King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Synthesis, spectral, thermal, potentiometric and antimicrobial studies of transition metal complexes of tridentate ligand

Sarika M. Jadhav [a], **Vinod A. Shelke** [a], **Sunil G. Shankarwar** [a], **Achut S. Munde** [b], **Trimbak K. Chondhekar** [a,*]

[a] *Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, Maharashtra, India*
[b] *Department of Chemistry, Milind College of Science, Aurangabad 431004, Maharashtra, India*

Abstract   A series of metal complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) have been synthesized with newly synthesized biologically active tridentate ligand. The ligand was synthesized by condensation of dehydroacetic acid (3-acetyl-6-methyl-(2*H*) pyran-2,4(3*H*)-dione or DHA), *o*-phenylene diamine and fluoro benzaldehyde and characterized by elemental analysis, molar conductivity, magnetic susceptibility, thermal analysis, X-ray diffraction, IR, ^{1}H-NMR, UV–Vis spectroscopy and mass spectra. From the analytical data, the stoichiometry of the complexes was found to be 1:2 (metal:ligand) with octahedral geometry. The molar conductance values suggest the non-electrolyte nature of metal complexes. The IR spectral data suggest that the ligand behaves as a dibasic tridentate ligand with ONN donor atoms sequence towards central metal ion. Thermal behaviour (TG/DTA) and kinetic parameters calculated by the Coats–Redfern and Horowitz–Metzger method suggest more ordered activated state in complex formation. To investigate the

Production and hosting by Elsevier

relationship between stability constants of metal complexes and antimicrobial activity, the dissociation constants of Schiff bases and stability constants of their binary metal complexes have been determined potentiometrically in THF–water (60:40%) solution at 25 ± 1 °C and at 0.1 M $NaClO_4$ ionic strength. The potentiometric study suggests 1:1 and 1:2 complexation. Antibacterial and antifungal activities *in vitro* were performed against *Staphylococcus aureus*, *Escherichia coli* and *Aspergillus niger*, *Trichoderma*, respectively. The stability constants of the metal complexes were calculated by the Irving–Rosotti method. A relation between the stability constant and antimicrobial activity of complexes has been discussed. It is observed that the activity enhances upon complexation and the order of antifungal activity is in accordance with stability order of metal ions.

1. Introduction

The Schiff base ligands and their metal complexes find applications in the fields of food and dyes industry, agriculture, analytical chemistry, catalysis, polymer sciences, biological science as antimicrobial agents, medical science as anticancer, antiseptic, antidiarrhoeal, antiulcer agents, in liquid crystal devices (LCD), metal corrosion inhibition and as myocardial perfusion imaging agents (Koubek et al., 1966). These compounds are regarded as the model system of biochemical interest (Dey, 1974). Various studies have shown that, the azomethine group (>C═N–) in Schiff base metal complexes has considerable biological significance and found to be responsible for biological activity such as fungicidal and insecticidal (Popp, 1961). Schiff bases of amino guanidine and aromatic aldehydes were studied for their antiviral, tuberculostatic and antipoliovirus activities (Mane et al., 2001).

The structural and interesting biological properties of DHA appeal to inorganic chemists working in the field of coordination chemistry. Schiff bases and their metal complexes exhibit a wide range of biological activities and various structural features. In view of the enormous importance of DHA and its metal complexes it is thought worthwhile to synthesize the Schiff base of DHA and its metal complexes. One of the oxygen heterocyclic compounds 3-acetyl-6-methyl-2H-pyran 2,4(3H)-dione (DHA) was reported to be an excellent chelating agent and possesses promising fungicidal, bactericidal, herbicidal and insecticidal activities (Suryarao et al., 1978, 1980; Schleiffenbaum et al., 1992; Stanley et al., 1996). It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems (Levai and Jeko, 2006).

The structural and interesting biological properties of DHA appeal to inorganic chemists working in the field of coordination chemistry. In view of the enormous importance of DHA and its metal complexes it is thought worthwhile to synthesise the Schiff bases of DHA and their metal complexes. Literature survey reveals that little attention has been given on tridentate Schiff bases of DHA containing ONN donor systems. In continuation of our earlier work (Munde et al.,2009, 2010; Halpern et al., 1971; Shirodkar et al., 2001), we have prepared tridentate Schiff base and its metal complexes, whose structure agrees with the above mentioned structural and coordinative patterns for biological activity. The solid complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) with this ligand have been prepared and characterized by different physicochemical methods. Stability constants of these complexes are also determined potentiometrically. The structure-activity correlation of Schiff base and its metal complexes is discussed on the basis of their stability constants.

