Synthesis, Spectral and Antimicrobial Studies of some Co(II), Ni(II) and Cu(II) Complexes Containing 2-Thiophenecarboxaldehyde Moiety

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Abstract: Some new Schiff base metal complexes of Co(II), Ni(II) and Cu(II) derived from 3-chloro-4-fluoroaniline (HL¹) and 4-fluoroaniline (HL²) with 2-thiophenecarboxaldehyde have been synthesized and characterized by elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, ESR and magnetic susceptibility. The complexes exhibit coordination number 4 or 6. The complexes are colored and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal: ligand) ratio. FAB-mass data show degradation pattern of the complexes. The Schiff base and metal complexes show a good activity against the bacteria; *B. subtilis*, *E. coli* and *S. aureus* and fungi *A. niger*, *A. flavus* and *C. albicans*. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the Schiff bases.

Keywords: 2-Thiophenecarboxaldehyde, N, S donor, biological activity.

Introduction

Schiff base ligands have been widely studied in the field of coordination chemistry mainly due to their facile syntheses, easily availability, electronic properties and good solubility in common solvents. Transition metal complexes containing the Schiff base ligands have been of interest for many years because the transition metal complexes play a central role in the conduction of molecular materials, which display unusual conducting, magnetic, thermal properties and find applicability in material chemistry and biochemistry¹⁻³. A Transition metal complexes which usually contain nitrogen, sulphur/or oxygen as ligand atoms are becoming increasingly important because these Schiff base can bind with different metal centers involving various coordination sites and allow successful synthesis of metallic

complexes with interesting stereochemistry. Heterocyclic compounds are widely distributed in the nature and essential to many biochemicals, analytical and industrial processes. Compounds containing these heterocycles have important properties in the field of material science and biological systems⁴⁻⁷.

Experimental

Melting points were taken in open glass capillaries and are uncorrected. Progress of reaction was monitored by silica gel-G coated TLC plates using MeOH:CHCl₃ system (1:9). The spot was visualized by exposing dry plate at iodine vapours chamber. All the used chemicals and solvents were of Anal R grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were purchased from Loba Chemie. Elemental analyses were performed on an Elemental Vario EL III Carlo Erba 1108 analyzer. FAB-mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Electronic spectra (in DMSO) were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10⁻³ M solutions of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using mercuric tetrathiocyanatocobaltate(II) as the calibrant. FT-IR spectra were recorded in KBr medium on a Perkin Elmer RX1 spectrophotometer in wave number region 4000-400 cm⁻¹. X-band EPR spectra were recorded on a Varian E-112 spectrometer using TCNE as the internal standard.

Synthesis of Schiff bases

The Schiff bases (HL¹ and HL²) have been synthesized by adding the methanolic solution of 3-chloro-4-fluoroaniline and 4-fluoroaniline with methanolic solution of 2-thiophenecarboxaldehyde in equimolar ratio. The reaction mixture was then refluxed on water bath for about 4-6 hours. The condensation product was filtered, thoroughly washed with ethanol and ether, recrystallized and dried in vacuo. The Purity of the synthesized compound was monitored by TLC using silica gel G (Yield: HL¹ - 78%; HL² - 82%).

Preparation of Schiff Base Metal Complexes

The metal complexes have been prepared by mixing the methanolic solution of CoCl₂·6H₂O, NiCl₂·6H₂O and CuCl₂·2H₂O to the methanolic solution of Schiff bases (HL¹ and HL²) in

1:2 molar ratio. The resulting mixture was then refluxed on water bath for about 5-8 hours. A colored product appeared on standing and cooling the above solution. The complex was filtered, washed with ether and dried under reduced pressure over anhydrous CaCl_2 in a desiccator. It was further dried in an electric oven at 50-70°C.

Biological activity

The *in-vitro* biological activity of the investigated Schiff base and its metal complexes was tested against the bacteria *B. subtilis*, *E. coli* and *S. aureus* by disc diffusion method using nutrient agar as medium and streptomycin as control. The antifungal activities of the compounds were also tested by the Well diffusion method against the fungi *A. niger*, *A. flavus* and *C. albicans*, on potato dextrose agar as the medium and Griseofulvin as control. The stock solution was prepared by dissolving the compounds in DMSO. In a typical procedure, a well was made on agar medium inoculated with microorganism. The well was filled with the test solution using a micropipette and the plate was incubated 24 h for bacteria at 37 °C and 72 h for fungi at 30 °C. During this period, the test solution diffused and the growth of the inoculated microorganism was affected. The inhibition zone was developed, at which the concentration was noted.

