Synthesis and spectral Studies of Macrocyclic Ni (II) Complexes with Schiff base ligands

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ABSTRACT

Recent progress in several field of coordination chemistry shows that the stereochemical considerations are gaining an increasing importance. 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 Diacetylmonoxime and 1,3– 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 chelating ligands have a general formula $[Ni(H_2Mahe^{1-2})(NO_3)_2]$ and $[Ni(H_2mahe)^{1-2}(ClO_4)_2]$.The IR observations suggest that the ligands have coordinated through oxime and amine nitrogen atom and forming upper and lower axial directional mode of five members chelating ring. While the remaining center of central metal ion are satisfied by the O^- ion of two NO_3^- or ClO_4^- above and below in a layer lattice structure in axial inter facial mode of one another with Ni (II) but coordinated two hydroxyl group of two oximes provide extra bonding and extra stability due to extra number of bonding of Intramolecular hydrogen bond as a result arise six members chelating ring with 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 high spin, 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 carbon atoms between two amino groups in the terminal and intramolecular hydrogen bonding. Biological activity studies have also been presented.

Keywords– Size of cavity, Dry alcoholic medium, Axial mode, Metal chelating ring, Magnetic susceptibility.

INTRODUCTION

Over the world wide attraction has been given to comparative studies on macrocyclic metal Ni (II) complexes with macrocyclic ligands. Consequently we in the present communication, in coordination of our earlier interest. 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. 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-(dimethyl glyoximato) and Ni(II). The stereochemistry of the complexes have been found to be of the types, $[Ni(H_2Mahe^{1-2})(NO_3)_2]$ and $[Ni(H_2(mahe^{1-2})(ClO_4)_2]$. Where H_2 (mahe^1) = 3, 9-demethyl – 4, 8-diaza-2, 10-dihydroximino-3, 8-undecadiene.

H_2 (Mahe^1) = 3, 10- dimethyl- 4-9-diaza-2, 11-dihydroximino-3, 9-dodecadiene. The chelating ligand with Ni (II) is expected to form complexes with different structural geometry. It may enhance their biological activity after chelate[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 works were of reagent grade solvents, and were purified by standard method and dry before use.

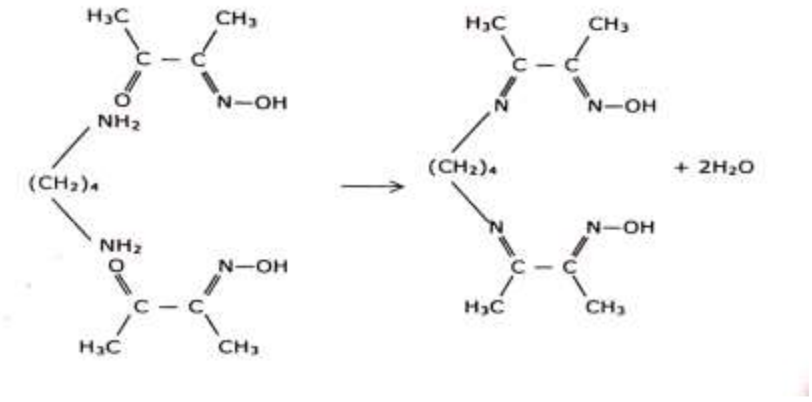
Ligands Synthesis.

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 powder and recrystallized from an alcoholic solution and kept in 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 recrystallized from an alcoholic solution and kept in 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 the preparation of ligands can be shown below in the form of figure.



n = 3,4

Synthesis and Structure of Ni (II) complexes

Preparation of Dinitro-3,9-dimethyl-4,8-diaza-2,10-dihydroximino-3,8-undecadiene,nickel (II), [Ni (H_2mahe^1) (NO_3)$_2$]

An alcoholic solution of Ni(II) nitrate hexahydrate (2.85 g, 0.01 mol) was added to an alcoholic solution of the ligand (2.4 g, 0.01 mol) and the mixture was vigorously shaken when the color of the solution changed from green to yellowish green and yellowish green crystals were obtained which were filtered, washed with alcohol followed by ether, dried under vacuum and analyzed

2. Preparation of Diperchlorato-3,9-dimethyl-4,8-diaza-2,10-dihydroximino 3,8-undecadiene, nickel (II), [Ni (H_2mahe^1)(ClO_4)$_2$]

Ni(II) perchlorate hexahydrate (1.8 g, 0.005 mol) dissolved in 20 mol of alcohol was added to the ligand (1.2 g, 0.005 mol) in alcohol and the mixture was vigorously shaken for a few minutes when a dark brown crystalline precipitate was obtained within a few minutes. It was filtered, washed with small quantities of alcohol, and finally with ether. It was subsequently dried under vacuum analyzed.