2. Experimental

o-Phenylenediamine and benzaldehyde AR grade were used for synthesis of ligand. DHA (Purity ⩾ 99%) was purchased from E. Merk and used as supplied. AR grade metal nitrates were used for complex preparation. AR grade solvents were used for spectral measurements. The carbon, hydrogen and nitrogen contents were determined on Perkin–Elmer (2400) CHNS analyzer. IR spectra in the range of 4000–400 cm^{-1} were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets. ^{1}H-NMR spectra of the ligand was recorded in $CDCl_3$ using TMS as an internal standard. The TG/DTA and XRD were recorded on Perkin–Elmer TA/SDT-2960 and Philips 3701, respectively. The UV–Vis spectra of the complexes were recorded on JascoUV-530 Spectrophotometer. Magnetic susceptibility measurements of the metal complexes were done on a Guoy balance at room temperature using Hg.$[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM-180 conductometer using 1 mM solution in dimethyl sulphoxide. Elico digital pH metre (model Li-127) equipped with a CL-51B combined electrode was used for pH measurements. The pH metre was calibrated against standard buffers (pH 4.02 and 9.18) before measurements. pH metre readings were corrected for organic-aqueous media. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M ($NaClO_4$). The solutions were titrated pH metrically against (0.2 N) NaOH.

2.1. General procedure for the synthesis of ligand

2.1.1. Step I

The ligand was prepared by modification of reported method (Jha and Joshi, 1984; Qayyoom et al., 1982) In a 50 mL solution of 0.001 mol (0.168 g) of DHA, 0.001 mol (0.108 g) of *o*-phenylenediamine was refluxed in super dry ethanol for about 3 h. Then it was cooled to room temperature. On cooling, the solid white colored intermediate compound, mono-Schiff base was obtained with 80% yield.

2.1.2. Step II

0.001 mol of intermediate (0.258 g) was then refluxed with 0.001 mol (0.10 mL) of fluoro benzaldehyde (0.107 mL) in super dry ethanol for 6 h. The precipitate thus formed was filtered, dried in vacuum over $CaCl_2$ and recrystallised in ethanol (yield: 73%).

2.2. General procedure for the synthesis of metal complexes

To a hot methanolic solution (0.02 mol) of ligand in (25 mL) methanolic solution, (25 mL) of metal nitrate (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 °C) and dried over calcium chloride in a vaccum dessicator (yield 62%).

2.3. Potentiometric study

Since the Schiff base and its metal complexes were found to be either insoluble or sparingly soluble in water, a reaction mixture consisting (60:40) THF–water solution was used as a solvent for potentiometric studies. THF used in the present investigation was obtained from E. Merk and was further purified by known literature method (Vogel, 1989). All metal ion solutions were prepared from their AR grade metal nitrates and standardized by known literature methods. A standard 0.2 N NaOH solution (E. Merk) was used for titrations. Standard solutions of AR grade $HClO_4$, $NaClO_4$ (1.0 M) were prepared and standardized by known methods (Ramarao et al., 1985). The ligand solution (0.1 M) was prepared in distilled THF.

3. Results and discussion

The analytical data of ligand and metal complexes is given in (Table 1). The elemental analysis show 1:2 (metal:ligand) stoichiometry for the complexes. It corresponds well with the general formula $[ML_2]$ where M = Cu(II), Ni(II), Co(II), Mn(II) and Fe(III). The magnetic susceptibilities of all complexes at room temperature are found to be consistent with octahedral geometry. The metal complex solutions in DMSO show low conductance which supports their non electrolyte nature.

3.1. ^{1}H-NMR spectra of ligand

The ^{1}H-NMR spectra of the ligand was recorded in $CDCl_3$. It shows following signals at 2.18δ, (s, C6–CH_3), 2.55δ (s, 3H, N=C–CH_3), 5.8δ (s, 1H, C5–H), 7.3–8.0 (m, 8H, phenyl), 8.8δ (s, 1H, N=C–H) and 15.87δ (s, 1H, enolic OH of DHA moiety).

3.2. Mass spectra of the ligand

Mass spectral data confirmed the structure of the ligand HL as indicated by the peaks corresponding to their molecular mass.

3.3. FTIR spectra

The FTIR spectrum of free ligand shows characteristic bands at 3435, 3070, 1698, 1602, 1361 and 1220 cm^{-1} assignable to intramolecular hydrogen bonded υ(OH), carbon–hydrogen stretching frequency υ(C–H), lactone carbonyl υ(C=O), methyl azomethine υ(C=N), arylazomethine υ(C–N) and phenolic υ(C–O) stretching modes, respectively (Tan et al., 1988; Venketeswar and Venkata, 2003). In the IR spectra of metal complexes, the absence of broad band in the range of 3300–3500 cm^{-1} region indicates deprotonation of the intramolecular hydrogen bonded OH group on complexation. This is supported by upward shift in phenolic υ(C–O) (Sari et al., 2006). The υ(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 υ(C–N) values. The IR spectra of metal complexes showed new bands in 457–740 cm^{-1} region which can be assigned to υ(M–O) and (M–N) stretching vibrations, respectively (Eichhorn and Bailar, 1953). From the above facts it is evident that the coordination takes place via azomethine nitrogen and phenolic OH of the ligand molecule.

