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Synthesis and spectroscopic studies of Ni(II) complexes of the tetraaza cyclohexadeca macrocyclic ligand.

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Abstract

In our present investigation,Synthesis and spectroscopic studies of Ni(II) complexes of the tetraaza cyclohexadeca macrocyclic ligand. The electronic spectra of Ni(II) complexes display a broad band in thecharge transfer region indicative of their square planar geometry. The square planar geometry of Ni(II) complexes is furthersupported by their diamagneticnature. Comparision of the infrared spectra of ligands and the complexes reveals facts.The appearance of a new band in IR spectraof $[NiL_1]Cl_2$*,* $[NiL_2]Cl_2$ *and* $[NiL_3]Cl_2$ *at 610* cm^{-1} *may beassigned to □Ni(II) mode of vibration.This also supports the coordination of the ligands to Ni(II) through nitrogenatoms. During the Preparation of the complex of Ni (II) with 1,5,9,13- tetraaza-2,10-dimethyl-4,12-diphenyl cyclohexadeca- 1,4,9,12-tetraene (*L_1*), Preparation of the complex of Ni (II) with 1,5,9,13- tetraaza-2,4,10,12-tetramethyl cyclohexadeca-1,4,9,12- tetraene (*L_2*) and Preparation of the complex of Ni (II) with1,5,9,13- tetraaza-2,4,10,12-tetraphenyl cyclohexadeca-1,4,9,12- tetraene (*L_3*).*

Keyword:- electronic spectra Ni(II), tetraaza, Dimethyl, diphenyl, tetraphenyltetramethyl, cyclohexadeca, tetraene.

INTRODUCTION

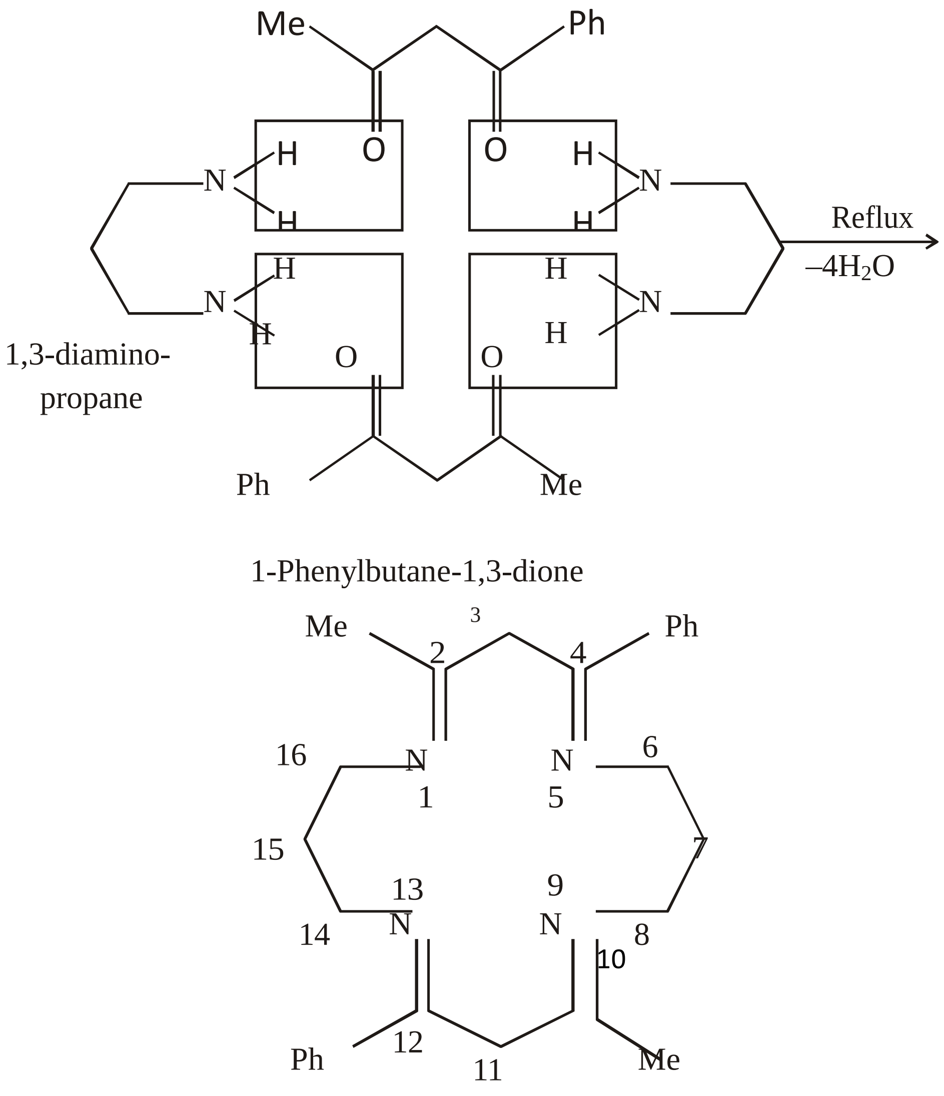
