

Synthesis and characterization of Tetra dentate N₈-MacrocyclicLigand and its Complexes.

P.Victor Arockiadoss* and Dr.M.Amaladasan

Postgraduate and Research Department of Chemistry,
St.Joseph's college (Autonomous), Tiruchirappalli-620002(T.N) India

*Corres.author: avemaria.p@gmail.com

Abstract: A new series of tetra dentate N₈-Macrocyclic complexes of type [M(ML)] X₂. Where M= Co^{II}. ML = MacrocyclicLigand. It has been prepared from Trimethoprim and Oxalic acid by Template method. X = clo₄⁻. Another type of complex have been formulated as [M(ML) X₂] Where M= Ni^{II}, X = cl, Macrocyclic Ligand is same. The ligand coordinates through all the four azomethine nitrogen's but pyridine nitrogen do not take part in coordination confirmed by absence of (M-py) vibration. These complexes have been characterized with the help of various physic-chemical techniques like IR, Electronic spectra, Molar conductance and magnetic susceptibility. Tetrahedral geometry has been proposed for per chlorate complex. Octahedral geometry has been proposed for chloride complex.

Key words: Synthesis ,characterization ,Tetra dentate N₈-MacrocyclicLigand ,Complexes.

INTRODUCTION

During the last few decades macrocyclic chemistry has attracted the attention of both inorganic and bioinorganic chemists. Macrocyclic metal complexes are of great importance due to their resemblances with many natural systems such as porphyrins and cobalamines and used in DNA recognition oxidation and cleavage¹⁻³. The chemistry macrocycli complexes are also important due to their use as dyes and pigments⁴. From the literature survey, it is found that great deal of interest has been shown in pyrimidine and its derivatives due to their biological importance as constituents of nucleic acids⁵⁻⁷. In the present paper new series of macrocyclic complexes of Co^{II} and Ni^{II} obtained by template condensation reaction of trimethoprim and oxalic acid has been reported.

EXPERIMENTAL

All the reagents used in the preparation of macrocyclic Ligands and their metal complexes were of reagent grade(Merck). The solvents used for the synthesis of macrocyclic ligands and metal complexes were distilled before use. All other chemicals were of AR grade and used without further purification. The electronic spectra (Propanol) were on the Beckman model 25 spectrometer. IR spectra (KBr) on a bruker IFs-60-VFT-IR Spectrometer. The conductivity was measured on a conductivity bridge using dip type platinised platinum electrode. The magnetic moments were measured out using gouy balance. Purity of the compound checked by TLC.

Synthesis of Tetra dentate N₈ – Macrocylic Ligand

Trimethoprim and oxalic acid were condensed to give macrocyclic ligand by the reported method⁸. Trimethoprim (0.01m) was dissolved in 1-Propanol (50 ml) solvent. Oxalic acid (0.01 m) was dissolved in 1-Propanol (50 ml) solvent. Both the solutions taken into round bottom flask. Then add two drops of Con.Hcl. The reaction mixture was allowed to reflux up to six hours at 60°C. It was then concentrated to half of the volume and set aside for two days. The resulting white crystals were washed with 1-propanol and ether then dried. The crude products was recrystallised from 1-propanol. the desired products was obtained.

Synthesis of Tetra dentate N₈ – Macrocylic complexes

A solution of the hydrated metal or per chlorate (0.01m) in 1-propanol (50 ml) was added to a round bottom flask containing solution of the macrocyclic ligand in 1-Propanol (50 ml). the mixture was reflux up to five hours. It was then concentrated to half of the volume and set aside for two days. The microcrystalline compound which separated out was filtered washed with 1-propanol-ether mixture (1:1) and dried in vacuum over anhydrous calcium chloride⁹.

Fig:1 Macrocylic ligand.(R=3,4,5-trimethoxybenzyl.)

