



Study of Nickel (II) and Mercury (II) Schiff Bases Metal Complexes

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ABSTRACT

Novel heterocyclic based metal complexes of Ni (II) and Hg (II) were synthesized from Schiff bases of 3-Acetyl 4-Hydroxy Quinolin-2(1H)-one (AHQ). The Schiff bases 4-hydroxy-3-(1-((4-methylpyridin-2-yl)imino)ethyl)quinolin-2(1H)-one(L₁), 4-hydroxy-3-(1-((5-methylpyridin-2-yl)imino)ethyl)quinolin-2(1H)-one(L₂) were prepared by condensation of AHQ with substituted pyridine moiety. These complexes were characterized by elemental analysis, magnetic moment, electronic and IR spectral analysis. In vitro biological screening effects of the synthesized Complexes were tested for their antibacterial and antifungal activity. For antibacterial activity the bacterial species used were Bacillus subtilis, Escherichia coli, Salmonella typhi, and Staphylococcus aureus while fungal species used were, Aspergillus flavus, Penicillium chrysogenum, Aspergillus niger and Fusarium moneliforme. The antibacterial activity was screened using agar well diffusion method and antifungal activity with poison plate method.

Keywords: AHQ, substituted pyridine, Metal Complexes, Spectral Analysis, Biological Activity.

1. INTRODUCTION

Many Schiff base have drawn wide attention because of their diverse biological and pharmaceutical activities.¹ Azomethine nitrogen in the Schiff base has significant chemical and biological relevance since it not only facilitates binding sites for metal ions but also associate with different substrates of biomolecules, such as proteins and amino acids which are essential components of biological systems.^{2,3} Many Schiff bases derived from heterocyclic moiety possess a wide spectrum of medicinal properties and thus, have been studied for activity against antituberculosis,⁴ antiinflammatory,⁵ antibacterial,⁶ antifungal,⁷ anticancer,⁸ antioxidant,⁹ and many more. Transition metals like nickel, iron, cobalt and copper among others, can form extremely stable complexes with the dynamic schiff base molecule, which can also be a chelating ligand.¹⁰ Usually metal chelates are more effective against bacteria and fungi than the isolated ligands.¹¹ Metal complexes biological potential and chelating power have attracted a lot of attention. The pharmacological activity of metal complexes is highly dependent on the nature of the metal ions and the donor sequence of the ligands because different ligands exhibit different biological properties.¹² The catalytic function of Schiff base metal complexes are observed in various reactions such as oxidation,¹³ epoxidation,¹⁴ polymerisation,¹⁵ condensation,¹⁶ reduction,¹⁷ and other reactions.

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The present investigation deals with the synthesis, spectral characterization (IR, electronic) and antimicrobial activities (antibacterial and antifungal) of Schiff base ligand metal complexes of Ni (II) and Hg(II) derived from AHQ and substituted amino pyridine.

II. EXPERIMENTAL

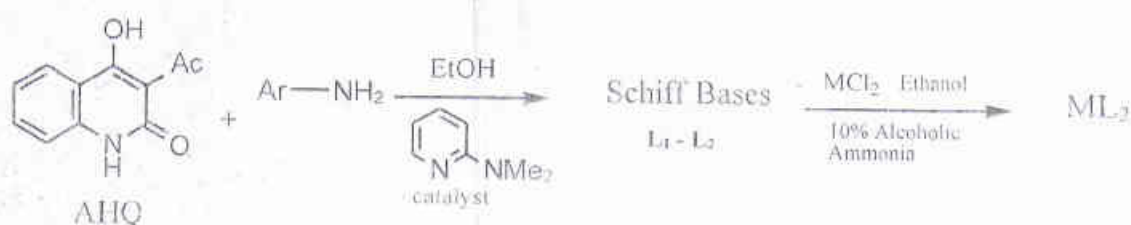
Melting points were determined by open capillary method and were uncorrected. IR spectra were carried out as KBr discs on a Shimadzu, IR-470 Spectrometer. The elemental analysis was determined using the Thermo Fisher Scientific CHN/S/O analyzer instrument. The magnetic susceptibilities of complexes were measured by the Gouy's method at room temperature using the Sherwood scientific magnetic susceptibility balance and using distilled water as the calibrant. Molar conductance of the metal complexes was measured using the Fisher Scientific PH/conductivity meter. The molar conductance measurements were performed using 0.001 M solutions of the complexes in DMSO at room temperature.

