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Synthesis, characterization and antimicrobial activity of mixed ligand complexes of Mn(II), Co(II), Ni(II), Cu(II) and Fe(III) ions with N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine and N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide

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ABSTRACT

Mixed schiff base ligand complexes of Mn(II), Co(II), Ni(II), Cu(II), and Fe(III) with N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine and N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide have been synthesized and characterized by elemental analyses, molar conductivity, thermal analysis, magnetic susceptibility, FT-IR, Electronic and ESR spectra. Analytical and spectroscopic data for all mononuclear metal complexes revealed 1:1:1(metal: ligand$_1$: ligand$_2$) formation ratio. Presence of two water molecule in the coordination site of complexes is confirmed from the thermal analysis. Octahedral geometry is suggested for all the complexes. Conductance measurement for all complexes in DMF solvent indicates their non-electrolytic nature. The antibacterial activity of the ligands and complexes indicate that the complexes show more potent activity than the free ligand.

Keywords: Schiff base, Metal complexes, ESR, Anti-microbial activity.

INTRODUCTION

Many transition metal complexes having oxygen and nitrogen donor schiff bases possess unusual configuration, structural liability and are sensitive to the molecular environment [1-2]. A systematic survey of literature have shown that many biologically important Schiff bases possesses antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant and antitumor properties [2-10], in review of this the present study involves the study of mixed ligand complexes of Mn(II), Co(II), Ni(II), Cu(II), and Fe(III) with N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine (L_1H) and N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide (L_2H).

Synthesis of Schiff base Ligands

The schiff bases (L_1H- L_2H) were synthesized by the condensation of 1:1equimolar ratio of 5-notrisalicylaldehyde with substituted aniline in methanol, refluxed on hot water bath for 2-3 hrs and reaction was monitored by TLC. On cooling to room temperature, schiff base crystallizes out as yellow to orange solids, which were filtered, washed with cold methanol and recrystalised using appropriate solvents.

N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine (L_1H) synthesis: 5-notrisalicylaldehyde (1.67gm, 0.01mol), 2-chlorobenzylamine (1.42gm, 1.21ml, 0.01mol) and methanol afforded 2.46gm (85%) of title compound as yellow solids:mp-138-140^{o}C.^{1}H NMR ($CDCl_3$) δ 14.56(s, 1H), 8.47 (s, 1H), 8.27 (d, J =2.7 Hz, 1H), 8.23 (d, J =2.7Hz, 1H), 8.19 (d, J = 3.0Hz,1H), 7.46 (d, J =3.6 Hz, 1H), 7.35 (d, J = 3.9 Hz, 1H),7.29 (d, J = 6.6 Hz, 1H), 7.02 (d, J = 6.6 Hz, 1H), 4.96 (s, 2H).

N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide (L_2H) synthesis: 5-notrisalicylaldehyde (1.67gm, 0.01mol), 4-aminobenzene-1-sulfonamide(1.72gm, 0.01mol) and methanol afforded 2.66gm (83%) of title compound as orange solids: mp-252-254^oC. ^1H NMR (DMSO-d6) δ10.26(s, 1H), 9.08 (s, 2H),8.65 (s, 1H), 8.42 (d, J =2.7 Hz, 1H), 8.23 (d, J = 3.0Hz, 1H), 7.51 (d, J = 8.4Hz,1H), 7.44 (d, J = 8.7 Hz, 1H), 7.09 (d, J = 6.0Hz, 1H), 7.06(d, J = 5.4 Hz, 1H), 6.57 (d, J = 8.7 Hz, 1H).

Synthesis of Mixed ligand complexes

N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine(L_1H), N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide (L_2H), methanol and aqueous solution of Metal chloride/ acetate were mixed in 1:1:1 equimolar ratio and stirred continuously. pH of the solution mixture was slowly raised to 7-7.5 pH for all bivalent metals except for Fe(III) 4-4.5 pH using 0.1N NaOH aqueous solution, reaction was monitored by TLC, metal complex obtained were digested on hot water bath for 1-2 hr, and solution was reduced to half using Rota-evaporator. Solid product obtained was filtered washed several times with methanol till colourless filtrate was obtained and dried in hot air oven at 80-100^oC.

