IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

SYNTHESIS AND CHARACTERIZATION OF NOVEL COMPLEXES OF Mn(III), Co(II), Cu(II) AND Zn(II) WITH SCHIFF BASE DERIVED FROM 1,2-BIS (*p*-AMINOPHENOXY) ETHANE AND 5-METHYL SALICYLALDEHYDE

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Abstract: Several novel complexes of Schiff base ligand were prepared and synthesized by the condensation of 1, 2-Bis (p-aminophenoxy) ethane and 5-methyl salicylaldehyde. Characterization of complexes has been done on the behalf of several parameter including magnetic measurements, elemental analyses, $^1\boldsymbol{H}$ NMR, UV-VIS and IR spectra. Schiff base ligand is coordinated to central metal as a tetradentate ONNO ligand. Azomethine nitrogen and $\boldsymbol{o-OH}$ groups are the four bonding sites.

Index Terms **- Schiff base, Tetradentate, NMR**

I. INTRODUCTION:

Schiff base ligand derived from aliphatic/aromatic amines and aromatic aldehydes represent a very important series of broadly studied organic ligands. Schiff base ligand and appropriate transition metal complexes are found to be of a fascinating interest in the field of inorganic chemistry [1-7]. Some Schiff base complexes are recognized to exhibit antifungal activity which intensified by presence of OH group. Consequently it is valuable thought to synthesize Schiff base complexes with hydroxo substituent on phenyl and heterocyclic rings [7-14]. Synthesis of Mn(III), Co(II), Cu(II) and Zn(II) complexes with Schiff base ligand were derived from the condensation of 1, 2-Bis (p-aminophenoxy) ethane and 5-methyl salicylaldehyde. Characterization of the complexes has been done on the basis of magnetic measurements, elemental analyses, 1H NMR, UV-VIS and IR spectra.

II. EXPERIMENTAL:

1, 2-Bis (p-aminophenoxy) ethane and 5-methyl salicylaldehyde were obtained according to literature [15]. N.N'-1,2-Bis(5-methyl salicylidene)-1,2–bis-(p-aminophenoxy) ethane was synthesized here for first time. Electronic spectra of complexes in UV Visible region were noted in DMF solution using Shimadzu model 160. UV visible spectrophotometer, IR Spectra of Complexes in pellets of KBR where recorded with Midac 1700 instrument. ^1H NMR Spectra in DMSO-d6 was recorded on Bruker GmbH DPX-400 Mhz. Digital FT NMR Spectrometer; magnetic susceptibility was measured on Sherwood scientific magnetic susceptibility balance (Model No-MK1) at 25 degree Celsius. Utilizing $Hg[Co(SCN)_2]$ as calibrant. Diamagnetic correlation was calculated by Pascal's Constant.

