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Synthesis, Characterisation And Biological Studies On Fe(II) AND Zn(II) Quinoline Schiff Base Complexes

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Abstract: The synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their application as catalyst in many reactions and related to synthetic organic and natural oxygen carriers. Molecules containing donor-acceptors such as Schiff bases have ability to serve as polymeric ultraviolet stabilizers, laser dyes .The present work is focused on the study of co-ordination behaviour of thiosemicarbazone Schiffbase with hydrated Fe(II) and Zn(II) chlorides. Analytical and spectral data confirmed the structure of the complexes.Also absorption at 305nm might be due to the extended conjugation of the ring or may be due to the ring residue. Antibacterial and Antifungal activities were carried out using Disc diffusion method and the compounds were found to be active.
Keywords: Schiff base complexes, Antibacterial activity, Antifungal activity.

Introduction

Coordination compounds have found application in medicine in the treatment and diagnosis of diseases [1].Coordination compound, any of a class of substances with chemical structures in which a central metal atom is surrounded by nonmetal atoms or groups of atoms, called ligands, joined to it by chemical bonds. Many enzymes, the naturally occurring catalysts that regulate biological processes, are metal complexes [2].. A hydrolytic enzyme important in digestion, contains a zinc ion coordinated to several amino acid residues of the protein. The divalent cations Zn^{2+}, Ca^{2+} and Mg^{2+} prevent cytotoxicity Among the transition metals iron, cobalt, nickel,zinc and copper complexes are extensively studied because of their application towards novel biological properties [3].Transition metal complexes acts as a homogeneous catalyst in many industrially important reactions such as hydrogenation, hydrosilation, hydroformylation, polymerization, isomerisation, acylation and oxidative hydrolysis of olefins and related to synthetic organic and natural oxygen carriers [4] and [5].Bimetallic coordination complexes may serve as model for variety of biological reactions such as oxygen transport, oxygen activation, photosynthetic water reduction, the study of electron transfer process, metal-metal interactional multi centered catalysis [6]. Iron plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin [7] & [8]. The color of blood is due to the hemoglobin, an iron-containing protein. Finely divided Nickel is used as a catalyst in the hydro generation of oils and fats [9]. In coenzyme B^{12} cobalt is bound to a tetraazamacrocyclic ligand [10]. In addition to the varied magnetic property and catalytic activities, the transition metal Schiff base complexes can also serve as efficient models for metalloproteins and enzymes [11] & [12]. Molecules containing donor-acceptors such as Schiff bases have ability to serve as their implication in biology [13].

Experimental Work

All the chemicals used were of analar grade. The solvents used were neat and dried. The TLC Plates were prepared by using silica gel G. Petroleum ether, Ethyl acetate and ethanol were used as irrigants. Microwave oven was used for the irradiation of reactions.

Preparation of Ligands:

Preparation of 2-Hydroxy-7-Methyl-quinoline-4-Carboxy Thiosemicarbazone (1):

When equal moles of 7-methyl-quinoline-3-carbonyl chloride and thiosemicarbazone in ethanol was refluxed for 18-22 hours on irradiation give 2-Hydroxy-7-methyl-quinoline-4-carboxy thiosemicarbazone. The completion of the reaction confirmed by thin layer chromatography and the reaction mixture, washed with Petroleum ether and dried.

Melting Point: 174˚c. Yield: 5.2g (87%).

Preparation of 7-Methyl -2- Hydroxy- Quinoline-4-Carboxy Thiosemicarbazone-Schiff base (2):

An ethanolic solution of 0.500g , 7-methyl quinoline thiosemicarbazone was irradiated for 40 seconds with 0.3ml of benzaldehyde which give **7-methyl 2- hydroxy quinoline-4-carboxy thiosemicarbazone-schiff base** the excess solvent was evaporated, washed and recrystallised from ethyl acetate.

Melting Point :140˚c. Yield : 3.8. g (73%).

Preparation of Iron Complex (3):

An ethanolic solution 0.080g of ferrous chloride was slowly added to the quinoline semicarbazone Schiff base(III) and the mixture was irradiated for 30 seconds. The reaction mixture was allowed to stand for 2 days at room temperature. A Light brown coloured needles were obtained.

Appearance: Needles Color: Light brown

Melting point : 230˚C.

