



Synthesis, Spectroscopic and Thermal Studies of Fe(III) and VO(IV) Complexes of Heterocyclic Schiff Base Ligand

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ABSTRACT

The present article describes the synthesis, characterization and thermal studies of newly synthesized Fe(III) and VO(IV) complexes from heterocyclic Schiff base ligand. The new Schiff base ligand has been synthesized by refluxing chalcone 3-chloro-6-hydroxy-2-methylphenyl-3-(3,4-dimethoxyphenyl)prop-2-en-1-one with isonicotinic hydrazide in the ethanolic medium. The reaction of this ligand with metal salts results in the formation of respective metal complexes. The compounds were characterized on the basis of elemental analysis, molar conductance, infrared (IR), ultraviolet-visible, mass, and ¹H-nuclear magnetic resonance spectroscopic techniques. IR spectral data show that ligand act as monobasic tridentate ONO donor toward Fe(III) ion and monobasic bidentate ON donor toward VO(IV) ion. Thermal stability and decomposition behavior of complexes have been studied with the help of thermogravimetric technique at a heating rate 10°C min⁻¹ in a nitrogen atmosphere.

Key words: Schiff base, Metal complexes, Infrared, Thermal analysis.

1. INTRODUCTION

During recent years metal complexes synthesized from Schiff base ligand play a key role in the development of coordination chemistry because of their role as a model in biological, biochemical, analytical, antibacterial, and antifungal activities [1-6]. They can also use effectively as a catalyst for oxidation, reduction, and hydrolysis reactions [7-11]. The Schiff base used for the synthesis of complexes are generally prepared by the condensation of carbonyl compound with primary amine, and they generally coordinate to metal ion through azomethine N and hydroxyl O. Recently, heterocyclic coordination chemistry has received great attention as they use as a versatile ligand in the formation of transition metal complexes [12-14]. The current study focused on the synthesis of heterocyclic Schiff base ligand and its Fe(III) and VO(IV) complexes which to be proven using thermal and spectroscopic characterization.

2. EXPERIMENTAL

All chemicals used were of analytical reagent grade, highest purity available, and purchased from SD-Fine and Merck Chemical companies. They included FeCl₃.6H₂O, VO(acac)₂, organic solvent (ethanol, methanol, dimethylformamide, and dimethyl sulfoxide).

The amounts of metal present in the complexes were estimated by metal oxide method [15]. The molar conductance of the complexes in dimethyl formamide (DMF) solution (10⁻³ M), at room temperature, was measured using the consort type c-533 conductivity instrument. The infrared Fourier-transform infrared (IR) spectra of ligand and complexes were recorded as KBr pellets using Perkin Elmer spectrometer. The thermal analysis was performed with a Perkin Elmer (TGS-2 model) thermal analyzer at a heating rate of 10°C min⁻¹ in the temperature range 40-800°C.

2.1. General procedure for the synthesis of Schiff Base Ligand

The chalcone-(3-chloro-6-hydroxy-2-methylphenyl)-3-(furan-2-yl) prop-2-en-one (0.01 mol) and isoniazid (0.01 mol) was added to the hot ethanolic solution, reflux up to 6-8 h and progress of reaction was checked by thin layer chromatography using methanol hexane system. The crude product formed pores into ice water and solid obtained washed by petroleum ether and dried in an oven. General scheme for the synthesis of Schiff base ligand is shown in Figure 1.

Yield: 72%. The ¹H nuclear magnetic resonance (NMR) spectra of Schiff base ligand was recorded in dimethyl sulfoxide (DMSO) using TMS as an internal

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standard. The spectrum shows following peaks.

^1H NMR (DMSO) δ ppm: 11.87 (s, 1H, phenolic OH), 3.83 (dd, 1H, CH_A pyrazoline), 4.30 (dd, 1H, CH_B pyrazoline), 6.73-7.61 (m, 9 H, aromatic), 3.76 (s, 6H, CH_3O), and 2.45 (s, 3H, methyl) [16,17].

2.2. General Procedure for the Synthesis of Fe(III) and VO(IV) complexes

Both the complexes were synthesized by adding ligand and respective metal salt, i.e., $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{VO}(\text{acac})_2$ in 1:1 ratio to the ethanol as solvent and the reaction mixture was refluxed in water bath for about 14-16 h. The colored solid product obtained was filtered, dried and washed several times using petroleum ether.

3. RESULTS AND DISCUSSION

All the complexes are colored solid, insoluble in common organic solvents such as ethanol and methanol but soluble in DMF and DMSO. The analytical data show that 1:1 metal to ligand ratio in Fe(III) complex whereas 1:2 in VO(IV) complex. Lower values of molar conductance indicate that complexes are nonelectrolytes. The analytical and physical data of ligand and its complexes are given in Table 1.