The chemistry of macrocyclic ligands has been a fascinating area of current research interest to the chemists all over the world. The continued interest and quest in designing new macrocyclic ligands stem mainly from their use as models for protein-metal binding sites in biological systems, as models for metalloenzymes, as sequestering reagents for specific metal ions, as models to study the magnetic exchange phenomena, as chemical sensors and batteries, as therapeutic reagents for the treatment of metal intoxication, as medical imaging agents, as catalysts, and in biomedical and fuel cell applications.The macrocycles and their complexes have attracted the interest of both inorganic and bioinorganic chemists in recent years and have been the domain of their research work in view of their wide range of applications. The studies of macrocycles have undergone tremendous growth in past few decades and their complexation chemistry with a wide variety of metal ions has been extensively studied. Macrocyclic compounds are interesting ligand systems as they are good hosts for metal ions, neutral molecules and organic cation guests. The host-guest chemistry of metal- ions and macrocyclic compounds is quite significant in fundamental studies like phase-transfer catalysis. Macrocyclic complexes are considered to mimic the synthetic models of metalloporphyrins and metallocorrins due to their interinsic structural properties. Efforts have been made to achieve peripheral substitution, the appended substitution might create the possibility of synthesis of more complex compounds serving as new biologically important models. These compounds have received considerable attention due to their possible applications in medicine.

