



SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF FURAN-2-CARBOXALDEHYDE SCHIFF BASE Sn (II) AND Hg (II) COMPLEXES

K.Rajesh^{*1} and D.Ramachandiran¹

^{*1}Department of Chemistry, Arignar Anna Govt. Arts & College, Cheyyar, Taminadu.

¹Department of Chemistry, Indian Arts and Science College, Kondam, Tamilnadu.

*Corresponding Author Email: krisrajesh77@yahoo.co.in, ramchemistryphd.2016@gmail.com

ABSTRACT

Schiff base have been prepared from Furan-2-Carboxaldehyde and 1,4 Diaminobutane. Ligand are synthesized in a 1:2 mol ratio, and their Sn (II) and Hg (IV) complexes in a 1:1 mol ratio (Ligand:Metal). Ligand and metal complexes were characterized by FTIR, UV, ¹H NMR, SEM and Antimicrobial activity. The compounds were confirmed by the presence of an imine band stretching in the 1615-1648cm⁻¹ and νMetal –N and νMetal –O at <600 cm⁻¹. The ¹H NMR of Ligand a singlet signal at δ 7.72 ppm observed isomethine nitrogen (s, C=N) on complexation Hg (II) and Sn (II) are observed δ 7.37 ppm, δ 7.77 ppm. The UV Vis spectrum of ligand show band at 347 nm on complexation Hg (II) and Sn (II) shows longer wavelengths at 645 nm and 543 nm. Surface morphologies were analyzed with SEM. Generally, the Schiff base ligand had a smooth surface morphology, while the Hg (II) and Sn (II) complexes presented heterogeneous features with smooth and rough surface regions and Antimicrobial activity the free ligand and their metal complexes have been screened for their in vitro biological activities against bacteria and fungi. The metal complexes show more potent activities compared with Schiff base ligand.

Key words:

KEY WORDS

Antimicrobial activities, Furan-2-carboxaldehyde, Schiff base, Stannous (II), Mercury (II), 1, 4 Diaminobutane.

INTRODUCTION

Schiff bases have been a subject of intense interest as a result of their synthetic accessibility and rich coordination chemistry. These are functional groups derived from the condensation of ketones (or) aldehydes with primary amines and are generally prepared under acid (or) base catalysis or with heat¹. The Schiff bases are characterized by the imines (-HC=N-) linkage, which is considered as responsible for their remarkable antibacterial, antitumor, antifungal, anticancer, diuretic and herbicidal activities². The synthesis of Schiff base is a reversible process and conditions have

to be optimized to maximize the yield, which often pose a serious challenge. Equally stimulating is the purification and recrystallization of the product as degradation of the Schiff bases can occur during the purification step³.

Schiff bases are regarded as "Privileged Ligands" because these are able to coordinate different metals and stabilize them in various oxidation states⁴. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities⁵. The complex formation usually makes Schiff bases effective and stereo specific catalysts for

oxidation, reduction, hydrolysis and other transformations of organic and inorganic chemistry⁶. These complexes are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of organisms, and have found potential applications in many fields such as oxidation catalysis, Electrochemistry, Analytical chemistry, Food industry, Agrochemical, Pharmaceutical and biological fields⁷. Schiff bases are generally excellent chelating agents, especially when a functional group like –OH (or) SH group is present close to the azomethine group so as to form a five (or) six membered ring with the metal ion. Nowadays, the research field dealing with Schiff bases coordination chemistry has expanded enormously.

However, few studies have been performed regarding Hg^{2+} and Sn^{2+} complexes with Schiff base derived from Furan-2-carboxaldehyde mercury and stannous play an important role in biological and chemical process mercury is considered as one of the most dangerous metal ions for environment and has most commonly toxic risks for human contacting areas as result of natural processes, because it is widely distributed in air, water, and soil and it is toxic element that exists in metallic, inorganic and organic forms. Mercuric ion (Hg^{2+}), the most stable form of inorganic mercury⁸, exists mostly in surface water due to its high-water solubility and it can cause several developmental delays and health problems that can damage the brain, nervous system, Kidneys and endocrine system. Therefore, it is critical to able to detect and measure the level of Hg^{2+} in both environmental and biological samples under aqueous conditions with high sensitivity and selectivity and without interference of other metal ions. the chemistry of mercury and its compounds has attached the interest of both the chemistry and chemical engineering communities over the years, due

to potential applications in the paper industry, as a preservative, in fluorescent lamps, in cosmetics, paints, in sensors, as well as for mercury batteries are widely used for mercury metal ion⁹.

Stannous compared to mercury it has low toxicity the use of stannous ion was key to development of many radiopharmaceuticals. None showed a reducing agent, so far, an efficiency of marking the radioactive tracer superior to that obtained with the use of stannous chloride, not only in nuclear medicine, but also the marking of various structures of biomedical applications one of the feature of biological importance of $SnCl_2$ is its ability to form cationic organ metallic compounds and exert its toxic effects within the cells¹⁰.

In this paper we report on a series of new Schiff base mixed ligand is perhaps the most important step in the development of metal complexes are mercury and stannous which display moderate until good antimicrobial activities^{11,12}.

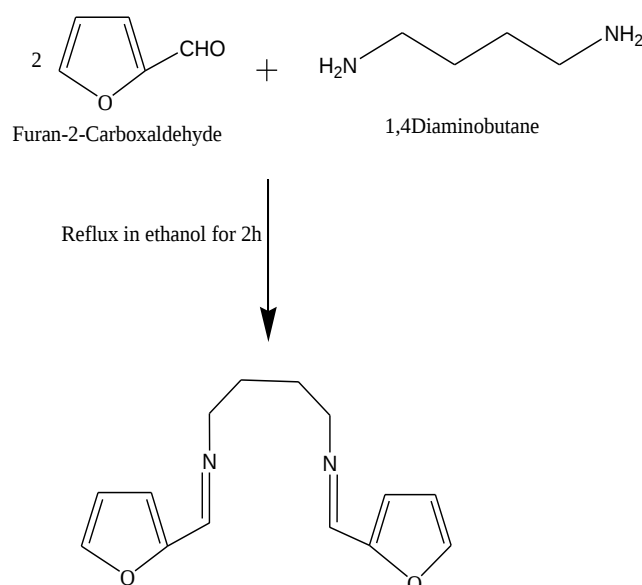
2. MATERIALS AND METHODS:

2.1 Materials

Furan-2-carboxaldehyde, 1, 4 diaminobutane and ethanol were purchased from sigma Aldrich and used without solvents were purchased from Merck.

2.2 Synthesis of Schiff base Ligand

1, 4 diaminobutane (3.52 ml, 40mmol) was added to a solution of Furan-2-carboxaldehyde (4.32ml, 40mmol) in absolute ethanol 50ml in 1:2 ratio. The reaction mixture was refluxing the solution for 2h. It was filtered. The resulting dark red colour solid product was extracted with absolute ethanol, purified by recrystallization from ethanol, washed with ethanol and then dried¹³. Scheme 1.



