Research Article **Available online www.ijsrr.org** **ISSN: 2279–0543**

International Journal of Scientific Research and Reviews

Studies of Macrocyclic Ni(II) Complexes with Multidentate Schiff base ligands

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ABSTRACT

Studies on coordination chemistry of Nickel (II) is fast gaining importance due to its enormous organometallic and catalytic chemistry. The complexes of NI(II) with multidentate schiff base ligand H_2(Mahe$^{1-2}$) derived from the reaction between Diacetylmonoximeand1,3– Diaminopropane or, 1, 4– Diaminobutane in dry alcoholic medium have been synthesized and characterized on the basis of elemental analyses, magnetic susceptibility, infrared, electronic spectral and conductivity data. The metal chelate ligand have a general formula [Ni(H_2 Mahe$^{1-2}$)X_2].The IR observations suggest that the ligand have coordinated through two oxime and two amine nitrogen atoms while two axial halogen ions are coordinated in facial mode of one another with Ni (II) but two hydroxyl group of two oximes also combine to one another by intramolecular hydrogen bond and forming six members chelating ring which enhance the extra stability of complexes. During the course of present investigation of magnetic susceptibility along with electronic and IR spectral data Indicates a greenish yellow color distorted paramagnetic Octahedral structure for the Ni(II) complexes. The stability of the macrocyclic complexes have been found to be dependent on the ring size of the cavity of the macrocyclic ligands which can be varied by changing the number of intervening atoms between two amino groups in the terminal and intramolecular hydrogen bonding. Biological activity studies have also been presented.

KEYWORDS– Macrocyclic complexes, Dry alcoholic medium, Axial halogen atoms, Metal chelates ligand. Intramolecular hydrogen bond.

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INTRODUCTION

Over the world wide attraction has been given to comparative studies on macrocyclic metal Ni (II) complexes with macrocyclic ligands. Very recently there has been a phenomenal growth in studies of Ni (II) complexes[1-5] consequently in the present communication in continuation of our earlier interest in the field[6-8].In the recent years, it has been the trends to synthesize the ligand molecules having definite framework of donor atoms and stitch them with different metal ions. Studies of new kind of Schiff bases and their complexes are now attracting the attention of biochemists. Schiff base metal complexes have widely studied subject, because of their industrial and biological application. Such complexes have been further explored for their catalytic and biological activities. For the last few years much attention has been cast on polyfunctional ligands, which can be encapsulate the metal ions. Schiff base complexes of later transition metals have been receiving the considerable research attention because of their use in biological and medicinal application[9-12].In recent years there has been growing interest in preparing the Schiff base complexes which show high activity. Now the chemistry of metal clusters is also gaining the momentum, the metal complexes have acquired a position of significance in the area of bioinorganic chemistry. Many enzymes and proteins involving metal systems and Various spectrochemical methods have been used to elucidate the structure of the complexes and sometimes to locate the coordination centers in ligand molecules and to know the preponderance of one coordination site over the other, the molecular orbital calculated have been used.NI(II) macrocyclic complexes obtained by macrocyclization between Bis-(dimethylglyoximato) and Ni(II). The stoichiometry of the complexeshavebeen found to be of the type $[Ni(H_2Mahe^{1-2})X_2]$. Where H_2 (mahe^1) = 3, 9-demethyl – 4, 8-diaza-2, 10-dihydroximino-3, 8-undecadiene.

H_2 (Mahe^2) = 3, 10- dimethyl- 4-9-diaza-2, 11-dihydroximino-3, 9-dodecadiene. The chelation of ligands with Ni (II) is expected to form complexes with different structural geometry. It may enhance their biological activity after chelation also.[13-15] which may find their importance in the applied medicinal chemistry and other area of industries.

EXPERIMENTAL

The Salts of the metal are used for synthetic and analytical workswere of reagent grade solvents, and were purified by standard method and dry before use.

