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Microwave Assisted Synthesis and Characterisation of Cobalt (III) complexes with Macrocyclic ligands

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Abstract- **Cobalt has been chosen as central metal ion because of its ability to form stable complexes in an octahedral environment. Macrocyclic ligand 3, 8–Dimethyl- 4, 7–diazodeca –3, 7- diene-2, 9-dione dioximate has been synthesised by the condensation of 1, 2- Diamino ethane and 2, 3 – Butanedionemonooxime in 1:2 molar ratio. The ligand and parent cobalt (III) dioxime have been characterised by elemental analysis, electronic and IR spectral data. Macrocyclic ligands are receiving considerable attention as they are proved to be superior sequestering agents for various radio nuclides of interest for radio pharmaceutical purposes.**

Keywords: Macrocyclic ligands, Dimethyl glyoxime, Cobalt (III) dioximes, Electronic Spectroscopy, IR spectroscopy.

INTRODUCTION

A macrocyclic ligand is a cyclic compound with nine or more members including all the hetero atoms and with three or more donor atoms. The donor atoms are usually positioned so that upon coordination preferably five or six membered chelate rings are formed with the metal ion1. Based on donor atom type , macrocyclic ligands can be classified as crown ethers (oxygen donor atoms), polyazamacrocycles or azacrown ethers (nitrogen donor atoms), macrocycles containing sulphur, phosphorous, arsenic atoms and macrocyclic ligands with mixed donor atoms (polyzapolyoxamacrocycles). Macrocycles with pendant functional groups include polyazamacrocycles that have coordinating side arms attached to the nitrogen. These ligands are capable of axial metal ion coordination. Chelation will be more efficient because the donor atoms are held near to the central metal ion. The development of bi functional chelating agents to sequester metal ions when conjugated to monoclonal antibodies (mAbs) or other biological molecules for targeted radiotherapy and diagnostic applications remains an active area of endeavour.

Cobalt is a chemical element with symbol Co and atomic number 27. It is essential to the metabolism of all animals. It is a key substituent of cobalamin. Cobalt(III) compounds containing direct Co-C bond that occupies an axial coordination position about a coronoid ring system2. Naturally occurring macrocyclic ligand transition metal complexes such as complexes of the porphyrin or corrin ring systems and the metal phtahlocyanin complexes have drawn considerable attention in the study of the coordination chemistry of biological interest3.

The Cobalt (III) complexes of macrocyclic ligands can serve as a model system for the study of vitamin-B124. Many other oxime complexes similar to complexes of DOH series were subsequently developed to know the trend in their red-ox behaviour. The qudridentate ligands are invariably macrocyclic with oxime group at one end. The structure of the oximes mostly depend on the alkyl or aryl group attachéd to the oxime carbon5.

The present study is focussed on the possibility of microwave assisted synthesis and characterisation of a dioxime ligand and to use it to prepare cobalt (III) complexes similar to cobaloximes containing pyridine and their derivatives as axial ligands6.

2. EXPERIMENTAL METHODS

2.1 Materials Used

2.1.1. Solvents: Double distilled water (distilled over alkaline permanganate) was used throughout. Acetone and ethanol were used for the preparation of the complexes. Ether was used for washing the complexes to remove excess ligands.

2.1.2. Chemicals and Reagents:
All chemicals were of analytical reagent grade. Cobaltous chloride and 4- Methyl pyridine were used for the preparation of the complexes. Ethylene diamine was used for the preparation of ligands.

2.2. PREPARATION OF THE COMPLEXES

2.2.1. Synthesis of theLigand, enbmo

About 0.05 mole of ethylene diamine was added to 200ml of distilled water and the solution was exposed to microwave in an unmodified microwave oven for 30 seconds. To this 0.1 mole of diacetylmonoxime was added and again exposed to microwave for about 30 seconds. The solution was set aside for 10 or 24hrs to get straw yellow product. It was filtered, washed with cold water and recrystallised from hot water.

2.2.2. Synthesis of [Co(enbmo)Cl2]

About 0.01 mole (1.0895g) of CoCl2.6H2O was dissolved in 75ml of acetone with constant stirring for about 10 minutes. It was then mixed with 0.01 mole (1.5794g) of enbmo and stirred well. A green colour core complex was formed. It was then allowed to stir for one hour. The product was filtered and washed with ether.