2:3 Syntheses of the metal complexes

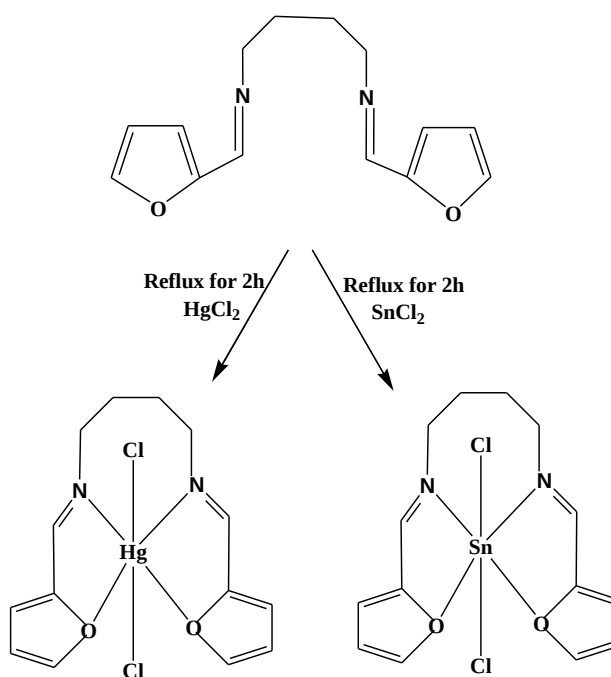
2:3:1 Synthesis of Hg (II) complex:

The Hg (II) complex was prepared by adding a ethanol solution of HgCl₂ (0.549g, 2mmol) in small quantities with stirring to hot ethanolic solution of the Schiff base ligand (0.488g, 2mmol) in ethanol (50ml) was added drop wise. After the addition was completed. The mixture was stirred and heated to reflux for 2h. the volume of the reaction mixture was reduced to 20-30 ml. the strong reddish brown colour solid complex

which separated out was suction filtered washed first with aqeous ethanol and finally with ether and dried. Scheme 2.

2:3:2 Synthesis of Sn (II) Complex:

Similarly, SnCl₂ (0.451g, 2mmol) the mixture was stirred and heated to reflux 2h. The brown colour solid crystals were separated out was suction filtered washed first with aqeous ethanol and finally with ether and dried¹⁴. Scheme 3.



Scheme – 2

Scheme - 3

2:4 Characterization of Schiff base ligand and metal complexes:

The FTIR spectra were recorded in Perkin-Elmer spectrophotometer in the range of 400cm⁻¹ to 4000cm⁻¹ in KBr phase. To observe optical property separated for Schiff base ligand and metal complexes were periodically analyzed with UV-Vis spectrometer (JSCOV-670) using the range 200 to 800 nm. The ¹H NMR spectra were recorded in DMSO d₆ 400 MHz (Bruker) spectrometer. And chemical shifts calculated in ppm with respect to TMS ($\delta=0$). The shape of the Schiff base ligand and metal complexes were observed by SEM using model EVO18 (ZEISS).

2.5 Biological Activity

The synthesized Schiff base and metal complexes were screened for antibacterial and antifungal activity.

2.5.1. Antibacterial Activity Study:

Characteristics of the medium:

The main characteristics of the medium were to support the growth of the organisms normally tested and not contain antagonist of antimicrobial activity. The medium must allow free diffusion of plant extract from the well.

The sterilized medium was poured into a Petri dish in a uniform thickness and kept aside for solidification. Using sterilized swabs, even distribution of lawn culture was prepared using bacteria such as *Escherichia coli*, *Staphylococcus aureus* and *Bacillus cereus* in Muller Hinton agar (MHA) Plates¹⁵.

Muller Hinton Agar (MHA) and Sabouraud's dextrose Agar (SDA) were prepared with lawn culture using desired test organism and the ingredients are Dextrose 4.0g, Mycological peptone 1.0g, Agar 2.0g, Distilled water 100ml and P^H 5.0 medium. The inoculated plates were kept aside for few minutes. Using well cutter 4 wells were made in those plates at required distance. In each step of well cutting, the well cutter was thoroughly wiped with alcohol. Using sterilized micropipette, 20 μ l of compounds are ligand and metal complexes extract were added in the three different wells and in another well the same volume of *ciprofloxacin* was taken as reference.

After diffusion, the plates were incubated at 37°C for 24 hours. After incubation, the inhibition of growth was analyzed. The antibacterial activity was evaluated by measuring the diameter of the zone of inhibition in mm against the test fungal strain. The tests were carried out in triplicates.

Muller Hinton Agar (MHA) and Sabouraud's dextrose Agar (SDA) were prepared with lawn culture using desired test organisms and the ingredients are used dextrose(4.0g), Mycological peptone(1.0g), Agar(2.0g), Distilled water (100 ml) and medium of P^H (5.0). The inoculated plates were kept aside for few minutes¹⁶. Using well cutter 4 wells were made in those plates at required distance. In each step of well cutting, the well cutter was thoroughly wiped with alcohol. Using sterilized micropipette, 20 μ l of compounds are ligand and metal complexes extract were added in the three different wells and in another well the same volume of *ciprofloxacin* was taken as reference.

After diffusion, the plates were incubated at 37°C for 24 hours. After incubation, the inhibition of growth was analyzed. The antibacterial activity was evaluated by measuring the diameter of the zone of inhibition in mm against the test fungal strain. The tests were carried out in triplicates.

The agar well diffusion method:

Simple susceptibility screening test using with agar-well diffusion method as adapted earlier was used. Each microorganism was suspended in Brain Heart Infusion (BHI) broth and diluted to approximately 10⁶ colony forming unit (cfu)/ml. They were "flood-inoculated" onto the surface of BHI agar and *Sabouraud Dextrose* Agar (SDA) and then dried. For *C. albicans* and *C. tropicalis*, SDA was used Five-millimeter diameter wells were cut from the agar using a sterile cork-borer, and 100 μ l of the sample's solutions were delivered into the wells. The plates were incubated for 18 hours at 35°C. Antimicrobial activity was evaluated by measuring the zone of inhibition against the test microorganisms. *Ceftazidime* (Fortum) (10 μ g) and *Trifulcan* (5 μ g) were the standard drugs for antibacterial and antifungal activities, respectively. Acetone was used as solvent control. The tests were carried out in duplicates. Results were interpreted terms of diameter of inhibition zone in mm.

The estimation of the Minimal Inhibitory Concentration (MIC) and Minimal Bactericidal Concentration (MBC) was carried out by the broth dilution method. Dilutions of essential oil from 2.0 to 0.075 mg/ml were used. Test bacteria culture was used at the concentration of 105 CFU/ml. MIC values were taken as the lowest essential oil concentration that prevents visible bacterial growth after 24 hrs of incubation at 37°C, and MBC as the lowest concentration that completely inhibited

bacterial growth. Chloramphenicol was used as reference and appropriate controls with no essential oil were used. Each experiment was made three times. The bactericidal kinetic assay was performed by using appropriate concentrations of essential oil (corresponding to $\frac{1}{2}$ MIC and MBC).

2.5.2. Anti-Fungal Activity:

The sterilized medium was poured to a Petri in a uniform thickness and kept aside for solidification and the ingredients are Beef extract 0.2g, Peptoe 1.75g, Starch 0.15g, Agar 1.70g, Distilled water 100ml and P^H 7.5 medium. Using sterilized swabs, even distribution of lawn culture was prepared using desired fungi such as *Aspergillus niger*, *Candida albicans* and *Aspergillus fumigatus* in SDA plates¹⁷.

