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Synthesis, Spectral Characterization, Thermal Behavior and Biological Studies of Co(II), Cu(II), Mn(III) and Fe(III) Metal Complexes of Schiff Base Ligand

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Abstract: ***N'-((E)-4-bromobenzylidene)-2-((E)-2-hydroxybenzylidene) hydrazine-1- carbothiohydrazide and its metal complexes with Co(II), Cu(II), Mn(III), and Fe(III) were synthesized. The synthesized complexes were characterized using infrared spectra, ^{1}H NMR, thermal studies and elemental analysis. Molar conductance analysis reveals that none of the developed complexes was naturally electrolytes. 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, ^{1}H NMR, Thermal Study, Antibacterial activity

1. Introduction

The thiocarbohydrazone metal complexes have great interest of chemists. So many 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. They have antibacterial, antifungal, anticancer and antitumor properties [2-5]. The work focuses on the preparation of metal complexes of Co(II), Cu(II), Mn(III) and Fe(III) with thiocarbohydrazone. All the synthesized metal complexes are characterized and studied for further investigations.

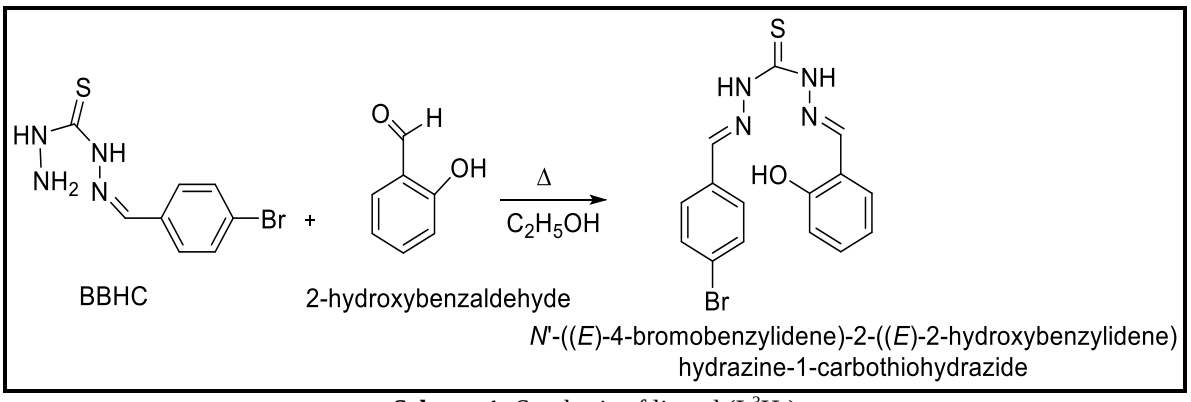
2. Experimental

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, Cobalt chloride, Manganese acetate and copper salt 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.

2.2 Synthesis of (N'-((E)-4-bromobenzylidene)-2-((E)-2 hydroxybenzylidene)hydrazine-1- carbothiohydrazide

The starting material thiocarbohydrazide were prepared by reported method. 2-hydroxybenzaldehyde (0.01mol), 4-bromo benzaldehyde (0.01mol) and thiocarbohydrazide (0.01mol) were combined and refluxed for two hours in absolute ethanol (25ml) (Scheme-1). The reaction composition was then cooled at room temperature about one hrs. After a yellow precipitate formation, it was filtered, cleaned with ice-cold distilled water, and vacuum-dried. Recrystallization has been done with ethanol, the yield was 80% and M.P. of 181°C.



Scheme 1: Synthesis of ligand (L^3H_2)

2.3 Synthesis of metal complexes

The synthesized ligand and the Co(II), Cu(II), Mn(III) and Fe(III) metal salts were independently dissolved in absolute ethanol in stoichiometric amounts (0.02 mol). The resulting mixture was refluxed by using water bath about 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.

The given scheme shows that thiocarbohydrazide condensation with 2-hydroxy benzaldehyde and 4-bromo benzaldehyde in ethanol, yield the Schiff base L^3H_2 ligand. All complexes are colored, stable, non-hygroscopic in the air and are soluble in DMF as well as DMSO. Table-1 provides all 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.