Preparation of Zinc complex (4):

An ethanolic solution of 0.0756 g of zinc chloride was slowly added to the quinoline semicarbazone Schiff base (2) and the mixture was irradiated for 30 seconds. The reaction mixtures were allowed to stand for 2 days at room temperature. A colourless needle was obtained.

Appearance: Needles Color: Colourless

Melting point:218˚c.

Results and Discussion

The present work is focused on the study of co-ordination behavior of thiosemicarbazone Schiffbase with hydrated Fe(II) and Zn(II) chlorides (Reaction Schemes 1 & 2).

The complex thiosemicarbazone Schiff base was obtained via 7-methyl quinoline-4-carboxy-thiosemicarbazone synthesized by refluxing equal moles of 7-methylquinoline -4-carbonylchloride and thiosemicarbazide in ethanol for 18-22 hrs.The 7-methyl quinoline -4-carboxythiosemicarbazone and benzaldehyde in equal moles were refluxed in ethanol for 18hrs at 80^{o}C.

IR spectrum of the compound (1) showed absorption peaks at1692cm^{-1}(CO),1670 cm^{-1} (CO),1635 cm^{-1} (CN of quinoline ring),1646cm^{-1} (CH=N,)1215cm^{-1} (C=S) **fig(1).** UV spectrum of the compound showed absorption at 280nm, 271nm, 227nm.

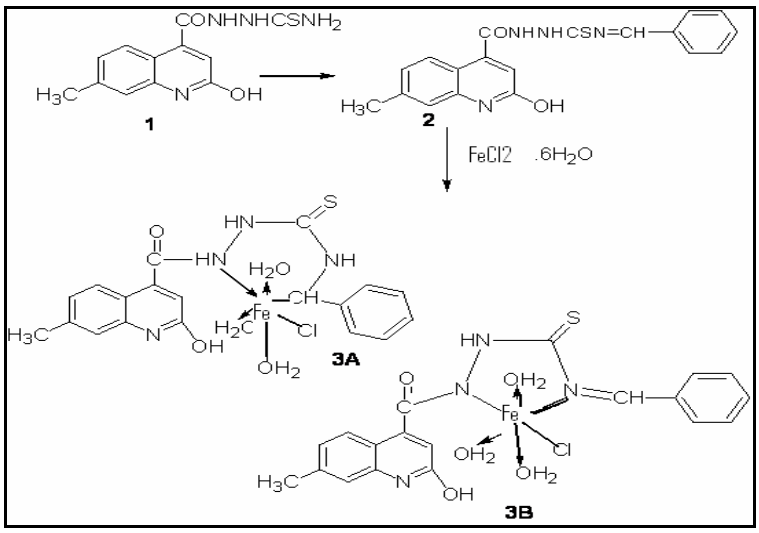
The Schiff base obtained was then irradiated with the ethanolic solution of ferrous chloride to form the Iron complex. 0.500g(0.00031mol) of Schiff base and 0.080g(0.00031mol) of $FeCl_2.6H_2O$ was taken in hot solution of ethanol and irradiated in microwave oven.a light brown crystal of needle shape was obtained.

IR spectrum of the compound 2-Hydoxy-7-methyl-quinoline-4-carboxy thiosemicarbazone showed absorption peaks at 1699 cm^{-1} (CO),1672 cm^{-1} (CO),1635 cm^{-1} (CN of quinoline ring),)1212cm^{-1} (C=S) disappearance of peak at 1636 cm^{-1}.

