Synthesis and Structural Characterization of Some Cobalt (II) Complexes with a Mannich Base Derived From Morpholine and Maleic Hydrazide

P.R.Santhi[1], G.Selvanathan[1], G.Poongothai[2]

[1]*Department of chemistry,A.V.C College(Autonomous),Mannampandal-609305, Tamil Nadu, (INDIA)*

[2]*Department of chemistry,Government Arts College for Men(Autonomous),Nandanam,Chennai-35,Tamil Nadu, (INDIA)*

Abstract:

A new Mannich base N-(1-morpholinomethylmaleichydrazide) ,(MMMH) was synthesized through Mannich reaction and its Cobalt(II) chloro, bromo and nitrato complexes have been prepared. Their structures have been elucidated on the basis of analytical, elemental analyses, electrical conductivity, magnetic moment and spectral studies such as UV,IR,NMR and Mass spectra for elucidating the structure of ligand (MMMH),DRS,IR and Far IR for cobalt(II) coloured complexes. The complexes exhibit monomeric as well as polymeric structure.

Key Words: *A new Mannich base, Morpholinomethylmaleichydrazide (MMMH) , Co(II) complexes, monomeric and polymeric structure.*

INTRODUCTION

The Mannich reaction is a three component- condensation in which a new base produced is known as a Mannich base.The mannich reaction of maleichydrazide and related compounds are reported in the literature[1].Maleichydrazide is a structural isomer of Uracil and it was found to be a potent inhibitor of leukemia[2],its derivatives are used as novel bioactive agents[3] and especially Mannich–N-bases were proved to be pharmacologically more active than maleichydrazide[4,5].The present work the N-mannich base,Morpholino Methyl Maleic Hydrazide(MMMH) was synthesized by introducing morpholinomethyl moiety in place of active hydrogen atom attached to nitrogen of maleic hydrazide through mannich reaction.By using the ligand MMMH coloured complexes of cobalt(II) chloro,bromo and nitrato complexes have been prepared.The structure of newly synthesized mannich base is given in Fig:1.

EXPERIMENTAL

All the solvents used for the synthesing ligand and the complexes were of analar grade and used as such.The elemental analysis were performed using LECO-CHN600 Elemental Analyser and was calibrated using standard EDTA prier to the determination.The conductance data were obtained in 10^{-3}m DMF solutions of the complexes at room temperature using Systronics Direct –Reading Digital conductivity Meter304 with a dip type conductivity cell.

The UV-VIS spectra[11] were recorded using JASCO-UVIDEC-430B double beam spectrophotometer provided with the quartz cells.DRS for solid state complexes were recorded in $MgCO_3$ medium using Hitachi UV-VIS-NIR Spectrophotometer.IR spectral measurements were for free ligand and their metal complexes as KBr pellets using Perkin Elmer 1430 Ratio Recording Sectrophotometer.

Far IR were recorded on a polytech PE983 and Bruker IFS66v FT-IR Spectrometer in polyethylene support.Magnetic measurements of the complexes at room temperature were made by using a Guoy Magnetic Balance and the Guoy tube was calibrated using Mercury(II)tetrathiocyanatocobaltate(II).

The ^{1}H and ^{13}C NMR of the ligand[11]were recorded on Bruker 400 Mhz Spectrometer.The mass spectral[12] study of the ligand were carried out using Finningn MAT-8230 mass spectrometer.

2.1.Synthesis of Mannich base

An equimolar mixture of maleichydrazide(11.20g),formaldehyde(3.0g) and morpholine (8.7g) was dissolved in 400ml of ethanol and refluxed for about 5 hours. The formation of the product MMMH and the completion of the reaction was identified by the formation of a clear solution.The resulting solution was concentrated to 200ml by distillation under reduced pressure.The concentrate on cooling yielded a colourless solid and recrystallized from ethanol.(Yield:98% : m.p:298^{0}C)

2.2. Synthesis of Metal complexes

The MMMH complexes of the Cobalt(II) chloride,bromide and nitrate were prepared by solvating the metal salt in ethanol and the ligand in ethanol.A hot solution of the ligand (MMMH) was added slowly with constant stirring to a hot solution of the metal salt(1:1mole ratio) when an insoluble complex was formed.This was then washed with hot

ethanol to remove the unreacted metal and ligand.The precipitated complexes were filtered ,washed with ethanol and dried in vacuo.

