



SYNTHESIS AND CHARACTERISATION OF NEW MN (II), FE (III), CO (II), METAL COMPLEXES DERIVED FROM 2-HYDROXY 3-METHOXY BENZALDEHYDE AND DHA

Shyam R. Annapure*

P.G. Department of Chemistry, Milind College of Science, Aurangabad-431002, Maharashtra, India.

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*Corresponding Author

Shyam R. Annapure

P.G. Department of
Chemistry, Milind College
of Science, Aurangabad-
431002, Maharashtra, India.

ABSTRACT

New Solid asymmetrical complexes of Mn (II), Fe (III), and Co (II) of Schiff bases are synthesized from, 3-Acetyl-6-methyl-pyran-2, 4-dione (DHA), 4-methyl benzene 1,2-diamine and 2-hydroxy 3-methoxy benzaldehyde. The structures of ligands and complexes are characterized by thermal analysis, X-ray diffraction, ¹H-NMR, mass, IR, UV-visible spectra, elemental analysis, magnetic susceptibility, and conductometry. Thermal study carried out to calculate kinetic parameter through TGA/DSC. The ligand field parameters have been characterized for Mn (II), Fe (III), Co (II) complexes, which recommend high spine octahedral geometry. The x-ray diffraction data

proposes monoclinic crystal system for all three complexes. The ligand and their metal complexes were subjected for fungicidal activity against Trichoderma and Aspergillus Niger and antibacterial activity against Escherichia coli and Staphylococcus aureus.

KEYWORDS: Dehydroactacid, Powder X-ray diffraction, Thermal analysis Antimicrobial activity.

INTRODUCTION

Coordination chemistry contribute huge number of publication in the field of chemical science due to its bio-chemical significance. So it is daunting challenge for chemists to synthesize various imines from carbonyl carbon and amines and their metal complexes. It is imperative to use metal complexes as anti-oxidant, anti-inflammatory, antiviral, antitumor, anti-cancer, DNA-cleavage.^[1-6] DHA appeared as a striking ligand to synthesize tetradentate

Schiff bases. In continuation of our work^[7-8] we synthesized complexes of various color, of Mn (II), Fe (III), and Co (II) with tetradentate ligands formed by the reaction of, 4-methyl benzene 1,2-diamine, DHA, and 2-hydroxy 3-methoxy benzaldehyde [Fig.1(a)], and characterized by different spectral methods, evaluated for microbial activity.

EXPERIMENTAL

Materials: Reagents and solvents used as it is obtained from Merck. DHA, 4-methyl benzene 1, 2-diamine and 2-hydroxy 3-methoxy benzaldehyde of AR grade were used for synthesis of ligand. AR grade metal chlorides were also used for the formation of the complexes.

Instrumentation

The CHN analysis was carried out on Thermo Scientific (FLASH 2000) CHN elemental analyzer. ¹H-NMR spectra of ligand were recorded on FT NMR spectrometer (400 MHz) model Advance-II (Bruker) in CDCl₃ as a solvent using tetramethylsilane as internal standard. IR study has been carried out on Perkin Elmer-Spectrum RX-I FTIR spectrometer using KBr pellets. The TGA/DSC and XRD were recorded on TA Inc. SDT-2790 and Pananalytical X'Pert Pro respectively. All electronic absorption spectra of the complexes and ligand were chronicled on Shimadzu 1800 spectrometer.

Synthesis of ligand

It's a two-step synthesis process; in the first step mono-Schiff base compound was prepared by refluxing 50ml solution of (10 mmol) of DHA and (10mmol) 4-methyl benzene 1, 2-diamine in absolute ethanol for about 4hr. The progress of reaction was monitored by thin layer chromatography. The thus obtained mono-Schiff base was then refluxed with 10mmol of 2-hydroxy 3-methoxy benzaldehyde to synthesis asymmetric ligand. Product was then cooled at room temperature and collected by filtration, followed by recrystallization in super dry ethanol. (Yield: 85%).

Synthesis of metal complexes

Metal complexes were prepared by mixing a stoichiometric ratio (1:1) by dissolving in methanol. The ligand (0.01mol) and metal chloride (0.01mol) are mixed in hot condition with continuous stirring. The mixture was heated at reflux for about 3-4 h. On cooling, the volume of reaction mixture is reduced to half, then colored solid metal complex is appeared. Thus obtained solid metal complex was purified by petroleum ether and dried over vacuum desiccator (yield: 83%).

RESULTS AND DISCUSSION

CHN analysis, MP, Color, Mol. Wt and molar conductance data of ligand and metal complexes is depicted in **Table 1**. The data shows equimolar stoichiometry (metal: ligand) and satisfying general formula $[ML(H_2O)_2]$ [where M =, Mn (II), Fe (III) Co (II)].