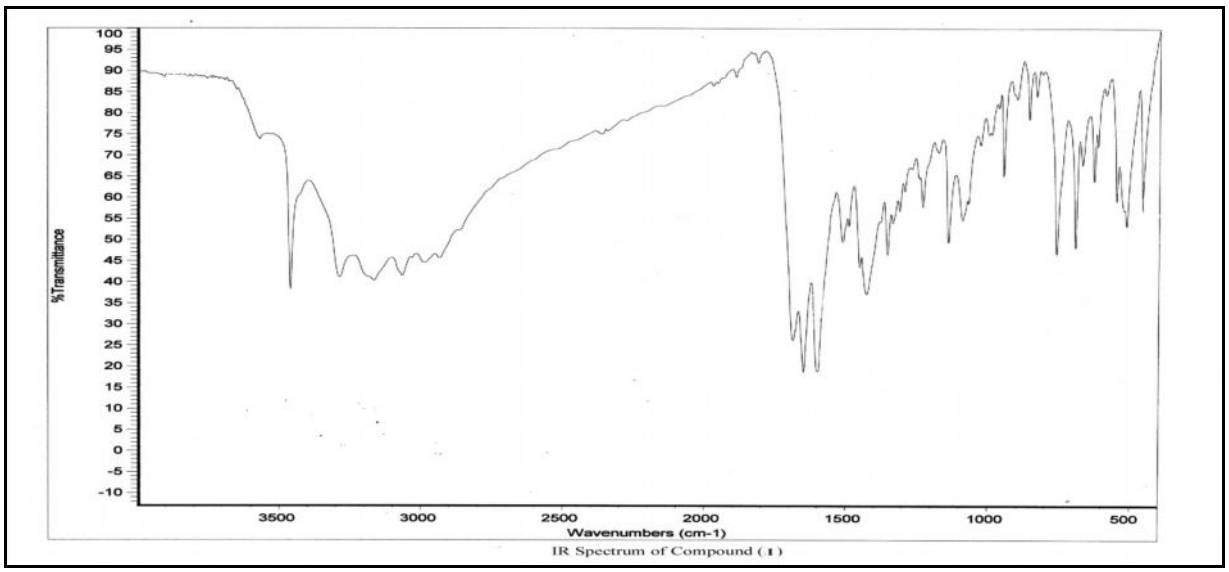
UV spectrum of the compound showed absorption at 280nm, 232nm,a disabsorption at 279 nm which might be due to the loss of one extended conjugation.Disappearance of peak at 1624 cm^{-1} infers that the C=N group of the Schiff base is utilized in the formation co-ordinaton between the metal and the complex ie .,(-N-C-Fe-) bond.

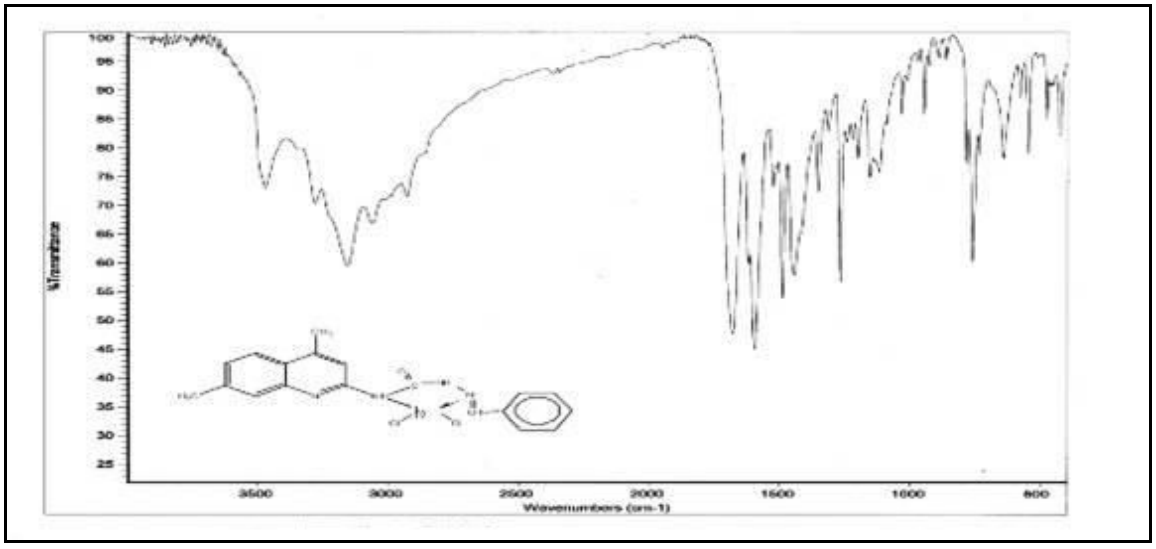
A desorption at 279nm in the UV absorption spectrum indicates the non existence of one extended conjugation during co-ordination.

Thus from the spectral and analytical data the structure of the compound formed was confirmed to be 3A and not 3B.

