WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 5.045
Volume 3, Issue 7, 798-806. Research Article ISSN 2277 –7105

MICROWAVE ASSISTED SYNTHESIS AND SPECTRAL CHARACTERIZATION OF BIOLOGICALLY ACTIVE Hg(II) COMPLEX WITH 2-AMINOBENZONITRILE AND OCTANOATE ION

R.Govindharaju[*1], S. Balasubramaniyan[1], K. Rajasekar[1] & T. Ramachandramoorthy[2]

[1]Department of Chemistry, Govt. Arts College, Ariyalur-621 713, Tamil nadu, India.

[2]PG & Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli- 620 017, Tamil nadu, India.

Article Received on
13 July 2014,

Revised on 07 August 2014,
Accepted on 02 Sept 2014

***Correspondence for Author**
R. Govindharaju
Department of Chemistry,
Govt. Arts College,
Ariyalur 621 713, Tamil nadu, India

ABSTRACT

Microwave irradiation was used for the preparation of Hg(II) complex with 2-Aminobenzonitrile (ABN) and octanoate ion as ligands. The prepared complex was characterized by elemental analysis, metal estimation, electrical conductivity, UV-Visible, IR, Far-IR and NMR spectral studies. The antibacterial and antifungal activities of both ABN and Octanoate ligands and the Hg(II) complex was carried out by disc diffusion method at various concentrations. From the analytical data the molecular formulae of the complex was arrived. The geometry of the complex from the UV-Visible spectrum, ligand entry and metal-linkage atom from IR and Far-IR spectra was arrived. The antibacterial and antifungal activity of the complex is higher than that of the free ABN and Octanoate ion.

KEYWORDS: Hg(II)complex, 2-Aminobenzonitrile, Octanoate, Microwave, Antibacterial, Antifungal

INTRODUCTION

Microwave irradiation nowadays is an accepted tool for accelerating the organic and inorganic reactions. It leads to the higher reaction selectivity and utilization of the expansive reagents. In addition to providing an eco-friendly "green chemistry" approach to the reaction, it is free of environmental impacts.[1-4] The application of microwave irradiation towards the acceleration of a wide range of organic and inorganic reactions, has received considerable attention. It is also allows a greener approach.[5-8] The aromatic nitriles have a wide variety of applications in pharmaceuticals, pesticide and dye industries.[9,10] Among the

aminobenzonitrile 2-Aminobenzonitrile (ABN) is used for the induction of nitrilase activity in Arthrobacter, radio protective agent and starting materials for the synthesis of biologically active compounds.[11-14] The ABN can coordinate to the metal ions through different modes *viz.*, monodentate, bidentate or bridging. The present work aims at the microwave irradiated synthesis, analytical, spectral and biological characterization of Hg(II) complex with 2-aminobenzonitrile and octanoate ion as ligands. The complex was screened for antibacterial and antifungal activities and the results were discussed.

MATERIALS AND METHODS

2-aminobenzonitrile and sodium octanoate were purchased from Sigma Aldrich Company. Mercury chloride, DMSO, DMF, methanol, ethanol were of Anala R grade, and used as such without further purification.

INSTRUMENTS

The elemental analysis of the complexes was carried out by using (Thermo Finnegan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The electrical conductivity measurements were conducted using 10^{-3} solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge (model number-304) at 30°C. The UV spectra of Hg(II) complex was recorded on Varian, Cary 5000 model UV Spectrophotometer. The IR spectra of the complex was recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in 4000-400 cm^{-1} range with KBr pellet technique. The Far-IR Spectra of the complex was recorded by Bruker 3000, FT IR Spectrometer. The NMR spectra were recorded by500 MHz (Bruker AV III). The antimicrobial and antifungal activities of the ligands 2-aminobenzonitrile, octanoate and their complex was done by disc diffusion method.

PREPARATION OF COMPLEX

(i) Preparation of Hg(II) Complex

0.44g (3.64 mmol) of ABN in ethanol and 1.21g (7.23 mmol) of sodium octanoate in ethanol were added to the mercury chloride 1.00g (3.64 mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. A pale yellow colour complex was precipitated (yield: 55.16%).