3.1. IR Spectra

To study the binding modes of ligand toward metal ion IR spectral data of Schiff base ligand compared with the complexes (Table 2). The IR spectrum of free Schiff base ligand shows a peak of azomethine group $-\text{CH}=\text{N}$ at 1598 cm^{-1} , which is shifted to a lower frequency in both VO(IV) and Fe(III) complexes at 1580 and 1573 cm^{-1} , respectively, indicates that azomethine nitrogen coordinate to metal ion. This decrease in IR stretching frequency occurs due to decrease in electron density during coordination. A broad band at 3376 cm^{-1} is assigned to hydrogen bonded $-\text{OH}$ in the spectrum of ligand which is disappeared in metal complexes shows the involvement of hydroxyl O in coordination to the metal ion. This is again proved due to shifting of phenolic C-O stretching band to a higher frequency ($30\text{-}31\text{ cm}^{-1}$) in the complexes. The very weak band which is absent in ligand but present in metal complexes are in the ranges $455\text{-}470\text{ cm}^{-1}$ and $475\text{-}519\text{ cm}^{-1}$, assigned to stretching frequencies of $\nu(\text{M-N})$ and $\nu(\text{M-O})$ bands. A characteristic band for neutral carbonyl group in ligand is appeared at

1655 cm^{-1} , shifted to lower frequency $53\text{-}56\text{ cm}^{-1}$ in Fe(III) complex shows that coordination of carbonyl "O" to metal ion while in VO(IV) complex the stretching band does not shifted to that much lower frequency indicates involvement of carbonyl "O" in coordination [18-21].

3.2. Mass Spectra

Mass spectrometry has been successfully used to determine the molecular ion peak for Schiff base ligand. The various fragmentation peaks obtained for ligand, Fe(III), and VO(IV) complexes are in good agreement with proposed structure. The mass spectral data show that Fe(III) complex is monomeric while VO(IV) is dimeric. Mass spectrum of ligand was shown in Figure 2.

3.3. Electronic Spectra

The electronic absorption spectra of metal complexes were recorded in DMSO in the range $200\text{-}800\text{ nm}$. The electronic spectrum of Fe(III) complex shows bands at 520 , 425 and 380 nm corresponding to transition ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$, respectively, indicates octahedral geometry around Fe(III) ion [14].

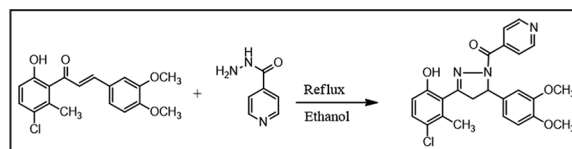


Figure 1: Synthesis of Schiff base ligand.

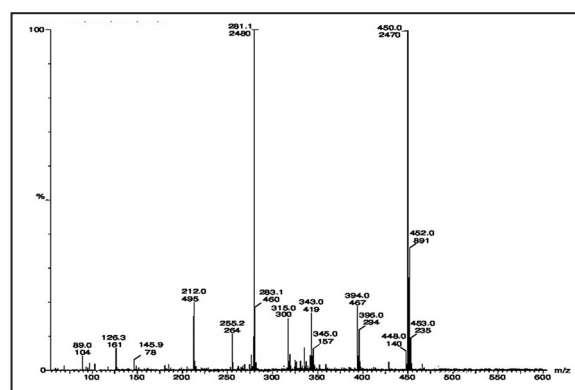


Figure 2: Mass spectrum of Schiff base ligand.

Table 1: Analytical and physical data of ligand and its metal complexes.

Compounds	Molecular formula	F.Wt.	Color	MP (°C)	C %	H %	N %	M %
LH	$\text{C}_{24}\text{H}_{22}\text{ClN}_3\text{O}_4$	451.13	Brown	165	63.72/63.79	4.93/4.91	9.27/9.30	
[Fe(L) $\text{Cl}_2 \cdot \text{H}_2\text{O}$]. H_2O	$\text{C}_{24}\text{H}_{25}\text{Cl}_3\text{FeN}_3\text{O}_6$	612.02	Green	>300	46.11/46.97	4.60/4.11	6.72/6.85	8.92/9.10
[VO(L) $_2$]	$\text{C}_{48}\text{H}_{42}\text{Cl}_2\text{N}_6\text{VOO}_8$	967.18	Red	>300	59.11/59.51	4.39/4.37	8.17/8.68	5.24/5.26

The fourth band appears at 331 nm was due to the ligand to metal charge transfer. For VO(IV) complex band appears at 710, 598, 455, and 360 nm for transition ${}^2B_2 \rightarrow 2E$, ${}^2B_2 \rightarrow 2B_1$, and ${}^2B_2 \rightarrow 2A_1$. The fourth band may be due to charge transfer spectra. All these transitions indicate square pyramidal geometry for VO(IV) complex [22,23]. The absorption region, band assignment and proposed geometry of the complexes are given in Table 3.

