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Synthesis and characterization of 18-membered tetraaza macrocyclic ligand and it complexes of Mn^{II} , Co^{II} , Ni^{II} and Cu^{II}.

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Abstract: A new series of tetra dentate N_6-Macrocyclic complexes of type [M(ML) X_2].Where M= Mn^{II} ,Co^{II} , Ni^{II} and Cu^{II} .ML = MacrocyclicLigand. It has been prepared from Trimethoprim and Phthalic acid by Template method. X =cl. 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 Spectra, Electronic spectra, Molar conductance, and magnetic susceptibility. Octahedral geometry has been proposed for all the complexes.

Key words: Synthesis ,characterization, 18- membered tetraaza macrocyclic ligand ,complexes of Mn^{II} , Co^{II} , Ni^{II} and Cu^{II}.

Introduction

Coordination Chemistry of macrocyclic ligand has been a fascinating area of current research in inorganic chemistry all over the world due to its wider applications and the unusual binding abilities.the award of 1987 Nobel prize in chemistry to Pederson,Lehn and Cram is a testimony to the importance of this field[1-3]. Synthesis and characterization of macro cyclic ligand has been very important area of current research in coordination chemistry at all over the world due to it's wider application in all the field, particularly antibiotic, transport of ion and unusual binding properties.[4] In the present article new series of macrocyclic complexes can be prepared by the interaction of synthesized macrocyclic ligand with some metal chlorides like Mn^{II} ,Co^{II} , Ni^{II} and Cu^{II} .

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. IR spectra (KBr) on a bruker IFs-60-VFT-IR Spectrometer.. The electronic spectra (Ethanol) were on the Beckman model 25 spectrometer.The magnetic moments were measured out using gouy balance. The conductivity was measured on a conductivity bridge using dip type platinised platinum electrode Purity of the compound checked by TLC.

Synthesis of Tetra dentate N_8 – Macrocyclic Ligand

Trimethoprim and Phthalic acid were condensed to give macrocyclic ligand by the reported method[5-7]. Trimethoprim (0.01m) was dissolved in Ethanol(50 ml) solvent. Phthalic acid (0.01 m) was dissolved in Ethanol (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 60^0C.It was then concentrated to half of the volume and set aside for two days. The resulting white crystals were washed with Ethanol and ether then dried. The crude products was recrystalised from Ethanol .the desired products was obtained.

Synthesis of Tetra dentate N_8 – Macrocyclic complexes

A solution of the hydrated metal chloride (0.01m) in Ethanol (50 ml) was added to a round bottom flask containing (0.01) solution of the macrocyclic ligand in Ethanol (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 Ethanol-ether mixture (1:1) and dried in vacuum over anhydrous calcium chloride[8-10].

Fig:1 Macrocyclic ligand, R=3,4,5-trimethoxybenzyl.

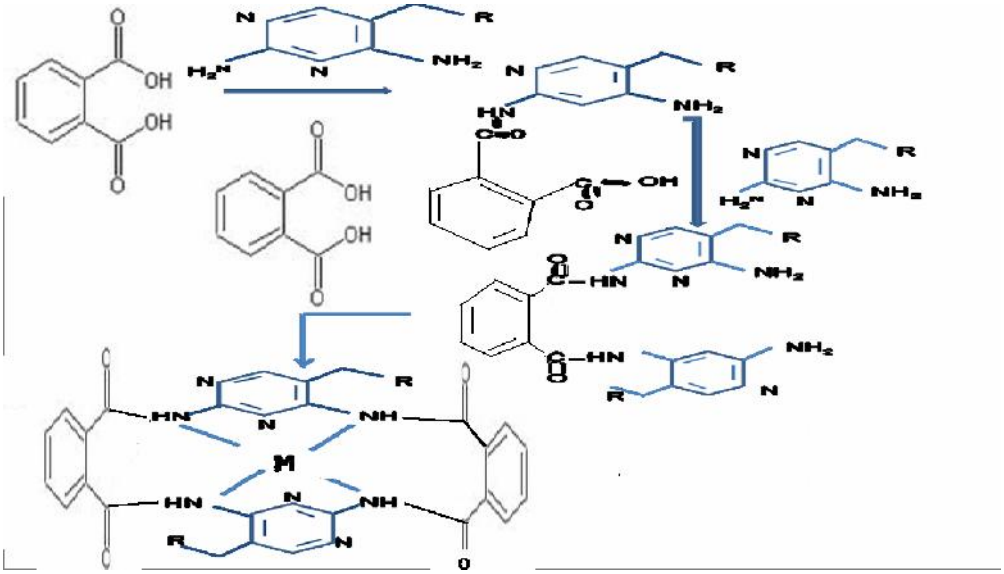
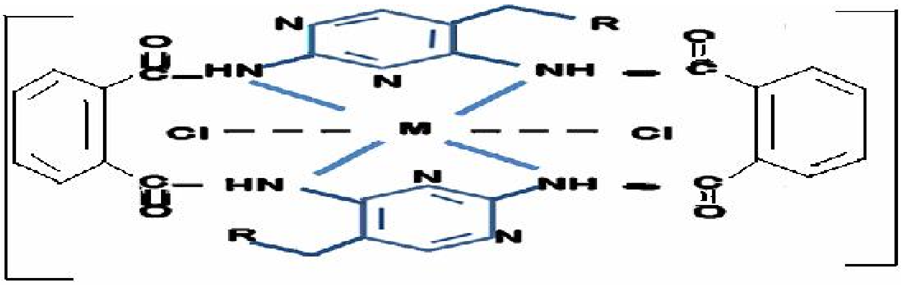


