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Studies of Binuclear Macrocyclic Ni (II) Complexes with Polydentate 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 fluoroborobridged macrocyclic complexes have been synthesized by refluxing inner complexes salts of [Ni(mahe$^{1-2}$)] in 1-butanol medium with fluoroboroesters. The stoichiometry of the complexes have been determined and characterized on the basis of elemental analyses, magnetic susceptibility, infrared, electronic spectral and conductivity data. The metal chelating ligands have a general formula $[Ni(H_2\ Mahe^{1-2})BF_2]BF_4$.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 Boron capsulation with two oxime groups forming 6-membered cyclic chelating ring. During the capsulation the two oxygen atom of oxime group coordinated with boron by coordinate covalent bond. The nitrogen atom of oxime and amine groups are coordinated with central metal ion with equatorial mode and the electronic and infrared features provide unequivocal evidence in favors of the postulated structures of the precursor low spin diamagnetic square planar complexes geometry. Biological activity studies have also been presented.

KEYWORDS– Macrocyclic complexes,1-butanal medium, Chelating ligand, Boran capsulation. Equatorial mode

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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[6-9].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. In recent years there has been growing interest in preparing the Schiff base complexes which show high activity[10-12]. 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. The fluoroborobridged macrocyclic complexes have been synthesized by refluxing inner complexes salts of [Ni(mahe$^{1-2}$)] in 1-butanol medium with fluoroboroesters. The stoichiometry of the complexes have been found to be of the type [Ni(H_2Mahe$^{1-2}$)BF_2]BF_4.It may enhance their biological activity after chelation also.[13-15] 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.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 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 166 $\pm 2^0$C (literature value 166^0C).

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). Analysis was in satisfactory agreement with the below formulation in Figure – 1.

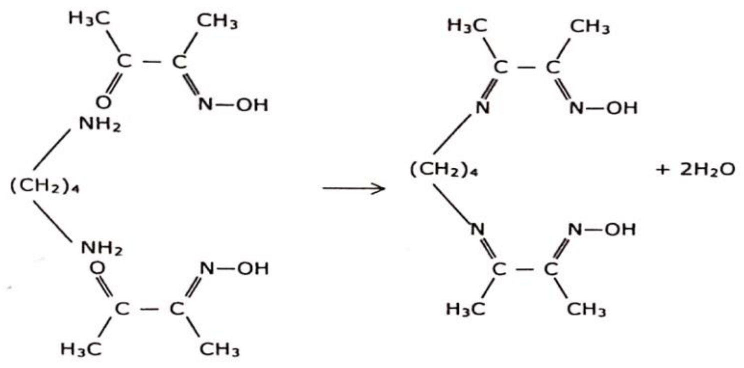

Figure – 1 - The chemical reaction of Synthesis of th ligands

Synthesis and Structure of Ni (II) complexes

1. **Preparation of Difluoroboro-3,9-dimethyl-4,8-diaza-2,10-dihydroximino-3,8-undecadienato nickel (II) tetrafluoroborate, [Ni(H_2mahe[1])BF_2] BF_4**

The inner complex salt [Ni(H_2mahe[1])] (3.0 g, 0.01 mol) was finely triturated and suspended in 1-butanol and stirred at room temperature. To the suspension, freshly distilled boron trifluoride etherate (1mol) was added drop wise while stirring till slightly in excess. The product was allowed to stand for 12 hours in a closed vessel. The chocolate colored product thus formed was filtered, washed with 1-butanal followed by petroleum spirit. The product was recrystallized from acetonitrile and dried in vacuum.

2. **Preparation of Difloroboro-3,10-dimethyl-4,9-diaza-2,11-dihydroximino-3,9-dodecadienato nickel (II) tetrafluoroborate, [Ni(H_2mahe[2]) BF_2] BF_4**

The inner complex salt [Ni(H_2 mahe[2])](3.0 g, 0.01 mol) was finely triturated and suspended in 1-butanol and stirred at room temperature. To the suspension, freshly distilled boron trifluoride etherate (1.0 mol) was added drop wise while stirring till slightly in excess. The product was allowed to stand for 12 hours in a closed vessel. The chocolate colored product thus formed was filtered, washed with 1-butanol followed by petroleum spirit. The product was recrystallized from acetonitrile and dried in vacuum.

RESULT AND DISCUSSION

Very recently the fluoroborobridged macrocyclic complexes have been synthesized by refluxing inner complexes salts of [Ni(mahe[1-2])] in 1-butanol medium with fluoroboroesters. The stoichiometry of the complexes have been determined 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_2 Mahe[1-2])BF_2]BF_4.

Infrared spectra

Infrared spectra of the complexes [Ni (H_2mahe [1-2])BF_2] BF_4 have been recorded in the frequency region 4000-600 cm^{-1} and vibrational bands of structural significance are shown below in Table-1.The Infrared spectra of the complexes are quite complex structurally important vibration bands such as (O-H) stretch, N-OH scissoring, C— N stretch N-O stretch, B—F stretch and B—O stretch are quite discernible and provide unequivocal concerning the nature of bonding of the ligands with the metal ions.

