

Synthesis, Characterization and Antimicrobial Activities of some Transition Metal Complexes of Biologically Active Asymmetrical Tetradentate Ligands

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ABSTRACT

The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with asymmetrical tetradentate Schiff bases derived from *o*-phenylenediamine (H_2L_1)/4-methyl *o*-phenylenediamine (H_2L_2), 3-Acetyl-6-methyl-pyran-2,4-dione (Dehydroacetic acid) and 2-hydroxy-1-naphthaldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, uv-visible, i.r., ¹H-nmr. spectra, X-ray diffraction, thermal analysis, and screened for antimicrobial activity. The IR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donor atoms sequence towards central metal ion. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand). The physico-chemical data suggests square planar geometry for Cu(II) and Ni(II) complexes and octahedral geometry for Co(II), Mn(II) and Fe(III) complexes respectively. The x-ray diffraction data suggests orthorhombic crystal system for Cu(II) complex, monoclinic crystal system for Ni(II) and Fe(III). Thermal behaviour (TG/DTA) 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 antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* and fungicidal activity against *Aspergillus Niger* and *Trichoderma*.

INTRODUCTION

Tetradentate Schiff bases with N_2O_2 donor atoms are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry [1-5]. Schiff bases of *o*-phenylenediamine reported to have variety of applications including biological [6], clinical [7] and analytical [8] fields. Many symmetrical tetradentate bis-Schiff bases of 1, 2-diamines with *o*-hydroxy aldehyde/ketone have been prepared and studied intensively. However much less attention has been focused on asymmetrical tetradentate Schiff bases derived from 1, 2-diamines and different aldehydes/ketones. In particular, those derived from aromatic 1, 2 diamines have been under-investigated [9] It is worthwhile to mention here that asymmetrical Schiff bases of this type are difficult to obtain and not easily isolated [10]

A search of literature reveals that no work has been done on the transition metal complexes of the asymmetrical Schiff bases derived from aromatic 1, 2- diamine, dehydroacetic acid and 2-hydroxy-1-naphthaldehyde. In this communication we report the synthesis of asymmetrical tetradentate Schiff bases formed by the condensation of *o*-

phenylenediamine/4-methyl o-phenylenediamine, dehydroacetic acid and 2-hydroxy-1-naphthaldehyde (Fig.1). The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with these ligands have been prepared and characterized by different physico-chemical methods.

MATERIALS AND METHODS

Reagents and solvents

Dehydroacetic acid obtained from Merck was used as supplied. o-phenylenediamine/4-methyl o-phenylenediamine and 2-hydroxy-1-naphthaldehyde of AR grade were used for synthesis of ligand. AR grade metal chlorides were used for the complex preparation.

Synthesis of ligand

The ligand was prepared by a modification of the reported methods [11-13]. Asymmetric tetradentate Schiff base ligand has been synthesized via a stepwise approach. In the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of 10 mmol of dehydroacetic acid and 10mmol o-phenylenediamine/4-methyl o-phenylenediamine in super dry ethanol for about 3 h. Mono-Schiff base thus formed was then refluxed with 10mmol 2-hydroxy-1-naphthaldehyde to prepare asymmetric ligand. Asymmetric Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol. (Yield: 70%).

Synthesis of metal complexes

To a hot methanol solution (25ml) of the ligand (0.01 mol), methnolic solution (25ml) of metal chloride (0.01 mol) was added with constant stirring. The pH of reaction mixture was adjusted to 7.5-8.5 by adding 10% alcoholic ammonia solution and refluxed for about 3 h. The precipitated solid 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: 55%)

Physical Measurement

The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. IR spectra were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets. ¹H-NMR spectra of ligand were measured in CDCl₃ using TMS as internal standard. The TG/DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701 respectively. The UV-visible spectra of the complexes were recorded on JascoUV-530 spectrometer. Magnetic susceptibility measurements of the metal chelates were done on a Guoy balance at room temperature using Hg[Co(SCN)₄] as a calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10⁻³ M solution in DMF.