The inoculated plates were kept aside for few minutes. Using with well cutter, four wells were made in those plates at required distance. In each step of well cutting, the well cutter was thoroughly wiped with alcohol. Using sterilized micropipette, 20 ml of compounds A, B, C extract were added in the three different wells and in another well the same volume of Amphoterecin - B or *ketoconazole* was taken as reference.

After diffusion, the plates were incubated at temperature for 24 hours for yeast like fungus and 48-72 hours for molds. After incubation, the inhibition of growth was analyzed. The antifungal activity was evaluated by measuring the diameter of the zone of inhibition in mm against the test fungal strain. The tests were carried out in triplicates.

Determination of Minimum Inhibitory Concentration (MIC):

One ml of extract (1mg/ml) was incorporated into one ml of nutrient broth and *sabouraud's* dextrose broth and was serially diluted to obtain concentration of 1000 $\mu\text{g/ml}$, 125 $\mu\text{g/ml}$, 62.5 $\mu\text{g/ml}$, 31.25 $\mu\text{g/ml}$ respectively. 20 μl of the inoculum was added to each of the test tubes. The tube without the extract served as control. The tubes were incubated at room temperature and readings were recorded after a period of 24 hrs for bacteria and 3 days for fungi. MIC was recorded as the lowest concentration of the extract at which no visible growth of the bacterial and fungal occurred after a period of seven days incubation.

3. RESULTS:

3:1 UV:Vis Spectra analysis:

The UV-Vis spectrum of Ligands shows band at 347 nm Fig 1(a), The adsorption Hg(II) spectrum metal complex shows band at 645 nm Fig 1 (b) and Sn(II) spectrum of adsorption band shows at 543 nm fig1(c) with a shoulder band around longer wavelength. The complex Hg (II) and Sn (II) two adsorption bands can be safely assigned to the charge transfer transitions and compared to the ligand adsorption bands with two metal complexes are adsorbed band shows at longer wavelengths^{18, 19}.

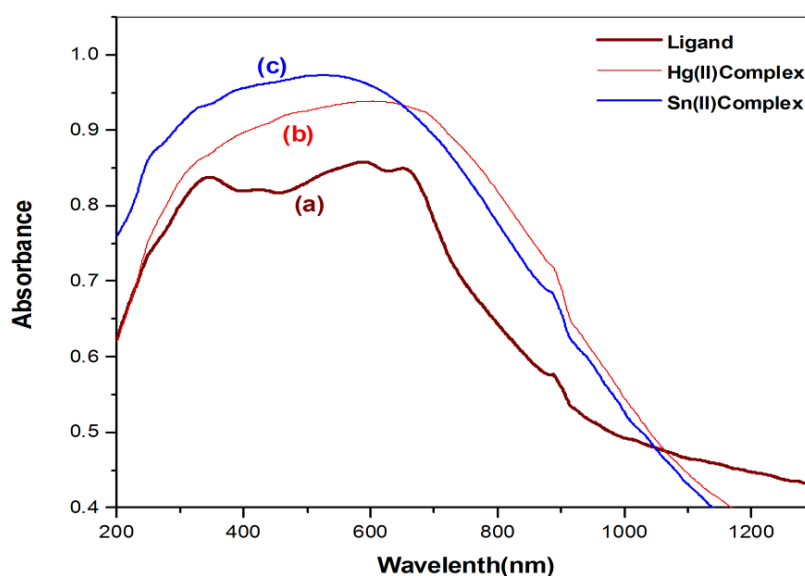


Fig. 1. UV:Vis Spectra (a) Schiff base ligand; (b) Hg (II) complex; (c) Sn (II) complex

3:2 FTIR-spectral Analyses

FT-IR analysis was performed to the ligand and metal complexes before and after complex preparations, The spectrum obtained for ligand shows bands at 1648 cm^{-1} , 1569 cm^{-1} , 1451 cm^{-1} , 1382 cm^{-1} , 1271 cm^{-1} , 1153 cm^{-1} , and 752 cm^{-1} . The Hg(II) complex shows

bands at 1617 cm^{-1} , 1326 cm^{-1} , 1210 cm^{-1} , 1107 cm^{-1} , 743 cm^{-1} , 590 cm^{-1} and 473 cm^{-1} and Sn (II) complex shows bands at 1615 cm^{-1} , 1465 cm^{-1} , 1401 cm^{-1} , 1250 cm^{-1} , 1157 cm^{-1} , 742 cm^{-1} , 594 cm^{-1} and 437 cm^{-1} Table 1.

Table 1:IR data of the Schiff and their metal complexes (cm^{-1})

Compound	ν (C=N)	ν (C-N)	ν (C-O-C)	ν (M-O)	ν (M-N)	Phenyl ring Vibrations
Ligand	1648	1382	1271	-	-	752
Hg (II) Complex	1617	1326	1210	590	438	743
Sn (II) Complex	1615	1401	1250	594	437	742

The study of IR stretching frequencies of the ligand and metal complexes will give an idea about mode of bonding in complexes and they also indicate the arrangement of atom in space and bond angles most of the assignments of IR absorptions frequencies have been based on the concept of group frequency. In large molecule factors both external as well as internal influence the force constant and determine the precise position of the infrared adsorption bands. On complexation with metal ions, the characteristic IR frequencies of the coordinating groups are influenced by the force constant of the metal ligand bond resulting in the shifting of the group frequencies. These shifts are useful in identifying the coordination sites. The important vibrating group in a free Schiff base ligand is naturally the imino group. The strong absorption due to this found to lie in the region C=N 1648 cm^{-1} . However, on complexation the group frequency of the free azomethine is altered. The band shows 2926 cm^{-1} in the presence of alkane C-H stretching frequency. The band 1569 cm^{-1} show the presence of aromatic C=C stretching vibration the band show at 1451 cm^{-1} the presence of aromatic C-C stretching Frequency and other band show in shift base ligand in adsorption bands at stretching vibrations are C-N band in 1382 cm^{-1} . A medium intensity band due to ν (C-O-C) stretching vibration of furan appeared at 1271 cm^{-1} in the ligand and the band 752 cm^{-1} shows that phenyl ring vibration in the presence of Schiff base ligand²⁰. Fig2 (a) The dark reddish-brown

Furan-2-carboxaldehyde, 1,4 diamino butane to mercury (II) if obtained from Hg (II) chloride and Schiff base. The complex is soluble in alcohol. The infrared spectrum of the Schiff base ligand shows a strong band at 1648 cm^{-1} , which assigned to the C=N stretching vibration. On complexation this band shifted to 1617 cm^{-1} . This indicates that the azomethine nitrogen is coordinated to the metal ion. The band in 1382 cm^{-1} in C-N aromatic stretching frequency shifted to 1326 cm^{-1} in metal complexation. The band show 752 cm^{-1} phenyl ring vibration show lower frequency in metal complex 743 cm^{-1} and the new bond show that 438 cm^{-1} - 590 cm^{-1} range indicating the formation of a linkage between ν (M-O) and ν (M-N) stretching vibrations²¹. Fig 2(b). Similarly, the brown colour of Sn (II) complex if obtained from Sn (II) chloride and Schiff base and the complex is also soluble in alcohol. The IR spectrum of the Schiff base ligand shows a strong band at 1648 cm^{-1} , which is assigned to the C=N stretching vibration on complexation this band shifted lower frequency 1615 cm^{-1} . This indicates that the azomethine nitrogen is coordinated to the metal ion. The band 1382 cm^{-1} in C-N aromatic stretching vibration shifted to 1401 cm^{-1} in metal complexation. The band show 752 cm^{-1} phenyl ring vibration show lower frequency in metal complex 742 cm^{-1} and the new bond show that 437 cm^{-1} - 594 cm^{-1} range indicating the formation of a linkage between ν (M-O) and ν (M-N) stretching vibrations²². Fig. 2(c).

