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Research Article

SYNTHESIS AND CHARACTERIZATION OF MACROCYCLIC COMPLEXES OF Mn^{II}, Co^{II}, AND Cu^{II}.

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Abstract

A new series of tetra dentate N₆-Macrocyclic complexes of type [M(ML) X₂], Where M = Mn^{II}, Co^{II}, and Cu^{II}. ML = Macrocyclic Ligand, X = Cl₂ and SO₄. It has been prepared from Trimethoprim and L-Alanine by Template method. The ligand coordinates through the macrocyclic ring imine and amine nitrogen atoms. These complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility measurements and the spectral studies like IR Spectra, Electronic spectra and NMR spectra. The spectral data suggest that the complexes of metal chlorides have octahedral geometry and that of metal sulphates have tetrahedral geometry.

Keywords: Synthesis, Characterization, 12- membered tetradentate macrocyclic ligand , complexes of Mn^{II} , Co^{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 field¹⁻⁴. In this work, incorporation of pyrimidine moiety into the macrocyclic frame work is found to enhance the rigidity and binding ability of the ligands towards the transition metal ions⁵. The present work also deals with the interaction of Mn^{II}, Co^{II} and Cu^{II} metal ions with the ligand⁶. The study of stereochemistry and chemical reactivity of the Coordination compounds of the macrocycles will help us to understand the relationship between chemical structure and biological activity of macrocycle.

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 were recorded (KBr) on a Bruker IFs-60-VFT-IR Spectrometer. The electronic spectra (methanol) 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 platinumised platinum electrode.

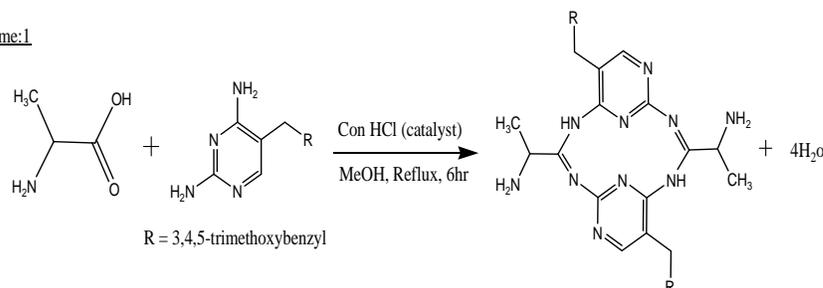
Synthesis of Tetra dentate N₆ – Macrocylic Ligand

Trimethoprim and L-Alanine were condensed to give macrocyclic ligand by the reported method⁷. Trimethoprim (0.01 M) was dissolved in methanol (50 ml) solvent. L-Alanine (0.01 M) was dissolved in methanol (50 ml) solvent. Both the solutions are 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 methanol and ether then dried. The crude recrystallised from methanol.

Synthesis of Tetra dentate N₆ – Macrocylic complexes

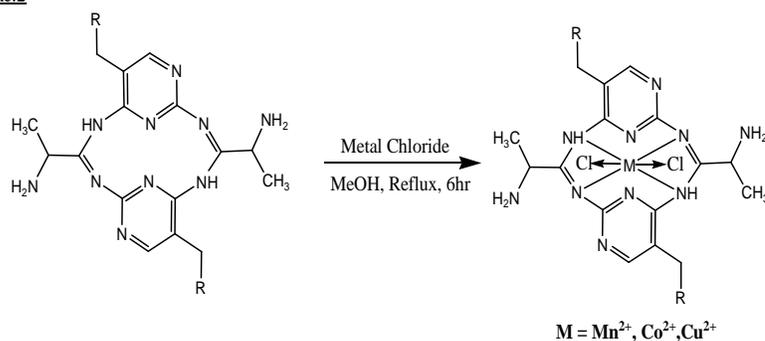
A solution of the hydrated metal chloride and metal sulphate (0.01 M) in methanol (50 ml) was added to a round bottom flask containing (0.01 M) solution of the macrocyclic ligand in methanol (50 ml) the mixture was reflux up to 6 hours. It was then concentrated to half of the volume and set aside for two days. The microcrystalline compound which separated out was filtered washed with methanol-ether mixture (1:1) and dried in vacuum over anhydrous calcium chloride⁸⁻¹⁰