RESULTS AND DISCUSSION

Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveals 1:1 molar ratio (metal: ligand) and corresponds well with the general formula [ML] (where M = Cu(II) and Ni(II)) and [ML(H₂O)₂] (where M = Co(II), Mn(II) and Fe(III)). The magnetic susceptibilities of Cu(II) and Ni(II) complexes at room temperature are consistent with square-planar geometry and that of Co(II), Mn(II) and Fe(III) complexes with high spin octahedral structure with two water molecules coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TG-DT analysis. The metal chelate solutions in DMF show low conductance and supports their non-electrolyte nature. (Table 1)

¹H-NMR spectra of ligand

The ¹H-n.m.r. spectra of free ligand in CDCl₃ at room temperature shows the following signals. 2.05-2.15 δ (s, 3H, C₆-CH₃), 2.40-2.55 δ (s, 3H, N=C-CH₃), 4.75 δ (s, 1H, phenolic OH), 5.80 δ (s, 1H, C₅-H), 6.6-7.9 δ (m, aromatic protons), 8.4 δ (s, 1H, N=C-H) and 15.90-16.00 δ (s, 1H, enolic OH of DHA moiety). In addition to these peaks (H₂L₂) shows a peak at 2.30 δ (s, 3H, phenyl-CH₃).

FTIR spectra

The IR spectrum of free ligands shows characteristic bands at 3200-3400, 1684-1699, 1640-1660, 1338-1344 and 1219-1275 cm⁻¹ assignable to ν OH (intramolecular hydrogen bonded), ν C=O (lactone carbonyl), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively [14-15] The absence of

a weak broad band in the 3200-340 cm^{-1} region, in the spectra of the metal complexes suggests deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by upward shift in ν C-O [16] (phenolic) to the extent of 20-50 cm^{-1} . On complexation, the ν (C=N) band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of azomethine group is coordinated to the metal ion. This is supported by upward shift in ν C-N to the extent of 20-40 cm^{-1} [17] The Ir spectra of metal chelates showed new bands in the 495-565 and 409-485 cm^{-1} regions which can be assigned to ν M-O and M-N vibrations respectively [18] The Ir spectra of Co(II), Mn(II) and Fe(III) show a strong band in the 3050-3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840 cm^{-1} region, assignable to the rocking mode of water [19] The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

Magnetic susceptibility and electronic absorption spectra

The magnetic and electronic spectral data is in relevance with proposed geometry of complexes (Fig 2). The electronic absorption spectrum of Cu(II) show three bands at 17577, 25906 and 29585 cm^{-1} for L_1 and 17360, 27624 and 30030 cm^{-1} for L_2 assignable to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and two intraligand charge transfer bands. These electronic transitions and observed 1.80-1.81 B.M magnetic moment value suggests square-planar geometry around Cu(II) [18,20] The electronic absorption spectra of Ni(II) complex consists of two bands at about 17123 cm^{-1} and 25706 cm^{-1} for L_1 and 18083, and 25906 cm^{-1} for L_2 assignable to ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and charge transfer transitions respectively. Observed electronic transitions, the diamagnetic nature and red colour of the complex suggests square-planar geometry for Ni(II) complex [21,22] Co(II) complex show three bands at 10857, 19011 and 27027 cm^{-1} for L_1 and 10775, 17421 and 25706 cm^{-1} for L_2 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 4.48-4.66 B.M. suggest high spin octahedral geometry for Co(II) complex [23,24] The octahedral geometry is further supported by ratio $\nu_2/\nu_1 = 1.750$ and 1.616 which is close to the value expected for octahedral geometry. Spectra of Mn(II) complex contains three bands at 16313, 22371 and 30487 cm^{-1} for L_1 and 14814, 24449 and 29673 cm^{-1} for L_2 assignable to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and charge transfer respectively. Electronic transitions along with magnetic moment value 5.74-5.73 BM which is almost close to spin only value (5.92 BM) suggest high spin octahedral geometry for Mn(II) complex [23,25] The electronic absorption spectra of Fe(III) complex show three weak bands at 13513, 18867 and 29154 cm^{-1} for L_1 and 13460, 19801 and 32573 cm^{-1} for L_2 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 5.84-5.78 BM suggests high spin octahedral geometry for Fe(III) complex [23,26]

