



NOVEL Ni (II) TETRAAZA MACROCYCLIC COMPLEX : SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Novel tetraaza macrocyclic ligand has been synthesized from condensation of ethylene diamine and ethyl acetoacetate and its Ni (II) complex is prepared by non-template condensation reaction. The bonding and stereochemistry of the complex has been characterized by elemental analysis, magnetic susceptibility, IR, UV-visible, ¹H NMR and mass spectral studies. The magnetic and spectral data indicate octahedral geometry of the complex.

Key words : Nickel, Tetraaza, Macrocyclic, Complex

INTRODUCTION

The field of coordination chemistry of macrocyclic complexes has undergone spectacular growth during the past few decades. This enormous growth is due to the synthesis of a large number and variety of synthetic macrocycles, which behave as coordinating agents for metal ions^{1,2}. Nitrogen containing macrocycles have a strong tendency to form stable complexes with transition metals³. A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications⁴. Macrocyclic transition metal complexes have been regarded as being better model compounds for metalloporphyrins and metallocorrins⁵⁻⁸.

The aim of this work was the production of novel macrocyclic ligand and its nickel (II) complex by using non-template condensation method (**Scheme 1**). Thus, macrocyclic ligand and its complex were synthesized and characterized by using different techniques.

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EXPERIMENTAL

All chemicals and solvents were reagent grade and used as received. C, H, N and M analyses (Table 1) were determined at the analytical unit of RSIC Chandighr University, Chandighr. IR spectra (as KBr pellets) were recorded ($4600-400\text{ cm}^{-1}$) on a Perkin-Elmer 681 spectrophotometer. Electronic spectra in the 200-900 nm regions were recorded on a Perkin-Elmer 550 spectrophotometer. Mass spectra were recorded on Jeol SX-102 (FAB), ^1H NMR spectra were obtained with a Perkin-Elmer R32-90 MHz spectrometer using TMS as internal standard and DMSO-d_6 as solvent from CDRI, Lucknow. Magnetic susceptibility of a complex was measured at 25°C by the Gouy's method using mercuric tetrathiocyanatobaltate (II) as the magnetic standard at Department of Chemistry RTM Nagpur University, Nagpur.

Preparation of 5, 12 - dioxo - 7, 14 - dimethyl - 1, 4, 8, 11 - tetraaza-cyclotetradeca-1, 8-diene (L) :

1, 2-Diaminoethane (0.01 mol, 0.6 mL) in ethanol (25 mL) and ethyl acetoacetate (0.01 mol, 1.2 mL) were dissolved in ethanol (25 mL). A mixture of both the reactants was refluxed for 6 h. Then volume was concentrated on the steam bath until white colored crystals begin to form. The product has been purified by crystallization from hot alcohol and 1 g of activated charcoal (to remove colored impurities, if any). Thus, white crystalline pure macrocyclic ligand has been collected. (Yield: 1.8 g; 75%). The purity of the crystalline ligand was checked by TLC.