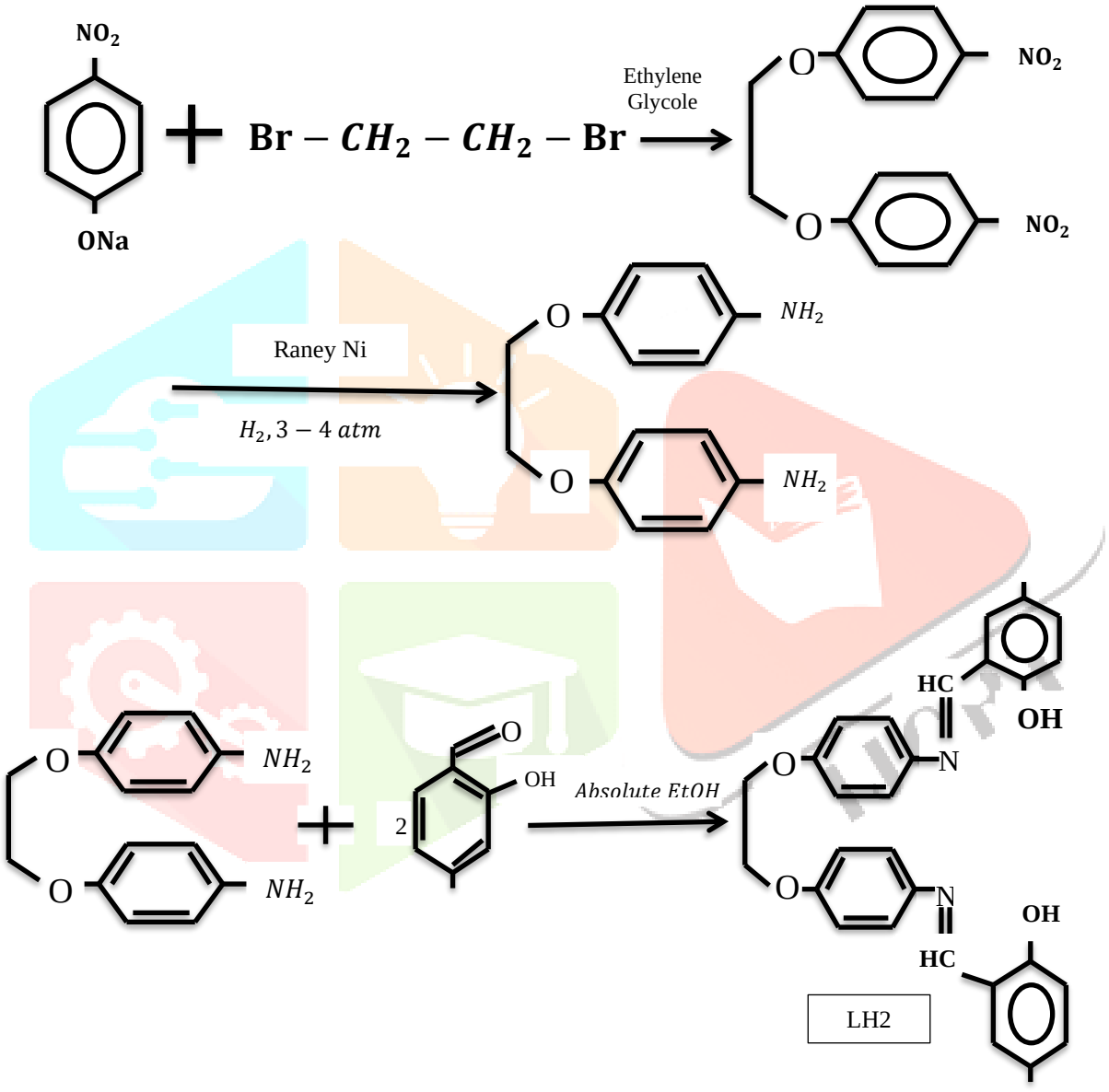
a) **SYNTHESIS OF LIGAND**:- 5-methyl salicylaldehyde (10.00mmole,1.06g) was added in 25 ml absolute ethanol drop wise over 5 hour to stirred solution of 1,2-bis(p-aminophenoxy) ethane (5.00 mmole,1.22g) in absolute 25 ml warm ethanol on cooling a solid mass was separated out[16]. That was kept in refrigerators for the better crystallization. Then it was filtered washed with EtOH, Et_2O and subsequently dried over $CaCl_2$ anhydrous in desiccator. The ligand was insoluble in all common organic solvent (acetone, alcohol, benze etc.) and soluble in polar solvent (DMF and DMSO).Yellow imines were purified recrystallization with DMF.

b) **SYNTHESIS OF COMPLEXES:** - Solution of metal acetate (20.00 mmole) with DMF(50ml) was mixed in Schiff base (20.00 mmole is to 9.04 gram) with DMF (50ml) in 1:1(M:L) ratio and content was heated in oil bath for 2,3 hours[16]. Than refluxed solution was poured into ice cold water, when colored solid separated out. Which was segregated by filtration and washed with Et_2O

Resulting Solid was recrystallized in 25 ml $(CH_3)_2SO$/25 ml (DMSO) and dried over $CaCl_2$ anhydrous in vacuum at room temperature. Yield was 55-60 percentages in all complexes with respect to ligand. They decompose at 280 Celsius which is insoluble in water approximately, but Sparingly Soluble in polar solvent (DMSO and DMF).

III. RESULT AND DISCUSSION;

1, 2-Bis (p-nitrophenoxy) ethane has been synthesized from the reaction of sodium *p*-nitrophenolate and 1, 2-Dibromoethane. In 2nd Step 1, 2-Bis (*p*-phenoxy) ethane was obtained from the reaction of 1,2-Bis(*p*-nitrophenoxy) ethane and Raneynickel as a catalyst. In 3rd step N,N'-Bis(5-methyl salicylidene)-1,2-Bis(*p*-aminophenoxy) ethane was obtained by the reaction of 1,2- Bis(*p*-aminophenoxy) ethane and 5-methyl salicylaldehyde.