¹H-NMR spectra of ligand

The ¹H NMR spectra of free ligand in CDCl₃ at room temperature shows the following signals. 2.06 δ (s, 3H, C4-CH₃), 2.17 δ (s, 3H, C6-CH₃), 2.44 δ (s, 3H, N=C-CH₃), 3.29 δ (s, 3H, -OCH₃), 5.85 δ (s, 1H, C5-), 6.75-7.16 δ (m, aromatic protons), 8.96 δ (s, 1H, N=C-H), 6.05 δ (s, phenolic (OH) hydrogen of phenyl ring) and 15.55 δ (s, 1H, enolic OH of DHA moiety).^[9]

IR spectra

The IR data of ligand (H₂L) and its metal complexes are listed in (**Table 2**). It depicts prominent bands at 3362, 1685, 1657, 1342 and 1221 cm⁻¹ assignable to ν OH, ν C=O (lactone carbonyl), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively.^[10] The presence of a strong broad band in the 3362 cm⁻¹ region, in the spectra of the ligand, which is not observed in complexes elucidates coordination of phenolic oxygen to the metal ion by deprotonation.^[11] Chelation by nitrogen of azomethine (C=N) is confirmed by observing band at 1657 cm⁻¹ in the spectra of ligand, which shifts to lower frequency 1602-1636 cm⁻¹ when complex is formed.^[12] This change can be supported by transfer of electrons from nitrogen to the vacant d-orbitals of the metal. Finding new bands in the 560-660 and 464-470 cm⁻¹ regions confirms the M-O and M-N bonding respectively.^[13] No change in skeletal vibrations (C=C) upon complexation. The presence of coordinated water is confirmed by the appearance of strong band in the 3267-3310 cm⁻¹ region in case of Mn (II), Fe (III) and Co (II), which is also supported by appearance of non-ligand band in 825-845 cm⁻¹ region, quoted for rocking mode of water.^[14]

Magnetic susceptibility and electronic absorption spectra

The electronic absorption spectrum of Mn (II) complex contains three bands at 650, 410, 324 nm assignable to the transitions $6A_{1g} \rightarrow 4T_{1g}$, $6A_{1g} \rightarrow 4T_{2g}$ and charge transfer respectively. Magnetic moment value 5.89 BM matches with standard value (5.92 BM) corresponding to octahedral geometry for Mn (II) complex.^[15] The electronic absorption spectra of Fe(III) complex show three strong bands at 766, 520, 324 nm, which may be assigned to the

transitions $6A_{1g} \rightarrow 4T_{1g}(4D)$, $6A_{1g} \rightarrow 4T_{1g}$ and charge transfer respectively. Electronic transitions together with magnetic moment value 5.87 BM indicates high spin octahedral geometry for Fe (III) complex.^[16] Co(II) complex show three bands at 922,524,392 nm which may be attributed to the transitions $4T_{1g} \rightarrow T_{2g}(F)$, $4T_{1g} \rightarrow 4A_{2g}(F)$ and charge transfer respectively. Electronic transitions along with magnetic moment value 4.51 B.M.^[17] suggest high spin octahedral geometry for Co(II) complex. The octahedral geometry is further supported by ratio $\nu_2/\nu_1=1.750$ which is close to the value expected for octahedral geometry.

Table 1: Physical characterization, analytical and molar conductance data of compounds.

Compound Molecular formula	Mol.Wt.	M.P/Decomp Temp. °C	Color	Molar conduc. Mho cm ² mol ⁻¹	Found (calculated)			
					C	H	N	M
(H ₂ L) C ₂₃ H ₂₂ N ₂ O ₅	406.43	194	Yellow	----	67.85 (67.97)	5.43 (5.46)	6.83 (6.89)	-----
[LMn(H ₂ O) ₂]	461.37	234	Brown	18.21	59.76 (59.88)	3.79 (3.81)	6.01 (6.07)	11.87 (11.91)
[LFe(H ₂ O) ₂]	462.28	224	Reddish Brown	35.40	59.71 (59.76)	3.18 (3.20)	6.01 (6.06)	12.03 (12.08)
[LCO(H ₂ O) ₂]	465.36	236	Yellow	22.21	59.32 (59.36)	3.71 (3.77)	6.00 (6.02)	12.63 (12.66)

Table 2: IR data of ligand and metal complexes.

