Synthesis, Structure, Characterization and Antimicrobials Studies of Fe(II) and Mn(II) complexes with 3-amino-2-methylquinazolin-4-phenylydrazone (HAQP)

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ABSTRACT

Quinazolin-4 (3H)-one and its derivatives form a number of complexes with transition metal ions. Quinazoline based Schiff base ligand 3-amino-2-methylquinazolin-4-phenylhydrazone (HAQP) was synthesized in the laboratory from 3-amino-2-methylquinazolin-4-one and phenylhy- drazine. Complexes of Fe(II) and Mn(II) with HAQP were synthesized and characterized by elemental analysis, infrared spectral, electronic transition, thermogravimetry, magnetic susceptibility, molar conductivity, NMR datas and solubility test. I.R. spectra of ligand shows a sharp band at 1650cm^{-1} attributed to $\upsilon_{C=N}$, which is a feature of azomethine group. The same band was observed in respective metal complexes. There is no band between 1700 cm^{-1} to 1800 cm^{-1} indicating absence of >C=O group. The band at 3300cm^{-1}, 3160cm^{-1} and 1470cm^{-1} attributed to $\upsilon_{a}NH2$, $\upsilon_{s}NH2$, $\upsilon_{\delta}NH2$ respectively of amino group present at -3 position in ligand. The different type of signals were observed in NMR spectra due to different type of protons, Molar conductance values 15 and 23 ohm^{-1} cm^{2}mol^{-1} show that Fe(II) and Mn(II) complexes were non electrolyte in nature. The magnetic moment values was found to be positive revealing that complexes are paramagnetic. The result of antimicrobial studies indicated that, the metal(II) complexes exhibited better antibacterial and antifungal activity than ligand.

Keywords: *Quinazoline, Azomethine, IR, NMR, Electronic Transition, Antibacterial and Antifungal Activities etc.*

1. INTRODUCTION

Schiff base compounds are very popular ligands because of their easy formation and rich co-ordination chemistry with a large variety of metal ions, that has allowed their use as catalysts in different asymmetric synthesis. Schiff base is a

compound containing an immine or azomethine group (-N=CH-). It is a condensation product of aldehyde or ketone with primary amine and was first reported in 1864 by a German chemist Hugo Schiff. Schiff base is very important structure for synthetic organic chemistry. The azomethine (-N=CH-) linkage is essential for biological activity. Azomethine nitrogen in the Schiff base ligand not only provides binding sites for metal/metal ions but also makes attchmetnts in various substrate of bio-molecules like proteins and amino acids in biological systems. Several important hydrometallurgical processes utilize metal complexes. Nickel, cobalt and copper can be extracted from their ores as ammine complexes using aqueous ammonia. Transition metal complexes are important in catalysis, material synthesis, photochemistry, and many biological systems. Medicinal inorganic chemistry can exploit the unique properties of metal ions for the design of new drugs. The multidentate Schiff base ligands are capable of producing very stable complexes with transition metals like Ni, Fe, Co, Cu, V, Mn *etc*. Most of the metal chelates have generally higher antibacterial and antifungal activities than the individual ligands. Many transition metal complexes were reported to have antitumor, anti-inflammatory, antioxidant, antimalarial and antimicrobial activities. Metal complexes with N,O as their donor atoms are very noticiable because of their important biological activities like anticancer, herbicidal and pesticidal activities.

In the present paper the ligand 3-amino-2-methylquinazolin-4-phenyly-drazone (HAQP) was synthesized from 3-amino-2-methylquinazolin-4-one and Phenyl hydrazine. In order to determine the nature of interaction of ligand (HAQP) with different metal ions like Fe(II), Mn(II), we have used them for the synthesis of their complexes. The complexes have been characterized on the basis of analytical data, conductivity measurement, magnetic susceptibility, thermo-gravimetry, infrared, nuclear magnetic resonance and electronic transition datas. The antimicrobial activities of ligand and complexes were determined.

2. EXPERIMENTAL SECTION

2.1 Materials

All the reagents and chemicals used in this research work were of analytical grade and used without further purification.

