

A Study on the interaction of a Mannich base Piperidino Methyl Maleic Hydrazide (PMMH) with Zinc(II), Cadmium(II) and Mercury(II) Complexes

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Abstract

A new Mannich base 1-Piperidinomethylmaleichydrazide is synthesized by the condensation of maleichydrazide, formaldehyde and piperidine and its Zinc(II), Cdium(II) and Mercury(II) complexes have been synthesized. The structure of the complexes have been elucidated on the basis of electrical conductivity,spectral study and elemental analyses.The monomeric, polymeric and non-electrolytic nature of the complexes is evidenced by their low conductance and spectral data.The complexes exhibit four and six co-ordinate geometry have been confirmed by analytical and spectral data.

Keywords -Mannich base, Piperidinomethylmaleichydrazide(PMMH), Zn(II), Cd(II), Hg(II) Complexes.

INTRODUCTION

The Mannich reaction of maleic hydrazide and related compounds are reported in the literature¹. Maleic hydrazide is a structural isomer of Uracil and it exists in three polymorphic forms^{2,3,4}and in all three polymorphs the molecules are present in the lactim-lactum form of three hydroxy-6-pyridazinone and the same pattern of hydrogen bonds is formed.Since the property varies, polymorphism of substances, is of crucial importance for material science and for technological applications,especially in pharmaceutical industry.However ,there is no report on metal complexes of piperidinomethylmaleichydrazide(PMMH).As a part of our contuning efforts to synthesise the transition metal(II) complexes using Mannich bases,the present work describes the synthesis and characterization of Zn(II),Cd(II) and Hg(II) complexes from the Mannich base ,1-Piperidinomethylmaleichydrazide.The infrared studies of the complexes and the free ligand help to a very great extent in the determination of the point of coordination^{5,6,7}.The UV and Visible electronic spectra⁸⁻¹¹ coupled with paramagnetic susceptibility measurements^{12,13} act as a powerful tool in the determination of the geometry and stereochemistry of the complexes.

EXPERIMENTAL

2.1 General Manipulations

All the reagents and solvents were purchased from Sd-fine chemicals and they were used as received.Elemental analyses were performed LECO-CHN 600 model and it was calibrated using standard EDTA prior to the determination. Conductance were recorded in 10⁻³ DMF solutions of the complexes at room temperature using a Systronics Direct Reading Digital Conductivity Meter 304 with a dip type conductivity cell.The electronic spectra of the ligand in the UV-visible region were measured using JASCO UVIDEC-430 B double beam spectrophotometer. Infra-red spectral measurements were made for the free ligand and its metal complexes as KBr pellets using Perkin Elmer 1430 Ratio Recording Spectrophotometer.¹H NMR of the ligand and d¹⁰ metal complexes were recorded on BRUKER 400MHz spectrometer.

2.2. Synthesis of Mannich base

The ligand piperidinomethylmaleichydrazide was synthesized by introducing piperidinomethyl at the first position of maleichydrazide by taking recourse to Mannich synthetic route.Equimolar mixture of maleic hydrazide,formaldehyde and piperidine was suspended in 300ml ethanol and refluxed.After five hours the completion of the reaction and the formation of the product was indicated by resulting a clear solution as opposed to a suspension at the start of the reaction.The clear reaction mixture was concentrated to 100ml by distilling of ethanol and cooled to obtain the crude product.The yellow crude product was washed with ether to remove the unreacted substrate and undesirable product. The ligand (PMMH)was recrystallized and dried.

2.3.Synthesis of Metal complexes

The Zn(II), Cd(II) and Hg(II) complexes of PMMH ligand were isolated using hot ethanol as the solvating medium. A hot solution of the ligand (PMMH) was added slowly with constant stirring to hot solution of the metal salts(1:1mole ratio) where insoluble complexes were formed.The complexes were then washed with hot ethanol to remove the unreacted metal and ligand.The precipitates were filtered and washed with acetone and dried.

RESULTS AND DISCUSSION

3.1.Structural characterization of Piperidinomethylmaleichydrazide

The ligand(PMMH) melting point is 220 °C and the molecular weight was found to be 209.The results of the elemental analyses indicates the molecular formula C₁₀H₁₅N₃O₂.The ligand is completely soluble in cold water,DMF,DMSO and hot methanol,ethanol and propanol.

