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Synthesis and Spectral Study of Mixed Ligand Complexes of Chromium (III) and Iron (III) Dibasic Tridentate Schiff bases as Primary and Naphthoic Acid as Co-Ligand

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Abstract

The transition metal complexes of Schiff bases have been widely researched on account of their importance as biochemical, analytical and antimicrobial reagent. Herein, the transition metal ion complexes of Fe(III) and Cr(III) with dibasic tridentate Schiff base derived by condensation of thiosemicarbazide with acetoacetanilide as primary ligand and 1-hydroxy-2-naphthoic acid as co-ligand have been prepared. The mixed ligand complexes of the above mentioned metal ions were characterized by analytical, magnetic and electronic spectral study. The transition metal complexes were also evaluated for antifungal activity against *Drechsleratetramera*, *Fusariumoxysporum* and *Macrophomiphoseoli* at different concentrations using growth method.

Keywords: Tridentate Schiff base, Mixed ligand, Naphthoic acid, Electronic spectral study, Antifungal activity

Introduction

Transition metal complexes of Schiff bases have been amongst the most widely studied coordination compounds in the last few years because of their importance as biochemical, analytical and antimicrobial reagents¹⁻⁶. Metal complexes formed by ligands which are capable of coordinating with two or more sites with metal ions have evoked much interest in the field of coordination chemistry⁷⁻⁹. The Schiff bases derived from a large number of carbonyl compounds and amines have been reported and they are found to form complexes with metal ions. The metal complexes formed from ligands 2-amino-4-phenyl-5-arylazothiazole and salicylaldehyde have been reported in literature¹⁰⁻¹¹.

The reaction of potassium hexathiocyanatochromate (III) with β -diketone and nitrogen donor ligand in ethanolic medium form complexes¹² of the type $[Cr(b_2b_2)(\gamma\text{-pic})_2(NCS)_2]$, $[Cr(b_2b_2)L(NCS)_2]$, $[Cr(b_2ac)(\gamma\text{-pic})_2(NCS)_2]$ and $[Cr(b_2ac)L(NCS)_2]$ where b_2b_2H = Dibenzoylmethane, b_2acH = benzoylacetone, $\gamma\text{-pic}$ = γ - picoline and L = 2,2' bipyridine or o-phenanthroline. The newly prepared mixed ligand complexes were characterized on the basis of their elemental analysis, magnetic, spectral and electrolytic conductance studies. They are paramagnetic and non-electrolytic in nature, having octahedral geometries. Complexes of Cr(III) and Fe(III) with 1-(2'-pyridyl) benzothiazole-2-thione have been studied by Khan and co-workers¹³. The spectrophotometric study of reaction between Fe (III) and 2-hydroxy-1-naphthaldoxime has been carried out¹⁴.

Kumar and Sethi¹⁵ have made spectral, magnetic, Mossbauer and chemotherapeutical studies of Fe(III) complexes with various new derivatives of isonicotinic acid hydrazide. Complexes of the composition $H[M(C_{18}H_{31}NO_4)_2]$ [$M=Cr^{+3}$, Mn^{+3} or Fe^{+3}] with N-4-methyl-7-hydroxy-8-acetocoumarinylidene-o-aminophenol ($H_2MHACAP$) have been prepared and characterised¹⁶ on the basis of elemental analysis, conductivity, electronic, infrared, and magnetic measurements. All these metal complexes have been found to exhibit octahedral geometry. Cr(III) and Fe(III) complexes of Schiff bases derived from salicylhydrazide and 6-methyl-4-hydroxy-3-acetyl-coumarin were reported in literature¹⁷.

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3-Hydroxy-3-phenyl-1-o-hydroxyphenyl triazene is commonly used as a reagent for spectrophotometric determination of chromium¹⁸.

The stability constant¹⁹ of Fe(III) and Cr(III) complexes of N-(8-aceto-7-hydroxy-4-methyl coumarin)-o-phenylenediamine was determined at 25°C and $\mu \approx 0.1M$ (NaClO₄) 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 was carried out by Agrawal and Tutlani²⁰. Octahedral complexes of Cr(III) with 2,5-dihydroxyacetophenone Schiff bases was studied²¹. Magnetic and spectral studies of octahedral complexes of Fe(III) with β -phenylamino -2,4,2,5 dihydroxypropionophenone, β -benzidinyl-2,5 dihydroxypropionophenone and β -benzidinyl-2,3,4 -trihydroxypropionophenone have been carried out²². Synthesis and structural determination of Fe(III) compounds with N,O and S containing ligands was also studied²³. Mossbauer studies on Fe(III) complexes with some nitrogen donor ligands was carried out²⁴.