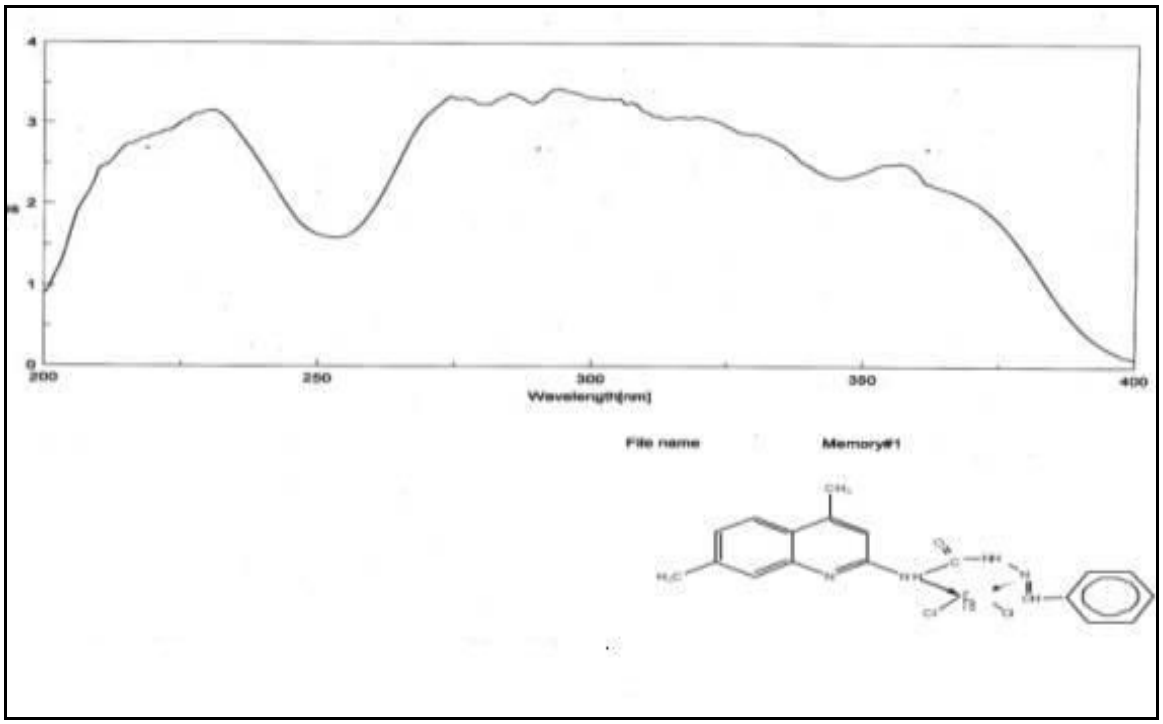


Reaction Scheme for the Formation of Iron Complex





IR Spectrum of Compound 3A



UV Absorption Spectrum of Iron Complex

The 7-methyl 2 hydroxy quinoline-4-carboxy thiosemicarbazone-schiff base was then subjected to salt to coordinate with Iron to form the Iron complex.

To a hot ethanolic solution of 0.500g(0.00031mol) of Schiff base(2) and 0.0756 g (0.0031mol) of NiCl2.6H2O in ethanol was added and irradiated in the microwave oven for 50 seconds a colourless needle was obtained.