Compound	IR band frequency (cm ⁻¹)							
	$\nu(\text{OH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	C=C	C-N	C-O	M-O	M-N
L	3362	1685	1657	1570	1342	1221	-	-
M _n -L	3267	1680	1636	1566	1335	1266	660	470
F _e -L	3310	1679	1604	1568	1375	1245	659	464
CO-L	3310	1680	1602	1560	1381	1242	560	464

Powder x-ray diffraction

Scanning of x-ray diffractogram of Mn(II), Fe(III), Co(II) metal complexes of L is done at wavelength 1.543 Å in the range 5-100°. The x-ray diffraction pattern of these complexes compared with major peaks of relative intensity greater than 10% has been indexed to their hkl value by using computer program.^[18]

Table 3: Unit Cell Parameter, Cell Volume of Metal Complexes.

Metal complexes	No. of Reflection	2θ at maxima	d value	Lattice constants Å	β	Unit Cell Volume Å ³
Mn (II)	13	13.745	9.963	a=19.235,b=8.568,c=7.879	β=99.897	926.33
Fe (III)	18	14.95	4.56	a=11.982,b=9.847,c=20.785	β=105.458	938.66
Co (II)	11	20.095	4.415	a=9.0427,b=8.0930,c=4.7048	β=110.279	322.97

In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that Mn (II), Fe (III), Co (II), complex of L has monoclinic crystal system.

Thermal analysis

The TG/DSC analysis of all Mn (II), Fe (III), and Co (II) complexes was done from ambient temperature to 1000°C in nitrogen atmosphere using α -Al₂O₃ as reference.

The TG curve of Mn (II) complex show first mass loss 11.40% (calcd.11.34%) in the range 160-250°C and an endothermic peak in this region $\Delta T_{min.} = 225.66^\circ\text{C}$, indicate removal of two coordinated water molecules. The second step fast decomposition from 250-550°C with 23% mass loss. This can be further confirmed by observing broad exotherm in DSC with $\Delta T_{max.} = 419.80^\circ\text{C}$ indicates removal of non-coordinated part. In third step from 550-850°C slow weight loss 39.15%, confirmed by endotherm $\Delta T_{min.} = 593.37^\circ\text{C}$ indicate loss of coordinated part. The thermal profile of Fe(III) complex shows mass loss 9.5% (calcd.9.3%) in the range 170-240°C and an endothermic peak in this region $\Delta T_{min} = 225^\circ\text{C}$ indicates loss of two coordinated water molecules.^[19] The anhydrous complex first show slow decomposition from 240-650°C with mass 32.74% (calcd.32.64%) loss and a broad exotherm $\Delta T_{max} = 425^\circ\text{C}$ in DSC may be attributed to removal of non-coordinated part of ligand. The second step decomposition is sharp from 650 to 750°C with mass loss of 18.60% (calcd. 18.85%) a sharp endotherm in DTA at 740°C is observed for this step. The third step decomposition is from 750 to 850°C with 19% mass loss. The mass of the final residue 5.2% does not corresponds to any stoichiometry of end product. The thermogram of Co (II) complex show continuous stepwise mass loss. First 7.304% (calcd.7.8%) in the range 150-270°C and an endothermic peak in this region $\Delta T_{min} = 235^\circ\text{C}$, indicates loss of two coordinated water molecules. The anhydrous complex first show stepwise decomposition in 270-450°C range with 13% mass loss (calcd.13.01%) and a broad endotherm $\Delta T_{min} = 420^\circ\text{C}$ in DSC may be attributed to removal of non-coordinated part of ligand. The second step decomposition at 450-900°C, with mass loss of 37.30% (calcd.37.45%) corresponds to decomposition of coordinated part of ligand. A broad endotherm at $\Delta T_{min} = 850^\circ\text{C}$ DSC is observed for this step.

Kinetic calculations

The kinetic and thermodynamic parameters viz ΔG (free energy change), ΔS , z (pre-exponential factor), E_a and n (order of reaction), together with correlation coefficient (r) for

non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method^[20] and Coats-Redfern integral method. The data is arranged in (Table 4). The results show that the values obtained by two methods are analogous. Low values of E_a of the complexes are indicating the autocatalytic effect of metal ion after thermal decomposition.

Table 4: The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzer (HM) and Coats-Redfern (CR).