Review of Literature

The coordination chemistry of transition metals and their derivatives has received attention by researchers mainly due to their biological importance²⁵⁻²⁷. The metal thiosemicarbazones compounds are emerging as a new class of experimental anticancer chemotherapeutic agent²⁸ which shows activity against most of the cancers through inhibition of a crucial enzyme obligatory for DNA biosynthesis and cell division^{29,30}. The complexes of manganese play an important role in photo chemical reactions³¹. Nitrogen, oxygen and sulphur donor ligands possess a range of biological applications such as antitumor³², antiviral³³, antibacterial³⁴, antimalarial³⁵ and antifungal activities³⁶. Manganese ethylene bisdithiocarbamate is known to exhibit antifungal activity and is successfully used against a wide variety of diseases³⁷ specially vegetables and fruits³⁸. Manganese complexes of some thiosemicarbazones are potent antileukemic agents³⁹⁻⁴⁰.

Aim of the Study

Metal complexes play a vital role in metabolic and toxicological functions in the biological system.

To use metal complexes as anticancer drug, antimicrobial and antiviral agents and in the treatment of arthritic and inflammation.

To use mixed ligand complexes in environment, medicinal, analytical, industrial chemistry.

Experimental

Materials and Method

All the chemicals used were of chemically pure analytical grade. The solvent were dried and

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distilled before use. Metal(II) chloride, thiosemicarbazide, acetoacetanilide, o-chloro-acetoacetanilide, 1-hydroxy-2-naphthoic acid and 3-hydroxy-2-naphthoic acid were procured from Fischer Scientific, India. Dimethyl formamide (DMF) and alcohol were also purchased from Fischer Scientific, India. The elemental analysis was performed at Central Drug Research Institute, India. Conductance of the metal complexes were measured in nitromethane at 25°C on Toshniwal conductivity bridge CL01/01 using dip type cell. The following accepted range of molar conductivity for water at concentration equal to M/1000 and temperature 25°C were taken to determine the number of ions present in solution. The standard range of molar conductivity in mhos of uni-divalent electrolyte is 215-273 mhos. Infrared spectra of the ligand and their metal complexes were recorded on Beckmann IR 120 Spectrophotometer and Perkin Elmer improved 137 spectrophotometer in Nujol mull and KBr in the range 200 to 400 cm⁻¹ and 400-4000 cm⁻¹ at room temperature. The electronic spectra of the complexes were recorded in ethanol at room temperature on CZ-specord UV-vis-spectrophotometer provided with an automatic recorder. The magnetic susceptibility at room temperature was determined on Gouy's electromagnetic balance and corrected for diamagnetism.

Preparation of Primary Ligand (Schiff Bases)

Schiff bases were prepared by refluxing thiosemicarbazides with acetoacetanilide or o-chloro-acetoacetanilide in 1:1 molar ratio in alcohol for 1h. 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 2h 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 over phosphorous pentoxide.

The mixed ligand complexes were prepared by treating the ethanolic solution of binary complexes with the ethanolic solution of 1-hydroxy-2-naphthoic acid. The reaction mixture was refluxed over water bath for about 4h in each case and the reaction mixture was kept overnight at room temperature. The precipitated compounds were filtered, washed with acetonitrile and dry ether to remove unreacted ligands if any. They were recrystallised from ethanol: chloroform mixture. The crystalline complexes were dried in vacuum.

