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Thiocarbohydrazone Schiff Base Metal Complexes: Synthesis, Characterization and Applications

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Abstract:

(E)-N'-((E)-4-hydroxy-3-methoxybenzylidene)-2-(1-(2 hydroxyphenyl)ethylidene)hydrazine-1-carbothiohydrazide and its metal complexes with Co(II), Cr(III), Mn(III), Fe(III) and VO(IV) were synthesized. Elemental analysis, ^{1}H NMR, Infrared spectra, magnetic measurements, molar conductance and thermal investigations were used to characterize the synthesized complexes. 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. Calculations of the free energy, activation energy, and reaction pattern of the complexes were made using the weight change as a function of temperature. The synthesized ligand and its complexes exhibited significant antimicrobial activity.

Keywords: Thiocarbohydrazide, Metal complexes, IR, NMR, TGA, Electronic Spectra, Antibacterial activity.

1. INTRODUCTION

The complexes of thiocarbohydrazide have attracted the attention of chemists. These compounds have been generated by many researchers as a target structure, and they have evaluated their anti-tuberculosis and anti-tumor properties[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), Cr(III), Mn(III), Fe(III) and VO(IV) with thiocarbohydrazone.

2. EXPERIMENTAL

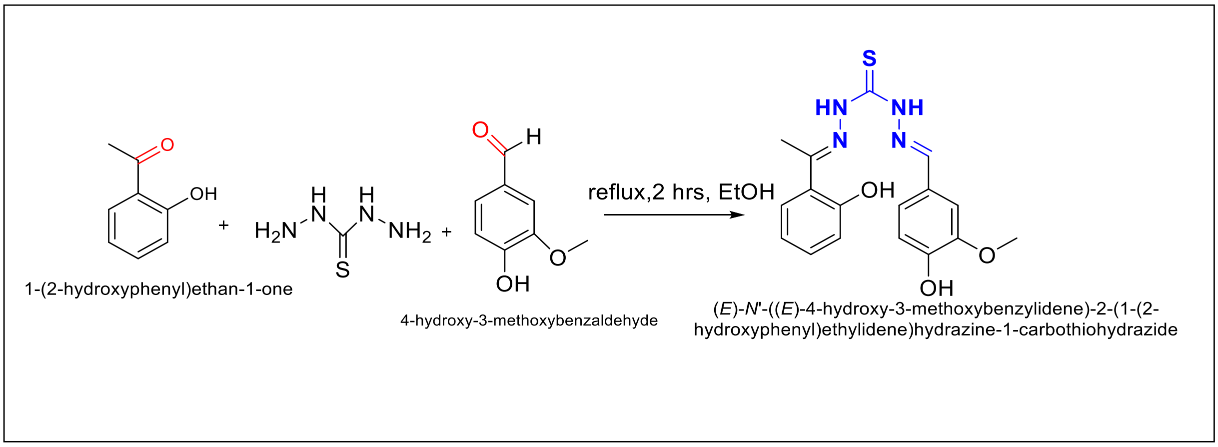
2.1 Material and measurement

The reagent-grade solutions as well as compounds utilized for the synthesis were obtained commercially. 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 $Mn(OAc)_2.4H_2O$ was oxidized using Christensen's technique to produce $Mn(OAc)_3.2H_2O$. 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 (E)-N'-((E)-4-hydroxy-3-methoxybenzylidene)-2-(1-(2-hydroxyphenyl)ethylidene)hydrazine-1-carbothiohydrazide

By using the procedures described, thiocarbohydrazide were prepared by reported method.[6-7] 4-hydroxy-3-methoxy benzaldehyde (0.01mol), 2-hydroxy acetophenone (0.01mol) and thiocarbohydrazide (0.01mol) were combined and refluxed for two hours in absolute ethanol (20ml) (Scheme-1). The reaction composition was then let to cool at normal temperature conditions for 60 minutes. 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 85% and M.P. of 162°C.

Scheme 1: Synthesis of ligand (L^2H_2)



2.3 Synthesis of metal complexes

The synthesized ligand and the 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 $CaCl_2$ at room temperature[8-9]

3. RESULT AND DISCUSSION

The given plan demonstrates that thiocarbohydrazide condensation with 4-hydroxy 3-methoxy benzaldehyde and 2-hydroxy acetophenone in ethanol, yield the Schiff base L^2H_2 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 L^2H2 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^2H_2	358.42	Yellow	162	---	56.91 (56.97)	5.01 (5.06)	15.54 (15.63)	8.78 (8.94)	---
$[Co(L^2H)OAc(H_2O)_2].3H_2O$	565.35	Pale brown	>300	10.12 (10.42)	40.13 (40.32)	5.25 (5.30)	9.78 (9.90)	5.62 (5.67)	---
$[Cr(L^2H)Cl_2(H_2O)]$	498.31	Brown	>280	9.97 (10.43)	40.91 (40.93)	3.72 (3.81)	10.98 (11.23)	6.12 (6.43)	(14.02)
$[Mn(L^2)OAc(H_2O)].2H_2O$	524.35	Black	>300	10.01 (10.47)	43.32 (43.48)	4.6 (4.76)	10.12 (10.67)	6.01 (6.11)	---
$[Fe(L^2H)Cl_2(H_2O)]$	502.16	Deep umber	>280	10.72 (11.11)	40.59 (40.62)	3.55 (3.78)	11.01 (11.15)	6.31 (6.38)	(13.93)
$[VO(L^2H)OAc].H_2O$	501.36	Brown	>300	10.03 (10.16)	45.33 (45.47)	4.28 (4.38)	10.92 (11.16)	6.12 (6.39)	---