2.2 Physical Measurements

The analytical data (C,H,N) for ligand and their metal complexes were analysed through Cario Erba 1108 elemental analyzer. Fe and Mn in the complexes after heating to decomposition were estimated by using standard Potassium permanganate solution and EDTA Solution. All weighing were carried out using an electric balance model AB54. The IR spectra of ligand and its metal complexes were recorded using KBr pellets in the range 4000-400cm^{-1} on a perkin-Elmer IR spectrophotometer, Model-883. Conductance measurements of the complexes were done in water and dimethylsulfoxide (DMSO) solvent using a HANNA instrument equipped with a HI 8820N conductivity cell. Melting point and decomposition temperature measurements were done with a SMP10 STVART melting point apparatus. The Magnetic susceptibility measurements of the complexes in solid state were carried out on a Guoy balance at room temperature using $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were applied using pascals constant. Electronc absorption spectra were recorded on a Schimadzu UV-visible spectrophotometer, Model-MPS-5000. $^1H_1$ spectra was recorded on a 200 MH_Z varian Gemini instrument. For want of neat solubility of the complexes in DMSO, quantitative spectra could not be recorded. The antimicrobial activity of ligand and metal complexes were screned against different types of bacteria and fungi. The result of the antimicrobial studies showed that the Metal(II) complexes have superior activity than its free ligand.

2.3 Synthesis of the Intermediate

3-amino-2-methylquinazolin-4-one

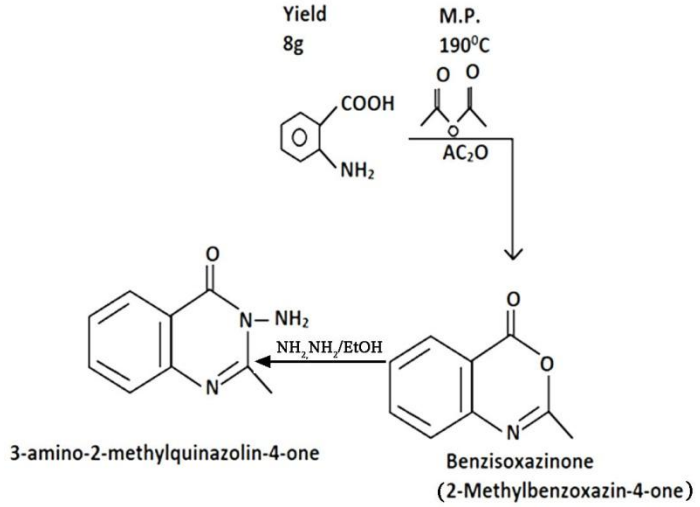
13.7g (0.1 mol) Anthranilic acid was added to aqueous acetic anhydride (30 c.c) and subsequent solution was heated under reflux condition on water bath about

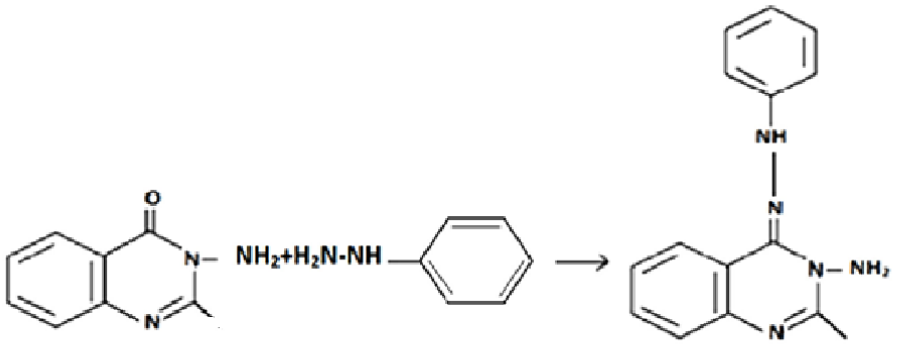
an hour. Excess acetic anhydride was distilled off. The concentrated solution was taken into another beaker and cooled on ice bath. Acetanthraline was filtered. 50% aqueous solution of hydrazine hydrate (100 c.c) was added to prepared acetanthraline gradually with continuous stirring. White bulky ppt. of 3-amino-2-methylquinazolin-4-one was separated out. It was allowed to cooling and filtered. It was recrystallized from aqueous ethanol followed by diethylether. The reaction is shown in (Scheme1).

