

Transition Metal Complexes of Novel Mannich Base Derived From Salicylideneacetone Spectral and Antimicrobial Study

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Abstract: In this study, we report the synthesis of a novel Mannich base, salicylideneacetone methyl dimethylamine (SAMDM), and its transition metal complexes. Salicylideneacetone, a condensation product from salicylaldehyde was used as a precursor and treated with formaldehyde and dimethylamine. The so formed base is complexed with transition metals. The progress of the reaction was monitored by TLC. The structure of the synthesized compounds are confirmed by UV, IR, and ¹H NMR spectroscopic techniques. The free ligand as well as the metal complexes were subjected to antimicrobial activity against gram positive and gram negative bacteria.

Keywords: Antimicrobial activity, Dimethylamine, Formaldehyde, Mannich base, Salicylideneacetone

I. Introduction

Chelating agents derived from organic compounds containing amide moiety as a functional group have a strong ability to form metal complexes and exhibit a variety of biological activities such as antibacterial, antifungal, anti tuberculosis activity, anti HIV activity, antiviral, antiulcer, anti-hypertensive [1- 7]. A number of studies have been done in the various mannich base complexes formed by the condensation of secondary amines with different aldehydes and amides [8-11]. From the survey of existing literature, it appears that metal complexes of mannich bases played a vital role in the development of coordination chemistry and their analytical utility in the determination of both transition and non transition metal ions is well established. Literature studies revealed that during the past decades, there has been a great deal of interest in the synthesis and structural elucidation of transition metal complexes containing amide moiety. However, there is no study on any metal complexes of Salicylideneacetone methyl dimethylamine. In the present work, we described synthesis, characterization and biological studies of new mannich base Salicylideneacetone methyl dimethylamine. derived from the condensation of salicylideneacetone, formaldehyde and dimethylamine and its metal complexes obtained with Cu (II), Ni (II), and Co (II) metals.

II. Experimental

2.1 Materials and methods

Reagents such as salicylaldehyde, acetone, formaldehyde and dimethylamine were of Merck products and were used as such. The melting point of all the synthesized compounds were 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 Perkin-Elmer FT-IR spectrophotometer using KBr pellets and ¹H 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 in 1:1 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 spirit. The sample was dried in vacuo over fused calcium chloride and then analysed. The scheme for this reaction is shown Fig.1

2.2.2 Synthesis of Salicylideneacetone methyl dimethylamine (SAMDM)

0.1 mol of Dimethylamine (1mL) and 0.1 mol of Formaldehyde (2 mL) are dissolved in 50mL of ethanol and taken in a 100mL RB flask. The contents of the flask are stirred well using magnetic stirrer for about 2 hrs and kept in ice bath for overnight. Then 0.1 mol of the Salicylideneacetone is added gradually with constant stirring to the reaction mixture kept in ice bath and the stirring was continued for about 1hr. Then it is kept in refrigerator for overnight. Then the contents are refluxed in 50mL alcohol for about 4hrs. After that it is kept in refrigerator for overnight. 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%. The scheme of this reaction is given in Fig. 2.

2.3 Synthesis of complexes

Hot ethanolic solution of the ligand (1 equivalent) was slowly mixed with hot ethanolic solution of metal chloride (1 equivalent) under reflux condition with constant stirring. The mixture was refluxed 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. The physical data of the synthesized ligand and the complexes are tabulated in Table.1.

III. Results and Discussion

3.1 ¹H NMR Spectra

The ¹H NMR spectra (Fig.3) of the Mannich base under study exhibit a multiplet at 7.2-7.5ppm for the hydrogens of the aromatic rings. The appearance of peaks at 2.1 & 4.2 ppm indicates the methylene hydrogens & methyl hydrogens respectively. Further, the formation of the ligand is ascertained by the disappearance of a signal at ~6.5 ppm corresponding to the –NH proton of secondary amine as it was eliminated in the Mannich reaction.

