Asian Journal of Chemistry; Vol. 24, No. 3 (2012), 1058-1060

ASIAN JOURNAL OF CHEMISTRY

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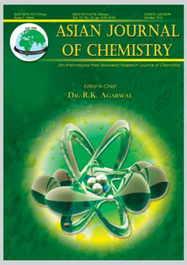

Synthesis, Characterization, Antimicrobial Activity and DNA Studies of Novel Schiff's Base Complexes of Some Transition Metal Ions

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(*Received*: 1 February 2011; *Accepted*: 7 November 2011) AJC-10593

A bidentate chelating Schiff base (L) and its complexes with Fe(II), Co(II), Ni(II), Cu(II) and Ru(III) metal ions have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectral studies. The cyclic voltammetric studies were carried out to understand the redox characteristics of some of these complexes. EPR spectral studies and calculation of LFSE, 10Dq, β and μ_{eff} have been carried out to prove the existence of covalency in the M-L bond. Interactions of these complexes with calf thymus DNA were investigated by UV-visible absorption spectroscopy and gel electrophoresis. Antimicrobial activity of these compounds have also been studied.

Key Words: Complexes, Transition metal, DNA binding, Antimicrobial, EPR studies.

INTRODUCTION

There has been considerable interest in the coordination chemistry of transition metal complexes having (N,N) donor Schiff bases because of the increasing recognition of the role of these metal ions in biological systems. These complexes are significant not only for their redox active role in several biochemical processes but also for their diversity in their magnetic behaviour. The present study was undertaken to unravel the novel stereochemical aspects (unusual magnetic behaviour, redox characteristics, antimicrobial activity and DNA binding) of the complexes of bidentate (N,N) donor Schiff base ligand formed by the condensation of *p*-methyl thioaniline with acetylacetone and its complexes with Fe(II), Co(II), Ni(II), Cu(II) and Ru(III) metal ions[1,2].

EXPERIMENTAL

All the reagents were of AnalaR grade and the solvents were purified by standard methods. Elemental analyzer and standard methods were employed to estimate the amount of elements. Electrical conductance was determined on a Systronics conductivity meter type 304 with a dip type cell having platinum electrode. Magnetic susceptibility measurements of the complexes were made by vibrating sample magnetometer EG & G model: 155. The UV-visible spectra of the ligands and its complexes were run on Cary-5E spectrometer. Infrared spectra (4000-450 cm^{-1}) were studied on KBr disc using a Perkin-Elmer spectrum ONE-N0174-1159. The magnetic resonance of the ^{1}H NMR and ^{13}C NMR were recorded using the instrument Brucker 300 FT NMR. The electrochemical behaviour of the complexes was inferred using the instrument CH1660B electrochemical workstation using tetrabutyl ammonium perchlorate as background electrolyte, glassy carbon as working electrode, Ag/Ag$^+$ electrode as reference electrode and platinum wire as auxiliary electrode. The EPR spectrum of the Cu(II) complex was recorded using Brucker EMX Plus.

Synthesis of the Schiff base, L ($C_{19}H_{22}N_2S_2$): A methanolic solution of *p*-methyl thioaniline was added drop wise with stirring to acetylacetone in 2:1 molar ratio and refluxed to get the Schiff base L.

Synthesis of metal complexes: A methanolic solution of corresponding metal salts of Fe(II), Co(II) and Ru(III) and the Schiff base ligand L in 1:3 molar ratio on heating under reflux gives the trischelate metal complexes. The bischelate Ni(II)and Cu(II) complexes were synthesized by the above method from a 1:2 molar solution of the metal ion and the ligand in methanol.

RESULTS AND DISCUSSION

A millimolar solution of these complexes in DMSO showed molar conductance corresponding to 1:1 electrolytic nature of Fe(II), Ni(II) and Cu(II) complexes,1:2 and 1:3 electrolytic nature of Co(II) and Ru(III) complexes, respectively.

