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Research Article

STUDIES ON THE SYNTHESIS AND CHARACTERIZATION OF THE TRANSITION METAL COMPLEXES OF NOVEL MANNICH BASE

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ABSTRACT

In this study, we report the synthesis of a novel Mannich base derived from Salicylidene acetone and its transition metal complexes . Here Salicylidene acetone was used as a precursor and treated with formaldehyde and piperidine. The so formed base is complexed with transition metals. The structure of the synthesized compounds are confirmed by UV,IR, and ^{1}H NMR spectroscopic techniques.The antibacterial activity of the ligand and the complexes were examined and found that the metal complexes showed good activity than the free ligand.

Keywords: Mannich base, Piperidine, Salicylideneacetone, transition metal complex.

1.INTRODUCTION

During last two decades, there has been increased research activity in the field of organometallic complexes particularly derived from Mannich bases. Mannich reaction is a three component condensation in which a compound containing an active hydrogen (substrate) is reacted withformaldehyde and a secondary amine.It is a prototype of carbon-carbon bond forming reaction involves the addition resonance stabilized nucleophile to iminiumions.During the course of the reaction, three compounds condense with concomitant release of water to produce a new base, called Mannich base in which the active hydrogen in the substrate is replaced with an aminomethylgroup.The formation of both C-C bond and C-N bond makes this reaction a extremely useful synthetic procedure.Literature survey reveals that some Mannich bases possess broad spectrum biological activities which include Antineoplastic[1], Antibacterial [2,3], Antifungal [4,5],Anti HIV [6,7], Anti cancer[8,9],and Antimalarial [10-14].In the present work, we report the synthesis, characterization, antibacterial studiesof a new Mannich base and its transition metal complexes.

2.EXPERIMENTAL

2.1 MATERIALS AND METHODS

Reagents such as salicylaldehyde, acetone, formaldehyde and piperidine were of Merck products and were used as such. The melting point of all the synthesized compounds was determined in open capillaries and is uncorrected. The UV-Vis spectra were recorded in DMSO solvent on Shimadzu UV mini-1240 spectrophotometer, IR spectra were recorded on Agilent Resolutions FT-IR spectrophotometer using KBr pellets and ^{1}H NMR spectra were recorded with Bruker AMX400 NMR spectrophotometer using DMSO solvent.

2.2 Synthesis of the ligand

2.2.1. Synthesis of Salicylideneacetone

This compound was synthesised in the following manner. A mixture of salicylaldehyde and acetone in1:1 molar ratio was prepared. It was added to a solution of NaOH (10 gm in 100 ml water and 80 ml ethanol) with a constant stirring, during which a red coloured precipitate was formed. The precipitate was filtered and washed with cold water to eliminate unreacted NaOH and was dried at room temperature upon filter paper. It was recrystallised from hot rectified sprit. The sample was dried in vacuo over fused calcium chloride and then analysed. The reaction is given in Scheme.1.

2.2.2 Synthesis of Salicylidineactenomethylpiperidine (SAMP)

0.1 mol of Piperidine(8.5mL) and 0.1 mol of Formaldehyde (3 mL) are dissolved in 50mL of ethanol and taken in a 100mL RB flask. The contents of the flask are stirred well in ice bath using magnetic stirrer for about 2 hrs. Then 0.1 mol of the Salicylideneacetone is added gradually with constant stirring to the reaction mixture kept in icebath and the stirring was continued for about 1hr.Then it is kept in refrigerator for overnight.Then the contents are refluxed for about 4hrs.After that it is kept in refrigerator again.Next day, the solvent was recovered from the mixture by distillation.Mannich base separates out. It is filtered and washed with hot water, recrystallised in alcohol and dried in air-oven at 60°C.The yield is found out to be about 72%.Reaction is given in scheme.2.

2.3 Synthesis of complexes

Hot ethanolic solution of the ligand (1 equivalent) was slowly mixed withhot ethanolic solution of metal chloride (1 equivalent) under reflux condition with constant stirring.The mixture was refluxed for 1-2 hours and after that it was cooled and kept in refrigerator for few hours. The colored solid complexes were separated out in each case.It was filtered ,washed with 50% alcohol and finally dried.