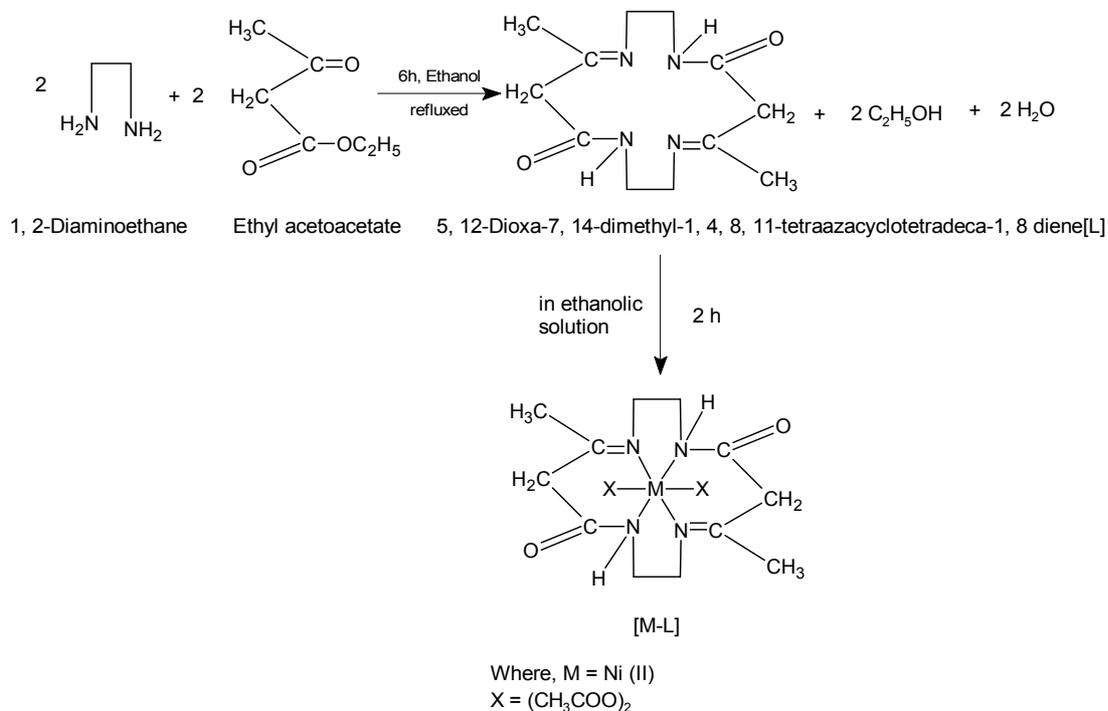
Preparation of $\{\text{Ni (II)- (L)- (CH}_3\text{-COO)}_2\}$

To the hot ethanolic solution of ligand (L) (0.01 mmol, 2.5 g), hot ethanolic solution of nickel acetate ($\text{Ni (CH}_3\text{-COO)}_2\cdot 4\text{H}_2\text{O}$; 0.01 mmol, 2.4 g) with few drops of acetic acid was added. The solution was then refluxed for 2 h. On cooling, a light green colored precipitate formed, which was then filtered and washed with cold ethanol and dried under vacuum.

RESULTS AND DISCUSSION

Table 1 : Analytical data of tetraaza macrocyclic ligand (L) and its complex

Comp.	Decomposition temp. (°C)	Colour	Elemental analysis (%) Calcd (found)				Molecular weight
			M	C	H	N	
[L]	220	White	-	57.14 (56.96)	7.93 (7.04)	22.22 (22.39)	252
[Ni-L]	320	Light green	13.55 (12.91)	44.85 (44.50)	6.07 (5.95)	13.08 (13.76)	428



Scheme 1

IR spectra

The preliminary identification of the macrocyclic ligand has been obtained from its IR spectrum, which shows the absence of uncondensed functional groups such as ethylenediamine and ethyl acetoacetate *i. e.*, stretching modes of starting materials. The appearance of strong absorption band in the region $1600\text{--}1650\text{ cm}^{-1}$ corresponds to $\nu\text{>C=N}$ stretching frequency. A single sharp band observed for the ligands in the region 3300 cm^{-1} corresponds to $\nu\text{N-H}$ in secondary >CO-NH group. The absorption bands in the region $2900, 2950$ and 3000 cm^{-1} and $1380, 1460$ and 1460 cm^{-1} in the ligand may, reasonably, assign to $\nu\text{C-H}$ stretching and $\nu\text{C-H}$ bending vibration modes, respectively.