[Mn(II)L_1-L_2)2H_2O]: N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine(L_1H) (0.642gm, 0.002mol), N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide(L_2H) (0.582gm, 0.002mol), ($Mn(CH_3COO)_2.4H_2O$) (0.490gm; 1.5 $cm^3$0.002mol), 300cm^3methanol and pH adjusted to 7-7.5 with 0.1N NaOH(aq)the mixture was kept overnight to afforded 0.750gm brown solids.

[Fe(III)L_1-L_2)2H_2O]: N-(5-nitro-2-hydroxybenzylidene)-2-chlorobenzylamine(L_1H) (0.642gm, 0.002mol), N-(5-nitro-2-hydroxybenzylidene)-4-aminobenzene-1-sulfonamide(L_2H) (0.582gm, 0.002mol), ($FeCl_3$.unhydr) (0.324gm; 1.5 $cm^3$0.002mol), 300cm^3methanol and pH adjusted to 4-4.5 with 0.1N NaOH(aq)afforded 0.711gm reddish brown solids.

[Ni(II)L_1-L_2)2H_2O], [Co(II)L_1-L_2)2H_2O] and [Cu(II)L_1-L_2)2H_2O]: N-(5-nitro-2-hydroxybenzylidene)-2-chloro benzylamine(L_1H) (0.642gm, 0.002mol), N-(5-nitro-2-hydroxy benzylidene)-4-amino benzene-1-sulfonamide (L_2H)(0.582gm, 0.002mol), ($NiCl_2.6H_2O$) (0.476gm; 1.5 cm^3 0.002mol)/($CoCl_2.6H_2O$) (0.476gm; 1.5 cm^3 0.002mol)/ ($CuCl_2.2H_2O$) (0.342gm; 1.5 $cm^3$0.002mol), 300cm^3methanol and pH adjusted to 7-7.5 with 0.1N NaOH(aq)afforded 0.590gm greenish yellow and 0.612gm orange brown solids and 0.821gm grey green solids of complexes respectively.

RESULTS AND DISCUSSION

The molar conductance was measured on an Equiptronic EQ-664A conductivity meter for all the complexes in DMF. Elemental and Thermal analysis was carried out using Thermo finnigan, Italy FLASH EA 1112 series and PERKIN ELMER,USA Diamond TG/DTA thermal analyzer in an inert atmosphere of nitrogen respectively was performed at SAIF, IIT Bombay, Mumbai. The magnetic susceptibility measurements at room temperature were performed in Pune university on faradays balance using $HgCo(NCS)_4$ as calibrant. The ^{1}HNMR spectrum of the ligands was recorded at university of Mumbai on 300 MHz spectrometer using TMS as internal standard and $CDCl_3$/(D_6) DMSO as a solvent. The IR spectra of ligands and their complexes were recorded on a JASCOFTIR–8400S spectrometer in KBr pellets in the range of 4000-350 cm^{-1}. UV-Visible spectra were recorded on a JASCO Corp.V-550 UV-Visible spectrometer in the range 200-1100 nm. Electron spin resonance spectra at Liquid nitrogen temperature in DMF of the Cu(II) complex was recorded in TIFR, on Varian E-112x-band ESR spectrometer, using DPPH as 'g' marker (g = 2.0023). The antimicrobial activities of ligands and their mixed ligand complexes were screened by agar well diffusion method. The elemental analysis presented in Table No.1 indicates that, all the metal complexes have 1:1:1stoichiometry with respect to L_1H: L_2H: M {where M = Mn(II), Co(II), Ni(II), Cu(II) and Fe(III)} and are dark colored amorphous substances, soluble in DMF and DMSO. Metal ion percentage in the complex was determined by standard method [11]. The molar conductance values (6.94-18.70) ohm^{-1} mol^{-1} cm^2) for 10^{-3} Molar solutions in DMF indicate that the metal complexes are non-electrolytic in nature [12].

