Asian Journal of Chemistry; Vol. 28, No. 8 (2016), 1721-1728

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19800

Synthesis, Characterization, DNA Cleavage, Antimicrobial and Catalytic Studies of Tridentate (N_3) Schiff Base Ligand and its Complexes with Transition Metal Ions

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Received: 28 December 2015; *Accepted*: 13 February 2016; *Published online*: 30 April 2016; AJC-17880

Transition metal complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions have been synthesized from cinnamaldehyde and diethylenetriamine. The complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility, FT-IR, electronic spectra, ^{1}H NMR, ^{13}C NMR, ESR, mass spectra and thermal studies. Their ligand field parameters have also been calculated. Hydrolysis of ethyl acetate has been studied by using the complexes as homogeneous catalysts. The DNA cleavage activities of Schiff base and its metal complexes have been monitored by agarose gel electrophoresis method in the presence of hydrogen peroxide. The antimicrobial activities of ligand and its metal complexes have been examined on the fungi *Candida albicans* and *Aspergillus niger* and bacteria *Staphylococcus aureus, Escherichia coli* and *Bacillus cereus.*

Keywords: Tridentate Schiff base ligand, Ligand field parameters, Hydrolysis of ester, DNA cleavage, Antimicrobial studies.

INTRODUCTION

Cinnamaldehyde contains an α,β-unsaturated carbonyl moiety which can be considered as Michael acceptor that binds with proteins and is employed in drug designing [1-3]. As it records low toxicity on human exposure it is used as an effective fungicide and insecticide to annihilate mosquito larve. It exhibits inhibitory activities towards proliferation, invasion and tumor growth in a murine A375 model of Human melanoma. It also inhibits par tuberculosis with an MIC of 25.9 µg/mL and its derivatives show enormous antimicrobial inhibition on *Escherichia coli* and *Salomonella typhimurium* [4-6].

The Schiff bases are widely employed as ligands in coordination chemistry. These ligands containing various donor atoms O, N, S depict broad physico-chemical, antitubercular, antitumor, fungicidal and antibacterial activities [7,8]. The Cu(II) based metal complexes are widely used in recent research mechanism of photovoltaic and photo sensitizers. Their Schiff base complexes are similar to the biomolecules in nature. The biological activities of mixed ligand carbonyl Schiff base metal complexes containing nitrogen donors have attached recent interest in anticancer activity. The catalytic studies of Schiff base metal complexes are effectively conducted on oxidation of alcohols, oxidative cleavage, hydroformylation, hydrolysis of esters, *etc*. The synthesis and characterization of tridentate ligand having nitrogen donor atoms and their metal complexes are interesting as they have significant catalytic, antimicrobial and DNA cleavage applications. In this study, a new series of transition metal complexes had been designed and synthesized using a new type of Schiff base derived from the condensation of cinnamaldehyde and diethylenetriamine [9].

EXPERIMENTAL

All the reagents were of AnalaR grade and the solvents were purified by standard methods. The IR spectra (4000-400 cm^{-1}) had been taken on KBr disc using a Perkin Elmer Spectrum ONE-N017-1159 spectrophotometer. Micro analysis of carbon, hydrogen and nitrogen was carried out using elemental analyzer and magnetic moments were measured at room temperature on vibrating sample magneto meter EG&G Model: 155 using Hg[Co(CN)$_4$] as one standard. The potential for electrical conductance of the complexes was determined on a systronic conductivity meter type 304 in DMSO with a dip type cell fitted with a platinum electrode. The UV-visible spectra were run on a carry-5E spectrometer (200-900 nm) in nujol mull. The TGA-DTA graphs were obtained by tapping NETZCH STA-409C/CD thermal analyzer. The electrochemical behaviour of the complexes had been studied with the help of cyclic voltammetry obtained on a CHI-600A electrochemical analyzer under oxygen free condition using a three electrode cell in which glassy carbon acted as a working electrode, calomel as a reference electrode and platinum wire as an auxiliary electrode supported by sodium perchlorate as the background electrolyte. The ^1H NMR, ^{13}C NMR spectra were recorded on JKM-ECS 400 in DMSO-d_6 and $CDCl_3$ solvents respectively. The mass spectrum was recorded using WATERS-Q-T of premier-HAB213, electro spray ionization-MS electrode. The ESR spectrum of Cu(II) complex was obtained at 300 K on Bruker BioSpin GmbH using DPPH as the g-markers.

Synthesis of Schiff base (L): A solution of cinnamaldehyde (0.2M, 0.7 mL) in 25 mL ethanol was added drop wise to diethylenetriamine (0.1M, 0.25 mL) in 25 mL of ethanol and the mixture was stirred for about 1 h. The resulting solution was allowed to cool and then poured into an ice bath. The yellow precipitate was filtered and after getting washed with ethanol [10-13], the precipitate was recrystallized from hot solution of ethanol and chloroform. The yield was quantitative and the purity of the product was checked by TLC.

