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Comprehensive Study on the Synthesis and Characterization of Cr (III), Mn (III), Fe (III) and Co (II) of Thiocarbohydrazone Metal Complexes

[1]Rathod S.B., [2]Mandlik P.R.

[1]Assistant Professor, Department of Chemistry, Hon. B. J. Arts, Commerce & Science College, Ale – 412411
Email- santoshchem21@gmail.com
[2]Professor, Department of Chemistry, Shri. Shivaji Science College, Amravati- 444602

Abstract

Thiocarbohydrazones are versatile O, S, N-donor ligands that form stable chelates with transition metals. We have carried out the synthesis, characterization and thermal study of a thiocarbohydrazone ligand (L^1H_2) derived by the condensation of 2-hydroxybenzaldehyde and p-nitrobenzaldehyde with thiocarbohydrazide and its metal complexes obtained by the reflux with Cr(III), Mn(III) Fe(III) and Co(II). The ligand and metal complexes were characterized by elemental analysis, FT-IR, ^{1}HNMR, mass spectrometry and thermogravimetric analysis (TGA). The spectroscopic results reveals that the ligands behavior towards the metal ion, the coordination number were shown to be six. The comparative thermal stability of the ligand and its metal complexes were studied.

Keyword- Thiocarbohydrazones, metal complexes, FT-IR, ^{1}HNMR, TGA.

1. Introduction

Thiocarbohydrazones represent a significant group of Schiff base ligands obtained by condensing thiocarbohydrazide with 2-hydroxybenzaldehyde and p-nitrobenzaldehyde. This reaction produces mixed thiocarbohydrazone derivatives that contain both electron-releasing and electron-withdrawing functional groups. These molecules include azomethine (–C=N–) linkages, thioamide sulphur, and several donor sites, which make them effective chelators. The phenolic –OH group in the 2-hydroxybenzaldehyde portion enhances coordination through intramolecular hydrogen bonding. In contrast, the p-nitro group contributes to greater structural rigidity and alters the ligand's electronic behavior. Thiocarbohydrazones can bind to a variety of transition metals such as Cr(III), Mn(III), Fe(III) and Co(II), forming complexes with notable magnetic and thermal characteristics. Owing to their rich donor set and structural flexibility, these ligands and their metal complexes are highly relevant in modern coordination chemistry and materials research.

2. Experimental

2.1. Synthesize of N'-((E)-2-hydroxybenzylidene)-2-((E)-4-nitrobenzylidene)hydrazine-1-carbothiohydrazide (L^1H_2)

Thiocarbohydrazide (1 mmol) is suspended in 25 mL ethanol and warmed to aid dissolution. To this, 2-hydroxybenzaldehyde (1 mmol) and p-nitrobenzaldehyde (1 mmol) are added. The reaction mixture is refluxed for 2 hours with constant stirring. During reflux, the solution gradually becomes colored indicating Schiff base formation. After completion, the mixture is cooled to room temperature and then placed in an ice bath to induce crystallization. The solid product formed is filtered, washed with cold ethanol to remove unreacted aldehydes. Finally, the crude solid is dried and purified by recrystallization.