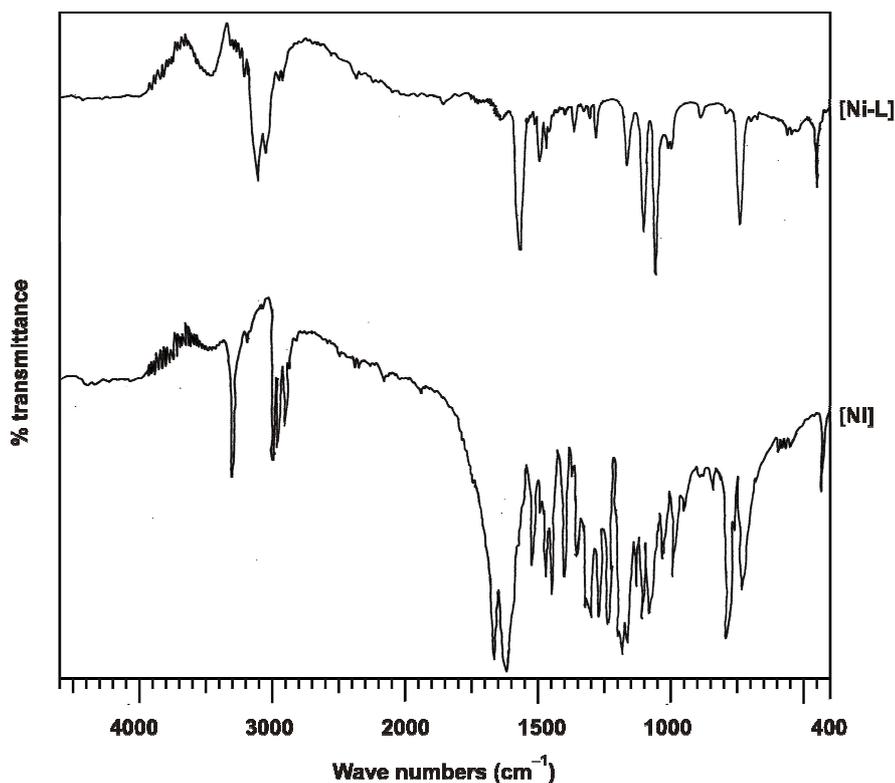


Fig. 1

The red shift in the $\nu\text{>C=N}$ and $\nu\text{N-H}$ modes appears at 1590 and 3280 cm^{-1} , respectively in the nickel complex⁹. The negative shift in $\nu\text{N-H}$ mode along with appearance of the new band at 470 cm^{-1} assignable to $\nu\text{M-N}$ vibration suggests that the imide nitrogen is coordinating to the metal ion. The position of amide band, which does

not undergo any change and the absence of a band attributable to $\nu_{\text{M-O}}$ [$500\text{--}550\text{ cm}^{-1}$] vibration indicates that the amide oxygen is non-coordinating. IR spectra of macrocyclic ligand and its coordination compounds Ni (II) are given in the Fig. 1.

^1H NMR Spectra

The ^1H NMR spectrum of the macrocyclic ligand shows triplet in the region δ 1.10 – δ 1.15 and singlet at δ 1.88 corresponding to CH_3 (6H) protons and CH_2 (4H) protons of acetoacetate¹⁰, respectively. The ^1H NMR spectrum of [L] shows a broad signal observed at δ 8.53 that may be attributed to amide protons¹¹ (2H). A quartet observed in the region δ 3.91- δ 3.98 and singlet at δ 4.35 possibly will be ascribed to methylene CH_2 (8H) protons of¹² diaminoethane moiety.

The ^1H NMR spectrum of the macrocyclic complex shows multiplet in the region δ 1.03 -1.36 attributable to CH_3 (6H) protons and the methylene protons (4H) of acetoacetate moiety, respectively. The transition metal complex shows broad singlet at δ 8.23 for Ni (II); a small singlet is observed for Ni (II) δ 8.2, which is attributable to amide protons (2H). Singlets and multiplets observed in the region δ 3.03 – 3.57 for the above macrocyclic complex may possibly assigned to methylene protons ($>\text{CH}_2$) adjacent to nitrogen. The shift of the signals towards lower field is an identification of the coordination of macrocycle. ^1H NMR spectrum of the ligand [L] is given in Fig. 2.