The structure of Maleichydrazide and PMMH are given Figs.1&2.The UV visible spectrum of PMMH in DMF exhibits absorption bands at 320nm(31250cm⁻¹) and 251nm (39840cm⁻¹). These can be assigned to n-π* and π-π* transitions and this bathochromic shift may indicate the substitution of piperidinomethyl group in place of active hydrogen atom in the pyridazine ring.The IR spectra of MH and PMMH are shown in Figs.3and 4.

3.2. Structural Characterization of Zinc(II),Cadmium(II)bromo complexes and Mercury(II) chloro complex of PMMH.

To find out the stoichiometries of the complexes,the metal,anion,carbon,hydrogen and nitrogen contents were determined.The electrical conductance measurements of the 10⁻³M DMF solutions at room temperature was done in order to ascertain wheather the anion is within or outside the coordination sphere of the complexes.The conductance data exhibit that the complexes are non-electrolytes.Elemental analyses and conductance data are presented in Table.1.The analytical and conductance data indicate that the stoichiometries of the complexes as MX₂.PMMH. ,where M= Zn,Cd,Hg and X=Br&Cl.

3.3.Structure of Zinc(II)bromo complex of PMMH.

There is no evidence in the IR region of 3200-3600cm⁻¹the presence of co-ordinated water molecules.The important IR^{14,15} absorption peaks of Zinc(II)bromo complex is given in Table.2 and Fig.5.The comparison of IR absorption spectrum of Zinc(II)bromo complex with the free ligand PMMH, ν_{C=O} and δ_{OH} suffer negative shifts by 97 and 84 cm⁻¹.This shows that the ligand PMMH is coordinated to zinc in bidentate fashion through hydroxyl oxygen and carboxyl oxygen of PMMH.

The various resonance signals¹⁴ exhibited by Zinc(II)bromo complex(Fig.6) is compared with those for free ligand PMMH(Table.3).As a result of electron drift from CNC group,the N-CH₂-N and N(CH₂)₂ suffer the downfield shift on complexation of the ligand with the metal atom.Based on analytical,conductance, IR and ¹H NMR data a tentative four co-ordinate polymeric structure is assigned to Zinc(II)bromo complex(Fig.7).

3.4.Structure of Cadmium(II)bromo and Mercury(II)chloro complexes

The result of the elemental analyses of Cadmium(II)bromo and Mercury(II)chloro complexes are in good agreement with the proposed composition as CdBr₂.PMMH and HgCl₂.PMMH.The conductance values show that the complexes are non-electrolytes.

The IR spectra of Cadmium(II)bromo and Mercury(II)chloro^{14,15} complexes are shown in Fig.8 & 9.Comparison of IR data of both complexes and the ligand PMMH show reduction in frequency of ν_{CNC} and δ_{OH} bands.It is inferred that PMMH is bidentately coordinated to enolic group of pyridazine ring and CNC of piperidinomoiety. A negative shift by 104cm⁻¹in δ_{OH} and 40cm⁻¹ in ν_{CNC} in the IR spectrum.The position of bands 1492(δ_{OH}) and 1039 cm⁻¹(ν_{CNC}) is compared to the spectrum of PMMH confirms coordination through hydroxyl oxygen and the nitrogen of piperidine ring.

The IR spectrum of Mercury (II)chloro complex with of free ligand the δ_{OH} decreased from1492 to 1409cm⁻¹ and ν_{CNC} decreased from 1081 to 1052cm⁻¹.The chloro complex experience negative shift of 83 and 29cm⁻¹ respectively in δ_{OH} and ν_{CNC} values.It also confirms the ligand PMMH coordinates with the Mercury in bidentate fashion.

The ¹H NMR spectra of Cadmium(II)bromo and Mercury(II)chloro¹⁴complexes are shown in (Figs.10 & 11,Table.3).No signal due to coordinated water in the ¹H NMR spectra of both the complexes.The CNC group,N-CH₂-N and >N(CH₂)₂ signals suffer downfield shift on complexation of the ligand with the metal atom.The methylene protons which connect the amino moiety and maleic hydrazide are not much effect.This further supports the mode of coordination suggested

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by IR studies. Based on analytical ,conductance, IR and ¹H NMR spectral data a plausible four coordinate symmetry is assigned to Cadmium(II)bromo and Mercury(II)chloro complexes(Fig.12).

CONCLUSION

Based on the analytical and spectral studies the structure of PMMH ligand as well as the Zn(II),Cd(II)bromo and Hg(II)chloro complexes are established.The analytical data reveals 1:1 (metal:ligand) ratio in Zn(II),Cd(II) and Hg(II) complexes.The electrolytic conductivity data of the complexes indicate their non-electrolytic nature.The analytical and spectral data confirmed the polymeric structure of Zinc(II)bromo complex and monomeric nature of Cadmium(II)bromo and Mercury (II) chloro complexes.