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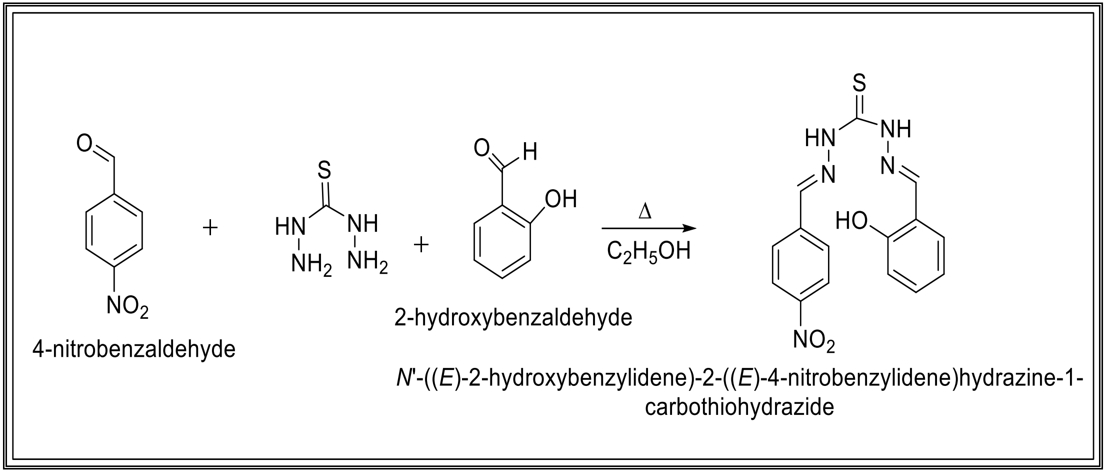


2.2 Preparation of metal complexes of Cr(III), Mn(III) Fe(III) and Co(II) with thiocarbohydrazones.

Thiocarbohydrazone ligand is dissolved or suspended in hot ethanol to obtain a clear solution. A metal salt solution of Cr(III), Mn(II), Fe(III) and Co(II) is prepared separately in warm ethanol mixture. The metal salt solution is added slowly to the ligand solution with continuous stirring. The reaction mixture is heated under reflux for about 2 hours to ensure complete coordination. During heating, a colored precipitate of the metal complex gradually forms. The mixture is cooled and the solid complex is filtered, washed with ethanol to remove unreacted materials. The purified metal complex is finally dried in air or in a desiccator and taken their melting points.

3. Results and discussion.

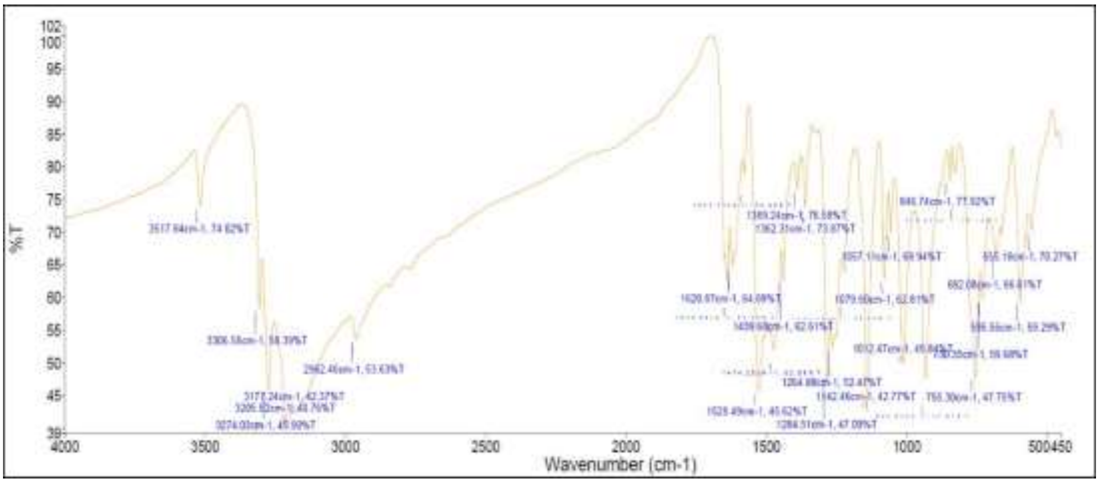
The given synthesis demonstrates that thiocarbohydrazide condensation with 2-hydroxybenzaldehyde and p-nitrobenzaldehyde in ethanol, yield the Schiff base L^1H_2 ligand. The ligand is yellow in colour. All the metal complexes are colored, stable, non-hygroscopic in the air and are soluble in DMF as well 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/z 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 data of the Ligand and its metal complexes

