



SPECTRAL STUDIES ON NICKEL (II) COMPLEXES WITH SCHIFF BASE LIGANDS

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Abstract

A series of new structurally novel unsymmetrical tetra dentate Schiff base metal (II) complex of nickel (II) was prepared by refluxing together the relevant unsymmetrical Schiff bases with the corresponding nickel (II) acetate in methanolic medium.

The ^1H NMR spectral data of the free ligand were recorded in CDCl_3 against tetramethylsilane (TMS) as internal reference.

The appearance of two different peaks for each of the azomethine protons and phenolic protons confirm the unsymmetrical nature of the Schiff bases in the series.

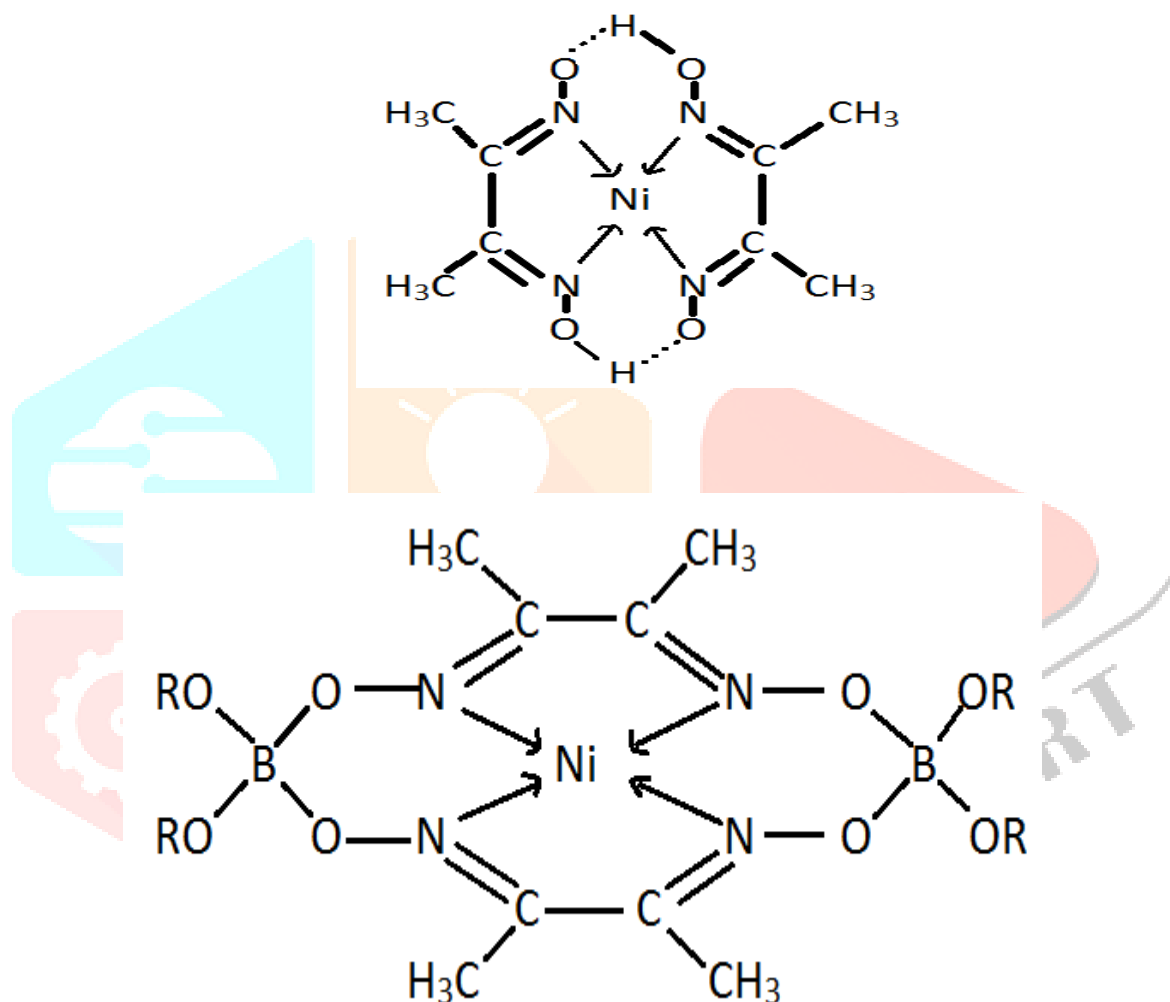
The absorption bands due to amino group disappeared in the IR spectra of all the four ligands [H_2L^{1-4}] which showed that the amino group in the diaminopyridine condensed with the aldehydes. The bands appearing at $1600\text{-}1640\text{ cm}^{-1}$ due to azomethine group of the ligands is shifted to lower frequency at $1570\text{-}1600\text{ cm}^{-1}$ in the nickel (II) complexes indicating the participation of the azomethine nitrogen in coordination with the metal ion.

