Microwave Synthesis, Characterization, Electrochemistry and Antimicrobial Activity of Manganese Acyclic Schiff Complexes

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Abstract— **A series of Manganese (II) Schiff base complexes were synthesized by microwave irradiation method, the Schiff bases are derived from substituted salicylaldehyde With 1,4-diaminobutane and o-phenylnediamine. The manganese complexes were characterized by UV-Visible, Infrared (FT-IR) and Electron Paramagnetic Resonance (EPR) spectroscopic techniques. The electrochemical redox behaviour of manganese complexes were analyzed by cyclic voltammetry (CV). The manganese complexes show good antimicrobial activity against the following microorganisms: E.coli, S.typhi, S.aureus, S.typhi ParaA and P.aeruginosa. The antimicrobial activity of the complexes was varied based on the ligand structure. The high activity is shown against Salmonella typhii.**

Keywords- Manganese Schiff base complex, microwave synthesis, antimicrobial activity,

I. INTRODUCTION

Manganese complexes with salen-type ligands have been extensively studied mainly due to their biological importance, catalytic applications, photocatalytic water splitting, and magnetic property. The manganese Schiff base complexes in different oxidation states are having major important roles in metalloenzymes, redox and non-redox proteins [1-3]. In addition to this an interest was shown to use the manganese complexes for MRI applications and it has been approved for clinical practice. In the MR imagining, manganese complexes show sufficient difference with the Gd metal complexes. In fact, while Gd-complexes are designed to maintain their integrity and to be excreted as they are, Mn-DPDP (manganese dipyridoxal diphosphate) generates relaxation mainly after release of manganese (II) ions which are coordinated by bio macromolecules, these ions are picked up by macromolecular structures generating really high relaxivities and strong contrast in MR images [4]. Halogenated salicylaldehyde Shiff base derivatives and their metal complexes show biological activities such as antitumor, antibacterial, antifungal activities and anti-carcinogenic properties. These studies show that the Schiff bases of 5-bromo salicylaldehyde would possess potential antimicrobial properties [5]. Designing new kind of manganese Schiff base complexes with halogenated salen derivatives are becoming more important in biological field. In the present work we synthesized manganese Schiff base complexes by the green chemical method with the help of microwave irradiation. This method gives high yield and cost effective. The halogenated salen derivatives synthesized from the diamines (1,4-diaminobutane and o-phenyldiamine) and substituted salicylaldehyde like 5-methylsalicylaldehyde, 5-bromosalicylaldehyde and salicylaldehyde. The manganese Schiff base complexes have been tested in vitro to assess their antibacterial activities against some common reference bacteria and the results were compared with similar doses of commercial antibiotic Ciprofloxacin.

II. EXPRIMENTAL

A. Reagents

5-methylsalicyaldehyde was prepared by the following literature method, 5-bromosalicylaldehyde was purchased from sigma Aldrich, salicylaldehyde was purchased from Alfa Aesar, the 1,4-diaminobutane was Sisco Research Laboratories and o-phenyldiamines were purchased from Quilogens. All the solvents were purchased Commercially and used without purification.

B. General synthesis of 5-methylsalicylaldehyde

A mixture of glycerol (150 g, 1.63 mol) and boric acid (35 g, 0.76 mol) were heated for 30 min at 170 °C to expel the water. Then a mixture of 4-methylphenol (25 g, 0.23 mol) and hexamethylenetetramine (25 g, 0.18 mol) was added. The mixture was stirred for 15 min. The thick brown liquid obtained was allowed to cool to 110 °C. A solution of concentrated sulphuric acid (30 mL) in water (70 mL) was added and the whole mixture was boiled in a current steam. The product was collected by steam distillation. The solid obtained was recrystallized from 75mLof 80% ethanol. Yield: 8.2 g (26%) M.P.: 55 °C.

C. Synthesis of Schiff base Ligands

An absolute solution of substituted salicylaldehyde [5-methylsalicylaldehyde (0.272g, 2 mM) or 5-bromosalicylaldehyde (0.402g 2mM) or Salicylaldehyde (0.243g 2mM)] in 5ml of methanol was added drop wise with the stirred solution of 1,4-diaminobutane(0.088g, 1mM) in 5ml of methanol. It was stirred about 30 min. The solution was allowed to microwave irradiation 160 W at 5 min and cooled to room temperature, yellow colour precipitate was appeared, it was filter and recrystallized by methanol. Reaction procedure was repeated instead of 1 mM 1,4-diaminobutane by 1 mM of o-phenyldiamine. Scheme for the Schiff base synthesis was shown in the following Figure-1.

