International Journal of Advanced Technology in Engineering and Science
Vol. No.5, Issue No. 03, March 2017
www.ijates.com
ijates
ISSN 2348 - 7550

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

*** Kumari Anandi, **Dr. Ravindra Singh**

**Research Scholar Dept. of Chemistry, Jai Prakash University Chapra, Saran Bihar*

***Assiciate Prof. P.G. Dept. of Chemistry, Jai Prakash University Chapra, Saran Bihar*

Abstract

In the present investigationSynthesis and spectroscopic studies of Pd(II) complexes of the tetraaza cyclohexadeca macrocyclicligand. During the experimental workthe preparation of the complex of Pd (II) with1, 5, 9, 13- tetraaza-2, 10-dimethyl-4, 12-diphenylcyclohexadeca- 1,4,9,12-tetraene (L_1), Preparation of the complex of Pd (II) with1,5,9,13- tetraaza-2,4,10,12-tetramethyl cyclohexadeca-1,4,9,12- tetraene (L_2),Preparation of coordination compounds of Pd (II) with 1, 5, 9, 13-tetraaza-2,4,10,12-tetraphenyl cyclohexadeca- 1, 4, 9, 12-tetraene (L_3).During the experiment of Electronic spectra of the complexes of Pd(II) and Infrared Spectra of complexes A new weak band at 345 cm^{-1} is observed in the infrared spectra of $[PdL_1]Cl_2$, $[PdL_2]Cl_2$ and$[PdL_3]Cl_2$ which may be assigned to ν_{Pd-N} mode of vibration.

Keyword :-spectroscopic,tetraaza, Dimethyl,diphenyl, tetramethyl cyclohexadeca tetraene,

Introduction

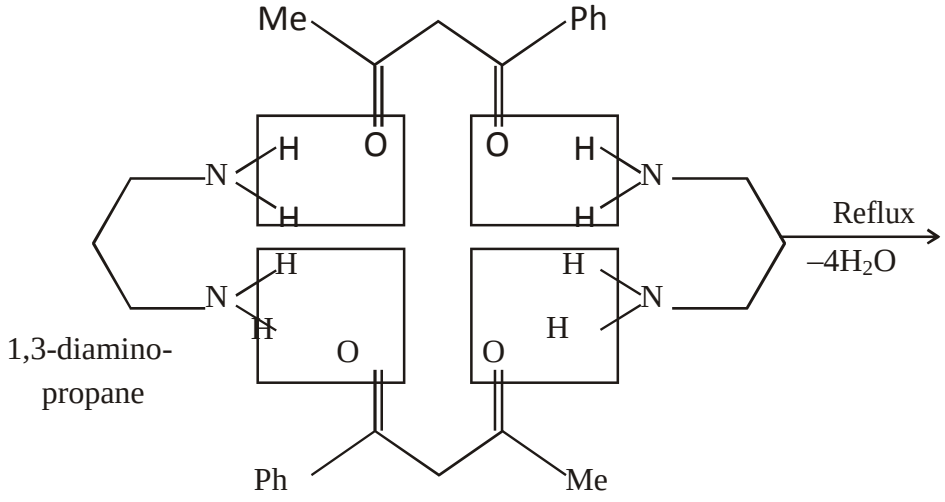
The studies of macrocycles have undergone tremendous growth in past few decades and their complexation chemistry with a wide variety of metal ions has been extensively studied. Macrocyclic compounds are interesting ligand systems as they are good hosts for metal ions, neutral molecules and organic cation 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

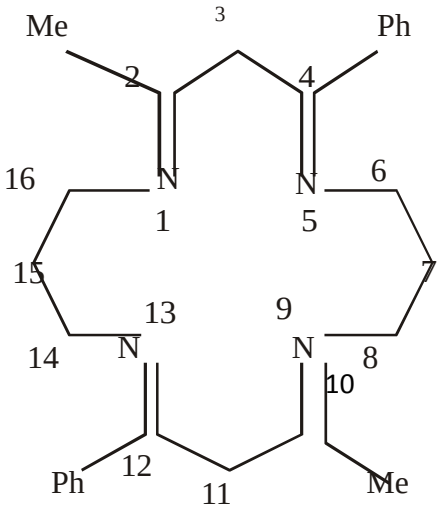
PREPARATION OF LIGANDS

(i) Preparationof 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-Phenylbutane-1,3-dione