The infrared spectra of both the ligands and complexes have no bands between 3100 and 4000 cm^{-1} indicating the absence of uncoordinated N-H and uncoordinated -OH groups. Due to

unsymmetrical nature of the ligands and the complexes two bands were observed for each of the following modes. $\nu_{C=N}$, ν_{M-N} and ν_{M-O} .

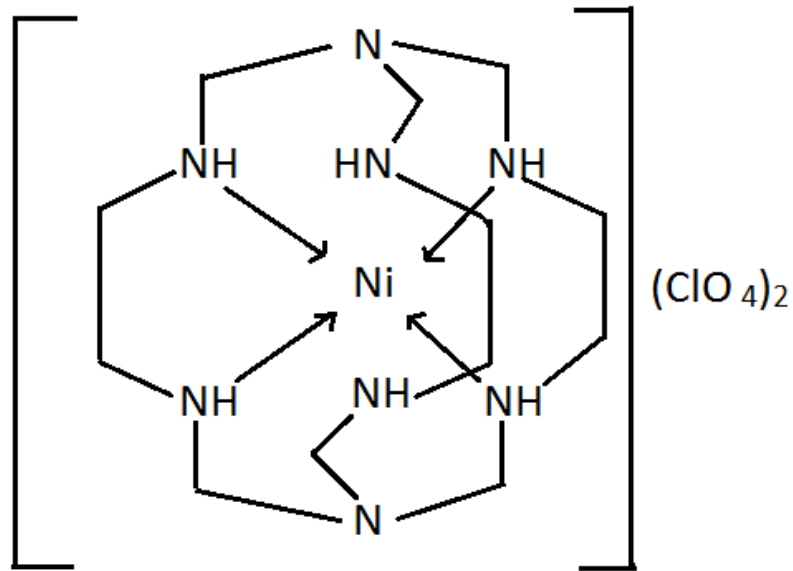
Introduction

ligands are encapsulation ligands and compartmental ligands. One representative example of each type is shown in Fig.



Alkoxyborobridged nickel(II) macrocycle

Fig



A encapsulation compound of nickel(II)

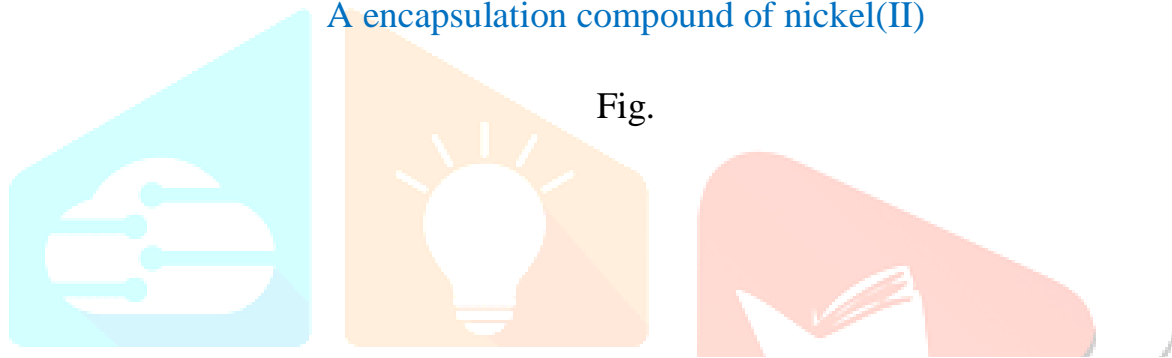


Fig.