Synthesis scheme for preparation of ligand (LH2) described above

Characterization of the three compounds has been done on the basis of IR and ^1H NMR analytical data and other data are given in Table 1, 2.

Table 1. The Formulas, and Elemental analyses Results of the ligand and the complexes

Compounds	Elemental Analyses Calculated (found), Percentage				
	C	H	N	$\mu_{eff}(B.M)$	M
Ligand(LH_2) $C_{30}H_{30}N_2O_4$	74.64 (74.66)	6.23 (6.25)	5.81 (5.83)		
CuL $C_{30}H_{28}N_2O_4Cu$	66.64 (66.66)	5.11 (5.12)	5.11 (5.13)	2.01	11.71 (11.72)
MnL(OH) $C_{30}H_{29}N_2O_5Mn$	65.55 (65.56)	5.21 (5.24)	5.11 (5.14)	4.86	9.95 (9.97)
CoL $C_{30}H_{28}N_2O_4Co$	67.75 (67.77)	5.21 (5.23)	5.22 (5.23)	4.45	11.11 (11.12)
ZnL $C_{30}H_{28}N_2O_4\ Zn$	66.61 (66.63)	5.11 (5.12)	5.12 (5.13)	Dia	12.10 (12.12)

Table 2. Characteristic IR Bands(cm^{-1}) of the ligand and complexes in KBr pellets

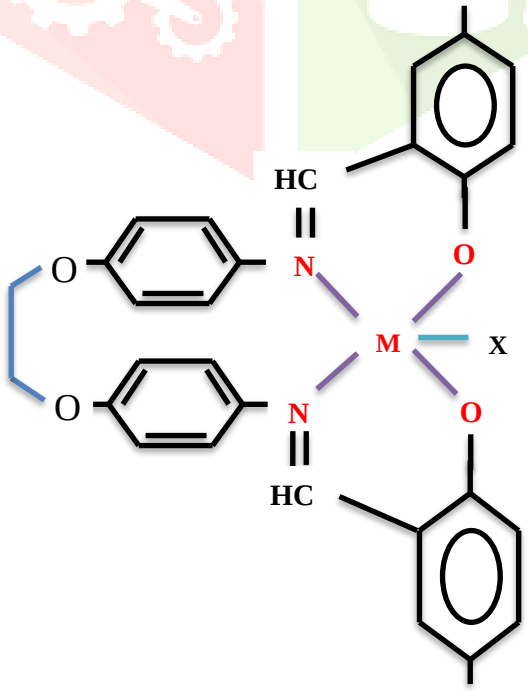
Ligand (LH_2)	CuL	CoL	MnL(OH)	ZnL	Assisgnment
2892S					Intermolecular H-bonded-OH
16275	1610S	1620S	1620S	1620S	C=N Stretching
1282m	1280m	1279m	1280m	1280m	Phenolic C-O Stretching
3041m	3045m	3054m	3045m	3045m	C-H Aromatic
2892S	2892S	2892S	2892S	2894S	C-H Aliphatic

Ligand LH2 on interaction with Mn(II), Co(II), Cu(II) and Zn(II) acetate yields complexes cross ponding to general formula ML, in the case of Mn(III),ML(OH). Analytical data of all these complexes are given in Table 1,2. The complexes where obtained from general reaction given below;

$$LH_2 + M(OOCCH_3)_2.nH_2O \rightarrow ML + 2CH_3COOH + nH_2O$$
$$M = Co(II), Cu(II), Zn(II)\ \ LH_2 = C_{28}H_{24}N_2O_4$$
$$n = 4 \quad 1 \quad 1$$

$$4LH_2 + 4Mn(OOCCH_3)_2.4H_2O + 7O_2 \rightarrow 4MnL(OH) + 8CH_3COOH + 14H_2O$$

Metal to ligand ratio Mn(III), Co(II), Cu(II) and Zn(II) complexes where found to be 1: 1 but Mn(II) complex has one extra hydroxo ligand.