Thermal analysis

The simultaneous TG/DT analysis of Cu(II) and Ni(II) complexes of L_1 and Co(II), Mn(II) and Fe(III) complexes of L_2 was done from ambient temperature to 1000°C in nitrogen atmosphere using α - Al_2O_3 as reference. In the TG curve of Cu(II) and Ni(II) complexes of L_1 , no mass loss up to 270°C indicates absence of coordinated water in these complexes [17]. In the TG curve of Cu(II) complex, the first step of decomposition from 285°C to 400°C, with a mass loss 24.70% (calcd. 23.11%), an exothermic peak $\Delta T_{\text{max}} = 335^\circ\text{C}$ in DTA may be attributed to the removal of non coordinated part of ligand. The second slow step from 410-905°C with mass loss 58.80% (calcd.61.46%), corresponds to decomposition of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue corresponds to stable CuO, 18.5% (calcd.17.82%). The TG curve of Ni(II) complex, show two step decomposition. The first step from 288°C to 435°C, with a mass loss 24.00% (calcd. 23.38%), an exothermic peak $\Delta T_{\text{max}} = 330^\circ\text{C}$ in DTA may be attributed to the decomposition of non coordinated part of ligand. The slow decomposition in second step from 565-868°C with mass loss 60.20% (calcd.62.05%), corresponds to removal of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue 10% does not corresponds to any stoichiometry of end product.

The thermogram of Co(II) complex show mass loss 7.5% (calcd.7.9%) in the range 180-230°C and an endothermic peak in this region $\Delta T_{\text{min}} = 207^\circ\text{C}$, indicates loss of two coordinated water molecules [27,28] The anhydrous complex first show slow decomposition in 240-550°C range with 28% mass loss (calcd.27.01%) and a broad exotherm $\Delta T_{\text{max}} = 248^\circ\text{C}$ in DTA may be attributed to removal of non coordinated part of ligand. The second step decomposition at 580-870°C, with mass loss of 51.30% (calcd.52.08%) corresponds to decomposition of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue corresponds to stable CoO with mass 12.25% (calcd.12.94%). The TG curve of Mn(II) complex show first mass loss

7.20% (calcd.7.97%) in the range 145-210°C and an endothermic peak in this region $\Delta T_{min} = 175^\circ\text{C}$, indicate removal of two coordinated water molecules. The anhydrous complex shows single step slow decomposition from 260-1000 °C with 52% mass loss. A broad endotherm in DTA indicates that the complex is thermally quite stable. The thermal profile of Fe(III) complex shows mass loss 7.5% (calcd.7.96%) in the range 160-250°C and an endothermic peak in this region $\Delta T_{min} = 207^\circ\text{C}$ indicates loss of two coordinated water molecules. The anhydrous complex first show slow decomposition from 250-625°C with mass 27% (calcd.27.20%) loss and a broad exotherm $\Delta T_{max} = 283^\circ\text{C}$ in DTA may be attributed to removal of non coordinated part of ligand. The second step decomposition is sharp from 655 to 665°C with mass loss of 14.50% (calcd. 14.85%) a sharp endotherm in DTA at 655°C is observed for this step. The third step decomposition is from 670 to 800°C with 22% mass loss. The mass of the final residue 9.2% does not corresponds to any stoichiometry of end product.

Kinetic calculations

The kinetic and thermodynamic parameters *viz* n (order of reaction), E_a (energy of activation), z (pre-exponential factor), ΔS (entropy of activation) and ΔG (free energy change) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Horowitz-Metzer (HM) approximation method [29] and Coats-Redfern integral method [30] The data is given in Table 2. The results show that the values obtained by two methods are comparable. The calculated values of energy of activation of the complexes are relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the complex [31,32] The negative value of entropy of activation indicates that the activated complexes are more ordered than the reactant and that the reactions are slow. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

(Table 2)