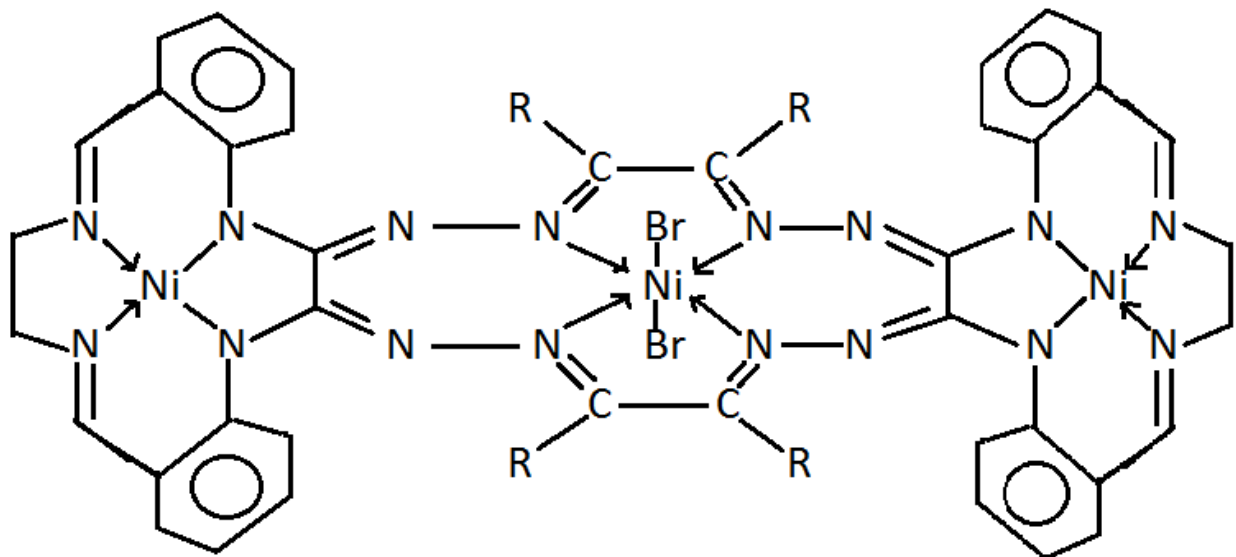


Fig.

R = methyl, phenyl, furyl A 40- membered tricomparmental (isolated) macrocyclic of nickel (II)