3.4. Magnetic measurements and electronic absorption spectra

The electronic spectra of Cu(II) complex in DMSO show bands at 13,812, 15,576 and 27,777 cm^{-1} assignable to a $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2E_g$ and charge transfer transitions, respectively. The electronic spectral data coupled with observed magnetic moment 1.81 µB suggest octahedral geometry for Cu(II) complex (Gudasi et al., 2007). Ni(II) complex displays three bands at 9433, 14,970 and 27,173 cm^{-1} assignable to $^3A_{2g} \rightarrow ^3T_{2g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ transitions, respectively. These electronic transitions along

Table 1 Physico-analytical data of ligand and metal compounds.

Compound/complexes	M.p. (°C)	Colour	Λ (Ω^{-1} cm^{1}cm^2)	Found (calcd.) (%)				
				C	H	N	F	M
HL	182	Cream White	–	69.40 (69.22)	4.90 (4.70)	7.80 (7.68)	5.50 (5.21)	–
CuL$_2$	265	Green	13.45	63.50 (63.67)	4.10 (4.07)	7.00 (7.07)	4.50 (4.79)	8.20 (8.02)
NiL$_2$	> 300	Yellow	11.02	64.50 (64.06)	4.20 (4.09)	7.30 (7.11)	4.90 (4.82)	7.60 (7.45)
CoL$_2$	245	Brown	15.03	64.10 (64.04)	4.00 (4.05)	7.25 (7.11)	4.85 (4.82)	7.36 (7.18)
FeL$_2$	255	Brown	12.02	64.35 (64.29)	4.10 (4.11)	7.15 (7.14)	4.90 (4.84)	7.20 (7.11)
MnL$_2$	277	Brown	17.24	64.40 (64.33)	4.20 (4.08)	7.20 (7.13)	4.90 (4.75)	7.50 (7.35)

HL = Schiff base ligand, 10^{-3} M solution in DMF.

Table 2 Ligand field parameters of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) complexes.

Compound	Ligand field splitting energy (Dq cm^{-1})	Racah interelectronic repulsion parameter (B cm^{-1})	Covalent factor (β)	$\beta\%$	v_2/v_1	Ligand field stabilization energy LFSE (kcal mol^{-1})
CuL$_2$	1381	30	–	–	1.127	39.364
CoL$_2$	1086	847	0.872	14.55	1.735	30.978
NiL$_2$	943	922	0.886	12.80	1.586	26.886
FeL$_2$	1347	681	0.671	32.83	1.410	38.409
MnL$_2$	1351	633	0.658	34.10	1.745	38.513

with magnetic moment 3.15 μB suggest octahedral geometry for Ni(II) complex (Lever, 1968; Hosney, 2007). The Co(II) complex shows three transitions at 10,869, 18,867 and 26,455 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow ^4A_{2g}$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transitions, respectively. These transitions and observed magnetic moment 4.6 μB indicate high spin octahedral geometry of the complex (Syamal and Maurya, 1986; Satpathy et al., 1991; Mane et al., 2002; Jadhav et al., 2010). Fe(III) complex exhibit bands at 13,477, 19,011 and 31,645 cm^{-1}assignable to $^6A_{1g} \rightarrow ^4T_1(^4D)$, $^6A_{1g} \rightarrow ^4T_{1g}$ and $^6A_{1g} \rightarrow ^4T_{2g}$, respectively. The observed magnetic moment 5.80 μB along with electronic transitions corresponds to octahedral geometry (Patel and Patel, 1989; Yaul et al., 2009). In case of Mn(II) complex the observed magnetic moment 5.85 μB and the spectral bands at 13,513, 23,584 and 26,455 cm^{-1} assignable to $^6A_{1g} \rightarrow ^4T_1(G)$, $^6A_{1g} \rightarrow ^4T_{2g}(G)$ and $^6A_{1g} \rightarrow ^4E_g$ transitions, respectively, indicate octahedral geometry for the complex (Makode et al., 2009; Badwaik et al., 2009; Carvajal et al., 2004). The calculated values of ligand field splitting energy (10Dq), Racah interelectronic repulsion parameter (B), covalent factor (β), ratio υ$_2$/υ$_1$ and ligand field stabilization energy (LFSE) data given in (Table 2) supports the proposed geometry for all the complexes.