Fig:2 Macrocyclic complexes



Results and Discussion

All the complexes were soluble in water, acetonitrile, ethanol and 1-propanol. They were thermodynamically stable up to 220^0C.

Molar conductivities

The molar conductance of these macrocyclic complexes in acetonitrile were measured and then calculated molar conductance value are reported in Table-1.The conductivities of the complexes were in the range of 10 – 30 Ohm^{-1} Cm^2 mol^{-1} [11]. Which is characteristics of 1:0 electrolytes, suggest that all of them are non –electrolytes. The presence of chloride ions is evident only after decomposition of the complexes, probably due to their presence in the coordination sphere. Based on the conductance, metal chloride complexes are assigned the structure [M (ML) cl2].ML-Macrocyclic ligand. M-Metal.

Magnetic moments

The magnetic moments of the complexes showed that they are all high spin type. The magnetic moment of the complexes are given in Table-1.the metal chloride complexes have magnetic moments, which suggest octahedral configuration around metal ions. Mn^{II} complex has magnetic moment 5.60 B.M. Mn^{II} high spin complexes show in general magnetic moment very close to the spin only value of 5.92 B.M. suggest octahedral geometry. The prepared cobalt complex has magnetic moment of 4.1 B.M. this value is very close to the spin only value of 3.88 B.M for octahedral complexes. The magnetic moment of octahedral Ni^{II} complexes are between2.9 – 3.4 B.M. the synthesized Ni^{II} complexe exhibit magnetic moment of 2.86 B.M suggest distorted octahedral geometry. The magnetic moment of Cu^{II} complex was lower than the spin only value of 1.73 B.M. which may be due to distortion. The macrocyclic→ complex of Cu^{II} exhibit magnetic moment 1.40 B.M supported that the distorted octahedral geometry[12].

Electronic spectra

Mn^{II} complex exhibits two to three very weak bands at 16,000 Cm^{-1}, 21,000 Cm^{-1} and 26,600 Cm^{-1} which are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ transition respectively. These observations reveal that the stereochemistry of this complex is consistent with the six coordinated octahedral geometry. The electronic spectral of Co^{II} complexes consist in general of three spin-allowed transition, although it will not always be possible to observe all the three bands. In the electronic spectra of high spin octahedral complexes of Co^{II} .one should expect three bands corresponding to the transitions.$^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{2g*}$ and $^4T_{1g} \rightarrow {}^4T_{1g(p)}$.once the Co^{II} complex display a very broad band at 22,380 Cm^{-1} which is assigned to $^4T_{1g} \rightarrow {}^4T_{1g(p)}$ transition of distorted octahedral geometry. Ni^{II} complex one should expect three bands corresponding to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ AT 10,000 Cm^{-1},14,000-18,000 Cm^{-1} and 25,000-30,000 Cm^{-1} respectively. The Ni^{II} complex display a band at 24,400 Cm^{-1} which is due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, suggesting octahedral geometry. In most of the Cu^{II} complexes bands in region 12,000-16,000 Cm^{-1}.The synthesized macrocyclic complex of Cu^{II} displays a band at 13,100 Cm^{-1} due to $^2E_g \rightarrow {}^2T_{2g}$ transition, characteristics of octahedral geometry[13].

