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SYNTHESIS, CHARACTERIZATION, STUDY OF THERMAL, X-RAY AND ANTIMICROBIAL NOVEL TRANSITION METAL COMPLEXES OF ASYMMETRICAL LIGAND

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ABSTRACT

The complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with asymmetrical tetradentate Schiff bases derived from 3-Acetyl-6-methyl-pyran-2,4-dione,*o*-phenylenediamine, and 2-hydroxy 3-methoxy benzaldehyde have been synthesized and characterized by CHN analysis,^{1}H-NMR, mass, IR,UV-visible spectra, magnetic susceptibility, thermalanalysis, X-ray diffraction, conductometry. The study reveals high spine octahedral geometry for Mn(II), Fe(III)and Co(II), and square planar geometry for Ni(II) and Cu(II) complexes. The x-ray diffraction data suggests monoclinic crystal system for all five complexes. Thermal behavior (TG/DSC) of the complexes was studied and kinetic parameters were determined by Horowitz-Metzger and Coats-Redfern method. The ligand and their metal complexes were screened for antimicrobial activity.

KEYWORDS: Asymmetrical ligand, Dehydroaceticacid, TGA/DSC, PowderX-ray diffraction.

INTRODUCTION

3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one(DHA) is good chelating[i] moiety with antibacterial [ii], antifungal[iii]antiviral[iv],antitumor [v], properties, DNA cleavage[vi]agents, used as a preservative. So researchers are preparing wide variety of heterocyclic compounds from it. Tetradentate Schiff bases with N_2O_2 donor atoms are well known to co-ordinate with various metal ions. In continuation of our research work[vii]in present study by using DHA, a versatile nucleus, *o*-phenylenediamine, 2-hydroxy 3-methoxy benzaldehyde, novel asymmetrical tetradentate Schiff bases with N_2O_2 donor atoms have been synthesized and its complexes with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II), and characterized by different physic-co-chemical methods.

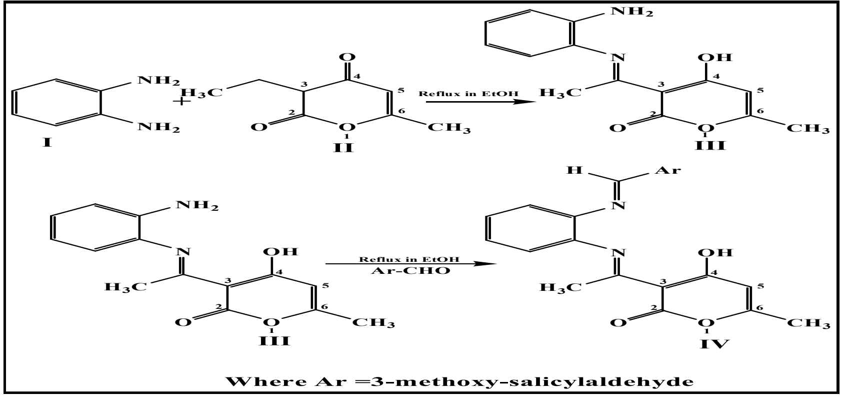
EXPERIMENTAL

Reagents and solvents dehydroacetic acid obtained from Merck was used as supplied.*o*-phenylenediamine, and 2-hydroxy 3-methoxy benzaldehyde of AR grade were used for synthesis of ligand. AR grade metal chlorides were used for the synthesis of complexes.

Synthesis of ligand

In the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of 10mmol of DHA and 10mmol *o*-phenylenediamine in super dry ethanol for about 3 h. The progress of reaction was monitored via thin layer chromatography. Mono-Schiff base thus formed was then refluxed with 10mmol 2-hydroxy 3-methoxy benzaldehyde to prepare asymmetric ligand. Product then cooled at room temperature and collected by filtration, and recrystallized by ethanol. (Yield: 85%).

Scheme 1



Where Ar =3-methoxy-salicylaldehyde

Synthesis of metal complexes

To a hot methanol solution (25ml) of the ligand (0.01 mol), methanolic solution (25ml) of metal chloride (0.01 mol) was added with constant stirring, and refluxed for about 3 h. The precipitated solid colored metal complex was filtered off in hot condition and washed with hot methanol, petroleum ether(40°-60°) and dried over calcium chloride in vacuum desiccator.(yield: 80 %)

RESULTS AND DISCUSSION

Table 1 indicates Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes.Molar ratio of (metal: ligand) is 1:1 and found in good relevance with the general formula [ML(H2O)2] (where M =, Mn(II) , Fe(III) Co(II) and [ML] (where M = Ni(II)andCu(II)) .