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. Whereas the second band is weak and appears in the form of a shoulder. These bands are almost unaffected in the metal complexes.IR spectra of the complexes are remarkably different from the free ligand as well as its precursor [Ni(mahe$^{1-2}$)]. The most spectacular change is observed near 1050 and 1160 cm^{-1}. A new band appear at about 820 cm^{-1}.The first band observed at 1050 cm^{-1} is very strong and fairly broad and is characteristic of BF_4^- and B-F stretching vibrations. This band overlap on the sharp intensity ν_{N-O} band present in the precursor complex. The bands at 1160 cm^{-1} and 820 cm^{-1} arises due to B-O stretching vibration and their energies are in agreement with earlier reported literature values. Only one ν_{N-O} band is clearly recognized for the macrocyclic complex and is located near 935cm^{-1}. From energy consideration the ν_{N-O} band appears at a lower frequency region compared to the precursor complex and lowering in energy manifests bonding of the oxygen of N-O groups with an electronegative BF_2 bridgehead. The highest energy ν_{N-O} band at 1115 cm^{-1} for the precursor could not be recognized in the macrocyclic complex since it is buried under the higher energy vibrational band ν_{B-O}. Another spectacular feature of the fluoroborobridged macrocyclic complexes is the splitting of the C—N stretching vibration which appears as a doublet at 1640 cm^{-1} and 1600 cm^{-1} respectively are the splitting is most probably due to macrocyclization. These vibrational bands originate due to deformation mode of vibration of $-CH_3$ and-CH_2- groups.

Table-1 Characteristic i.r.spectral bands of ligands H_2(mahe$^{1-2}$) complexes of [NiH_2(mahe$^{1-2}$)BF_2] BF_4

Complex / Ligand	ν_{O-H}	$\nu_{C...H}$ 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)BF_2]BF_4	3375 m	1610 S	1465 m	1045 S	1195	810		450
[Ni(H_2mahe^2)BF_2]BF_4	3380 m	1615 S	1470 m	1055 S	1200	805		455

S= Strong m=Medium b= Broad

Magnetic susceptibility and electronic spectra of Nickel (II) complexes.

The electronic spectra of these complexes have been measured in the range 10,000 – 25,000 cm^{-1}The spectra consist of a broad band in the region 20,000 – 22,000 $cm^{-1}$and can be reasonable interpreted in the light of the development just described. The width of the spectra manifests that the band represents a group of two to three transitions assignable to the transitions, $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1A_{1g}\rightarrow{}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ under a square planar environment possessing the chromophore, NiN_4.The fluoroborobridged macrocyclic complexes of Ni(II) as well its precursors are diamagnetic and are believed to possess square geometry. The electronic spectra of the complexes have been measured in visible and ultraviolet regions in dichloromethane medium. The electronic spectra of the complexes are dominated by an intense in the region 18,000 to 21,000 cm^{-1}. This electronic transition has been assigned to $^1A_{1g}\rightarrow {}^1A_{2g}$ for spin-paired Ni(II) ion under a square planar ligand field. The band position is recorded in Table-2.

Table-2 Electronic spectral bands for precursors [Ni(H_2mahe$^{1-2}$)] and macrocyclic complexes,[Ni(H_2mahe$^{1-2}$) BF_2] BF_4

Complexes	$^1A_{1g}\rightarrow{}^1A_{2g}$
[Ni(H_2mahe^1)]	18,800
[Ni(H_2mahe^2)]	20,800
[Ni(H_2mahe^1)BF_2] BF_4	18,600
[Ni(H_2mahe^2) BF_2] BF_4	20,800

Conductivity measurement

Conductivity of the complexes was measured in the solvent DMSO. The macrocyclic complexes of [Ni(H_2mahe$^{1-2}$)BF_2] BF_4 have conductivity in the range 90–100 ohm^{-1} cm^2 mol^{-1} and are expected to be electrolytic of the type 1:1[16-17] .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(H_2mahe^1)	10
Ni(H_2mahe^2)	12
[Ni(H_2mahe^1) BF_2] BF_4	90
[Ni(H_2mahe^2) BF_2] BF_4	95

Biological activity.

On the basis of experiment the Ni(II) complexes have more active and more effective than free ligands. The complexes are highly active due to the greater lipophilic and absorbing nature. The complexes are more 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 overlap with ligand filled orbital and vacant outer d- orbital of the metal ion with donor nitrogen atom of oxime groups. Further it increasing the delocalization of electrons of metal ion over the whole chelate ring as a result decreases or controlled the growth or increases the ratio of death of bacteria. The results indicated that chelation improved the antibacterial activity compared to the ligand[18-19] and known as antibiotic drugs.

On the basis of chemical and spectral analysis of the complexes, it may be concluded that the complexes seen to have diamagnetic Square planer geometry. The following tentative structure

May be proposed for these complexes in Figur-2

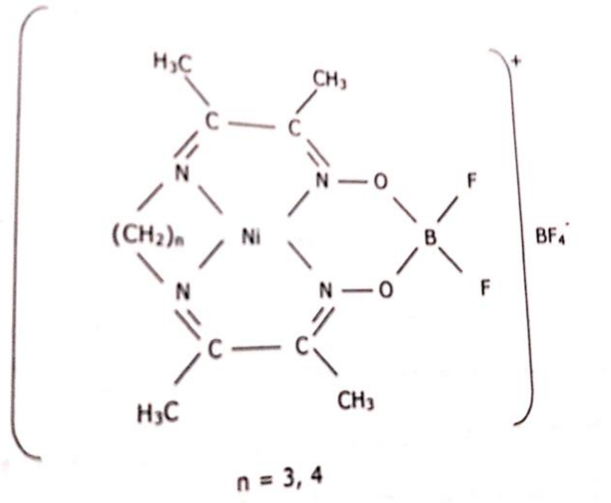

Figure - 2 The square planar geometry of [Ni(H_2 Mahe$^{1-2}$)BF_2]BF_4 complexes.

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 with central metal ion of complexes while two oxygen atom of the oxime group capsulated with boron and proposed 6-membered capsulated ring structure. On the basis of physicochemical and spectroscopic observation it is proposed that the geometry of the complexes of the type [Ni(H_2mahe$^{1-2}$)BF_2]BF_4 are monomeric low spin diamagnetic square planar complexes.

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