RESULTS AND DISCUSSION

Analytical and conductance data of the complexes is given Table.1 which indicate the stoichiometry of the complex as $MX_2.MMMH.2H_2O$,where M = Co^{II} and X= Cl,Br and NO_3 except for chloro and bromo complex of cobalt(II).The stoichiometry of the cobalt(II) chloro and bromo complexes are $CoCl_2.MMMH$ and $CoBr_2.MMMH$.The molar conductance values(∧M) exhibited that all the complexes are non-electrolytes[6,12].

3.1.IR and Far IR Spectra[7,8,11]

The IR spectra of cobalt (II) chloro,bromo and Nitrato complexes complexes are given in Table.2.(Figures:2,3,4).The appearance of very broad band in the region 3040-3600 cm^{-1} for cobalt (II) nitrato complex indicate the presence of co-ordinated water molecules.The chloro and nitrato complexes experience negative shifts in δOH and νCNC when compared with those of free ligand frequencies.In cobalt (II) bromo complex the δOH and νC=O are lowered from 1711 to 1660 and 1612 to 1547 when compared to free ligand.Three new strong bands appear at 1270 (ν_5),1201(ν_1) and 1126(ν_2)cm^{-1} in cobalt nitrato complex,which point to the unidatebehavior of nitrato group.

In far IR the absorptions around 382 and 327 are assigned to νCo-o and νCo-N respectively.The additional bands at 273 and 244 cm^{-1} for cobalt(II) chloro and bromo complexes are due to νCo-Cl and νCo-Br .The far IR cobalt complexes are shown in Figures-5,6.

3.2.Electronic absorption spectra[9,10,12]

The diffuse reflectance spectra of cobalt(II) chloro,bromo and nitrato complexes were recorded to cover the range of 200-2000nm.The absorption bands are listed in Table.3. and the ligand field parameters of cobalt (II) complexes are given in Table.4.

The cobalt(II) nitrato complex recorded three bands at 7513(ν_1)cm^{-1},16694(ν_2) and 19120(ν_3) cm^{-1} respectively.The cobalt(II) nitrato complex has three spin allowed transitions are characteristic of octahedral environment around cobalt(II) ion.

The cobalt(II) chloro complex exhibits two absorption bands 8695 cm^{-1}(ν_2) and 14999(ν_3) cm^{-1}.They are assigned (ν_2) $^4T_1(F) \leftarrow {}^4A_2$, (ν_3) $^4T_1(P) \leftarrow {}^4A_2$ transitions respectively. These transitions are characteristic of cobalt ion in a tetrahedral environment.For a cobalt (II) ion in a tetrahedral environment the (ν_1) band is not usually observed as it lies in the near IR region.

The cobalt (II) bromo complex also exhibits two bands 6939 and 16260 cm-1.The first band certainly cannot be assigned to ν_1 transition because the resulting (Dq)Td will be too high for a Td geometry.Therefore,the possible assignment is ν_2,so that (Dq) Td=386cm^{-1}.Taking the transition at 16260cm^{-1} as ν_3,we arrive at B=775cm^{-1} since Bo=971cm^{-1}.We have β =0.79 and the percentage of β = 14.The ratio ν_3/ν_2 was determined using the Tanabe-Sugano diagram to get the information regarding ν_1 .The results of the calculation indicate that the transition energy for "ν_1" lies in the near IR region and cannot be easily located because of vibrational effects.

The magnetic moment value for the cobalt(II) nitrato complex point to a six coordinate geometry,whereas in the case of cobalt(II) chloro and bromo the μ eff value supports a four coordinate geometry.On the basis of analytical and spectral data the MMMH complexes of Co^{II} has been assigned tentatively the monomeric structures for $CoCl_2.MMMH$, $Co(NO_3)_2.MMMH.2H_2O$ and polymeric structure for $CoBr_2.MMMH$. The structures are shown in Figs:7,8,9.

CONCLUSION

A new Mannich base N-(morpholinomethylmaleichydrazide) and its cobalt (II) chloro,bromo and nitrato complexes have been synthesized and characterized by analytical and spectral study.It is concluded from the study that the chloro and nitrato complexes are monomer and cobalt(II) bromo complex has a polymeric structure.

