respect to the blank per assay broth were noted after 24 hrs.The presence of the zone of inhibition around a particular disc indicates the anti microbial activity of the compound. The activity was tested on two bacteria., i.e., *Staphylococcus.aureus* and *Escherichia.coli*, respectively the gram +ve and gram –ve bacteria. The results are tabulated.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry for providing facilities, recording IR spectra and Magnetic Susceptibility measurements. The authors are also indebted to the Head, SAIF, IIT, Chennai and the Director, IICT for recording spectra. The authors are thankful to Dr. Gopal Reddy, Department of Microbiology, Osmania University and his group for assisting in screening the compounds against the bacteria.

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