^{1}H-NMR spectra of ligand

The ^{1}H NMR spectra of free ligand in $CDCl_3$ at room temperature shows the following signals. 2.15 δ (s, 3H, C6-CH_3), 2.45 δ (s, 3H, N=C-CH_3),3.40 δ (s, 3H,-OCH_3), 5.85 δ (s, 1H, C5-), 6.72-7.14 δ (m, aromatic protons), 8.97 δ (s, 1H, N=C-H), 6.38 *δ*(s, phenolic (OH) hydrogen of phenyl ring) and 15.64 δ (s, 1H, enolic OH of DHA moiety).

FTIR spectra

A comparative study of IR data of ligand and its metal complexes is listed in Table 2. It shows major band at 3216, 1674, 1647, 1566, 1361, 1214 cm^{-1} assignable to υ OH,υ C=O (lactone carbonyl), υ C=N (azomethine), C=C, υ C-N (aryl azomethine) and υ C-O (phenolic) stretching modes respectively[viii].Lack of broad band in region of 3216 cm^{-1} in the spectra of metal complexes reveals chelation of phenolic oxygen to the metal ion[ix]. Difference of 10-40 cm^{-1}in frequency is observed in case of azomethine υ (C=N) band in metal complexes, with compared to ligand which is 1647 cm^{-1}indicating involvement of azomethine nitrogen in coordination to metal[x]. Metal complexes shows new band in the 521-554 and 461-487 cm-1 regions can be assigned to υ M-O and M-N vibrations respectively. While (C=C) ring skeletal band is constant in all metal complexes.The presence of coordinated water inMn(II), Fe(III) and Co(II) metal complexes is confirmed by observing broad band in 3067-3088 cm-1 region. Hence it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule to the transition metal ions.

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

Compound Molecular formula	Mol.Wt.	M.P /Decomp Temp. ^{0}C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (calculated)			
					C	H	N	M
(H$_2$L) $C_{22}H_{20}N_2O_5$	392.40	155	Yellow	-------	66.71 (67.34)	5.35 (5.14)	7.35 (7.14)	-----
[LMn(H$_2$O)$_2$]	447.34	223	Brown	19.20	57.58 (58.58)	3.56 (3.47)	6.15 (6.21)	12.86 (13.01)
[LFe(H$_2$O)$_2$]	448.25	222	Coffee Brown	42.21	58.45 (58.95)	3.63 (3.55)	6.13 (6.25)	13.86 (12.46)
[LCO(H$_2$O)$_2$]	451.34	225	green	12.40	58.34 (58.54)	3.21 (3.47)	6.12 (6.21)	12.81 (13.86)
[LNi]	451.10	230	Yellow	21.20	58.89 (58.58)	3.36 (3.47)	6.88 (6.21)	13.10 (13.01)
[LCu]	455.95	231	Brown	18.10	57.25 (57.95)	3.24 (3.42)	6.23 (6.14)	13.50 (13.94)

Table 2. IR and UV data of ligand and metal complexes

Compound	**IR band frequency (cm^{-1})**								**λ max(nm)**	**Magnetic Moment(BM)**
	***ν*(OH)**	***ν*(C=O)**	***ν*(C=N)**	**C=C**	**C-N**	**C-O**	**M-O**	**M-N**		
L	3216	1674.3	1647.7	1566.8	1361	1214	-	-	283,318,377	-
$\mathrm{M_n}$-L	3067	1674.2	1636	1566.7	1331	1236	522.9	487.1	322,414,656	5.84
$\mathrm{F_e}$-L	3076	1672.1	1632	1566.1	1329	1247	547.8	462.5	322,530,794	5.79
CO-L	3088	1671.0	1624	1567.0	1339	1265	554.2	463.2	322,529,928	4.77
Ni-L	3025	1673.0	1620	1567.0	1325	1260	521.2	461.1	390,592	Diamagnetic
Cu-L	3034	1672.2	1603	1566.0	1327	1267	522.1	485.1	326,387,596	1.75