Synthesis of metal complexes: 1 mmol ethanolic solution of manganese sulphate, ferric chloride, cobaltus nitrate, nickel chloride and cupric chloride was refluxed with 2 mmol ethanolic solution of Schiff base for 3-5 h on a water bath [14-17]. The precipitated complexes were filtered and washed thoroughly with ethanol and recrystallized using a hot solution of ethanol and chloroform. The yield was quantitative and the purity of the product was checked thoroughly by TLC.

Hydrolysis of esters: A solution of Co(II) and Ni(II) was prepared by dissolving known amount of it in a solvent mixture of 20 mL DMSO and 20 mL distilled water (and whose pH was adjusted to 2.5) and then by adding 5 mL of ethyl acetate the contents were stirred uniformly [18]. The extent of the reaction was estimated by withdrawing 5 mL of the reaction mixture at regular intervals and then titrate it against standard NaOH solution using phenolphthalein as an indicator. The reaction was carried out at 25, 35 and 45 °C in a thermostat with an accuracy of ± 0.01 °C. The quantity of catalysts used was in the range 0.01-0.05 g.

The reaction rates were compared with the rates obtained by using HCl as a conventional catalyst 40 mL of HCl of known strength was taken in a stoppered bottle to which was added 5 mL of ester and the extent of reaction was measured as mentioned above. The reaction was carried out at 25, 35 and 45 °C also using 0.001, 0.01, 0.02 and 0.03 M HCl and the activation energy (E) was calculated from the Arrhenius plots. The changes in the enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) were recorded.

DNA cleavage studies: The DNA cleavage experiment was conducted using pUC19 DNA by agarose electrophoresis with the corresponding metal complex in the presence of H_2O_2 as an oxidant. The oxidative cleavage of DNA was examined by keeping the concentration of the compound 30 µM and pUC19 DNA as 2 µL to make up the volume to16 µL with 5 mM tris-HCl/5 mM NaCl buffer solution [19]. The resulting mixture was incubated at 37 °C for 2 h and electrophoresed for 2 h at 50 V in tris-acetate-EDTA(TAE) buffer (pH 8.3) using 1 % agarose gel containing 1.0 µg/mL ethidium bromide and photographed under UV light at room temperature.

Antimicrobial activity: *in vitro* biological screening effects of the synthesized Schiff base and metal complexes were tested against the bacteria *S. aureus*, *E. coli* and *B. cereus* by the well-diffusion method using agar nutrient as the medium, kept at 45 °C and then poured into Petri dishes to solidify. The holes of 5 mm diameter were punched carefully using a sterile cork borer and were filled with to the bring test solution (1 mg/mL in DMSO). The plates were incubated for 24 h at 37 °C. The zone of inhibition for all the test compounds was measured and the results were compared with the standard drug ciprofloxacin under identical conditions [20].

The antifungal activities of the compounds were evaluated by the well-diffusion method against the fungi *C. albicans* and *A. niger* cultured on potato dextrose agar as medium by adapting the procedure described above. The plates were incubated at 37 °C for 72 h. The diameters of the zone of inhibitions for Schiff base and metal complexes were measured and the results were compared with standard drug fluconazole under identical conditions. The stock solution (10^{-6} M) was prepared by dissolving the compounds in DMSO and the solutions were serially diluted to find MIC values. In a typical procedure, a well was made on the agar medium inoculated with microorganisms. It was filled with the test solution using a micropipette and the plate was incubated for 24 h in case of bacteria and 72 h for fungi at 37 °C. During this period, it was noticed that the test solution started diffusing affecting the growth of the inoculated microorganisms [21]. The inhibition zone was developed and its diameter was measured.

RESULTS AND DISCUSSION

The analytical data for the Schiff base and its metal complexes with some physical properties are shown in Table-1. The analytical data reveals that the Schiff base acts as a tridentate ligand (N_3) [22,23].

The Schiff base ligand and metal complexes are soluble in ethanol and DMSO. The molar conductance values of the Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes are 148.5,

TABLE-1
ELEMENTAL ANALYSIS OF SCHIFF BASE AND METAL COMPLEXES

Compound	m.w.	Elemental analysis (%): Calcd. (Found)				μ_{eff} (BM)	Λ_M (S cm^2 mol^{-1})
		M	C	H	N		
L = $C_{22}H_{25}N_3$	331.463	–	79.72 (79.64)	7.60 (7.55)	12.68 (12.61)	–	–
$[Mn(L)_2]SO_4$	811.910	6.77 (6.70)	65.09 (65.06)	6.21 (6.18)	10.35 (10.29)	5.88	148.5
$[Fe(L)_2]Cl_3$	825.130	6.77 (6.69)	64.05 (63.99)	6.11 (6.06)	10.18 (10.14)	5.86	206.3
$[Co(L)_2](NO_3)_2$	845.867	6.96 (6.90)	62.48 (62.42)	5.96 (5.91)	13.25 (13.19)	4.20	143.3
$[Ni(L)_2]Cl_2$	792.525	7.41 (7.38)	66.68 (66.63)	6.36 (6.32)	10.60 (10.57)	2.78	156.7
$[Cu(L)_2]Cl_2$	797.378	7.96 (7.92)	66.28 (66.25)	6.32 (6.29)	10.54 (10.50)	1.85	137.6

206.3, 143.5, 156.7 and 137.6 S cm^2 mol^{-1} (Table-1), respectively. The molar conductance values indicate that these complexes have electrolytic character. The Fe(III) complex acts as 1:3 electrolyte (range 200-240 S cm^2 mol^{-1} in DMSO). The Mn(II), Co(II), Ni(II) and Cu(II) complexes behave as 1:2 electrolytes (range 110-195 S cm^2 mol^{-1} in DMSO).