Tables and Figures

Table:1 Analytical and conductance data of cobalt (II) complexes of MMMH

Compound	Elemental analysis(%)					∧M*
	Carbon Obs (cal.)	Hydrogen Obs (cal.)	Nitrogen Obs (cal.)	Metal Obs(cal.)	Anion Obs (cal.)	
$CoCl_2.MMMH$	31.43 (31.68)	3.62 (3.81)	12.08 (12.32)	16.98 (17.29)	20.04 (20.82)	8.3

$CoBr_2$.MMMH	25.19 (25.13)	2.36 (3.03)	9.15 (9.77)	14.05 (13.71)	36.94 (37.18)	6.7
$Co(NO_3)_2$.MMMH.$2H_2O$	24.58 (25.12)	2.93 (3.02)	9.68 (9.77)	14.15 (13.71)	- (28.84)	9.0

Table:2 Important IR absorption bands(cm^{-1}) of MMMH complexes of cobalt(II)

Compound	ν_{OH}	ν_{CH}	ν_{CO}	δ_{OH}	ν_{CNC}
MMMH	3021	2956	1711	1612	1109
CoCl2.MMMH	3066	2959	1663	1550	1002
CoBr2.MMMH	3024	2958	1660	1547	1006
$Co(NO_3)_2$.MMMH.H_2O	3680-3040	2960	1661	1547	1005

Table: 3.Colour,electronic spectral bands,transitionassignments,metal environment and magnetic moment values of cobalt(II) complexes of MMMH

Complex	Colour (μ eff)BM	Environment	Absorption maxima(cm^{-1})	Transition assignment
CoCl2.MMMH	Blue (4.15)	1O,2Cl,1N	8695 14999	$^4T_1(F) \leftarrow {}^4A_2$ $^4T_1(P) \leftarrow {}^4A_2$
CoBr2.MMMH	Blue (4.05)	2O,Br	3855 6939 16260	$^4T_1(F) \leftarrow {}^4A_2$ $^4T_1(P) \leftarrow {}^4A_2$
Co(NO3)2.MMMH.2H2O	Pink (5.38)	5O,1N	7513 16,694 19,120	$^4T_2g(F) \leftarrow {}^4T_1g(F)$ $^4A_2g(F) \leftarrow {}^4T_1g(F)$ $^4T_1g(P) \leftarrow {}^4T_1g(F)$

Table:4.Ligand field parameters of Co^{II}Complexes of MMMH

Parameter	$CoCl_2$.MMMH	$CoBr_2$.MMMH	$Co(NO_3)_2$.MMMH.$2H_2O$
ν_3/ν_2	1.725	2.343	1.145
ν_2/ν_1	1.800	1.800	2.222
ν_3/ν_1	3.105	4.218	2.545
ν_3/B	24.428	20.98	21.60
B(cm^{-1})	614	775	885
Dq(cm^{-1})	483	386	939
Dq/B	0.786	0.49	1.06
B	0.63	0.79	0.91
LFSEcal mol^{-1}	16.56	13.23	32.19

MMMH-Morpholinomethylmaleichydrazide, Free ion value for Co^{II}=971cm^{-1} , LFSE=12Dq; 1Kcal/mol=350cm^{-1}