3.5. Powder X-ray diffraction analysis

The X-ray diffractogram of metal complexes was scanned in the range 5°–10° at wavelength 1.543 Å. The diffractogram and associated data depict 2θ values for each peak, relative intensity and interplanar spacing (d-values). The diffractogram of Cu(II) complex shows 15 reflections with maxima at 2θ = 37.798 corresponding to d value 2.377 Å. The diffractogram of Ni(II) complex had eleven reflections with maxima at 2θ = 89.953° Corresponding to d value 1.089 Å, where as the diffractogram of Fe(III) complex had fourteen reflections with maxima at 2θ = 23.11° corresponding to d value 3.845 Å. The X-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% have been indexed by using computer programme (Shoemaker and Garland, 1989). Cu(II) complex yielded values of lattice constants, a = 8.364 Å, b = 7.848 Å, c = 7.761 Å and α = γ = 90°, β = 113.20° and unit cell volume V = 468.09 (Å)^3. Ni(II) complex yielded values of lattice constants, a = 14.152 Å, b = 6.147 Å, c = 4.432 Å, α = β = γ = 90° and unit cell volume V = 385.603 (Å)^3. Fe(III) complex yielded values of lattice constants, a = 14.546 Å, b = 5.732 Å, c = 9.940 Å, α = γ = 90°, β = 97.396, and unit cell volume V = 821.942 (Å)^3. Cu(II), Fe(III) complexes of the condition a ≠ b ≠ c and α = γ = 90° ≠ β required for the compound to be monoclinic were found to be satisfactory. While for Ni(II) complex, the condition such as a ≠ b ≠ c and α = β = γ = 90° required for the compound to

be orthorhombic was found to be satisfactory. Experimental density values of the complexes were determined by using specific gravity method (Coats and Redfern, 1964) and found to be 2.809, 2.478 and 2.673 g·cm^{-3} for Cu(II), Ni(II), and Fe(III) complexes respectively which were exactly equal to the theoretical calculated values.

3.6. Thermal analysis

The Cu(II), Fe(III) and Mn(II) complexes were chosen for thermal study. The TG/DT analysis of metal complexes was carried from ambient temperature to 1000 °C in nitrogen atmosphere using α-Al$_2$O$_3$ as reference. In the thermogram of Cu(II) complex, the first step decomposition was shown in the range 220–490 °C with a mass loss 48.60% (calcd. = 49.79%). Similarly exothermic peaks ΔT_{max} = 220 and 320 °C in DTA were attributed to decomposition of non coordinated part of ligand. The second step of decomposition in the range 480–800 °C corresponds to mass loss due to decomposition of coordinated part of ligand 39.20% (calcd. = 40.17%), afterward the weight loss remained constant corresponding to stable metal oxide CuO 10.00% (calcd. = 10.03%).

In Fe(III) complex, the first weight loss in the range 290–440 °C, indicated the decomposition of non-coordinated part of complex corresponding to weight loss 49.80% (calcd. = 50.40%). An exothermic peak at temperature 437.51 °C in DTA corresponds to sudden weight loss. The second step of decomposition, from temperature 450 °C to 950 °C with weight loss 40.00% (calcd. = 40.67%) is due to coordinated part of the complex. Finally stable metal oxide with 9.00% (calcd. = 9.13%) weight loss was obtained.

In the TG curve of Mn(II) complex, the first weight loss 89.70% (calcd. = 89.90%) in the range 260–900 °C, indicated the decomposition of non-coordinated part of complex. Exothermic peaks at 267, 302 °C in DTA correspond to sudden weight loss. Finally stable metal oxide with weight loss 9.00% (calcd. = 9.02%) was obtained Table 3.

3.6.1. Kinetic calculations

The kinetic and thermodynamic parameters for decomposition of metal complexes have been determined by the Coats–Redfern method and Horowitz–Metzger method (El-Award, 2000; Nakamoto, 1961) and given in (Table 4). The calculated free energy of activation is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of metal complexes (Impura et al., 1983; Irving and Rossotti, 1954; Nakamoto, 1978). Negative ΔS values indicate more ordered activated states that may be possible through chemisorptions of oxygen and other decomposition products. The more ordered nature may be due to the polarization of bonds in

Table 3 Magnetic and electronic absorption spectral data (in DMSO) of the compounds.