The magnetic studies of the complexes at room temperature are consistent with octahedral geometry for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) and exhibit paramagnetic nature. The magnetic moment values of Mn(II), Fe(III), Co(II) and Ni(II) complexes are 5.88, 5.86, 4.20 and 2.78 BM, respectively, suggesting a high spin octahedral environment. The observed magnetic moment of the Cu(II) complex is 1.85 BM which suggests a distorted octahedral geometry [24,25].

Mass spectral and fragmentation of the Schiff base: The mass spectrum of the Schiff base ligand (Figs. 1 and 2) shows a molecular ion peak $(M+H)^+$ at *m/z* 332.21 which corresponds to its proposed molecular formula ($L = C_{22}H_{25}N_3$). The molecular ion peak at *m/z* 322 (96 %) and the values of peaks at *m/z* are 216 (100 %), 141 (33 %) and 104 (10 %) due to the elimination of C_8H_9, C_6H_6 and $C_5H_{13}N_3$, respectively.

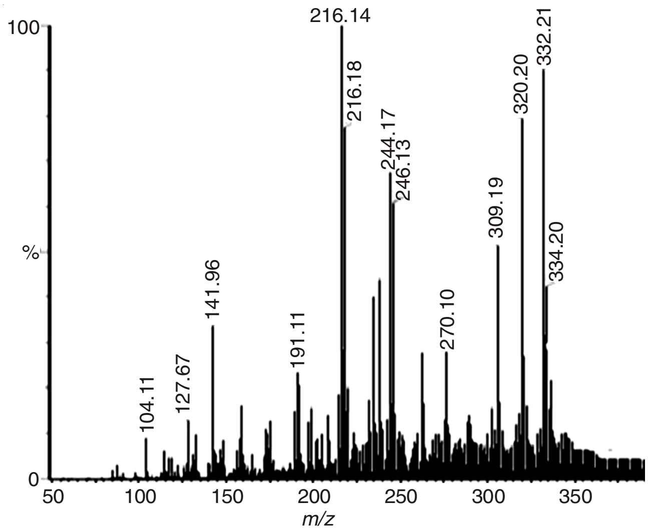

Fig. 1. Mass spectrum of Schiff base

Infrared spectra: The IR spectral data of Schiff base and metal complexes are given in Table-2. The appearance of band at 1649 cm^{-1} is due to the presence of azomethine moiety and this band gets shifted to lower frequency on complexation with metal ions [26]. The characteristic band at 3313-3272 cm^{-1} is because of ν(N-H) vibration of diethylenetriamine. The new vibrations at 518-483 cm^{-1} which are absent in the free Schiff base are attributed to the existence of ν(M-N) in the complexes. The appearance of these vibrations confirms the involvement of nitrogen atoms in chelation [27].