Electronic absorption spectra and Magnetic susceptibility

The electronic absorption spectrum of Mn(II) complex contains three bands at 656, 414 and 322nm, assignable to the transitions 6A1g → 4T1g, 6A1g → 4T2g and charge transfer respectively(Table 2). The electronic absorption spectra of Fe(III) complex show three strong bands at 794, 530 and 322 nm, which may be assigned to the transitions 6A1g → 4T1g(4D), 6A1g → 4T1g and charge transfer respectively. Co(II) complex show three bands at 928, 529 and 387 nm, which may be attributed to the transitions 4T1g → T2g(F), 4T1g → 4A2g(F) and charge transfer respectively, Cu(II) show three bands at 596, 387 and 268 nm assignable to the transitions 2B1g → 2A1g and two intraligand charge transfer bands. The electronic absorption spectra of Ni(II) complex consists of two bands at about 592,390 nm assignable to 1A1g → 1T2g and charge transfer transitions respectively. Magnetic moment value are 5.84, 5.79, 4.77 B.M. for Mn (II) , Fe(III) Co(II) suggest high spin octahedral geometry for them[xi] (Table 2). The data, diamagnetic nature and red color of the complex suggests squareplanar geometry for Ni(II) complex .These electronic transitions and observed 1.75 B.M magnetic moment value suggests square-planar geometry around Cu(II) [xii].

Thermal analysis

The TG/DSC analysis of all Mn (II), Co(II), Ni(II) and Cu(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.11.50%) in the range 200-270°C with endothermic peak in this region ΔTmin = 225°C, indicate removal of two coordinated water molecules[xiii]. In the second slow step decomposition from 270-600 °C with 23.80 % mass loss.Also supported by observing broad exotherm in DSCwith ΔTmax = 419°C indicates that the complex is thermally quite stable, by leaving 46.82 % residue. Thethermogram of Co(II) complex show weight loss 8.45% (calcd.8.35%) in the range 200-250°C and an endothermic peak in this region ΔTmin = 230°C, indicates loss of two coordinated water molecules. The anhydrous complex show fast decomposition in 250-600°C range with 52.68 % mass loss (calcd.53.62.%) and a broad exotherm ΔTmax = 403.65°c in DSC may be attributed to removal of non-coordinated part of ligand. Although decomposition is continues single step. The mass of the final residue corresponds to stable CoO with mass 22.25 % (calcd.22.35%).The TG curve of Ni(II) complex, show two step decomposition. No weight loss up to 270°C indicates absence of coordinated water in these complexes. The first step from 250°C to 350°C, with a mass loss 58.59 % (calcd. 58.64%), an endothermic peak ΔTmin = 250°C in DSC may be attributed to the decomposition of non-coordinated part of ligand. In second slow step from 350-800°C with mass loss 24.99 % (calcd.24.56 %), an exothermic peak ΔTmax = 411.73°C in DSC, may corresponds to removal of coordinated part of ligand. The mass of the final residue 16.41% does not corresponds to any stoichiometry of end product.In the TG curve of Cu(II) complexes no mass loss up to 270°C indicates absence of coordinated water in these complexes. The first step of decomposition from 270°C-400°C, with a mass loss 43.94 % (calcd. 43.75%), an exothermic peak ΔTmax = 285.62°C in DSC may be attributed to the removal of non-coordinated part of ligand. The second slow step from 400-700°C with mass loss 23.60% (calcd.24.61%),an exothermic peak ΔTmax = 404.66°c. in this region in DSC corresponds to decomposition of coordinated part of ligand. The mass of the final residue corresponds to stable CuO, 31.45 % (calcd.31.55%), indicate more thermal stability.

Kinetic calculations

The kinetic and thermodynamic parameters viz ΔG (free energy change), ΔS (entropy of activation), z (pre-exponential factor),Ea (energy of activation) 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 [xiv] and Coats-Redfern integral method[xv].The data is given in Table 3.

Table 3. The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	n	Method	E_a	Z	ΔS	ΔG	Correlation coefficient(r)
Mn(II)	I	0.55	HM	24.5	30168	-117.06	36.15	0.9996
			CR	25.98	50614364	-103.09	33.27	0.9972
	II	1.35	HM	15.75	22575	-149.64	32.69	0.9996
		0.55	CR	15.28	22268800	-74.47	22.69	0.9993
CO(II)	I	0.50	HM	9.75	17737	-171.79	26.24	0.9981
			CR	8.87	63753	-161.15	25.22	0.9995
	I	1.11	HM	34.18	158601	-152.10	46.39	0.9998
			CR	32.00	14085439	-114.79	42.56	0.9998

Ni (II)	II	1.01	HM CR	32.98 32.34	158277 5440062	-154.85 -125.43	46.98 42.94	0.9985 0.9996
Cu (II)	I	1.55	HM CR	88.28 85.11	145656 20742719	-151.60 -110.36	94.12 92.78	0.9992 0.9997
	II	1.12	HM CR	36.65 31.38	185926 159210	-152.86 -154.15	48.58 47.29	0.9970 0.9992

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

Powder x-ray diffraction

The x-ray diffractogram of mentioned five metal complexes of L was scanned in the range 5-100° at wavelength 1.543 Å, and by programing it through Powder x-ray, resulting data gives 2θ value for each peak,2θ at highest intensity,d-values (inter-planar spacing), hkl (Miller indices), lattice constant and unit cell volume are indexed in Table 4.