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

Compound Molecular formula	Mol. Wt.	M.P. / Decomp. Temp. °C	Colour	Molar conduc. Mho cm ² mol ⁻¹	Found (Calculated)			
					C	H	N	M
(H ₂ L ¹) [C ₂₅ H ₂₀ N ₂ O ₄]	412.45	153	Yellow	----	72.52 (72.80)	5.08 (4.89)	6.90 (6.79)	----
[L ¹ Cu]	474.00	250	Reddish Brown	57.50	64.10 (63.29)	3.85 (3.80)	6.12 (5.91)	13.52 (13.41)
[L ¹ Ni]	469.16	245	Red	37.07	64.35 (63.94)	4.21 (3.84)	6.25 (5.97)	12.78 (12.51)
[L ¹ Co (H ₂ O) ₂]	505.38	265	Coffee Brown	35.22	60.20 (59.36)	4.70 (4.35)	6.05 (5.54)	12.10 (11.66)
[L ¹ Mn (H ₂ O) ₂]	501.39	278	Brown	26.32	59.30 (59.83)	4.80 (4.39)	6.10 (5.58)	11.40 (10.96)
[L ¹ Fe (H ₂ O) ₂]	502.30	255	Brown	53.60	59.90 (59.73)	4.55 (4.38)	5.86 (5.57)	11.95 (11.12)
(H ₂ L ²) [C ₂₆ H ₂₂ N ₂ O ₄]	426.48	173	Yellow	----	74.15 (73.23)	5.15 (5.20)	6.80 (6.57)	----
[L ² Cu]	488.03	267	Brown	52.10	64.42 (63.93)	4.57 (4.10)	5.60 (5.74)	13.45 (13.02)
[L ² Ni]	483.19	258	Red	32.54	64.82 (64.57)	4.73 (4.14)	6.02 (5.79)	12.54 (12.15)
[L ² Co (H ₂ O) ₂]	519.41	273	Reddish Brown	27.85	60.86 (60.07)	4.35 (4.62)	5.60 (5.39)	11.75 (11.35)
[L ² Mn (H ₂ O) ₂]	515.42	290	Brown	25.20	60.01 (60.53)	4.52 (4.66)	5.50 (5.43)	10.80 (10.66)
[L ² Fe (H ₂ O) ₂]	516.33	288	Brown	59.50	60.25 (60.43)	4.32 (4.65)	5.95 (5.42)	11.20 (10.82)

Powder x-ray diffraction

The x-ray diffractogram of Cu(II), Fe(III) complexes of L₁ and Ni(II) complex of L₂ metal complexes was scanned in the range 5-100° at wavelength 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Cu(II) complex of L₁ had eight reflections with maxima at 2θ = 7.081° corresponding to d value 12.473 Å. The diffractogram of Ni(II) complex of L₂ shows thirteen reflections with maxima at 2θ = 9.654° corresponding to d value 9.154 Å. The diffractogram of Fe(III) complex of L₁ had eleven reflections with maxima at 2θ = 89.964° corresponding to d value 1.089 Å. The x-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been

indexed by using computer programme [33] The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cu(II) complex of L_1 yielded values of lattice constants, $a=24.7884 \text{ \AA}$, $b=7.5475 \text{ \AA}$, $c = 3.3399 \text{ \AA}$ and unit cell volume $V=624.8771 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ required for sample to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Cu(II) complex has orthorhombic crystal system. The unit cell of Ni(II) complex of L_2 yielded values of lattice constants, $a=18.8424 \text{ \AA}$, $b=3.8620 \text{ \AA}$, $c = 12.3857 \text{ \AA}$ and unit cell volume $V=751.0398 \text{ \AA}^3$. The unit cell of Fe(III) complex of L_1 yielded values of lattice constants, $a=11.3309 \text{ \AA}$, $b=5.6308 \text{ \AA}$, $c = 4.6692 \text{ \AA}$ and unit cell volume $V=295.3025 \text{ \AA}^3$. In concurrence with 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) complex of L_2 and Fe(III) complex of L_1 has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method [34] and found to be 2.5065, 2.1420 and 2.8406 gcm^{-3} for Cu(II), Ni(II) and Fe(III) complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were calculated. Number of molecules per unit cell were calculated by using equation $\rho = nM/NV$ and was found to be four, two, and one for Cu(II), Ni(II), and Fe(III) complexes respectively. With these values, theoretical density were computed and found to be 2.5188, 2.1363 and 2.8241 gcm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [35]