The elemental analysis data (Table-1) revealed that the stoichiometry of the Ni(II) and Cu(II) complexes is1:2 (metal: ligand) and 1:3 for Fe(II), Co(II) and Ru(III) complexes.

TABLE-1
PHYSICAL CHARACTERIZATION, ANALYTICAL, MOLAR CONDUCTANCE, MAGNETIC SUSCEPTIBILITY DATA OF THE SCHIFF'S BASE AND ITS COMPLEXES

m.f.	Elemental analysis (%): Found (calcd.)					m.w.	Yield (%)	Λ_M (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
	M	C	H	N	S				
L,($C_{19}H_{22}N_2S_2$)	–	66.66 (66.64)	6.50 (6.47)	8.16 (8.18)	18.68 (18.72)	342.5	64	–	–
$[Fe(L)_3]SO_4$	4.70 (4.73)	58.09 (58.04)	5.66 (5.64)	7.09 (7.12)	19.01 (19.03)	1179.4	54	79.8	5.26
$[Co(L)_3](NO_3)_2$	4.87 (4.86)	55.51 (56.55)	5.50 (5.49)	9.29 (9.25)	15.91 (15.89)	1210.5	55	144.2	4.30
$[Ni(L)_2]SO_4$	6.87 (6.99)	54.33 (54.34)	5.30 (5.28)	6.66 (6.67)	19.06 (19.01)	839.8	58	78.3	Diamag.
$[Cu(L)_2]SO_4$	7.55 (7.52)	54.98 (54.03)	5.31 (5.25)	6.58 (6.63)	18.90 (18.98)	844.6	62	84.5	1.85
$[Ru(L)_3]Cl_3$	8.17 (8.18)	55.40 (55.43)	5.42 (5.38)	6.88 (6.80)	15.52 (15.57)	1235.0	53	226.6	1.77

TABLE-2
ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS

Complex	ν_1 cm^{-1} (nm)	ν_2 cm^{-1} (nm)	ν_3 cm^{-1} (nm)	Dq (cm^{-1})	B' (cm^{-1})	β	β %	ν_3/ν_2	ν_2/ν_1	LSE Kcal mol^{-1}
$[Fe(L^3)_3]SO_4$	10246(976)	–	–	1024.6	–	–	–	–	–	29.29
$[Co(L^3)_3](NO_3)_2$	11507(869)	17361(576)	23923(418)	1291.04	922.17	0.950	5.03	1.378	1.509	29.53
$[Ni(L^3)_2]SO_4$	19120(523)	–	–	1912.0	–	–	–	–	–	54.67
$[Cu(L^3)_2]$ SO_4	19608(510)	–	–	1960.80	–	–	–	–	–	56.06
$[Ru(L^3)_3]Cl_3$	16949(590)	–	–	1694.9	–	–	–	–	–	48.46

The effective magnetic moment values of Fe(II), Co(II) and Cu(II) complexes show that they contain 4, 3 and 1 unpaired electrons, respectively. The Ru(III) complex is low spin and contains one unpaired electron due to the electronic configuration $t_{2g}^5e_g^0$. The nickel (II) complex is diamagnetic[3,4].

The UV-visible absorption studies were carried out to determine the ligand field parameters such as Dq, LFSE and β to ascertain the geometry of the complexes[5,6].

The ligand L showed high intense bands at 380 nm and 268 nm, respectively due to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. The red shift of these bands in its complexes confirms the involvement of the ligand in complex formation.

The Fe(II) complex shows only one broad hand due to $^5T_{2g}\rightarrow{}^5E_g$ transition confirming the presence of octahedral geometry. Three *d-d* bands are observed in the spectrum of Co(II) complex due to the transitions from $^4T_{1g}(F)$ level to $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(P)$ levels. The value of $\nu_2/\nu_1 = 1.509$ indicates distorted octahedral geometry of the Co(II) complex. The reduction of the value of β of the complex (922 cm^{-1}) from that of free Co(II) ion (971 cm^{-1}) shows the covalent nature of the M-L bond.

