

Synthesis, structure and characterisation of Cr(III) and Fe(III) complexes of m-nitro benzaldehyde thio semicarbazone

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ABSTRACT

A new Ligand m-nitro benzaldehyde thio semicarbazone (m-NBTS) complexes with metal [M=Cr(III) and Fe(III)] to form [M(m-NBTS)(Py)₂Cl₂Cl], which have been characterized by elemental analysis, IR, UV-Visible, Conductivity measurement and Thermal studies. Elemental Analysis suggests 1:1:2(M:NBTS:Pyridine) Stoichiometry for the complex. Electronic Spectra revealed the geometry to be Octahedral in nature.

KEY WORDS: Ligand, Thiosemicarbazone, m-NBTS, Electronic Spectra.

1. INTRODUCTION

Chemical Compounds can be conveniently classified under two main categories: (i) simple compounds and (ii) Molecular compounds. The latter again can be subdivided into (a) double salts and (b) complex compounds, depending upon their chemical and physical behavior as determined from studies of their chemical reactions, migration in electric field, conductivity, solubility, distribution ratio, electrode potential, absorption spectra, freezing point of aqueous solution and magnetic susceptibility. Co-ordination compounds are very important in animal and plant kingdom. Chlorophyll (magnesium Complex) in green plants and Hemoglobin (iron complex) in the blood are two important compounds in the biological systems. In fact, metal complexes with these derivatives of hydrazines have occupied a very important place in the further development and progress of co-ordination chemistry. A study of complex with thio derivatives of hydrazine is therefore of particular interest. Although metal complexes of thiosemicarbazides (Campbell, 1975) and thio semicarbazones (Living Stone, 1965; Ali, 1974; Padhye, 1985) have been reviewed, a systematic study of the thio hydrazides and thio hydrazones, which are structurally very similar, has yet to be investigated.

About the Ligands: Functional groups such as, -CHO, -C=O, -C=N, -C=S and inorganic neutral moieties such as H₂O, NH₃ and N₂ can act as ligands. A group that can attach to the same metal ion through more than one of its atoms and thus producing one or more rings is termed as chelating group or multidentate Ligand. (Morgan, 1920) named this ring formation as chelation. In five and six membered rings, the chelate effect is more pronounced and they form the most stable species. Molecules which contain bridging chain between the N and S donor atoms (Singh, 2000) are used as ligands in the synthesis of Ni(II) complexes. Complexes of thiosemicarbazide, which is an N-S-bidentate ligand are well known in analytical chemistry.

2. EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Preparation of m-nitro benzaldehyde thio semicarbazone: One gram of thiosemicarbazide was dissolved in hot water in presence of 1-2 drops of acetic acid. Mixture of m-nitrobenzaldehyde (1g) and sodium acetate (2g) in ethanol was stirred with the solution of thiosemicarbazide for 30 minutes. The resulting yellow powder was crystallized from ethanol (Parihari, 2000).

Preparation of Chromium and Iron complexes of NBTS: Metal ion, m-nitrobenzaldehyde thiosemicarbazone and pyridine were taken in the ratio 1:1:2, and the resulting mixture in ethanol were refluxed for about 6 hours. The contents were cooled and then the separated solid was filtered and washed with hot water, methanol, benzene and petroleum ether. The washed solid was dried in vacuum desiccators.

3. RESULTS AND DISCUSSION

Elemental analysis: The micro analysis of carbon, hydrogen and nitrogen in the complexes were recorded and given in the Table 1:

Table.1. Analytical data of the ligand and the complexes

Compound	Molecular formula	Molecular weight	Found (Calc) %		
			Carbon	Hydrogen	Nitrogen
NBTS	C ₈ H ₈ N ₄ O ₂ S	224.0	42.10 (42.86)	3.45 (3.57)	24.65 (25.00)
[Cr(NBTS)(Py) ₂ Cl ₂ Cl]	C ₁₈ H ₁₈ N ₆ O ₂ SCrCl ₃	529.0	41.90 (42.19)	3.21 (3.51)	16.20 (16.40)
[Fe(NBTS)(Py) ₂ Cl ₂ Cl]	C ₁₈ H ₁₈ N ₆ O ₂ SFeCl ₃	533.5	41.30 (41.82)	3.27 (3.49)	16.10 (16.26)

In complex $[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ the percentage of Chromium was found to be 11.20% (theoretical value=11.52). In complex $[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ the percentage of Iron was found to be 11.97% (Theoretical value=12.20%). In complexes $[\text{M}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ the elemental analysis data suggest the formula as $[\text{MLL}'_2\text{X}_2]\text{Cl}$.

