

**STUDIES ON MIXED LIGAND COMPLEXES OF IRON (III)
WITH DIBASIC TRIDENTATE SCHIFF BASES AS PRIMARY AND
NAPHTHOIC ACIDS AS CO-LIGANDS**

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The metal complexes of Fe(III) with thiosemicarbazones as primary and naphthoic acid as co-ligand are synthesized and characterized. The structure of newly synthesized complexes and the ligands were established with U.V, I.R, Magnetic moment study and elemental analysis. The ligand and the complex were also screened for their fungicidal activity against different fungi viz-Drechlera tetramera, Alternaria alternata and Fusarium oxysporum.

KEYWORDS : Thiosemicarbazones, fungicidal activity & ML.

INTRODUCTION

The coordination chemistry of trivalent ions involving multidentate ligands have received limited attention. Complexes of Fe(III) with p-dimethyl aminoaniline-3-penten-2-one have been prepared and characterized by Agrawal and Chandra [1], Fe(III) is known to form high spin, ($s = 5/2$), low spin ($s = 1/2$) and intermediate spin ($s = 3/2$) complexes under influence of different ligand field. Spin-crossover phenomenon is usually observed with the Fe(III) compounds. B.K. Kanungo and his coworkers [2] have reported five and six coordinate low-spin Fe(II) complexes. Patel and Verma [3] have reported the formation of Fe(III) Chelates of N, N'-hexamethylene-bis-(2, 5-di-OH-acetophenone/propiophenone/benzophenone).

The reaction of potassium hexathiocyanatochromate (III) with β -diketone and nitrogen donor ligand in ethanolic medium form complexes [4] of the type $[Cr(b_z b_z)(\gamma\text{-pic})_2(NCS)_2]$, $[Cr(b_z b_z)L(NCS)_2]$, $[Cr(b_z ac)(\gamma\text{-pic})_2(NCS)_2]$ and $[Cr(b_z ac)L(NCS)_2]$ where $b_z b_zH =$ Dibenzoylmethane, $b_z acH =$ benzoylacetone, $\gamma\text{-pic} = \gamma$ - picoline and $L =$ 2, 2' bipyridine or o-phenanthroline. The complexes have been characterized on the basis of elemental analyses, molar conductance, and room temperature magnetic moment, infrared and electronic spectral data. They are paramagnetic and non-electrolytic in nature, having octahedral

geometries. Complexes of Fe(III) with 1-(2'-pyridyl) benzothiazole-2-thione have been studied by Khan and co-workers [5], Spectrophotometric study of reaction between Fe(III) and 2-hydroxy-1-naphthaldoxime has been carried out [6].

Kumar and Sethi [7] have made spectral, magnetic, mossbauer and chemotherapeutical studies of Fe(III) complexes with various new derivatives of isonicotinic acid hydrazide. Complexes of the composition $H[M(C_{18}H_{31}NO_4)_2]$ [$M=Fe^{+3}$] with N-4-methyl-7-hydroxy-8-acetocoumarinylidene-o-aminophenol ($H_2MHACAP$) have been prepared and characterized [8] on the basis of elemental analysis, conductivity, electronic, infrared, pmv and magnetic measurements. All these metal complexes have been found to exhibit octahedral geometry. Fe(III) complexes of the Schiff bases derived from salicylhydrazide and 6-methyl-4-hydroxy-3-acetyl-coumarin were reported in literature [9] 3-Hydroxy-3-phenyl-1-o-hydroxyphenyl triazine has been used as a reagent for spectrophotometric determination of chromium [10].

Stability constant [11] of Fe(III) complexes of N-(8-aceto-7-hydroxy-4-methyl coumarin)-o-phenylene diamine have been determined at 25°C and $\mu \approx 0.1M$ ($NaClO_4$) in 75% (V/V) aqueous-dioxane medium at different M : L ratio (where M = metal ion and L = ligand). Synthesis and structural characterization of Cr(III) complexes with terephthalic acid hydrazide Schiff bases has been carried out by Agrawal and Tutlani [12]. Octahedral complexes of Cr(III) with 2, 5-dihydroxyacetophenone Schiff bases have been studied [13]. Magnetic and spectral studies of octahedral complexes of Fe(III) with β -phenylamino-2,4, 2,5 dihydroxy propiophenone, β -benzidiny-2 : 5 dihydroxy propiophenone and β -benzidiny-2, 3, 4-trihydroxy propiophenone have been carried out [14]. Synthesis and structural determination of Fe(III) compounds with N, O and S containing ligands have been studied [15]. Mossbauer studies on Fe(III) complexes with some nitrogen donor ligands have been carried out [16].

The coordination chemistry of transition metals and their derivatives has received much attention in the recent years mainly due to their biological importance [17-19]. The metal thiosemicarbazones compounds are emerging as a new class of experimental anticancer chemotherapeutic agent [20], which shows activity against most of the cancers through inhibition of a crucial enzyme obligatory for DNA biosynthesis and cell division [21, 22]. The complexes of manganese play an important role in photochemical reactions [23]. Nitrogen, oxygen and sulphur donor ligands possess a range of biological applications such as antitumor [24], antiviral [25], antibacterial [26], antimalarial [27] and antifungal activities [28]. Manganese ethylene bisdithiocarbamate is known to exhibit antifungal activity and has been successfully used against a wide variety of diseases [29] specially of vegetables and fruits [30]. Manganese complexes of some thiosemicarbazones are potent antileukemic agents [31-32].