Results and Discussion

All the metal complexes are colored, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature, more or less soluble in common organic solvents. Analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula are given in Table 1. All the metal chelates have 1:2 (metal:ligand) stoichiometry. The molar conductance in DMSO of the complexes are 129.2, 49.5 and 56.2 $\text{Scm}^2\text{mol}^{-1}$ respectively, for Co(II), Ni(II) and Cu(II) complexes of HL^1 . This indicates the Co(II) complex is electrolytic nature while Ni(II) and Cu(II) complexes are non-electrolytic nature. The molar conductance values for Co(II), Ni(II) and Cu(II) complexes of HL^2 are 120.1, 39.6 and 46.5 $\text{Scm}^2\text{mol}^{-1}$ respectively. This indicates the nature of Co(II) as electrolytic and Ni(II) and Cu(II) complex are non-electrolytic.

FAB-mass spectrum

The FAB-mass spectra suggested that all the complexes have a monomeric nature. These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses.

The FAB mass spectrum gives additional information about the analyzed species. The FAB mass spectrum of $[\text{Co}(\text{HL}^1)_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ shows a molecular ion peak (M^+) at m/z 663 amu which suggests the monomeric nature of the complex thus confirming the proposed formula. The spectrum of complex shows a series of peak at 643, 608, 542, 375, 279 and 105 corresponding to various fragments. The value of 105 corresponds to Co with N donor S as ligand moiety. The FAB mass spectra of $[\text{Ni}(\text{HL}^1)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ shows a molecular ion peak (M^+) at m/z , 648 confirm the proposed formula. The spectrum of complex also shows a

series of peak 611, 543, 470, 375, 278 and 107 corresponding to various fragments. Their intensity gives an idea of stability of the fragments^{8,9}.

Table 1. Analytical and Physical Data of Ligand and its Metal Complexes.

Molecular formula/ Mol. Wt./(Colour)	Yield (%)	Elemental Analysis Found/Calcd. (%)				* Λ_m
		C	H	N	M	
C ₁₁ H ₇ NCIFS [HL ¹] 240 (Light Yellow)	78	54.54 (55.00)	2.89 (2.91)	5.78 (5.83)	-	-
[Co(C ₁₁ H ₇ NCIFS) ₂]Cl ₂ .3H ₂ O 664 (Bitter almond)	65	39.81 (39.75)	3.01 (3.01)	4.02 (4.21)	8.88 (8.87)	129.2
[Ni(C ₁₁ H ₇ NCIFS) ₂]Cl ₂ .2H ₂ O 646 (Green)	63	40.74 (40.86)	3.04 (3.09)	4.32 (4.33)	9.03 (9.06)	49.5
[Cu(C ₁₁ H ₇ NCIFS) ₂]Cl ₂ 614 (Black)	68	42.64 (42.99)	2.26 (2.28)	4.52 (4.56)	10.26 (10.34)	56.2
(C ₁₁ H ₈ NFS) [HL ²] 205 (Black)	82	64.39 (64.42)	3.90 (3.95)	6.82 (6.88)	-	-
[Co(C ₁₁ H ₈ NFS)]Cl ₂ .2H ₂ O 576 (Green)	68	45.83 (45.75)	3.47 (3.46)	4.86 (4.85)	10.23 (10.21)	120.1
[Ni(C ₁₁ H ₈ NFS)]Cl ₂ .2H ₂ O 576 (Green)	72	45.83 (45.75)	3.47 (3.46)	10.16 (10.14)	10.16 (10.14)	39.6
[Cu(C ₁₁ H ₈ NFS)]Cl ₂ .2H ₂ O 580 (Black)	70	45.50 (45.52)	3.41 (3.45)	4.79 (4.81)	6.22 (6.29)	46.5

*Conductance (Λ_m) = S cm² mol⁻¹.

The FAB mass spectrum gives additional structural information about the analyzed species. The FAB mass spectrum of [Cu(HL²)₂]Cl₂.2H₂O complex shows a molecular ion peak (M⁺) m/z = 580 amu, which suggest the monomeric nature of the complex. The spectrum of the complex also shows a series of peaks corresponding to various fragments 541, 469, 434, 354, 280 and 107. Their intensity gives an idea about stability of the fragments^{8,9}.

