

Synthesis, Spectroscopic Characterization, Thermal Analysis and Biological Studies of Thiocarbohydrazone Schiff base and its Co(II), Cu(II), Cr(III), Mn(III), Fe(III) and VO(IV) Metal Complexes

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Abstract:

N'-((E)-1-(2,5-dihydroxyphenyl)ethylidene)-2-((E)-3-methoxybenzylidene)hydrazine-1-carbothiohydrazide and its metal complexes with Co(II), Cu(II), Cr(III), Mn(III), Fe(III) and VO(IV) were synthesized. The synthesized complexes were characterized using thermal studies, molar conductance, magnetic measurements, ¹H NMR, infrared spectra, and elemental analysis. Molar conductance analysis reveals that none of the developed complexes was naturally electrolytes. The spectroscopic results revealed the ligand's behavior toward metal ions, where the complex coordination numbers were shown to be between four and six. The water molecule loss out or in of the coordination domain is shown by the thermogravimetric measurement of complexes. The weight change as a function of temperature was used to calculate the complexes' free energy, activation energy, and reaction pattern. The synthesized ligand and its complexes exhibited significant antimicrobial activity.

Keywords: Thiocarbohydrazone, Metal complexes, Infra-red, ¹HNMR, TGA, Electronic Spectra, Antibacterial activity.

1. INTRODUCTION

The thiocarbohydrazone complexes have caught the interest of chemists. Numerous researchers have created these compounds as target structures and assessed their anti-tumor and anti-tuberculosis qualities [1]. The atoms like oxygen, nitrogen and sulphur act as electron donor are found in metal complexes that have antibacterial, antifungal, anticancer, and antitumor properties [2-5]. The work focuses on the preparation of metal complexes of Co(II), Cu(II), Cr(III), Mn(III), Fe(III) and VO(IV) with thiocarbohydrazone. These synthesized complexes are characterized and studied for further investigations.

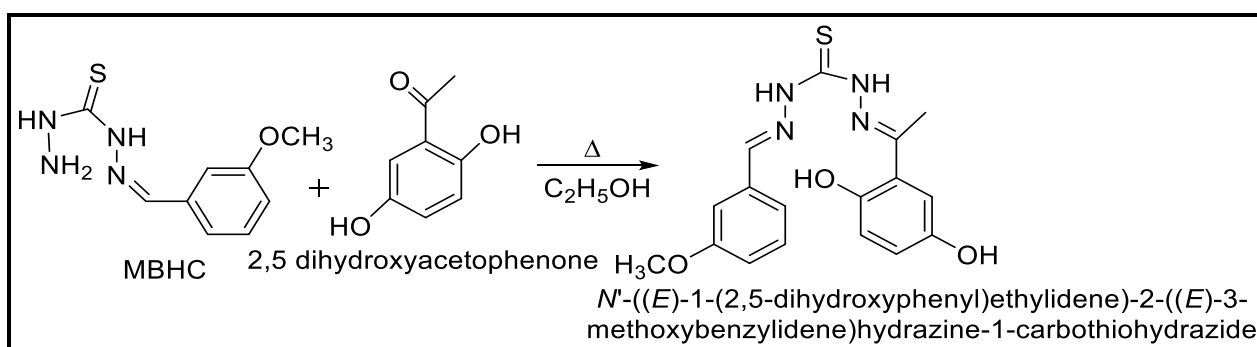
2. EXPERIMENTAL

2.1 Material and measurement

The chemicals and compounds used for synthesis were purchased from commercial sources and were of reagent-grade quality. Solvents were purified by standard methods reported in the literature. Commercially available chemicals used for the synthesis of the complexes viz. anhydrous ferric chloride, chromium chloride hexahydrate, Cobalt chloride, Manganese acetate, and vanadyl sulphate pentahydrate are purchased. The commercially available $Mn(OAc)_2 \cdot 4H_2O$ was oxidized using Christensen's technique to produce $Mn(OAc)_3 \cdot 2H_2O$. Perkin Elmer 842 spectrophotometer was employed to measure the IR spectrum of ligand and its complexes. Coleman's microanalyses were utilized to do an elemental analysis (C, H, and N). A ligand's 1H NMR spectrum was captured using a 300MHz NMR spectrometer in the presence of dimethyl sulfoxide (DMSO) and chloroform-d ($CDCl_3$). Dimethylsulphoxide (DMSO) was used to measure the complexes molar conductance using a range of solution concentrations between 10^{-3} molar.