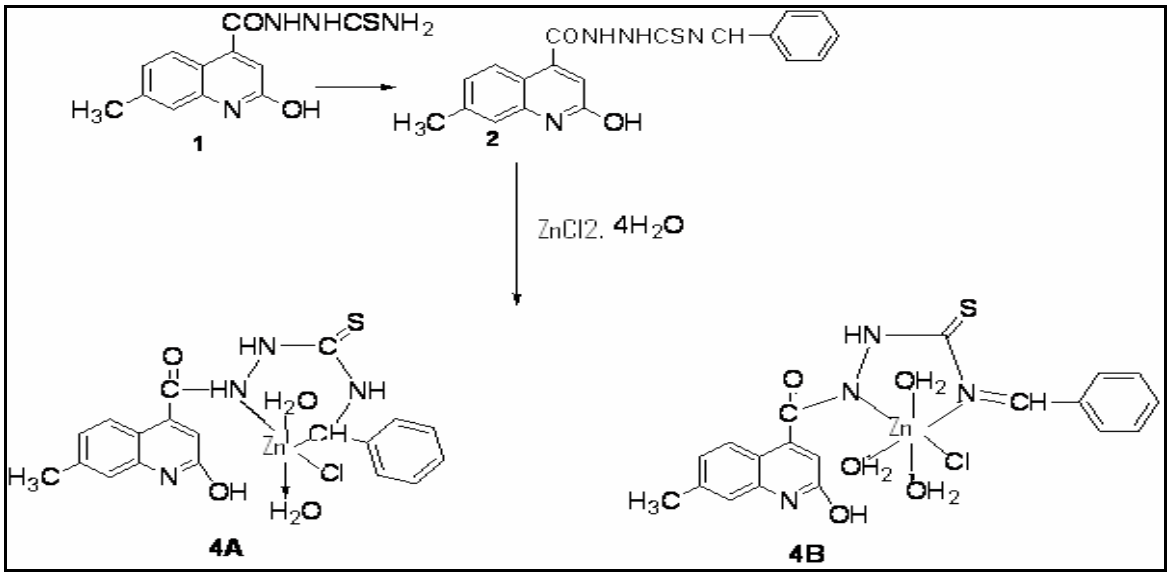
IR spectrum of the compound 2-Hydroxy-7-methyl-quinoline-4-carboxy thiosemicarbazone showed absorption peaks at 1713 cm-1 (CO),1630 cm-1 (CN of quinoline ring);1611 cm-1 (CH=n;)3288 cm-1 (NH=C=S ⟷ N=C-SH); 1213 cm-1 and 761 cm-1 (-C=S ⟷ C-SH) .

UV spectrum of the compound showed absorption at 302nm, 289nm, 280nm, 235nm Presence of absorption max at 302nm.

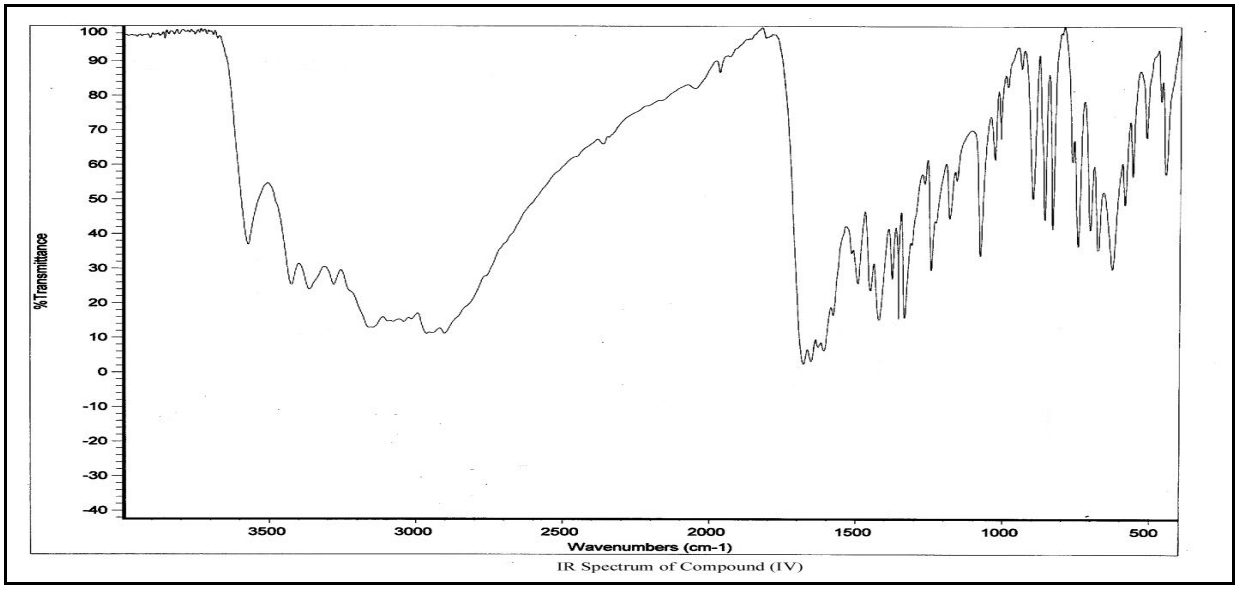
The tautomerism in the IR spectrum showed the NH=C moiety is not disturbed during co-ordination.