Compound	μ_{eff} μ_B	v (cm^{-1})	Band assignment	Geometry
HL	–	31,055	–	
		33,783		
CuL$_2$	1.81	13,812	$^2B_{1g} \rightarrow {}^2A_{1g}$	Octahedral
		15,576	$^2B_{1g} \rightarrow {}^2E_g$	
		27,777	Charge transfer	
NiL$_2$	3.15	9433	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	Octahedral
		14,970	$^3A_{1g} \rightarrow {}^3T_{1g}(F)$	
		27,173	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
CoL$_2$	4.60	10,869	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
		18,867	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		26,455	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
FeL$_2$	5.80	13,477	$^6A_{1g}(F) \rightarrow {}^4T_1(^4D)$	Octahedral
		19,011	$^6A_{1g} \rightarrow {}^4T_{1g}$	
		31,645	$^6A_{1g} \rightarrow {}^4T_{2g}$	
MnL$_2$	5.85	13,513	$^6A_{1g} \rightarrow {}^4T_1(G)$	Octahedral
		23,584	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	
		26,455	$^6A_{1g} \rightarrow {}^4E_g$	

Table 4 The kinetic parameters of degradation of the metal complexes calculated by the Horowitz–Metzer (HM) and Coats–Redfern (CR) methods.

Complex	Step	Decomposition temperature (°C)	n	Method	Ea (kJmol^{-1})	ΔG^* (kJmol^{-1})	ΔS^* (JK^{-1}mol^{-1})	Z (S^{-1})	Correlation coefficient (r)
CuL$_2$	I	355	1.5	HM	9.64	37.67	−274.89	7×10^{-2}	0.9942
				CR	9.52	30.69	−271.58	8.85×10^{-2}	0.9959
	II	640	0.3	HM	11.28	29.20	−173.72	1.12×10^{-1}	0.999
				CR	16.39	27.73	−159.49	1.769	0.9964
FeL$_2$									
	I	330	1.45	HM	50.29	84.28	−233.91	15.31	0.9936
				CR	50.35	80.45	−235.67	17.82	0.9945
	II	660	1.5	HM	18.53	46.63	−260.12	4.81×10^{-1}	0.9945
				CR	25.76	53.10	−253.21	1.11	0.9996
MnL$_2$	I	365	1.35	HM	11.58	36.60	−240.49	3.57	0.9903
				CR	17.01	35.40	−245.38	1.98	0.9993
	II	700	0.55	HM	11.58	36.60	−240.49	3.57	0.9903
				CR	17.01	35.40	−245.38	1.98	0.9993

activated state which might happen through charge transfer electronic transitions.

3.7. Potentiometry

Calvin–Bjerrum pH titration technique as modified by Irving and Rossotti was used to determine proton-ligand and metal-ligand stability constants in THF–water mixture (60% v/v) at a constant temperature 25 °C and ionic strength of 0.1 M NaClO$_4$. The Irving and Rossotti method was used to calculate $\bar{n}_A$, $\bar{n}$, pK and pL values from the pH titration curves. The constants of ligand and metal complexes are given in the (Table 5).

In the present ligand, protonation takes place in the initial stages of titration because of the presence of azomethine nitrogen. The pK$_1$ and pK$_2$ were determined at $\bar{n}_A$ = 1.5 and 0.5, respectively. The first stability constant pK$_1$ therefore refers to the imine nitrogen. However there are two imine nitrogens present in the ligand and only one pK value is displayed by it, suggesting that out of two nitrogens, one is not involved in protonation. This may be attributed to the intramolecular hydrogen bonding of nitrogen N^b (Fig. 1) which undergoes

chelation with enolic OH of dehydroacetic acid moiety and hence does not take part in protonation and deprotonation. Therefore the pK value shown by the ligand is due to the protonation of nitrogen N^a. The second pK observed as 9.98 in the ligand is due to the dissociation of enolic proton which is sufficiently acidic due to the resonance effect. All the metals form 1:1 and 1:2 chelates with this ligand. The 1:1 and 1:2 chelates are formed in a simultaneous process in all the systems. Hence, the method of least squares has been invariably used for getting accurate values of log k$_1$ and log k$_2$. These values are reported in (Table 5).

Coordination of metal ion with ligand takes place via protonated nitrogen and oxygen of the enolic group. The order of stability constants is Cu > Ni > Co > Fe > Mn which is in agreement with the Irving–Williams order (Douglas et al., 1991).

3.8. Antifungal activity

In the present investigation the free ligand, free metal salts, control (DMSO solvent), and newly synthesized metal

Table 5 Stability constants of the complexes at 25 ± 0.1 °C and $\mu = 0.1$ M.

Compound	CuL$_2$	NiL$_2$	CoL$_2$	FeL$_2$	MnL$_2$
logk_1	9.39	8.57	8.54	4.87	2.97
logk_2	8.84	8.01	5.05	2.87	2.93
logβ	18.23	16.58	13.59	7.74	5.90

Protonation constants of Schiff base pK_1 = 3.01 and pK_2 = 9.98.