Nickel(II) complex shows only one intense band at 19120 cm^{-1}. Absence of any band below 10000 cm^{-1}, the presence of only one band and its diamagnetic nature shows that the complex is square planar. The μeff value and the presence of only one intense *d-d* band at 19608 cm^{-1} due to the transition $^2B_{1g}\rightarrow{}^2A_{1g}$ reveal the presence of square planar geometry around the Cu(II) ion (Table-2).

The octahedral geometry of the Ru(III) complex is studied and show one band at 16949 cm^{-1} which is assigned to the $^2T_{2g}\rightarrow{}^2A_{2g}$ transition and its μ_{eff} value corresponding to the presence of one unpaired electron (Table-2). The LFSE values of these complexes obey the Irving-William order of stability Cu(II) > Ni(II) > Co(II) > Fe(II).

The formation of the Schiff base (L) is confirmed by the presence of a band at 1620 cm^{-1} due to the vibration of the -CH=N-group. This band shows a downward shift in its complexes indicating the coordination of azomethine nitrogen with the metal ions. The presence of new bands in the spectra of the complexes at 495-470 cm^{-1} due to ν(M-N) further confirms the formation of M-N bond in these complexes[7,8].

The absence of any significant change in the band at 1096 cm^{-1} due to ν(C-S) in the ligand on complexation and the absence of a band in the region 425-380 cm^{-1} due to ν(M-S) clearly indicate that the sulphur is not coordinated with the metal ions (Table-3).

TABLE-3
FT-IR SPECTRAL DATA OF THE COMPOUNDS (cm^{-1})

Compound	M-OH_2	ν(C=N) azomethine	ν(C-S)	ν(M-N)	ν(M-O)
L,($C_{19}H_{22}N_2S_2$)	-	1620	1096	-	-
$[Fe(L)_3]SO_4$	-	1596	1091	470	-
$[Co(L)_3](NO_3)_2$	-	1591	1086	476	-
$[Ni(L)_2]$ SO_4	-	1584	1084	484	-
$[Cu(L)_2]$ SO_4	-	1579	1083	489	-
$[Ru(L)_3]Cl_3$	-	1576	1080	494	-

The X band EPR spectra of the complex of Schiff base L with Cu(II) was recorded at room temperature and liquid nitrogen temperature. At the high field region it shows only one intense band due to the tumbling motion of the molecule at room temperature. However at liquid nitrogen temperature four well resolved peaks with low intensity are observed in the low field region. The values of g tensor g_{II} (2.2204) and $g_{\perp}$ (2.0420) give an insight about the ground state. In square planar complexes, the unpaired electron is present in the $d_{x^2-y^2}$ orbital with ground state $^2B_{1g}$. The relative magnitude of $g_{II} > g_{\perp} > g$ shows that the ground state is predominantly $d_{x^2-y^2}$ orbital.

The value of g_{II} is less than 2.3. The value of λ (497 cm^{-1}) is less than that of Cu(II) ion value (830 cm^{-1}). The value of γ^2 (0.7723) is less than 1.0. All these findings give supportive evidences to prove the existence of covalency in the metal-ligand bond in this complex. The value of β^2 is 0.8339 which shows the presence of covalency in in-plane π bonding and the value of γ^2 is 0.6072 which indicates that the out-of-plane π bonding has ionic character. For this complex the values of

TABLE-4
ANTIMICROBIAL ACTIVITY DATA

Compound	Zone of inhibition (mm)								
	Bacteria						Fungi		
	SA	ML	BC	EC	ST	PA	AN	CA	CN
L^3	16	12	07	06	10	06	08	09	05
Fe(II) complex	18	17	12	12	11	10	12	18	09
Co(II) complex	16	17	11	10	10	08	14	07	09
Ni(II) complex	18	18	14	13	12	10	16	09	10
Cu(II) complex	19	20	15	16	19	11	19	24	14
Ru(III) complex	12	10	08	07	06	05	09	11	06
Chloramphenicol	21	22	18	19	23	14	–	–	–
Ketoconazole	–	–	–	–	–	–	21	28	17

SA = *Staphylococcus aureus*, ML = *Micrococcus luteus*, BC = *Bacillus cereus*, EC = *Escherichia coli*, ST = *Salmonella typhi*, PA = *Pseudomonas aeruginosa*, AN = *Aspergillus niger*, CA = *Candida albicans*, CN = *Cryptococcus neoformans*.