IR spectra

The data of the IR spectra of Schiff base ligand and its metal complexes are listed in Table 2. The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared.

The IR spectra of HL¹ ligand exhibits a strong band at 1630 cm⁻¹ due to $\nu(\text{C}=\text{N})$ azomethine group. This band shifts to lower energy region by 20-27 cm⁻¹ in the complexes. It suggests bonding through azomethine nitrogen. A strong band was observed at 848 cm⁻¹, assignable to $\nu(\text{C-S-C})$ of thiophene. The band position of $\nu(\text{C-S-C})$ has shifted to lower side by 18-28 cm⁻¹ in the complexes on coordination of metal ions with sulphur of thiophene. The appearance of broad band around 3313, 3328 and 3350 cm⁻¹ in the spectra of complexes have been assigned to associated water molecule. In all complexes new bands at 490 $\pm$ 8 cm⁻¹ and 404 $\pm$ 2 cm⁻¹ are due to the formation of $\nu(\text{M-N})$ and $\nu(\text{M-S})$ bands respectively. The IR spectrum of HL² Schiff base shows a strong band at 1626 cm⁻¹ due to $\nu(\text{C}=\text{N})$ azomethine group. On the chelation with metal ion, it has shifted down (11-38 cm⁻¹) due to coordination of the azomethine nitrogen to the central metal ion. Thiophene ring $\nu(\text{C-S-C})$ shows absorption band at 842 cm⁻¹ in the Schiff base spectrum. This band shows lower shift by 24-27 cm⁻¹ in all complexes suggesting participation of thiophene $\nu(\text{C-S-C})$ sulphur in coordination. The appearance of broad band at 3397, 3387 and 3368 cm⁻¹ in complexes have been assigned to $\nu(\text{OH})$ water molecules¹⁰⁻¹⁶.

The IR data of both the Schiff base and its metal complexes show that the Schiff bases (HL¹ and HL²) is coordinated to the metal ion in bidentate manner with SN donor sites of thiophene sulphur and azomethine nitrogen.

Electronic spectra and magnetic moment

The electronic spectral data of the metal complexes in DMSO solution are given in Table 3. The nature of the ligand field around the metal ion has been deduced from the electronic spectra.

The electronic spectrum of Co(II) complex of HL¹ shows two bands of appreciable intensity at 15503 cm⁻¹ and 20125 cm⁻¹ which have tentatively been assigned to $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$ (ν_2) and $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$ (ν_3) transitions. The magnetic moment is 4.35 B.M. Thus the tetrahedral geometry has been suggested for this complex. The electronic spectrum of Ni(II) complex of HL¹, shows three bands at 11070 cm⁻¹, 18816 cm⁻¹ and 24125 cm⁻¹ corresponding to transition $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ (ν_2), $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{P})$ (ν_3) respectively. The magnetic moment is 3.19 B.M. These findings are in favor of an octahedral geometry for the Ni(II) complex. For Cu(II) complex of HL¹, a single broad band at 13320 cm⁻¹ has been observed, this attributes to $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transition. Its magnetic moment is 1.85 B.M. Thus the octahedral geometry has been suggested for complex. The electronic spectrum of Co(II) complex of HL² shows two bands of appreciable intensity at 12360 cm⁻¹ and 19806 cm⁻¹ which have tentatively been assigned to $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$ (ν_2) and $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$ (ν_3) transitions. The magnetic moment is 4.67 B.M. Thus, the tetrahedral geometry has been suggested for this complex. The electronic spectrum of Ni(II) complex of HL² exhibits three bands at 11220 cm⁻¹ and 20212 cm⁻¹ and 23645 cm⁻¹ which are assignable to $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ (ν_2) and $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$ (ν_3) transition respectively. The magnetic

moment is 3.14 B.M. These findings are in favour of an octahedral geometry for the Ni(II) complex. In the Cu(II) complex of HL² a single broad band at 16750 cm⁻¹ has been observed, this attributes to ²E_g→²T_{2g} transition. Its magnetic moment is 1.94 B.M. Thus the octahedral geometry has been suggested for complex¹⁷⁻²¹.