Electronic Spectra

Electronic spectral studies of Mixed Ligand Complexes were carried out in DMSO solution. The absorption spectrum of the Mn(II) complex showed two bands at ~20000cm^{-1}(ε ~18L mol^{-1} cm^{-1})assigned for the LMCT transition and another band at~10050cm^{-1}(ε ~ 95L $mol^{-1}cm^{-1}$) is due to the d-d transitions, the magnetic moments 4.11B.M are slightly lower for 5 unpaired electron may be due to presence of small magnetic exchange [13]. The mixed ligand Fe(III) complex exhibits spectral bands in the range at around 20000cm^{-1}(ε~100L$mol^{-1}cm^{-1}$) and assigned due to LMCT bands and a weak band at 10000 cm^{-1} (ε~22L$mol^{-1}cm^{-1}$) is assigned due to d-d transitions, also the magnetic moment values of 5.30B.M are in the required range for high spin Fe(III) complex indicating Octahedral geometry for Fe(III) complex [14]. The Co(II) complex showed bands at~9881.42 cm^{-1}(ε~25L mol^{-1} cm^{-}

[1]) and ~19417.50cm^{-1} were observed and are attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively in an octahedral field[10-11]. The spectral parameters of Co(II) complex are Dq = 1085cm^{-1}, B= 723.70cm^{-1}, β = 0.75 and β_0 = 25.47%. The reduction of Racah parameter from the free ion value 971cm^{-1} and β_0 value of 25.47% testify the presence of considerable covalence in the complex [15-16]. The Co(II) complex has magnetic moment 5.20B.M which suggest an octahedral geometry for the complex. Ni(II) complex exhibits two electronic spectral bands at ~10020cm^{-1} and ~16260.20cm^{-1} which can be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions in an octahedral field respectively. The transition due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) was completely obscured by the intense intra ligand transition band. The ν_2: ν_1 ratio is 1.62, which is in the usual range reported for an octahedral Ni(II) complexes [16-17]. The spectral parameters for Ni(II) complex are, Dq = 1002.00 cm^{-1}, B= 865.70cm^{-1}, β=0.84 and β_0= 15.95% . The reduction of Racah parameter from the free ion value 1030 cm^{-1} and β_0 value of 15.94% confirms the presence of considerable covalence in the complex. The Ni(II) complex has magnetic moment 3.12 B.M which also suggest the complex has octahedral geometry. The Cu(II) complex exhibit broad band centered at ~13333.33cm^{-1} mainly due to $^2E_g \rightarrow {}^2T_{2g}$ transition suggesting the octahedral geometry [14]. The observed magnetic moment value of 1.87B.M for Cu(II) complex suggest square planner or octahedral geometry.

Table No. 1. - Analytical and Physical data of Schiff bases (L_1H and L_2H) and their mixed ligand complexes

Ligand / Complex	Mol. Wt.	M.P. °C	Analysis % Found (Calculated)					Molar Conductance (λm) Ohm^{-1}cm^{2}mol	μ_{eff} B.M.
			C	H	N	S	M		
L_1H $C_{14}H_{11}N_2O_3Cl$	290.70	138-140	56.35 (57.83)	3.68 (3.78)	9.56 (9.63)	-	-	-	-
L_2H $C_{13}H_{11}N_3O_5S$	321.30	252-254	47.85 (48.59)	3.28 (3.42)	12.88 (13.08)	9.56 (9.98)	-	-	-
$[Mn(L_1\text{-}L_2)2H_2O]$ $C_{27}H_{20}N_5O_8ClSMn$	664.83	>250	46.80 (48.77)	2.84 (3.03)	10.47 (10.53)	4.75 (4.82)	8.92 (9.01)	6.94	4.11
$[Fe(L_1\text{-}L_2)2H_2O]$ $C_{27}H_{20}N_5O_8ClSFe$	665.75	>250	47.75 (48.71)	2.90 (3.03)	10.34 (10.52)	4.67 (4.82)	9.60 (9.65)	13.44	5.30
$[Co(L_1\text{-}L_2)2H_2O]$ $C_{27}H_{20}N_5O_8ClSCo$	668.83	>250	47.56 (48.48)	2.88 (3.01)	10.26 (10.47)	4.65 (4.79)	9.44 (9.52)	14.22	5.20
$[Ni(L_1\text{-}L_2)2H_2O]$ $C_{27}H_{20}N_5O_8ClSNi$	668.59	>250	47.25 (48.50)	2.94 (3.01)	10.34 (10.47)	4.71 (4.80)	8.99 (8.95)	15.33	3.12
$[Cu(L_1\text{-}L_2)2H_2O]$ $C_{27}H_{20}N_5O_8ClSCu$	673.44	>250	46.82 (48.15)	2.72 (2.99)	10.21 (10.40)	4.66 (4.76)	9.00 (9.15)	18.70	1.87