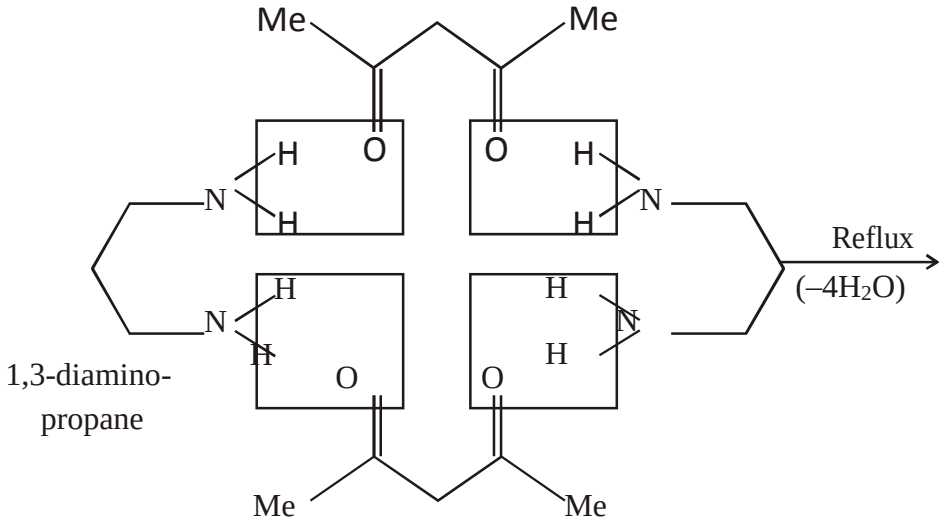
1,5,9,13-tetraaza-2,10-dimethyl-4,12-diphenyl cyclohexadeca-1,4,9,12 tetraene(L_1)

(Fig. -1)

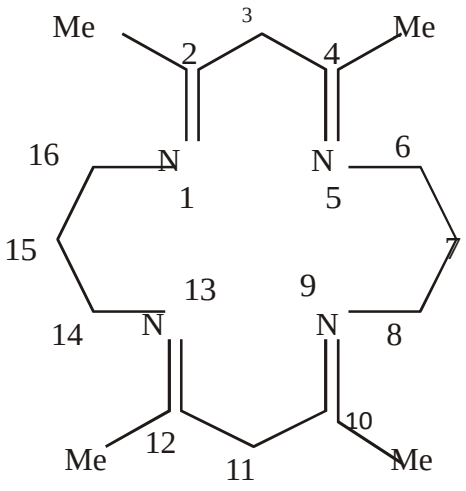
(ii) Preparation of 1,5,9,13-tetraaza-2,4,10,12- tetramethyl cyclohexadeca-1,4,9,12-

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.



Pentane-2,4-dione



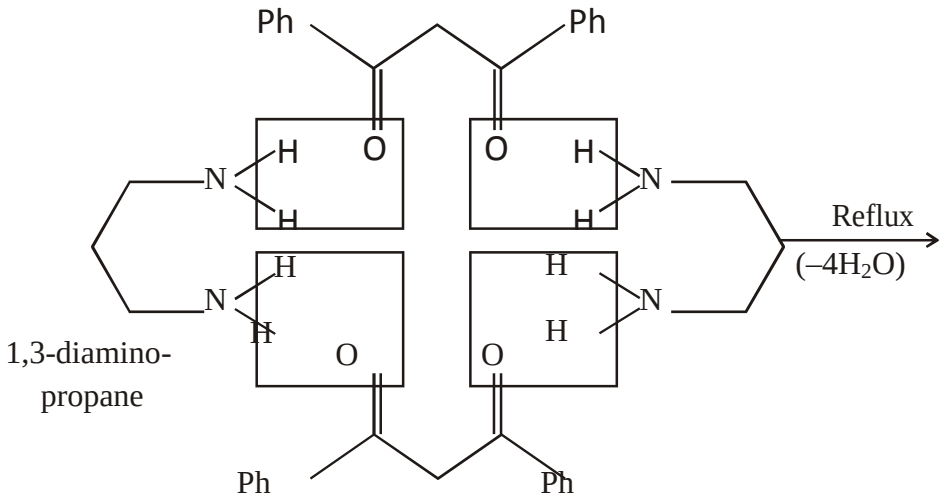
1,5,9,13-tetraaza-2,4,10,12-tetramethyl cyclohexadeca- 1,4,9,12-tetraene(L_2)

(Fig. -2)