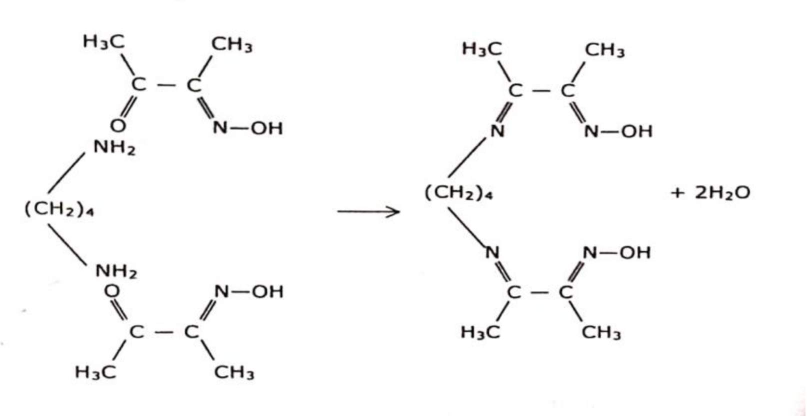
Ligands synthesis.

(1)Preparation of 3,9-dimethyl-4,8-diaza-2,10-dihydroximino-3,8-undecadiene, H_2 (mahe[1])

1,3 Diaminopropane (3.7 g, 0.05 mol) of Loba qualities was added to Diacetylmonoxime (10.1 g, 0.1 mol), an Aldrich reagent and the resulting mixture was continuously and vigorously stirred with a glass rod when it went into a clear solution. Stirring was continued for an hour when the solution started becoming thicker. Stirring was continued and the solution was cooled at about 0^0C when a light yellow solid was obtained. The sample was dried under vacuum and was powdered and recrystallised from an alcoholic solution and kept in a desiccators. It absorbs moisture and turns into a reddish viscous mass when exposed to atmosphere for a long period. Melting point of the compound was found to be 166 $\pm 2^0$C (literature value 166^0C). Analysis was in satisfactory agreement with formulation.

(2)Preparation of 3, 10-dimethyl - 4,9-diaza-2,11-dihydroximino-3,9-dodecadiene,H_2 (mahe[2])

1,4-Diaminobutane (4.4g, 0.05mol) of Loba qualities was added to Diacetylmonoxime (10.1g, 0.1 mol), an Aldrich reagent and the resulting mixture was continuously and vigorously stirred with a glass rod when it went into a clear solution. Stirring was continued for an hour when the solution started becoming thicker. Stirring was continued and the solution was cooled at about 0^0C when a light yellow solid was obtained. The sample was dried under vacuum and was powdered and recrystallised from an alcoholic solution and kept in a desiccators. It absorbs moisture and turns into a reddish viscous mass when exposed to atmosphere for a long period. Melting point of the compound was found to be 170 ± 2^0C (literature value 170^0C).The both synthetic reaction for preparation of ligands can be shown below in the form of the figure -1.



n = 3, 4

Figure - 1 Durring the reaction synthesis of ligands

Synthesis and Structure of Ni (II) complexes

1- Preparation of Dichloro-3,9-dimethyl-4, 8-diaza-2, 10-dihydroximino-3, 8-undecadiene, nickel (II),[Ni (mahe^1)Cl_2]

The ligand H_2(mahe^1) (2.40 g, 0.01 mol) was dissolved in minimum amount of absolute alcohol then an alcoholic solution of Nickel (II) chloride hexahydrate (2.4 g, 0.01 mol) was added. The reaction mixture was vigorously shaken for a few minutes, then the color of mixture solution immediately changes to red and fine crystals were obtained. The amount of solid products increased when the solution was allowed to stand for some time. It was filtered, washed with alcohol and finally with ether and analyzed after drying.