Scheme:1



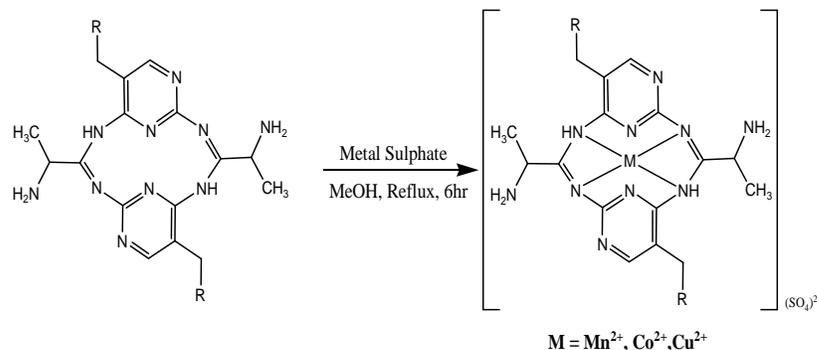
Scheme:1. Synthesis of ligand

Scheme:2



Scheme:2. Synthesis of Metal complex with Chloride

Scheme:3



Scheme:3. Synthesis of Metal complex with Sulphate

Results and Discussion

All the complexes were soluble in water, acetonitrile, ethanol and DMSO. They were thermodynamically stable up to 220 °C. From the analytical data (Table 1)

the complexes can be represented $[M(C_{34}H_{42}N_{10}O_6)Cl_2]$ and $[M(C_{34}H_{42}N_{10}O_6)SO_4]$ Where $M = Mn^{II}, Co^{II}, Cu^{II}$. The molecular mass and the analytical results were in good agreement with the proposed compositions of the complexes.

Table-1. Colour, Conductance, Magnetic moment and analytical data of the complexes of Ligand

S. No	Ligand/Complexes	Colour	Molar Conductance $Ohm^{-1} Cm^2 mol^{-1}$	Magnetic Moments (B.M)	Analysis %Found (Calculated)				
					C	H	N	M	x
1	$L2(C_{34}H_{42}N_{10}O_6)$	Pale brown			59.42 (59.46)	6.34 (6.16)	20.28 (20.39)	–	–
2	$[Mn(L2)Cl_2]$	Pale brown	4.50	6.10	50.30 (50.26)	5.24 (5.21)	17.26 (17.24)	6.78 (6.76)	8.73 (8.72)
3	$[Mn(L2)SO_4]_2$	white	85.20	5.73	48.76 (48.74)	5.06 (5.05)	16.74 (16.72)	6.57 (6.56)	3.86 (3.83)
4	$[Co(L2)Cl_2]$	pink	60.00	4.7	50.05 (50.01)	5.18 (5.19)	17.14 (17.16)	7.26 (7.22)	8.69 (8.67)
5	$[Co(L2)SO_4]_2$	Light violet	97.30	3.98	48.54 (48.51)	4.99 (5.03)	16.67 (16.64)	7.02 (7.00)	3.83 (3.81)
6	$[Cu(L2)Cl_2]$	green	46.70	1.56	49.67 (49.72)	5.12 (5.16)	17.06 (17.06)	7.76 (7.74)	8.55 (8.62)
7	$[Cu(L2)SO_4]_2$	Pistha green	112.00	1.86	48.30 (48.25)	4.97 (5.00)	6.57 (6.55)	7.56 (7.51)	3.84 (3.79)

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 12 – 48 $ohm^{-1} cm^2 mol^{-1}$ and 80-120 $ohm^{-1} cm^2 mol^{-1}$ which is characteristics of 1:0 electrolytes¹¹; suggest that all of them are non-electrolytes. The presence of chloride ions & sulphate 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 $[M(ML)cl_2]$, $[M(ML)So_4]$, 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 is given in Table 1. the metal chloride & sulphate complexes have magnetic moments, which suggest octahedral and tetrahedral configuration around metal ions. Manganese(II)chloride complex has magnetic moment 6.1 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. Manganese(II)sulphate are 5.73 BM respectively suggesting tetrahedral coordination

for the metal ion. The prepared cobalt(II)chloride complex has magnetic moment of 4.7 B.M. This value is very close to the spin only value of 3.25 B.M for octahedral complexes. Cobalt(II)sulphate it is higher than the spin only value of 3.98 B.M which indicates the tetrahedral geometry. The magnetic moment of Cu(II)chloride complex was lower than the spin only value of 1.56 B.M. which may be due to distortion. The macrocyclic complex of Cu(II)chloride exhibit magnetic moment 1.40 B.M supported that the distorted octahedral geometry¹². The Cu(II)sulphate complex with the magnetic moment 1.86 B.M indicated the presence one paramagnetic electron and tetrahedral geometry.