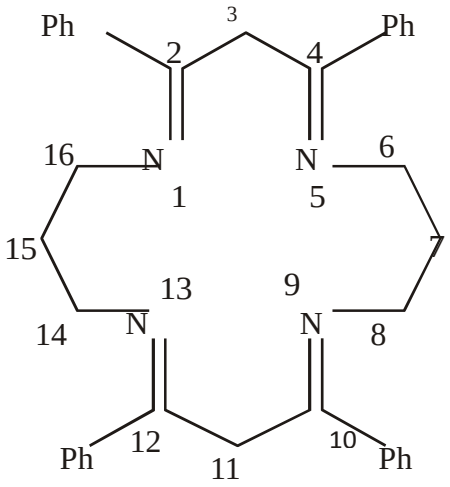
(iii) Preparation of 1,5,9,13-tetraaza-2,4,10,12- tetraphenyl cyclohexadeca-

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 addded 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 recrystallised twice from methanol-watermixture.



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 Pd (II), were prepared by template method.

(I) Preparation of the complex of Pd (II) with1,5,9,13- tetraaza-2,10-dimethyl-4,12-diphenylcyclohexadeca- 1,4,9,12-tetraene (L_1):

0.10 mole of $PdCl_2$ was dissolved in minimumvolumeofethanolandthesolutionwastakeninaround-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 solution was refluxed on a water-bath using a water condenser for about 8hours.

It was then allowed to cool for another 24 hours. Whitecrystals were separated which were filtered, washed with water and then with ethanol and dried in an electric oven at 110°C. Thecomplex was insoluble in water, benzene, CH_3OH, C_2H_5OH, ether, $CHCl_3$ and CCl_4. It was soluble in DMF and DMSO.Itsm.p. was recorded to be 234°C.

(II) Preparation of the complex of Pd (II) with1,5,9,13- tetraaza-2,4,10,12-tetramethyl cyclohexadeca-1,4,9,12- tetraene (L_2):

0.10 mole of $PdCl_2$ was dissolved in

minimumvolumeofethanolandthesolutionwastransferredto a round-bottom flask of 500 mlcapacity. 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 a water condenser for about 8 hours. It was then allowed to cool for about 24 hours. White crystals were separated out which were filtered, washed with water and then with ethanol. It was insoluble in water, benzene,CH_3OH,C_2H_5OH, $CHCl_3$ and CCl_4. It was soluble in DMF andDMSO.

The complex was dried in an electric oven at 110°C anditsm.p. was recorded to be 228°C.

(III) Preparation of coordination compounds of Pd (II) with 1,5,9,13-tetraaza-2,4,10,12-tetraphenyl cyclohexadeca- 1,4,9,12-tetraene (L_3)

0.10 mole of $PdCl_2$ was dissolved in minimumvolumeofethanolandthesolutionwastransferredto 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 1,3-diphenylpropane-1,3-dione. The mixture solution was refluxed on a water-bath using a water condenser for about 8 hours. The content was then allowwed to cool for 24 hours. White crystals were separated out which wre filtered, washed with water and then with ethanol. The complex was insoluble in water, benzene, CH_3OH, C_2H_5OH, $CHCl_3$ and CCl_4butwas soluble in DMF and DMSO. It was dried in an electricoven at 110°C and its m.p. was recorded to be241°C.

Results & Discussion

Spectroscopic investigations of Compleses

Electronic spectra of the complexes of Pd(II)

It is reported that Pd(II) generally coordinates with square planar stereochemistry with ligands and exhibits absorption bands which are due to following d- dtransitions[189].

$^1A_{1g} \rightarrow {}^1B_{1g}(\nu_1)$, $^1A_{1g} \rightarrow {}^1E_{1g}(\nu_2)$, $^1A_{1g} \rightarrow {}^1B_{2g}(\nu_3)$.

The spectra of Pd(II) complexes show the presence of d-d bands in the range 18000-20000 $cm^{-1}(\nu_1)$, 22400-24600 cm^{-1} (ν_2) and 29500-31200 cm^{-1} (ν_3). These bands are in fairly good agreement and suggest thatthecomplexes of Pd(II) have square planar

environment of ligands around Pd(II).This is further supported by the diamagnetic behaviour of Pd(II) complexes.

Infrared Spectra of complexes

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

(i) A new weak band at 345 cm^{-1} is observed in in the infrared spectra of $[PdL_1]Cl_2$, $[PdL_2]Cl_2$ and$[PdL_3]Cl_2$ whichmaybeassignedto ν_{Pd-N} modeofvibration.The appearance of this new band supports the coordinationofligands to Pd(II) through nitrogen atoms.