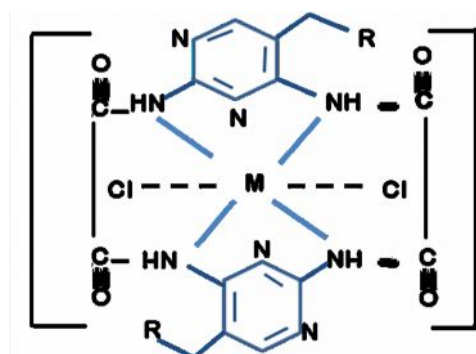
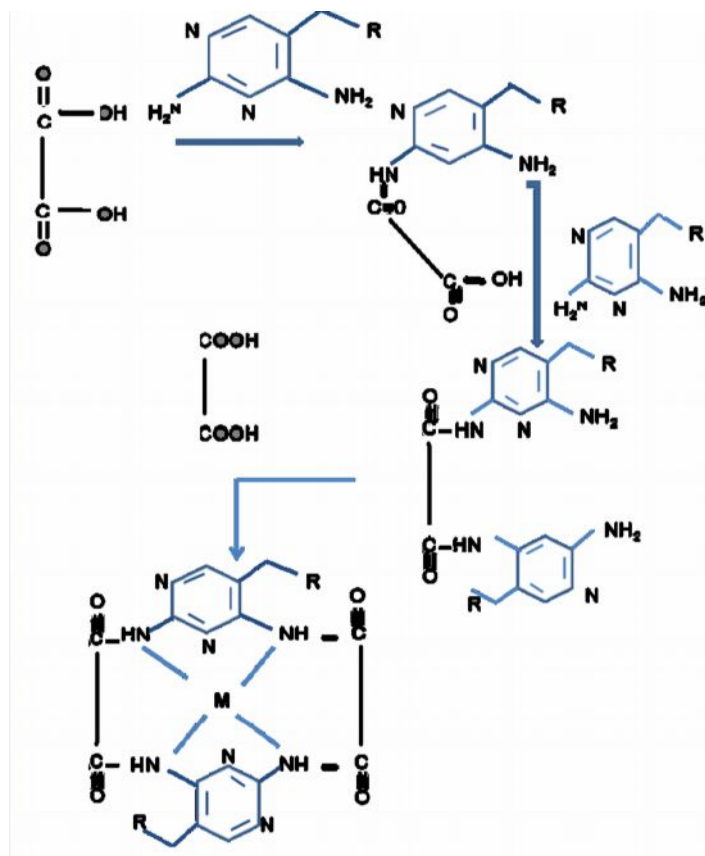


Fig:2 Nickel chloride complex

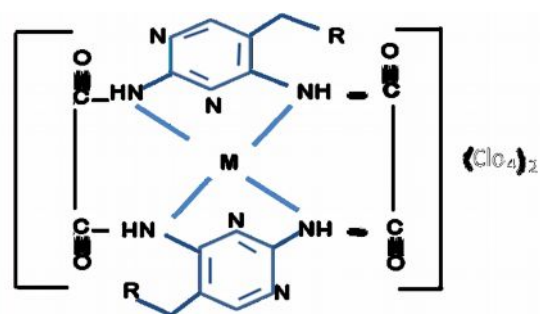


Fig:3 Cobalt per chlorate complex

RESULTS AND DISCUSSION

Nickel chloride complex were light green colour. Cobalt per chlorate complex was pale green blue colour. They were soluble in water acetonitrile ethanol and 1-propanol. They were thermodynamically stable up to 220°C.

Molar conductivities

The electrical conductance of these macrocyclic complexes in acetonitrile were measured and then calculated molar conductance. Molar conductivities of the cobalt per chlorate complex in acetonitrile were in $198 \text{ Ohm}^{-1} \text{ Cm}^2 \text{ mol}^{-1}$ which is characteristics of 1:2 electrolytes, indicating that per chlorate groups are ionic in nature. The conductivity of the Nickel chloride complex are $12.8 \text{ Ohm}^{-1} \text{ Cm}^2 \text{ mol}^{-1}$ suggest that non electrolytes¹⁰.

Magnetic properties

Synthesized macrocyclic cobalt per chlorate complex exhibit magnetic moment was 4.42BM.suggesting tetrahedral environment around cobalt (II) ion. Nickel chloride complex exhibit magnetic moment was 3.31BM.suggesting octahedral environment around nickel (II) ion¹¹.

Electronic spectra

The electronic spectral data of exhibited $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$ transition through a band in the 8500 Cm^{-1} in the visible region is due to which is good agreement with tetrahedral geometry for cobalt per chlorate complex. Nickel chloride complex showed broad band in the 9200 Cm^{-1} due to $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ transition of octahedral geometry¹¹.

IR Spectra

The coordination sites of the ligand have been determined by careful comparisons of the IR Spectra of the complexes with that of the parent macrocyclic ligand. N-H stretching of macrocyclic ligand at 3405 Cm^{-1} which is shifted to 3400 Cm^{-1} for cobalt complex and 3405 Cm^{-1} for nickel complex. N-H def of macrocyclic ligand at 3328 Cm^{-1} which is shifted to 3326 Cm^{-1} for cobalt complex and 3171 Cm^{-1} for nickel complex. C-H stretching of macrocyclic ligand at 2893 Cm^{-1} which is shifted to 2890 Cm^{-1} for cobalt complex