Table 6 Antibacterial activity of compounds (diameter of inhibition zone in mm) antifungal activity (weight in mg% inhibition) of the ligand and metal complexes.

Compound	Antibacterial activity				Antifungal activity			
	E. Coil		Staphylococcus		Aspergillus niger		Trichoderma	
	0.5 mg/mL	1 mg/mL	0.5 mg/mL	1 mg/mL	0.5 mg/mL	1 mg/mL	0.5 mg/mL	1 mg/mL
Ciprofloxin/control	40	45	42	44	75	72	65	60
HL	09	20	07	16	58(23)	46(36)	50(23)	39(35)
CuL$_2$	19	38	14	30	32(57)	17(76)	33(49)	28(53)
NiL$_2$	10	21	09	20	38(49)	18(75)	35(46)	29(52)
CoL$_2$	12	26	11	24	43(43)	19(73)	41(41)	30(50)
FeL$_2$	14	27	12	26	48(36)	27(66)	42(35)	31(48)
MnL$_2$	16	30	13	28	49(35)	25(65)	45(31)	35(42)
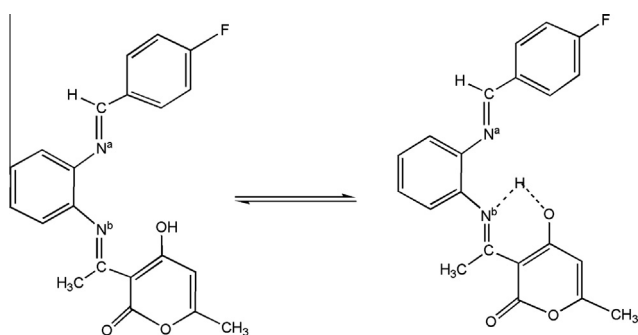
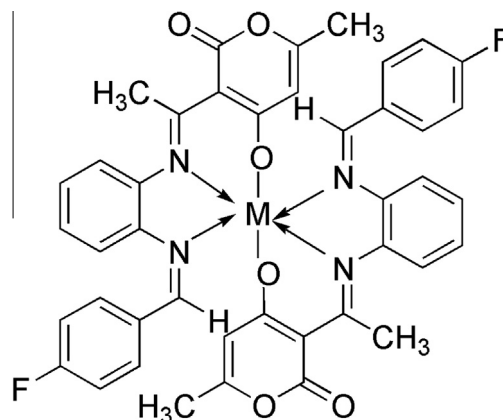**Figure 1** Resonance structure of the ligand.

complexes were screened for antifungal activity against fungi like *Aspergillus niger* and *Trichoderma* at 0.5 and 1 mg mL^{-1} levels separately. The cultures of the fungi were purified by single spore isolation technique. The concentrations of 0.5 and 1 mg mL^{-1} of each compound in DMSO were prepared. The fungi toxicity of Schiff base and its metal complexes in liquid medium were studied by the mycelia dry method (Sari et al., 2006) *in vitro* against *A*. niger and *Trichoderma*. The results of investigation indicate that all the ligands and their metal complexes arrested the growth of *A*. niger and *Trichoderma*. A considerable increase in fungi toxicity of metal complexes as compared to their ligands is observed for both 0.5 and 1 mg mL^{-1}.

3.9. Antibacterial activity

The antibacterial activity of ligand and metal complexes was tested *in vitro* against bacteria such as *Staphylococcus* aureus and *Escherichia coli*, by paper disc plate method (Sari et al., 2006). The compounds were tested at the concentration 0.5 and 1 mg mL^{-1} in DMSO and compared with known antibiot-

ics ciprofloxin given in (Table 6) The results obtained were compared with known antibiotics, ciprofloxin. Three replicate values were taken and average value is given in (Table 6).

From the results obtained, it clear that the antibacterial activity of metal salts is negligibly small. Inhibition by metal complexes is found to be higher than that of a free ligand and corresponding metal salts against the same organism under identical experimental conditions. This is similar to earlier observations (Badwaik and Aswar, 2007). This can be attributed to Tweedy's chelation theory, according to which, the chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole ring (Thangadurai and Natarajan, 2001). This increases the lipophilic character of the metal chelates. Transport of both, metal and ligand across lipophilic membranes to vital intramolecular sites is favored by chelation. Once intracellular, the