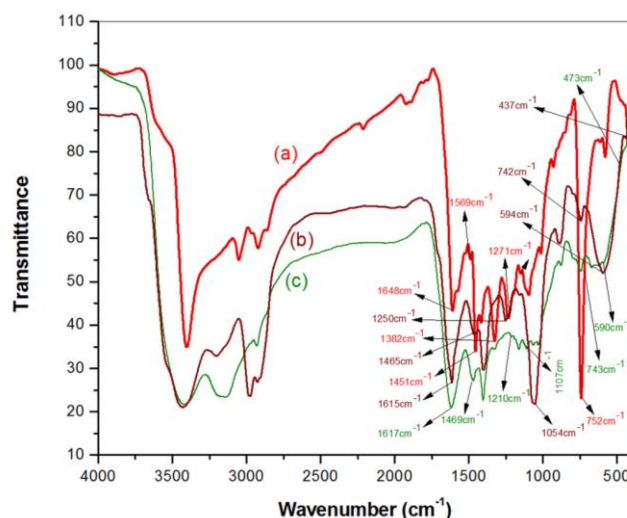


Fig. 2. FT-IR Spectra (a) Schiff base ligand; (b) Hg (II) complex; (c) Sn (II) complex

3:3 ¹H NMR Spectral Analysis:

The nuclear magnetic resonance spectra are the signals of the respective protons of the complexes are verified on the basis of its chemical shifts, multiplicities and coupling constants. The ¹H NMR spectra of ligand Hg (II) and Sn (II) complexes were recorded in DMSO –D₆. The ¹H NMR spectrum of ligand also revealed multiplets in the range downfield δ 6.55-7.72 ppm exhibits multiplets (m, 8H, 2ArH, 6Furon) which was attributed to aromatic and Furan ring protons are present δ 2.50 ppm (s, 6H, Methyl H) exhibits singlet free ligand methyl protons and the shielding protons are present δ 1.05 ppm and δ 3.42 ppm multiplet shows that free ligand²³. (Fig 3) a. The ¹H NMR spectrum of the Hg (II) complex in DMSO d₆ solvent confirms its proposed structure on complexation Hg (II) complex at the position of azomethine signal was shifted to higher region δ 8.16ppm in comparison with that of the free ligand

inferring coordination through the azomethine nitrogen atom of the ligand. The multiple's assigned to the aromatic and furan ring protons were displaced upper field around the region δ 6.79-7.77 ppm indicating the involvement of oxygen of Furan ring in the coordination. The shielding protons are present in δ 1.50 and δ 3.37 ppm at Hg (II) metal complex in the higher region of coordination. Fig. 3(b) similarly the ¹H NMR spectrum of the Sn (II) complex at the position of azomethine signal was shifted to lower region at δ 7.37 ppm in comparison with that of the free ligand, inferring coordination through the azomethine nitrogen atom of the ligand. The multiplets assigned to the aromatic and Furan ring protons were displayed lower field around the region δ 4.91-5.84ppm indicating the involvement of oxygen of Furan ring in the coordination. The shielding protons are present in δ 1.37 and δ 3.41 ppm at Sn (II) metal complex in the lower region of coordination²⁴. Fig 3(c).