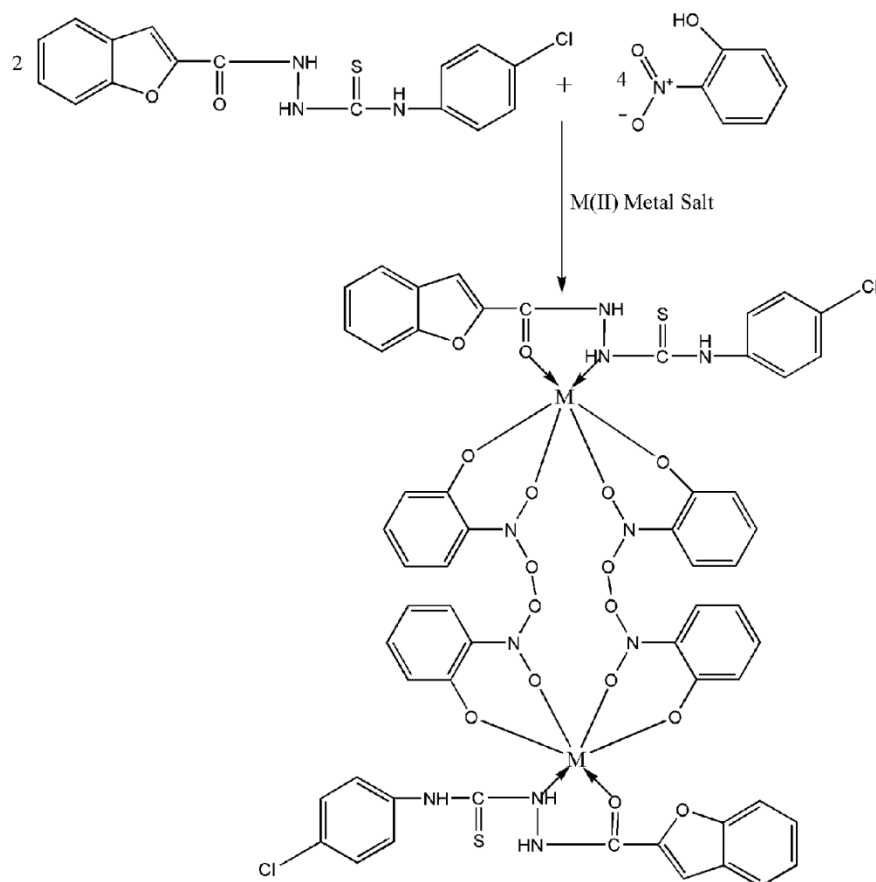


Fig1: Shows the structure of mixed ligand complexes of Cr(III) and Fe(III)

Antifungal Activity

The antifungal activity of ligands as well as their metal complexes was determined using 3 strains of fungus i-e

Drechsleratetramera, *Macrophomiaphoseoli* and *Fusariumoxysporum* at different concentration viz: 50, 100, 200ppm. The samples were inoculated in warm Czapeck'sDox agar medium and autoclaved at 15lbs for 15min and then shaken well to give uniform dispersal of chemical. The samples were poured into sterilized petri- dishes keeping 3 replications of each treatments and a check without chemicals. Then the plates were inoculated centrally with a mycelia disc from 7 days old culture of the fungi towards complex.

Results and Discussion

Analytical data of mixed ligand complexes suggest 1:1:1 (M:L:L:L) stoichiometry of isolated mixed ligand complexes (where $M = Cr^{3+}$, F_9^{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 $150^\circ C$ 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.

FTIR Study

On comparison of IR, spectra of free ligands with those of mixed ligand complexes confirm the coordination of thiosemicarbazone and naphthoic acid to the metal Fe(III) and Cr(III) IR 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 group⁴¹. 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 coordination of azomethene nitrogen to the metal.

The bands of strong intensities in the spectra of primary ligand around 1650 cm^{-1} are due to $\nu_{C=O}$. In the spectra of complexes, this band is absent and a new band is observed around 1620 cm^{-1} which can be attributed to the enolisation and subsequent coordination through the deprotonated oxygen atom of $-CH_2-C=O$ group⁴². The band due to $\nu_{C=S}$ appears around 830 cm^{-1} in free primary ligand which disappears on complexation and a new band appears around $720-750\text{ cm}^{-1}$. These observations may be attributed to thioenolisation of $-NH-C=S$ group and subsequent coordination through the deprotonated sulphur⁴³. From IR spectral data, it is concluded that the thiosemicarbazones are potentially dibasic tridentate ligands and the coordination sites are β -nitrogen, thiatosulphur and oxygen after deprotonation. The possibility of α -nitrogen coordination is ruled out because of considerable strain⁴⁴ as shown in Fig.2