RESULTS AND DISCUSSION

Elemental Analysis and Metal Estimation

The elemental analysis and metal estimation of the complex leads to the general formula $[Hg(ABN)(OC)_2]$ where ABN= 2-aminobenzonitrile and OC= octanoate. The elemental analytical data were in good agreement with the molecular formula arrived for the complex.

Electrical Conductivity

The electrical conductivity of the 10^{-3} M complex solution in DMSO was measured. The values at 59.46 $ohm^{-1}cm^2mol^{-1}$ which is quite lower than that expected for an electrolyte and reveal their non-electrolyte nature (1:0 type) and there is no ion present outside the coordination sphere.[15]

Table-1 Analytical and EC Values of the Complex.

Complex	EC ($ohm^{-1}cm^2mol^{-1}$)	%H	%C	%N	%M
$[Hg(ABN)(OC)_2]$	59.46	5.99 (5.97)	45.65 (45.68)	4.62 (4.65)	33.14 (33.17)

UV Spectra

The diamagnetic Hg(II) complex did not show any d-d transition and its spectrum is dominated only by a charge transfer transition (CT-band). The CT-band at 250 nm is assigned **pseudotetrahedral** geometry for the complex.[16]

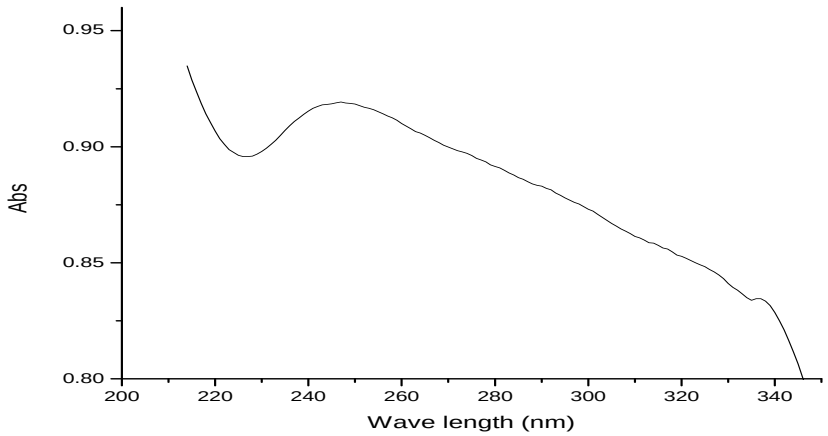

Fig.1 UV Spectrum of Hg(II) Complex

IR And Far-IR Spectrum

In the IR spectrum of free 2- aminobenzonitrile exhibit strong bands at 3453cm^{-1} and 3366 cm^{-1} respectively, indicating the asymmetric and symmetric stretching frequencies of NH_2

group. These bands are broadened in the complex (3464 cm^{-1}) which indicates the amino nitrogen atom as one of the coordinating groups. The ν (C≡N) stretching frequency at 2206 cm^{-1} in free ABN gets shifted to higher wave numbers, 2216 cm^{-1} in complex which indicate that the nitrogen atom of the (-C≡N) is another coordinating group to the metal ions. In free octanoate the ν(C-O) stretching at 1409 cm^{-1} get shifted to the frequencies 1456 cm^{-1} in complex which indicate the monodentate coordination of the Octanoate ion through oxygen atom. All above observations confirmed the entry of both 2- aminobenzonitrile and octanoate ion in to the coordination sphere of the metal ions.[17,18]