GENERAL PROCEDURE FOR SYNTHESIS OF COMPLEXES:

Each complex is synthesized by placing 0.02 moles of ligand (L₁-L₂) in a flask with a flat bottom and 50 milliliters of ethanol. After a brief period of heating, 0.01 moles of a metal salt solution that has been dissolved in 20 milliliters of ethanol is added gradually to the hot ligand solution. After two hours of refluxing, the mixture is chilled. In a cold container with refluxed contents, a freshly made 10% alcoholic ammonia solution is gradually added while being constantly stirred. Precipitation starts to form at pH eight.

For an hour, the precipitated complex is digested. If a pH shift is seen, it is corrected and digested for a further hour. The digested precipitate of complex is filtered in hot water, washed with hot ethanol, followed by hot petroleum ether, and dried in vacuum desiccators over calcium chloride.

REACTION SCHEME:



Where Ar_{i-ii} is Ar_i = 2-amino 4- methyl Pyridine
Ar_{ii} = 2-amino 5- methyl Pyridine

M = Ni(II) & Hg (II)

Fig. 1 Synthesis of Metal Complexes of Ni(II) and Hg (II)

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III. ANTIMICROBIAL STUDY

ANTI BACTERIAL ACTIVITY:

The agar well diffusion method was used to test the antibacterial activity.¹⁸Mueller Hinton Agar for bacteria was used for all tests for antibacterial activity. For positive control of bacteria Ampicillin was used. The solvent and positive control used was DMSO. Antibiotics and dehydrated media powder were brought from Hi-Media, India. Using sterile wire-loop, test organisms were aseptically added to sterile MH broth before being incubated at 37°C for 18 hours. This suspension was utilized as an inoculant. Wells in the media plates with a 10mm diameter were made using a sterile cork borer for the addition of compound solutions and controls. With the aid of a micropipette, 100 µl of the compound solution was aseptically added to the wells to reach a final concentration of 10 g of compound in each well. As controls, the same quantity of DMSO and ampicillin solution were introduced. The plates were cooled for 30 minutes to allow solutions to diffuse through the agar substrate. Plates were then incubated for 24 hours at 37°C. *Bacillus subtilis* and *Salmonella typhi* were gram positive bacteria that were utilized as test organisms, whereas *Staphylococcus aureus* and *Escherichia coli* were gram negative microorganisms. The zone margin should be regarded as the region that does not clearly display any expansion that the unaided eye can see. With a measuring scale in millimetres, the clean zone was measured.

ANTIFUNGAL ACTIVITY

The poison plate approach was used to provide antifungal activity.¹⁹For the evaluation of antifungal activities. *Aspergillus niger*, *Aspergillus flavus*, *Fusarium moniliforme*, and *Penicillium chrysogenum* species were selected. Potato Dextrose Agar (PDA) media was utilized as a culture. To sterilize the medium, it was autoclaved at 121°C for 25 minutes under 15 psi of pressure. 20 ml of sterilized, melted PDA was added to sterilized petri plates with 2 ml of each component, and the mixture was then gently stirred in a circular motion to get homogenized. With positive Neomycin and negative DMSO controls, the identical process was followed. The fungal spores from the slant culture were transferred to a test tube containing sterile saline and thoroughly mixed with a sterile wire loop. As an inoculant, this spore solution was employed. The plates were incubated for four days at room temperature. After incubation, the growth of the infected fungi was monitored on the plates. The outcomes were noted.


IV. RESULT AND DISCUSSION

The Ni (II) complexes prepared in the present work are greenish-yellow. These are stable to air and moisture. All Ni(II) complexes are not soluble in water, common polar and non-polar solvents but are sparingly soluble in methanol, ethanol and chloroform. They are appreciably soluble in dimethyl sulphoxide (DMSO). The observed solution conductivities of Ni (II) complexes are given in Table 1. The low solution conductivity values of the complexes in DMSO indicate their non-electrolytic nature.²⁰The elemental analysis data (Table 1) of metal complexes confirm the ligand to the metal ratio for Nickel complexes as 2:1, proposing a monomeric


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complex. The electronic spectra of Ni(II) complexes observed in the present work show absorption bands in three regions, $V_1 = 11495 - 11360 \text{ cm}^{-1}$, $V_2 = 16530 - 16390 \text{ cm}^{-1}$ and $V_3 = 26315 \text{ cm}^{-1}$. These observed bands may be assigned to three spin allowed transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) charge transfer band respectively, which are characteristic of the distorted octahedral field.^{21,22} The electronic spectral data are presented in Table 2.