3.1 Infrared Spectra

The ligand's IR spectra revealed bands at 3133, 3290, 1268, and 1616 cm^{-1} that might be attributed to several phenolics, including *v(NH)*, *v(OH)*, *v(C-O)*, & *v(C=N)*, correspondingly. The bands that are indicative of *v*(C=S) and the lack of an IR band about 2900 because of *v*(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 v (M-O) bands in the complex spectrum. In all the complexes' spectra, *v*(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 *v*(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.[11] 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 *v*(C-S).[11-14]

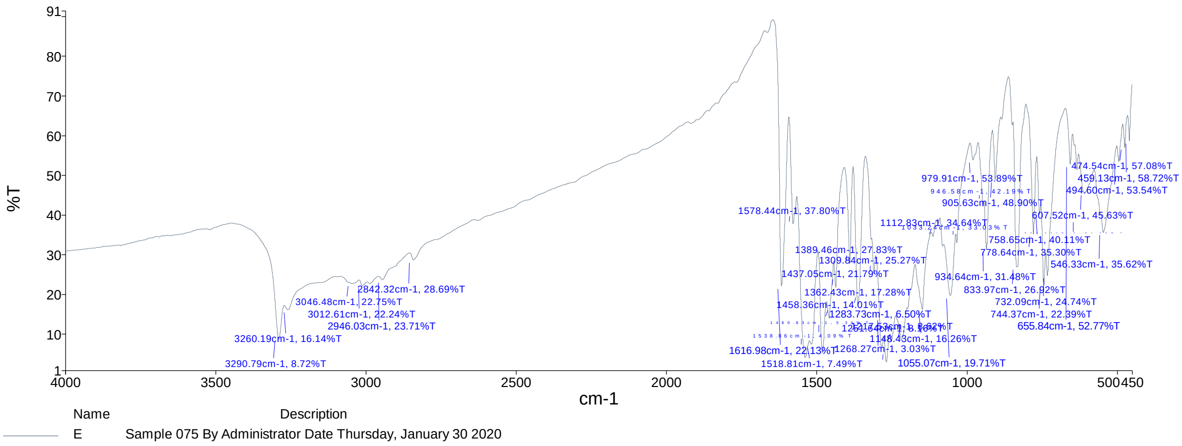


Table 2: IR spectrum data of ligand and metal complexes

Sr.No.	Ligand/Complexes	*ν*(O-H) Phenolic	*ν*(N-H)	*ν*(C=N)	*ν*(C-O) Phenolic	*ν*(C=S)	*ν*(M-O)	*ν*(M-N)
1	L^2H_2	3290	3133	1616	1268	1148,850	-	-
2	$[Co(L^2H)OAc(H_2O)_2].3H_2O$	-	3125	1586	1218	1145,862	552	422
3	$[Cr(L^2H)Cl_2(H_2O)]$	-	3045	1597	1214	1137,852	553	444
4	$[Mn(L^2)OAc(H_2O)].2H_2O$	-	3116	1599	1117	693	540	457
5	$[Fe(L^2H)Cl_2(H_2O)]$	-	2540	1589	1212	1133,854	528	453
6	$[VO(L^2H)OAc].H_2O$	-	3030	1594	1215	1141,874	554	456

3.2 1H NMR

The ligand's NMR spectra exhibit a signal at 12.09 ppm, which corresponds to the phenolic OH protons. The aromatic protons show signals at 6.8-7.4 ppm. The protons of the methoxy group are accountable for the signals seen at 3.82 ppm. The imino proton resonates at 3.23 ppm. The signals at 6.7 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. Table 3 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 745,610,510 and 425 due to $^5B1 \rightarrow {}^5B2$, $^5B1 \rightarrow {}^5B1$, $^5B1 \rightarrow {}^5E$ and LMCT. Mn (III) complex was discovered to have a magnetic moment of 4.87 BM. The spectrum supports the square pyramidal geometry.[15] The bands allocated to the area of 612, 464, 280 nm were seen in the Cr (III) complex spectra to $^4A2g(F) \rightarrow {}^4T2g(F)$, $^4A2g(F) \rightarrow {}^4T1g(F)$, $^4A2g(F) \rightarrow {}^4T1g(P)$ the transition indicates octahedral geometry.