Table 2 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)
Cu(II)	I	1.45	HM CR	21.15	22.68	6.788	7.013	-234.43	-234.15	37.22	38.73	0.9988 0.9999
	II	0.89	HM CR	13.47	14.34	0.129	0.151	-271.00	-269.71	42.28	43.09	0.9988 0.9936
Ni(II)	I	1.01	HM CR	26.41	26.13	14.02	8.334	-229.08	-233.41	43.46	43.50	0.9953 0.9929
	II	0.61	HM CR	27.47	28.16	1.012	1.404	-254.74	-252.02	57.43	57.80	0.9982 0.9946
Co(II)	I	1.20	HM CR	12.16	12.56	0.281	1.080	-262.27	-269.39	33.30	34.33	0.9999 0.9991
	II	0.95	HM CR	37.16	33.34	4.290	4.756	-242.78	-241.93	65.91	62.93	0.9995 0.9995
Mn(II)	----	1.42	HM CR	33.44	24.28	2.450	1.766	-247.42	-250.17	62.75	53.91	0.9936 0.9832
Fe(III)	I	1.40	HM CR	17.32	17.62	0.895	1.335	-252.86	-249.54	38.30	38.33	0.9921 0.9979
	II	0.35	HM CR	33.99	32.91	2.540	2.362	-247.22	-247.82	63.51	62.50	0.9990 0.9971

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

Table 3 Antibacterial activity of compounds

Test Compound	Inhibition zone (mm)			
	<i>E. Coli</i>		<i>Staphylococcus</i>	
	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciproflaxin	29	32	31	35
(H_2L^1)	10	12	11	15
[L^1Cu]	14	16	16	19
[L^1Ni]	12	12	13	17
[$L^1Co(H_2O)_2$]	12	14	14	17
[$L^1Mn(H_2O)_2$]	10	12	11	15
[$L^1Fe(H_2O)_2$]	10	12	11	15
(H_2L^2)	12	13	14	16
[L^2Cu]	16	18	18	20
[L^2Ni]	14	13	15	18
[$L^2Co(H_2O)_2$]	14	15	16	19
[$L^2Mn(H_2O)_2$]	13	14	15	17
[$L^2Fe(H_2O)_2$]	13	14	15	17

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 [36] The compounds were tested at the concentration 500ppm and 1000ppm. DMF and compared with known antibiotics *viz* ciproflaxin. (Table 3). For fungicidal activity, compounds were screened *in vitro* against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method [16] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (Table 4). From Table 3 and 4, 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 [16, 36] Such enhanced activity of metal chelates is due to the increased lipophilic nature of the metal ions in complexes [37]. 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 centre of cell constituents, resulting in interference with the normal cell process [38].

Table 4 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 ¹)	55 (30)	22 (72)	34 (51)	18 (74)
[L ¹ Cu]	35 (56)	10 (87)	14 (80)	01 (99)
[L ¹ Ni]	35 (56)	11 (86)	17 (76)	03 (96)
[L ¹ Co (H ₂ O) ₂]	40 (49)	15 (81)	24 (66)	03 (96)
[L ¹ Mn (H ₂ O) ₂]	48 (39)	17 (78)	29 (59)	07 (90)
[L ¹ Fe (H ₂ O) ₂]	50 (37)	18 (77)	31 (56)	10 (86)
(H ₂ L ²)	52 (34)	20 (75)	31 (56)	16 (77)
[L ² Cu]	26 (67)	08 (90)	12 (83)	01 (99)
[L ² Ni]	32 (59)	09 (89)	13 (81)	01 (99)
[L ² Co (H ₂ O) ₂]	38 (52)	11 (86)	15 (79)	02 (97)
[L ² Mn (H ₂ O) ₂]	43 (46)	12 (85)	23 (67)	06 (91)
[L ² Fe (H ₂ O) ₂]	45 (43)	16 (80)	24 (66)	08 (89)