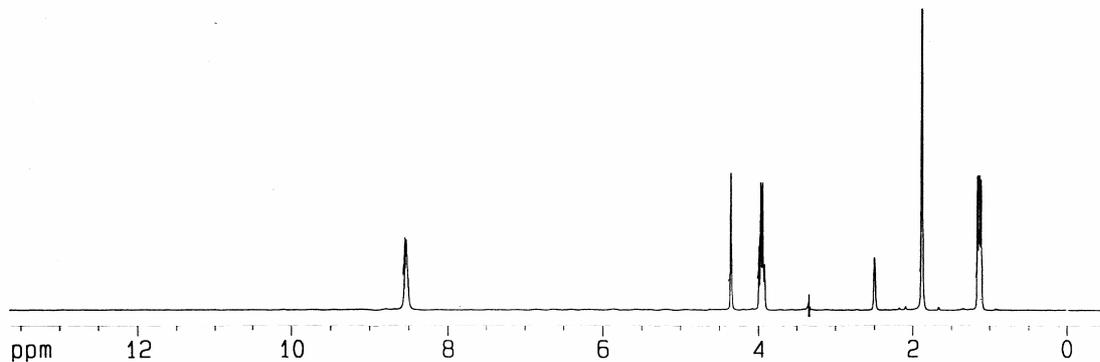


Fig. 2 : Proton NMR spectrum of macrocyclic ligand [L]

Mass spectra

The mass spectra of the macrocyclic ligand [L] and its Ni (II) complex have been traced which provide different molecular ion peaks corresponding to molecular reorganizations. The spectra show numerous peaks representing successive degradation of

the molecules. The observed molecular ion peaks (m/e), fragments and abundances of the macrocyclic ligand [L] is given in **Scheme 2**.

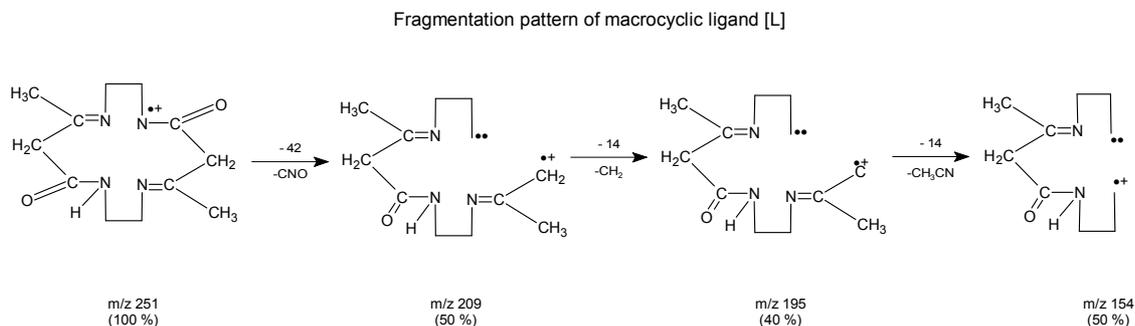


Table 2 : Magnetic moment and assignments of electronic spectra of Ni (II) complex

Compounds	Electronic spectra		Assignments/ geometry
	μ_{eff} (B. M.)	λ_{max} (cm ⁻¹)	
[Ni- L]	2.1	11, 440-11, 455 and	$^3A_{2g} \rightarrow ^3T_{2g}$ (F)
		16, 660-16, 680	$^3A_{2g}$ (F) \rightarrow $^3T_{1g}$ (F)
		28, 765-28, 778	$^3A_{2g} \rightarrow ^2T_{2g}$ (P)

Electronic spectra

The details of magnetic moment, tentative geometry and electronic spectral bands¹³ of macrocyclic complex observed are given in the Table 2.

CONCLUSION

The present investigation deals with the synthesis and characterization of tetraaza macrocyclic ligand and its nickel complex. On the basis of various physicochemical studies, the nature as well as to some extent structure and stereochemistry of macrocyclic ligand and its complex have been suggested.

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