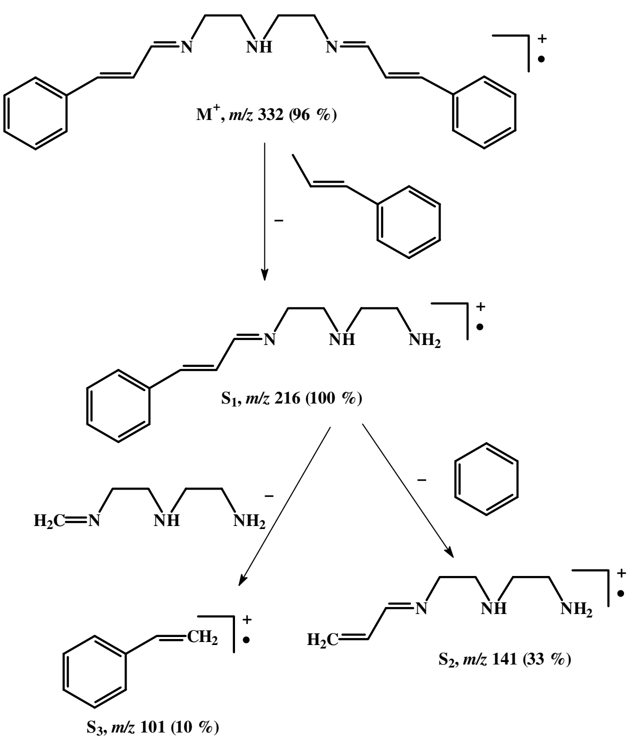

Fig. 2. Mass fragmentation of Schiff base

Electronic spectra: The electronic absorption spectral data of Schiff base and Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes are recorded in DMSO are shown in Table-3. The electronic absorption spectrum of the Schiff base shows a band at 30211 cm $^{-1}$ due to n → π* transition of -C=N- chromophore. This transition can be found again in the complex combination spectra but shifts towards lower frequencies which indicate the coordination of the ligand with the metal ions. The electronic spectrum of Mn(II) complex exhibits three bands at 11800 cm^{-1} (ν_1), 16393 cm^{-1} (ν_2) and 19400 cm^{-1} (ν_3) which are assigned to the transitions ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and ${}^6A_{1g} \rightarrow {}^4E_g$(G), respectively. The ligand field parameters Dq, B′, β and LFSE have been calculated using the secular equations given by Koing. The values of ligand field parameters Dq, B′, β, β % and LFSE for this complex are 1180.0 cm^{-1}, 874 cm^{-1}, 0.910, 8.96 and 141.23 KJ mol^{-1}, respectively. These values suggest a high spin octahedral environment [28].

The electronic spectrum of Fe(III) complex shows three bands at 13520 cm^{-1} (ν_1), 15867 cm^{-1} (ν_2) and 19600 cm^{-1} (CT) due to the transitions of ν_1 and ν_2 are ${}^6A_{1g} \rightarrow {}^4T_{1g}$(G), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) respectively. The ligand field parameter Dq and LFSE value for this complex are1352.0 cm^{-1} and 161.83 KJ mol^{-1},

TABLE-2
INFRARED SPECTRA OF SCHIFF BASE AND ITS METAL COMPLEXES

Compound	ν(N–H)	ν(C=O)	ν(C–H) (aliphatic)	ν(C=C)	ν(M–N)
$L = C_{22}H_{25}N_3$	3313.10	1649.84	2928.28	1587.47	–
$[Mn(L)_2]SO_4$	3279.52	1634.02.	2937.58	1569.24	518.06
$[Fe(L)_2]Cl_3$	3280.34	1621.79	2926.17	1601.39	491.21
$[Co(L)_2](NO_3)_2$	3272.85	1629.05	2940.47	1557.08	503.15
$[Ni(L)_2]Cl_2$	3278.43	1639.45	2928.47	1581.31	501.61
$[Cu(L)_2]Cl_2$	3279.76	1621.28	2928.28	1569.30	483.37

TABLE-3
UV-VISIBLE SPECTRA OF SCHIFF BASE AND METAL COMPLEXES

Compound	Frequency (cm^{-1})	Dq (cm^{-1})	B' (cm^{-1})	β	β (%)	ν_2/ν_1	ν_3/ν_2	LFSE (KJ mol^{-1})
L = $C_{22}H_{25}N_3$	30211	–	–	–	–	–	–	–
Mn(II) complex	11800 (ν_1) 16393 (ν_2) 19400 (ν_3)	1180.0	874.0	0.910	8.96	1.389	1.183	141.23
Fe(III) complex	13520 (ν_1) 15867 (ν_2) 19600 (CT)	1352.0	–	–	–	–	–	161.83
Co(II) complex	10850 (ν_1) 19011 (ν_2) 27020 (ν_3)	1085.0	840.90	0.866	13.40	1.752	1.421	129.86
Ni(II) complex	9427 (ν_1) 16026 (ν_2) 25016 (ν_3)	1178.4	861.00	0.826	17.3	1.70	1.561	141.03
Cu(II) complex	14450 (ν_1) 25200 (CT)	1445.0	–	–	–	–	–	172.94

respectively. These values suggest a high spin octahedral environment for the central metal ion [29].

The electronic spectrum of Co(II) complex exhibits three bands at 10850 cm^{-1} (ν_1), 19011 cm^{-1} (ν_2) and 27020 cm^{-1} (ν_3) which are assigned to the transitions $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F), $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F), $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (P), respectively. The intense band around 30200 cm^{-1} may be the charge transfer band. The ligand field splitting energy (Dq), inter electronic repulsion parameter (B′), nephelauxetic ratio (β), β % and LFSE for Co(II) complex have been calculated and their respective values correspond to 1085.0 cm^{-1}, 840.90 cm^{-1}, 0.866, 13.40 and 129.86 KJ mol^{-1}. The inter electronic repulsion parameter (B′) is less than free metal ion (971 cm^{-1}) and the nephelauxetic ratio (β) is less than 'one' which indicates a moderate covalent character of the metal-ligand bonds with octahedral environment. This is further supported by ratio ν_2/ν_1 = 1.750-1.626 which is close to the value expected for octahedral geometry.

The electronic spectrum of Ni(II) complex exhibits two bands at 16026 cm^{-1} (ν_2) and 25016 cm^{-1} (ν_3) assignable to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions, respectively in an octahedral environment. The lowest band $\nu_1 \approx$ (10 Dq) was not observed due to limited range of the instrument used. The ligand field splitting energy (Dq), inter electronic repulsion parameter (B′), nephelauxetic ratio (β), β % and LFSE for Ni(II) complex have been calculated and their respective values have seen to correspond 1178.4 cm^{-1}, 861.0 cm^{-1}, 0.826, 17.30 and 141.03 KJ mol^{-1}. The inter electronic repulsion parameter (B′) is less than free metal ion (1040 cm^{-1}) and the nephelauxetic ratio (β) is less than one which indicates a moderate covalent character of the metal-ligand bonds in an octahedral environment [30]. The ratio ν_2/ν_1 is usually 1.6-1.82 which is an identification of octahedral geometry in the Ni(II) complexes.