2.4 Synthesis of Ligand

3-amino-2-methylquinazolin-4-Phenylhydrazone (HAQP)

The ligand was synthesized by condensation of 3-amino-2-methyl-quinazolin-4-one (8g) with alcoholic solution of Phenylhydrazine (10g). The mixture was heated under reflux condition about 08 hours in the presence of three to four drops concentrated H_2SO_4. The reaction mixture was cooled to room temperature and then ligand was separated by filtration. It was washed with cold acetic acid to get a pure sample. Crystals possess brownish red colour but when dried it became yellow. The chemical reaction is represented in Scheme-2. The ligand was analysed as $C_{15}H_{15}N_5$.





3-amino-2-methylquinazolin-4-phenylhydrazone
(HAQP)

2.5 Antibacterial Activity Test

The same method was used in antibacterial test as used by Jorgensen (Jorgensen and Turnidge, 2003). In this method, Schiff base ligand and Metal(II) complexes were assayed by agar disc diffusion and using cultures of Escherichia coli, salmonella typhi and staphylococcus aureus. The samples were separated dissolved in DMSO to have different concentrations (1500, 2500, 3500) μ_g/disc. Each of these was separately placed on the surface of the culture media before incubation at 37^0C for 30 hours. The diameter of zone inhibition produced by the ligand and its metal(II) complexes was compared with standard drug, amoxicillin capsule.

2.6 Antifungal Activity Test

The in vitro antifungal activity of the ligand and its Fe(II) and Mn(II) complexes were assayed using three fungal isolates Aspergillus flarus, Aspergillus niger and Mucor indicus using different concentrations (1500, 2500, 3500) μ_g/disc by Disc Diffusion Technique. Potato Dextrosc Ager (PDA) was used to prepare the culture media and incubated at room temperature for seven days. The results obtained were compared with the activity of ketoconazole (200 mg) as a stanndrad antifungal drug and DMSO as negative control.

3. RESULT AND DISCUSSION

Schiff base ligand (HAQP) and its metal(II) complexes were prepared in good yield. The physical properties of the synthesized ligand and its complexes were analyzed and presented in Table 1. The percentage yield of ligand was 90% while that of Metal(II) complexes were 72% and 68% respectively. The ligand (HAQP) crystal was yellow when dried where as Fe(II) and Mn(II) complexes

were brown and pink respectively. It was measured that melting point of ligand was 190^0 and decomposition temperature of the Fe(II) and Mn(II) complexes were 300^0C and 305^0C. This is an indication of thermal stability of the complexes. The effective magnetic moments values of Fe(II) and Mn(II) complexes are 5.13 BM, 5.93 BM. This is an indication of paramagnetic behavior of complexes.

The complexes are stable at room temperature, non-hygroscopic, insoluble in water and many of the common organic solvents (Table 2) but soluble in DMF and DMSO. The molar conductance of the complexes in DMSO were found 15 and 23 $ohm^{-1}cm^2mol^{-1}$ for Fe(II) and Mn(II) complexes which is less than 26 $ohm^{-1}cm^2mol^{-1}$ thus indicationg the non electrolytic behavior. The analytical data of the complexes indicates that their stoichiometry range be represented as 1:2 (metal to ligand ratio) and presented in table 3. The ligand was analysed as $C_{15}H_{15}N_5$ while complexes were analysed as [Fe $(AQP)_2$ $(H_2O)_2$] and [Mn $(AQP)_2$ $(H_2O)_2$].

Table : 1

Physical Properties of the ligand and its Metal(II) complexes.

Ligand/Complexes	Colour	% yield	M.P (^{0}C)	D.Temp.	μeff	Molar conductance $ohm^{-1}cm^2mol^{-1}$
HAQP	Yellow	90	190	-	-	-
[Fe $(AQP)_2$ $(H_2O)_2$]	Brown	72	-	300	5.13	15
[Mn $(AQP)_2(H_2O)_2$]	Pink	68	-	305	5.93	23

Keys : M.P. = Melting Point, D. Temp. = Decomposition Temperature

Table : 2

Solubility test of the ligand and its metal(II) complexes

Ligand/Complexes	Solvents						
	Acetone	n-Hexane	DMF	DMSO	CCl_4	Ethanol	Water
HAQP	SS	IS	S	S	S	SS	IS
[Fe $(AQP)_2$ $(H_2O)_2$]	SS	IS	S	S	S	SS	IS
[Mn $(AQP)_2(H_2O)_2$]	SS	IS	S	S	S	SS	IS

Keys : S = Soluble, IS = Insoluble, SS = Sparingly Soluble.