Tables and Figures

Fig.1. Structure of Maleichydrazide (3-Hydroxy-6-pyridazinone)

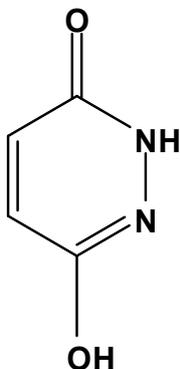


Fig.2. Structure of 1-Piperidinomethylmaleichydrazide (PMMH)

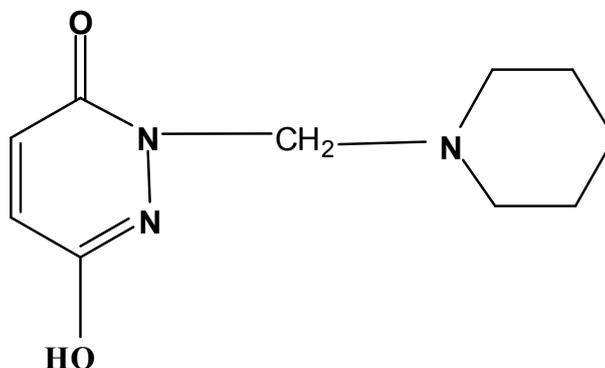


Fig.3. IR Spectrum of Maleichydrazide

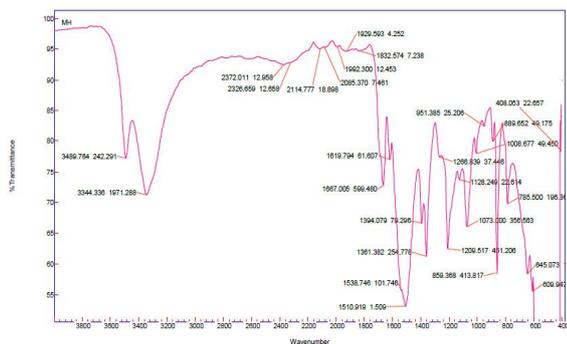


Fig.4. IR Spectrum of PMMH

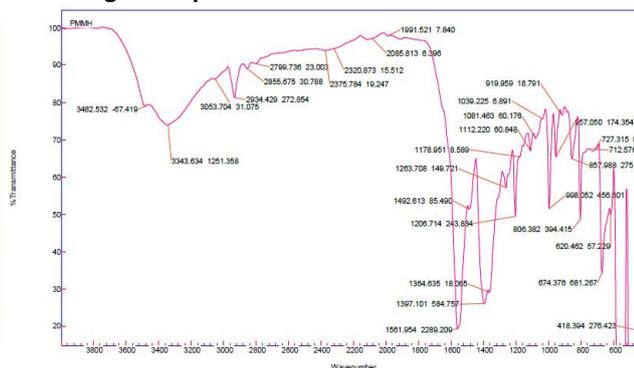


Table.1. Analytical data of the complexes of PMMH

Compound	Elemental analysis(%)					Λ M*
	Carbon obs (cal.)	Hydrogen obs (cal.)	Nitrogen obs (cal.)	Metal obs (cal.)	Anion obs (cal.)	
HgCl ₂ .PMMH	24.98 (24.65)	3.12 (3.48)	8.74 (8.53)	41.75 (41.93)	14.76 (14.85)	5.2
ZnBr ₂ .PMMH	27.64 (27.88)	3.46 (3.68)	9.67 (9.74)	15.06 (15.18)	36.81 (36.93)	10.4
CdBr ₂ .PMMH	24.94 (24.86)	3.12 (3.32)	8.73 (8.93)	23.36 (23.58)	33.21 (33.43)	4.7

Table.2.Important IR absorption bands (cm⁻¹) of PMMH complexes of Hg^{II},Zn^{II} and Cd^{II}

Compound	ν_{OH}	ν_{CH}	$\nu_{C=O}$	δ_{OH}	ν_{CNC}
PMMH	3053	2934	1664	1492	1081
HgCl ₂ .PMMH	3049	2945	1565	1409	1052
ZnBr ₂ .PMMH	3046	2945	1565	1408	999
CdBr ₂ .PMMH	3432	2940	1564	1388	997

Table.3 . ¹H NMR resonance signals for PMMH and its Hg^{II}, Zn^{II} and Cd^{II} Complexes