The electronic spectrum of Cu(II) complex exhibits three bands, a low intense broad band in the region 16411-12320 cm^{-1} with maxima at 14450 cm^{-1} due to $^2T_{2g} \rightarrow {}^2E_g$ transition, the high intense band in the region 22900-27100 cm^{-1} with maxima at 25200 cm^{-1} due to symmetry forbidden ligand → metal charge transfer transition. The band above 27100 cm^{-1} was assigned as ligand band. Therefore distorted octahedral geometry around Cu(II) ion due to John-Teller effect [31]. The ligand field splitting energy (Dq) and LFSE values are 1445.0 cm^{-1} and 172.94 KJ mol^{-1}, respectively.

^{1}H NMR and ^{13}C NMR spectra of the Schiff base: ^{1}H NMR spectrum of Schiff base ligand is recorded in DMSO-d_6 solvent using tetramethylsilane (TMS) as an internal standard (Fig. 3). The aromatic region was a set of multiples in the range 7.3-7.5 ppm for the Schiff base ligand, while the azomethine group protons were observed in the 7.73 ppm. The total number of protons present in the Schiff base exhibited signals, this confirms the formation of Schiff base ligand [32].

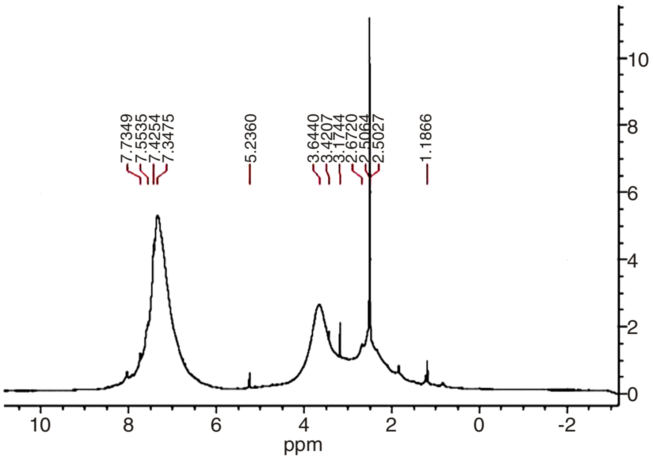

Fig. 3. ^{1}H NMR spectrum of Schiff base ligand

^{13}C NMR spectrum of Schiff base ligand is recorded in $CDCl_3$ solvent (Fig. 4).The chemical shift for aromatic region was a set of peak in the range 128.78 ppm, while the chemical shift of azomethine carbons were observed in the range 163.74 ppm. The chemical shift for aliphatic carbons was a set of multiples in the range 76.91-77.55 ppm. The found ^{1}H NMR and ^{13}C NMR spectra of the Schiff base ligand are shown in Table-4.

ESR spectra: The X-band EPR spectra of the Cu(II) complex that has been recorded in DMSO at room temperature 300 K (Fig. 5). The analysis of spectrum gives $A_{\parallel}$, $g_{\parallel}$ and $g_{\perp}$ values as 160 × 10^{-4} cm^{-1}, 2.270 and 2.083, respectively. These values indicate that the ground state of Cu(II) is predominantly

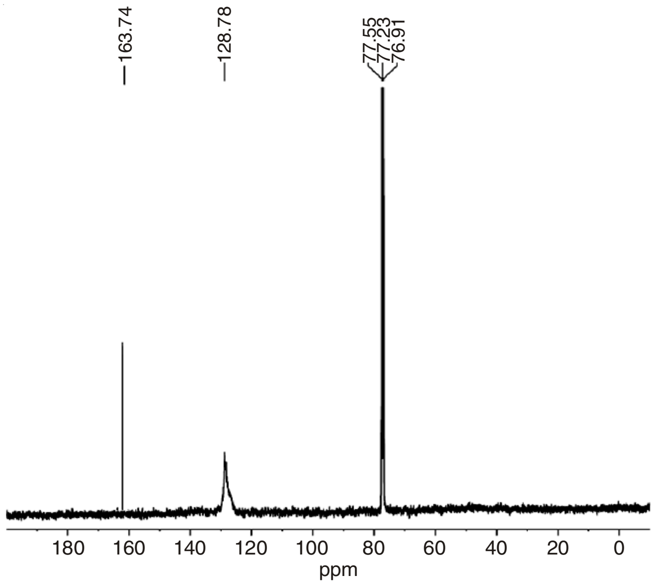

Fig. 4. ^{13}C NMR spectrum of Schiff base ligand

TABLE-4
^1H NMR AND ^{13}C NMR SPECTRUM
DATA OF SCHIFF BASE LIGAND ($L = C_{22}H_{25}N_3$)