Table-1.Colur,Conductance,magneticmoments and electronic spectra of the macrocyclic complexes.

Sl. no	Complexes	Colour	Molar conductance Ohm^{-1} Cm^2 mol^{-1}	Magnetic moments (B.M)	Electronic spectra		Stereo chemistry
					Energy Cm^{-1}	Assignment	
1	[Mn(ML)cl2]	Pink	24.14	5.60	26,600	$^6A_{1g} \rightarrow {}^4T_{2g}$(D	Octahedral
2	[Co(ML)cl2]	Purple	37.25	4.10	22,330	$^4T_{1g} \rightarrow {}^4T_{1g(p)}$	Octahedral
3	[Ni(ML)cl2]	LightGreen	21.88	2.86	23,540	$^3A_{2g} \rightarrow {}^3T_{1g(p}$	Octahedral
4	[Cu(ML)cl2]	Green	11.03	1.40	13,700	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral

IR Spectra

The Infra Red spectra of the macrocyclic complexes are very useful in determining the coordination groups of the ligand.the shifts in the peaks indicate the mode of linkage in the complexes.comparision of the IR spectra of macrocyclic ligand and the complexes confirmed the formation of the complexes. Spectra indicated that trimethoprim and phthalic acid moieties are present. Very strong bands appearing in the region 3443-3306 Cm^{-1} may be assigned to secondary amino group.. N-H stretching of macrocyclic ligand at 3324 Cm^{-1} which is shifted to 3330 $Cm^{-1}$for manganese, 3400 $Cm^{-1}$for nickel complex and 3405 Cm^{-1} for copper complex. N-H def of macrocyclic ligand at 3167 Cm^{-1} which is shifted to 3170 $Cm^{-1}$for manganese complex and 3171 Cm^{-1} for cobalt complex, 3154 Cm^{-1} for nickel complex and 3180 Cm^{-1} for copper complex. C-H stretching of macrocyclic ligand at 2727 Cm^{-1} which is shifted to 2890 $Cm^{-1}$for manganese complex and 2730 Cm^{-1} for cobalt complex, 2755 Cm^{-1} for nickel complex, 2742 Cm^{-1} for copper complex. C-H def of macrocyclic ligand at 1226 Cm^{-1} which is shifted to 12450 $Cm^{-1}$for manganese complex ,1230 $Cm^{-1}$for cobalt complex,1238 Cm^{-1} for nickel complex and 1230 $Cm^{-1}$for copper complex. C-N stretching of macrocyclic ligand at 1662 Cm^{-1} which is shifted to 1589 $Cm^{-1}$for manganese complex. 1689 $Cm^{-1}$for cobalt complex ,1425 Cm^{-1} for nickel complex and 1668 $Cm^{-1}$for copper complex. C-C stretching of macrocyclic ligand at766 Cm^{-1} which is shifted to 780 $Cm^{-1}$for manganese complex. 793 $Cm^{-1}$for cobalt complex, 800 Cm^{-1} for nickel complex and 743 $Cm^{-1}$for copper complex. . It indicates that all the four secondary amino group are coordinated to metal ion the slight upward shift of carbonyl frequency of of amide group from 1662 to 1635 Cm^{-1} supports the coordination through only secondary amino groups not through carbonyl group[14]. 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. Pyridine nitrogen is not involved in coordination because the lone pair of electron are engaged for resonance. The ring of flipping enhances the steric hindrance which prevents the carbonyl from coordination. At the same time amidic nitrogen with the lone pair is more readily available for coordination, thus only four secondary amino groups are involved in coordination. The appearance of a new moderately intense band in the region 495-485 Cm^{-1} assignable to stretching of (M-N) further confirms the involvement of nitrogen in coordination. It confirms the involvement of nitrogen in coordination. spectral data reveals bands at 481-429 Cm^{-1} which may be assigned Mn-cl, Co-cl, Ni-cl andCu-cl coordination[15].

Conclusion

Conductivity measurement indicates that the metal complexes are non-electrolytes in nature. The magnetic moments of all the complexes reveal that they are all of high spin type with paramagnetic nature. Electronic spectra data support that all the metal complexes have octahedral. The IR spectra data reveal that the macrocyclic ligand coordinated through four amino nitrogen of the macrocyclic ring and there is no indication of pyrimidine nitrogen in coordination. Based on the various physiochemical studies such as conductivity, magnetic susceptibility, electronic and IR spectral studies octahedral geometry may be proposed for all the complexes.

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