3. Result and Discussion

Table 1: Analytical and physical data ligand L^3H2 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.)
L^3H2	377.26	Yellow	181	---	47.81 (47.76)	3.41 (3.47)	14.71 (14.85)	8.42 (8.50)
$[Co(L^3H)OAc(H_2O)_2].3H_2O$	584.19	Pale brown	>280	9.98 (10.08)	34.80 (34.92)	4.19 (4.27)	9.77 (9.58)	5.41 (5.48)
$[CuL^3)_2$	877.60	Brown	>260	14.12 (14.48)	40.92 (41.02)	2.47 (2.50)	12.31 (12.76)	7.13 (7.30)
$[Mn(L^3)OAc(H_2O)].2H_2O$	543.19	Deep umber	>280	9.99 (10.11)	37.50 (37.55)	3.57 (3.68)	10.21 (10.30)	5.47 (5.90)
$[Fe(L^3H)Cl_2(H_2O)]$	521	Black	>300	10.32 (10.71)	34.51 (34.54)	2.51 (2.68)	10.34 (10.74)	6.01 (6.15)

3.1 Infrared Spectra

A medium intense band at 3174 cm^{-1} may be due to presence of *ν*(N-H) group. The ligand shows a band at 1168 cm^{-1} and 827 cm^{-1} due to *ν*(C=S) vibration. The absence of this band in the IR spectra of the metal complexes can be explained by the tautomerism of the C=S group with one of the imino groups to form the C-SH in the molecule of ligand [6]. This band appears in the Cu (II) and Mn (III) complex in the range 685-686 cm^{-1} and the sulphur atom of C-S group is not coordinated to the remaining metal ions. This further confirmed by the fact that, the ν(C=S) vibration does not show any remarkable shift in its position [7-9] However, there is little variation in the intensity of the band.

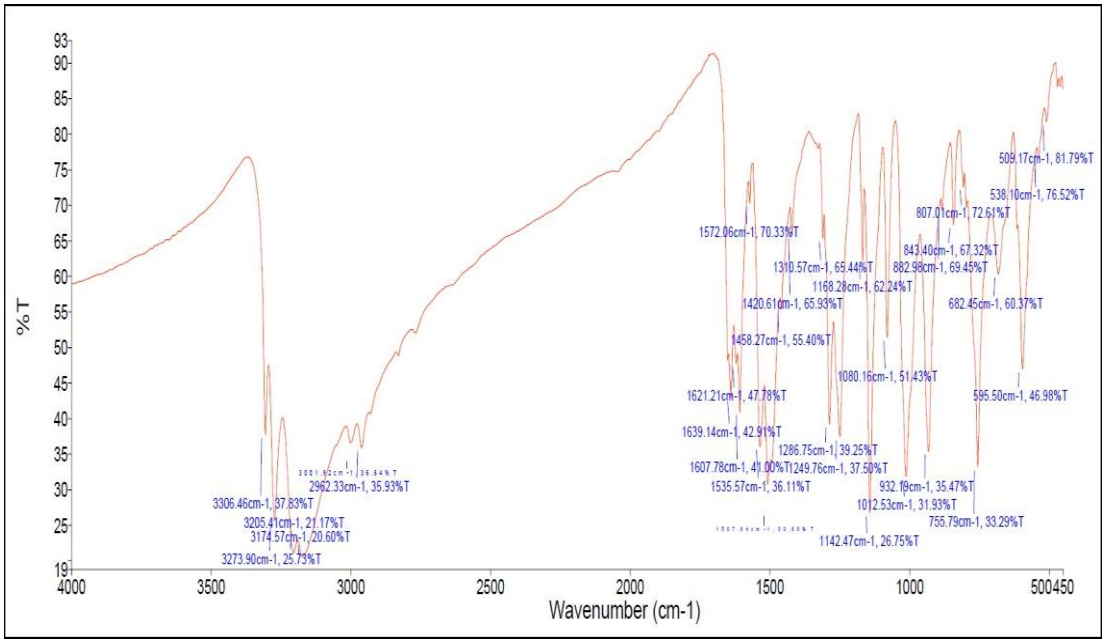


Figure 1: IR Spectrum of Ligand L^3H2

Table 2: IR spectrum data of ligand L^3H_2 and metal complexes

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)	*ν*(H_2O)
L^8H2	3306	3174	1621	1249	1168	---	---	---
$[Co(L^8H)OAc(H_2O)_2].3H_2O$	---	3095	1604	1205	1152,822	564	446	3475,1470, 820,755
$[CuL^8)_2$	---	3090	1603	1200	685	561	452	---
$[Mn(L^8)OAc(H_2O)].2H_2O$	---	3058	1602	1217	686	554	455	3467,1440, 824,749
$[Fe(L^8H)Cl_2(H_2O)]$	---	2881	1597	1205	1150,827	556	457	3466,1438, 828,754

3.2 ^{1}H NMR

The ^{1}HNMR spectrum of ligand exhibit a signal at 12.12 ppm, which corresponds to the phenolic OH protons [10-12]. The aromatic protons show signals at 7.86-7.92 ppm. The protons of the methoxy group are accountable for the signals seen at 3.86 ppm. The imino proton resonates at 8.71 ppm. The signals at 8.67 ppm may be due to the NH.