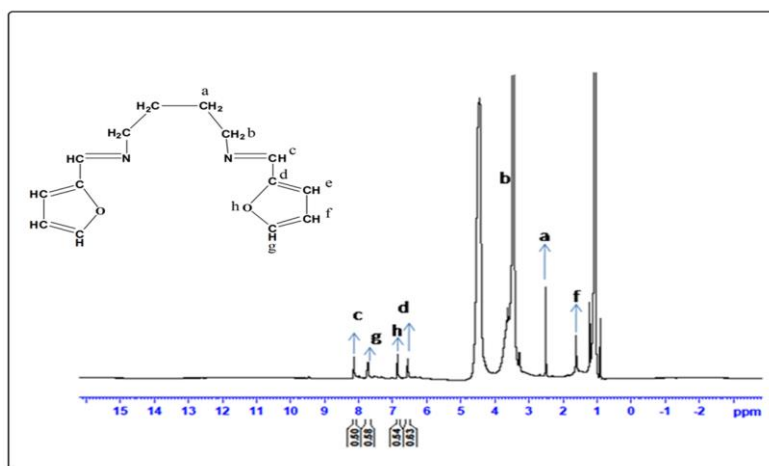


Fig. 3. (a) ¹H NMR spectrum of ligand

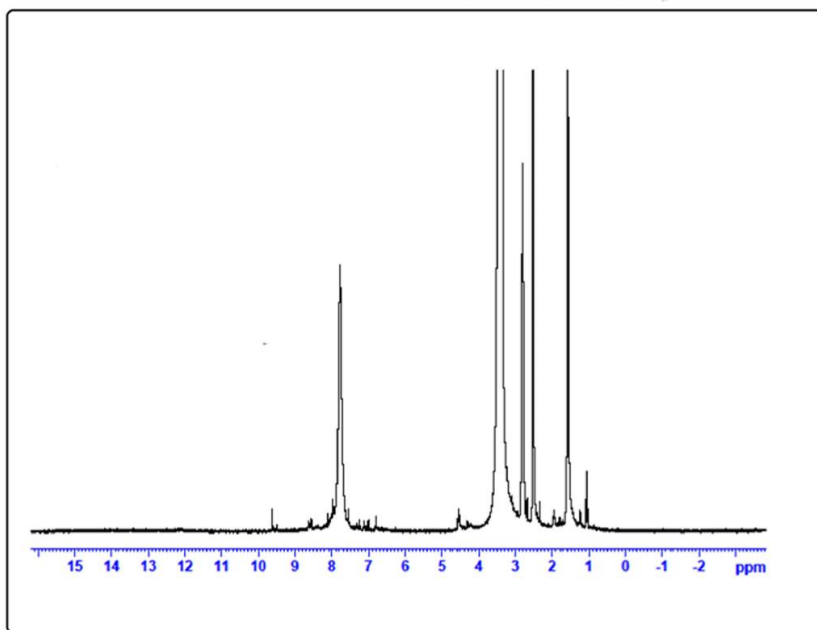


Fig. 3. (b) ¹H NMR spectrum of Hg (II) complex

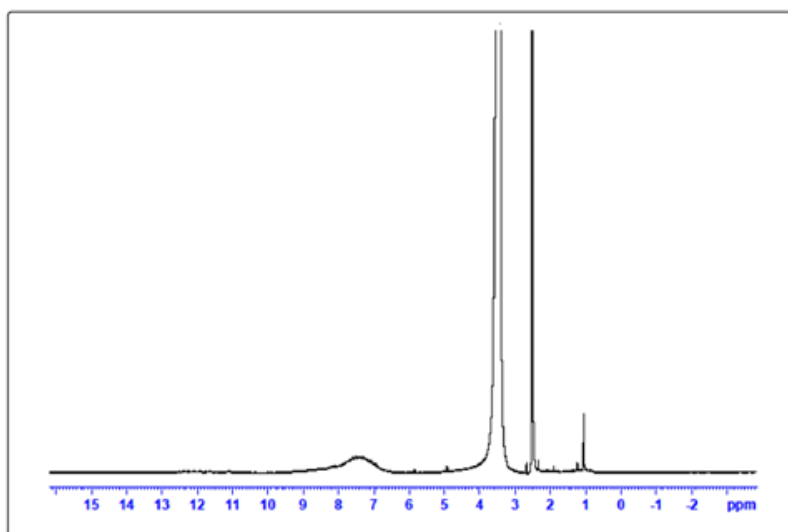


Fig. 3. (c) ¹H NMR spectrum of Sn (II) complex

Scanning Electron Microscopy (SEM) Analysis: -

The SEM images of ligand, Hg (II) and Sn (II) complexes are presented in respectively as a representative example. Generally the Schiff base ligand host a smooth surface morphology, while the complexes presented

heterogeneous features, with smooth and rough surface regions. The complexes were also with SEM in which was possible to verify brighter regions evidencing the presence of the metallic species are very rough surfaces²⁵. Fig 4(a,b,c)

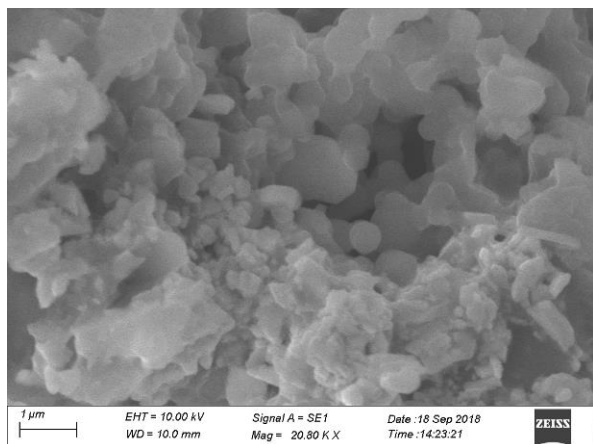


Fig. 4. (a) SEM image of ligand

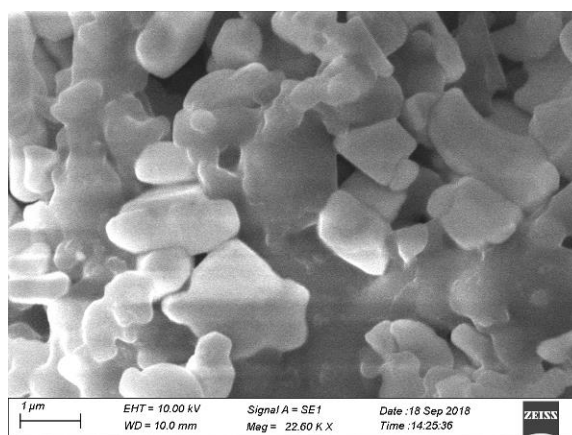


Fig. 4. (b) SEM image of Hg (II) Complex

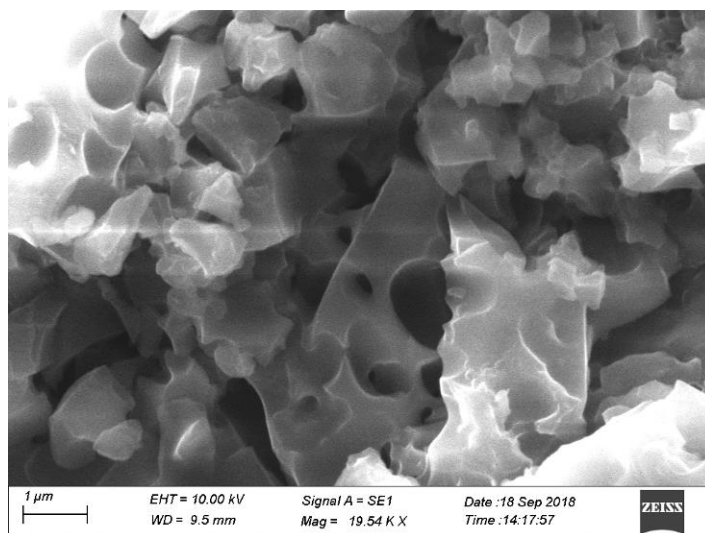


Fig. 4. (c) SEM image of Sn (II) Complex

3.5 Antibacterial Activity

The results of the antibacterial screening of the Schiff base ligand, Hg (II) and Sn (II) complexes at a

concentration of 20mg/ml against all bacteria have been found. The inhibition zones were measured in mm and results are shown in Table 2.

Table 2: The Antibacterial activity of ligand, Hg (II) and Sn (II) complexes against tested microorganisms.

S.No	Microorganisms	Zone of inhibition (mm)				
		Control	Ligand	Hg (II) complex	Sn (IV) complex	Ciprofloxazon
1.	<i>B. cereus</i>	-	-	34	12	24
2.	<i>S.aureus</i>	-	-	33	14	23
3.	<i>E.coli</i>	-	-	30	13	24

The results of antimicrobial screening, indicate that Schiff base ligand, Hg (II) and Sn (II) complexes significant activity against *Bacillus Cereus* (*B. cereus*), *Staphylococcus aureus* (*S.aureus*) and *Escherichia coli* (*E.coli*). The high zone of inhibition shows Hg (II) complex in *S.aureus* in 33 mm and Sn (II) complex show

that 14 mm and reference material *Ciprofloxacin* show that inhibition 23 mm. the *E.coli* bacteria shows that zone of inhibition in Hg (II) complex 30 mm, Sn (II) complex inhibition of 24 mm and the *B.cereus* bacteria shows that the zone of inhibition Hg(II) complex 34 mm, Sn (II) complex 14 mm and reference material

Ciprofloxacin zone of inhibition 23mm. The zone of inhibition only shows selected metal complexes, but no zone of inhibition shows that Schiff base ligand²⁶. Fig.5. (a,b,c)

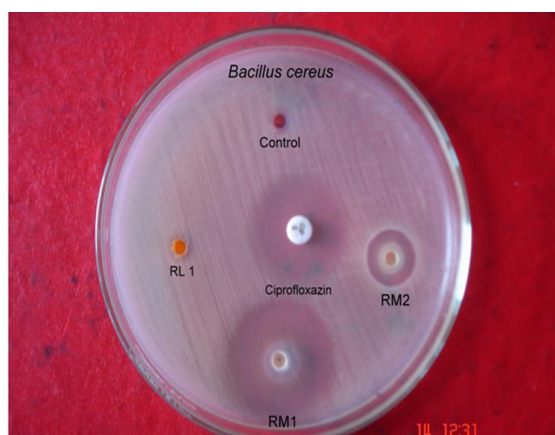


Fig.5. (a)Antibacterial activity of Ligand (RL₁), Hg (II) complex (RM₁) and Sn (II) complex (RM₂) against *B. cereus*