2.2 Synthesis of (N'-((E)-1-(2,5-dihydroxyphenyl)ethylidene)-2-((E)-3-methoxybenzylidene)hydrazine-1-carbothiohydrazide

By using the procedures described, thiocarbohydrazide were prepared by reported method [6-7]. 2,5 dihydroxyacetophenone (0.01mol), 3-methoxy benzaldehyde (0.01mol) and thiocarbohydrazide (0.01mol) were combined and refluxed for three hours in absolute ethanol (25ml) (Scheme-1). The reaction composition was then let to cool at normal temperature conditions for 1 hrs. After a yellow precipitate formation, it was filtered, cleaned with ice-cold distilled water, and vacuum-dried. Recrystallization was done with ethanol, the yield was 79% and M.P. of $158^\circ C$.



Scheme 1: Synthesis of ligand (L^8H_2)

2.3 Synthesis of metal complexes

The synthesized ligand and the Co(II), Cu(II), Cr(III), Mn(III), Fe(III) and VO(IV) metal salts were independently dissolved in absolute ethanol in equimolar amounts (0.02 mol). The resulting mixture was refluxed by using water bath about 3-4 hrs. After cooling, the solid end-product has been produced, and it was filtered before being washed with ethanol and finally with ether. All of these compounds were then dried on fused CaCl₂ at room temperature [8-9].

3. RESULT AND DISCUSSION

The given plan demonstrates that thiocarbohydrazone condensation with 3-methoxy benzaldehyde and 2,5 dihydroxy acetophenone in ethanol, yield the Schiff base L⁸H₂ ligand. All complexes are colored, stable, non-hygroscopic in the air and are soluble in DMF as well as DMSO. Table-1 provides the physical as well as analytical statistics about the ligand and complexes. By comparing the molecular weights of these complexes with the m/e values, the hypothesized molecular formulas of these complexes were validated. According to the molar conductance observations, none of the complexes are electrolytes.

Table 1: Analytical and physical data ligand L⁸H₂ and metal complexes

Composition of complex	Formula weight	Color	Melting point	% M Found (calc.)	% C Found (calc.)	% H Found (calc.)	% N Found (calc.)	% S Found (calc.)	% Cl Found (calc.)
L ⁸ H ₂	358.11	Yellow	158	---	56.87 (56.97)	5.01 (5.06)	15.55 (15.63)	8.81 (8.95)	---
[Co(L ⁸ H)OAc(H ₂ O) ₂].3H ₂ O	565.04	Pale brown	>300	10.38 (10.43)	40.27 (40.35)	5.21 (5.30)	9.86 (9.91)	5.58 (5.67)	---
[CuL ⁸] ₂	841.30	Brown	>300	15.01 (15.10)	48.29 (48.49)	3.72 (3.80)	13.25 (13.31)	7.52 (7.61)	---

[Cr(L ⁸ H)Cl ₂ (H ₂ O)]	498	Brown	>280	10.33 (10.43)	40.76 (40.96)	3.71 (3.81)	11.12 (11.24)	6.34 (6.43)	14.01 (14.07)
[Mn(L ⁸)OAc(H ₂ O)] .2H ₂ O	524.04	Black	>300	10.37 (10.48)	43.39 (43.50)	4.79 (4.77)	10.53 (10.68)	6.02 (6.11)	---
[Fe(L ⁸ H)Cl ₂ (H ₂ O)]	501.85	Pale umber	>280	11.07 (11.12)	40.58 (40.64)	3.25 (3.38)	11.09 (11.15)	6.27 (6.38)	13.85 (13.96)
[VO(L ⁸ H)OAc].H ₂ O	501.05	Brown	>300	10.11 (10.16)	45.32 (45.50)	4.23 (4.39)	11.08 (11.17)	6.33 (6.39)	---