2. Preparation of Dibromo-3,9-dimethyl-4, 8-diaza-2, 10-dihydroximino-3, 8-undecadiene, nickel (II),[Ni (mahe^1) Br_2]

About 1.6 g (0.005mol) of Nickel (II) bromide hexahydrate was dissolved in 50 ml of alcohol. The solution was treated with an alcoholic solution of the ligand (1.2 g, 0.005 mol) when a dark brown solution was obtained. After allow the solution was to stand for some time. Dark brown crystals were obtained. The compound was filtered, washed first with alcohol and then with ether and analyzed after drying.

3. Preparation of DiIodo-3,9-Dimethyl-4,8-diaza-2,10-dihydroximino-3,8-undecadiene Ni(II), [Ni (H_2 mahe^1) I_2]

An alcoholic solution of the ligand (2.40 g, 0.01mol) was allowed to react with Nickel (II) iodide hexahydrate (4.28 g, 0.01mol). The colors of the solution immediately changed to dark red and dark red crystals were obtained. When the solution was allow to stand for some time. The solid compound was filtered, washed first with alcohol and then with ether, dried and analyzed.

4. Preparation of Dichloro-3,10-Dimethyl-4,9-diza-2,11-dihydroximino-3,9-dodecadiene Ni(II), Ni(H_2mahe^2)Cl_2]

The ligand H_2(mahe^2) (2.5 g, 0.01 mol) was dissolved in minimum amount of absolute alcohol and then an alcoholic solution of Ni(II) chloride hexahydrate (2.5 g, 0.01 mol) was added. The mixture was vigorously shaken. The color of the mixture solution immediately changes to red and fine crystals were obtained. The amount of solid product increased when the solution was allowed to stand for some time. It was filtered, washed with alcohol and finally with ether and analyzed after drying.

5. **Preparation of Dibromo-3,10-Dimethyl-4,9-diaza-2,11-dihydroximino-3,9-dodecadiene Ni(II), [Ni (H_2 mahe^2) Br_2]**

About 1.6 g (0.005 mol) of N(II) bromide hexahydrate was dissolved in 50 ml of alcohol .The solution was treated with an alcoholic solution of the ligand (1.2 g, 0.005 mol) when a dark brown solution was obtained. After allowing the solution to stand for some time, dark brown crystals were obtained. The compound was filtered, washed first with alcohol and then with ether and analyzed after drying.

6. **Preparation of DiIodo-3,10-Dimethyl-4,9-diaza-2,11-dihydroximino-3,9-dodecadiene Ni(II),[Ni(H_2 mahe^2)I_2]**

An alcoholic solution of the ligand (2.5 g, 0.01mol) was allowed to react with Ni (II) iodide hexahydrate (4.28 g, 0.01mol).The colors of the solution immediately changed to dark red and dark red crystals were obtained. When the solution was allow to stand for some time. The solid compound was filtered, washed first with alcohol and then with ether, dried and analyzed.

RESULT AND DISCUSSION

Very recently oximes and amines have been used for preparation of Schiff base ligands and macrocyclic Ni(II) complexes by condensing diacetylmonoxime with 1,3–diaminopropane / 1,4-diaminobutane and to attempt to synthesize and characterize Ni(II) macrocyclic complexes with these ligands .The complexes [Ni(H_2mahe$^{1-2}$)X_2] have been synthesized and characterized on the basis of elemental analyses, magnetic susceptibility, infrared. electronic spectral and conductivity data.