Fig:1 Structure of Synthesised Mannich base MMMH

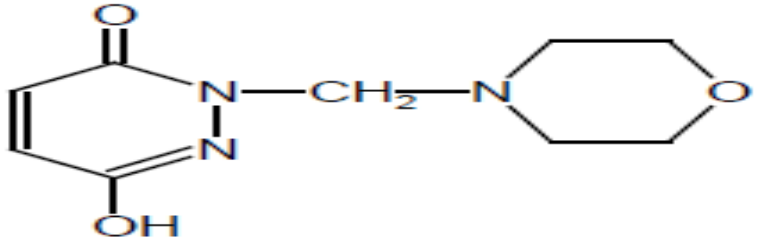


Fig:2 IR Spectrum of $CoCl_2$.MMMH

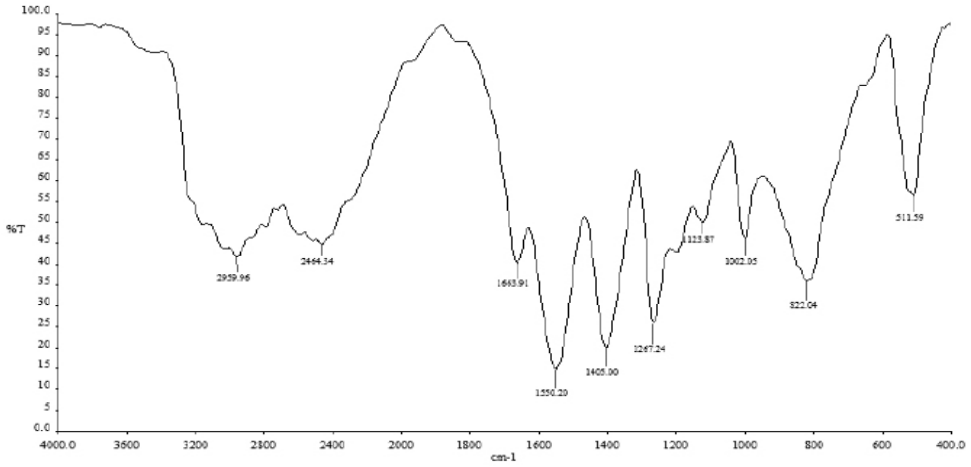


Fig:3 IR Spectrum of $CoBr_2$.MMMH

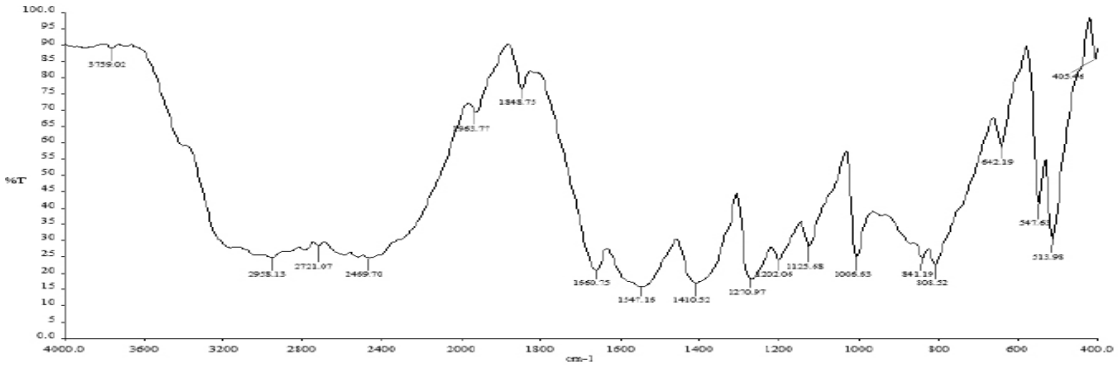


Fig:4 IR Spectrum of $Co(NO_3)_2$.MMMH.$2H_2O$

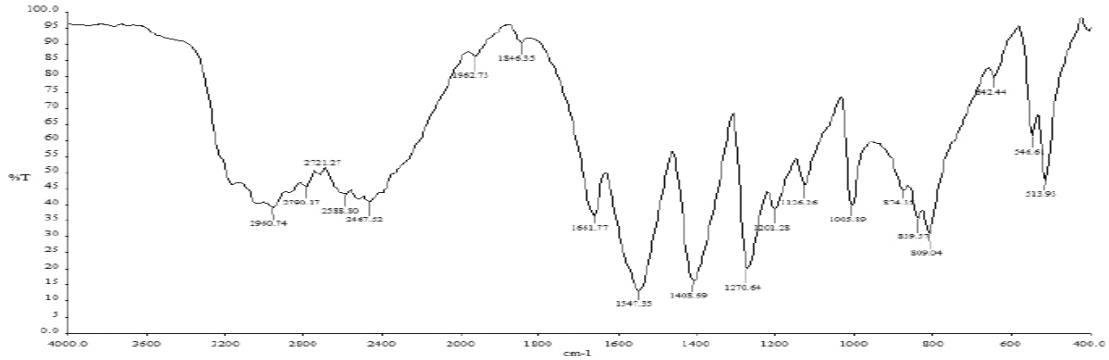


Fig:5 Far IR Spectrum of $CoCl_2$.MMMH

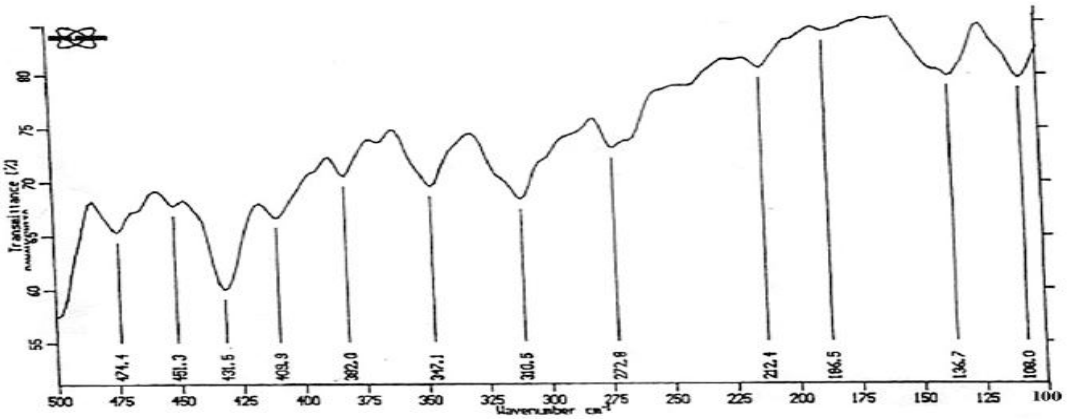