3.2 IR Spectra

From the IR spectra of the ligand (Fig.4), important observation is made as the presence of an intense band at ~ 1656 cm⁻¹ which is due to νC=O carbonyl group. The most notable change in the IR spectra is the disappearance of the –NH stretching vibration and appearance of an intense band at ~ 1229 cm⁻¹ due to νC-N stretching. The absence of band at 3300 cm⁻¹ due to amino –NH disappears implying its condensation after deprotonation. In the case of the complexes (Fig.5), 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 748 cm⁻¹ corresponding to M-O bond and a signal at 424cm⁻¹ corresponding to M-Cl bonds. The presence of coordinated water molecules is determined by the presence of bands around 3440cm⁻¹ and a band at 852 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 were recorded in the range of 200-1100 nm. The Cu (II) complex (Fig.6) under the present study exhibits a broad band in the region 26336 cm⁻¹. due to transition between ²E_g → ²T_{2g} which indicated octahedral geometry. Co (II) complex displays bands at 25650 cm⁻¹ and 30120 cm⁻¹ were assigned to ⁴A_{2g} → ⁴T_{1g} and ⁴A_{2g} → ⁴T_{2g} transitions supported tetrahedral geometry. The Ni (II) complex showed broad bands at 25764cm⁻¹ and 30310 cm⁻¹ which is assigned to ³A_{2g} → ³T_{1g} and ³A_{2g} → ³T_{2g} transition respectively confirmed the octahedral geometry. Based on the foregoing results we suggest the structure (Fig.7) for the complexes synthesized using the Mannich base ligand.

3.5 Antimicrobial activity

For the antibacterial study, nutrient agar was used as the medium. All the compounds were screened for antibacterial activity against certain pathogenic bacteria by disc diffusion method at concentration of 10µg / ml in DMSO using gram positive *Bascillus subtilis*, *Staphylococcus aureus*, and gram negative *Proteus vulgaris*, *Klesiella pneumoniae* The zone of inhibition was measured in mm and the activity was compared with Gentamycin in 1 µg / disc. The results are tabulated in Table 3. From the results it may be observed that the complexes are possessing better activity against both types of bacterias than the free ligand. Among them, copper complex has more active than all other complexes.

IV. Figures and Tables

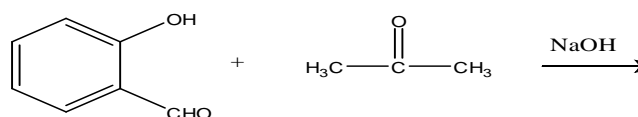


Fig. 1 Scheme of the reaction – formation of Salicylideneacetone

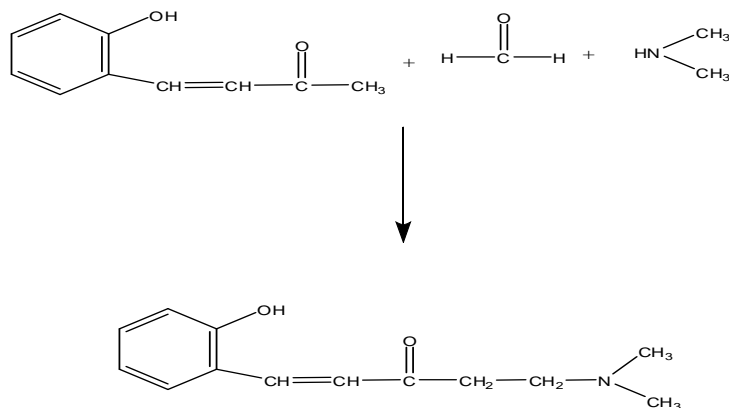


Fig. 2 Scheme of the Mannich Reaction

Table .1 Physical data of the ligand and complexes

Compound	Colour	Yield %	MP (°C)
SAMDMA - Ligand	Brownish	72	184
Cu-SAMDMA	Green	64	220
Co-SAMDMA	Pale pink	56	246
Ni-SAMDMA	Pale green	62	262