Electronic spectra

The electronic spectra of the Mn^{II} complex exhibits two to three bands at 51,546 cm^{-1} , 47,169 cm^{-1} and 37,068 cm^{-1} which are assigned to ${}^6A_{1g}$ ${}^4T_{1g}(G)$, ${}^6A_{1g}$ ${}^4T_{2g}(G)$ and ${}^6A_{1g}$ ${}^4T_{2g}(D)$ 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. ${}^4T_{1g}(F)$ ${}^4T_{2g}(P)$, ${}^4T_{1g}(F)$ ${}^4T_{2g}(F)$ and

${}^4T_{1g}(F)$ ${}^4A_{2g}(F)$. Once the Co(II)chloride complex display a very broad band at $19,379\text{ cm}^{-1}$ which is assigned to ${}^4T_{1g}(F)$ ${}^4T_{1g}(P)$ transition of distorted octahedral geometry. The Co(II)sulphate complex and gave a bands $19,379\text{ cm}^{-1}$, $10,142\text{ cm}^{-1}$ it was for the ${}^4T_{1g}(F)$ ${}^4A_{2g}(F)$ transition of tetrahedral geometry. The electronic spectra of these complexes display bands corresponding to the transitions ${}^2B_{1g}$ ${}^2A_{1g}$, ${}^2B_{1g}$ ${}^2B_{2g}$, ${}^2B_{1g}$ 2E_g . Copper(II)chloride complex displays a band at $11,560\text{ cm}^{-1}$ due to 2E_g ${}^2T_{2g}$ transition, characteristics of octahedral geometry¹³. The copper(II)sulphate complex was observed to show a stronger charge transfer transition than the d-d transition.

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. Comparison of the IR spectra of macrocyclic ligand and the complexes confirmed the formation of the complexes. Spectra indicated that trimethoprim and L-Alanine moieties are present. The stretching and bending vibrations of the –NH₂ group of amino acid were observed at 3506 and 850 cm^{-1} respectively in the IR spectrum of the free macrocyclic ligand as well as in the macrocyclic complexes of Mn^{II}, Co^{II}, Cu^{II} chlorides and sulphates. This clearly indicated that the amino group did not take part in coordination. The bands at 3328 and 1240 cm^{-1} observed for the N-H and C= N vibrations for free ligand were found to have a negative shift of $40-70\text{ cm}^{-1}$ and $20-30\text{ cm}^{-1}$ ¹⁴⁻¹⁸ respectively in all the complexes of Mn^{II}, Co^{II}, Cu^{II}. The band $519-489\text{ cm}^{-1}$ was assigned to M-N stretching in the complexes as there was coordination through nitrogen. The M-Cl vibration was identified through the bands appear around $380-320\text{ cm}^{-1}$ for those complexes that were involved in the chloride coordination¹⁹. In the sulphate complexes a very strong and broad band appeared near 1100 cm^{-1} which was indicative of the non-coordinating sulphate species²⁰. The bands at 615 and 762 cm^{-1} were assigned to the in-plane and out-of – plane bending motions of aromatic ring indicating the non-coordination of the nitrogens in the pyrimidine ring. Thus, it might be quadridentate and macrocyclic compound the macrocyclic ring not involving the nitrogen atoms of the pyrimidine. It was in accordance with the fact that quadridentate macrocycles could be formed more readily than the hexa- or quinquidentate ligands²¹. It was very interesting to note that the imine and amine nitrogens were equally active and excluded the weak and less stable coordination by the pyrimidine nitrogen²².

¹H NMR Spectra

The proton magnetic resonance spectrum of the macrocycle ligand was taken in DMSO solvent. The spectrum shows eight different types of protons since signals are observed at eight different regions from the TMS (Internal standard). The intensities of the peaks are in the ratio 1:2:3:9:1:2:1:2 ¹H NMR spectrum of the macrocyclic ligand (L2) display peaks at 6.8 (2H, S, ring NH); 1.1 (4H, S, free NH₂); 1.2-1.4 (6H, d, C-CH₃); 3.7 (18H, S, O - CH₃); 6-6.5 (2H, q, -CH); 6.0 (4H, S, pyrimidine- CH₂ -Ar); 8.7 (2H, S, pyrimidine - H) and 8.9 (4H, d, Ar - H). Thus the ¹H NMR spectrum confirms the presence of trimethoprim and L-alanine moieties in the macrocycle L2. The ¹H NMR spectrum of macrocycle L2 do not show any signal corresponding to amino acid protons suggesting that the proposed macrocyclic skeleton has been formed through condensation reaction. From the ratio of the intensities of the peak the number of protons can be calculated as 42.

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