3.1 Infrared Spectra

The ligand's IR spectra revealed bands at 3518, 3240, 1250, and 1654 cm⁻¹ that might be attributed to several phenolic, including $\nu(NH)$, $\nu(OH)$, $\nu(C-O)$, & $\nu(C=N)$, correspondingly. The bands that are indicative of $\nu(C=S)$ and the lack of an IR band about 2900 because of $\nu(SH)$ both indicate the ligand's thione nature in the solid state. Although there are five donor sites, the TCH acts as a tridentate ligand. The lack of the O-H band in the complex spectrum suggested that both the hydroxyl oxygen and the metal ion were involved in coordination through deprotonation. This is additionally validated by the C-O phenolic shifting by 13–42cm⁻¹ to a lower frequency and the formation of a new spectrum in the region of 565–625cm⁻¹ owing to $\nu(M-O)$ bands in the complex spectrum. In all the complexes' spectra, $\nu(C=N)$ ligand band moved to a lower frequency by 14–51cm⁻¹, showing that azomethine nitrogen was coordinated with the metal ion[10]. The frequencies for $\nu(C=S)$ in all compounds are either unaltered or have not moved to upper frequencies, indicating that the C=S group is not participating in the coordination. Therefore, the bands that occur at 679 and 693cm⁻¹ in the IR spectra of the Mn(III) complex are allocated to the stretching vibration of $\nu(C-S)$ [11-14].