Table : 3

Analytical data of the ligand and its metal(II) complexes

Ligand/Complexes	Found (Calculated)%			
	Metal	C	H	N
HAQP	-	67.81 (67.92%)	5.54 (5.66%)	26.32 (26.41%)
[Fe $(AQP)_2$ $(H_2O)_2$]	9.01 (9.03%)	58.01 (58.06%)	4.41 (4.51%)	22.45 (22.58%)
[Mn $(AQP)_2(H_2O)_2$]	8.74 (8.88%)	58.01 (58.15%)	4.38 (4.52%)	22.43 (22.61%)

4. SYNTHESIS OF METAL(II) COMPLEXES

4.1 Synthesis of Bis(3-amino-2-methylquinazolin-4-Phenylhydrazone)-diaquo-Iron(II).

1.954g (0.005 mol) Mohr's salt in ethanol was added to solution of 3.54g (0.01 mol) 3-amino-2-methylquinazolin-4-phenylhydrazone prepared in mixture of ethanol and acetone (4:1). The mixture was heated under reflux condition about 5 hours and P^H was maintained 8.3. Green crystal separated out on cooling the mixture. It was filtered, washed with alcohol and dried. It was analysed as [Fe $(C_{15}H_{15}N_5)_2$ $(H_2O)_2$].

4.2 Synthesis of Bis(3-amino-2-methylquinazolin-4-phenylhydrazone)-diaquo Manganese(II).

Ethanolic solution of 1.384g (0.05 mol) Manganese sulphate heptahydrate was added to the alcoholic and acetone (4:1) solution of 3.54g (0.01 mol) 3-amino-2-methylquinazolin-4-phenylhydrazone. This was heated under reflux condition about six hours and P^H was maintained 8 during whole reaction. On cooling solid mass settled. It was filtered and washed with ethanol and ether. It was dried at room temperature and analysed as [Mn $(C_{15}H_{15}N_5)_2$ $((H_2O)_2$].

4.3 Thermogravimetry Analysis

Complexes $[Fe(C_{15}H_{15}N_5)_2((H_2O)_2]$ on heating looses mass equivalent to two mole of water at 170^0C, which suggests water molecules in coordination. Complex decomposes at 300^0C.

When 0.5g of $[Mn(C_{15}H_{15}N_5)_2(H_2O)_2]$ complex was heated upto 235^0C, the loss in weight was 4.5mg, which is equivalent to two mole of water. This indicates water molecules are in Co-ordination sphere. Complexes decomposes at 305^0C.

4.4 IR and NMR Spectroscopy

The important absorption frequencies of ligand and complexes along with their assignment are presented in table 4. The IR spectra of ligand and its complexes were recorded in nujol and KBr in the range of 4000-400cm^{-1}. IR spectra of ligand shows a sharp band at 1650cm^{-1} attributed to stretching vibration, $\upsilon_{C=N}$. The band at 3300, 3160, and 1470 cm^{-1} were observed assigned to υ_{aNH2}, υ_{sNH2} and $\upsilon_{\delta NH2}$ of amino group present at 3-position in ligand. The band at 3090 cm^{-1} and above indicating the stretching vibration frequency of the following moiety :

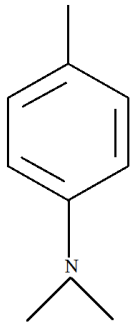


Figure : I

The NMR spectra was recorded on a 200 MH_Z varian Gemini instrument. $^1H_1$ spectra recorded in neutral solution (acetone) shows signals at τ = 1.00, 1.50, 1.65, 1.75, 1.90 and 2.10 attributed to different ring protons. Signals at τ = 7.3 and 6.9 assigned to amino and anilino protons respectively. The NMR spectra recorded in alkaline medium shows nearly same signal due to ring protons. The doublet signals appeared in netural solution at τ = 7.5 without resolution indicative of

deprotonation due to removal of anilino proton and diminishing of spin interaction of $–NH_2$ Proton. So, only one unresolved signal was appeared at τ = 7.5. The signals at 8.1 attributed to methyl proton present at 2-position in ligand and signals at τ = 7.6 are due to methyl proton of acetone. Thus, ligand may be represented as:

$$HAQP \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} AQP^- + H^+$$

Yellow *Brownish* Red

The NMR data for different types of proton is presented in table 5.