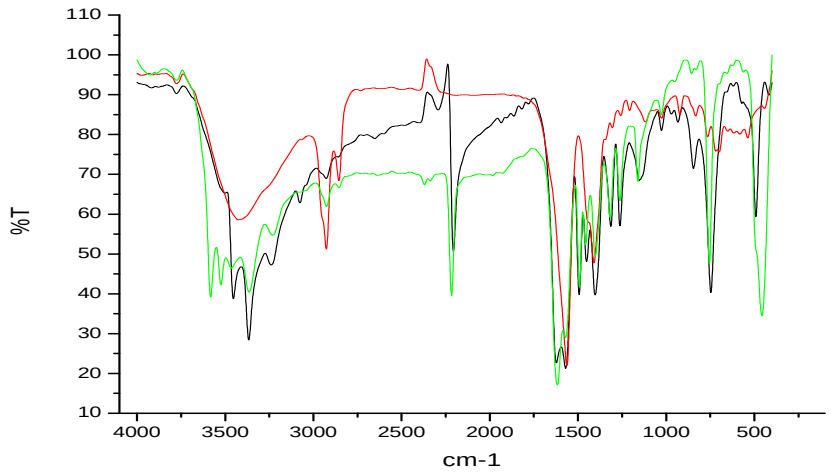

Fig.2 IR Spectra Of 2-Aminobenzonitrile, Sodium Octanoate And $[Hg(ABN)(OC)_2]$

From far–IR spectra, the metal-ligating atom linkage may be assigned. In Hg(II) complex, the bands at 240 cm^{-1}, 494 cm^{-1} and 445 cm^{-1} correspond to δ(M-CN), δ(M-N) and δ(M-O) coordination respectively which indicates the bidentate nature of 2-aminobenzonitrile and the monodentate nature of octanoate ion.[19]

^{1}H And ^{13}C NMR Spectra of Ligands And Hg(II) Complex

The ^{1}H-NMR analysis of the ligands (ABN and Octanoate) and their Hg(II) complex were carried out in DMSO-d6 solvent tetramethylsilane used as an internal reference. The spectrum of ligand ABN shows the peaks at 3.46 ppm and at 6.33-7.50 ppm are assigned the amino and aromatic protons of ABN. On coordination the amino nitrogen gets shifted to downfield at 3.24 ppm which indicate the amino nitrogen is one of the coordinating group. In ^{13}C-NMR the C-NH_2 at 152.04 ppm shifted to up field at 152.13 ppm which also confirmed the coordinating group.[20-22]