and 2730 Cm^{-1} for nickel complex¹². C-H def of macrocyclic ligand at 1314 Cm^{-1} which is shifted to 1125 Cm^{-1} for cobalt complex and 1238 Cm^{-1} for nickel complex. C-N stretching of macrocyclic ligand at 1598 Cm^{-1} which is shifted to 1421 Cm^{-1} for cobalt complex and 1425 Cm^{-1} for nickel complex. C-C stretching of macrocyclic ligand at 774 Cm^{-1} which is shifted to 995 Cm^{-1} for cobalt complex and 981 Cm^{-1} for nickel complex. Stretching and bending vibration of the C=O group of carboxylic acid were observed 1667 Cm^{-1} and 910 Cm^{-1} are not shifted. This clearly indicated that C=O group not take part in the coordination. There are fairly strong IR spectral bands in the region 3175 to 2635 Cm^{-1} due to the C-H and C-C-C stretching of the Pyrimidine ring, benzyl aromatic ring and methoxy groups also appear in the spectra of the complexes in the same region indicates that they do not take part in coordination. The appearance of a new moderately intense band in 515 Cm^{-1} that is assignable to stretching of M-N. It confirms the involvement of nitrogen in coordination. The M-cl vibrations were identified through the bands appeared in 380 Cm^{-1} for nickel chloride complex that were involved in chloride coordination that confirms octahedral geometry¹³. In the per chlorate complex a broad band of strong intensity is observed 1125 Cm^{-1} which is characteristics of uncoordinated per chlorate ion and confirms its presence in the outer sphere of the complex ion.

CONCLUSION

Based on the various physiochemical studies such as conductivity, magnetic susceptibility, electronic and IR spectral studies octahedral geometry may be proposed for chloride complex and tetrahedral geometry may be proposed for per chlorate complex.

ACKNOWLEDGEMENT

I have great pleasure in expressing my deep sense of gratitude to Dr.M.Amaladasan, Associate Professor, Department of chemistry, St.Joseph's college(Autonomous), Trichy-2 for having motivated and supervised me into this work .I extended my sincere thanks to authorities of St.Joseph's college(Autonomous), Trichy-2 for the facility and support .

REFERENCES

1. L. F. Lindoy, Ed., The Chemistry of Macrocyclic Ligand Complexes, L. F. Lindoy, Ed., Cambridge University Press, Cambridge, UK, 1989.
2. E. C. Constable, Ed., Coordination Chemistry of Macrocyclic Compounds, E. C. Constable, Ed., Oxford University Press, Oxford, UK, 1999.
3. K. Gloe, Ed., Springer Current Trends and Future Perspectives, , New York, NY, USA, 2005.
4. D.P.Singh, Ramesh kumar "one pot template synthesis and characterization of trivalent transition metal complex derived from di amino pyridine and glyoxal, Rasayan journal of chemistry Vol.1 No.2(2008) 349-354.
5. Amaladasan.M studies on the interaction of Mn (II), Co(II), Ni(II), Cu(II) and Zn with tetradentate- N_8 macrocycles. Ph.D Thesis(1998).
6. Dharam pal singh, vanda malik and Ramesh kumar (2009) Synthesis and characterization of 10 membered tetraaza macrocyclic complexes of Cr(III), Mn(III), and Fe(III). Research letter in inorganic chemistry.
7. Dr.M.Amaladasan and P.Victor Arockiadoss "Synthesis and Characterization of Copper(II) and Nickel (II) Complexes of 14-Membered Tetradentate Macrocyclic ligand " Retail
8. Amaladasan.M "synthesis of N_8 macrocyclic ligands by poly phosphoric acid-catalysed condensation of trimethoprim and amino acids. Indian journal of chemistry section –B 1998.
9. Dr.M.Amaladasan , Prasanna devi and Mr.P.Victor Arockiadoss Synthesis and Characterization of 20-Membered N_6 macrocyclic ligand. Retail.
10. L. K. Gupta and S. Chandra, "Physicochemical and biological characterization of transition metal complexes with a nitrogen donor tetradentate novel macrocyclic ligand," Transition Metal Chemistry, vol. 31, no. 3, pp. 368–373, 2006.
11. Lodeiro, R. Bastida, E. Bértolo, A. Macías, and A. Rodríguez, "Synthesis and characterisation of four novel N_xO_y -Schiff-base macrocyclic ligands and their metal complexes," Transition Metal Chemistry, vol. 28, no. 4, pp. 388–394, 2003.
12. L. Pavia, G. M. Lampman, and G. S. Kriz, Introduction to Spectroscopy, Harcourt College Publishers, New York, NY, USA, 2001.
13. K. Mohamed, K. S. Islam, S. S. Hasan, and M. Shakir, "Metal ion directed synthesis of 14–16 membered tetraamine macrocyclic complexes," Transition Metal Chemistry, vol. 24, no. 2, pp. 198–201, 1999.