2.2.3. Synthesis of [Co(enbmo)(H2O)Cl]Cl

About 0.01 mole of the dichloro complex was added to 75ml of ethanol and allowed to stir for five minutes. The solution under stirring condition was treated with 3ml of water and exposed to micro wave for 3 minutes. The mixture was stirred for one hour. The light green colour due to dichloro complex gradually changed into brown. The precipitate was filtered by using sintered crucible, washed with ether and dried over desiccators.

3. CHARACTERISATION BY PHYSICAL MEASUREMENTS AND SPECTRAL DATA

3.1. Elemental Analysis:

The microanalysis for C and H, N and S in the complexes were recorded on PERKIN ELMER – COLMAN MODEL-33, Carbon – Hydrogen analyzer at Central Drug Research Institure (CDRI) Lucknow.

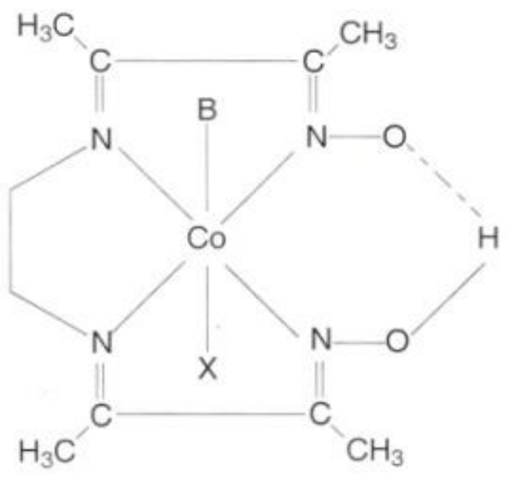
3.2. Electronic spectra:

UV –Visible spectrum of the complexes were obtained from LAMBD-125 spectrophotometer using 1cm matched quartz cells. Alcoholic solutions of the complexes of suitable concentrations were used.

3.3. IR spectra:

IR spectra of the complexes were obtained using PERKIN ELMER SPECTRUM – 1 in KBr disc. The spectra were recorded at Loyola College, Department of Chemistry, Instrumentation laboratory, Chennai.

General Structure of the Complex, [Co(enbmo)(B)X]



B= Base, H2O; X = Cl

4. RESULTS AND DISCUSSIONS

4.1 ELEMENTAL ANALYSIS

The element analysis data obtained by analytical methods agree well with theoretical data expected for the formula of the complexes proposed.

Table 1: Elemental Analysis

S. No	Complex	M.F	M.W	% of C		% of H		% of N	
				Cal	Obs	Cal	Obs	Cal	Obs
1	$[Co(enbmo)Cl_2]$	$C_{10}H_{17}N_4O_2CoCl_2$	354.93	33.81	33.17	4.79	4.42	15.78	15.52
2	$[Co(enbmo)(H_2O)Cl]\ Cl$	$C_{10}H_{19}N_4O_3CoCl_2$	372.93	32.18	32.08	5.10	5.21	15.02	14.82

4.2 ELECTRONIC SPECTRA

The macrocyclic dioxime exhibits a sharp intense peak at 220nm whereas the complexes show a broad peak in UV region center around 270nm.(Fig-1). This may be attributed to the overlapping of π-π^* transition bands occurring almost in the same range.

4.3 INFRA RED SPECTRA OF THE COMPOUNDS

The absorption at various frequencies can be assigned to the functional groups present in the complex. The figures (2-4) and the table (2) list the expected and observed range of frequencies for the functional groups present in the complex

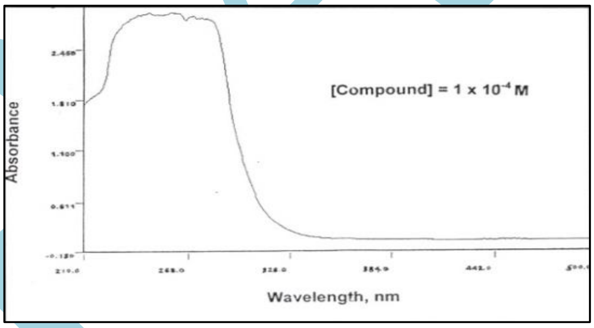


Fig-1: Electronic Spectrum of [Co(enbmo)Cl2]