Figure 2 Proposed structure of the metal complexes, where M = Cu(II), Ni(II), Co(II), Mn(II) and Fe(III).
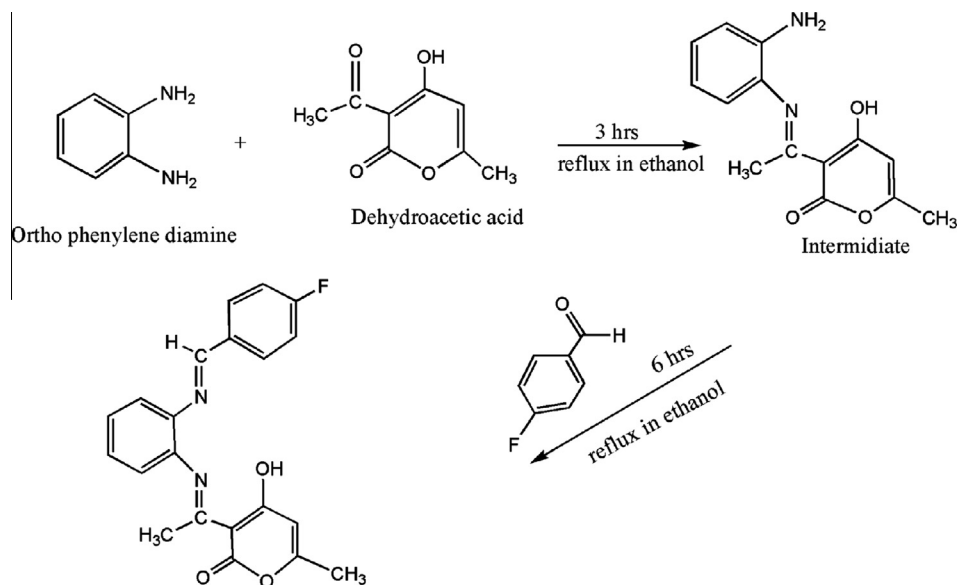
Scheme 1   Synthesis of the ligand.

fully coordinated complex or one of its derivatives, including the dissociated metal or ligand may be the active entity. For each class of microorganism, higher activity is shown by Cu(II) complex. Because of its high stability the Cu(II) chelate as a whole may be considered to be the most active component.

Investigation of antifungal activity of the ligand and its metal complexes revealed that, all the metal chelates are more fungi toxic than their parent ligand (Table 6). The antifungal activity of the ligand is found to enhance several times on being coordinated with metal ions. Antifungal activity of these complexes is found to be increased as the stability of the complex increased. The activity of these complexes follow the order Cu > Ni > Co > Fe > Mn which is exactly same as the order of stability constants of these complexes. Comparison of activities of the ligand and its metal chelates shows that the copper complex is more active as the ligand, against *A. niger*. Activity of ligand against *Trichoderma* is found to increase after chelation. However the extent of the increase is less than that of *A. niger*. The high antifungal activity of ligand and its metal complexes may be due to the fluoro substituents present in the ligand (Ismail, 2002).

4. Conclusion

On the basis of physicochemical and spectral data discussed above, octahedral geometry for Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) complexes is proposed. From IR spectra it is assumed that the ligand behaves as ONN tridentate, coordinating via phenolic oxygen and imino nitrogen as illustrated in (Fig. 2a and b) Thermal study reveals that the complexes are thermally stable. The XRD study suggests the orthorhombic crystal system for Ni(II) and monoclinic crystal system for Cu(II) and Fe(III) complexes. The antimicrobial activity of the complexes is more as compared to the ligand. Antibacterial activity shows that the copper complex is more biologically active in all complexes. Antifungal activity of these complexes is found to be increased in the similar order of increase in the stability constants of metal complexes Scheme 1.