3.3 Thermal Analysis

Thermal decomposition results data of L^3H_2 reveals that the Cu (II) complex show two stage decomposition pattern, Cr (III), Fe (III) and VO(IV) complexes show a three stage decomposition pattern while Co(II) and Mn(III) complexes show a four stage decomposition pattern[13-14]. The analysis of the thermograms of Co (II) and Mn (III) complexes shows that water eliminated in between 140-260 °C indicating the presence of two coordinated water molecule in Co (II) complex and further loss in weight upto 250°C indicating the presence of one coordinated water molecule in Mn (III) complex. Weight loss in Cr (III) and Fe (III) upto 140-230°C corresponds to removal of one coordinate water molecules, for coordinated water [%wt loss, obs/calcd: Co(II): 6.76/6.63, Cr(III): 3.85/3.78, Fe(III): 3.76/3.74 and Mn(III): 3.69/3.66]. The Co (II), Mn (III) and VO(IV) complexes are stable upto 70°C, elimination of three lattice water molecule from Co (II) complex upto 130°C, two lattice water molecule from Mn (III) complex upto 120°C and one lattice water molecule from VO(IV) complex, for lattice water [%wt loss, obs/calcd: Co(II): 11.13/10.04, Mn(III): 7.35/7.15 and VO(IV): 3.78/3.79].

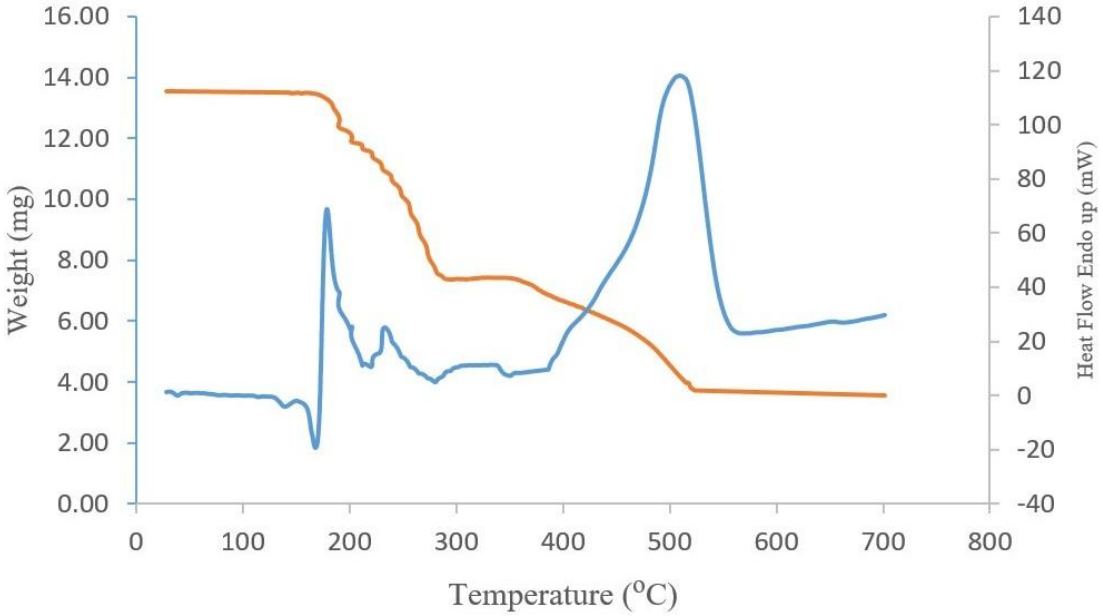


Figure 2: Thermogram of Co (II) metal complex

3.5 Antibacterial activity

The ligand L^3H_2 and its complexes were screened for their antibacterial study. The ligand is resistant against most resistant bacterial strain S. typhi and P. vulgaris and found to be bacteriocidal towards other bacteria[15-16]. The growth of E. coli and S. aureus is more whited by almost all the compounds as compared the other bacterial species. The Mn(II) complex are highly active against E. coli and S. aureus whereas bacteriostatic past S. typhi and P. vulgaris. The Fe(III) complex is bacteriostatic against E. coli and P vulgaris and show moderate activity against the other organisms. The VOIV) complex eviances good zone of inhibition against E. coli and S. aureus and low sensitive against S. typhi and P. vulgaris. The Co(II) complex possesses good antibacterial activity against E. coli, S. aureus and P. vulgaris. The Cu(II) complex is found to be bacteriostatic against S. typhi and P. vulgaris and low to moderately sensitive to other bacteria.

4. Conclusion

Through azomethine, the thiocarbohydrazone ligand interacts in dibasic tetradentate coordination with the metal center (1:1mole ratio). 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 Mn (III), no coordinated water molecule was seen. There is considerable agreement between the activation energy estimates provided by the Sharp-Wentworth and Freemann-Caroll approaches.

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