On the basis of elemental analysis, IR spectra and NMR signals, the following structure was proposed for ligand (HAQP)

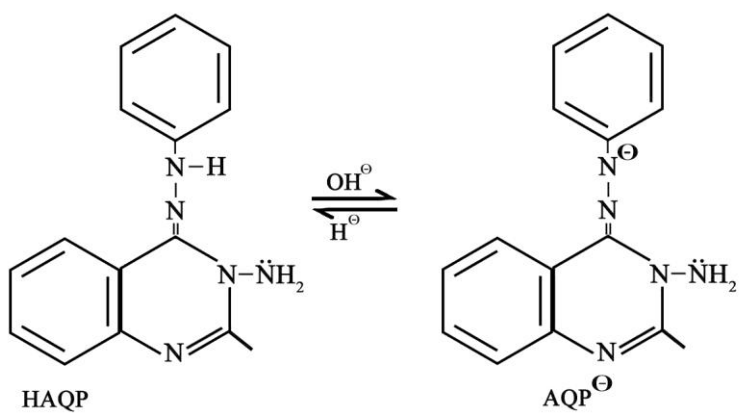


Figure : 2

The deprotonation and complex formation in alkaline meduium support the Co-ordination through anilino nitrogen (not by azomethine nitrogen) and amino nitrogen. This is further supported by IR spectra of complexes where there is no shift in the azomethine (>C=N-) frequency.

AQP^- acts as bidentate ligand in alkaline medium and Co-ordinate to metal ion as :

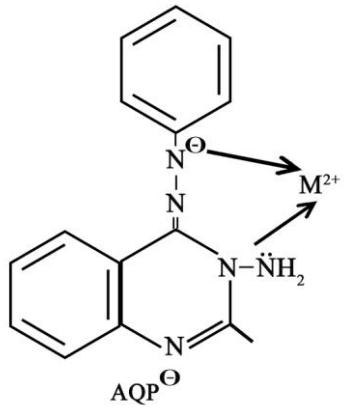


Figure : 3

IR spectra of [Fe $(AQP)_2$ $(H_2O)_2$] Shows band at 3260 and 3120 cm^{-1} assigned to υ_{aNH2} and υ_{sNH2} which are less by 40 cm^{-1} as compared to ligand. IR spectral band at 1480 cm^{-1} assigned to $\upsilon_{\delta NH2}$ in complex is higher by 10cm^{-1} than that of ligand. This indicates Co-ordination through amino nitrogen. Band at 3430 cm^{-1} attributed to O-H frequency in complex but its appearance at lower frequency shows O-atom in Co-ordination. Band at 370 and 315 cm^{-1} further support the Fe-N and Fe-O bonding respectively.

[Mn $(AQP)_2$ $(H_2O)_2$] complex shows band at 3250, 3100 and 1480 cm^{-1} correspond to $–NH_2$ group. The first two bands are lowered by 50 and 60 cm^{-1} while third band is enhanced by 10cm^{-1} as compared to bands observed in ligand for these stretching vibrations. This clearly indicates co-ordination through amino nitrogen. There is no band at 3090 cm^{-1} indicating deprotonation of anilino proton and co-ordination through anilino nitrogen. The band appears at 300 and 400 cm^{-1} assigned to Mn-N and Mn-O bonding. The band at 3450 cm^{-1} indicates O-H stretching vibration lowered by nearly 100 cm^{-1} than free O-H bond. The band appears in complex at 1650 cm^{-1} assigned to >C=N- group at the same position as in the ligand shows non participation of azomethine nitrogen in Co-ordination.

Table : 4

IR spectra data for ligand and its metal(II) complexes.