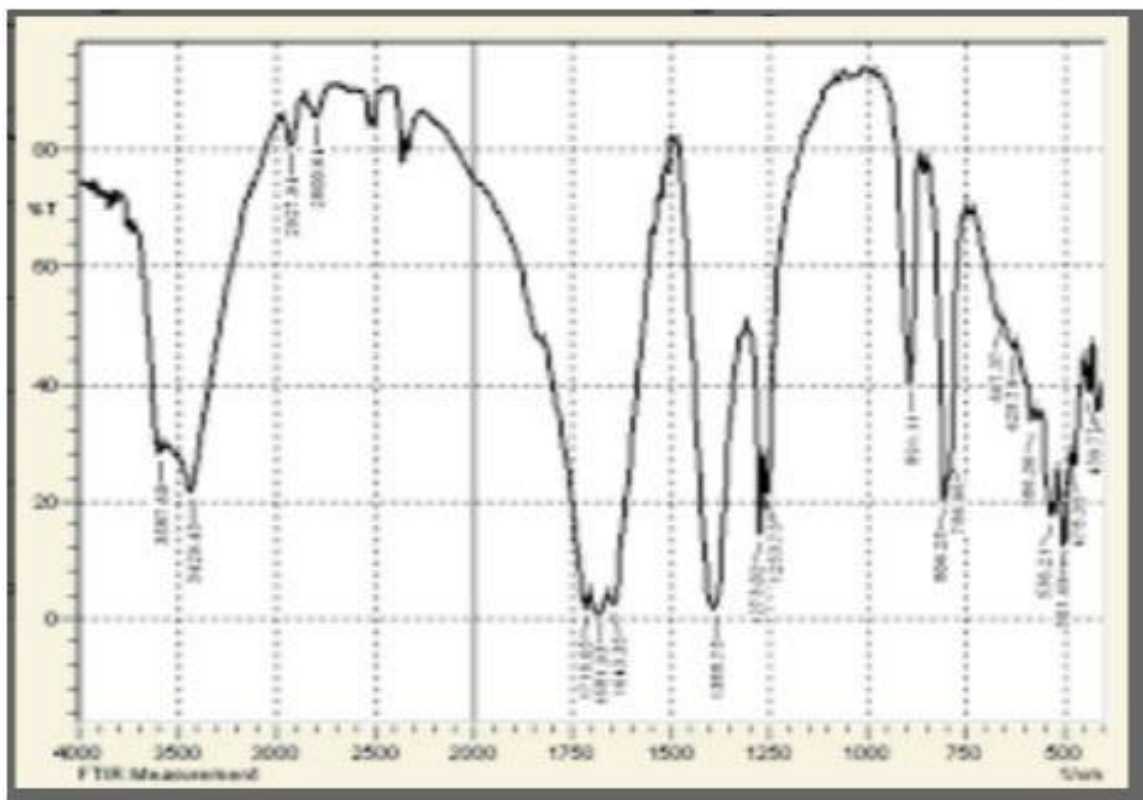


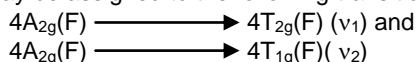
Fig 2: IR spectrum of dibasic tridentate Schiff base

ν OH (of COOH group) observed as a broad intense band at 2650 cm^{-1} in naphthoic acid is not traceable in the spectra of mixed ligand complexes indicating that the carboxylic proton has been removed in complexation. The symmetrical and asymmetrical stretching vibrations of $-\text{COO}^-$ of free ligand are observed at 1410 and 1630 cm^{-1} respectively that shifted to $1440\text{--}1450\text{ cm}^{-1}$ and $1570\text{--}1580\text{ cm}^{-1}$ in the complexes indicating coordination of carboxylate oxygen to metal ion. The broad band centered at 2960 cm^{-1} in the spectra of complexes indicating non-participation of phenolic-OH present in naphthoic acids.

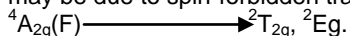
Magnetic and Electronic Spectral Studies

Cr(III) Mixed Ligand Complexes

Cr(III) complexes under study showed magnetic moment of $3.80\text{--}3.84$ B.M. corresponding to three unpaired electrons and sp^3d^2 hybridization. These values lie in the range expected for octahedral stereochemistry. The electronic spectra of acetonitrile solution of Cr(III) compounds exhibit bands in the range $17200\text{--}17900\text{ cm}^{-1}$ and $23000\text{--}23400\text{ cm}^{-1}$ which may be assigned to the following transitions.



These transitions are characteristics of an octahedral Cr(III) ion. In addition, a low energy band in the range $12700\text{--}12950\text{ cm}^{-1}$ is also observed which may be due to spin-forbidden transition.