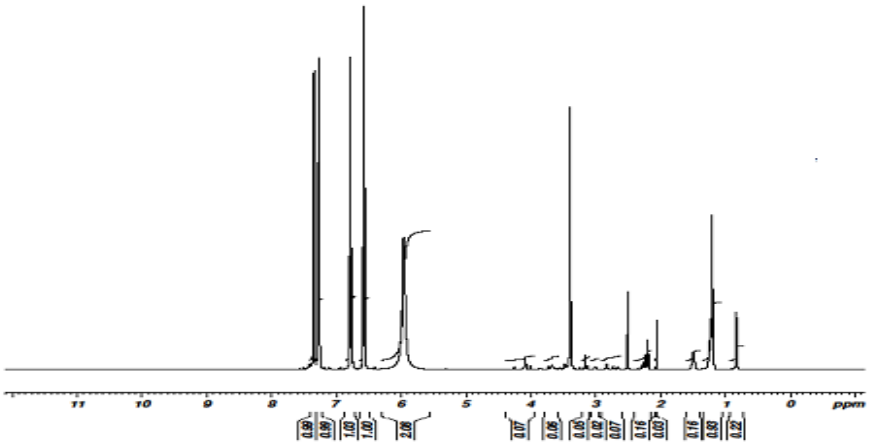

Fig.3 ^{1}H-NMR Spectrum of Hg(II) Complex

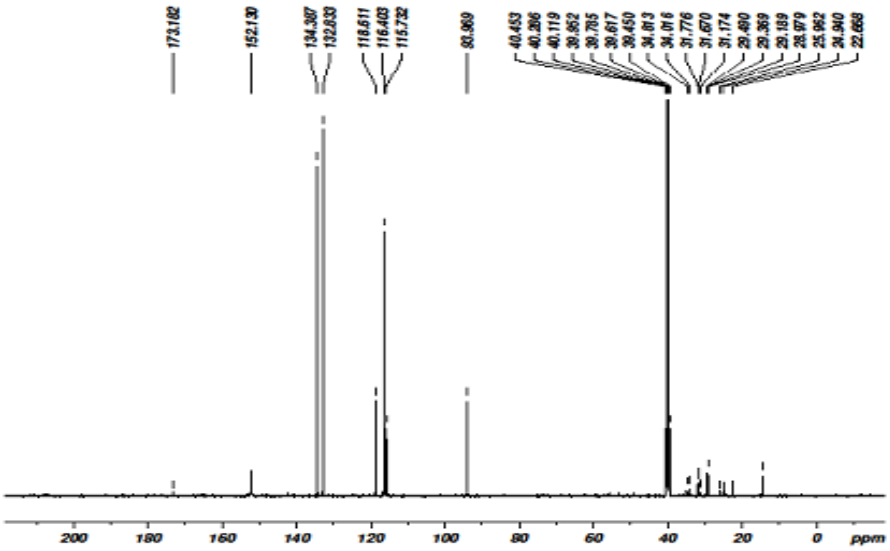

Fig.4 ^{13}C-NMR Spectrum of Hg(II) Complex

Antimicrobial Activities

The antibacterial and antifungal activities of the ligands 2-aminobenzonitrile, sodium Octanoate and the Hg(II) complex were determined by disc diffusion method using following microorganisms *viz., E-coli, Enterobacter, Klebsiella, Staphylococcus aureus, Streptococci, Salmonella typhi, P.aeruginosa, C.albicans, Aspergillus Flavus* and *Aspergillus niger*. The complex has potent active as compared to the free ligands at various concentrations for all the tested microorganisms except *S.aureus and Klebsiella*. Such increase in activity may be due to the nature of ligands and structure of the complexes. [23,24]