References

Badwaik, V.B., Aswar, A.S., 2007. Russ. J. Coord. Chem. 33, 755–760.
Badwaik, V.B., Deshmsukh, R.D., Aswar, A.S., 2009. Russ. J. Coord. Chem. 35, 247–252.
Carvajal, J.R., Roisnel T., Winplotr, A. Graphic 2004. Tool for Powder Diffraction Laboratories leon brillouin (ceal/enrs) 91191 gif suryvette cedex France.
Coats, A.W., Redfern, J.P., 1964. Nature 201, 68–75.
Dey, K., 1974. J. Sci. Res. 33, 76–97.
Douglas, X.W., Cinda, S., Carlson, Anthoney, 1991. Trans. Met. Chem. 16, 53–56.
Eichhorn, G.L., Bailar, J.C., 1953. J. Am. Chem. Soc. 75, 2905–2907.
El-Award, A.M., 2000. J. Therm. Anal. Cal. 197, 163–177.
Gudasi, K., Patil, M., Vadvai, R., Shenoy, R., Patil, S., 2007. J. Serb. Chem. Soc. 72, 357–566.
Halpern, P., Marzilli, L.G., Marzilli, P.A., 1971. J. Am. Chem. Soc. 93, 1374–1378.
Hosney, N.M., 2007. J. Coord. Chem. 60, 2755–2764.
Impura, A., Inoue, Y., Yasumori, I., 1983. Bull. Chem. Soc. Jpn. 56, 2203–2207.
Irving, H., Rossotti, H.S., 1954. J. Chem. Soc., 2904–2910.
Ismail, F.M.D., 2002. J. Fluorine Chem. 118, 27–33.
Jadhav, S.M., Shelke, V.A., Munde, A.S., Shankarwar, S.G., Patharkar, S.R., Chondhekar, T.K., 2010. J. Coord. Chem. 63 (24), 4153–4164.
Jha, N.K., Joshi, D.M., 1984. Synth. React. Inorg. Met-Org. Chem. 14, 455–465.
Koubek, E., Ginsberg, A.P., Williams, H.J., 1966. J. Inorg. Chem. 5, 1656–1662.
Levai, A., Jeko, J., 2006. Monatash. Chem. 137, 339.
Lever, A.B.P., 1968. Inorganic Chem.. 4, 763.
Makode, J.T., Yaul, A.R., Bhandage, S.G., Aswar, A.S., 2009. Russ. J. Coord. Chem. 54, 1372–1377.

Mane, P.S., Shirodkar, S.G., Arbad, B.R., Chondhekar, T.K., 2001. Indian J. Chem. 40A, 648–651.

Mane, P.S., Shirodkar, S.G., Chondhekar, T.K., 2002. J. Indian Chem. Soc. 79A, 376–378.

Munde, A.S., Jagdale, A.N., Jadhav, S.M., Chondhekar, T.K., 2009. J. Korean Chem. Soc. 53, 407–414.

Munde, A.S., Jagdale, A.N., Jadhav, S.M., Chondhekar, T.K., 2010. Serb. Chem. Soc. 75, 349–359.

Nakamoto, K., 1961. In: Kirschner, S. (Ed.), Advances in the Chemistry of Coordination Compounds. Mc Millan, New York.

Nakamoto, K., 1978. Infrared and Raman Spectral of Inorganic Coordination Compounds, third ed. John Wiley, New York.

Patel, M.N., Patel, V.T., 1989. J. Synth. Rect. Inorg. Met. Org. Chem. 19, 137–155.

Popp, F.D., 1961. J. Org. Chem. 26, 1566–1568.

Qayyoom, M.A., Hanumanthu, P., Ratnam, C.V., 1982. Indian J. Chem. 21B, 883–885.

Ramarao, N., Rao, V.P., Jayage, R.V.J., Ganorrkar, M.C., 1985. Indian J. Chem. 24, 877–880.

Sari, N., Gurkan, Cete, P.S., Sakiyan, I., 2006. Russ. J. Coord. Chem. 32, 511–517.

Satpathy, K.C., Panda, A.K., Mishra, R., Pande, I., 1991. Transition Met. Chem. 16, 410–412.

Schleiffenbaum, B., Spertini, O., Tedder Thomas, F., 1992. J. Cell Biol. 119 (1), 229.

Shirodkar, S.G., Mane, P.S., Chondhekar, T.K., 2001. Indian J. Chem. 40A, 1114–1117.

Shoemaker, D.P., Garland, C.W., 1989. Experiments in Physical Chemistry, fifth ed. Mc Graw-Hill International Edition, New York.

Stanley, V.G., Woldesenbet, S., Gray Cassandra, 1996. Poultry Sci. 75 (1), 42.

SuryaRao, D., SubhaRao, B.L., John, V.T., Ganorkar, M.C., 1978. Nat. Acad. Sci. Lett. 1, 402.

SuryaRao, D., Sadasiva Reddy, C., John, V.T., Ganorkar, M.C., 1980. Curr. Sci. 49, 511.

Syamal, A., Maurya, R., 1986. Trans. Met. Chem.. 11, 172.

Tan, S.F., Ang, K.P., Jatchandran, H.L., 1988. Trans. Met. Chem. 13, 64–68.

Thangadurai, D.T., Natarajan, K., 2001. Synth. React. Inorg. Met-Org. Chem. 31, 549–567.

Venketeswar, R.P., Venkata, N.A., 2003. Indian J. Chem. 42A, 1896–1899.

Vogel, A.I., 1989. A Text Book of Practical Organic Chemistry, fifth ed. ELBS & Longmann, London, pp. 289.

Yaul, S.R., Yaul, A.R., Pethe, G.B., Aswar, A.S., 2009. Am-Eura. J. Sci. Res. 4, 229–234.