



Synthesis and Characterization of Ni (II), Cu (II) metal Complexes of New Tetradentate Ligand derived from Dehydroacetic acid

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Abstract: Colored solid asymmetrical complexes of Ni(II), and Cu(II) of Schiff bases are synthesized from *o*-phenylenediamine, 3-Acetyl-6-methyl-pyran-2,4-dione (DHA) and 4-N, N Diethyl amino Salicylaldehyde. 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 behavior (TG-DSC) of the complexes were studied and kinetic parameter were determined by Horowitz Metzger and Coats Red Fern method. The ligand field parameters have been characterized for Ni (II), Cu(II) complexes, which endorse square planar geometry. The x-ray diffraction data proposes monoclinic crystal system for both 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 : Powder X-ray diffraction, Thermal analysis, Antimicrobial activity, Dehydroacetic acid.

Introduction

Huge number of publication has been devoted for Schiff bases and Co-ordination chemistry of transition metal complexes[1]. It reiterated the importance of ability of amines, to condense with carbonyl carbon. This fact had been pervade, so it is imperative for researcher to use it as antitumor, anti-oxidant, anti-cancer, antibacterial, antiviral, DNA-cleavage[2-7].

In continuation of our earlier work [8] in this unequivocal missive we synthesized complexes of Ni(II), and Cu (II) with tetradentate ligands formed by the condensation of *o*-phenylenediamine, DHA, and 4-N, N, Diethyl amino Salicylaldehyde[Fig.1(a)], and characterized by different spectral methods, also evaluated for microbial activity.

Experimental

Materials

Reagents and solvents Procured from sigma Aldrich are used without purification. DHA, *o*-phenylenediamine, and 4-N,N-Diethyl amino Salicylaldehyde of Analytical grade were used for synthesis of ligand. AR grade metal chlorides were used for the preparation of the complexes.

Instrumentation

$^1\text{H-NMR}$ spectra of ligand were recorded on FT NMR spectrometer (400 MHz) model Advance-II (Bruker) 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 at SAIF Chandigarh. All electronic absorption spectra of the complexes and ligand were chronicled on Shimadzu 1800 spectrometer. The CHN analysis was carried out on Thermo Scientific (FLASH 2000) CHN elemental analyzer.

Synthesis of ligand

It's a two-stepsynthesis;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 pouring on crushed ice and filtration, followed by recrystallization in super dry ethanol. (Yield: 92%).

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 continuousstirring .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: 90%).

Results and discussion

CHNanalysis, MP,Color, Mol.Wt, and molar conductance data of ligand and metal complexes is depicted in **Table1**.The data shows equimolarstoichiometry (metal: ligand) and satisfying general formula $[\text{ML}]$ [where M = Ni (II), Cu (II)].

$^1\text{H-NMR}$ spectra of ligand

The ^1H NMR spectra of free ligand in CDCl_3 at room temperature shows the following signals. 1.04-1.09 δ (t, 6H, $2\times\text{CH}_3\text{-CH}_2\text{-N}$), 1.11-1.16 δ (q, 4H, $2\times\text{N-CH}_2\text{-CH}_3$), 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) [9] [**Fig.2**] and mass spectra in [**Fig.3**].