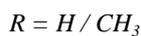
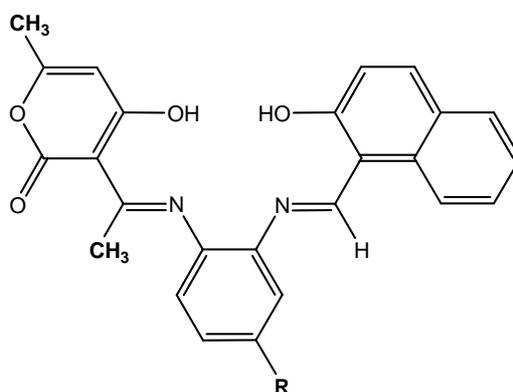


Figure 1. Structure of ligand

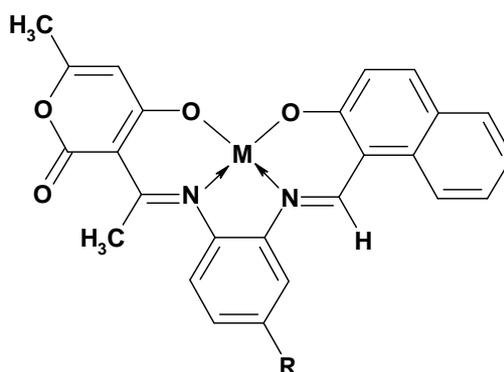


Figure 2(a)

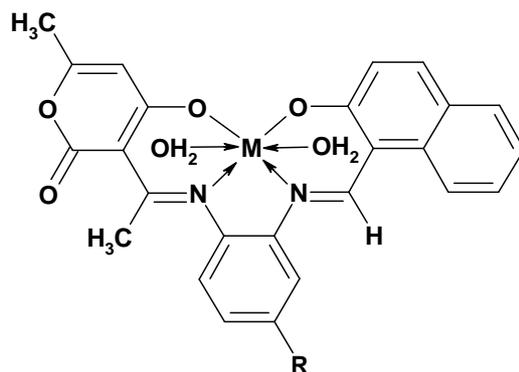


Fig. 2(b)

 $R = H / CH_3$ **Fig.2. The proposed structure of the complexes.**(a) When $M = Cu(II)$ and $Ni(II)$; (b) When $M = Co(II)$, $Mn(II)$ and $Fe(III)$

CONCLUSION

In the light of above discussion we have proposed square- planar geometry for Cu(II) and Ni(II) complexes and octahedral geometry for Co(II), Mn(II) and Fe(III) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, ONNO tetradentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig.2. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The XRD study suggests orthorhombic crystal system for Cu(II) complex and monoclinic crystal system for Ni(II) and Fe(III) complexes.