Where, $\text{M}=\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$

$\text{L}=\text{m-nitrobenzaldehydethiosemicarbazone}(\text{NBTS})$

$\text{L}'=\text{Pyridine} (\text{Py})$

$\text{X}=\text{Cl}^-$

Infrared Spectral Studies: The characteristic infrared stretching frequencies of the ligand and the complexes are given in the table 2.

Table.2. IR spectral data for ligand and complexes

Assignment	Ligand NBTS cm^{-1}	Chromium Complex cm^{-1}	Iron Complex cm^{-1}
$\nu\text{N-H}$	3396, 3246	3385, 3246	3384, 3247
$\nu\text{C}=\text{C}$	1470	1351	1469
$\nu\text{N}=\text{O}$	1349	1351	1349
$\nu\text{C}=\text{N}$	1623	1603	1605
$\nu\text{C}=\text{S}$	1295, 843	1275, 806	1277, 805
$\nu\text{C-H}$	3156, 2985	3160, 3084	3158, 3087
$\nu\text{M-N}$	-	412	411
$\nu\text{M-S}$	-	335	336
$\nu\text{M-Cl}$	-	305	306

Characterization of the ligand (NBTS): The IR spectrum of the ligand (NBTS) is given in fig.1. The ligand shows IR bands at 3396 and 3246cm^{-1} due to N-H stretching frequency of NH_2 group of thiosemicarbazone. The band at 3156 and 2985cm^{-1} are due to the C-H stretching. The strong band at 1623cm^{-1} is due to C=N stretching azomethine nitrogen. The appearance of these bands confirms the formation of linkage between aldehyde group of m-nitrobenzaldehyde and the nitrogen of thiosemicarbazone. The band at 1526cm^{-1} indicates the presence of nitrogen at meta-position of benzene ring. The strong band at 1349cm^{-1} is due to N=O stretching (Keshari, 1981) and the sharp band at 1295cm^{-1} is due to C=S stretching. The band at 1470cm^{-1} is due to aromatic C=C stretching. The other bands in the IR spectra of the ligand mainly fall in the finger print region.

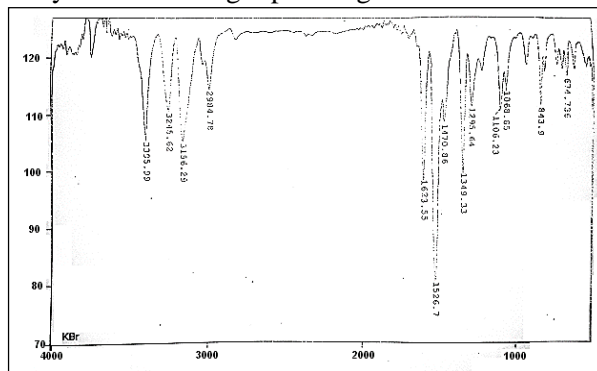
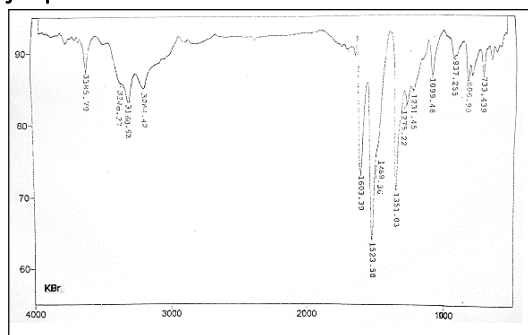
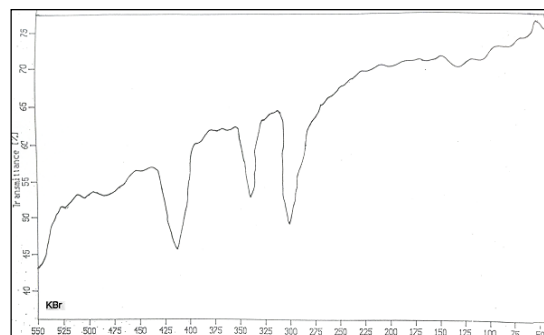
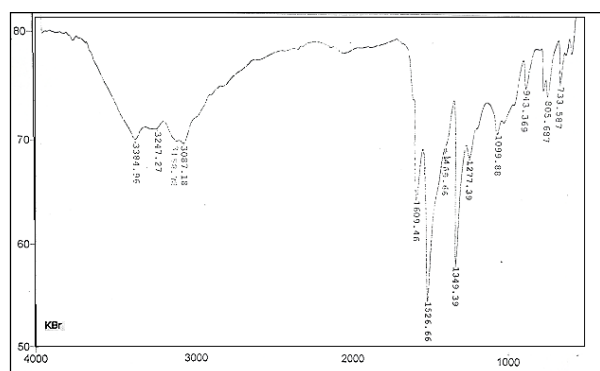
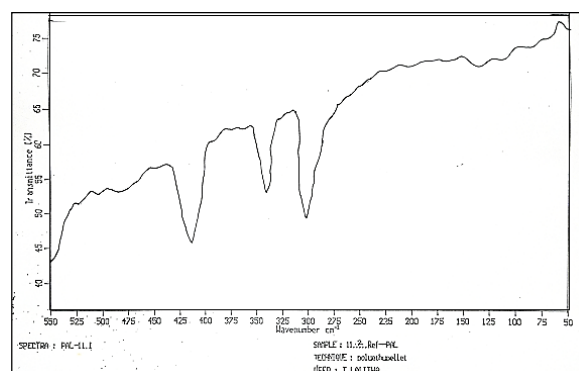