3.4. Thermal Analysis

Thermal analysis is performed to determine the thermal stability of complexes and its degradation pattern in which the change in the weight of the substance is recorded as function of temperature or time thermogravimetric analysis (TGA) was performed in nitrogen atmosphere with heating rate $10^\circ\text{C min}^{-1}$ and thermograms are recorded in temperature range $40\text{--}800^\circ\text{C}$. Using this technique several kinetic parameters such as activation energy (E_a), order of reaction (n), entropy change (S), apparent entropy change (S^*), and frequency factor (Z) were calculate. The thermal data have been analyzed using Freeman-Carroll (Figure 5) and Sharp-Wentworth methods.

The TGA curves of both the complexes are given in Figures 3 and 4 while kinetic parameters are assigned in Table 4.

Both the complexes are stable up to 50°C and further decomposed in which Fe(III) complex shows three

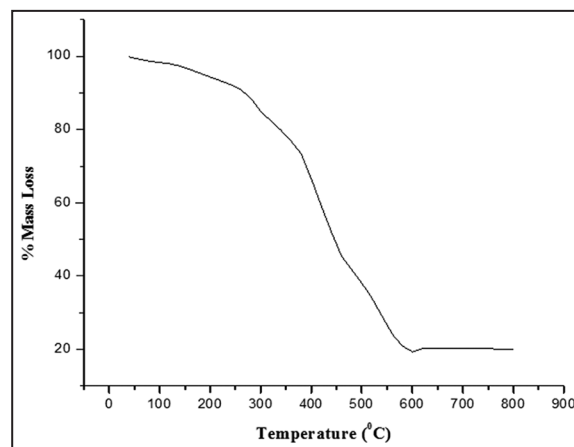


Figure 3: Thermal gravimetric analysis curve of Fe(III) complex.

Table 2: IR spectral data of ligand and its complexes.

Complexes	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{O-H})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	Pyridyl ring breathing	$\nu(\text{C-O})$
LH	1655	1598	3376	-	-	1066	1411
[Fe (L) Cl ₂ .H ₂ O].H ₂ O	1599	1573	-	455	475	1059	1442
[VO (L) ₂].H ₂ O	1654	1580	-	470	519	1060	1441

IR=Infrared

Table 3: Electronic absorption spectral data of the complexes.

Compounds	Solvent	Absorption (nm)	Band assignment	Geometry
[Fe (L)]	DMSO	520	${}^6A_{1g} \rightarrow 4T_{1g}$	Octahedral
		425	${}^6A_{1g} \rightarrow 4T_{1g} (G)$	
		380	${}^6A_{1g} \rightarrow 4E_g (G)$	
		331	LMCT	
[VO (L) ₂]	DMSO	710	${}^2B_2 \rightarrow 2E$	Square pyramidal
		598	${}^2B_2 \rightarrow 2B_1$	
		455	${}^2B_2 \rightarrow 2A_1$	
		360	LMCT	

DMSO=Dimethyl sulfoxide

Table 4: Kinetic parameter for Fe (III) and VO (IV) complexes.

Compounds	Half decomposition temperature (°C)	Activation energy Ea (kJ/mole)		Order of reaction (n)	Entropy change -ΔS (J/mol/K)	Free energy change ΔF (kJ/mol)	Frequency factor Z (S ⁻¹)	Apparent entropy change S* (kJ)
		FC	SW					
[VO (L) ₂].H ₂ O	410	24.98	23.86	0.93	-145.91	70.65	98.12	-89.65
[Fe (L) Cl ₂ .H ₂ O].H ₂ O	420	18.13	18.82	0.95	-148.58	64.63	112.34	-89.56

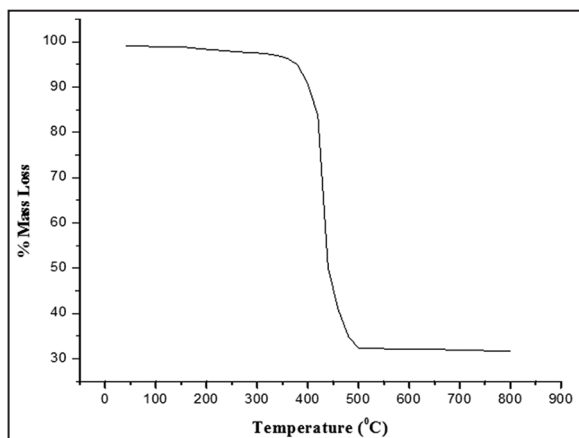


Figure 4: Thermal gravimetric analysis curve of VO(IV) complex.