K_{II} (0.6440) is greater than $K_{\perp}$ (0.4689). The value of g_{II}/A_{II} = 124 which is less than 140 clearly indicates that the geometry of this complex is square planar[9,10]. The monomeric nature of this complex can be understood from its G value of 5.49, its magnetic moment of 1.85 BM due to one unpaired electron and the absence of any band in the region below 1600 G due to the transition $\Delta Ms \pm 2$.

^{1}H NMR and ^{13}C NMR spectra are used to confirm the proposed structure of the ligand. Three singlets are observed at δ 0.91 ppm (6H), δ 1.39 ppm (2H) and δ 2.47 ppm (6H), respectively due to the protons of the methyl groups attached with azomethine group, the protons of methylene group in the acetyl acetone ring and the methyl protons attached to sulphur ($S-CH_3$)[11,12].

^{13}C NMR spectrum of the Schiff base L exhibits 8 signals indicating the presence of 8 different carbon atoms. The line at δ 17.52 ppm is due to methyl carbon attached to sulphur. The line at δ 20.21 ppm is due to methyl carbons attached to azomethine group. The line at δ 44.33 ppm is due to methylene carbon. The carbons of the benzene ring give 4 lines in the range δ 133 ppm to δ 172 ppm. These observations are in good agreement with the given structure of the ligand in Fig. 1.

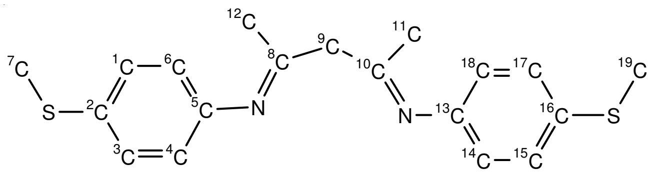

Fig. 1. Structure of Schiff base L

The electrochemical properties of the Fe(II), Cu(II) and Ru(III) complexes were studied through cyclic voltammetric techniques with glassy carbon as working electrode, Ag/Ag$^+$ electrode as reference electrode and Pt wire as auxiliary electrode[13]. The Fe(II) and Cu(II) complexes showed one quasi reversible redox couple with ipa/ipc and E_p of 0.567, 184 mV and 0.529, 190 mV, respectively. The Ru(III) complex shows two redox waves due to Ru^{4+}/Ru^{3+} and Ru^{3+}/Ru^{2+} couples. Oxidation of $Ru^{2+} \rightarrow Ru^{3+}$ and $Ru^{3+} \rightarrow Ru^{4+}$ takes place in the backward scan respectively at -0.222 V and +0.486 V. The forward scan exhibits two waves at 0.420 V and -0.300 V, respectively due to the reduction of $Ru^{4+} \rightarrow Ru^{3+}$ and $Ru^{3+} \rightarrow Ru^{2+}$. The quasi reversible nature and the involvement of one electron transfer is inferred from the values of i_{pa}/i_{pc} (0.618 and 0.613) and ΔE_p (78 mV and 66 mV), respectively.

The synthesized ligand and its complexes were tested for antimicrobial activity by well diffusion method in potatoes dextrose agar medium against the bacteria *Staphylococcus aureus*, *Micrococcus luteus*, *Bacillus cereus*, *Escherichia coli*, *Salmonella typhi* and *Pseudomonas aeruginosa* and fungi *Aspergillus niger*, *Candida albicans* and *Cryptococcus neoformans*. The zone of inhibition was measured using DMSO as control solvent, chloamphenicol as standard for bacteria and ketoconazole a standard for fungi. The compounds showed significant antimicrobial activity which increases on complexation[14,15] (Table-4).

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