Fig:6 Far IR Spectrum of $Co(NO_3)_2.MMMH.2H_2O$

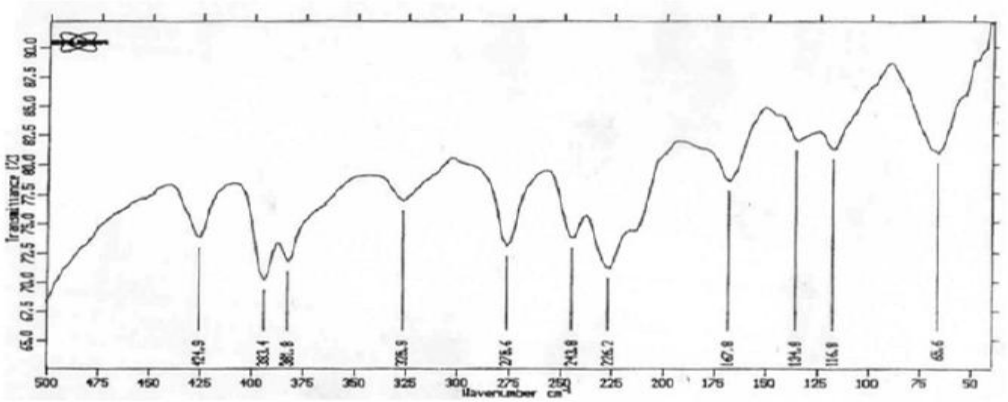
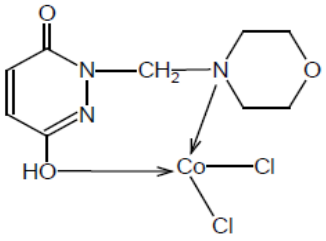


Fig:7,8 Monomeric structure of $CoCl_2.MMMH$ $Co(NO_3)_2.MMMH.2H_2O$



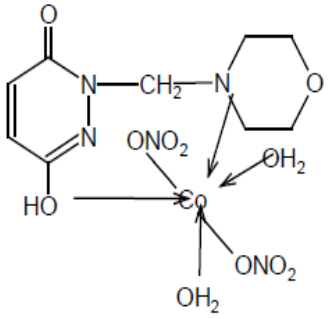
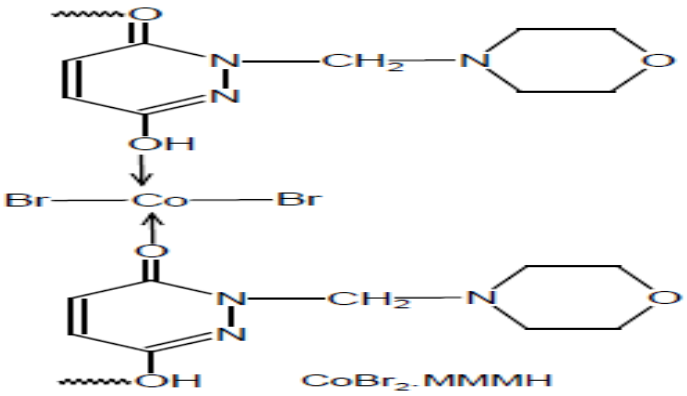


Fig:9. Polymeric structure of CoBr2.MMMH



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