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Synthesis, Spectral Characterization, Thermal and Biological Studies of Fe(III), Co(II), Cu(II), Mn(III), Cr(III) and Vo(IV) Complexes of Thiocarbohydrazone Ligand

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Abstract: ***N',2-bis((E)-2-hydroxy-3-methoxybenzylidene) hydrazine-1-carbothiohydrazide and its metal complexes with Fe(III), Co(II), Cu(II), Mn(III), Cr(III) and VO(IV) were synthesized. Elemental analysis, ^{1}H NMR, ESR, Infrared spectra, magnetic measurements, molar conductance, mass spectra, and thermal investigations (DTA & TGA) 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, TGA, Electronic Spectra, Biological activity

1. Introduction

The complexes of thiocarbohydrazide has attracted the attention of chemists[1]. These compounds have been generated by many researchers as a target structure, and they have evaluated their anti-tuberculosis and anti-tumor properties. ONS donors 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 2-hydroxy 3-methoxy benzaldehyde with Fe(III), Co(II), Cu(II), Mn(III), Cr(III) and VO(IV) metal and attempts to check the antimicrobial activity.

2. Experimental

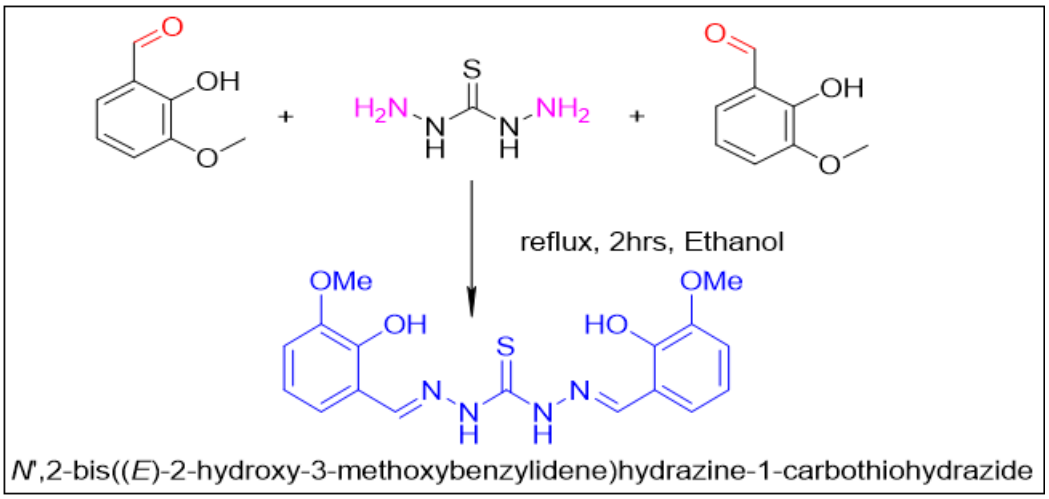
2.1 Materials and physical measurements

The chemicals utilized for the synthesis were obtained commercially and were used without further purification. The solvent were of analytical grade and purified by standard methods reported in 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. 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 ^{1}H NMR spectrum was captured using a 300MHz NMR spectrometer in the presence of dimethyl sulfoxide (DMSO) and chloroform-d (CDCl3). The electronic spectra of ligand and complexes were recorded on Shimadzu UV-200-800 series spectrophotometer. Dimethylsulphoxide (DMSO) was used to measure the complexes molar conductance using a range of solution at concentrations of 10^{-3} M.

2.2 Synthesis

2.2.1 Synthesis of N',2-bis((E)-2-hydroxy-3-methoxybenzylidene)hydrazine-1-carbothiohydrazide ligand

By using the literature described, thiocarbohydrazide were prepared by reported method.[6-7] 2-hydroxy-3-methoxy benzaldehyde (0.02mol, 3.04g) and thiocarbohydrazide (0.01mol, 0.91g) were combined and refluxed for two hours in absolute ethanol (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 76% and M.P. of 178°C.The analytical and physical data for the ligand LH2 and its metal complexes are listed in Table-1.