Ligand/Complexes	Spectral bands and their frequencies (in cm^{-1})						
	$\upsilon_{C=N}$	υ_{aNH2}	υ_{sNH2}	$\upsilon_{\delta NH2}$	υ_{N-H} (Anilino)	υ_{M-H}	υ_{M-O}
HAQP	1650 (s)	3300 (s)	3160 (b)	1470 (s)	3090 (w)	-	-
$[Fe (AQP)_2 (H_2O)_2]$	1650 (s)	3260 (b)	3120 (w)	1480 (s)	-	370 (s)	315 (s)
$[Fe (AQP)_2 (H_2O)_2]$	1650 (s)	3250 (b)	3100 (w)	1480 (s)	-	300 (s)	400 (s)

Keys : M = Fe, Mn, S = Sharp, b = broad, w= weak

Table : 5

NMR signals data of ligand, 3-amino-2-methylquinazolin-4-phenylhydrazone (HAQP)

$^1H_1$ NMR signals			
Aromatic Ring proton		Amino proton	Anilino proton
(A) In neutral solution	τ = 1.00, 1.50, 1.65, 1.75, 1.90 and 2.10	τ = 7.3	τ = 6.9
(B) In alkaline solution	τ = 1.00, 1.50, 1.65, 1.75, 1.90 and 2.10	τ = 7.5	-

4.5 Electronic Spectra of Metal(II) Complexes

Fe(II) complexes have d^6 configuration with 5_D ground state term. $[Fe (AQP)_2(H_2O)_2]$ complex shows a weak band at 10600 cm^{-1} in visible range and two bands 31500 cm^{-1} and 40400 cm^{-1}. The peak at 10600 cm^{-1} was attributed to 5_{T2g} (D)$\rightarrow 5E_{1g}$ (D) transition. 10Dq value for $[Fe(AQP)_2 (H_2O)_2]$ is 10600 cm^{-1} Which is very close to the 10Dq value found for octahedral Fe(II) Complexes. Other transitions are spin forbidden. Such transitions may take place at higher energy.

Electronic peaks at 31500 and 40400 cm^{-1} Were assigned to $5_{T2g}(H) \rightarrow 3T_{1g}$ (H) and 5_{T2g} (D) $\rightarrow$3Eg (H) respectively.

Mn(II) ion has d5 system with 6s ground term. $6A_{1g}$ is the ground state in octahedral field. There is no spin allowed as well as parity allowed transition in octahedral field. [Mn $(AQP)_2$ $(H_2O)_2$] complex shows one broad band at 18000cm^{-1} and three narrow bands at 21800, 25600 and 30450 cm^{-1} assigned to $^6A_{1g}$ (S)$\rightarrow^4T_{2g}$ (G), $^6A_{1g}$(s)$\rightarrow^4T_{1g}$(G), $^6A_{1g}$(S)$\rightarrow^4E_g$ (G)+4_{A1g}(G) transitions respectively.

The electronic spectral peaks of metal(II) complexes of structural importance are presented in table 6.

Table : 6

Electronic spectral peaks of Metal(II) complexes

Complex	Electronic transition and spectral peaks(In cm^{-1})			
[Fe $(AQP)_2$ $(H_2O)_2$]	$5_{T2g}(D) \rightarrow 5_{Eg}(D)$ 10600	$5_{T2g}(D) \rightarrow 3_{T1g}(H)$ 31500	$5_{T2g}(D) \rightarrow 3_{Eg}(H)$ 40400	
[Mn $(AQP)_2$ $(H_2O)_2$]	$6_{A1g}(S) \rightarrow 4_{T2g}(G)$ 18000	$6_{A1g}(S) \rightarrow 4_{T1g}(G)$ 21800	$6_{A1g}(S) \rightarrow 4_{T1g}(G)$ 25600	$6_{A1g}(S) \rightarrow 4_{Eg}(G)+4_{A1g}(G)$ 30450

4.6 Magnetic Susceptibility :

Fe(II) has $3d^6$ system. The spin only magnetic moment value for Fe(II) is 6.928. M. at room temperature.

Mn(II) ion has d^5 system with 6s ground term. μeff value for [Mn $(AQP)_2$ $(H_2O)_2$] is found as 5.93 B.M. at room temperature.