EXPERIMENTAL

PREPARATION OF LIGANDS

(i) Preparation of 1, 5, 9, 13-tetraaza-2,10-dimethyl- 4,12-diphenyl cyclohexadeca-1,4,9,12-tetraene (L_1):

0.10 mole of 1,3-diaminopropane was dissolved in 50 ml. of methanol and cooled in ice. To this solution, a solution of 0.10 mole of 1-phenylbutane-1,3-dione in 50 ml. of methanol was added. The mixture was stirred for24 hours at 5°C, refluxed for about 8 hours and then concentrated to about 30 ml. and placed in an ice-bath. White coloured crystals were separated which were washed with ice-cold methanol and recrystallised twice from methanol- water mixture.

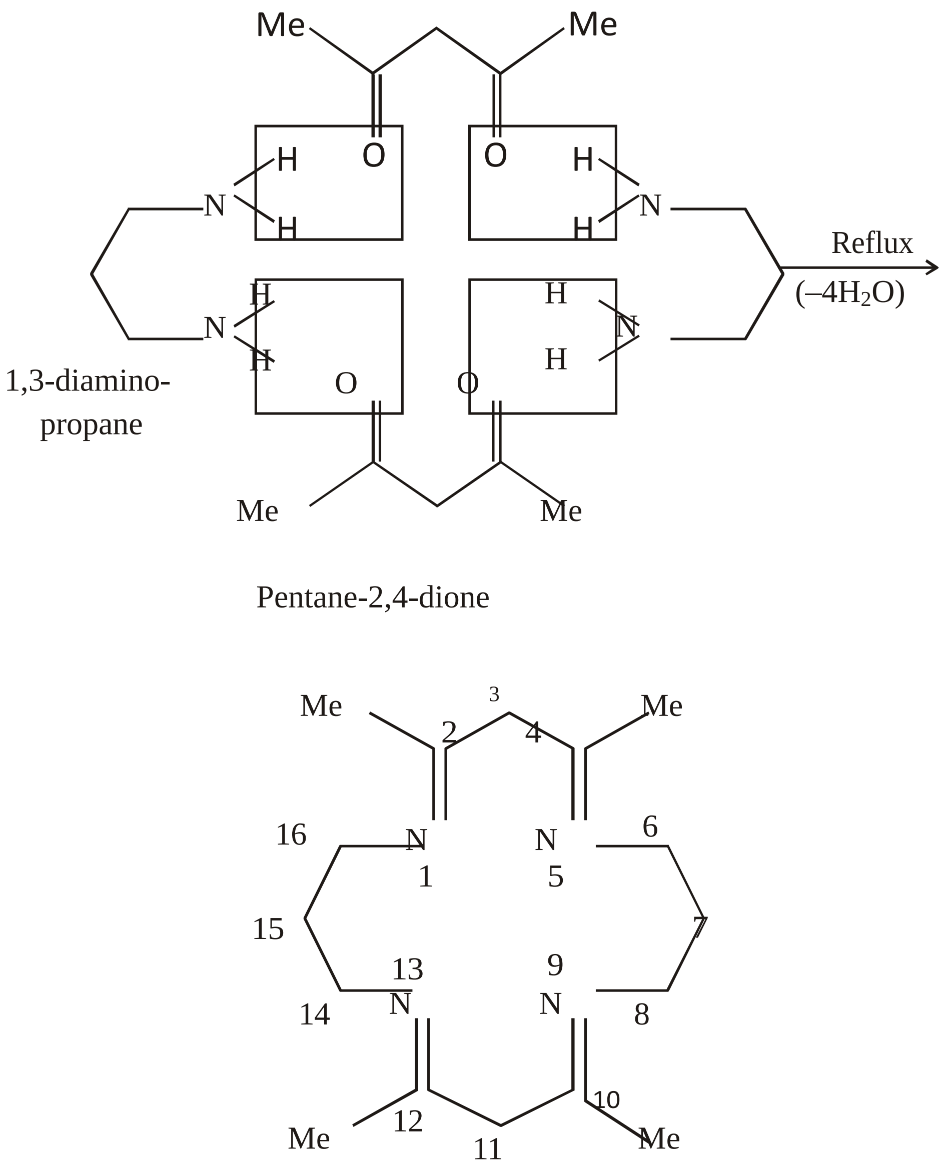


1,5,9,13-tetraaza-2,10-dimethyl-4,12-diphenyl cyclohexadeca-1,4,9,12 tetraene(L_1)

(Fig. -1)

(ii) Preparation of 1,5,9,13-tetraaza-2,4,10,12- tetramethyl cyclohexadeca-1,4,9,12-tetraene (L_2)

0.10 mole of 1,3-diaminopropane was dissolved in 50 ml. of methanol and cooled in an ice-bath. A solution of 0.10 mole of pentane-2,4-dione in 50 ml. of methanol was added to the methanolic solution of 1,3-diaminopropane. The mixture was stirred for about 24 hours at 5ºC, refluxed for about 8 hours and then concentrated to about 30 ml.and placed in an ice-bath. Yellowish-whitecrystals were separated which were washed with ice-methanol and recrystallised twice from methanol-watermixture.