Scheme 1

2.2.2 Synthesis of complexes of ligand with Fe(III), Co(II), Cu(II), Mn(III), Cr(III) and VO(IV) metals

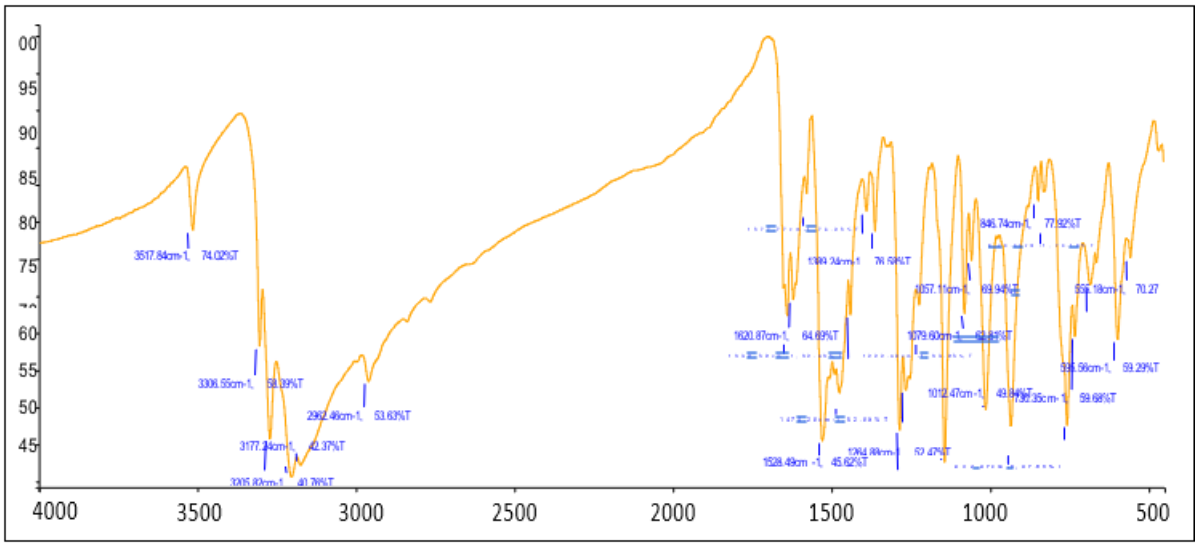
The synthesized ligand and the metal salts were independently dissolved in absolute ethanol in equimolar amounts. The resulting mixture was refluxed by using water bath about 4 hrs. After cooling, the solid end-product has been obtained, and it was filtered before being washed with ethanol and finally with ether. All of these compounds were then dried on fused $CaCl_2$ at room temperature[8-9]

3. Results and Discussion

Condensation of thiocarbohydrzide and 2-hydroxy-3methoxy benzaldehyde in ethanol yields the Schiff base ligand (LH2). All the complexes are colored solid, non-hygroscopic and stable at room temperature. They are insoluble in water and soluble in Dimethyl formamide (DMF) as well as Dimethyl sulphoxide (DMSO) and not in other typical organic mixtures. 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 is electrolytes.

3.1 Infrared Spectra

Through spectroscopic investigations, such as comparing the IR spectrum of ligand with the metal complex spectrum. The free ligand and complexes' structurally significant IR bands are included in Table 2. The ligand's IR spectra revealed bands at 3257, 3160, 1270, and 1617 cm^{-1} that might be attributed to several phenolic, including *ν(NH)*, *ν(OH)*, *ν(C-O)*, & *ν(C=N)*, correspondingly. The bands that are indicative of *ν*(C=S) and the lack of an IR band about 2900 because of *ν*(SH) both indicate the ligand's thione nature in the solid state. When the metal complex IR spectrum were contrasted with those of the TCH, it was discovered that the complex displayed bands between 3272 and 3204cm^{-1} that might be attributed to the *ν*(NH2) of the amine group of the TCH being moved to lower frequencies (3246-3148). 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, *ν*(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 *ν*(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 *ν*(C-S).[11-14]



3.2 Electronic absorption spectra 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 710,615,510 and 400 due to $^{5}B1 \rightarrow {}^{5}A1$, $^{5}B1 \rightarrow {}^{5}B1$, $^{5}B1 \rightarrow {}^{5}E$ and LMCT. Mn (III) complex was discovered to have a magnetic moment of 4.91 BM. The spectrum supports the square pyramidal geometry.[15] The bands allocated to the area of 740, 555, and 290 nm were seen in the Cr (III) complex spectra to $^{4}B1g \rightarrow {}^{4}B2g$, $^{4B1g} \rightarrow {}^{4}A2g$, $^{4A2g} \rightarrow {}^{4}T1g$ the transition indicates octahedral geometry. This complex supported octahedral geometry and had a magnetic moment of 4.41 BM.[16] The absorption band at 750, 615, and 465nm is seen in the Fe(III) complex spectra and may be allocated to $^{6}A1g \rightarrow {}^{4}T1g$, $^{6}A1g \rightarrow {}^{4}T2g$, $^{6}A1g \rightarrow {}^{4}Eg$ transition correspondingly, which indicates octahedral geometry of complex with magnetic moment 5,62 BM.[17] indicates the $d^{2}sp^{3}$ hybridization.[18-19] Two bands at 700 and 515 nm that may be classified as bands appear in the oxovanadium complex's electronic spectrum $^{1}B2 \rightarrow {}^{2}E$, $^{1}B2 \rightarrow {}^{2}A1$ suggesting a square pyramidal complex[20] with effective magnetic moment 1.85 BM

3.3 1H NMR Spetra

The ligand's NMR spectra exhibit a signal at 11.99 ppm, which corresponds to the phenolic OH protons. The aromatic protons show signals at 6.9-7.4 ppm. The protons of the methoxy group are accountable for the signals seen at 3.4ppm. The aldehydes proton resonates at 9.3 ppm. The signals at 6.9 ppm may be due to the NH.

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] Figure -3 shows the TGA thermal curves of the complexes that were produced in a nitrogen environment with a heat rate of $10^{o}C/min^{-1}$, whereas the Table contains the kinetic parameters.

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