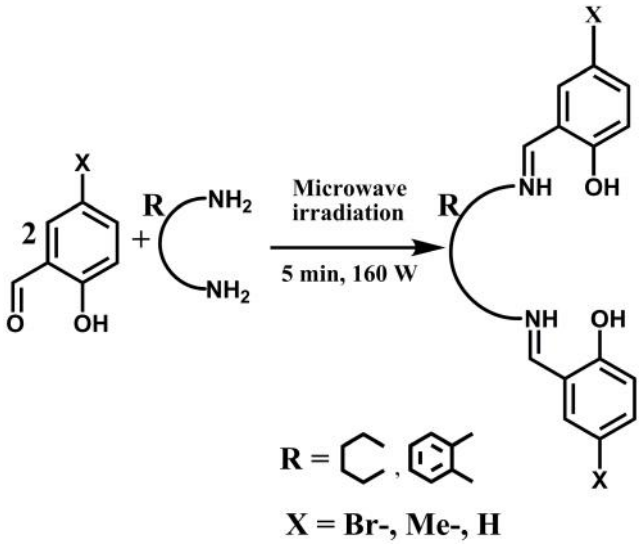

FIGURE-1: SYNTHESIS OF SCHIFF BASE LIGAND

D. Synthesis of Manganese Schiff base complexes

An absolute solution of Manganese(II)chloride tetrahydrate (0.198g 1mM) in 5ml of methanol was added with the stirred solution of 1 mM Schiff base ligands . The mixture of solution was kept on stirring 30 min. The solution was allowed to microwave irradiation 320 W at 7 min and cooled to room temperature, brown precipitate was appeared, it was filter and recrystallized by mixing solution of methanol and dichloromethane in 1:1 ratio. Complex formation was shown in the Figure-2.

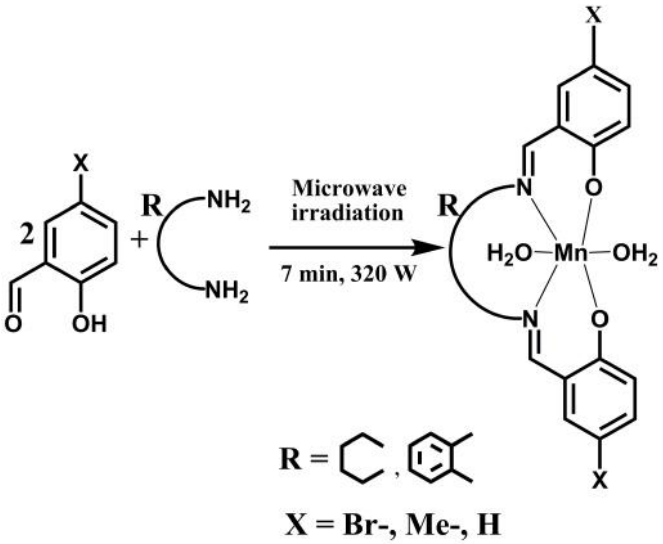

Figure-2: SYNTHESIS OF MANGANESE SCHIFF BASE METL COMPLEXES

E. Antibacterial activity

Newly synthesized compounds were screened for their in vitro antibacterial activity by agar well diffusion method against five bacterial strains viz., E.coli, S.typhi, S.aureus, S.typhi ParaA and P.aeruginosa. The bacteria were cultured for 24 h at 37 0C in an incubator. Stock solutions of the compounds were prepared by dissolving (2 mg/ml) it in DMSO solvent. The agar medium was prepared and autoclaved at 121 0C for 15 min. The autoclaved medium was mixed well and poured onto a pre-sterilized petridish. Petridishes containing nutrient Muller Hinton medium were seeded with 24 h culture of bacterial strains using sterile L-rod. Wells were punched using a sterile cork borer and 10 µg/ml of the compound was added from stock solution. The inoculated plates were incubated for 24 h at 37 0C. After incubation, the diameter of the inhibition zone was measured and the results were recorded in millimeters (mm). Each solvent extracts were tested separately in triplicates. The antimicrobial screening concentrations of the compounds were estimated from the minimum inhibitory concentration (MIC). MIC is the lowest concentration of antimicrobial complex that will inhibit the growth of microorganisms [6].