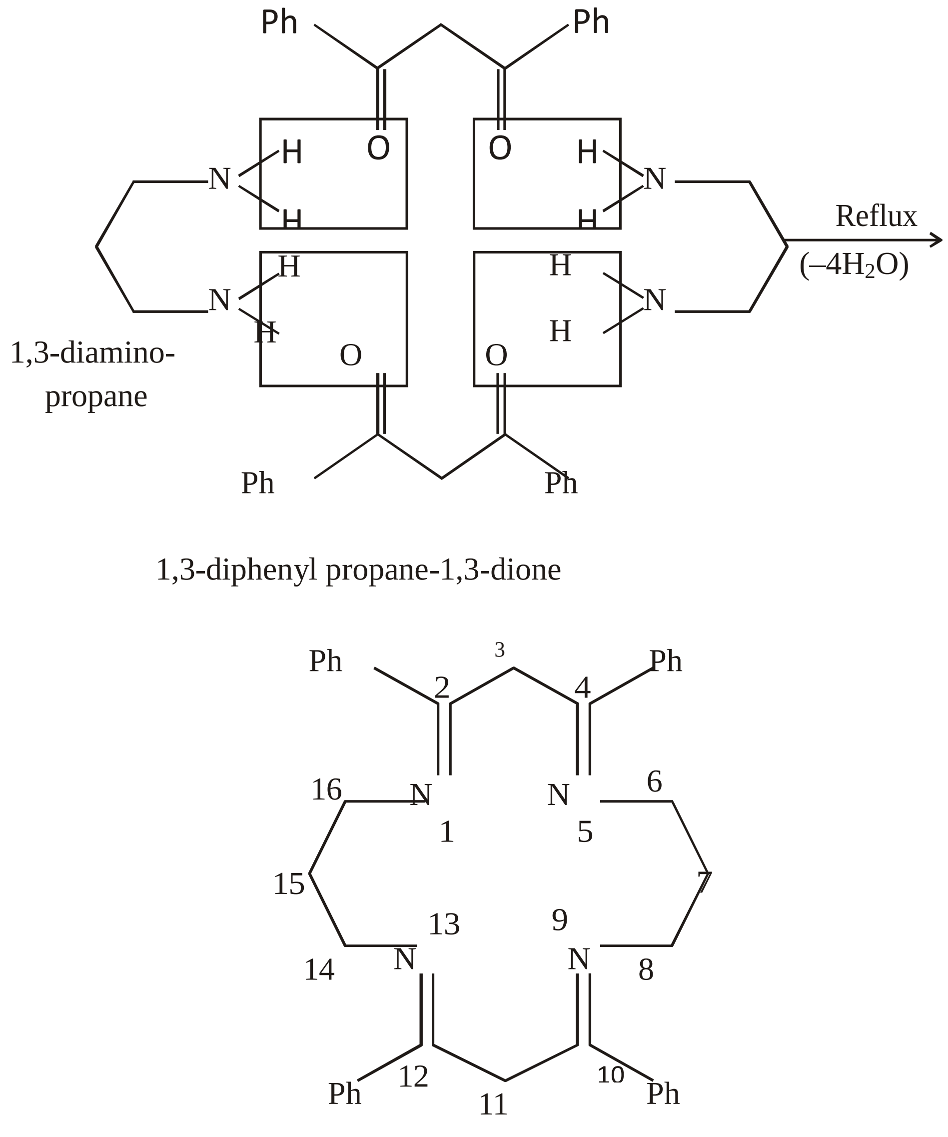


1,5,9,13-tetraaza-2,4,10,12-tetramethyl cyclohexadeca- 1,4,9,12-tetraene(L_2)

(Fig. -2)

(iii) Preparation of 1,5,9,13-tetraaza-2,4,10,12- tetraphenyl cyclohexadeca-1,4,9,12-tetraene (L_3)

0.10 mole of 1,3-diamino propane was dissolved in 50 ml. of methanol and cooled in an ice-bath. A solution of 0.10 mole 1,3-diphenylpropane-1,3-dione in 50 ml..of methanol was prepared and added to the methanolic solution of 1,3-diaminopropane. The mixture was stirred for about 24 hours at 5°C, refluxed for about 8 hours and then concentrated to about 30 ml.. and placed in an ice- bath washed with ice-cold methanol and re-crystallized twice from methanol-watermixture.



1,3-diamino-propane

1,3-diphenyl propane-1,3-dione

1,5,9,13-tetraaza-2,4,10,12-tetraphenyl cyclohexadeca- 1,5,9,12-tetraene(L_3)

Fig. -3

MICROANALYTICAL DATA RELATED TO LIGANDS :

Table-1

Sl. No.	**Ligands**	**% Found (% Calculated)**			**Molecular Formula**	**Colour**
		C	**H**	**N**		
1.	L_1	79.28 (78.00)	7.92 (8.00)	13.84(14.00)	$C_{26}H_{32}N_4$	White
2.	L_2	69.82 (69.56)	10.26 (10.14)	20.29 (20.28)	$C_{16}H_{28}N_4$	Yellowish White
3.	L_3	82.21 (82.44)	6.74 (6.87)	10.53 (10.88)	$C_{36}H_{36}N_4$	White

Microanalytical data of ligands are in confirmity with the molecular formula of corresponding ligands.