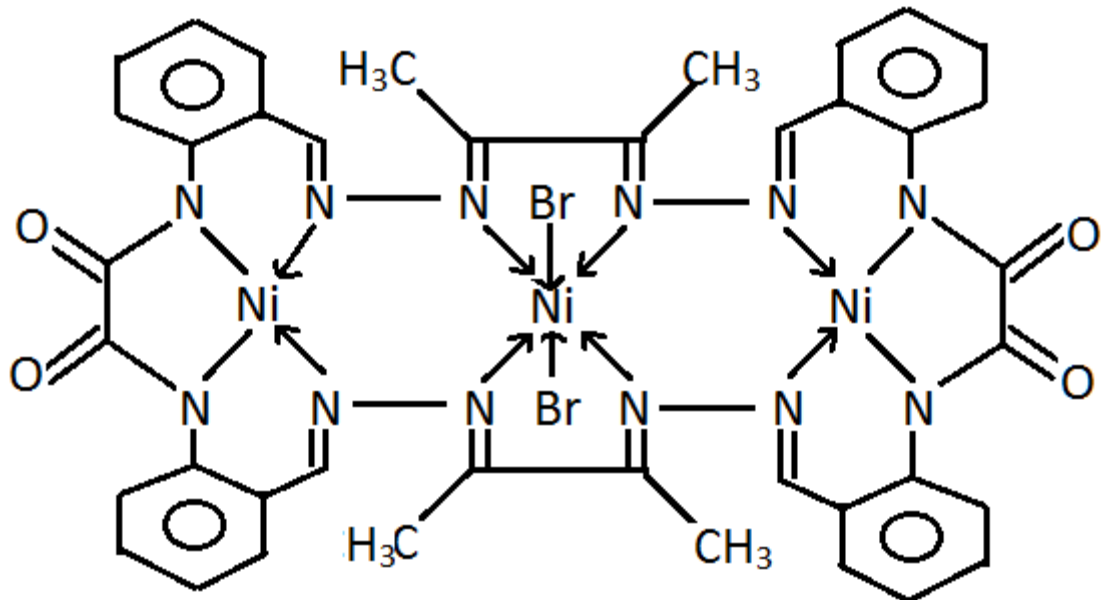
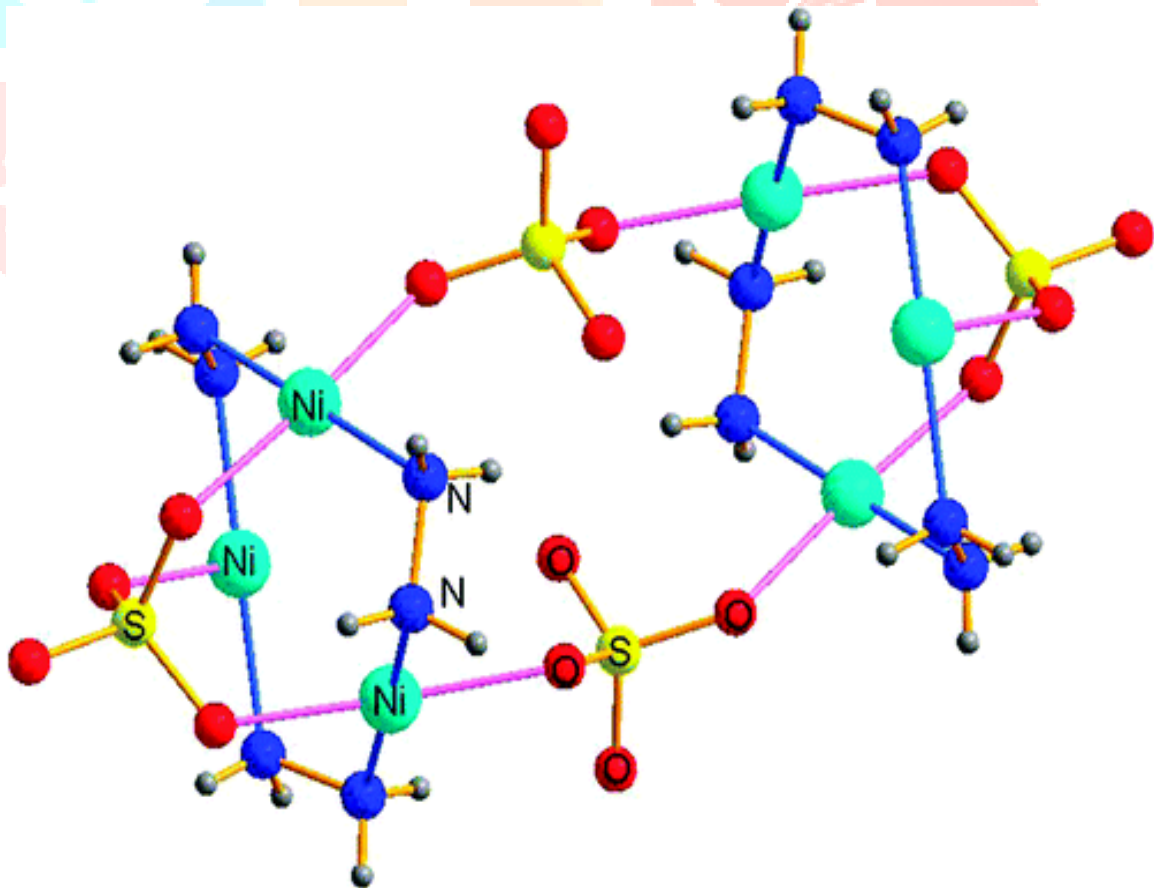