Table 4. Unit Cell Parameter,Cell Volume of Metal Complexes

Metal complexes	No. of Reflection	2θ at maxima	d value	Lattice constantsÅ	β	Unit Cell Volume A^3
Mn (II)	11	11.832	7.473	a=18.408,b=7.482,c=6.801	β=99.456	924.20
Fe (III)	11	13.301	6.651	a=9.248,b=12.973,c=8.068	β=104.365	937.87
Co (II)	10	17.726	4.999	a=14.894,b=5.404,c=14.508	β=126.157	942.90
Ni (II)	10	11.896	7.433	a=14.741,b=9.112,c=7.706	β=119.622	899.93
Cu (II)	09	11.781	7.505	a=9.264,b=13.189,c=7.983	β=101.275	956.73

In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = γ = 90° ≠ β 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), Ni(II)andCu(II) complex of L has monoclinic crystal system[xvi].

Antimicrobial activity

The antimicrobial activity of ligand and metal complexes were tested in vitro against bacteria such as *Staphylococcus aureus* and *Escherichia coli* by paper disc plate method [xvii].The compounds were tested at the concentration 500ppm and 1000ppm. DMF and compared with known antibiotics viz. *Ciproflaxin*. (Table 5). For fungicidal activity, compounds were screened in vitro against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method[xviii]with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (Table 6).

Table 5 Antibacterial activity of compounds

Test Compound	Inhibition Zone (mm)			
	E.Coli		*Staphylococcus*	
	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciproflaxin	29	32	31	35
(H_2L)	10	12	11	15
[$LMn(H_2O)_2$]	11	13	12	16
[$LFe(H_2O)_2$]	11	13	12	16
[$LCO(H_2O)_2$]	13	15	15	18
[LNi]	13	13	14	18
[LCu]	15	17	17	20

From Table 4 and 5, it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes .Such enhanced activity of metal chelates is due to the increased lipophilic nature of the metal ions in complexes . The increase in activity with concentration is due to the effect of metal ions on the normal cell process. The action of compounds may involve the formation of hydrogen bond with the active center of cell constituents, resulting in interference with the normal cell process.

Table 6 Yield of Mycelial dry weight in mg (% inhibition)

Test Compound	*Aspergillus Niger*		*Trichoderma*	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
(H_2L)	56(30)	22(72)	34(51)	18(74)
$[LMn(H_2O)_2]$	48(39)	17(78)	29(59)	07(90)
$[LFe(H_2O)_2]$	50(37)	18(77)	31(56)	10(86)
$[LCO(H_2O)_2]$	40(49)	15(81)	24(66)	03(96)
[LNi]	35(56)	11(86)	17(76)	03(96)
[LCu]	35(56)	10(87)	14(80)	01(99)

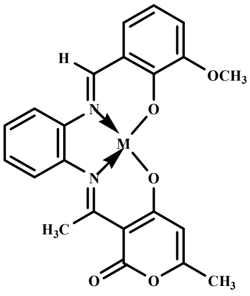


Figure 2 (a)

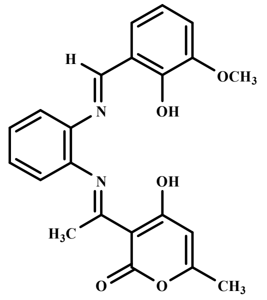


Figure 1 Sructure of ligand

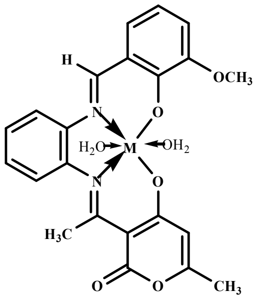


Figure 2 (b)

The proposed structure of the complexes.

2(a) Where M= Ni(II),Cu(III); 2(b)Where M=Mn(II),Fe(III),CO(II).

CONCLUSION

In the present investigation we reported synthesis of asymmetrical ligand and its first transition metal complexes. Spectral study probes chelation by azomethine nitrogen and phenolic oxygen are involved in the coordination with metal ions (fig.A [2,a,b]). Proposing octahedral geometry for Mn(II), Fe(III)and Co(II), and square- planar geometry forNi(II)andCu(II) complexes . It is assumed that the ligand behave as dibasic and are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The XRD study suggests monoclinic crystal system for all Mn(II), Fe(III) ,Co(II), Ni(II)andCu(II) complexes.

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