Mercury complexes Prepared in the present research work are white. They are stable in air and moisture. The Hg(II) complexes decompose at high temperature (above 300°C).²³ They are insoluble in non-polar and common polar solvents. At a very low concentration, solutions can be prepared in CH₃OH and DMSO. The molar conductance value of the complexes in DMSO (10^{-3}M) is very low ($16.02 - 16.61 \text{ mhos}^{-1} \text{ cm}^2 \text{ mol}^{-1}$), indicating the non-electrolytic nature of complexes.²⁴ The metal to ligand ratio was shown as 1:2, predicting a monomeric structure. All Hg (II) complexes are diamagnetic. These findings agree with the previously reported experimental work.²⁵

In the present investigation IR spectrum data of Ni (II) and Hg (II) was given in table-4. The stretching vibration for lactum C=O observed in range of $1664 - 1660 \text{ cm}^{-1}$ for Ni (II) while in Hg (II) complexes found within the range $1665 - 1663 \text{ cm}^{-1}$.

The band assigned to the azo-methine C=N stretching frequencies in the free ligand were observed around $1617 - 1600 \text{ cm}^{-1}$. In the IR spectra of the Ni (II) and Hg (II) complexes, medium to weak bands appeared in the region $1599 - 1590 \text{ cm}^{-1}$ were assigned to azo-methine C=N stretching vibration mode. A decrease in a shift of this band observed on complexation indicates that the imine group of each ligand is coordinated to metal ion via its nitrogen.²⁷

The medium intensity absorption bands in the region $1276 - 1270 \text{ cm}^{-1}$ in the spectra of metal complexes were predictable to enolic C-O stretching frequency. These bands in the corresponding free ligands spectra were observed in the range $1269 - 1224 \text{ cm}^{-1}$. Thus the observed upward shift of this band by $18 - 22 \text{ cm}^{-1}$ and the disappearance of broad absorption due to phenolic -OH in metal complexes confirms the participation of enolic oxygen bonded to 4C of 4-hydroxyquinolin-2(1H)-one part in the formation of the complex.

The band in the range $498 - 472 \text{ cm}^{-1}$ were assigned for Metal Oxygen bond while band in the range $448 - 428 \text{ cm}^{-1}$ were assigned to Metal Nitrogen bond.²⁸

The antibacterial activity was tested for the synthesized Ni (II) and Hg (II) complexes. The outcomes are summarized in Table 5. Across all bacterial species under study, metal complexes of Ni (II) and Hg (II) have shown good antibacterial activity in zones of inhibition ranging from 14 to 19 mm in diameter. Metal complexes with all ligands showed substantial activity in the antifungal test. It has been found that complexes of Ni (II) complexes have shown higher antibacterial and antifungal activity as compare to Hg (II) complexes.²⁹

VI. CONCLUSION

In conclusion, we reported the synthesis, characterization, and antimicrobial properties of metal complexes of Ni (II) and Hg (II) with Schiff bases obtained from heterocyclic ligands such as pyridine and AHQ with the


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goal of developing a contribution to coordination chemistry. Ni (II) metal complexes that have been prepared are monomeric and have an octahedral orientation, whereas Hg (II) metal complexes are monomeric and have a tetrahedral geometry. Thus according antimicrobial studies all complexes have significant antibacterial and antifungal action.

Table No. 1 Elemental Analysis of Ni (II) and Hg(II)Complexes

S. No.	Complexes	Molecular formula	Colour	M.P. ^o C	Mol. Wt.	Soln cond μv	Elemental analysis Found(Calculated)			
							%C	%H	%N	%M
1	[Ni (L ₁) ₂]	[Ni(C ₁₇ H ₁₄ N ₃ O ₂) ₂ (H ₂ O) ₂]	Greenish Yellow	265	679.36	16.21	60.06 (60.11)	4.66 (4.75)	12.38 (12.37)	8.50 (8.64)
2	[Ni (L ₂) ₂]	[Ni(C ₁₇ H ₁₄ N ₃ O ₂) ₂ (H ₂ O) ₂]	Greenish Yellow	248	679.36	16.26	60.02 (60.11)	4.54 (4.75)	12.30 (12.37)	8.58 (8.64)
3	[Hg (L ₁) ₂]	[Hg(C ₁₇ H ₁₄ N ₃ O ₂) ₂]	White	>300	785.23	16.61	51.90 (52.01)	3.65 (3.59)	10.74 (10.70)	25.51 (25.55)
4	[Hg (L ₂) ₂]	[Hg(C ₁₇ H ₁₄ N ₃ O ₂) ₂]	White	>300	785.23	16.02	51.88 (52.01)	3.63 (3.59)	10.60 (10.70)	25.61 (25.55)