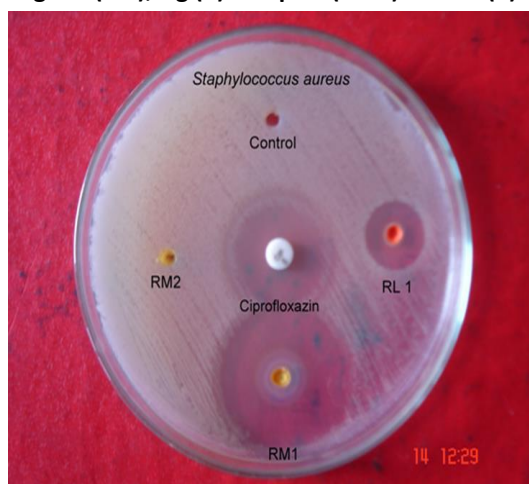


Fig. 5. (b)Antibacterial activity of Ligand (RL₁), Hg (II) complex (RM₁) and Sn (II) complex (RM₂) against *S.aureus*

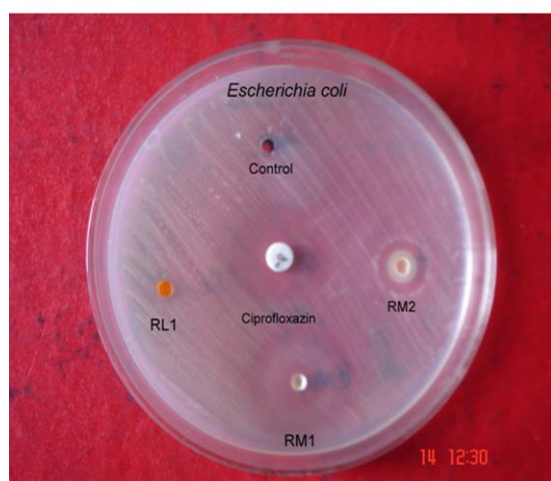
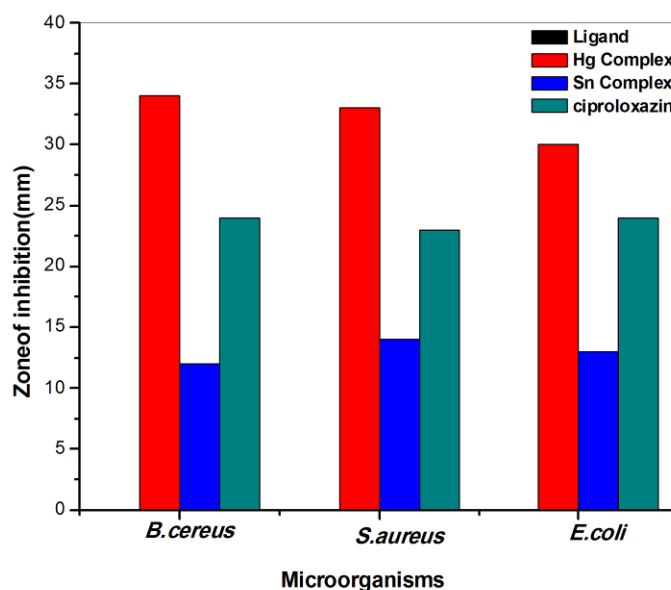


Fig. 5. (c)Antibacterial activity of Ligand (RL₁), Hg (II) complex (RM₁) and Sn (II) complex (RM₂) against *E.coli*

Graph 1: Zone of inhibition (mm) of Antibacterial Activity



3.6 Anti-Fungal Activity:

The antifungal screening effect of the synthesized Schiff base ligand, Hg (II) complex and Sn (II) complex were evaluated against *Aspergillus niger* (*A. niger*), *Candida albicans* (*C. albicans*) and *Aspergillus Fumigatus*

(*A. fumigatus*) using *Amphoterecing* – B standard antifungal reference by well diffusion method. The inhibition zones were measured in mm and results are shown in Table. 3.

Table 3: The Antifungal activity of ligand, Hg (II) and Sn (II) complex's against tested microorganisms.

S.No	Microorganisms	Zone of inhibition (mm)				
		Control	Ligand	Hg (II) complex	Sn (II) complex	Ciprofloxaion
1.	<i>A. niger</i>	-	-	50	12	14
2.	<i>A. fumigatus</i>	-	-	50	11	13
3.	<i>C. albicans</i>	-	4	47	10	-

The results showed that the Hg (II) complex 50 mm in *A. niger* and antifungal reference *Amphoterecin* – B Show at 14mm. The zone of inhibition in *candida albicans* show 37mm and reference *Amphoterecin* – B show at 14mm. The zone of inhibition in *C. albicans* show 47 mm and reference *Amphoterecin* – B indicate at no zone of inhibition and the *A. fumigatus* shows that zone of inhibition 50 mm and *Amphoterecin* – B at 11 mm. Similarly Sn (II) complex show that zone of inhibition in

12 mm *A. niger*, The standard antifungal reference *Amphoterecin* – B shows that zone of inhibition 14 mm, *A. Fumigatus* 11 mm and reference *Amphoterecin* – B indicate at 13mm and *c. albicans* show that 10 mm and no zone of inhibition *Amphoterecin* – B. Therefore, the results showed that the Hg (II) complex than the Sn (II) complex exhibited potent inhibitory activity against all the three Fungal strains²⁷. Fig. 6 (a, b, c).



Fig. 6 (a) Antifungal activity of Ligand (RL₁), Hg (II) complex (EM₁) and Sn (II) complex (RM₂) against *A.niger*

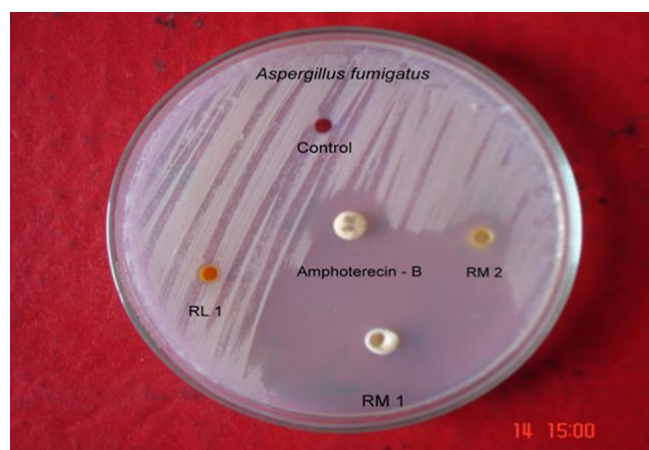


Fig. 6 (b) Antifungal activity of Ligand (RL₁), Hg (II) complex (RM₁) and Sn (II) complex (RM₂) against *A.fumigatus*