III. RESULT AND DISSCUSION

A. FT-IR SPECTRAL ANALYSIS

The FT-IR spectra of the Manganese complexes are shown Figure-3. In the IR spectra the [ν (C=N)] absorption band shifted towards the lower frequencies due to the bond formation between the imine group nitrogen with the central metal ion. This peaks are appeared around 1610-1650 cm^{-1}. The azomethine nitrogen binds with the manganese ion through its lone pair of electrons. This azomethine nitrogen and carbon double normally appeared at 1690-1700cm^{-1}, in the Schiff base complexes this band appears at the lower frequencies, it shows that the complexation of the nitrogen atom with the manganese metal ion [7] . If there is any substitution in the para position of phenyl ring a strong peak appeared at the range of 810-850cm^{-1}, in these IR spectra a strong peak exhibit at the 810-840cm^{-1} it shows that the presence of para substitution in phenyl ring, i.e., 5-substituted salicylaldehydes. The complex formation was confirmed by the presence of peaks in the region of 650-700cm^{-1}, this peak suggest the bond formation between the manganese metal ion with the oxygen atom ν (Mn-O) [8].

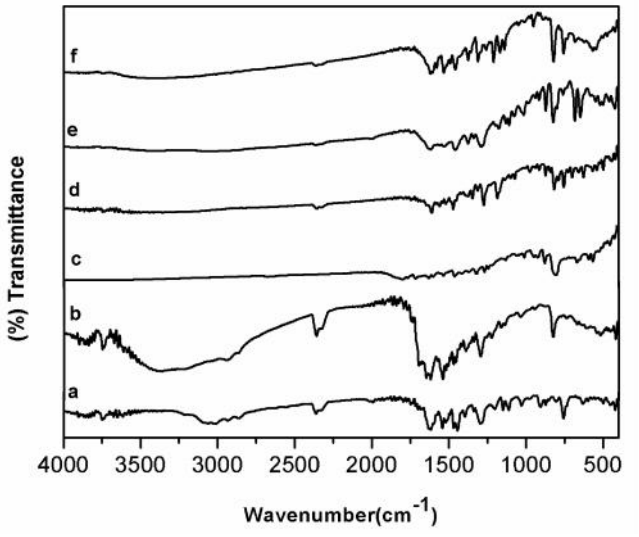

Figure -3: FT-IR spectra of Mn Schiff base complexes

B. Electronic Spectrial analysis

The electronic spectra of the Schiff base and their manganese complexes are recorded in the range of 200-800 nm, in the methanol solution. The spectra are recorded in Perkin Elmer Lambda instrument. The electronic spectra of the manganese Schiff base complexes shows a broad absorbance peak at 320-340 nm is exhibit the n → π* transition of the organic moieties present in the complexes. In the electronic spectra a band appeared at the range of 240-300 nm is suggest that the electronic excitation from π to π* transition, i.e., π → π*. The d-d transition of the cobalt metal ion is exhibit in the region of 400-470nm. The characteristic transitions suggest

the geometry of the manganese Schiff base complexes is octahedral geometry. The complexes are in high spin and the, calculated magnetic momentum is 5. 92 BM, it highly matched with the observed magnetic momentum of manganese Schiff base complexes [9].

C. EPR spectral analysis

The EPR spectra of the synthesized manganese Schiff base complexes are recorded at solution phase in methanol solvent, and normal room condition. The EPR spectrum of the manganese complex was shown Figure-4. The liquid state EPR spectrum of complex 1 and 2 at 298 K is characterized by a broad signal with g value of 2.156. However, in the spectrum of 2, in addition to the signal at 2.018, there is another broad weak signal with g value of 2.345. The g values indicate that the Mn(II) in these complexes are rhombically distorted. Manganese hyper-fine splitting is not observed in the spectra of any of these complexes. The observed g values are very close to the free electron spin value, suggestive of the absence of spin orbit coupling in the ground state. Also they are in agreement with the values reported previously for structurally similar Mn(II) complexes and is indicative of the distorted octahedral geometry of Mn(II) [10,11]