Table No. 2 Electronic Spectral Data of Ni (II) Complexes

Sr. No.	Complexes of Ligand (L ₁ -L ₂)	Absorption Maxima cm ⁻¹ (nm)		
		V ₁	V ₂	V ₃
1	Ni [(L ₁) ₂ (H ₂ O) ₂]	11495 (870)	16530 (605)	26315 (380)
2	Ni[(L ₂) ₂ (H ₂ O) ₂]	11360 (880)	16390 (610)	26315 (380)

Table No. 3Magnetic Susceptibility Data of Ni (II) Complexes

Sr. No.	Ni (II) Complexes of ligand	χ _M x 10 ⁶ (CGS)	χ _A x 10 ⁶ (CGS)	μ _{eff} (B.M.)
1	Ni [(L ₁) ₂ (H ₂ O) ₂]	3964.55	4263.75	3.19
2	Ni[(L ₂) ₂ (H ₂ O) ₂]	3675.57	3974.77	3.08

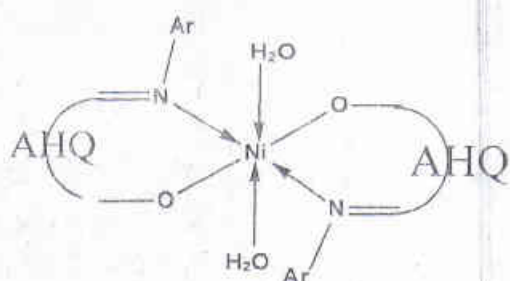
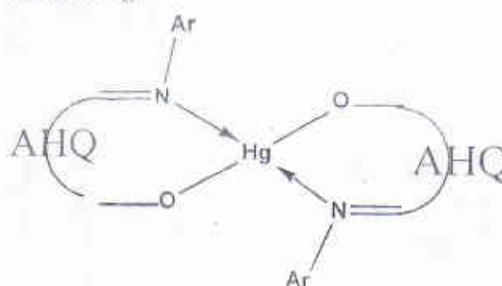
Table No. 4 Infrared Absorption Frequencies (cm^{-1}) of

Sr. No.	Ligand / Complex	Bond vibrational modes (stretching - ν)					
		Lactam	Pyridine	Azo-methine	Enolic	New Peaks	
		(C=O)	(C=N)	(C=N) \downarrow	(C-O) \uparrow	M-O	M-N
1	Ni [(L ₁) ₂ (H ₂ O) ₂]	1664	1605	1599	1270	498	448
2	Ni[(L ₂) ₂ (H ₂ O) ₂]	1660	1600	1590	1272	492	440
3	Hg(L ₅) ₂	1665	1603	1593	1276	472	430
4	Hg(L ₅) ₂	1663	1600	1592	1270	475	422

Table No.5 Anti- Bacterial and Anti-Fungal Activity

Synthesized Schiff base ligands	Antibacterial Study Zone of Inhibition(diameter in mm)				Antifungal Study Growth of Fungi			
	Gram Positive		Gram Negative		A. niger	A. flavus	E. moniliforme	P. chrysogenum
	S. typhi	B. subtilis	E. coli	S. aureus				
Ampicillin (Reference)	18	19	17	18	Neomycin (Reference)	-	-	-
Ni [(L ₁) ₂ (H ₂ O) ₂]	17	18	19	18	-	-	-	-
Ni[(L ₂) ₂ (H ₂ O) ₂]	18	18	18	19	-	-	-	-
Hg(L ₅) ₂	16	15	15	17	++	+	+	+
Hg(L ₅) ₂	16	17	14	14	+	+	-	-

Moderate growth (++), Reduced growth (+) and No growth (-) of fungi

Structure I: Monomeric octahedral Structure of Ni(II) Complexes of Ligand L₁ & L₂

Structure II: Monomeric tetrahedral Structure of Hg(II) Complexes of Ligand L & L

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