Infrared Spectra

The important infrared frequencies exhibited by the ligands L_1H and L_2H and their mixed ligand complexes are given in the Table No.2. Infrared spectra of the schiff bases L_1H and L_2H show a band at 3073 and 3117cm^{-1} due to the phenolic hydroxyl group respectively in free ligands, which disappeared in spectra of their complexes indicating probably the coordination through phenolic oxygen moiety. The schiff base L_2H show two band at 3356cm^{-1} and 3256cm^{-1} due to the amine group and at 1317cm^{-1} and 1153cm^{-1} due to SO_2 group in free ligand, these bands does not show any considerable shift in the spectra of complex and remain unchanged, hence it can be conclude that the amine group attached to the SO_2 group and SO_2 group both are not involved in the complexation. Both schiff bases L_1H and L_2H show a medium intensity band at around 1285cm^{-1} due to phenolic ν(C-O) group which is shifted to higher region at around 1312-1301cm^{-1} indicating the coordination through the phenolic oxygen atoms [18-20]. The IR spectra of the schiff bases L_1H and L_2H exhibit a strong band at 1638 and 1620cm^{-1} due to ν(C=N) (azomethine)which has been shifted to lower regions at 1629-1617cm^{-1} and 1607-1604cm^{-1} respectively in the spectra of complexes indicating the participation of the azomethine groups in the complex formation [18-20]. The spectra of the complexes show a broad diffused bands in the region at around 3100-3700cm^{-1}, strong bands at 1538-1535cm^{-1} and week intensity bands at 735-700 cm^{-1} due to ν(OH), δ(OH) and ρr(OH)respectively of the coordinated water molecules [20-21]. The coordination through nitrogen of azomethine and oxygen of (C-O) group of ligands are further evidenced by the appearance in the complexes of non-ligand bands around 460-687cm^{-1}and 411-445cm^{-1} are due to M-N and M-O bonds respectively [20-21]

Thermal Studies

The complexes Mn(II), Co(II), Ni(II), Cu(II) and Fe(III) lose their weight in the temperature range~147-158°C, 262-281°C, 230-245°C, 260-285°C and 213-241°C corresponding to two coordinated water molecules. Loss of water molecules at higher temperature [22-24] is in accordance with literature, Second Peak may be attributed to lose of one Chloride ion [24]. The occurrence of endothermic peak and elimination of the two water molecules at comparatively higher temperature unambiguously confirm earlier observation based upon the IR spectra that the

water molecules are coordinated in the metal complexes. The complexes do not decompose completely even after 800°C, thus indicating more thermal stability of the complexes

Table No.2- IR Spectral data of Schiff bases (L_1H and L_2H) and their mixed ligand complexes

Ligand / Complex	ν_{O-H} phenolic	ν_{O-H} coordinated water	ν_{NH} SO_2 NH_2	$\nu_{C=N}$	ν_{O-H} coordinated water	ν_{C-O} phenolic	δ_{O-H} coordinated water	ν_{SO2} SO_2 NH_2	ν_{M-N}	ν_{M-O}
L_1H	3073	-	-	1638	-	1285	-	-	-	-
L_2H	3117	-	3358,3256	1620	-	1285	-	1314,1153	-	-
$[Mn(L_1\text{-}L_2)2H_2O]$	-	3326-3637	-	16171607	1538	1301	700	1320,1156	513	411
$[Fe(L_1\text{-}L_2)2H_2O]$	-	3400-3700	3357,3255	16191605	1535	1308	801	1320,1153	469	445
$[Co(L_1\text{-}L_2)2H_2O]$	-	3200-3700	-	16181604	1536	1308	723	1317,1158	687	443
$[Ni(L_1\text{-}L_2)2H_2O]$	-	3200-3700	-	16201607	1536	1310	660	1320,1161	460	439
$[Cu(L_1\text{-}L_2)2H_2O]$	-	3200-3690	-	16291605	1536	1312	735	1320,1161	514	440