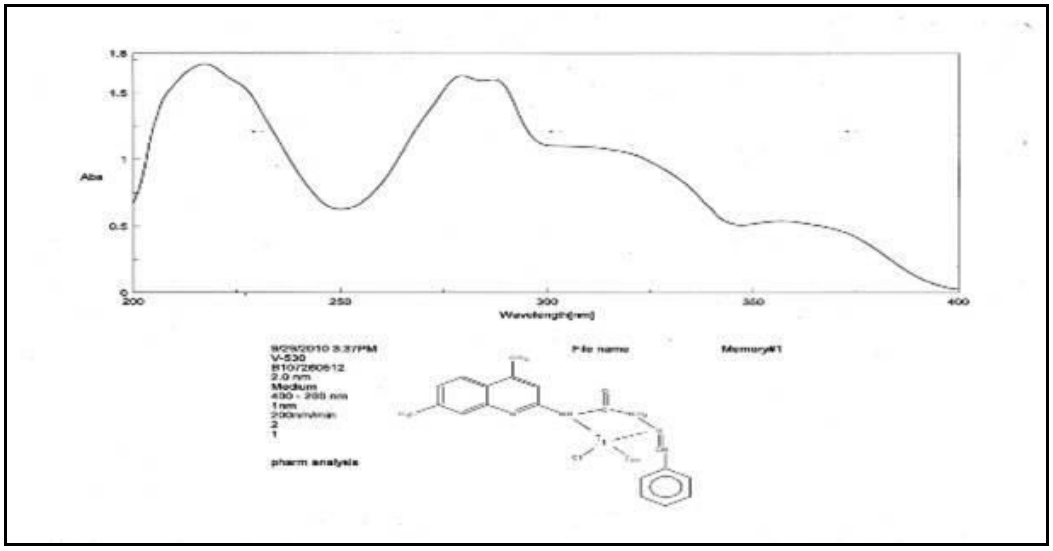
Absorption at 302nm might be due to the extended conjugation of the ring or may be due to the ring residue. This shows that the the coordination is formed between the lone pair of nitrogen and hence a 5-membered -6-coordination was confirmed.

From the spectral and analytical data the structure of the compound formed was confirmed to be 4B and not 4A.



Reaction Scheme for the Formation of Iron Complex





Biological Activity

The disc diffusion method uses filter paper discs, 6.0mm in diameter, charged with appropriate concentrations of the drugs. The disc are stored dry in cold. A suitable dilution of a broth culture or a broth suspension of the test bacterium is flooded on the surface of a solid medium (Mueller-Hinton agar).Compounds **1, 2, 3A** and **4B** were tested against the bacterias E.Coli and staphylococcus albus and the fungi candida species and Aspergillus niger at various concentrations 100µg/L, 50µg/L, 25µg/L.

Antibacterial & Antifungal Activities :

Antibacterial and antifungal activities were carried by Kirby-Bauer Method (Disc diffusion method). The media for antibacterial study is Muller Hintan Agar(MHA). The media for antifungal study is Sabouraul Dextrose Agar(SDA). The standard used was Gentamycin for antibacterial studies. The standard used for antifungal studies was Ketocandizole.

Table-1 shows the antibacterial activity of the compounds 1, 2, 3A and 4B against E.coli and Staphylococcus albus. It was found that all the compounds were active. Among the four compounds 3A and 4B are active than their precursors.

The antibacterial activity of the compound was almost closer to the standard gentamycin.