Infrared spectra

The complexes [Ni (H_2mahe $^{1-2}$) X_2] have been recorded in the frequency region 4000-600 cm $^{-1}$ and vibrational bands of structural significance are shown below in Table-1.The complexes show a strong band centered at 3400 cm^{-1}.The band be assigned to $\nu_{O\text{-}H}$ of the N-O-H group involved in hydrogen bonding, most probably intramolecular in nature and suggests that the ligand still exists in its neutral from. Intramolecular hydrogen bonding in oxime complexes where the protons of the N-O-H groups have not be ionized. The structural features of the complexes involve bonding of amine groups with the metal center and the macrocyclic ligand exists in a dianionic form. The dianionic form of the ligands for the group of macrocycles appears to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands, enclosing the metal ion in the macrocyclic cavity forming 5-membered chelate rings with the amine moieties and 6-membered rings involving oxime groups with intramolecular hydrogen bonding. The spectra of the ligands and complexes show absorption maximum of medium intensity at 1700cm^{-1} The four bands in the spectra of the ligand are found near 1590, 1570, 1500 and 1442 cm^{-1} respectively. The first and last two bands are having medium intensity. Where the second band is weak and appears in the form of a shoulder. These bands are almost unaffected in the metal complexes. The spectra of complexes show yet another band in far Infrared region in the range 530-510 cm^{-1} which can be assigned to $\nu_{Ni\text{-}O}$ or $\nu_{Ni\text{-}X}$.

Table-1 Characteristic i.r spectral bands of ligands and complexes

Complex / Ligand	$\nu_{O\text{-}H}$	$\nu_{C\overset{\cdots}{\,}H}$ Azomethine	$\nu_{C=N}$ oxime	$\nu_{N\text{-}O}$	$\nu_{B\text{-}O}$	$\delta_{B\text{-}F2}$	$\nu_{Ni\text{- }x}$	$\nu_{Ni\text{-}N}$
H_2(mahe^1)	3360 S	1630 S	1440 S	1010 S	-	-	-	-
H_2(mahe^2)	3365 S	1635 S	1445 S	1015 S	-	-	-	-
[Ni(H_2mahe^1)Cl_2]	3360 b	1600 S	1460 m	1095 S	-	-	510	435
[Ni(H_2mahe^1)Br_2]	3365 b	1595 S	1455 m	1090 S	-	-	515	430
[Ni(H_2mahe^1)I_2]	3355 m	1590 S	1465 m	1100 S			520	425
[Ni(H_2mahe^2)Cl_2]	3360 b	1595 S	1455 m	1095 S			520	440
[Ni(H_2mahe^2)Br_2]	3365 b	1590 S	1460 m	1090 S			525	445
[Ni(H_2mahe^2)I_2]	3360 b	1605 S	1465 m	1100 S			520	440

S= Strong m=Medium b= Broad

Magnetic properties and electronic spectra of complexes.

The electronic spectra of these complexes consist of three bands, one in the region 13000-14500 cm^{-1},the next one in the vicinity of 20000 cm^{-1} followed by strong intense band near 24000 cm^{-1}. The band in the lower frequency region can be assigned to the transition,$^3A_{2g} \leftarrow {}^3B_{1g}$whereas the higher frequency band can be assigned to the transition, $^3E_g \leftarrow {}^3B_{1g}$, $^3A_{2g}$ and ^3E_g are the two split components of $^3T_{1g}$ state in octahedral field upon tetragonal distortion and thus the appearance of two bands in the region 12000-20000 cm^{-1} suggests the central Ni(II) ion to be present in an octahedral field with certain amount of tetragonal distortion. The band at 24000 cm^{-1} can be assigned to the transition $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ which in some cases overlaps with strong charge transfer bands. During the course of present investigation the Ni(II) complexes with the range of magnetic moment data 2.7-3.1 B.M. at room temperature which suggests paramagnetic octahedral arrangement of the ligand atoms around the central Ni (II) ion. The band positions of Ni(II) complexes are recorded in Table-2.

