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Synthesis and Charactrisation of Dehydroacetic acid based New Mn(II),Fe(III),Co(II), metal Complexes of Asymmetrical Ligand

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Abstract: Solid asymmetrical complexes of Mn(II),Fe(III), and Co(II)of Schiff bases are synthesized from o-phenylenediamine,3-Acetyl-6-methyl-pyran-2,4-dione (DHA)and4-N,N, Diethyl amino Salicylaldehyde. The structures of ligands and complexes are characterized by thermal analysis, X-ray diffraction,^{1}H-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 spineoctahedral 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 : Dehydroactic acid, Powder X-ray diffraction, Thermal analysis Antimicrobial activity.

Introduction

In search of novel chemical nuclease, the method designed by Hugo Schiff appeared in a paper entitled *"A New Series of Organic Bases"*is a milestone for researchers (1). So chemists started to synthesize various imines from carbonyl carbon and amines and their metal complexes and used it as medicinal power house. These metal complexes have numerous potential to use it as anti-inflammatory, antiviral, antitumor, anti-oxidant, anti-cancer, DNA-cleavage(2-7).DHA appeared as an striking ligand to synthesize tetradentate Schiff bases. In present study we synthesized complexes of various color, of Mn(II), Fe(III),and Co (II) with tetradentate ligands formed by the reaction of o-phenylenediamine, DHA, and 4-N, N, Diethyl amino Salicylaldehyde[**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,*o*-phenylenediamine, and 4-N,N, Diethyl amino Salicylaldehyde 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. ^{1}H-NMR spectra of ligand were recorded on FT NMR spectrometer (400 MH_Z) model Advance-II (Bruuker) in $CDCl_3$ 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; in the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of (10 mmol) of DHA and (10mmol)*o*-phenylenediamine in absolute ethanol for about 3 hr. The progress of reaction was monitored via thin layer chromatography. The resulting mono-Schiff base thus formed was then refluxed with 10mmol of 4-N, N, Diethyl amino Salicylaldehyde to synthesis final product. Product was then cooled at room temperature and collected by filtration, followed by recrystallization in super dry ethanol. (Yield: 89%).

Synthesis of metal complexes

Metal complexes were prepared by mixing a stoichiometric ratio (1:1) by dissolving in methanol. The ligand (0.01 mol) and metal chloride (0.01 mol) 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: 87%).

Results and discussion

CHN analysis, MP,Color, Mol.Wt, and molar conductance data of ligand and metal complexes is depicted in **Table1**.The data shows equimolar stoichiometry (metal: ligand) and satisfying general formula $[ML(H2O)_2]$ [where M =, Mn (II), Fe(III) Co(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. 1.04-1.09 δ (t, 6H, $2\times CH_3$-CH_2-N), 1.11-1.16 δ (q, 4H, $2\times$N-CH_2-CH_3), 2.12 δ (s, 3H, C6-CH_3),2.51 δ (s, 3H, N=C-CH_3), 5.79 δ (s, 1H, C5-), 6.75-7.16 δ (m, aromatic protons), 8.59 δ (s, 1H, N=C-H), 6.18 δ (s, phenolic (OH) hydrogen of phenyl ring) and 9.50 δ (s, 1H, enolic (OH/NH) of DHA moiety)(8,9) .