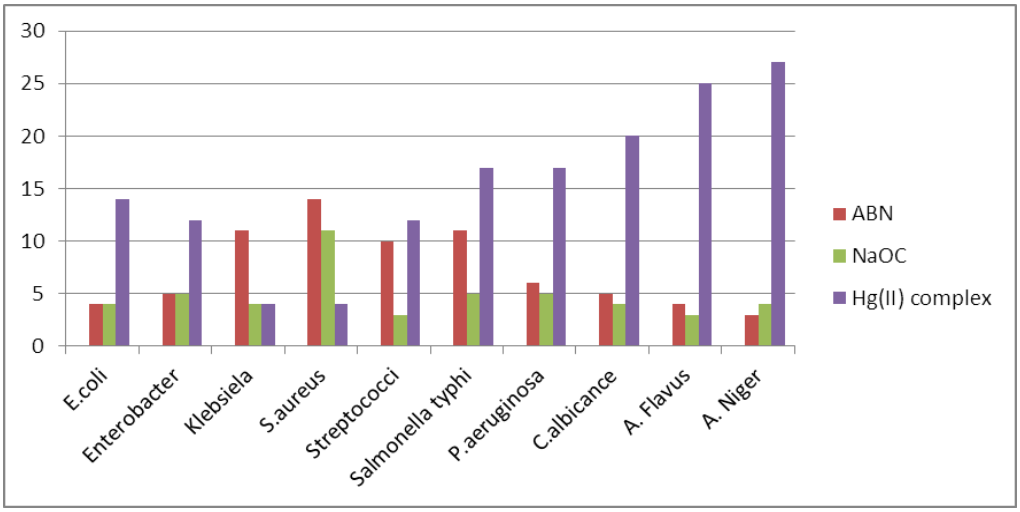

Fig.5 Zone of inhibition for ABN, NaOC and Hg(II) complex at 50µg/ml

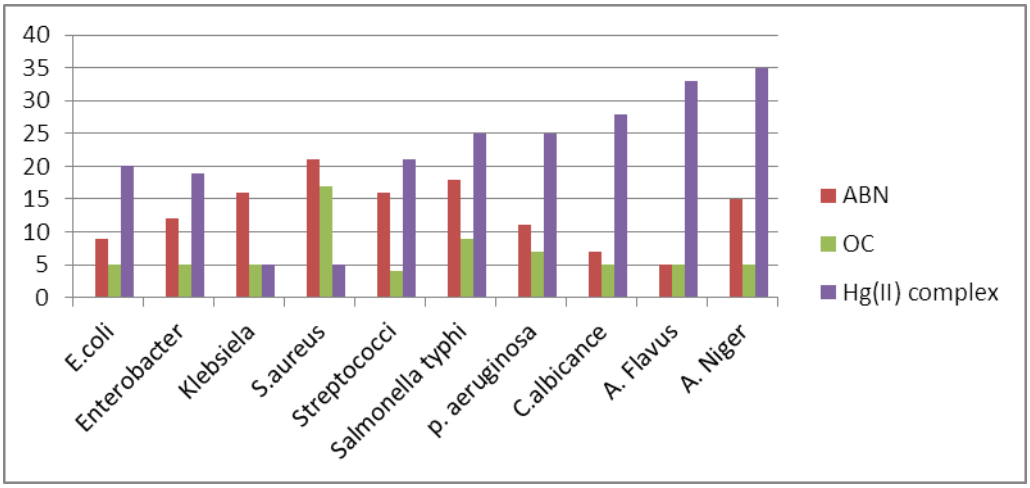

Fig.6 Zone Of Inhibition For ABN, NaOC And Hg(II) Complex At 100µg/ml

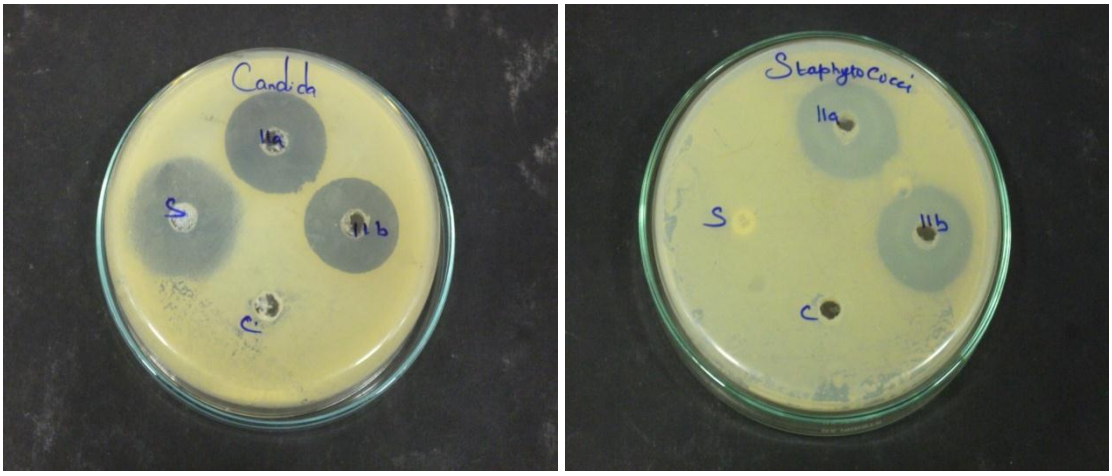

Fig.7 Antimicrobial Activities of ABN, NaOC And Hg(II) Complex

CONCLUSION

In this paper the microwave assisted synthesis of 2-aminobenzonitrile and octanoate complex of Hg(II) is given. The structural features of the complex are confirmed by elemental analysis, metal estimation, electrical conductivity and spectral studies. The complex is non-electrolyte and antibacterial and antifungal activity of the complex is higher than the free ABN & Octanoate ion.

ACKNOWLEDGEMENT

The authors thank the Principal, Government Arts College, Ariyalur for the facilities provided to carry out the work; they also thank to the Head and Staff members of STIC, Cochin, SAIF Mumbai and Chennai and St. Joseph's College, Tiruchirappalli for providing instrumental data.

REFERENCES

1. Mohammed Fakruddin Ali Ahmed, Mahammadyunu V. Microwave Synthesis and Antimicrobial Activity of Some Copper (II), Cobalt (II), Nickel (II) and Chromium (III) Complexes with Schiff Base 2,6-pyridinedicarboxaldehyde-Thiosemicarbazone. Oriental Journal of Chemistry, 2014; 30(1): 111-117.
2. Kappe Co, Loupy A. "microwave inorganic synthesis" (wiley-VCH, Weinheim) 2002, pp.405.
3. Kappe CO. High Speed Cobinatorial Synthesis utilizing microwave irradiation. Curr.opinion Chem. Bio, 2002; 6: 314-320.
4. Dandida A, Arya K, Sati M, Gautam S. Microwave Assisted Green Chemical Synthesis of Novel Spiro[indole-pyrido thiazine] a system reluctant to be formed under thermal conditions. Tetrahedron, 2004; 60: 5253-5258.
5. Gedye R, Smith F, Westaway K, Ali H, baldisera l, Laberge L, Rousell J. The use of Microwave Oven for Rabid Organic Synthesis. Tetrahedrn Lett. 1986; 27: 279-282.
6. Caddick S. Microwave Assisted Organic Reactions. Tetrahedron, 1994: 50: 10403-10432.
7. Mingos DMP, Baghurst DR. Tilden Lecture, Applications of Microwave Dielctric Heating Effects to Synthetic problems in Chemistry. Chem.Rev. 1991;1-47.
8. Whitakkar AG, Mingos DMP. The Application of Microwave Heating to Chemical Synthesis. J.Microwave Power & Electromag.Energy. 1994; 29: 195-219.