Chemical shift (δ) ppm	Assignment
2.5027	(s, 1H, -NH-)
2.5064	(m, 2H,-C=N-CH_2-)
2.6720	(m, 2H, -NH-CH_2-)
3.6440	(m, 1H, -CH=CH-)
5.2360	(s, 1H, -CH-Ar)
7.3475-7.5535	(m, 5H, ArH)
7.7349	(d, 1H, -N=CH-, azomethine H)
76.91-77.55	-C-C- (aliphatic)
128.78	-C=C- (aromatic)
163.74	-C=N- (azomethine)

$d_{x^2-y^2}$. The trend $g_{\parallel} > g_{\perp} > 2.0023$ that has been observed for the complex indicates that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu(II) ion and is a characteristic of the axial symmetry. The g_{av} value has been calculated to be 2.145 using the equation $g_{av} = 1/3[g_{\parallel} + 2\, g_{\perp}]$. The deviation of g_{av} from that of free electron (2.0023) is due to the covalence character (Table-5). The parameter 'G' is calculated by using expression $G = g_{\parallel} - 2/g_{\perp}-2$. The G value indicates the interaction between metal centers in solid complex consistent with Hathaway approach. The covalency parameter α^2 has been calculated as:

$$\alpha^2 = (A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + (3/7)(g_{\perp} - 2.0023) + 0.04$$

If the value of $\alpha^2 = 0.5$, it indicates complete covalent bonding while the value of $\alpha^2 = 1$ suggests complete ionic bonding. The observed value of α^2 of the complex is less than unity, which indicates that the complex has some covalent character in the ligand environment. The EPR study thus suggests the distorted octahedral geometry [33].

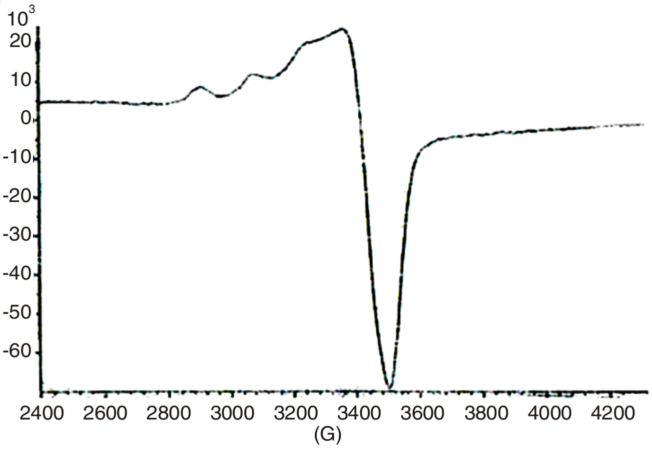

Fig. 5. ESR spectrum of Cu(II) complex

TABLE-5
ESR SPECTRAL DATA OF Cu(II) COMPLEX

Complex	$A_{\parallel} \times 10^{-4}$	$g_{\parallel}$	$G_{\perp}$	g_{av}	G	α^2
Cu(II)	160	2.270	2.083	2.145	3.309	0.786

Thermal studies: The TGA and DTA curves of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes show no endothermic peak at 100-160 °C. This indicates the absence of coordinated aqua molecules in these complexes and octahedral environment with *bis*-tridentate (N_3) Schiff base chelate ligands [34].

Electrochemical studies: The electrochemical behaviour of the complexes have been examined in DMSO solutions with 0.1 M $NaClO_4$ over the range of +2.0 V to –2.0 V using cyclic voltammetry at glassy carbon working electrodes. The electrochemical data of the complexes are summarized in Table-6. The Fe(III) and Cu(II) complexes show that both are quasi-reversible corresponding to one electron transfer process [35].

Hydrolysis of esters: Hydrolysis of ethyl acetate has been studied by employing complexes as homogeneous catalysts. At constant concentrations of ester, the quantity of the catalyst has been varied in the range 0.01-0.04 g. It has been found that the value of k (specific reaction) is proportional to the quantity of the catalyst (Table-7). The plot of rate constant *versus* the amount of catalyst is linear showing that the rate constant is directly proportional to the amount of catalyst used in the reaction (Fig. 6). A similar correlation has been established in the case of aliphatic ester.

Hydrolysis of ethyl acetate in presence of HCl is first order. In the present study, it is seen that as regards to Co(II) and Ni(II) complexes also the hydrolysis is first order as shown by the linear plot of log (a-x) against t (Fig. 7). The rate constants for the hydrolysis of ethyl acetate obtained by using different catalysts at various temperatures are given in Table-8. Keeping the quantity of the catalyst and ester constant, it has been observed that when the temperature has varied in the range

TABLE-6
ELECTROCHEMICAL DATA OF SCHIFF BASE METAL COMPLEXES

Complexes	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE (mV)	i_{pa} (μA)	i_{pc} (μA)
Fe(III)/Fe(II)	0.721	-0.802	0.761	81	49.250	-0.696
Cu(II)/Cu(I)	0.223	0.514	0.369	291	13.345	9.826