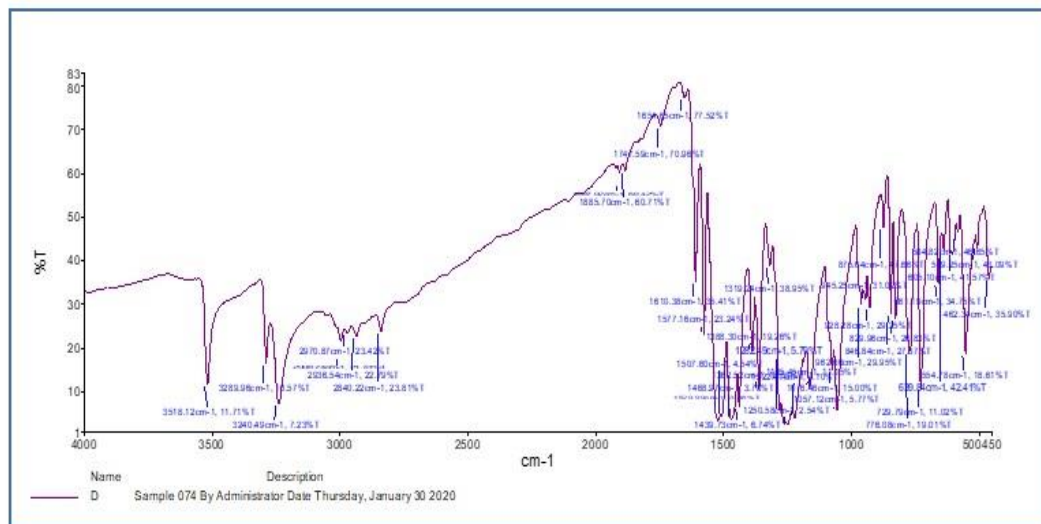


Figure 1- IR Spectrum of Ligand L⁸H

Table 2: IR spectrum data of ligand and metal complexes

Ligand/Complexes	$\nu(\text{O-H})$ Phenolic	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$ Phenolic	$\nu(\text{C=S})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{H}_2\text{O})$
L ⁸ H ₂	3518	3240	1654	1268	1150,833	-	-	---
[Co(L ⁸ H)OAc(H ₂ O) ₂].3H ₂ O	-	3175	1612	1215	1150,828	563	442	3466,1511, 831,740
[CuL ⁸] ₂	-	3199	1605	1177	677	562	457	-
[Cr(L ⁸ H)Cl ₂ (H ₂ O)]	-	3186	1605	1232	1169,831	563	461	3452,1533, 835,754
[Mn(L ⁸)OAc(H ₂ O)].2H ₂ O	-	3121	1572	1185	691	564	452	3455,1513, 823,752
[Fe(L ⁸ H)Cl ₂ (H ₂ O)]	-	3169	1607	1174	1171,823	535	432	3470,1509, 824,731
[VO(L ⁸ H)OAc].H ₂ O	-	3227	1604	1214	1173,830	569	455	3161

3.2 ¹H NMR

The ligand's NMR spectra exhibit a signal at 11.84 ppm, which corresponds to the phenolic OH protons. The aromatic protons show signals at 7.12-7.94 ppm. The protons of the methoxy group are accountable for the signals seen at 3.86 ppm. The imino proton resonates at 9.97 ppm. The signals at 8.7 ppm may be due to the NH.

3.3 Electronic absorption spectrum and magnetic moments

The electronic spectrum of the ligand and complexes have been captured using the DMF solvent. Given data shows the comparative analysis of the ligands, and all of the complexes exhibit a change in the absorption band upon coordination. The Mn (III) electronic spectra complex exhibit spectrum at 708, 587, 516 and 428 nm due to ${}^5B_1 \rightarrow {}^5B_2$, ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5E$ and LMCT. Mn (III) complex was discovered to have a magnetic moment of 4.83 BM. The spectrum supports the square pyramidal geometry [15]. The bands allocated to the area of 616, 469, 273 nm were seen in the Cr (III) complex spectra to ${}^4A_2g(F) \rightarrow {}^4T_2g(F)$, ${}^4A_2g(F) \rightarrow {}^4T_1g(F)$, ${}^4A_2g(F) \rightarrow {}^4T_1g(P)$ the transition indicates octahedral geometry. This complex supported octahedral geometry and had a magnetic moment of 4.62 B [16]. The absorption band at 709, 565, and 427 nm is seen in the Fe(III) complex spectra and may be allocated to ${}^6A_1g(S) \rightarrow {}^4T_1g(G)$, ${}^6A_1g(S) \rightarrow {}^4T_2g(G)$, ${}^6A_1g(S) \rightarrow {}^4E_g$ transition correspondingly, which indicates octahedral geometry of complex with magnetic moment 5.92 BM [17] indicates the d^2sp^3 hybridization [18-19].

3.4 Thermal Analysis

Thermal decomposition of the ligand and its metal complexes results reveals that the Co(II) and Mn(III) complexes decomposed in four stages, the Cr(III), Fe(III) and VO(IV) complexes in three stages Cu(II) complex in two stages (Fig 2). The analysis of thermogram of Co(II) and Mn(III) complexes indicates that the complexes are stable upto 70°C, elimination of three water molecule from Co(II) complex upto 120°C, two water molecule from Mn(II) complex upto 130°C and one water molecule from VO(IV) complex indicating the presence of lattice water molecule. [%wt loss, obs/caled: Co(II): 9.62/9.53, Mn(III): 6.90/6.87 and VO(IV): 3.68/3.54 for lattice water]. Whereas Co(II) and Mn(III) complexes shows that water eliminated in between 130-230°C indicating the presence of two coordinated water molecule in Co(II) complex and further loss in weight upto 270°C indicating the presence of one coordinated water molecule in Mn(III) complex [20-21]. The thermogram of Cr(III) and Fe(III) complexes show a weight loss corresponding to one coordinate water molecule in each complex is observed in the range 140-210°C indicates that the presence of one coordinated water molecule in each complex [%wt

loss, obs/calcd: Co(II): 6.41/6.33, Mn(III): 3.47/3.41, Cr(III): 3.68/3.64 and Fe(III): 3.66/3.54 for coordinated water).