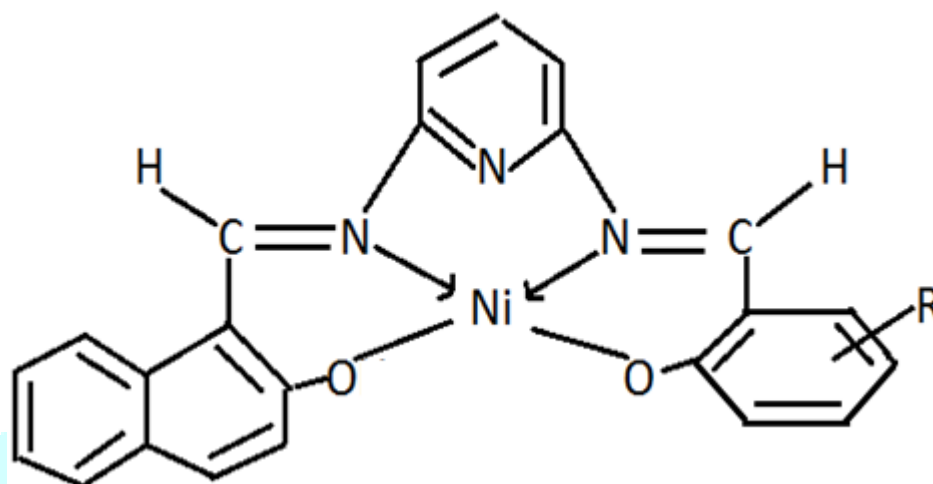
Fig.

Very recently a hexanuclear complex of nickel (II) with hydrazine ligand, a nanomaterial used for the synthesis of nanotubes of silicon has created rejuvenated interest in the field of nickel complexes.



Fig

Inspired by the above mentioned attracting and fascinating scenario of nickel (II) complexes with Schiff base ligands, we in the present programme propose to synthesize and characterize a few nickel (II) complexes with a series of novel unsymmetric Schiff base ligands derived by the nickel(II) ion catalysed template condensation of 2,6-diaminopyridine with (substituted and unsubstituted) salicylaldehyde and 2-hydroxy naphthaldehyde.



Unsymmetrical Schiff base ligand obtained by condensation of 2,6-diaminopyridine, salicylaldehyde and 2-hydroxy naphthaldehyde.

Fig

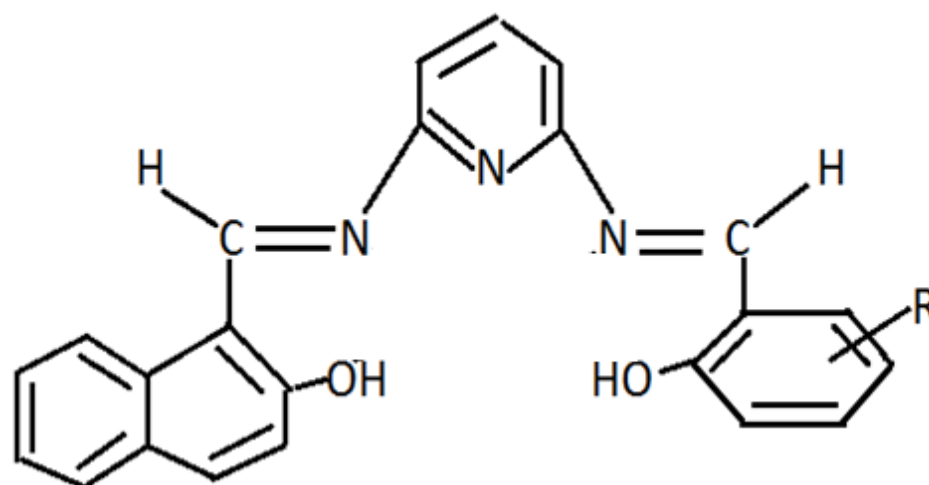
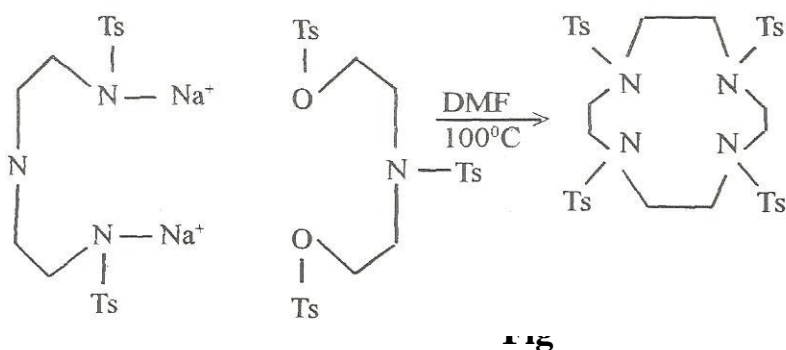