Figure.1. IR Spectrum of NBTS

Characterization of the complexes: The band around 400cm^{-1} , 410cm^{-1} region is assigned to M-N (Sigel., et. al., 1994) and the band at nearly 350cm^{-1} is assigned to the stretching frequency of M-S bands. The bands around 3385 and 3246cm^{-1} in the complexes indicate the presence of free NH_2 group. The bands around 3160 and 3084cm^{-1} are due to C-H stretching. The strong band for ligand at 1623cm^{-1} exhibit a negative shift by 20cm^{-1} in the complex (nearly 1603cm^{-1}) indicating the coordination of metal through azomethine nitrogen. The band in the spectrum of the ligand at 1295cm^{-1} is shifted to 1275 and 1277cm^{-1} in the complexes indicating the co-ordination through S atom of C=S group. The bands at 1526cm^{-1} and 1394cm^{-1} in the ligand indicate nitro group at meta-position of benzene ring does not involve in the co-ordination. The band around 1468cm^{-1} is assigned to aromatic C=C stretching. The shifting of the band at 843cm^{-1} to lower frequency by 50cm^{-1} (733cm^{-1}) further suggest the co-ordination of C=S group to the metal. There are also sharp bands in the finger print region. All the above observations indicate the both nitrogen and sulphur atoms are involved in co-ordination to the metal. In the far-infrared region, the complexes display a band around 300cm^{-1} , which is assigned to M-Cl stretching frequency (Lata Nobria., et. al., 1999).

Figure.2. IR Spectrum of $[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ Figure.3. Far IR Spectrum of $[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ Figure.4. IR Spectrum of $[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ Figure.5. IR Spectrum of $[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$

Electronic Spectral Studies: The electronic spectra of these complexes in DMF solution were recorded in the 200 to 1000 cm^{-1} . The UV-spectra of the ligand and complexes are given in figures 6, 7 and 8. The results obtained from these spectra are given in Table 3. The electronic spectrum of the ligand (NBTS) is given in Fig. 6. It shows band at 354 nm. The UV-visible spectra of Cr(III) and Fe(III) complexes show band in the lower wave length region at 325 nm and 322 nm. This shift in the absorption bands indicates the formation of the complex.