3. Preparation of Dinitro-3,10-Dimethyl-4,9-diaza-2,11-dihydroximino-3,9-dodecadiene Ni(II), [Ni (H_2 mahe^2) $(NO_3)_2$]

An alcoholic solution of Ni(II) nitrate hexahydrate (2.85 g, 0.01 mol) was added to an alcoholic solution of the ligand (2.5 g, 0.01 mol) and the mixture was vigorously shaken when the color of the solution changed from green to yellowish green and yellowish green crystals were obtained which were filtered, washed with alcohol followed by ether, dried under vacuum and analyzed.

4. Preparation of Diperchlorato-3,10-Dimethyl-4,9-diaza-2,11-dihydroximino-3,9-dodecadiene Ni (II), [Ni(H_2 mahe^2) $(ClO_4)_2$]

Ni(II) perchlorate hexahydrate (1.8 g, 0.005 mol) dissolved in 20 mol of alcohol was added to the ligand (1.2 g, 0.005 mol) in alcohol and the mixture was vigorously shaken for a few minutes when a dark brown crystalline precipitate was obtained within a few minutes. It was filtered, washed with quantities of alcohol, and finally with ether. It was subsequently dried under vacuum and analyzed.

RESULT AND DISCUSSION

very recently oximes and amines have been used for preparation of Schiff base ligands and macrocyclic Ni(II) complex 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$^{1-2}$)$(NO_3)_2$] and [Ni(H_2mahe$^{1-2}$)$(ClO_4)_2$] have been synthesized and characterized on the basis of elemental analyses, magnetic susceptibility, infrared. electronic spectral and conductivity data. The complexes were colored and insoluble in common organic solvents but easily soluble in DMSO and DMF.

Infrared spectra

The complexes [Ni (H_2mahe $^{1-2}$)$(NO_3)_2$] and [Ni(H_2mahe$^{1-2}$)$(ClO_4)_2$] 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 ν_{O-H} of the N-O-H group involved in hydrogen bonding, most probably intramolecular hydrogen bonding in nature and suggests that the ligand still exists in its neutral from. The intramolecular hydrogen bonding in hydroxyl group of oximes of complexes in which the protons of the N-O-H groups have not be ionized and involved the formation of intramolecular hydrogen bonding.The structural features of these complexes involve bonding of oxime group with the metal centers and 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 5-membered chelate rings with the amine moieties and 6-membered ringed involving dioxime group with intramolecular hydrogen bond. The spectra of the ligands and complexes show absorption maximum of medium intensity at 1700 $cm^{-1.}$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 ν_{Ni-O} or ν_{Ni-X}.

Table-1

Characteristic i.r. spectral bands of ligands H_2 (mahe$^{1-2}$) complexes of [Ni(H_2mahe$^{1-2}$)$(NO_3)_2$] and [Ni(H_2mahe$^{1-2}$)$(ClO_4)_2$]

Complexes / Ligand	ν_{O-H}	$\nu_{C\underline{...}H}$ Azomethine	$\nu_{C=N}$ oxime	ν_{N-O}	ν_{B-O}	δ_{B-F2}	ν_{Ni-X}	ν_{Ni-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)$(NO_3)_2$]	3360 m	1600 S	1460 m	1110 S	-	-	510	430
[Ni(H_2mahe^1)$(ClO_4)_2$]	3355 m	1605 S	1465 m	1105 S	-	-	515	435
[Ni(H_2mahe^2)$(NO_3)_2$]	3355 m	1610 S	1455 m	1105 S			525	440
[Ni(H_2mahe^2)$(ClO_4)_2$]	3370 b	1605 S	1460 m	1110 S			520	445

S= Strong m=Medium b= Broad

Magnetic properties and electronic spectra of complexes.

The Ni(II) macrocyclic complexes are paramagnetic and their electronic spectra of these complexes consist of three bands, one in the region 13000-14500 cm^{-1},the next one in the vicinity of20000 cm^{-1} followed by strong intense band near 24000cm^{-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 four-nitrogen atoms of the macrocyclic ligand shift 4-coordinations in planar framework, the remaining two axial coordination satisfied by the O^- ion of NO_3^- and ClO_4^- above and below in a layer lattice structure. While two – OH group of Oxime combine to one another by intramolecular hydrogen bond with cyclic structure. The band positions of Ni(II) complexes are recorded in Table-2.