IR spectra

The IR data of ligand (H_2L) and its metal complexes are listed in (**Table 2**).It depictprominent bands at 3427, 1693, 1660, 1360 and 1212 cm^{-1} assignable to υ OH, υ C=O (lactone carbonyl), υ C=N (azomethine), υ C-N (aryl azomethine) and υ C-O (phenolic) stretching modes respectively (10).The presence of a strong broad band in the 3427 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 1660 cm^{-1}in the spectra of ligand,which find at lower frequency 1634-1636 cm^{-1}whencomplex 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 565-666 and 464-472 cm-1 regions confirms the M-O and M-N bonding respectively(13).No any change in skeletal vibrations (C=C) upon complexation.The presence of coordinated water is confirmed by the appearance of strong band in the 3067-3086 cm-1 region in case ofMn(II), Fe(III)andCo(II),which is also supported by appearance of non-ligand band in 825-846 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 608,514,382 nm assignable to the transitions 6A1g → 4T1g, 6A1g → 4T2g and charge transfer respectively. Magnetic moment value 5.86 BM matches with standard value (5.92 BM) corresponds octahedral geometry for Mn (II) complex (15). The electronic absorption spectra of Fe(III) complex show three strong bands at 689,530,353 nm, which may be assigned to the transitions 6A1g → 4T1g(4D), 6A1g → 4T1g and charge transfer respectively. Electronic transitions together with magnetic moment value 5.83 BM indicates high spin octahedral geometry for Fe (III) complex (16). Co(II) complex show three bands at 921,526,357 nm which may be attributed to the transitions 4T1g → T2g(F), 4T1g → 4A2g(F) and charge transfer respectively. Electronic transitions along with magnetic moment value 4.67 B.M.(17) suggest high spin octahedral geometry for Co(II) complex .The octahedral geometry is further supported by ratio υ2/ υ1 = 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. ^{0}C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (calculated)			
					C	H	N	M
(H_2L) $C_{25}H_{27}N_3O_4$	433.50	87	Dark Red	----	68.25 (69.27)	6.06 (6.28)	9.23 (9.69)	-----
[$LMn(H_2O)_2$]	488.44	195	Coffee Brown	28.35	60.56 (61.48)	4.35 (4.45)	8.55 (8.60)	11.15 (11.25)
[$LFe(H_2O)_2$]	489.34	257	Dark Brown	51.20	61.30 (61.36)	4.48 (4.50)	8.46 (8.59)	11.39 (11.41)
[$LCO(H_2O)_2$]	492.43	267	Green	36.21	60.89 (60.98)	3.55 (4.60)	8.44 (8.53)	11.89 (11.97)

Table-2 IR data of ligand and metal complexes

Compound	IR band frequency (cm^{-1})							
	v(OH)	*v*(C=O)	*v*(C=N)	C=C	C-N	C-O	M-O	M-N
L	3427	1693.3	1660	1566.8	1360	1212	-	-
M_n-L	3067	1683.2	1636	1556.7	1335	1266	666	472
F_e-L	3086	1680.1	1634	1557.1	1329	1267	568	465
CO-L	3078	1679.0	1634	1566.0	1331	1275	565	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 Åin 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**).

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 A^3
Mn (II)	17	18.463	4.801	a=9.294,b=11.282,c=6.546	β=98.204	679.433
Fe (III)	16	13.74	3.02	a=10.5663,b=8.5469,c=19.456	β=104.365	936.87
Co (II)	18	14.86	3.00	a=8.9125,b=9.6354,c=14.568	β=122.157	932.90

In respect of these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$ 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-Al_2O_3 as reference.