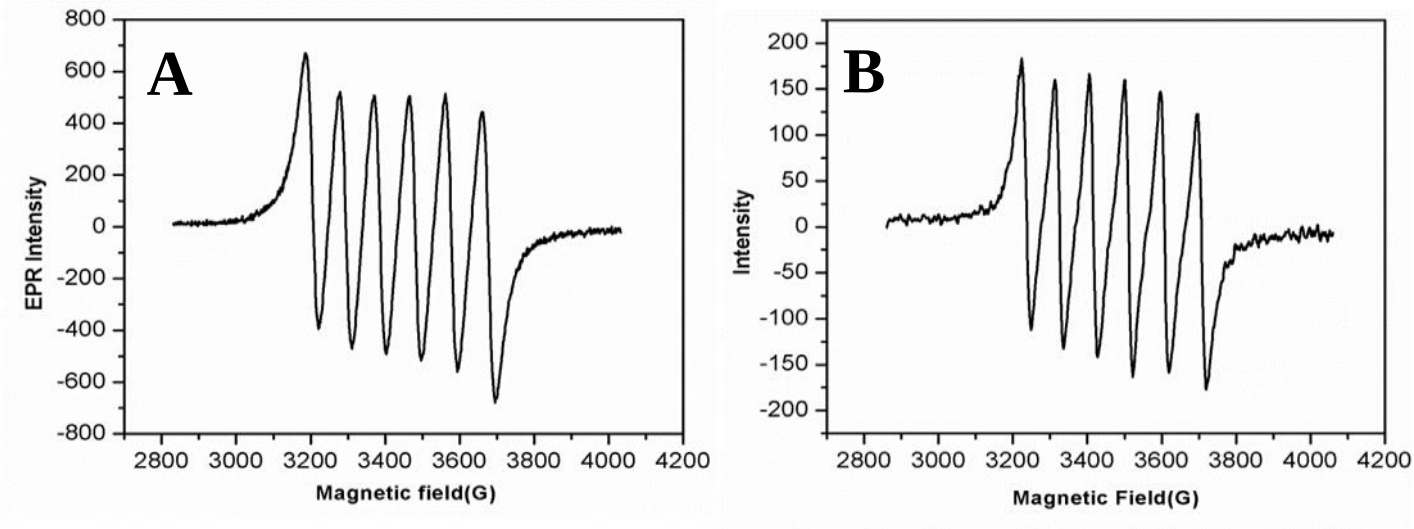

Figure – 4: EPR spectra of A) N,N'-bis(5-methylsalicylidene)-1,4-diaminobutane, B) N,N'-bis(5-bromosalicylidene)- o-phenylenediamine manganese complexes

D. Electrochemical Studies

The redox behaviour of the manganese Schiff base complexes are examined by cyclic voltammetry, in three electrode system. The glassy carbon electrode was the working electrode, silver and silver chloride (Ag/AgCl) was the reference electrode and platinum wire used as counter electrode. Voltammetry measurement was carried in the acetonitrile solution. The TBAP was used as supporting electrolyte. The obtained cyclic voltammograms was explained the electrochemical properties and redox level of the manganese metal ion. The metal ion has positive potential, it shows that the central metal ion has lower oxidation state and strongly binds with the ligand. It reveals that central metal ion have equal approach towards donor atoms. The manganese Schiff base complexes show one oxidation potential, and two reduction potential. Cyclic voltammogram of manganese complexes show one oxidation wave one at 0.440- 0.850 V due the oxidation of Mn(II)/Mn(IV). It gives a broad peak hence it shows that the two electron transfer process. The manganese complexes show two reduction processes. It reviles that the reaction carries via Mn(IV)/Mn(III) and Mn(III)/Mn(II). Each reduction process takes via one electron transfer. The two reductions appear around 0.7 V and 0.1 V. All the complexes show the electrochemical active of the central metal ion Mn(II) [12].

E. Antibactrial activity

The in vitro antibacterial activity of the manganese Schiff base complexes were screened separately against five human pathogenic bacteria (E.coli, S.typhi, S.aureus, S.typhi ParaA and P.aeruginosa..,) by well diffusion method. The manganese (II) complexes showing highest activity against Salmonella typhii at the concentration of 125 µM. Complex $[Mn(II)L^5]$ has the highest antimicrobial activity against all the organisms, in contrast $[Mn(II)L^2]$ showed the lowest antimicrobial activity. The data are given in Table - 1. This difference in inhibition may be due to the differences between the cell structures of bacteria, yeast, and not depend upon the

number of alkyl group present in the complex. In addition, the difference in the antibacterial activity of manganese (II) complexes studied in this work probably is associated to ligand type and its space distribution around the complex core [13]. The inhibition activity of the complex was determine by measuring the size of inhibition diameter. The inhibition zone of bacteria in all compounds are given in Table 1. The obtained results suggest that the metal complexes are less active than the standard against all the bacteria tested. The antibacterial activity varied in the metal complexes due to their impermeability of the cell or the differences in ribosome in microbial cell [14]. Antibacterial activity of the complexes are affected by the hydrogen formation between imine nitrogen with active centers of cell constituent.