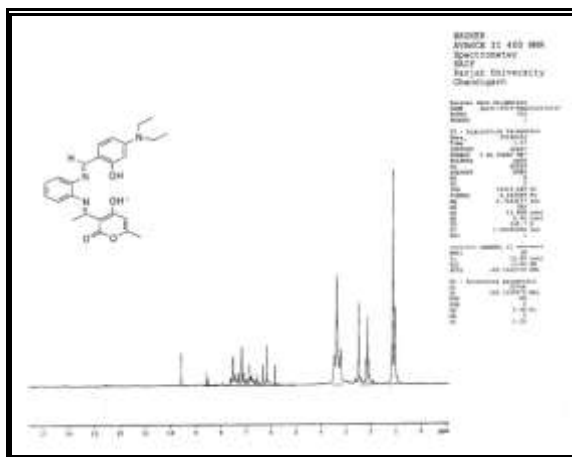


Fig.2

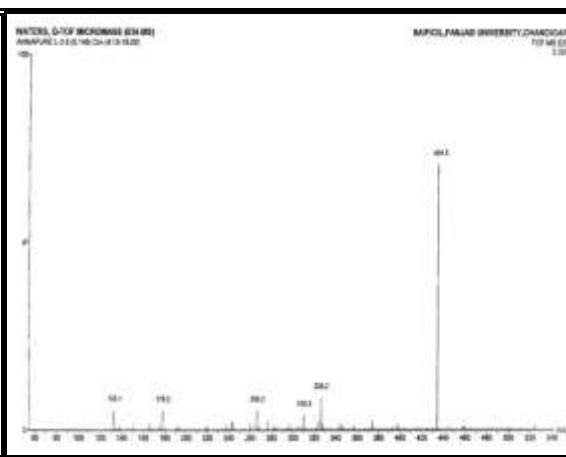


Fig.3

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 ₂₅ H ₂₇ N ₃ O ₄	433.50	87	Dark Red	----	68.25 (69.27)	6.06 (6.28)	9.23 (9.69)	-----
[LNi]	492.19	210	Dark Maroon	38.08	60.96 (61.01)	4.45 (4.53)	8.49 (8.54)	11.86 (11.92)
[LCu]	497.05	208	Reddish Brown	55.80	60.36 (60.41)	4.31 (4.35)	8.39 (8.45)	12.68 (12.78)

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	3427	1693.3	1660	1566.8	1360	1212	-	-
Ni-L	3075	1681.2	1633	1565.7	1345	1214	445	415
Cu-L	3078	1685.0	1631	1565.4	1350	1215	542	460

IR spectra

The IR data of ligand (H₂L) and its metalcomplexes are listed in (Table 2). It depicts prominent bands at 3427, 1693, 1660, 1360 and 1212 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 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 found at lower frequency 1631-1633 cm⁻¹ when complex 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 445-542 and 415-460 cm⁻¹ regions confirms the M-O and M-N bonding respectively [13]. No any change in skeletal vibrations (C=C) upon complexation.

Powder x-ray diffraction

Scanning of x-ray diffractogram of Ni (II), Cu (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 [14]. The diffractogram of Ni (II) complex of L had Nine reflections with maxima at $2\theta = 9.468^\circ$ corresponding to d value 7.28254 Å. The unit cell of Ni(II) complex of L yielded values of lattice constants, $a=13.35775\text{Å}$, $b=7.297302\text{Å}$, $c = 6.383613\text{Å}$ and unit cell volume $V=868.18815\text{Å}^3$. The diffractogram of Cu(II) complex of L had Twelve reflections with maxima at $2\theta = 11.647^\circ$ corresponding to d value 9.78456 Å. The unit cell of Cu(II) complex of L yielded values of lattice constants, $a=12.75326\text{Å}$, $b=10.066585\text{Å}$, $c = 9.844085\text{Å}$ and unit cell volume $V=856.83415\text{Å}^3$.

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 Ni(II), Cu(II), complex of L has monoclinic [15] crystal system.

Magnetic susceptibility and electronic absorption spectra

The electronic absorption spectra of Ni (II) complex consists of two bands at about 17123 cm⁻¹ and 28089 cm⁻¹ assignable to $1A_{1g} \rightarrow 1T_{2g}$ and charge transfer transitions respectively. Observed electronic transitions, the diamagnetic nature and red color of the complex suggests squareplanar geometry for Ni (II) complex. Cu(II) show three bands at 14577, 25906 and 30581 cm⁻¹ assignable to the transitions $2B_{1g} \rightarrow 2A_{1g}$

and two intraligand charge transfer bands. These electronic transitions and observed 1.86 B.M magnetic moment value suggests square-planar geometry around Cu (II) [16].