The survey of the literature revealed that the mixed ligand complexes of Fe(III) with dibasic tridentate Schiff bases derived by the condensation of thiosemicarbazides with acetoacetanilide and o-chloro-acetoacetanilide as primary and 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acid as co-ligands have not been studied so far. In the present chapter, above mentioned complexes were synthesized. The newly synthesized complexes were characterized on the basis of their elemental analysis, magnetic, spectral and electrolytic conductance studies. Different ligand field parameters have also been calculated. These complexes were also screened for their fungicidal activity against *Drechlera-tetramera*, *Fusarium-oxysporum* and *Macrophomera-phaseoli* at different concentration viz. 100, 50 and 20 ppm.

EXPERIMENTAL

All the reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard methods reported in literature. The analysis of carbon, hydrogen and nitrogen were performed at CDRI Lucknow.

PREPARATION OF PRIMARY LIGANDS (SCHIFF BASES) :

Schiff bases were prepared by refluxing thiosemicarbazides with acetoacetanilide or o-chloro-acetoacetanilide in 1 : 1 molar ratio in alcohol for an hour. After refluxing it was concentrated on water bath upto half of its volume. The precipitate obtained after condensation were filtered and dried. The formation of Schiff bases were confirmed by elemental analysis and infrared spectral studies.

PREPARATION OF MIXED LIGAND COMPLEXES :

To a warm absolute ethanolic solution of anhydrous metal (III) Chloride, hot ethanolic solution of Schiff base was added drop wise. The reaction mixture was thoroughly stirred and refluxed at 70-80°C for two hours on water bath. Crystalline complexes separated out on cooling at room temperature. They were filtered off washed with ethanol and finally with ether and dried in vacuum over P_4O_{10} .

The mixed ligand complexes were prepared by treating the ethanolic solution of binary complexes with the ethanolic solution of 1-hydroxy-2-naphthoic acid or 3-hydroxy-2-naphthoic acid. The reaction mixture was refluxed over water bath for about four hours in each case and the reaction mixture was kept over night at room temperature. The precipitated compounds were filtered, washed with acetonitrile and dry ether to remove unreacted ligand if any. They were recrystallised from ethanol chloroform mixture. The crystalline complexes were derived in vacuum yield 70%.

RESULT AND DISCUSSION

Analytical data of mixed ligand complexes suggest 1:1:1 (M:L:L'/L'') stoichiometry of isolated mixed ligand complexes (where $M = Cr^{3+}$ Fe^{3+} and $L = C_{11}H_{14}N_4SO$, $L' = C_{11}H_{13}N_4SOCl$ $L'' = C_{11}H_8O_3$, $L''' = C_{11}H_8O_3$). The compounds are stable upto 150°C showing that they are non-hygroscopic. All the complexes are soluble in common organic solvents. The conductance data shows that they are having non-electrolytic nature.

I.R. Studies :

On comparison of I.R. spectra of free ligands with those of mixed ligand complexes confirm the coordination of thiosemicarbazone and naphthoic acid to the metal Fe(III) I.R. spectra of free thiosemicarbazone ligands display two bands around 3450 and 3300 cm^{-1} due to ν_{as} and ν_{sym} of terminal NH_2 group [33]. These bands remain practically unaltered in the corresponding metal complexes showing the non-involvement of this group on complexation. The absorption due to $\nu_{C=N}$ of the free ligand appearing in the region 1620 cm^{-1} undergoes a negative schiff by 5-15 cm^{-1} in the spectra of complexes indicating the coordination of azomethene nitrogen to the metal.

The bands of strong intensities in the spectra of the primary ligand around 1650 cm^{-1} are due to $\nu_{C=O}$. In the spectra of complexes, this band is absent and a new bands observed around 1620 cm^{-1} which can be attributed to the enolisation and subsequent coordination through the deprotonated oxygen atom of the $-CH_2-C=O$ group [34]. The band due to $\nu_{C=S}$ appears around 830 cm^{-1} in free primary ligand disappears on complexation and a new band appears around 720-750 cm^{-1} . These observations may be attributed to thioenolisation of the $-NH-C=S$ group

and subsequent coordination through the deprotonated sulphur [35]. From the I.R. spectra data it is concluded that the thiosemicarbazones are potentially dibasic tridentate ligands and the coordination sites are the β -nitrogen and thiolato sulphur and oxygen after deprotonation. The possibility of α -nitrogen coordination is ruled out because of considerable strain³⁶.

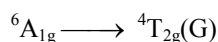
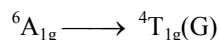
The ν OH(of COOH group) observed as a broad intense band at 2650 cm^{-1} in naphthoic acids is not traceable in the spectra of the mixed ligand complexes indicating that the carboxylic proton has been removed in complexation. The symmetrical and asymmetrical stretching vibrations of COO of free ligand observed at 1410 and 1630 cm^{-1} respectively shifted to 1440 - 1450 cm^{-1} and 1570 - 1580 cm^{-1} in the complexes indicating coordination of carboxylate oxygen to metal ion.

The broad band centred at 2960 cm^{-1} in the spectra of complexes indicating non-participation of phenolic OH present in naphthoic acids.

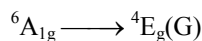
Magnetic and Electronic Spectral Studies:

Fe(III) MIXED LIGAND COMPLEXES:

The magnetic moment values of Fe(III) complexes lie in the range 5.92 - 5.99 B.M. These values are in the range usually found for high spin octahedral Fe(III) complexes. These values of magnetic moment corresponds to five unpaired electrons and suggest six coordinated high, spin stereochemistry to these complexes. The electronic spectra of Fe(III) complexes shows bands in the range 16700 - 17000 , 21700 - 22000 and 24750 - 25150 cm^{-1} . These bands may be assigned to



and



The bands observed at 27900 cm^{-1} is expected to be the charge transfer band (L \rightarrow M). The band observed at around 17600 and 29700 cm^{-1} may be due to splitting of ${}^4T_{1g}$ and thus the complexes has distorted octahedral stereochemistry.

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