Complex	Type of protons (δ ppm)				
	-CH=CH	OH	Bridging(CH ₂) (or) -N-CH ₂ -N	-N(CH ₂) ₂	(CH ₂) ₂ O
PMMH	6.87	3.51	3.028	2.595	1.457
HgCl ₂ .PMMH	6.55	3.359		2.504	1.642
ZnBr ₂ .PMMH	6.54	3.35		2.50	1.64
CdBr ₂ .PMMH	6.66	4.376		2.99	1.732

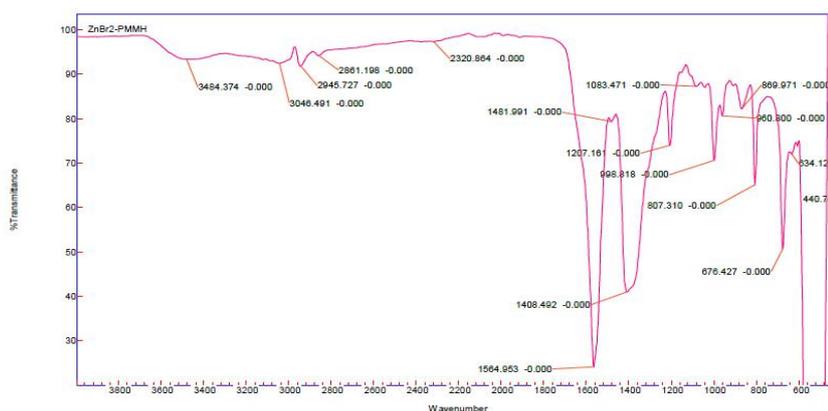


Fig.5. IR absorption spectrum of Zinc(II)bromo complex

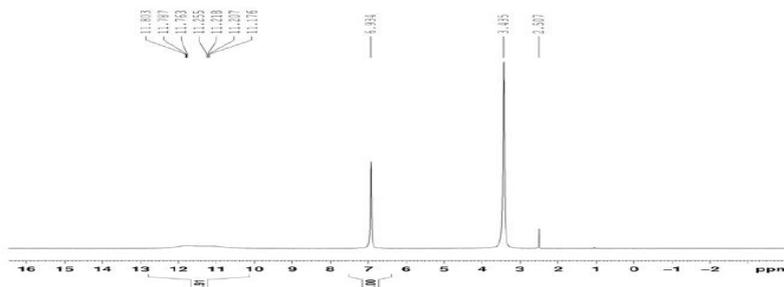


Fig.6. ¹H NMR Spectrum of Zinc(II)bromo complex

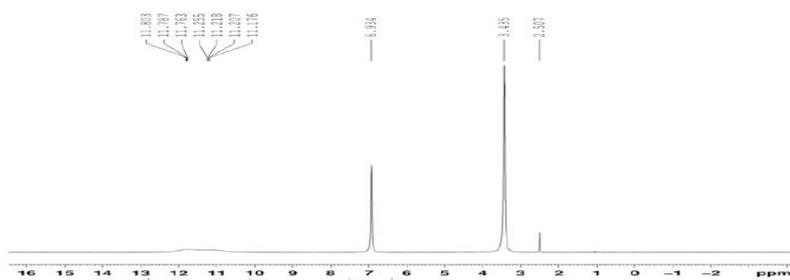


Fig.7.Polymeric Structure of Zinc(II)bromo complex

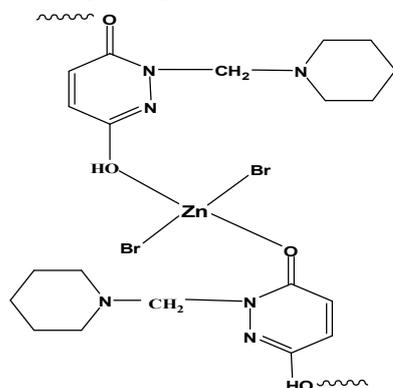