Thermal analysis

The TG/DSC analysis of 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 Ni(II) complex [Fig.4] show no mass loss up to 230 °C indicates absence of coordinated water. First mass loss 11.57% (calcd.11.67%) in the range 240-340°C and an endothermic peak in this region $\Delta T_{min} = 243.25^\circ\text{C}$, indicate removal of non-coordinated part of ligand [17]. The second step decomposition from 340-400 °C with 10.51% mass loss. In third step from 400-575 °C sudden weight loss 17.99 %, confirmed by exotherm $\Delta T_{max} = 432.91^\circ\text{C}$ indicate loss of coordinated part.

The thermal profile of Cu (II) complex shows mass loss 8.08 % (calcd.8.15%) in the range 200-370°C and an endothermic peak in this region $\Delta T_{min} = 270^\circ\text{C}$ indicates loss of coordinated part of ligand. The complex show slow decomposition from 370-650°C with mass 25.34% (calcd.25.44%) loss and a broad exotherm $\Delta T_{max} = 405^\circ\text{C}$ in DSC may be attributed to removal of coordinated part of ligand [18]. No mass loss observed after 700 °C indicates more thermal stability of complex.

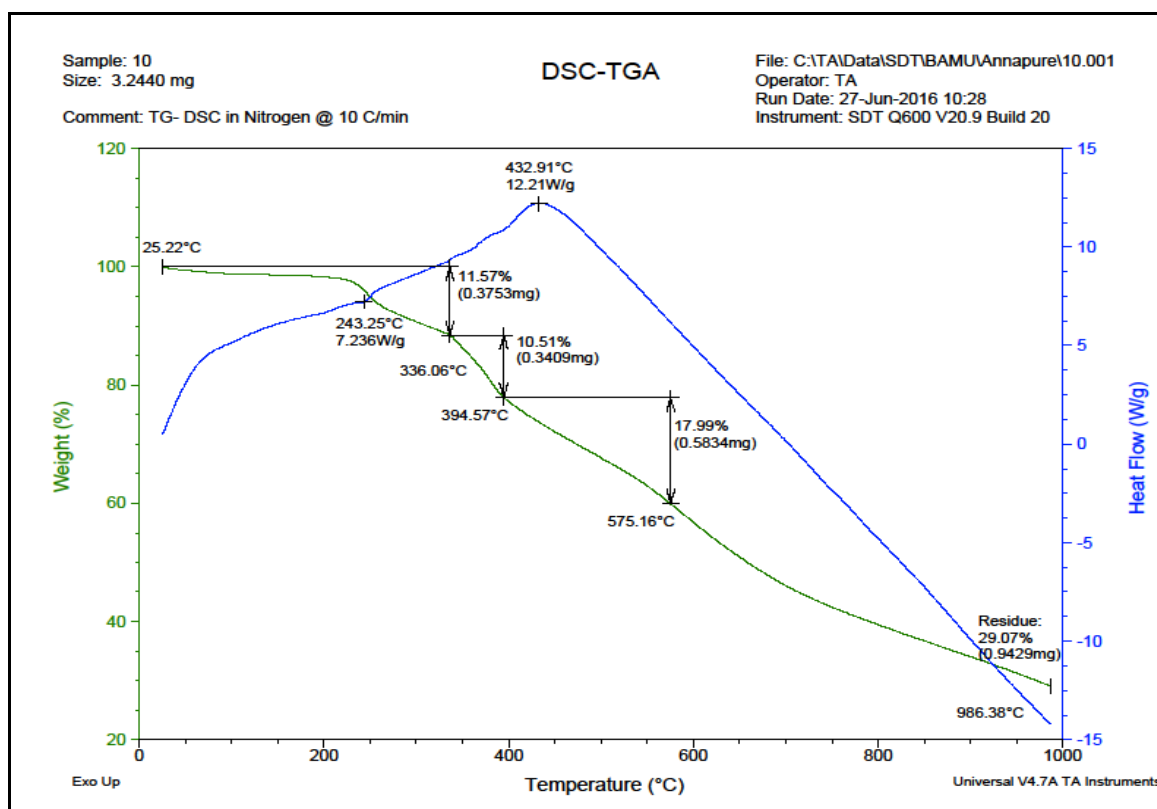


Fig.4

Kinetic Calculation

The kinetic and thermodynamic parameters viz ΔG (free energy change), ΔS (entropy of activation, Z (pre-exponential factor), E_a (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 [19] and Coats-Redfern Integral method [20].

The data is arranged in (Table 3). The results show that the values obtained by two methods are analogous.

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)
Ni(II)	I	1.12	HM	32.66	85264	-155.85	46.25	0.9995
			CR	31.23	1112456	-158.45	42.56	0.9995
	II	115	HM	28.42	154623	-122.26	35.46	0.9948
			CR	25.49	19684752	-120.45	32.89	0.9956
Cu(III)	I	1.25	HM	35.61	90886	-155.10	46.81	0.9987
			CR	30.60	13622935	-114.05	42.33	0.9989
	II	1.10	HM	43.57	192815	-153.11	60.47	0.9971