M=Mn(III), Co(II),Cu(II),Zn(II)
X=OH

Proposed structure of the tetrahedral Co(II),Zn(II),square-planar Cu(II) and trigonal bipyramidal Mn(III) compexes of the ligand LH_2

A. **IR SPECTRA:-** Tentative designation of important bands of Schiff base under exploration and there corresponding metal complex are noted in table 2. The significant features of the Schiff based ligand and its complexes can be given as follows;

I. Broad band of Schiff based ligand appeared at 2892 cm^{-1} is identified as the starching vibration of intra-molecular H bonded OH in the molecule similar band were obtained for 5-Methyl salicylaldehyde at same frequency. This band dissipates in IR spectrum of the complexes. The band at 1282 cm^{-1} in IR spectra the ligand is assigned to the phenolic C-O stretching vibration. This band is found in the region 1279-1280 cm^{-1} of IR spectra of complexes. These vibrations proposed the o-OH group of this Schiff base component has taken part in complex formation.

II. Solid state IR Spectra(in KBr Pellets) of complexes compare with those of ligand assigned that the C=N band 1627$cm^{-1}$is shifted to the lower frequency for complexes of Mn(III), Co(II), Cu(II) and Zn(II). This band is found at the region 1610-1620cm^{-1}in IR spectra of complexes.

B. 1H NMR SPECTRA OF THE SCHIFF BASE (LH2 and Zn(II)) COMPLEX:-

i. 1H NMR Spectra (DMSO-d6) of ligand LH2 shown signal on 13.48(s, 2H), 8.73(s, 2H), 7.32(m, 14H), 3.30(s, 4H) and2.4(s, 6H) ppm. Which are assigned to OH HC=N aromatic CH, O-CH3 and Ph-C-H hydrogen respectively.

ii. 1H NMR spectra (DMSO-d6) of Zn(II) Complex shown signal on 8.81(s,2H), 7.26(m,14H),3.11(s,4H) and 2.33 (s,6H) ppm. Which are indicated to HC=N aromatic CH and O-CH2 hydrogen respectively.

C. **ELECTRONIC SPECTRA: -**

Electronic spectral data of synthesized complexes were noted in dimethyl formamide (DMF) solutions. Absorption spectra of Schiff base is characterized mainly by two absorption band at the region 275-560 nm. In spectra of Schiff base ligand the aromatic band on 210-307nm (ε=14427L mol^{-1} cm^{-1}) are allocated to a benzene $\pi \rightarrow \pi^*$transition. The band on 425nm (ε =6710L mol^{-1} cm^{-1}) is entrusted to the amino $\pi \rightarrow \pi^*$ transition. Compared to free ligand, imine $\pi \rightarrow \pi^*$transition of the complexes were shifted to few extends probably due to coordination of nitrogen atom of the ligand imine group to metal ion. Electronic spectra of Mn(III) complex shows absorption band on 555nm (ε =662L mol^{-1} cm^{-1}) attribute to 6A1-4T1(G) transition that is compatible with the complex having trigonal bipyramidal geometry. Electronic spectra of Co(II) complex shows absorption band on 625 nm(ε =785L mol^{-1} cm^{-1}) attribute to 4A2-4T1(P) transition that is compatible with the complex having a tetrahedral geometry.
Electronic spectra of Co(II) complex shown absorption band on 605 nm (E=292L mol^{-1} cm^{-1}) attribute to 2T2g-2Eg(G) transition that is compatible with the complex having a square planar geometry. Electronic Spectra of Zn(II) Complex shows absorption band on 430 nm (ε =2652 mol^{-1} cm^{-1}) attribute to L-M (charge transfer) transition that is compatible with the complex having tetrahedral geometry.

D. **MAGNETIC PROPERTIES: -**
Mn(III), Co(II) and Cu(II) Complexes are Paramagnetic and their magnetic susceptibility are 4.87, 4.44, 2.02 B.M. respectively. Since Mn(III), Co(II) and Cu(II) complex are paramagnetic, but Zn(II) Complex are Diamagnetic.

E. CONDUCTIVITY:-
Complexes are non-electrolyte are shown by its molar conductivity in DMF which are under range 6-14 (ohm) ^ (-1) (cm)^(2) (mol)^(-1).

Acknowledgment

Author would like to thank the Department of Chemistry Bihar University for providing Lab facilities. Author would also like to thank Sigma-Aldrich for providing required chemicals.

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