ESR Spectra

The ESR spectrum of the Cu(II) complex was recorded at liquid nitrogen temperature in DMF. Observed value for the $[Cu(L_1\text{-}L_2)2H_2O]$complex are $g\|=2.28$, $g^{\perp}=2.06$ and G = 4.59. The observed g|| value is less than 2.3 in agreement with the covalent character of the metal-ligand bond[21,]. The trend $g\| > g^{\perp} > ge(2.0023)$observed for this complex shows that the unpaired electron is localized in $d_{x^2\text{-}y^2}$orbital of Cu(II) ion and the spectral features are characteristic of axial symmetry; tetragonal elongated structure may be assumed for this Cu(II) complex [14,25-28]. The anisotropic G values have been calculated by using the equation $G = (g\|-2.002)/ (g^{\perp}-2.002)$. The G value is more than 4.0, thus the ligand forming the Cu(II) complex is regarded as weak field ligand [27-28].

Antimicrobial Activity

Synthesized Schiff bases and their corresponding mixed ligand metal complexes were screened against *S.aurious, P.aeruginosa* and *Candida albicans* to assess their potential as antimicrobial agent by agar well diffusion method. The results suggest that the complexation increases the antimicrobial activity. Following conclusions are drawn based on the measured zone of inhibition against the growth of various microorganisms as listed in Table No.3.

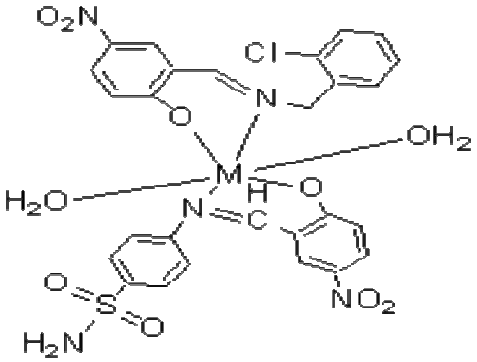
1. The ligands show slight antibacterial activity against gram positive and slight to moderate antifungal activity, while they show no activity against gram negative bacteria
2. For the gram-positive bacteria only Ni complex show moderate activity, while all others are inactive
3. In case of gram-negative bacteria all complexes show slight to moderate activity, order of activity is Fe =Co=Ni>Cu
4. While all complexes are inactive against the fungal strain under study

Schiff base / Complex	Zone of inhibition		
	Staphylococcus aureus	*Pseudomonas aeruginosa*	*Candida albicans* (fungus)
L_1H	+	-	+
L_2H	+	-	++
$[Mn(L_1\text{-}L_2)(H_2O)_2]$	-	++	-
$[Fe(L_1\text{-}L_2)(H_2O)_2]$	-	++	-
$[Co(L_1\text{-}L_2)(H_2O)_2]$	-	++	-
$[Ni(L_1\text{-}L_2)(H_2O)_2]$	++	++	-
$[Cu(L_1\text{-}L_2)(H_2O)_2]$	-	+	-
Highly active = +++ (inhibition zone > 8.2 mm); moderately active = ++ (inhibition zone > 5.0-8.2 mm); slightly active = + (inhibition zone > 2.5-5.0 mm); Inactive = - (inhibition zone < 2.5mm)			

CONCLUSION

The elemental analysis, magnetic susceptibility, electronic, IR and ESR spectral observation s suggest the octahedral geometry for the Mn(II), Co(II), Ni(II),Cu(II) and Fe(III) complexes. The general structure of the complexes is shown in figure 1. The Schiff bases do show some antimicrobial activity to certain extent but their complexes exhibit comparatively greater amount of activity against the microorganisms.

Figure No. 1- Proposed structure for the complexes



M=Mn(II),Co(II),Ni(II),Cu(II)and Fe(III)

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