REFERENCES

- [1] R. Atkins, G. Breweg, E. Kakot, G. M. Mockler, E. Sinn, *Inorg. Chem.*, **1985**, 24, 127.
- [2] R. Yuan, Y. Chai, D. Liu, D. Gao, J. Li and R. Yu, *Anal. Chem.*, **1993**, 65, 2572.
- [3] R. Ramesh, P. K. Saganthy, K. Natarajan, *Synth. React. Inorg. Met-Org. Chem.*, **1996**, 26, 47-60.
- [4] Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **1997**, 70, 1319.
- [5] B. Jeog, C. Rim, H. Chae, K. Chjo, K. Nam, Y. Choi, *Bull. Korean Chem. Soc.*, **1996**, 17, 688.
- [6] P. Singh, R. L. Geol, B.P. Singh, *J. Indian Chem. Soc.*, **1975**, 52, 958.
- [7] A. M. Mahindra, J. M. Fisher, M. Rabinovitz, *Nature.*, **1983**, 303, 64.
- [8] P. R. Patel, B.T. Thaker, S. Zele, *Indian J. Chem.*, **1999**, 38A, 563.
- [9] N. T. S. Pan, D. H. Brown, H. Adams, S. E. Spey, P. Styring, *J. Chem. Soc. Dalton Trans.*, **2004**, 9, 1348.
- [10] S. F. Tan, K. P. Ang, *Trans. Met. Chem.*, **1988**, 13, 64-68.
- [11] L. G. Marzilli, P. A. Marzilli, J. Halpern, *J. Am. Chem. Soc.*, **1984**, 93, 1374.
- [12] N. K. Jha, D. M. Joshi, *Synth. React. Inorg. Met-Org. Chem.*, **1984**, 14, 455.
- [13] M. A. Qayyoom, P. Hanumanthu, C. V. Ratnam, *Indian J. Chem.*, **1982**, 21, 883.
- [14] N. Ramarao, V. P. Rao, R. V. J. Jayage, M. C. Ganorrkar, *Indian J. Chem.*, **1985**, 24(4), 877.
- [15] S. F. Tan, K. P. Ang, H. L. Jatchandran, *Trans. Met. Chem.*, **1984**, 9, 390-395.
- [16] R. P. Venketeswar, N. A. Venkata, *Indian J. Chem.*, **2003**, 42A, 896.
- [17] D. C. Dash, A. K. Panda, P. Jena, S. B. Patjoshi, A. Mahapatra, *J. Indian Chem. Soc.*, **2002**, 79, 48-50.
- [18] R. Natrajan, K. Antonysamy, C. Thangaraja, *Trans. Met. Chem.*, **2003**, 28, 29-36.
- [19] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York, **1970**, pp 159, 167, 214.
- [20] N. Raman, Y. Pitchaikaniaraja, A. Kulandaisamy, *Proc. Indian Acad. Sci.*, **2001**, 113 (3), 183-189.
- [21] K. M. Reddy, M. B. Halli, A. C. Hiremath, *Indian J. Chem. Soc.*, **1994**, 17, 118.
- [22] M. Mokhles, Abd-Elzaher, *J Chinese Chem. Soc.*, **2001**, 48, 153-158.
- [23] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1968** pp 275-361.
- [24] K. C. Satpathy, A. K. Panda, R. Mishra, I. Pande, *Trans. Met. Chem.*, **1991**, 16, 410.

-
- [25] L. Sacconi, *Trans. Met. Chem.*, **1968**, 61, 943.
[26] M. N. Patel, V. J. Patel, *Synth. React. Inorg. Met. Org. Chem.*, **1989**, 19, 137.
[27] N. S. Bhave, R. B. Kharat, *J. Inorg. Nucl. Chem.*, **1980**, 42, 977.
[28] V. K. Revankar, V. B. Mahale, *Indian J. Chem.*, **1979**, 28A, 683.
[29] H. H. Horowitz, G. Metzger, *Anal. Chem.*, **1963**, 35, 1464.
[30] A. W. Coats, I. P. Redfern, *Nature.*, **1964**, 20, 68.
[31] A. M. El-Awad, *J. Therm. Anal. Cal.*, **2000**, 61, 197.
[32] A. Impura, Y. Inoue, I. Yasumori, *Bull. Chem. Soc. Jpn.*, **1983**, 56, 2203.
[33] J. R. Carvajal, T. Roisnel, Winplotr, **2004**, A Graphic Tool for Powder Diffraction, Laboratoire Leon Brillouin (cea/enrs) 91191 gif suryvette cedex, France.
[34] D. P. Shoemaker and C. W. Garland, *Experiments in Physical Chemistry*, 5th edn, Mc Graw-Hill International Edition, New York, **1989**, pp 17-27.
[35] M. B. Deshmukh, S. Dhongade, S. Desai, S. S. Chavan, *Ind. J. Chem.*, **2005**, 44, 1659.
[36] P. S. Mane, S. G. Shirodkar, B. R. Arbad, T. K. Chondhekar, *Ind. J. Chem.*, **2001**, 40, 648.
[37] L. Mishra; V. K. Singh, *Ind. J. Chem.*, **1993**, 32A, 446.
[38] N. Dharamraj, P. Viswanathamurthi, K. Natarajan, *Trans. Met. Chem.*, **2001**, 26, 105.