9. Friedrich K, Wallenfels K. "The chemistry of Cyano group", 2nd Edn., Zvirappor Interscience Publisher, London, 1970.
10. Sun D, Liu FJ, Hao HJ, Li YH, Haung RB, Zheng LS, Six low – dimensional Silver (I) coordination complexes derived from 2-aminobenzonitrile and carboxylates. Inorg. Chim. Acta, 2012; 387: 271-276.
11. Taylor EC, Knopf RI, Borror, The dimerisation of 2-amino-5-nitrobenzonitrile. J.Am.Chem.Soc, 1960; 82: 3152-3157.
12. Segarra V, Crespo MI, Pujol F, Belata J, Domonech T Miralpix M, Palacios JM, Castro A, Martinez A, Phospodiesterase inhibitory properties of losartane.Design and synthesis of new lead compounds. Bio. Org. Med. Chem, 1998; 8: 505-510.
13. Kabri Y, Gellis A, Vanelle P, Microwave-assisted Synthesis in aqueous medium of new quinozoline derivatives as anticancer agent precursors. Green. Chem, 2009; 11: 201-208.
14. Patil YP, Tambade PJ, Parghi KD, Jeyaram RV, Bhanage BM. Synthesis of quinozoline-2,4(1H,3H)-Diones from Carbon dioxide and 2-aminobenzonitrile using MgO/ZrO as a solid base catalyst. Catal.Lett, 2009; 133: 201-208.
15. Geary WJ, The Use of Conductivity Measurements in Organic Solvents for the Characterization of Coordination Compounds. Coordi.Chem.Rew, 1971; 7,1, 81-122.
16. Mangaiyarkkarasi P and Arul Antony S, Synthesis, Characterization And Biological Significance of Some Novel Schiff Base Transition Metal Complexes Derived from 4-Aminoantipyrine And Dihydropyrimidine of Vanillin, Journal of Applicable Chemistry, 2014; 3(3): 997-1006.
17. Abbas Noor Al, Shareefi, SalihHadiKadhim and Waleed Abbas Jawad, Journal of Applicable Chemistry, 2013; 2(3): 438-446.
18. Rao CNR, Ferraro JR. Spectroscopy in Inorganic Chemistry. Academics Press, New York, 1970; 10.
19. Nakamoto K, Infrared and Raman Spectra of Inorganic Coordination Compounds, III Edition. (Wiley, NewYork), 1997.
20. Kulkarni A D, Patil S A, Badami P S. Electro Chemical Properties of some transition metal complexes: synthesis characterization and in-vitro antimicrobial studies of Co(II), Ni(II) Cu(II), Mn(II) and Fe(III) complexes. Int J.Electrochem Sci. 2009; 4: 717-729.
21. Afaf H. E, Fahmy H H, Ali Abdelwahed S H. Synthesis and Antimicrobial Activity of Some New Benzimidazole Derivative. Molecules. 2000; 5: 1429–1438.

22. Rajasekar K and Ramachandramoorthy T, Synthesis, Spectral Characterization and Biological Activities of Cr(III), Co(II) and Cd(II) with 4-aminoantipyrine and thiocyanate ion as ligands, Int J Pharm Bio Sci, 2013; 4(2): 271 – 276.
23. Jian L, Tingting L , Sulan C, W. Xin, L. Lei and Yongmei , W. Synthesis, structure and biological activity of Co(II) and Cu(II) complexes of Valline-derived Schiff bases. *J. Inorg. Biochem., 2*006; 100(11): 1888-1896.
24. Abou-Melha KS and Faruk H. Bimetallic Complexes of Schiff Base bis-[4-hydroxy cuomarin-3-yl]-N, N-thiocarbohydrazone as a potentially Dibasic penta dentate ligand. Synthesis, Spectral and Antimicrobial Properties. *Iran. Chem. Soc*, 2008; 5(1): 122-134.