^{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.

The ^{1}H NMR signals at δ = 1.0 ppm to 1.2 ppmare due to methyl ($-CH_3$) protons. The multiplet bandsat δ =13ppmto1.6ppmareduetomethylene($-CH_2$) protons of $-CH_2-CH_2-CH_2-$ moiety. The singletsignals at δ = 1.3 ppm to 1.8 ppm are due to the allylic protons of methylene($-CH_2-$)groups.Themultipletsignalscentredat δ = 7.3 ppm to 7.4 ppm are due to the aromatic protons of phenylgroups.

Table -2

^{1}H NMR Spectral data of complexes

Sl.No.	Complex	Position of ^{1}H NMR signals Compound
1.	$[PdL_1]Cl_2$	δ = 1.0 ppm (s, 6H), δ = 1.3 ppm (m, 12H), δ = 1.6 ppm (s,4H), δ = 7.4 ppm (m, 10H)
2.	$[PdL_2]Cl_2$	δ = 1.0 ppm (s, 12H), δ = 1.3 ppm (m, 12H), δ = 1.7 ppm(s, 4H)
3.	$[PdL_3]Cl_2$	δ = 1.2 ppm (m, 12H), δ = 1.8 ppm (s, 4H), δ = 7.3 ppm (m, 20H)

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 synthesize 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).

REFERENCES

1. Ashu Chaudhary Singh:- *Rasayan J. Chem., 2 (1), 191 and R. V.S (2009).*

2. B. H.M.Mruthyunjayswamy, B.I. Omkar,Y.Jadegoud.:- *J.Braz.Chem.Soc.,**16**, 783(2005).*

3. B.D.Busch:- *Rec. Chem. Progr.; **25**, 107(1964).*

4. Bartletetal.:- *J. Am. Chem. Soc.;**117**10025 (1995).*

5. C.N.Schrauzer:- *Chem. Ber; **95**, 1438(1962).*

6. D. E. Fenton,H.Okawa:-*Perspectivesof Bioinorganic Chemistry; JAI Press,London, **8** **(**1993)*

7. D. R.Bostonand N. j. Rose:- *Abstracts, 157th National Meetings of the American Chemical Society, Minnepolis, Minn, April 1969, No.INOR-96.*

8. Eugeniusz Kubaszewski, Tadeusz Malinski.:- *J. Heterocyclic Chem., **29**, 1417(1992).*

9. J.Eilmes.:- *Polyhedron., **6**, 943(1985).*

10. K. Shanker, A.M.Reddy, P. Muralidhar,R.Rohini, V.Ravinder.:- *International Journalof Chem Tech Research;**1**777(2009).*

11. L. T. Bozic, E.Marotta, P.Taraldi:-*Polyhedron; **26**,1663 (2007).*

12. L. T. Bozic, E.Marotta, P.Taraldi:-*Polyhedron; **26**,1663(2007).*

13. Levasonetal.:- *Inorg. Chem.; **30**, 331(1991); **34,** 1626(1995)*

14. M. B. Reddy,K.Shanker, P. Usha Rani,R.Rohini, K. Reddy, V.Ravinder:-*J. Indian Chem.Soc., **4**, 971 (2007).*

15. MayurA.Panchbhai, L. J.Paliwaland N. S. Bhave:- *E-Journal of chemistry; **5(S1),** 1048(2008).*

16. P. M. Reddy,A. V. V. S Prasad R. Rohini,V.Ravinder:- *Spectrochim. Acta., **68A**, 1000(2007).*

17. P. M. Reddy,A.V.V.SPrasad, R. Rohini,V.Ravinder:- *Spectrochim. Acta.,**70A**, 704(2008).*

18. P.M. Reddy,A.V.V.SPrasad, V.Ravinder:- *Transition Met. Chem.,**32**, 507(2007).*

19. P.M. Reddy, Y.P. HO, K. Shankar,R.Rohini, V. Ravinder.:- *Eur.J.Med.Chem.;**10**,1(2009).*

20. R. Vaum, N.D.Heindel, H. D. Burns, J.Emrich.:-*J. Pharm. Sci., **71**,122 (1982).*

21. S. Chandra,A.Gautam,M.Tyagi:- *Transition Met. Chem., **32**, 1079(2007).*

22. S. Ilhan,H.Temel.:- *Transition Met. Chem., **32**, 1039(2007).*