Table.3. UV spectral data for ligand and complex

Ligand/Complex	Wave Length (nm)
Ligand (NBTS)	354
$[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$	325
$[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$	322

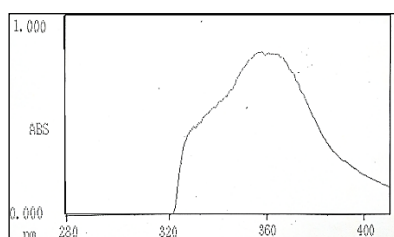
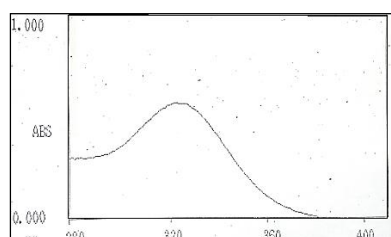
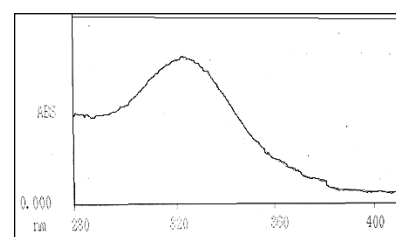


Figure.6: Electronic Spectrum of NBTS

Figure.7: Electronic Spectrum of $[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ Figure.8: Electronic Spectrum of $[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$

Conductivity Studies: The conductance were measured in DMF solution. The conductivity of the solvent and the solution of the complexes were measured using conductivity bridge.

Table.4. Conductivity data for the complexes

Complex	Solvent	Conductance ($\wedge m$) $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	Remarks
$[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$	DMF	145.50	Electrolyte
$[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$	DMF	150.53	Electrolyte

The conductance value of the complexes are high and hence they are considered as electrolyte (Agarwal., et. al., 1996).

Thermal Studies: The ligand NBTS (m-nitro benzaldehyde thio semicarbazone) decomposes in a single step. The percentage of mass loss is more than 90% and the peak temperature is 507.8K. The thermogram of Chromium complex shows decomposition in four stages. Here the degradation starts at 377.2K. The mass loss corresponds to absorbed water moiety. In the second stage the mass loss corresponds to pyridine moiety at peak temperature 490.7K. In the third stage the mass loss is above 70% corresponds to NBTS moiety at peak temperature 524.8K. In the fourth stage the mass loss is above 50% at peak temperature 743.8K. The thermogram of Iron complex decomposes in five stages. Here the degradation starts at around 412.5K, where mass loss corresponds to pyridine moiety. In the second stage the mass loss due to NBTS moiety at peak temperature 578.2K. In the third, fourth stages the mass loss is above 70% at peak temperatures 572.4K and 629.2K respectively.

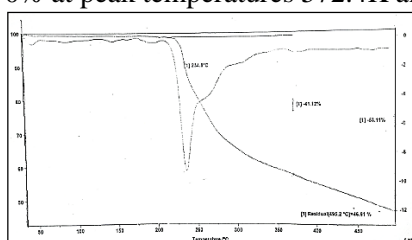
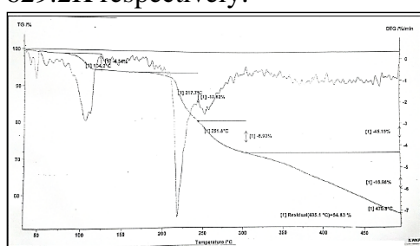
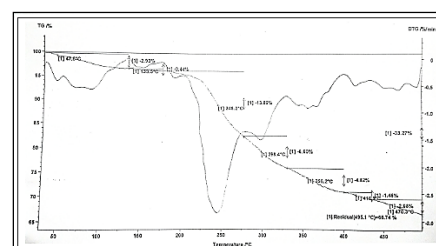
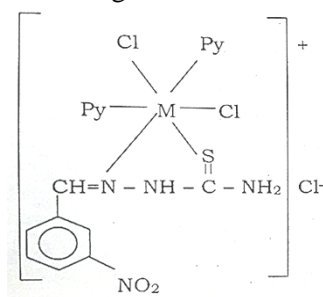


Figure.9. Thermogram of NBTS

Figure.10. Thermogram of $[\text{Cr}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$ Figure.11. Thermogram of $[\text{Fe}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$

4. CONCLUSION

From the studies, it is concluded that the ligand m-nitro benzaldehyde thio semicarbazone (NBTS) binds the metal atoms (Chromium and Iron) through one nitrogen (Azomethine nitrogen) and one sulfur atom, two pyridine molecules also bind to the metal through two nitrogen atoms in the same complexes. From our studies both complexes show a stoichiometry of $[\text{ML}(\text{Py})_2\text{Cl}_2]\text{Cl}$. The co-ordination environment and the metal centers appear to be octahedral. Considering the facts, the following structure has been proposed for these types of complexes.



$\text{M}=\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$

$[\text{M}(\text{NBTS})(\text{Py})_2\text{Cl}_2]\text{Cl}$

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