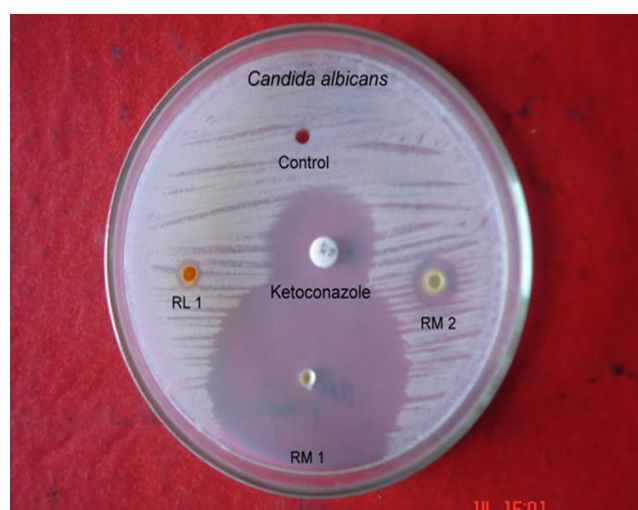
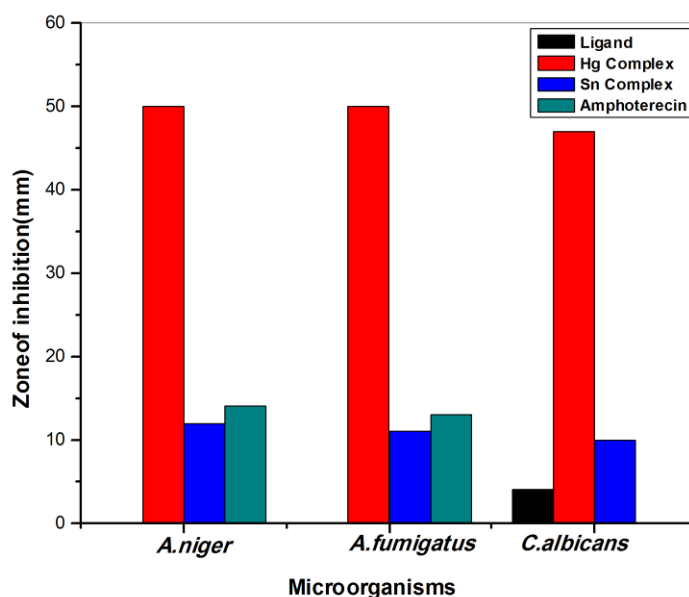


Fig. 6. (c) Antifungal activity of Ligand (RL₁), Hg (II) complex (RM₁) and Sn (II) complex (RM₂) against *C. albicans*

Graph 2: Zone of inhibition (mm) of Antibacterial Activity



4. DISCUSSION

The new Schiff base ligand was prepared by the 1:2 ratio reaction between Furan-2-Carboxaldehyde and 1,4 diaminobutane in ethanol. The complexes Hg (II) and Sn (II) were synthesized by the reaction of the ligand with the appropriate chlorine salts in a 1:1 molar ratio. The complexes were characterized by optical and elemental analysis. The UV- Vis spectrum of ligand show band at 347 nm and the adsorption spectrum of Hg complex indicate that at higher wavelength 645 nm than Sn (II) complex show at 543 nm. The two metal complexes are adsorbed band shows at longer wavelengths compare to Schiff base ligand due to charge transfer transitions are involved.

The infrared spectrum of ligand shows a strong intensity band at 1648cm^{-1} , which may reasonably assign to the imine function ($\text{C}=\text{N}$) in the Schiff base ligand. The strong adsorption band shows that 1569cm^{-1} show the presence of aromatic $\text{C}=\text{C}$ stretching vibration and other bands shows in Schiff base ligand in adsorption band at stretching vibrations are C-N band in 1352 cm^{-1} , C-C band at 1451 cm^{-1} and the band 752cm^{-1} show that phenyl ring vibration. The IR spectra of the complexes show a sharp band in the $1615\text{-}1617\text{ cm}^{-1}$ region, which is attributed to the $\nu(\text{C}=\text{N})$ stretch, indicating coordination of the azomethine nitrogen to the metals bands at $1326\text{-}1401\text{ cm}^{-1}$ associated with $\nu(\text{C}-\text{N})$ vibrations from the aromatic rings are also present in the spectra and the new bands shows the two complexes at $590\text{-}594\text{cm}^{-1}$ and $437\text{-}438\text{cm}^{-1}$ the range

indicating the formation of a linkage between ν (M-O) and ν (M-N) stretching vibrations.

Further evidence of the bonding mode of the ligands were also provided by the ^1H NMR spectra of the Schiff base ligand and their Hg (II) and Sn (II) complexes. The chemical shifts of the different types of protons in the ^1H NMR spectra of the parent ligand showed singlet in the region δ 8.12ppm which was attributed to the azomethine ($-\text{CH}=\text{N}-$) protons. The ligand also revealed multiplets in the range δ 6.55- 7.22 ppm which was attributed to aromatic and Furan ring protons on complexation of Hg (II) and Sn (II) complexes the position of azomethine signal was shifted to higher region δ 7.37 -8.16 ppm in comparison with that of the free ligand, inferring coordination through the azomethine nitrogen atom of the ligand. The multiplets, assigned to the aromatic and furan around the region δ 5.84 -7.77ppm, indicating the involvement of oxygen of furan ring in the coordination.

The SEM images of ligand, Hg (II) and Zr (II) complexes are presented in respectively as a representative example, Generally the Schiff base ligand host a smooth surface morphology, while the complexes presented heterogeneous features, with smooth and rough surface regions. The complexes were also with SEM in which was possible to verify brighter regions evidencing the presence of the metallic species are very rough surfaces.

The antimicrobial activity of both ligand and two metal complexes are screening of against bacteria and fungi

the good zone of inhibition of bacteria *S.aures* in Hg(II) complex show at 34 mm and reference material *ciprofloxacin* show that inhibition 24 mm. Then the Sn(II) complex show that *S.aures* 14 mm and reference material *ciprofloxacin* show that inhibition zone at 23 mm. The antifungal activity the high zone of inhibition of Fungi *A.Niger* in Hg (II) complex show at 50 mm and antifungal reference material *Amphoterecin – B* show at 14 mm that the Sn(II) complex show that *A.fumigatus* in 11 mm and *Amphotercin- B* at 13 mm inhibition. These compounds exhibited significant activity against all tested microorganism.

CONCLUSION

The synthesis of the complexes Hg (II) and Sn (II) with Furan-2-Carboxaldehyde and their characterization using FT-IR and NMR studies are reveal the presence of different mode of linkages of the ligand with two metals. The synthesized ligand and its Hg (II) and Sn (II) complexes have been screened for their antimicrobial activity, most of the Hg(II) complex as well as HgCl₂, exhibit moderate antibacterial activity and good antifungal activity.