Complex	Step	n	Method	E_a	Z	ΔS	ΔG	Correlation coefficient(r)
Mn(II)	I	1.30	HM	8.96	56234.56	-160.23	18.46	0.9989
			CR	7.87	56489723	-161.44	17.89	0.9992
	II	1.30	HM	31.45	59867.59	-123.46	44.09	0.9987
			CR	30.58	89574625	-121.89	42.87	0.9979
Fe(III)	I	0.55	HM	35.86	56247	-105.48	40.66	0.9990
			CR	36.78	54756232	-106.45	40.23	0.9998
	II	0.55	HM	49.54	89635	-121.36	56.47	0.9989
			CR	50.23	78965784	-123.47	55.68	0.9990
CO(II)	I	0.47	HM	33.15	56234	-135.45	35.56	0.9909
			CR	31.56	45672341	-136.42	34.54	0.9982
	II	0.47	HM	15.45	25364	-175.79	32.89	0.9987
			CR	14.89	25437624	-179.22	31.64	0.9993

E_a in kJ mol^{-1} , Z in S^{-1} , ΔS in $\text{JK}^{-1}\text{mol}^{-1}$ and ΔG in kJ mol^{-1}

Antimicrobial activity

Ligand and metal complexes are subjected for antifungal activity, by using Mycelia dry weight method. Compounds were tested against *Trichoderma* and *Aspergillus Niger*.^[21] The activity is tested at 250 and 500 ppm in DMF and depicted in (Table-5) by comparison with standard. Compounds were tested for antimicrobial activity against bacteria such as *Escherichia coli* and *Staphylococcus aureus* by paper disc plate method.^[22] The compounds were tested at the concentration 500ppm and 1000ppm in DMF, considering Ciproflaxin as standard (Table-6). Perceiving the values of Table-5 and 6, inference made that the inhibition by metal complexes is more than a ligand. Solubility of metal complexes in organic solvents increase its activity. Hydrogen bonding with active center of cell may responsible for enhanced activity.

Table 5: Yield of Mycelial dry weight in mg (% inhibition).

Test Compound	<i>Aspergillus Niger</i>		<i>Trichoderma</i>	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
(H ₂ L)	52(34)	20(75)	31(56)	16(77)
[LMn(H ₂ O) ₂]	43(46)	12(85)	23(67)	06(91)
[LFe(H ₂ O) ₂]	45(43)	16(80)	24(66)	08(89)
[LCO(H ₂ O) ₂]	38(52)	11(86)	15(79)	02(97)

Table 6: Antibacterial activity of compounds.

Test Compound	Inhibition Zone (mm)			
	<i>E.Coli</i>		<i>Staphylococcus</i>	
	500 ppm	1000 ppm	500 ppm	1000 ppm
<i>Ciproflaxin</i>	29	32	31	35
(H ₂ L)	12	13	14	16
[LMn(H ₂ O) ₂]	13	14	15	17
[LFe(H ₂ O) ₂]	13	14	15	17
[LCO(H ₂ O) ₂]	14	15	16	19

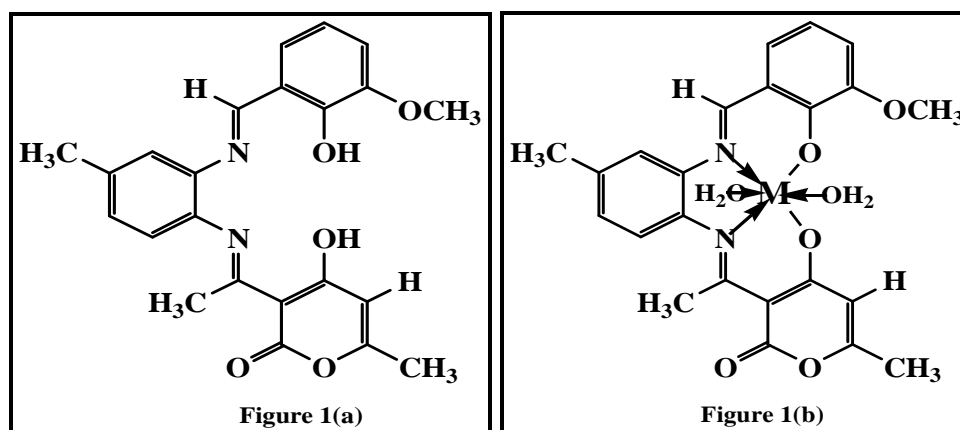


Fig.1 a Structure of the Ligand, Fig. 1 b proposed structure of the complexes, Where M=Mn (II), Fe (III), CO (II).

CONCLUSION

In present study we report synthesis of asymmetrical ligand and its transition metal complexes. Spectral study suggest that azomethine nitrogen and phenolic oxygen are involved in the co-ordination with metal ions (**fig.1 (b)**). Proposing octahedral geometry for Mn (II), Fe (III) and Co (II), complexes. It is concluded that the ligand is dibasic in nature and N2O2 tetradentate metal complexes are biologically active and show enhanced antimicrobial activities compared to its free ligand. The XRD reveals monoclinic crystal system for all Mn (II), Fe (III), and Co (II) complexes. Thermal study forecasts thermal behavior of complexes.

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