3. RESULTS AND DISCUSSION

3.1 ^{1}H NMR Spectra

The ^{1}H NMR spectra (Fig.1) of the Mannich base under study exhibit a multiplet at 7.2-7.4ppm for the hydrogens of the aromatic rings. The appearance of peaks at 3.5 & 2.5 ppm indicates the methylene hydrogens attached with the phenolic ring& methylene hydrogens of the piperidine ring respectivelyand the aromatic –OH is appears at 10ppm.Further, the formation of the ligand is ascertained by the disappearance of a signal corresponding to the –NH proton of secondary amine as it was eliminated in the Mannich reaction.

3.2 IR Spectra

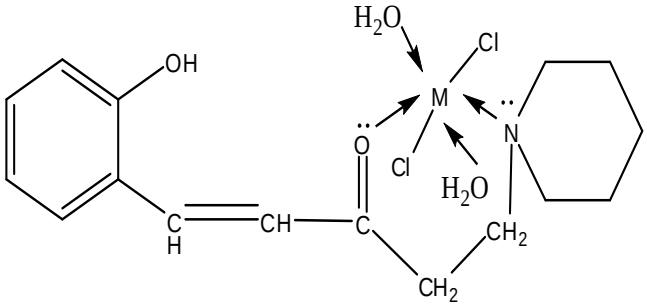
The important observation is the presence of an intense band at ~ 1670 cm-1 which is due to νC=O carbonyl group (Fig.2).The most notable change in the IR spectra is the disappearance of the – NH stretching vibration and appearance of an intense band at ~ 1211 cm-1 due to νC-N-C stretching. The absence of band at 3300 cm-1 due to amino -NH disappears implying its condensation after deprotonation. In all the complexes, (Fig.3) band due to νC=O and νC-N shifted towards lower frequency clearly indicating the nitrogen and carbonyl oxygen are involved in coordination with metal ions.The new bands at 730 cm-1 corresponding to M-O bond.The presence of coordinated water molecules is determined by the presence of bands around 3391cm-1 and a band at 833 cm-1 is assignable to –OH stretching mode of vibration.The presence of phenolic –OH group in all the complexes in between 3443- 3360 cm-1 indicates that which was not involved in coordination.

3.3 UV-Visible spectra

The UV-Visible spectra of the complexes(Fig.4) were recorded in the range of 200-1100 nm. The UV spectrum mostly showed two intense maxima bands around 47540 cm-1 and 29890 cm-1 which belong to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively.The Cu (II) complex under present study exhibit a broad band in the region 26700cm-1 due to transition between $^2E_g \rightarrow {}^2T_{2g}$ which indicated the octahedral geometry.The Ni (II) complex showed broad signals at 26255 cm-1 and 28540 cm-1which is assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$and $^3A_{2g} \rightarrow {}^3T_{2g}$transitions respectively which further confirms its octahedral geometry. The position of bands observed for Co (II) complex also shows it is also having the octahedral geometry.

3.4 Suggested structure of the complexes

Based on the foregoing results we suggest the following structure for the complexes synthesized using the Mannich base ligand.



Where M – Cu(II), Co(II) or Ni(II)

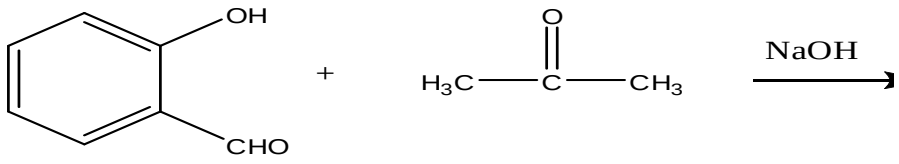
3.5 Antimicrobial activity

The synthesized compounds were screened for antibacterial activity against certain pathogenic bacteria by disc diffusion method at concentration of 10µg / mlin DMSO using the microbes*Bascillussubtilis, Escherichia coli,Staphaylococcusaureus,*and*Pseudomonas aeruginosa.*The zone of inhibition was measured in mm and the activity was compared with Ciprofloxacin in 1µg / disc.The results showed