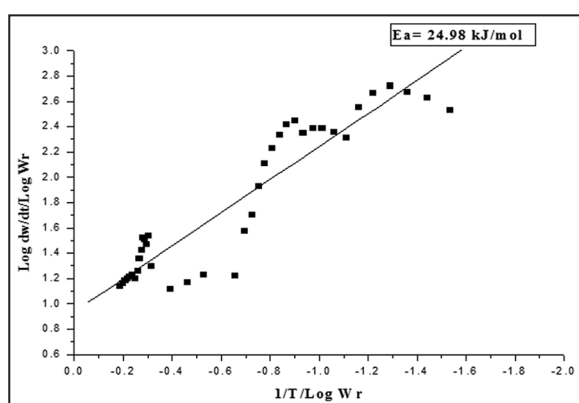


Figure 5: Freeman-Carroll plot of Fe(III) complex.

steps decomposition pattern while VO(IV) complex decomposed in only one step. In Fe(III) complex first decomposition step was observed for the removal of one lattice water molecule in between 40 and 120°C having weight loss 2.01 (calculated 2.94%), and second for one coordinated water molecule in between 120 and 220°C showing weight loss 3.64 (calculated 2.94%). The decomposition in the temperature range 220-360°C is assigned for the removal of three Cl atoms with a mass loss 17.46 (calculated 17.40%). Above 360°C decomposition of coordinate part of ligand start having mass loss 35.15 (calculated 34.47%). In VO(IV) complex there is no significant weight loss up to 220°C indicates the absence of any lattice and coordinated water molecule, while above 380°C actual decomposition of ligand moiety starts. Both the complexes do not decompose completely; there was the formation of their respective metal oxide [24-26].

4. CONCLUSIONS

The present article includes the synthesis and characterization of new Schiff base ligand and its Fe(III) and VO(IV) complexes. Characterization of compounds includes IR, mass, ^1H NMR, and TGA. From this, a flexidentate nature of ligand was observed toward different metal ion. It coordinates to Fe(III)

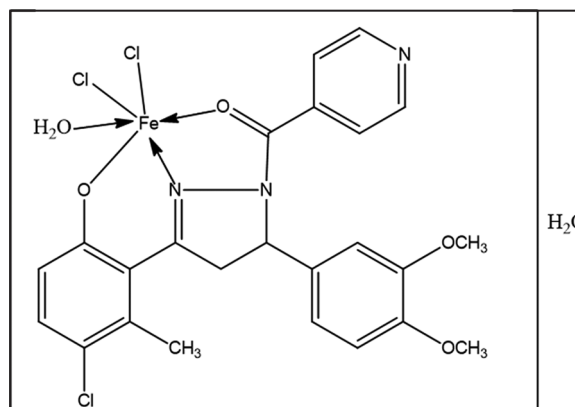


Figure 6: Proposed structure for Fe(III) complex.

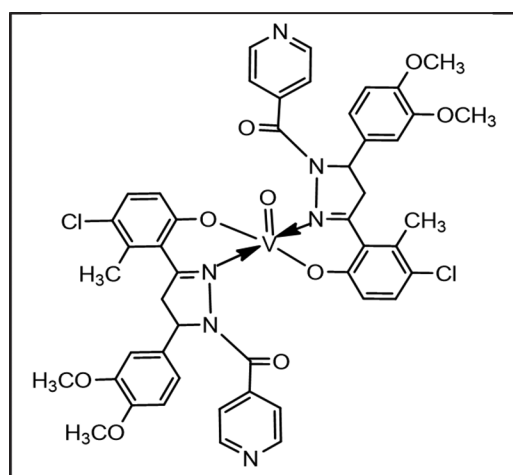


Figure 7: Proposed structure for VO(IV) complex.

metal ion through hydroxyl oxygen, azomethine nitrogen and neutral carbonyl oxygen and act as a monobasic tridentate ligand (metal ligand ratio 1:1) while in case of VO(IV) complex binding through neutral oxygen was not appeared shows that ligand act as a monobasic bidentate (metal ligand ratio 1:2). The thermal data show that complexes were highly stable and its thermal decomposition, as well as thermodynamic parameters, was studied. Proposed structure of Fe(III) and VO(IV) complexes is shown in Figure 6 & 7.

5. ACKNOWLEDGMENT

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