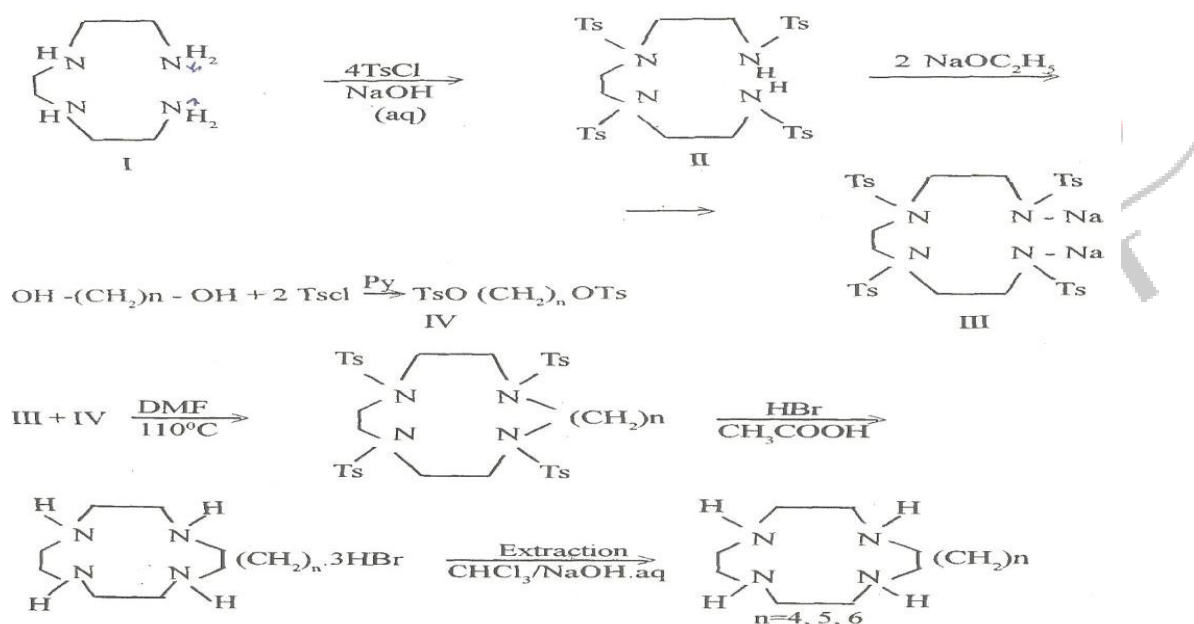
Fig.

Since the present thesis deals with the synthesis and characterization of nickel (II) complexes with novel unsymmetrical Schiff base ligands, it would be appropriate to present an up-to-date and elaborate review of earlier work done in these fields in order to present a background to the present work.

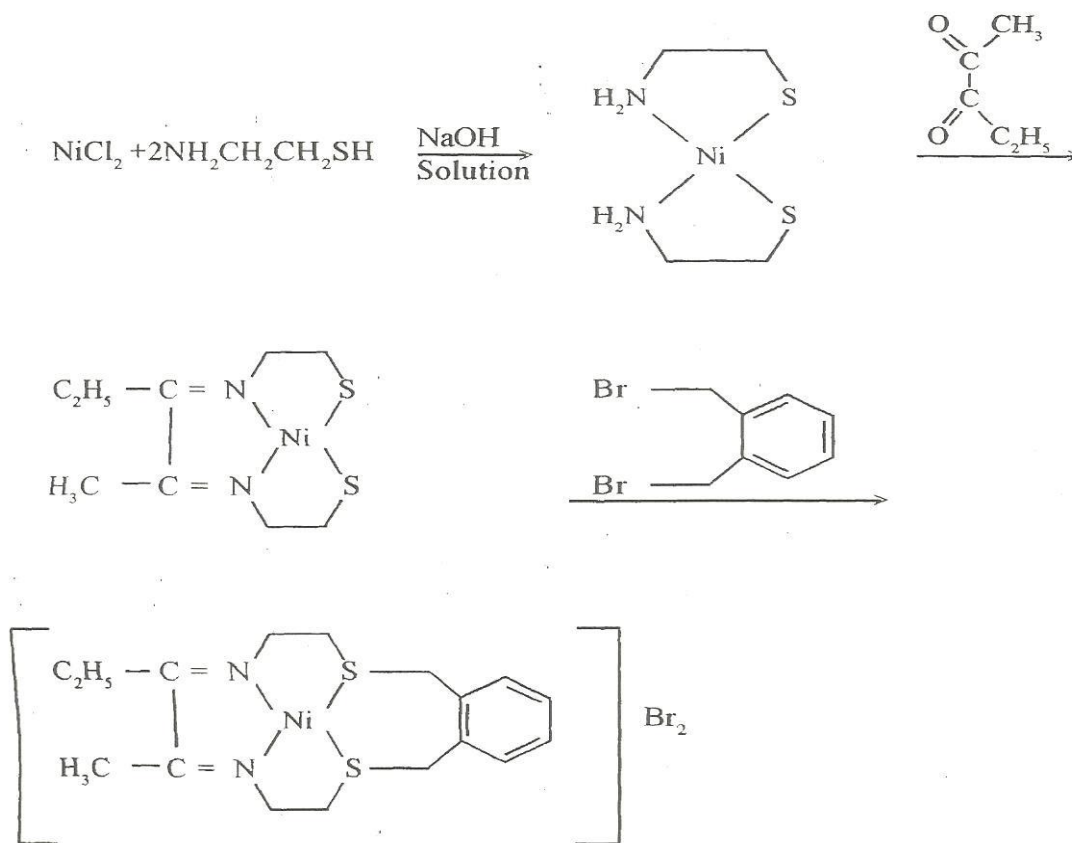
Several new methods for obtaining cyclic amines in reasonable yields are known. Tosylated reactants condense by heating in dimethyl formamide at elevated temperatures and are example of such exotic reactions. The tetratosyl derivative has been obtained in 80% yield and the tosyl groups can be conveniently removed by heating the product in sulphuric acid medium.