TABLE-7
INFLUENCE OF THE AMOUNT OF CATALYST ON THE HYDROLYSIS OF ETHYL ACETATE BY REPRESENTATIVE COMPLEXES $[Co(L)_2](NO_3)_2$ AND $[Ni(L)_2]Cl_2$

Complexes	Amount of catalyst (g)	Specific reaction rate ($k \times 10^{-4}$, min^{-1})
$[Co(L)_2](NO_3)_2$	0.010	0.32
	0.020	0.51
	0.030	0.95
	0.040	1.21
$[Ni(L)_2]Cl_2$	0.010	0.21
	0.020	0.44
	0.030	0.76
	0.040	0.91

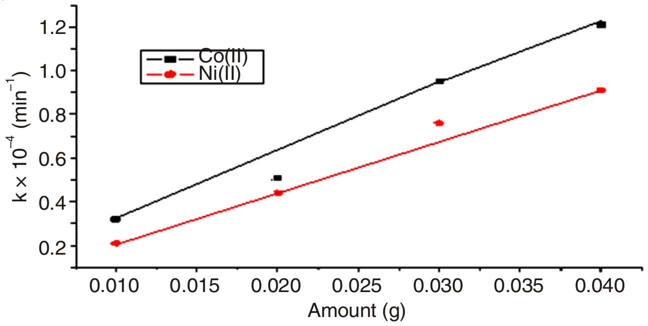

Fig. 6. Plot of rate of reaction *versus* amount of catalysts at 313 K, volume of ethyl acetate: 5.0 mL

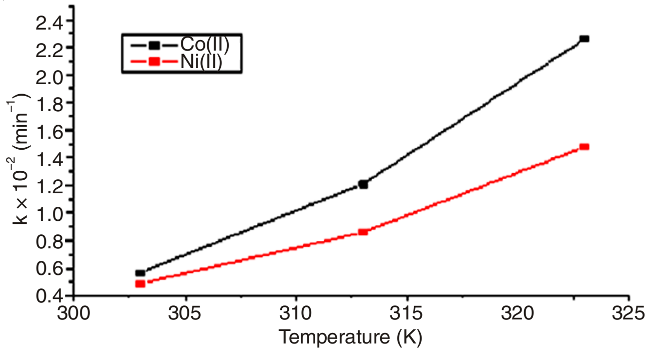

Fig. 7. Plot of rate of reaction *versus* temperature

303-313 K, the value of k has increased with increase in temperature. HCl is more an efficient catalyst than the Co(II) and Ni(II) complexes.

It is observed that $\Delta H^{\neq}$ values are closer to E values in accordance with absolute reaction rate theory for solution. The value of $\Delta G^{\neq}$ is found to be higher in all the cases and glaring difference is nit traced found in the two systems. The values of $\Delta S^{\neq}$ were found to be negative in all the cases indicating that molecules in transition state are more ordered than the reactants in the ground state.

DNA cleavage studies: The DNA cleavage efficiency of the Schiff base and its metal complexes has been compared with that of the control. The Schiff base and metal complexes are able to convert super coiled DNA into open circular DNA [36]. The oxidative cleavage involves the oxidation of deoxyribose by absorption of sugar hydrogen or oxidation of nucleobases in the presence of an oxidative agent. The oxidative cleavage implies by hydroxyl radical species of $O_2(OH)$. In the present study, the pUC19 DNA gel electrophoresis experiment has been analyzed in the presence of the oxidant H_2O_2 (50 µg/mL) with Schiff base and Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes (Fig. 8). The results show that Fe(III), Co(II), Ni(II) and Cu(II) complexes have effectively degraded the pUC19 DNA in presence of the oxidant and Schiff base and Mn(II) complex does not show any significant cleavage. The descending order of DNA cleavage results are:

$$[Cu(II)\ complex + H_2O_2] > [Ni(II)\ complex + H_2O_2] > [Co(II)\ complex + H_2O_2] > [Fe(III)\ complex + H_2O_2] > [Schiff\ base + H_2O_2] > [Mn(II)\ complex + H_2O_2]$$