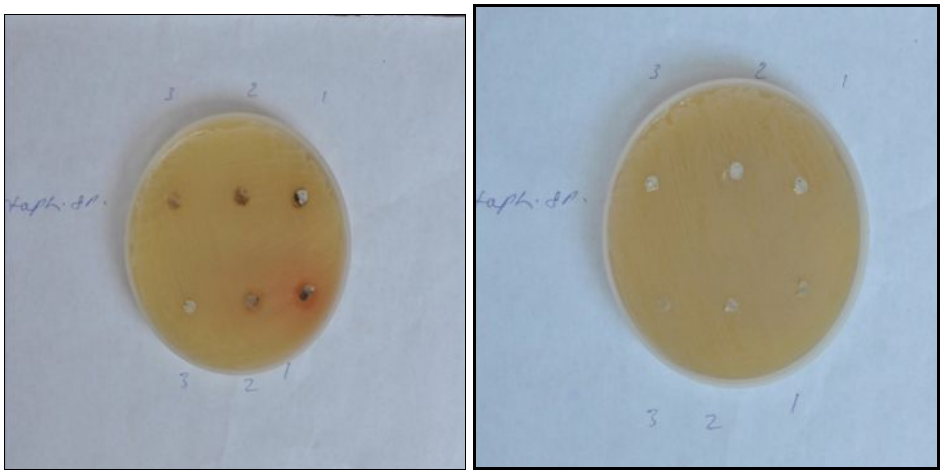
Table-3 shows the antifungal activity of the compounds 1, 2, 3A and 4B against Candida species and Aspergillus niger. It was found that all the compounds were active. Among the four compounds 3A and 4B are active than their precurors.

The Fungi Candida species was found to be active than Aspergillus niger. Aspergillus niger shows only moderate activity.

The antifungal activity of the compound was almost closer to the standard Ketocandizale.

Table-1 Antibacterial Activity

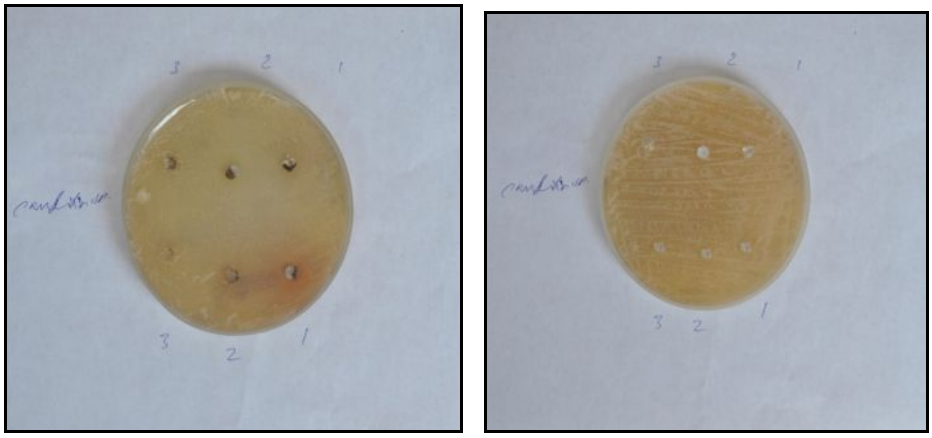
Samples	Concentrations (100µg/l)	(50µg/L)	(25µg/L) in mm	Concentrations (100µg/l)	(50µg/L)	(25µg/L) in mm
	E.Coli			**Staphylococcus albus**		
Compound 3A	5	3	3	5	3	2
Compound 3B	5	4	4	7	5	1
Compound 4A	7	5	4	7	4	2
Compound 4B	7	3	2	8	6	2
Gentamycin	10	8	8	12	10	8



Antibacterial Activities of the compounds 3A and 4B against Staphylococcus albus

Table-2 Antifungal Activity

Samples	Concentrations (100µg/l) (50µg/L) (25µg/L) in mm			Concentrations (100µg/l) (50µg/L) (25µg/L) in mm		
	Candidaspecies			Aspergillus niger		
Compound 3A	6	3	4	5	3	2
Compound 3B	5	4	4	4	2	2
Compound 4A	5	3	3	6	2	2
Compound 4B	8	6	2	6	2	2
Ketocandizale	10	8	8	8	6	6



Antifungal Activities of the compounds 3A and 4B against Candida species.

Conclusion

Co-ordination behaviour of Fe(II) and Zn(II) complexes and the antibacterial activity and antifungal activity were studied in the present work.The acid chloride(1) was reacted with thiosemicarbazide at 80°C for 16-22 hours and to obtained thiosemicarbazone(2).Equal moles of thiosemicarbazone(2) and $FeCl_2.6H_2O$ were irradiated under microwave oven to obtain the complex 3A.Equal moles of thiosemicarbazone(2) and $ZnCl_2.6H_2O$ were irradiated under microwave oven to obtain the Zn complex(4B).Analytical and spectral data confirmed the structure of the complex as 3A and 4B. Antibacterial and Antifungal activity were carried out using Disc diffusion method and the compounds were found to be active.

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