The TG curve of Mn(II) complex show first mass loss 7.931% (calcd.7.23%) in the range 150-250°C and an endothermic peak in this region ΔTmin. = 167.58°C, indicate removal of two coordinated water molecules. The second step slow decomposition from 250-550 °C with 32% mass loss. This can be further confirmed by observing broad exotherm in DSC with ΔTmax. = 434.93°C indicates removal of non co-ordinated part. In third step from 550-960 °C sudden weight loss 37.19 %, confirmed by endotherm ΔTmin. = 761.80°C indicate loss of coordinated part. The thermal profile of Fe(III) complex shows mass loss 7.5% (calcd.7.3%) in the range 160-230°C and an endothermic peak in this region ΔTmin = 220°C indicates loss of two coordinated water molecules(19). The anhydrous complex first show slow decomposition from 230-650°C with mass 29.54% (calcd.30.44%) loss and a broad exotherm ΔTmax = 420°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 16.50% (calcd. 16.85%) a sharp endotherm in DTA at 750°C is observed for this step. The third step decomposition is from 750 to 950°C with 16% mass loss. The mass of the final residue 6.2% does not corresponds to any stoichiometry of end product. The thermogram of Co(II) complex show continuous stepwise mass loss. First 6.304% (calcd.6.8%) in the range 150-270°C and an endothermic peak in this region ΔTmin = 239°C, indicates loss of two coordinated water molecules. The anhydrous complex first show stepwise decomposition in 270-450°C range with 11% mass loss (calcd.11.01%) and a broad endotherm ΔTmin = 416°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 17.30% (calcd.17.45%) corresponds to decomposition of coordinated part of ligand. A broad endotherm at ΔTmin = 843°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-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	n	Method	E_a	Z	ΔS	ΔG	Correlation coefficient(r)
Mn(II)	I	1.26	HM	6.68	49647.43	-159.94	16.64	0.9980
			CR	5.52	80954269	-159.64	16.62	0.9992
	II	1.27	HM	33.62	171720.43	-153.32	49.07	0.9937
			CR	28.78	96239402	-119.15	45.62	0.9940
Fe(III)	I	0.57	HM	30.99	45893	-108.45	48.88	0.9990
			CR	29.54	56981234	-109.36	46.71	0.9977
	II	0.57	HM	43.54	85469	-118.37	63.12	0.9989
			CR	42.29	78456825	-111.78	61.78	0.9990
CO(II)	I	0.45	HM	23.77	33023	-165.27	37.24	0.9909
			CR	21.73	224291732	-126.11	34.04	0.9972
	II	0.45	HM	14.76	22028.4	-170.79	32.79	0.9983
			CR	13.81	156563107	-153.22	30.94	0.9993

Ea in kJ mol^{-1}, Z in S^{-1}, ΔS in $JK^{-1}mol^{-1}$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 Ciprofloxacin 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	***Aspergillus Niger***		***Trichoderma***	
	250 ppm	**500 ppm**	**250 ppm**	**500 ppm**
Control	79	79	70	70
(H_2L)	61(23)	24(70)	40(43)	19(73)
[$LMn(H_2O)_2$]	53(33)	18(77)	34(51)	08(89)
[$LFe(H_2O)_2$]	54(32)	18(77)	35(50)	12(83)
[$LCO(H_2O)_2$]	50(37)	16(80)	32(54)	04(94)

Table 6 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)	08	11	11	14
[$LMn(H_2O)_2$]	10	13	11	15
[$LFe(H_2O)_2$]	10	13	11	15
[$LCO(H_2O)_2$]	12	13	14	17

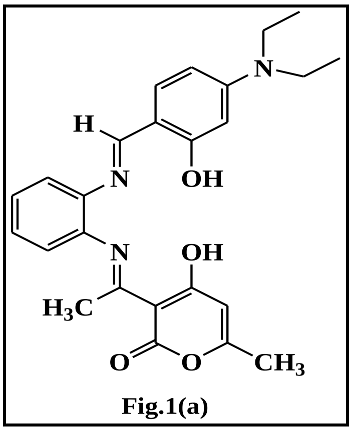

Fig.1(a)

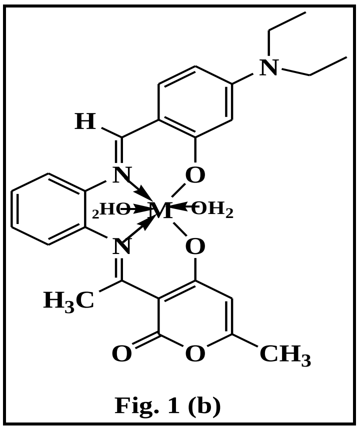

Fig. 1 (b)

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 investigation we report synthesis of 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)andCo(II),complexes. It is concluded that the ligand is dibasic in nature and ONNO 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 predicts thermal behavior of complexes.

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