Table 1: Antimicrobial activity (MIC) of [Mn(II)L^1- Mn(II)L^6] complexes

Complex		E.coli	S.typhi	S.aureus	S.typhi ParaA	P.aeruginosa
MnL^1	25	3.00 ±1.0	4.00 ±1.0	5.00 ±1.0	8.00 ±1.0	-
	50	4.00 ±1.0	4.00 ±1.0	6.00 ±1.0	8.00 ±1.0	-
	75	5.00 ±1.0	5.00 ±1.0	6.00 ±1.0	9.00 ±1.0	-
	100	6.00 ±1.0	6.00 ±1.0	7.00 ±1.0	10.00 ±1.0	-
	125	6.00 ±1.0	7.00 ±1.0	8.00 ±1.0	10.00 ±1.0	-
MnL^2	25	0.50 ±0.0	3.00 ±1.0	2.00 ±1.0	0.60 ±0.0	2.00 ±1.0
	50	0.60 ±0.0	4.00 ±1.0	2.00 ±1.0	0.80 ±0.0	3.00 ±1.0
	75	0.60 ±0.0	6.00 ±1.0	3.00 ±1.0	0.90 ±0.0	4.00 ±1.0
	100	0.80 ±0.0	6.00 ±1.0	4.00 ±1.0	1.00 ±0.0	4.00 ±1.0
	125	1.00 ±0.0	6.00 ±1.0	5.00 ±1.0	1.00 ±0.0	5.00 ±1.0
MnL^3	25	6.00 ±1.0	8.00 ±1.0	2.00 ±1.0	-	2.00 ±1.0
	50	7.00 ±1.0	8.00 ±1.0	2.00 ±1.0	-	4.00 ±1.0
	75	8.00 ±1.0	9.00 ±1.0	3.00 ±1.0	-	5.00 ±1.0
	100	8.00 ±1.0	10.00 ±1.0	4.00 ±1.0	0.50 ±0.0	6.00 ±1.0
	125	9.00 ±1.0	10.00 ±1.0	5.00 ±1.0	0.50 ±0.0	7.00 ±1.0
MnL^4	25	4.00 ±1.0	5.00 ±1.0	-	0.00 ±0.0	0.30 ±0.0
	50	5.00 ±1.0	6.00 ±1.0	-	0.00 ±0.0	0.50 ±0.0
	75	6.00 ±1.0	7.00 ±1.0	-	0.00 ±0.0	0.60 ±0.0
	100	7.00 ±1.0	8.00 ±1.0	-	0.00 ±0.0	0.80 ±0.0
	125	7.00 ±1.0	9.00 ±1.0	0.00 ±0.0	0.00 ±0.0	0.90 ±0.0
MnL^5	25	9.00 ±1.0	12.00 ±1.0	7.00 ±1.0	6.00 ±1.0	5.00 ±1.0
	50	10.00 ±1.0	13.00 ±1.0	8.00 ±1.0	6.00 ±1.0	6.00 ±1.0
	75	10.00 ±1.0	15.00 ±1.0	8.00 ±1.0	7.00 ±1.0	7.00 ±1.0
	100	11.00 ±1.0	16.00 ±1.0	9.00 ±1.0	8.00 ±1.0	7.00 ±1.0
	125	12.00 ±1.0	18.00 ±1.0	10.00 ±1.0	8.00 ±1.0	8.00 ±1.0
MnL^6	25	2.00 ±1.0	4.00 ±1.0	0.00 ±0.0	-	-
	50	2.00 ±1.0	5.00 ±1.0	0.00 ±0.0	-	-
	75	3.00 ±1.0	6.00 ±1.0	0.00 ±0.0	-	-
	100	4.00 ±1.0	6.00 ±1.0	0.00 ±0.0	0.00 ±0.0	-
	125	5.00 ±1.0	7.00 ±1.0	1.00 ±0.0	0.00 ±0.0	-

IV. CONCULUTION

In summary, we have synthesized Schiff base and their manganese complexes were synthesized by microwave irradiation method and characterized their structural properties. The spectral studies suggest that the Schiff base have tetradentate nature and coordinate with manganese ion. The results indicate that Mn(II) complex show octahedral geometry. Antibacterial activity of the synthesized complexes was investigated from the result the 5-bromo substituted manganese [MnL^5] has better inhibition activity against all the five bacteria. All the complexes show good inhibition activity against S.typhi.

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