PREPARATION OF COORDINATION COMPOUNDS

As the yield of the macrocyclic ligands were very low, their complexes with Ni (II), were prepared by template method.

(i) Preparation of the complex of Ni (II) with 1,5,9,13- tetraaza-2,10-dimethyl-4,12-diphenylcyclohexadeca- 1,4,9,12-tetraene (L_1):

0.10 mole of $NiCl_2.6H_2O$ wasdissolvedin 50 ml.. of water-methanol mixture (1:1 volume ratio). Itwas taken in a round-bottom flask of 500 ml.capacity. To this solution were added 50 ml.methanolic solution of 0.20 mole of 1,3-diaminopropane and 50 ml.methanolic solution of 0.20 mole of 1-phenylbutane-1,3-dione. The mixture was refluxed on a sand-bath using water condenser for about 8 hours and then left for about 24 hours. Green crystals were separated out which were filtered, washed with water and then with methanol. The product was dried in an electric oven at 110°C. The product was insoluble in water, methanol, ethanol, $CHCl_3$ and CCl_4 butitwassolubleinDMFandDMSO.Them.p.ofthe complex was recorded to be 212°C.

(ii) Preparation of the complex of Ni (II) with 1,5,9,13- tetraaza-2,4,10,12-tetramethyl cyclohexadeca-1,4,9,12- tetraene (L_2):

0.10 mole of $NiCl_2.6H_2O$ was dissolved in 50 ml.. of water-methanol mixture (1 : 1 volume ratio). Itwastaken in a round-bottom flask of 500 ml.capacity. To this solution were added 50 ml.methanolic solution of 0.20 mole of 1,3-diaminopropane and 50 ml.methanolic solution of 0.20 mole of pentane-2,4-dione. The mixture was refluxed on a water-bath using water-condenser for about 8 hours and then left for about 24 hours. Green crystals were separated out which were filtered, washed with water and then withmethanol. The product was dried in an electric oven at 110°C. It was insoluble in water and common organic solvents such as methanol, ethanol, benzene, ether, $CHCl_3$ and CCl_4 but wassoluble in DMF and DMSO. The m.p. of the complex wasrecorded to be 204°C.

(iii) Preparation of the complex of Ni (II) with1,5,9,13- tetraaza-2,4,10,12-tetraphenyl cyclohexadeca-1,4,9,12- tetraene (L_3):

0.10 mole of $NiCl_2.6H_2O$ was dissolved in 50 ml. of water-methanol mixture (1:1 volume ratio). Itwastaken in a round-bottom flask of 500 ml.capacity. To this solution were added 50 ml. of methanolic solution of 0.20 mole of 1,3-diaminopropane and 50 ml.methanolic solution of 0.20 mole of 1,3-diphenylpropane-1,3-dione. The mixture was refluxed on a water-bath using a water condenser for about 8 hours. It was then allowed to cool for another 24 hours. Green crystals were separated which were filtered, washed with water and then with methanol. The complex was insoluble in water and common organic solvents suchasbenzene, ether, methanol, ethanol, $CHCl_3$, CCl_4. It was soluble in DMF and DMSO. The complex was dried in an electricfurnace at 110°C and its m.p. was recorded to be 119°C.

Result & Discussions

Spectroscopic Investigations of Complexes

Electronic spectra of complexes of Ni (II):