4.7 Antimicrobial and Antifungal Activity

The result of antibacterial and antifungal activities on ligand (HAQP) and its metal(II) complexes is presented in table 7 and 8. Then ligand and its complexes were screened for their antibacterial activities against the few selected bacteria isolates of Eschirichia coli, salmonella typhi and staphylococcus auresu, by diffusion method (Table 7). It was found that the metal(II) complexes are more effective than free ligand in inhibiting the microbial growth. Similar result was also recorded in table 8 for antifungal activity shown by selected fungi isolates of Aspergillus flarus, Aspergillus niger and Mucor iudicus respectively.

Table : 7

Antibacterial activity on the ligand and its metal(II) complexes.

Compound	Concentration ($\mu g.cm^{-3}$)	Bacterial inhibitiaon zones in mm.		
		staphylococcus auresu	Eschirichia coli	salmonella typhi
Ligand	1500	09	11	10
	2500	08	10	12
	3500	11	09	11
$[Fe (AQP)_2 (H_2O)_2]$	1500	12	12	11
	2500	13	16	16
	3500	17	19	15
$[Mn (AQP)_2 (H_2O)_2]$	1500	10	11	12
	2500	12	14	14
	3500	14	19	17

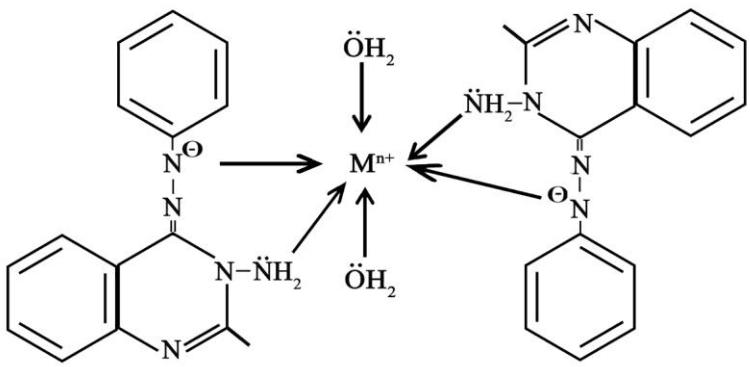
Table : 8

Antifungal activity on the ligand and meta(II) complexes

Compound	**Concentration ($\mu g.cm^{-3}$)**	**Fungal inhibitiaon zones in mm.**		
		Aspergillus flarus	**Mucor ludicus**	**Aspergillus Niger**
HAQP	1500	08	05	06
	2500	10	07	08
	3500	11	09	09
$[Fe (AQP)_2 (H_2O)_2]$	1500	13	11	13
	2500	17	14	16
	3500	20	16	18
$[Mn (AQP)_2 (H_2O)_2]$	1500	12	13	14
	2500	14	18	17
	3500	22	22	21

4.8 Structure of metal(II) complexes

Elemental analysis, molar conductivity, thermogravimetric analysis, spectroscopic tools and magnetic moment data showed that the complexes can be formulated as [M $(AQP)_2$ $(H_2O)_2$] and assuming octahedral geometry.



Proposed Octahedral Geometry of [M(AQP)$_2$ (H$_2$O)$_2$]

Keys : M = Fe, Mn

n = 2

Figure : 4

5. CONCLUSION

The Fe(II) and Mn(II) complexes derived from 3-amino-2-methylqunazolin-4-phenylhydrazome were synthesized and characterized. The molar conductance values of Fe(II) and Mn(II) complexes were found low, indicating the non hygroscopic and non electrolytic behavior of the metal(II) complexes. The elemental analysis data indicates stoichiometry as 1:2 (metal to ligand ratio). The IR data indicated that ligand Co-ordinated to Fe(II) and Mn(II) ions in a bidentate manner via anilino and amino nitrogen atoms. Deprotonation of anilino proton occurred in alkaline medium and complex formation in the same medium supports the co-ordination through anilino nitrogen. Meanwhile, water molecules acts also as a monodentate ligand and co-ordinate through oxygen atom to the central ion, M^{++} (M=Fe, Mn).The complex was formulated as [M $(AQP)_2$ $(H_2O)_2$] . The metal(II) complexes were found to be more active than the ligand but less than the reference drugs Amoxicilln and ketoconazole used.

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