			CR	44.90	34082919	-110.08	57.05	0.9919

E_a in kJ mol⁻¹, Z in S⁻¹, ΔS in JK⁻¹mol⁻¹ and ΔG in kJ mol⁻¹

Antimicrobial activity

Ligand and metal complexes are subjected for antifungal activity; by using Mycelia dry weight method [21] compounds were tested against *Trichoderma* and *Aspergillus Niger*. The activity is tested at 250 and 500 ppm in DMF and depicted in (Table-4) 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-5). Perceiving the values of Table-4 and 5, inference made that the inhibition by metal complexes is more than a ligand. Solubility of metal complexes in organic solvents increase its activity. Hydrogenbonding with active center of cell may responsible for enhanced activity.

Table 4Yield 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)	61(23)	24(70)	40(43)	19(73)
[LNi]	43(46)	13(84)	22(69)	03(96)
[LCu]	40(49)	10(87)	20(71)	02(97)

Table 5 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)	08	11	11	14
[LNi]	12	12	13	17
[LCu]	13	14	16	19

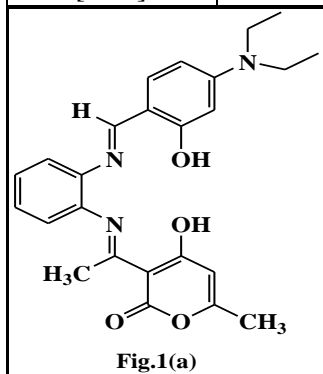


Fig.1(a)

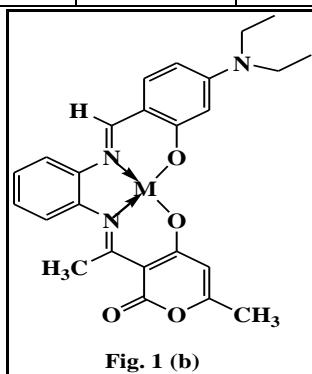


Fig. 1 (b)

Fig.1a Structure of the Ligand, Where M=Ni(II), Cu(II).**Fig. 1b** Proposed structure of the complexes,

Conclusion

In this publication we report synthesis of ligand and its metal complexes of first transition series. Spectral study suggest that azomethine nitrogen and phenolic oxygen are involved in the co-ordination with metal ions (**fig.1 (b)**). Proposing square planar geometry for Ni(II), and Cu(II), complexes. It is resolved that the ligand is dibasic in nature. Tetradentate N₂O₂ donor metal complexes are biologically active and indicates heightened antimicrobial activities compared to its free ligand. The XRD reveals monoclinic crystal system for Ni(II), and Cu (II) complexes. Thermal study predicts thermal behavior and stability of complexes.

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