Table-2 Electronic spectra of complexes

Complexes	$^3B_{1g} \rightarrow {}^3A_{2g}$	$^1B_{1g} \rightarrow {}^3E_g$	$^3T_{1g}(P) \leftrightarrow {}^3A_{2g}$	μ_{eff}(B.M)
$[Ni(H_2mahe^1)Cl_2]$	13,800	17,800	24,000	2.80
$[Ni(H_2mahe^1)Br_2]$	13,900	18,100	24,300	2.85
$[Ni(H_2mahe^1)I_2]$	14,000	18,300	24,100	2.95
$[Ni(H_2mahe^2)Cl_2]$	13,700	17,700	24,100	2.90
$[Ni(H_2mahe^2)Br_2]$	13,800	18,000	23,200	2.45
$[Ni(H_2mahe^2)I_2]$	14,100	18,200	24,000	2.95

Conductivity measurement

Conductivity of the complexes in the solvent DMSO. The complexes of $[Ni\ (H_2mahe^{1\text{-}2}X_2]$ have been found to possess conductivity in the rang 10–21ohm^{-1}cm^{2}mol^{-1} and indicate their non-electolytic nature[16-18], which clearly indicates that anions are coordinated with metal ion. The molar conductance values also supported the structure assigned on the basis of physicochemical and spectroscopic measurements. The conductivity measurement data have been presented below in Table-3.

Table- 3 Conductivity data of the complexes

Complexes	Λ_m ohm^{-1} cm^2 mol^{-1}
$Ni(mahe^1)$	10
$Ni(mahe^2)$	12
$[Ni(H_2mahe^1)Cl_2]$	14
$[Ni(H_2mahe^1)Br_2]$	13
$[Ni(H_2mahe^1)I_2]$	15
$[Ni(H_2mahe^2)Cl_2]$	18
$[Ni(H_2mahe^2)Br_2]$	20
$[Ni(H_2mahe^2)I_2]$	21

Biological activity.

On the basis of experiment the activity of Ni(II) complexes have more effective than free ligands. The ligands have many donor atoms (N, O) and are analogous to biological environment to some extent. The complexes are highly active due to the greater lipophilic nature of the complexes. Which enhance the antimicrobial activity on chelate then the probability of the metal ion will be reduced to greater extent and increase the lipophilic and absorbing nature of complexes due to the equatorial overlapping of ligand filled orbital with vacant outer d- orbital of the metal ion. Further it increasing the delocalization of electrons of metal ion with absorbing power over the whole chelating ring as a result decreases the growth or increase the ratio of death of bacteria. The results indicated that chelating improved the antibacterial activity compared to the ligand[19-20]and known as antibiotic drugs.

CONCLUSION

Thus on the basis of above studies it is concluded that the ligand H_2 (mahe$^{1-2}$) acts in bidentate manner and coordination is proposed through oxime and amine N atom. The remaining centers of metal ions in complexes are satisfied by two axial facial modes of negative halogen ions such as Cl^-, Br^-,I^-.But the macrocyclic ligands exists in a dianionic form. The dianionic form of the ligand for the group of macrocycles appears to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands, enclosing the metal ion in the macrocyclic cavity forming two 5-membered chelate rings in axial mode of upper and lower direction with the amine moieties. While two hydroxyl groups of two oximes combine to one another by intramoleculer hydrogen bond and forming 6-membered chelating ring in complexes which enhance the extra stability of the complexes. On the basis of physicochemical and spectroscopic observation it is proposed that the geometry of the complexes of the types [$Ni(H_2mahe^{1-2})X_2$] are monomeric high spin paramagnetic octahedral in geometry. The following tentative structure may be proposed for these complexes in figure -2.

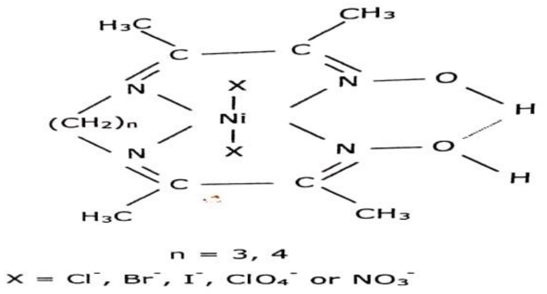


Figure -2 Tentative octahedral structure of the complexes.

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