Table 2. IR bands of Schiff base ligands and their complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C-S-C})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$
[HL ¹]	1630	848	-	-	-
[Co(HL ¹) ₂]Cl ₂ .3H ₂ O	1603	820	3350	486	402
[Ni(HL ¹) ₂]Cl ₂ .2H ₂ O	1608	830	3313	490	408
[Cu(HL ¹) ₂]Cl ₂	1610	825	-	488	410
[HL ²]	1626	842	-	-	-
[Co(HL ²)Cl ₂ .2H ₂ O	1600	816	3397	488	410
[Ni(HL ²)Cl ₂ .2H ₂ O	1598	818	3387	485	408
[Cu(HL ²)Cl ₂ .2H ₂ O	1605	815	3368	482	406

ESR spectra

The ESR spectra of Cu(II) provide information about the extent of the delocalization of unpaired electron. The X-band ESR spectra of Cu(II) complexes were recorded in the solid state at room temperature, their $g_{\parallel}$, $g_{\perp}$, Δg , g_{av} , G have been calculated. The values of ESR parameters $g_{\parallel}$, $g_{\perp}$, g_{av} , Δg , G for Cu(II) complex of HL¹ are 2.1775, 2.0977, 2.1030, 0.0526 and 1.83 respectively. Similarly, the corresponding values for Cu(II) complex of HL² are 2.2454, 2.0665, 2.1048, 0.7254 and 3.77 respectively.

ESR spectra of the complexes revealed two g values ($g_{\parallel}$ and $g_{\perp}$). Since the $g_{\parallel}$ and $g_{\perp}$ values are closer to 2 and $g_{\parallel} > g_{\perp}$ suggesting a tetragonal distortion around the Cu(II) ion. The trend $g_{\parallel} > g_{\perp} > g_e(2.0023)$ shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital in the ground state of Cu(II), spectra are characteristic of axial symmetry. The $g_{\parallel} > 2.3$ is characteristic of an ionic environment and $g_{\parallel} < 2.3$ indicates a covalent environment in metal ligand bonding. The $g_{\parallel}$ values for these complexes are less than 2.3 suggesting the environment is covalent. The exchange coupling interaction between two Cu(II) ions is explained by Hathaway expression $G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$. According to Hathaway, if the value G is greater than four ($G > 4.0$), the exchange interaction is negligible; whereas when the value of G is less than four ($G < 4$) a considerable exchange coupling is present in solid complex. The G values for these Cu(II) complexes are less than four indicate, considerable exchange interaction in the complexes^{22,23}.

Antimicrobial activities

The bactericidal and fungicidal investigation data of the compounds are summarized in Tables 5 and 6. The results of the investigations account for the antipathogenic behavior of the compounds and this efficacy is positively modified on complexation. Overtone's Concept and Chelation Theory explain well this drug action²⁴⁻²⁶.

Table 3. *In-vitro* antibacterial activity of compounds and their inhibition zone (%).

Compound	Antibacterial activity						Antifungal activity					
	<i>B. subtilis</i>		<i>E. coli</i>		<i>S. aureus</i>		<i>A. niger</i>		<i>A. flavus</i>		<i>C. albicans</i>	
	50	100	50	100	50	100	50	100	50	100	50	100
	pp	pp	pp	pp	pp	pp	pp	pp	pp	pp	pp	pp
	m	m	m	m	m	m	m	m	m	m	m	m
HL ¹	10	21	14	20	13	20	10	19	15	21	12	18
Co(II)	23	34	22	30	19	30	20	30	22	32	18	32
Ni(II)	25	33	20	31	18	32	21	31	20	31	15	31
Cu(II)	22	30	22	29	19	31	20	32	22	31	18	31
HL ²	15	21	12	20	18	24	15	23	14	22	10	22
Co(II)	22	35	19	25	22	33	18	31	20	33	12	34
Ni(II)	20	35	20	33	22	32	19	30	18	32	22	33
Cu(II)	24	36	21	34	20	35	20	32	17	34	20	35
Streptomycin	28	37	26	34	27	35	-	-	-	-	-	-
Griseofulvin	-	-	-	-	-	-	22	32	20	35	24	36

Conclusion

In the present research studies, our successful efforts are synthesized of some newly compounds. These synthesized compounds Characterized by various physicochemical and spectral analyses. The synthesized Schiff base ligands bind with the metal ions in a bidentate manner, with SN donor sites of thiophene-S and azomethine-N. FAB-mass shows

degradation pattern of the complexes. The antimicrobial data show that the metal complexes to be more biological active compared to those parent Schiff base ligand against all pathogenic species. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased.

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