This complex supported octahedral geometry and had a magnetic moment of 4.08 BM.[16] The absorption band at 747, 548, and 446 nm is seen in the Fe(III) complex spectra and may be allocated to $^6A1g(S) \rightarrow {}^4T1g(G)$, $^6A1g(S) \rightarrow {}^4T2g(G)$, $^6A1g(S) \rightarrow {}^4Eg$ transition correspondingly, which indicates octahedral geometry of complex with magnetic moment 5,91 BM.[17] indicates the d^2sp^3 hybridization.[18-19]

3.4 Thermal Analysis

A key approach for determining the thermal complex stability and the capacity of water to coordinate, whether outside or within the coordination sphere, is the thermal analysis of metal complexes. All metal complexes were analyzed for their thermal stability. Activation energy, half decomposition temperature, evident activation entropy, frequency factor, and free energy variation of complexes have all been computed using the Freemann-Carolland Sharp Wentworth technique[21-22]. With the lowest half decomposition temperature, the ligand exhibits two-step decomposition patterns. The complexes of Co(II) and Mn(III) decompose in four steps, the Cr(II), Fe(III) and VO(IV) complexes in two steps while Cu(II) complex in one step only. The presence of water molecule (lattice or coordinated) in Co(II), Mn(III), Cr(III), Fe(II) and VO(IV) complexes suggested from IR spectra is confirmed by weight-loss observed in the first decomposition step of these complexes[23-24]. The weight loss in Co(II) upto 115°C, in Mn(III) upto 145°C and in VO(IV) upto 140°C corresponds to loss of three, two and one lattice water molecules respectively. [%wt loss, obs/calcd: Co(II): 9.81/9.77, Mn(III): 7.11/7.08 and VO(IV): 3.72/3.66 for lattice water]. The further weight loss in Co(II) and Mn(III) complexes upto 145- 240°C and weight loss in Cr(III) and Fe(III) upto 145-230°C corresponds to removal of two coordinate water molecules in Co(II) and one coordinate water molecules in Mn(III), Cr(III) and Fe(III) complexes, respectively. [%wt loss, obs/calcd: Co(II): 6.65/6.52, Mn(III): 3.62/3.51, Cr(III): 3.76/3.73 and Fe(III): 3.72/3.68 for coordinated water].

The thermal data of the compounds is given in Table-3. On the basis of half decomposition temperature the thermal stability order of compounds was found to Cr(III) > Mn(III) > Fe(III) > VO(IV) > Co(II) > L^2H_2.

Table 3 : Thermal analysis data metal complex data

Sr .No.	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			
1	L^2H_2	290	15.31	14.93	0.92	-136.66	13.65
2	$[Co(L^2H)OAc(H_2O)_2].3H_2O$	380	18.23	20.40	0.93	-147.45	64.58
3	$[Cr(L^2H)Cl_2(H_2O)]$	645	18.21	20.52	0.93	-164.46	69.63
4	$[Mn(L^2)OAc(H_2O)].2H_2O$	610	18.56	17.10	0.91	-147.19	64.08
5	$[Fe(L^2H)Cl_2(H_2O)]$	420	11.77	12.31	0.94	-136.51	13.55
6	$[VO(L^2H)OAc].H_2O$	400	19.05	18.66	0.96	-166.29	55.25

3.5 Antibacterial activity

The ligand L^2H_2 and its complexes are found to show low bacteriocidal behavior against most of the bacterial culture used in the present study and are resistant towards the others[25]. The ligand is found to be moderately active against E. coli and S. aureus and resistant to other bacterial strain. The Co(II), Fe(III) and VO(IV) complexes are almost bacteriostatic against E. coli and P. vulgaris and show weak or good activity against other bacteria. The Cr(III) complexes shows a good zone of inhibition against all bacteria. The Mn(III) complex show pronounced sensitivity to E. coli and P. vulgaris. The Co(II) complex exhibit bacteriostatic behavior (resistant) towards all the bacterial strain used. The Cr(III) and VO(IV) complexes are found to show moderate bacteriocidal nature and ligand, Co(II), Mn(III) and Fe(III) complex show bacteriostatic nature against S. typhi. The antibacterial screening data of the ligand L^2H^2 and its metal complexes is summarized in Table 4.

Table 4. Antimicrobial activity of ligand (L^2H_2) and its metal complexes

Sr. No.	Ligand and its metal complexes	E. coli (mm)	S. aureus (mm)	S. typhi (mm)	P. vulgaris (mm)
1	L^2H_2	S_{13}	S_{16}	R	R
2	Co-L^2H_2	R	R	R	S_{18}
3	Cr-L^2H_2	S_8	S_{16}	S_{11}	R
4	Mn-L^2H_2	S_{16}	R	R	S_{19}
5	Fe-L^2H_2	R	S_{20}	R	S_{13}
6	VO-L^2H_2	R	S_{13}	S_{18}	S_9

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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