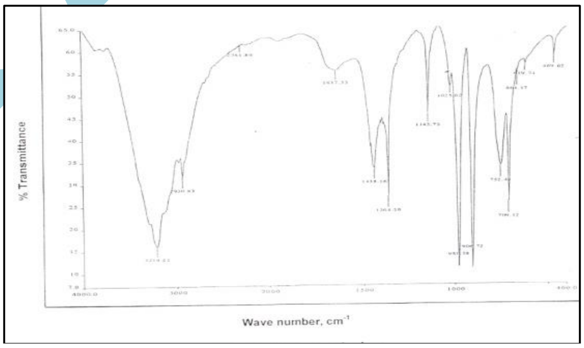


Fig-2: IR Spectrum of enbmo

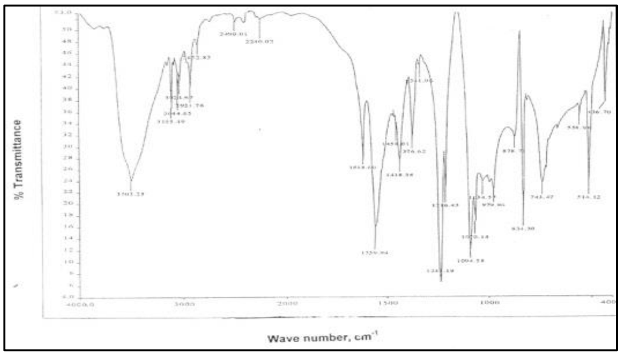


Fig-3: IR Spectrum of [Co(enbmo)Cl2]

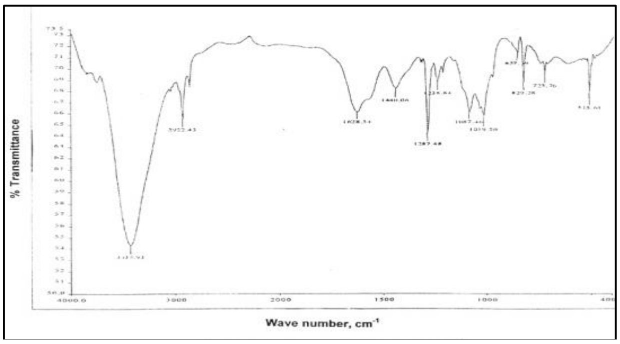


Fig-4: IR spectrum of [Co(enbmo)(H2O)Cl] Cl

Table 2: Assignment of IR frequencies to the functional groups present in the complex

S. No	Functional Groups	Observed range of frequency in (enbmo) cm^{-1}	Observed range of frequency in [Co(enbmo) Cl_2] cm^{-1}	Observed range of frequency in [Co(enbmo)(H_2O)Cl]Cl cm^{-1}	Expected range of frequency cm^{-1}
1	-OH	3215	3605	3503	3300-3400
2	$-CH_3$	2930	-	-	2965-2940
3	$-CH_2$ symmetric bending	1440	-	-	1485
4	-C=N-	1640	1440	1438	1600-1430
5	-C=C-	1635	1560	1559	1600-1430
6	Co-N	-	515	514	530-500
7	Py	-	1618,743	1618,743	1600-1430,748-704
8	4 –Substituted pyridine	-	835	834	520-794
9.	$Ar-CH_3$	-	2920	2921	2930-2920

CONCLUSIONS

The macrocyclic dioxime (enbmo) prepared and used in this study has four nitrogen donors and can form an equatorial square-planar network. Dihalocobalt (III) octahedral complexes with four equatorial nitrogen such as [Co(dmgH)2X2] where X= Cl , Br were reported to be green in colour. Incidentally cobalt (II) chloride treated with macrocyclicdioxime prepared in acetone medium gave similar green colour complex supporting structural similarity of the complexes prepared with [Co(dmgH)2X2]. In conclusion it could be stated that the macrocyclicdioxime viz., enbmo behaves like dimethylglyoxime. So that the cobalt (III) macrocyclicdioxime prepared shows similarity to cobaloximes.

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