Composition	Formula weight	Colour	MP	%M	%C	%H	%N
L^5H_2	343.36	Yellow	183	---	52.41	3.77	20.37
$[Cr(L^5H)Cl_2(H_2O)]$	483.25	Brown	>280	10.63 (10.75)	37.10 (37.24)	2.75 (2.89)	14.31 (14.48)
$[Mn(L^5)OAc(H_2O)].2H_2O$	509.29	Black	>300	10.61 (10.78)	39.95 (40.05)	3.85 (3.92)	13.51 (13.74)
$[Fe(L^5H)Cl_2(H_2O)]$	487.10	Deep umber	>280	11.25 (11.46)	36.75 (36.95)	2.79 (2.87)	14.21 (14.37)
$[Co(L^5H)OAc(H_2O]_2].3H_2O$	550.29	Pale brown	>300	10.61 (10.70)	36.99 (37.07)	4.49 (4.54)	12.66 (12.72)

3.1 Infrared Spectral analysis

The ligand's IR spectra revealed bands at 3306, 3274, 1264, and 1620 cm^{-1} that might be attributed to several phenolic, 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 to a lower frequency and the formation of a new spectrum in the region of 563–553cm^{-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 showing that azomethine nitrogen was coordinated with the metal ion. 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. Therefore, the bands that occur at 807 and 861cm^{-1}.



3.2 ^{1}HNMR study

The NMR spectrum of the ligand shows a distinct downfield signal at 11.20 ppm, which is attributed to the phenolic –OH protons involved in hydrogen bonding. The aromatic region displays multiple peaks in the range of 7.21–7.92 ppm, corresponding to the protons of the benzene ring. A signal appearing at 8.71 ppm is assigned to the methoxy group protons, indicating their deshielded environment. The imino (–CH=N–) proton gives a characteristic resonance at 8.23 ppm, confirming the formation of the Schiff base. Additionally, another downfield signal observed at 10.92 ppm may be attributed to the –NH proton. These chemical shifts collectively support the structural features of the ligand. Overall, the ^{1}HNMR data strongly indicate successful synthesis and proper proton environments within the molecule.

3.3 Mass spectral study

The mass spectrum of the synthesized ligand further confirms its molecular structure and purity. A prominent molecular ion peak (M^+) appears at the 343.36 m/z value, supporting the proposed molecular formula. Fragmentation begins with the loss of the phenolic –OH group, producing a characteristic fragment peak. Cleavage near the imine (–CH=N–) bond results in another significant fragment, consistent with Schiff base behaviour. A peak corresponding to the loss of sulfur-containing fragments indicates the presence of the thiocarbohydrazone moiety. Additional peaks at lower m/z such as 225.25, 208.21, 196.25, 179.22, 136.13 and 107.13 m/z values represent stepwise breakdown of the aromatic ring system. The relative intensities of the fragments support the stability of the aromatic cation as a major contributor. The absence of unexpected peaks suggests that no side products or impurities are present. Altogether, the mass spectral data strongly validate the ligand's structural integrity and successful synthesis.

3.4 Thermal analysis

TGA of the thiocarbohydrazone metal complexes shows multi-step decomposition behaviour. The initial weight loss below 140 °C corresponds to the removal of lattice or coordinated water molecules. The second major decomposition step occurs between 200–350 °C, attributed to the breakdown of the organic ligand framework. Further weight loss in the range 350–450 °C indicates complete fragmentation of the thiocarbohydrazone moiety. The thermal stability of the complexes follows the order: Cr(III) > Fe(III) > Mn(III) > Co(II). Higher decomposition temperatures confirm the strong metal–ligand coordination in Cr(III) and Fe(III) complexes. The final residue obtained above 600 °C corresponds to the formation of stable metal oxides. TGA data supports the proposed composition and stoichiometry of all synthesized complexes.

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