The free ion ground term of Ni (II) is ^{3}F with ^{3}P as the first excited term. Under the influence of the cubic field, the ^{3}F term splits into $^3T_{1g}$(F), $^3T_{2g}$(F) and $^3A_{2g}$(F) states and the 3Ptermtransforms to $^3T_{1g}$(P) state only. Ni(II) complexes inweakoctahedral field, are expected to give three d-d bands corresponding to the transitions, $^3A_{2g}$(F) □ $^3T_{2g}$(F), $^3A_{2g}$(F)□ $^3T_{1g}$(F) and $^3A_{2g}$(F) □ $^3T_{1g}$ (P). In case of Ni(II)tetrahedralcomplexes, three d-d transition bands are also expectedcorresponding to the transitions $^3T_1$ □ $^3T_2$, $^3T_1$ □ $^3E_2$ and$^3T_1$ □ $^3T_1$ (P). Distorted octahedral complexes of Ni (II) are expected to give four d-d transition bands corresponding to the transitions $^3B_{1g}$ □ ^3E_g, $^3B_{1g}$ □ $^3B_{2g}$, $^3B_{1g}$ □ $^3T_{1g}$(^3E_g.$^3A_{2g}$) and $^3B_{1g}$ □ $^3T_{1g}$(P). Low spin Ni(II) square planarcomplexes should give two d-d transition bands but thereoccur at high energy in the charge transfer region and have not been satisfactorily interpreted. In high spin squareplanarcomplexesofNi(II),twotransitionscorrespondingto$^1A_{1g}$□$^1B_{2g}$ and $^1A_{1g}$ □ ^1E_g are expected.In our present investigation, the electronic spectra of Ni(II) complexes display a broad band in thecharge transfer region indicative of their square planar geometry. The square planar geometry of Ni(II) complexes is furthersupported by their diamagneticnature.

Infrared Spectra of complexes:

Comparision of the infrared spectra of ligands and the complexes reveals following facts :

(i) The appearance of a new band in IR spectraof[NiL$_1$]Cl$_2$, [NiL$_2$]Cl$_2$ and [NiL$_3$]Cl$_2$ at 610 cm^{-1} may be assigned to □$_{\text{Ni–N}}$ mode of vibration[193]. This also supports the coordination of the ligands to Ni(II) through nitrogenatoms.

^{1}H NMR spectra of complexes:

^{1}H NMR spectra of complexes further substantiate the proposed structure of complexes. The ^{1}H NMR spectral data of complexes are given in Table -2.

Table– 2

^{1}H NMR Spectral data of complexes

Sl.No.	**Complex**	**Position of ^{1}H NMR signals Compound**
1.	[NiL$_1$]Cl$_2$	□ = 0.90 ppm (s, 6H), □ = 1.2 ppm (m, 12H), □ = 1.7 ppm (s, 4H), □ = 7.5 ppm (m, 10H)
2.	[NiL$_2$]Cl$_2$	□ = 1.0 ppm (s, 12H), □ = 1.4 ppm (m, 12H), □ = 1.8 ppm(s, 4H)
3.	[NiL$_3$]Cl$_2$	□ = 1.2 ppm (m, 12H), □ = 1.5 ppm (s, 4H), □ = 7.2 ppm (m, 20H)

s = singlet, m =multiplet.

The ^{1}H NMR signals at □ = 0.90 ppm are due to methyl (–CH$_3$) protons. The multiplet bandsat□ =1.2ppmto1.4ppmareduetomethylene(– CH$_2$) protons of –CH$_2$–CH$_2$–CH$_2$– moiety. The singletsignals at □ = 1.5 ppm to 1.8 ppm are due to the allylic protons of methylene(–CH$_2$–)groups.Themultipletsignalscentredat□ = 7.2 ppm to 7.5 ppm are due to the aromatic protons of phenylgroups.

CONCLUSION

Macrocyclic compounds find useful applications:

(i) In removing heavy metals from aqueous solution for waterpurification.

(ii) As molecular switches and linear motors for constructing artificial nanoscale machinery (rotaxanes).

(iii) As chemicalsensors.

(iv) In mimicry ofcellular receptors.

(v) As molecular recognitionagents.

(vi) As recognition agent forpeptides.

(vii) As organic light emittingdiodes.

Keeping in view the wide range ofapplications of macrocyclic compounds and their complexes, we undertook a programme to synthesise and characterize complexes of Ni(II), Pd(II) and Pt(II) with 1,5,9,13-tetraaza-2,10-dimethyl- 4,12-diphenylcyclohexadeca-1,4,9,12-tetraene(L_1),1,5,9,13-tetraaza-2,4,10,12-tetramethylcyclohexadeca-1,4,9,12- tetraene (L_2) and 1,5,9,13-tetraaza-2,4,10,12-tetraphenyl cyclohexadeca-1,4,9,12-tetraene (L_3).

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