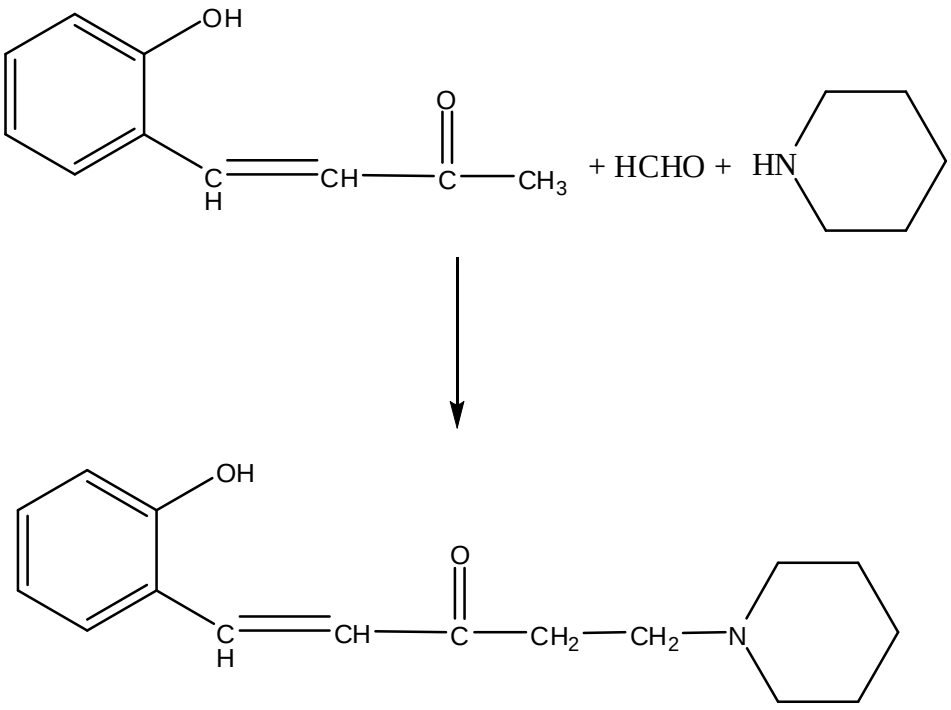
that the chelating tends to make the ligand to act as more potent bactericidal agents,thus destroying more bacteria than the free ligand.

4.CONCLUSION

It may be concluded that the newly prepared igand behaves as a bidentate chelating agent thro' the N and O donor sites and the spectroscopic data is in support of our expected structure. The antimicrobial property of the complexes were better than that of the free ligand observed.This may be attributed to the permeation of metal complexes through the cell membranes is much feasible due to coordinated bond than the free ligand.



Scheme . 1:



Scheme. 2:

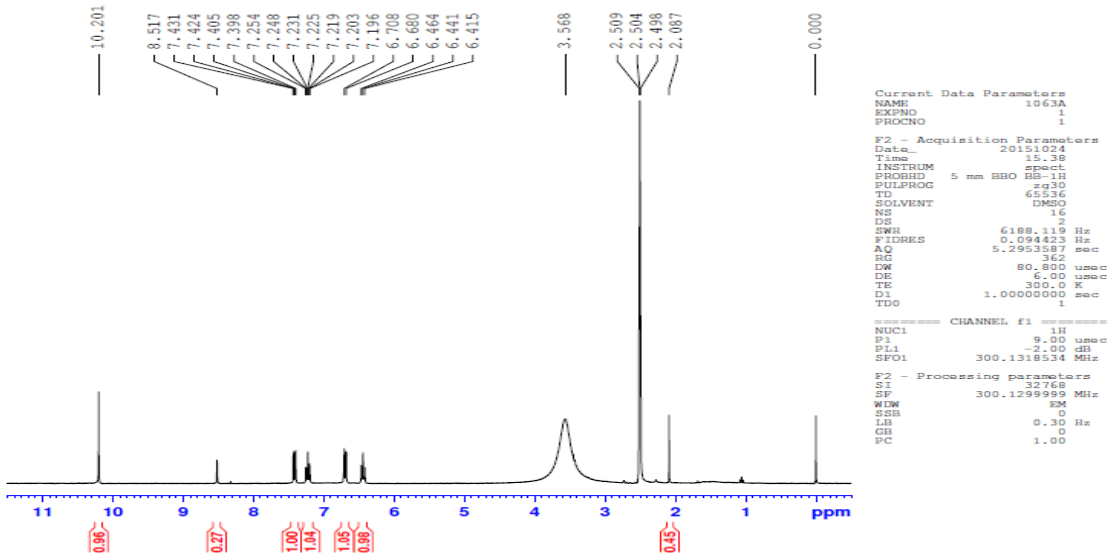


Fig. 1: NMR spectra of the ligand

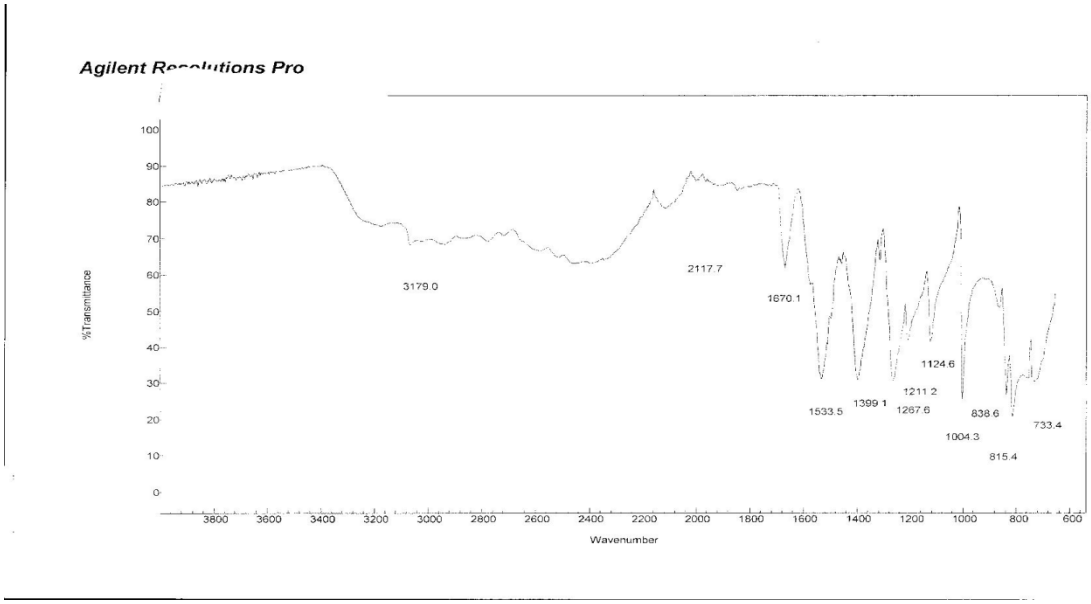


Fig. 2: IR Spectra of the ligand

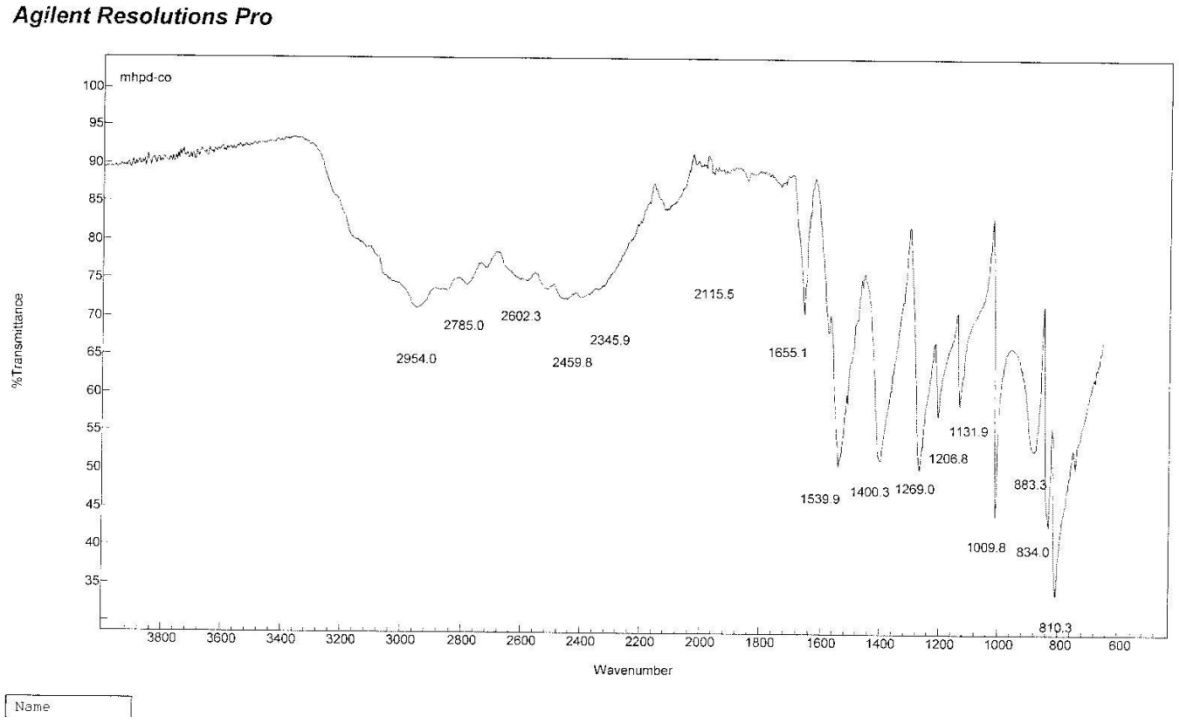


Fig. 3: IR Spectra of the metal Complex

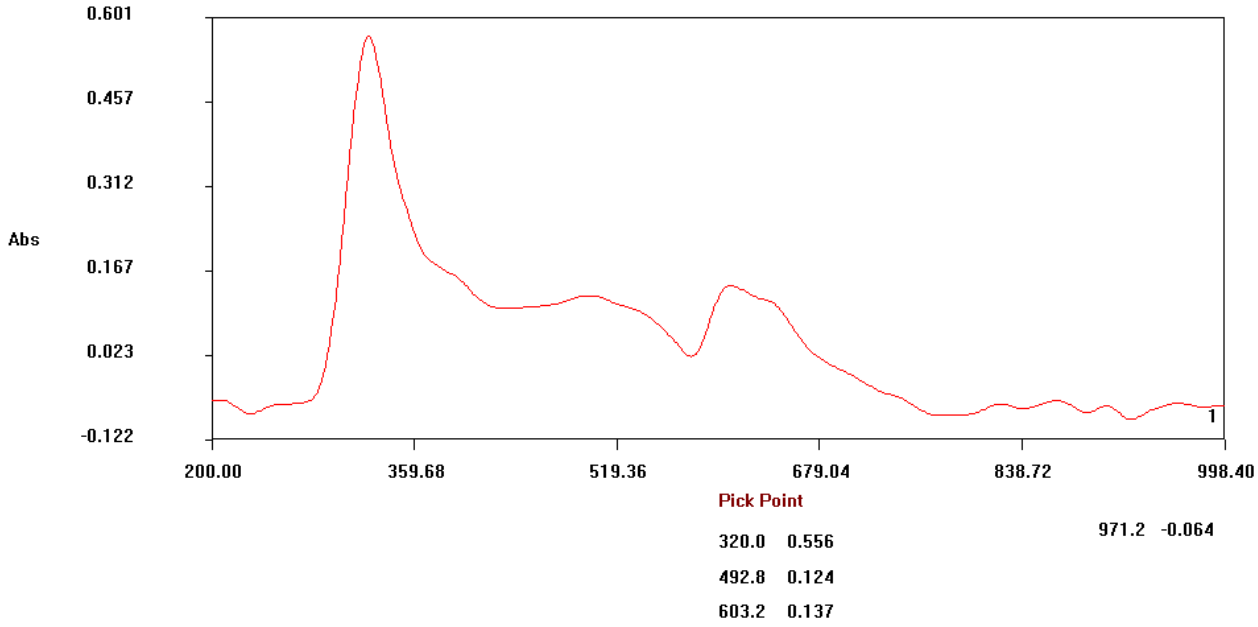


Fig. 4: UV Spectra of the metal complex

Table 1: Physical data of the ligand and the complexes

Compund	Yield (%)	Colour	Mp (°C)
SAMP Ligand	78	Colorless	253
SAMP-Co	75	Pale pink	255
SAMP-Ni	72	Pale green	232
SAMP-Cu	68	Pale blue	246

Table 2: IR Spectral data of the ligand and the complexes

Compound	IR Stetching Frequency (in cm^{-1})			
	-C=O	-CNC	M-N	M-O
SAMP Ligand	1670	1211	----	----
SAMP-Co	1655	1206	883	810
SAMP-Ni	1654	1207	882	808
SAMP-Cu	1655	1207	883	808

Table 3: Antibacterial activity

S. No.	*Bacteria*	Standard Antibiotic Disk(Ciprofloxacin)	Zone of inhibition mm in diameter (10µg/disc)			
			SAMP-L	SAMP-Co	SAMP-Ni	SAMP-Cu
1	*Staphylococcus aureus*	21	10	15	13	17
2	*Bascillussubtilis*	16	12	17	15	19
3	*Escherichia coli*	26	09	19	12	16
4	*Pseudomonas aeruginosa*	18	08	13	14	17

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