REFERENCES

- [1]. Qing –Rong Cheng, Hong Zhou, Zhi-Quan Pan, Jing-Zhong Chen. New Cu(II)₄ and Zn (II) ₄ complexes: Synthesis, characterization and magnetic and biological studies. Polyhedron, 30: 1171-1176, (2011)
- [2]. N.Sengottuvelan, D. Saravanakumar, M.Kandaswamy, Electrochemical, magnetic, catalytic and DNA cleavage studies of binuclear copper (II) complexes derived from pendant substituted tetraaza macrobicyclic compartmental ligands. Polyhedron, 26: 3825-3832, (2006)
- [3]. S.Samal, S. Acharya, R.K. Dey, A.R. Ray. Synthesis and metal ion uptake studies of chelating resins derived from formaldehyde-furfuraldehyde condensed phenolic Schiff base of 4,4' diaminodiphenylether and O hydroxyacetophenone. Talanta, 57:1075-1083, (2002)
- [4]. Allan G. Blackman. The coordination chemistry of tripodal tetraamine ligands. Polyhedron, 24: 1-39, (2004)
- [5]. Hamdi Temel, Umit Cakir, Birol Otludil & H. Ibrahim Ugras. Synthesis, spectral and biological studies of Mn (II), Ni (II), Cu (II) and Zn (II) complexes with a tetradentate Schiff base ligand. Complexation studies and the determination of stability constants. Synthesis and Reactivity in inorganic and Metal-Organic chemistry, 31(8): 1323-1337, (2011)
- [6]. Bushra Iftikhar, Kanwal Javed, Muhammad Saif Ullah Khan, Zareen Akhter, Bushra Mirza, Vickie Mckee. Synthesis, characterization and biological assay of Salicylaldehyde Schiff base Cu(II) complexes and their precursors. J of Molecular Structure, 1155: 337-348, (2007)
- [7]. Nobukatsu Nemoto, Makoto Asano, Tetsuya Asakura, Isami Hongo, Yukihiko Ueno, Koji Ikeda, and Nobuo Takamiya. Oxidation of 3-Methylindole Catalyzed by Cobalt (II) Phthalocyanines Covalently Bound to Polyorganosiloxane. J of inorganic and Organometallic Polymers, 1(2):147-152, (1991)
- [8]. Ghodrati Mahmoudi. Masoumeh Servati Gargari, Farhad Akbari Afkhami, Christos Lampropoulos. Mercury (II) coordination complexes bearing Schiff base ligands: What affects their nuclearity and/or dimensionality. Polyhedron, 93:46-54, (2015)
- [9]. Ante Milicevic, Nenad Raos. Estimation of stability constants of copper (II) chelates with triamines and their mixed complexes with amino acids by using topological indices and the overlapping spheres method. Polyhedron, 26: 3350-3356, (2007)
- [10]. C.R. Silva, M.B. Olivenra, S.F. Melo, F.J.S. Bantas, J.C.P de Mattos, R.J.A.C. Benzerra, A.Calderira-de- A raujo, A. Duatti and M. Bernardo- Fiho, Biological effects of stannous chloride; a substance that can produce stimulation or depression of the central nervous system. Brain Research Bulletin, 59: 213-216, (2002)
- [11]. Wei Sun, Dong-Yun Liu, Hai-Yan Zhu, Lei Shi, Qi Sun. A new efficient approach to 3-methylindole: Vapor –phase synthesis from aniline and glycerol over Cu – based catalyst. Catalysis, 12: 147-150, (2010)
- [12]. Yuichi Shimazaki, Tatsuo Yajima, Osamu Yamauchi. Properties of the indole ring in metal complexes. A comparison with the phenol ring. J of Inorganic chemistry, 12:79-84, (2015).
- [13]. Kishor Arora, D.Kumar, Kiran Burman, Sonal Agniotri, Bhoop Singh, Theoretical studies of 2-nitrobenzaldehyde and Furan-2-carbaldehyde Schiff base of 2-amino pyridine. J of Saudi chemical society, 15: 161-165, (2011)
- [14]. Kiran Singh, Yogender Kumar, paravesh Puri, Chetan Sharama, Kamal Raj Aneja, Antimicrobial, spectral and thermal studies of divalent cobalt, Nickel, Copper and Zinc complexes with triazole Schiff bases. Arbin J of chemistry, 1: S978-S987, (2017)
- [15]. C.F. Bagamboula, M.Uyttendaele, Debevere. Inhibitory effect of thyme and basil essential oils, carvacrol, thymol, estragol, linalool and P-cymene towards shigella sonneri and S.flexneri. J of Food microbial, 21:33-42, (2004)
- [16]. N.Erdemog, E.peli, E.yes. Antiinflammatory and antinociceptive activity assessment of plants used as remedy in Turkish folk medicine. J of Ethnopharmacol, 89:123-125, (2003).

- [17]. C.perez, M.pauli, P.Bazerque. An antibiotic assay by the agar-well diffusion method. *Acta Bio Med. Exp*, 15: 13-115, (1990)
- [18]. Aurel Pui, Theodor Malutan, Lucia Tatary, Corina Malutan, Doina Humelnicu, Gabriela Carja, New complexes of lanthanide Ln (III), (Ln =La, Sm,Gd,Er) with Schiff base derived From-2-Furaldehyde and phenyldiamines. *Polyhedron*, 30(20):127-2131, (2011)
- [19]. Priyanka Chakraborty, Sasankasekhar Mohanta. Mononuclear and heterometallic dinculear, trinuclear and dimer-of-dinculear complexes derived from single- and double-compartment Schiff base ligands having a less utilized diamine. *Polyhedron*, 87: 98-108, (2014)
- [20]. Veli T.Kasumov, Seniz Ozalp-Yaman, Esref Tas. Synthesis, spectroscopy and electrochemical behaviors of nickel (II) complexes with tetradentate Schiff bases derived from 3,5-Bu^t₂-Salicylaldehyde. *Spectrochimica Acta Part -A*, 62: 716-720, (2005)
- [21]. Baojiao Gao, Dandan Zhang, Yanbin Lit Synthesis and photoluminescence properties of novel Schiff base type polymer-rare earth complexes containing Furfural-based bidentate Schiff base ligands. *Opticals materials*, 77: 77-86, (2018)
- [22]. Panna Kitiphaisalnont, Santi Thohinung, Prapaipim Hanmugtum, Narongsuk Chaichit. Effect of metal ions and length of alkylene bridge on the strength of hydrogen bonds in diiminedioxime cobalt (III) and nickel (II) complexes. *Polyhedron*, 25: 2710-2716, (2006)
- [23]. Hassan Keypour, Nasibeh Rahpeyma, Majid Rezaeivala, Parisa Arxzhangi, Mehdi Bayat. Synthesis and structural characterization of a new Schiff base macrocyclic ligand containing a piperazine head unit and its metal complexes. Crystal structure of the Co (II) complex. *Polyhedron*, 51:117-122, (2013)
- [24]. Omyma A.M. Ali. Palladium (II) and Zinc (II) complexes of natural N₂O₂ donor Schiff base derived from furfuraldehyde: Synthesis, characterization, fluorescence and corrosion inhibitors of ligands. *Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy*, 132: 52-60, (2014)
- [25]. Eliene Leandro de Araujo Hellen Franciane Goncalves Bbarbosa Edward Ralph Dockal Eder Tadeu Gomes Cavaleiro. Synthesis, characterization and biological activity of Cu (II), Ni (II) and Zn (II) complexes of biopolymeric Schiff bases of salicylaldehydes and chitosan. *J of Biol macromolecule*, 95: 168-175, (2017)
- [26]. Omyma A.M. Ali, Samir M. El. Medani, Maha R. Abu serea, Abeer s S, Sayed, Unsymmetrical Schiff base (ON) ligand on complexation with some transition metal ions. Synthesis, spectral characterization, antibacterial, fluorescence and thermal studies, *spectrochimica Acta part A. Molecular and Bimolecular spectroscopy*, 136: 651-660, (2015)
- [27]. Kusai Alomar, Anne Landreau, Magali Allain, Gilles Bouet, Gerald Larcher, Synthesis, Structure and antifungal activity of thiopene-2,3-dicarboxaldehyde bis(thiosemicarbazone) and nickel (II), Copper (II) and Cadmium (II) complexes. Unsymmetrical coordination mode of nickel complex, *Journal of Inorganic Biochemistry*, 126: 76-83, (2013)