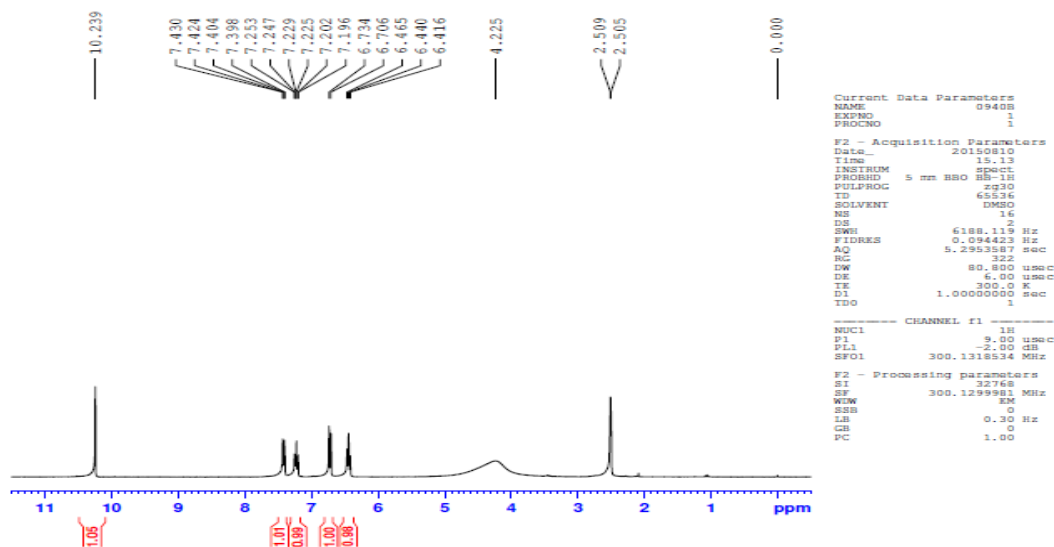


Fig.3.. ¹H NMR Spectra of the ligand

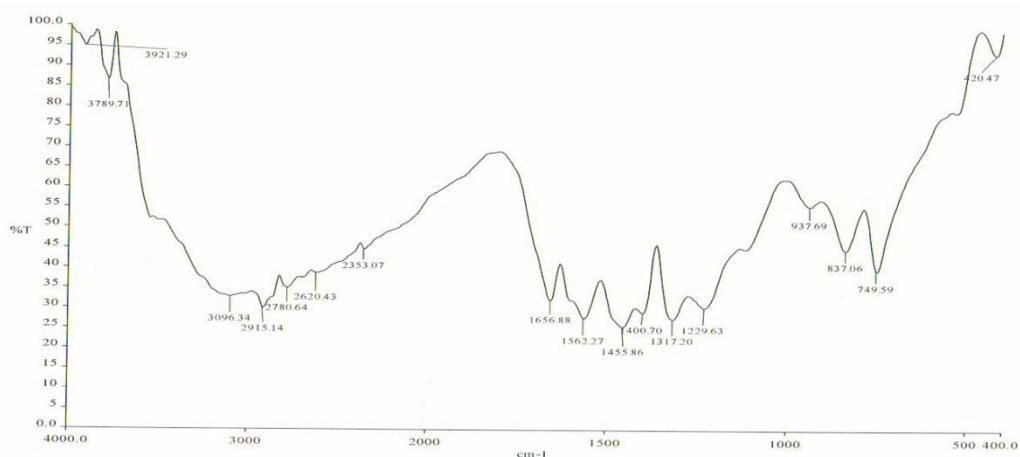


Fig.4 IR Spectra of the ligand

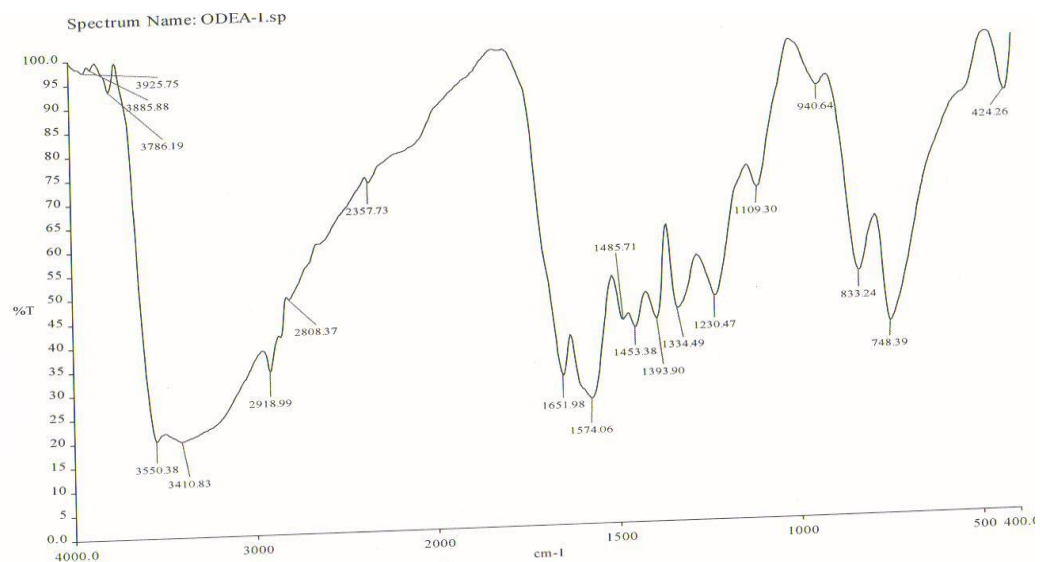


Fig.5 IR Spectra of the complex

Table 2. IR Spectral data

Compound	Vibrational frequency of various functional groups (in cm^{-1})				
	-OH	>C = O	-CNC	M-O	M-Cl
SAMDMA	3096	1656	1229	----	---
Cu-SAMDMA	3410	1651	1109	748	424
Co-SAMDMA	3415	1602	1118	753	493
Ni-SAMDMA	3435	1648	1114	748	425

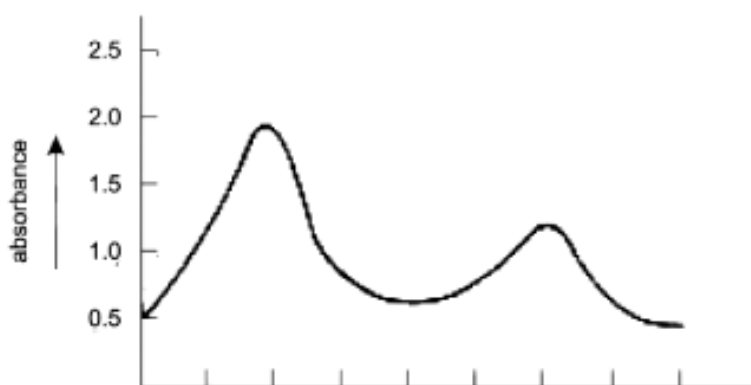


Fig.6 UV Spectra of the complex

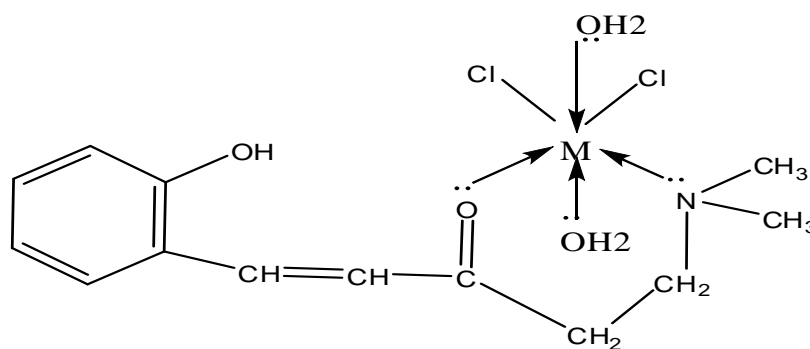


Fig.7 Suggested structure of complexes

Table 3: Antibacterial activity

Sl. No.	Bacteria	Standard Antibiotic Disc (Gentamycin)	Zone of inhibition mm in diameter (10 µg/disc)			
			SAMDM-L	SAMDM-Co	SAMDM-Ni	SAMDM-Cu
1	<i>Staphylococcus aureas</i>	22	10	14	14	15
2	<i>Bascilla susbtilis</i>	16	12	14	16	17
3	<i>Proteus vulgaris</i>	28	16	19	16	19
4	<i>Kllesiella pneumoniae</i>	16	12	15	14	19

V. Conclusion

We can come to a conclusion that the ligand behaves as a bidentate neutral chelating agent through the ketonic oxygen and the amino nitrogen atoms. Further, the spectroscopic data is in support of our proposed structure. The antimicrobial property of the complexes against both types of bacterias were better than that of the free ligand observed.

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