The thermogram of Cu(II) complex show almost horizontal curves upto 250°C indicating the absence of lattice or coordinated water molecules in the complex. A rapid loss in weights is observed in the temperature range 230-460°C indicative of decomposition of free part of the coordinated ligand. A gradual increase in temperature above 460°C was accompanied by degradation of coordinated part of ligand [22-24]. The thermal data of compounds is given in (Table 4). On the basis of half decomposition temperature the thermal stability order of compounds was found to be Cu(II) > Co(II) > Mn(III) > Fe(III) > VO(IV) > L⁸H₂ > Cr(III).

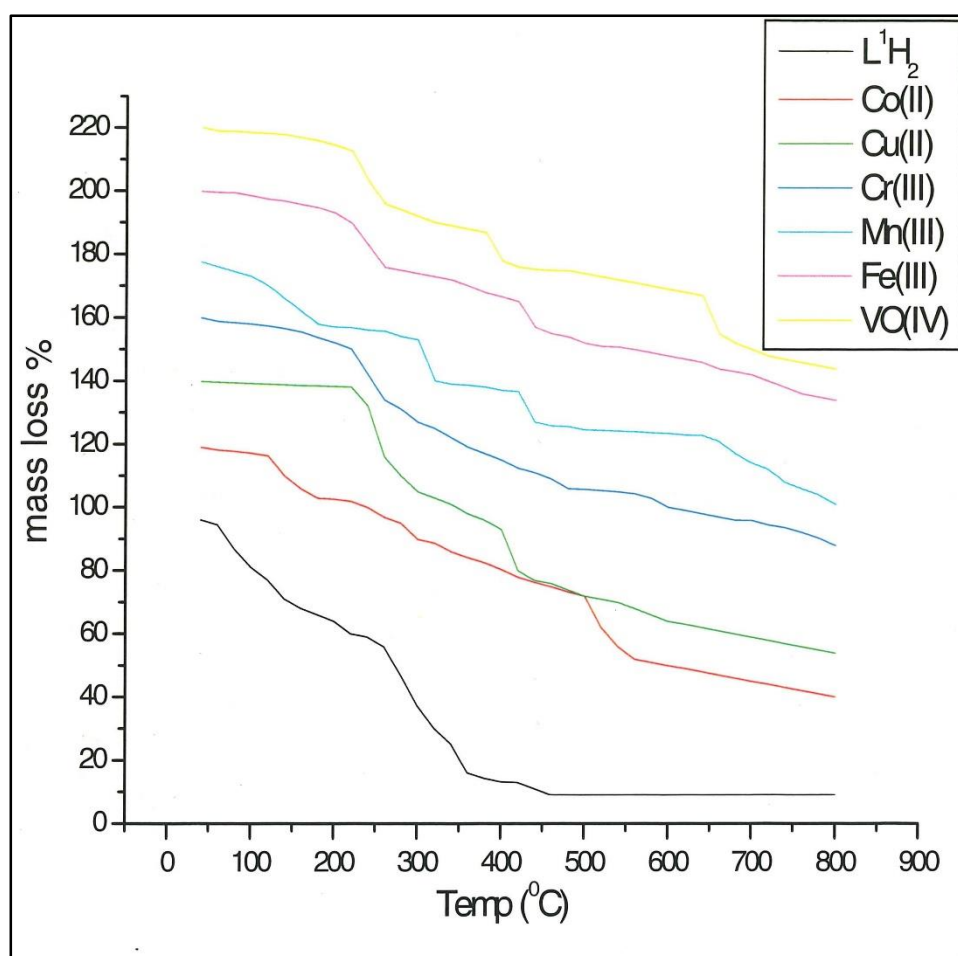


Figure 2- Thermogram of Ligand L⁸H₂ and its metal complexes

Table 3 : Thermal analysis data ligand L⁸H₂ and its metal complexes

Compounds	Half Decomposition Temperature (°C)	Activation Energy Ea (KJ)		Order of Reaction (n)	Entropy Change ΔS (J/mol/K)	Free Energy Change ΔF (KJ/mol)
		FC	SW			
L ⁸ H ₂	340	15.51	17.99	0.91	- 149.11	63.92
[Co(L ⁸ H)OAc(H ₂ O) ₂].3H ₂ O	430	18.17	19.31	0.93	- 167.69	54.57
[CuL ⁸] ₂	480	17.67	16.59	0.94	- 148.77	64.19
[Cr(L ⁸ H)Cl ₂ (H ₂ O)]	340	17.77	14.79	0.93	- 148.13	64.84
[Mn(L ⁸)OAc(H ₂ O)].2H ₂ O	430	16.77	14.29	0.92	- 137.52	11.31
[Fe(L ⁸ H)Cl ₂ (H ₂ O)]	410	17.82	18.66	0.95	- 129.55	58.90
[VO(L ⁸ H)OAc].H ₂ O	400	13.16	11.79	0.96	- 146.11	77.15

3.5 Antibacterial activity

Antimicrobial screening of ligand L^8H_2 and its complexes against *E. coli*, *S. aureus*, *S. typhi* and *P. vulgaris* strains were carried out. The results shows evidence that the ligand exhibits bacteriostatic behavior towards *S. typhi* and *P. vulgaris* except *E. coli* and *S. aureus*. The Co(II), Cu(II) and VO(IV) complexes are found to show almost good bacteriocidal nature against *E. coli* and *S. aureus*. The Co(II) complex show