Table-2

Electronic spectra of complexes of $[Ni(H_2mahe^{1-2})(NO_3)_2]$ and $[Ni(H_2mahe^{1-2})(ClO_4)_2]$ cm^{-1}

Complexes	$^3B_{1g} \rightarrow ^3A_{2g}$	$^1B_{1g} \rightarrow ^3E_g$	$^3T_{1g}(P) \leftrightarrow ^3A_{2g}$	μ_{eff}(B.M)
$[Ni(H_2mahe^1)(NO_3)_2]$	14,000	17,900	24,700	3.00
$[Ni(H_2mahe^1)(ClO_4)_2]$	13,700	18,000	24,500	2.80
$[Ni(H_2mahe^2)(NO_3)_2]$	14,100	17,800	24,600	2.85
$[Ni(H_2mahe^2)(ClO_4)_2]$	13,600	18,100	24,600	2.85

Conductivity measurement

conductivity of the complexes were measured in the solvent DMSO. Their molar conductance in DMSO solvent, the complexes of [Ni (H_2mahe$^{1-2}$(NO_3)$_2$] and [Ni(H_2mahe$^{1-2}$) (ClO_4)$_2$] have been found to possess conductivity in the rang 10-25 ohm^{-1} cm ^{2} mol^{-1} and indicate their non-electolytic nature[16-17].Which clearly indicates that anionic part of ligands are coordinated with metal atom / ions. 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

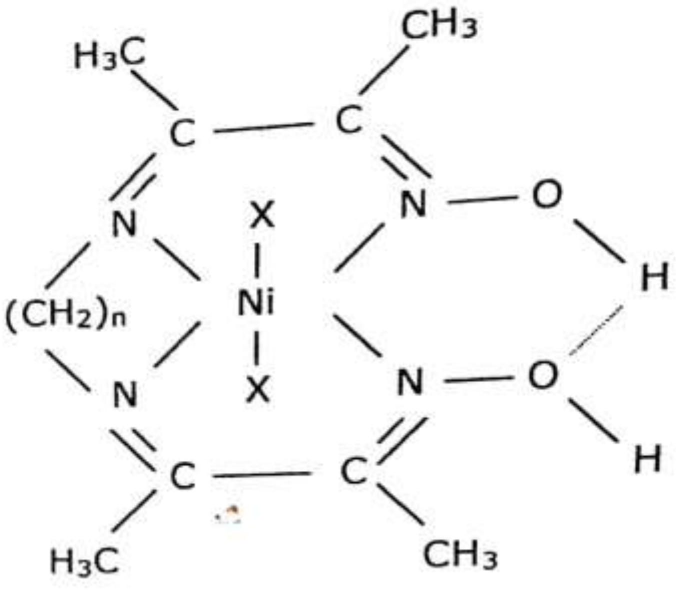
Complexes	Λ_m ohm^{-1} cm^2 mol^{-1}
Ni(mahe^1)	10
Ni(mahe^2)	12
[Ni(H_2mahe^1) (NO_3)$_2$]	16
[Ni(H_2mahe^1) (ClO_4)$_2$]	17
[Ni(H_2mahe^2) (NO_3)$_2$]	23
[Ni(H_2mahe^2) (ClO_4)$_2$]	25

Biological activity.

On the basis of experiment the biological antibacterial activity of Ni(II) complexes have more effective than free ligands. The complexes are highly active due to the greater dissolving ability in fats, oils, lipids and non-polar solvent such as hexane, toluene etc with more absorbing nature of the complexes. Which controls the antimicrobial activity on chelation, the probability of the metal ion will be reduced to greater extent due to the equatorial overlapping with ligand filled orbital and vacant outer d- orbital of the metal ion with donor oxime nitrogen group. Further it increasing the absorbing surface area of complexes with delocalization of electrons of metal ion over the whole chelate ring as a result prevents the growth or increase the ratio of death of bacteria. The results indicated that chelation improved the antibacterial activity compared to the ligand[18-20] 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 a bidentate manner and coordination is proposed through oxime and amine N moiety. The remaining center of central metal ion are satisfied by the O^- ion of two NO_3^- or ClO_4^- above and below in a layer lattice structure in axial inter facial mode of one another with Ni (II) but coordinated two hydroxyl group of two oximes provide extra bonding and extra stability due to extra number of bonding of Intramolecular hydrogen bond as a result arise six members chelating ring with extra stability of complexes.On the basis of physicochemical and spectroscopic observations it is proposed that the geometry of the complexes of the types $[Ni(H_2mahe^{1-2})(NO_3)_2]$ and $[Ni(H_2mahe^{1-2})(ClO_4)_2]$ are monomeric high spin paramagnetic octahedral in geometry. The following tentative structure may be proposed for these complexes.



n = 3, 4

$X = ClO_4^-$ or NO_3^-

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