Synthetic reactions of this type have become general as well as considerable simpler to prepare macrocycles with increased ring size.



A large fraction of synthetic macrocyclic complexes have been prepared via metal ion template methods. The cyclization occurs either by metal ion induced reactivity of one of the condensing functional groups or often by steric factors that govern the appropriate positioning of the reacting species in the ring closure process. Majority of template condensations followed from the work of Curtis involving condensation of metal-amine complexes with carbonyl compounds. An interesting example of metal ion template synthetic macrocyclic compound was obtained immediately after Curtis synthesis.



Results and Discussion

Unsymmetrical Schiff base nickel (II) complexes.

A series of new structurally novel unsymmetrical tetra dentate Schiff base metal (II) complex of nickel(II) was prepared by refluxing together the relevant unsymmetrical Schiff bases with the corresponding nickel (II) acetate in methanolic medium as shown in.

They were isolated as pure from methanol in very good yields. The purity of the metal complex was established by microanalyses as formulated. All the unsymmetrical Schiff base complexes did not melt or decompose when heated up to 250°C. The nickel (II) complexes were found to be red.

¹H NMR Spectra of the Schiff bases:-

The ¹H NMR spectral data of the free ligand were recorded in CDCl₃ against tetramethylsilane (TMS) as internal reference.

The appearance of two different peaks for each of the azomethine protons and phenolic protons confirm the unsymmetrical nature of the Schiff bases in the series.

The higher of the two signals for both the azomethine and phenolic protons is assigned to the azomethine / phenolic proton attached to the naphthaldehyde ring while the lower signal is assigned to the azomethine / phenolic proton attached to the salicylaldehyde ring. Signals for the methine proton of the azomethine group were observed between 8.2 and 9.0 ppm. The peak in the region 6.8 to 8.1 ppm. which appeared as a multiplet are assigned to chemical shifts for aromatic protons. The O-H protons of the phenolic group were observed as a singlet between 12.0 and 15.5 ppm and were generally shifted downfield due to intermolecular hydrogen bonding. The signal due to the methyl protons on the ethoxy substituent in H_2L^3 appeared as a triplet at 1.5 ppm while the signal at 4.1 ppm is assigned to the CH_2 proton.

For the unsymmetrical Schiff bases, the observed difference in the signal of the phenolic proton is attributed to the greater electron withdrawing effect of the naphthaldehyde ring and hydrogen bonding between the phenolic proton and the azomethine nitrogen.

The deshielding effect of electron withdrawing groups and hydrogen bonding are responsible for the proton signal being moved further downfield. Similarly the same trend is observed for the azomethine proton of the unsymmetrical Schiff bases.