Fig.8.IR Spectrum of Cadmium(II)bromo complex

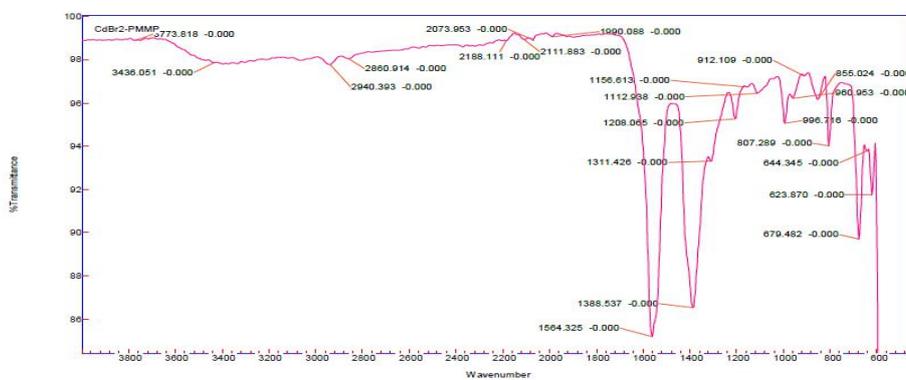


Fig.9.IR Spectrum of Mercury(II)chloro complex

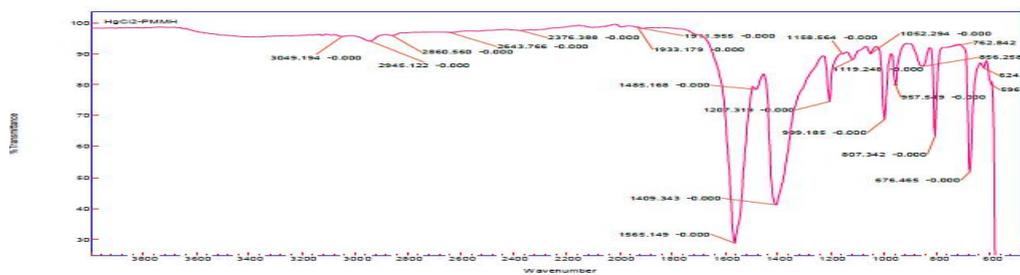


Fig.10.¹H NMR Spectrum of Cadmium(II)bromo complex

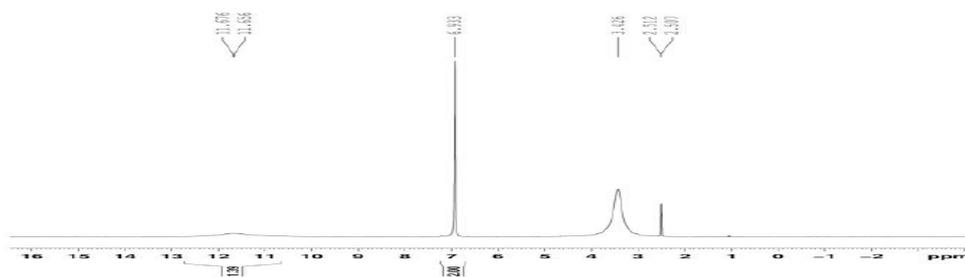


Fig.11. ¹H NMR Spectrum of Mercury(II)chloro complex

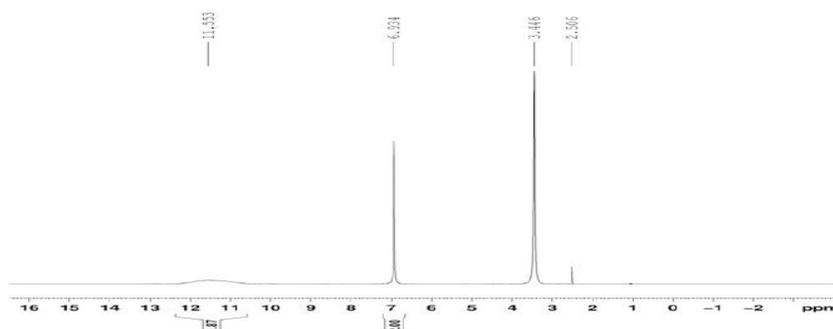
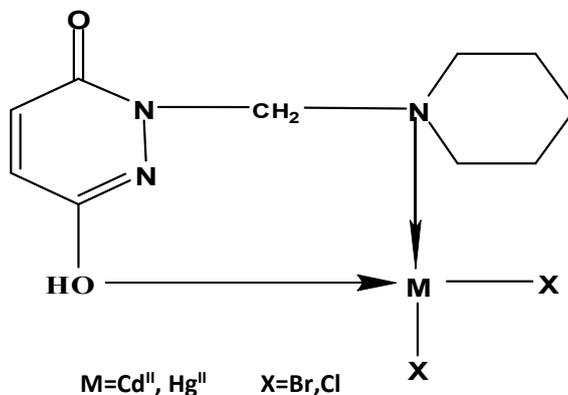


Fig.12. Structure of Cadmium(II)bromo and Mercury(II)chloro complexes



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