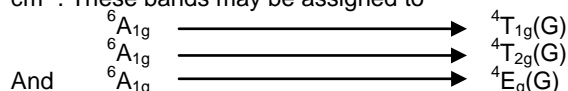


The higher energy spin allowed ν_3 band corresponding to $4A_{2g}(F) \longrightarrow 4T_{1g}(P)$ usually found above $30,000\text{ cm}^{-1}$ could however not be traced in the electronic spectra of Cr(III) mixed ligand

complexes. The spectral and magnetic moment values support the octahedral stereochemistry for the Cr(III) complexes.

Fe(III) mixed ligand complexes

The magnetic moment values of Fe(III) complexes lie in the range $5.92\text{--}5.99$ B.M. These values are in the range usually found for high spin octahedral Fe(III) complexes. These values of magnetic moment correspond 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 $16700\text{--}17000$, $21700\text{--}22000$ and $24750\text{--}25150\text{ cm}^{-1}$. These bands may be assigned to



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

Antifungal Study

The antifungal activities of ligands (dibasic tridentate Schiff base + naphthoic acid) and their mixed ligand complexes of Cr(III) and Fe(III) were screened against 3 fungus strains *Drechsleratetramera*, *Macrophomiphoseoli* and *Fusariumoxysporum* by the growth method. Czpeck's dox agar medium was used for culture of fungus at different concentrations 50 , 100 , 200 ppm. The growth response of the 3 fungus strains was measured as average % inhibition after 96h. Table 1 shows growth responses (average %

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inhibition) of *Drechsleratetramera*, *Macrophomiaphoseoli* and *Fusariumoxysporum* after 96h at 26+1°C on Czpeck'sdox agar medium at different concentration (50,100,200 ppm) in relation to the ligands and their metal complexes Cr (III) and

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Fe(III). The average % inhibition was observed to be good for Fe (III) metal complexes as compared to Cr (III) metal complexes. The ligands showed less antifungal activity as compared to metal complexes.

TABLE 1: Antifungal analysis of ligands (primary + secondary) and its Chromium(III) and Iron(III) metal complexes

Test Sample	Average % inhibition after 96 hours								
	<i>Drechsleratetramera</i>			<i>Macrophomiaphoseoli</i>			<i>Fusariumoxysporum</i>		
	Concentration used in ppm								
	200	100	50	200	100	50	200	100	50
Ligand (Primary + Secondary)	65	52	35	64	51	34	64.5	50.5	33.8
[Cr(C ₁₁ H ₁₂ N ₄ SO)(C ₁₁ H ₇ O ₃)H ₂ O]	50	38	28	51.0	37	20.4	51.0	30	20.4
[Cr(C ₁₁ H ₁₁ N ₄ SOCl)(C ₁₁ H ₇ O ₃)H ₂ O]	51.0	37.8	27	50.8	26.8	20.3	50.8	29	20.6
[Fe(C ₁₁ H ₁₂ N ₄ SO)(C ₁₁ H ₇ O ₃)H ₂ O]	52.0	36.7	28	50.6	26.5	21.0	51.2	28.6	20.4
[Fe(C ₁₁ H ₁₁ N ₄ SO)(C ₁₁ H ₇ O ₃)H ₂ O]	51.6	37.5	27	50.4	26.4	20.6	51.0	28.4	20.2

Conclusion

It is to be concluded that in this work mixed ligand complexes of Fe (III) and Cr(III) have been successfully synthesized along with tridentate Schiff base derived by condensation of thiosemicarbazides with acetoacetanilide as primary ligand and 1-naphthoic acid as co-ligand. The transition metal complexes were characterized by FTIR, elemental analysis and electronic spectral study. The spectral and magnetic moment values support the octahedral stereochemistry for the Cr(III) and Fe(III) complexes. The antifungal activity of the three compounds were performed with 3 fungus strains, *Drechsleratetramera*, *Macrophomiaphoseoli* and *Fusariumoxysporum* at different concentrations. The growth response and average % inhibition after 96h of exposure to fungi strain was observed in relation to the ligand and its metal complexes. The complexation of metal Cr(III) and Fe(III) with mixed ligands have increased antifungal activity as compared to mixed ligands individually.

Conflict of Interest

Author does not have any conflict of interest.

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