Table

1H NMR data for free ligands

Ligands	δ_{OH}	δ_{Ar-H}	δ_{CH_3}	δ_{CH_2}	$\delta_{N=O}$
H_2L^1	15.5(s, 1H) 10.2 (s, 1H)	6.9,8.1(m,13H)			8.9 (s, 1H) 9.0 (s, 1H)
H_2L^2	13.9 (s, 1H) 15.2 (s, 1H)	7.1,8.1(m,13H)			8.4 (s, 1H) 8.8 (s, 1H)
H_2L^3	12.9 (s, 1H) 15.0 (s, 1H)	6.8-8.1(m, 13H)	1.5(t,3H)	4.1 (q, 2H)	8.2 (s, 1H) 8.7 (s, 1H)
H_2L^4	12.0 (s, 1H) 15.7 (s, 1H)	6.9-8.0 (m,14H)			8.6 (s, 1H) 8.9 (s, 1H)

Infrared spectra

The important infrared spectral bands of the nickel (II) complexes are presented in Table. A representative IR Spectra of nickel (II) complex.

The tentative assignments of the observed band for the compounds were made by comparing the spectra with those reported in the literature on similar systems¹⁻⁷. The absorption bands due to amino group disappeared in the IR spectra of all the four ligands [H_2L^{1-4}] which showed that the amino group in the diaminopyridine condensed with the aldehydes. The bands appearing at 1600-1640 cm^{-1} due to azomethine group of the ligands is shifted to lower frequency at 1570-1600 cm^{-1} in the nickel (II) complexes indicating the participation of the azomethine nitrogen in coordination with the metal ion.

Similarly the $\nu_{C=O}$ band of the ligand which occurs at 1255-1330 cm^{-1} is shifted to 1270-1360 cm^{-1} in the complexes indicating deprotonation and co-ordination of the phenolic oxygen to the atom.

Thus it can be concluded that the Schiff bases acted as tetradentate ligands coordinating via the azomethine N and the phenolic O.

Further conclusive evidence of the co-ordination of the Schiff bases with the metal ions was shown by the appearance of new bands at 435-580 and 410-581 cm^{-1} assigned to the metal nitrogen (M-N) and metal oxygen (M-O) stretching vibrations respectively.

These bands were absent in the spectra of the uncomplexed schiff bases, thus confirming the participation of O and N atoms in the co-ordination. It has been established that the metal ligand vibrational modes are very sensitive to substituent effects.

The infrared spectra of both the ligands and complexes have no bands between 3100 and 4000 cm^{-1} indicating the absence of uncoordinated N-H and uncoordinated -OH groups. Due to unsymmetrical nature of the ligands and the complexes two bands were observed for each of the following modes. $\nu_{C=N}$, ν_{M-N} and ν_{M-O} .

The spectra of the ligands show two different C=N stretching frequency at 1610-1621 and 1570-1580 cm^{-1} which are shifted to lower frequency in the spectra of all the nickel complexes at 1600-1610 and 1560-1570 cm^{-1} respectively indicating the involvement of azomethine nitrogen in co-ordination with the metal ion.

The corresponding phenolic C-O stretching occur at 1313-1333 and 1276-1289 cm^{-1} for the ligand and at 1331-1366 cm^{-1} and 1287-1311 cm^{-1} for the complexes.

The shift to higher frequency of this band confirms the participation of the phenolic oxygen in bonding. Assignment of the proposed co-ordination sites is further supported by the appearance of new bands at 457-583 and 507-554 cm^{-1} which are assigned to $\nu_{(\text{Ni-N})}$ while 463-577 and 431 cm^{-1} are attributed to $\nu_{(\text{Ni-O})}$ ^{3,9}.

Table

Selected infrared spectral bands of legend and Nickel(II) complexes

Complex	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
H_2L^1	1610, 1580	1315, 1275	-	-
H_2L^2	1620, 1567	1335, 1290	-	-
H_2L^3	1610, 1569	1315, 1285	-	-
H_2L^4	1615, 1568	1310, 1285	-	-
NiL^1	1609, 1582	1330, 1290	457, 554	577, 431
NiL^2	1603, 1580	1365, 1310	457, 510	545, 431
NiL^3	1606, 1577	1345, 1295	478, 507	560, 431
NiL^4	1606, 1577	1340, 1290	583, 507	463, 431

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