moderate activity against *P. vulgaris* and resistant towards the *Styphu*. The Fe(III) complex shows more sensitivity against *S. aureus* whereas bacteriostatic in nature against all bacterial species. The Cu(II) complex show moderate activity against *S typhi* and resistant towards *P. vulgaris*. The Cr(III) complex exhibits a moderate zone of inhibition against *S. aureus* and *S. typhi* but resistant towards *E. coli* and *P vulgaris*. The Mn(III) complex exhibits more sensitivity towards *E. coli*, *S.aureus* and *P. vulgaris* whereas bacteriostatic in nature against *S. typhi*. The antibacterial screening data of the ligand L^8H_2 and its metal complexes is summarized in Table 4.

Table 4. Antimicrobial activity of ligand (L^8H_2) and its metal complexes

Sr. No.	Ligand and its metal complexes	<i>E. coli</i> (mm)	<i>S. aureus</i> (mm)	<i>S. typhi</i> (mm)	<i>P. vulgaris</i> (mm)
1	L^2H_2	S ₂₂	S ₂₁	R	R
2	Co- L^8H_2	S ₁₇	S ₁₉	R	S ₁₃
	Cu- L^8H_2	S ₁₄	S ₁₇	S ₁₄	R
3	Cr- L^8H_2	R	S ₂₀	S ₁₆	R
4	Mn- L^8H_2	S ₂₄	S ₂₀	R	S ₁₃
5	Fe- L^8H_2	R	S ₂₃	R	R
6	VO- L^8H_2	S ₁₈	S ₂₄	S ₂₂	R

4. CONCLUSION

Through azomethine, the thiocarbohydrazone ligand interacts in dibasic tetradentate coordination with the metal center (1:1mole ratio). Except for VO(IV) and Mn (III) complexes display square pyramidal geometry, all of the complexes may be identified by their nitrogen atoms, deprotonated phenolic oxygen atoms, and magnetic susceptibility data. In the thermogram of both complexes VO(IV) and Mn (III), no coordinated water molecule was seen. The square pyramidal structure of the [VOL] was validated by the

estimated spin Hamiltonian values. There is considerable agreement between the activation energy estimates provided by the Sharp-Wentworth and Freemann-Caroll approaches.

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