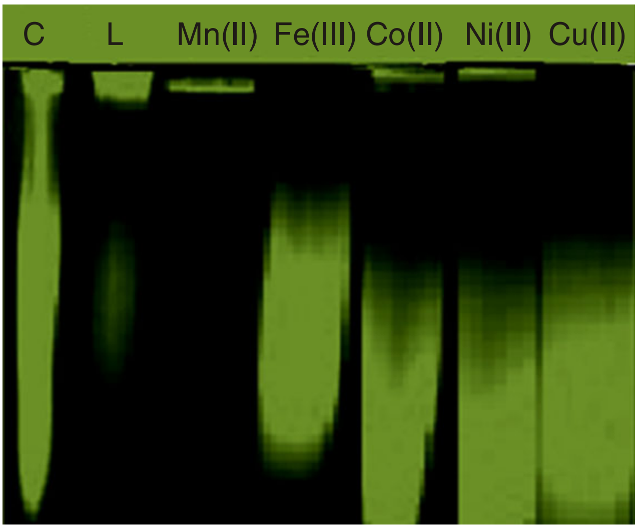

Fig. 8. DNA cleavage studies of Schiff base and complexes

Antimicrobial activity: The *in vitro* antimicrobial activity of the investigated compounds has been tested against bacteria and fungi as given in Table-9. The minimum inhibitory concentration (MIC) values of the investigated compounds are summarized in Table-10. The synthesized ligand shows inhibitory effect (MIC values of 50-100 µg/mL) on growth of the tested bacterial strains. All the complexes have shown greater bactericidal activities against *E. coli* (MIC 12.50-25 µg/mL), *S. aureus* (MIC 12.50-50 µg/mL) and *B. cereus* (MIC 12.50-25 µg/mL) than the ligand. In the fungal studies, the ligand has had an

TABLE-8
KINETICS OF HYDROLYSIS A OF ETHYL ACETATE IN PRESENCE OF SCHIFF BASE METAL COMPLEXES AS HOMOGENEOUS CATALYSTS (VOLUME OF ESTER: 5 mL, AMOUNT OF CATALYST: 50 mg)

Complexes	T (K)	$k \times 10^{-2}$ (min^{-1})	E (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Co(II)	303	0.57	56.335	53.732	-110.60	88.357
	313	1.21				
	323	2.26				
Ni(II)	303	0.49	44.995	42.390	-284.70	89.158
	313	0.86				
	323	1.48				

TABLE-9
ANTIMICROBIAL ACTIVITY OF SCHIFF BASE AND ITS COMPLEXES

Compound	Antibacterial inhibition (mm)			Antifugal inhibition (mm)	
	S. aureus	*E. coli*	*B. cereus*	*C. albicans*	*A. niger*
L	08	09	08	07	09
Mn(II)	10	11	09	09	12
Fe(III)	14	13	11	11	14
Co(II)	09	09	10	09	11
Ni(II)	10	10	09	12	10
Cu(II)	19	21	19	21	19
Ciprofloxacin	28	32	28	–	–
Fluconazole	–	–	–	36	30

TABLE-10
DETERMINATION OF MIC FOR ANTIMICROBIAL ACTIVITIES

Compound	Concentration (µg/mL)				
	S. aureus	*E. coli*	*B. cereus*	*C. albicans*	*A. niger*
L	100	50	50	100	50
Mn(II)	25	25	50	50	25
Fe(III)	25	25	12.5	25	25
Co(II)	12.5	25	25	25	12.5
Ni(II)	25	12.5	25	25	25
Cu(II)	12.5	12.5	12.5	25	12.5
Ciprofloxacin	6.25	6.25	6.25	–	–
Fluconazole	–	–	–	12.5	6.25

inhibitory effect (MIC values in range 50-100 µg/mL) on the growth of the tested strains. The complexes also have shown greater fungicidal activities against *C. albicans* (MIC 12.50-50 µg/mL) and *A. niger* (MIC 12.50-25 µg/mL). The values indicate that metal complexes posses higher antimicrobial activity than the free ligand [37,38]. Such increased activity of the metal chelates can be explained on the basis of chelation theory. The Schiff base and complexes also disturbed the respiration of the cell and block the synthesis of proteins, which further restricts the growth of the organisms. The Cu(II) complex has exhibited better activity when compared to Schiff base and other metal complexes.

Conclusion

A novel tridentate (N_3) Schiff base and mononuclear Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes were synthesized by the condensation of cinnamaldehyde and diethylenetriamine. The Schiff base ligand contained N_3 donors and the ligand and metal complexes were characterized by various spectral and analytical data. The results revealed the fact that the chelate would coordinate in a tridentate manner with the metal ions and the geometry of Mn(II), Fe(III), Co(II) and Ni(II) complexes were octahedral geometry but the Cu(II) complex showed a distorted octahedral geometry. All the complexes were in paramagnetic environment. The TGA-DTA study had shown the absence of coordinated aqua molecules. The catalytic study of the hydrolysis of ester in presence of metal complexes as catalysts followed a first order kinetics with higher $\Delta G^{\neq}$ in mild acidic medium. The DNA cleavage study of Schiff base and metal complexes had been carried out in presence of an oxidizing agent. All the metal complexes except Mn(II) had shown strong DNA damage. The Cu(II) complex exhibited powerful antimicrobial activity whereas the other molecules showed a moderate activity.

ACKNOWLEDGEMENTS

The authors thank to the Management, PG and Research Department of Chemistry, C. Abdul Hakeem College, Melvisharam, India. The authors are also thankful to SAIF, IIT Kanpur, India for providing the mass spectra, ESR, TGA-DTA analyzer, magnetic susceptibility data, FT-IR and electronic spectral studies. Sincere thanks are also due to PG and Research Department of Chemistry, Muthurangam Govt. Arts College, Vellore, India for providing cyclic voltammetry studies. Finally, the authors extended their heartfelt gratitude to VIT University, Vellore, India for providing the antimicrobial and DNA cleavage studies.

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