SUMMARY
Transition metal complexes of the acyl and aroylhydrazines and their hydrazones have received attention during the recent years because of their use as analytical reagents, varied bonding and stereochemical possibilities offered by them, as oxygen carriers and biochemical models and more recently, as effective catalysts for the epoxidation of olefins in the chemical and petrochemical industries. Although, there are extensive reports on synthesis and structure of 3d-metal complexes of six-membered heteroaryl hydrazines and their hydrazones, only few reports are available on the complexes of hydrazides and the Schiff bases derived from five-membered heterocyclic acid hydrazides, those of 2-furoyl- and 2-thenoylhydrazines.

In view of the inadequacy or complete absence of the previous work on the Cr(III), Fe(III), Ru(III), and Rh(III) complexes of Haff, Hatfh, Haphf and Haftf, it was thought of interest to undertake a systematic, preparative and structural studies of the complexes of above metals with the above ligands.
PREPARATION AND ANALYSIS OF COMPLEXES:

The isolated complexes may be divided into two categories, viz., the adducts and the neutral complexes having the non-deprotonated and deprotonated ligands, respectively.

The adduct complexes were generally prepared by mixing together an ethanolic/methonolic solution of the Haff or Hatfh or Hapfh or Haftfh and the appropriate metal salt in 1:1, 2:1 and 3:1 molar ratio. The complexes, either precipitated, immediately, or by stirring or the precipitation was invoked by adding ethyl ether after reducing the volume of the reaction solution. The neutral complex Fe(atfh)₃ was obtained by adding an aqueous solution of the appropriate metal salt (1 mmol) to the solution of the Hatfh (3 mmol) in ethanol and raising pH of the solution to ca.~7 by adding an aqueous N NaOH solution.

The complexes were collected through filtration and were purified by washing with the appropriate solvents. The complexes were dried in vacuo.
The complexes were analyzed for metal, chloride, hydrazine, and nitrogen. The structures of the complexes have been elucidated by employing a number of physicochemical techniques such as molar conductance, ir, magnetic susceptibility, electronic, Mössbauer and thermogravimetric analysis.

RESULTS AND DISCUSSION:

On the basis of elemental analyses and molar conductance measurements, the following formulae have been proposed for complexes.

(a) Fe(atfh)₃
(b) Fe(atfh)₂Cl.H₂O
(c) M(HL)Cl₃.H₂O  \( M=\text{Cr(III)} \) and \( \text{Fe(III)} \); HL=Haff, Hatfh and Hafth.
(d) Ru(Hatfh)Cl₃.H₂O
(e) Fe(Hapfh)Cl₃.H₂O
(f) M(HL)Cl₃  \( M=\text{Cr(III)} \) and \( \text{Fe(III)} \); HL=Haff, Hafth.
(g) Fe(Hapfh)Cl₃
(h) Fe(L)₂Cl  HL=Haff, Hapfh and Hafth.
(i) Cr(aff)₂Cl
(j) \( \text{M(HL)}_2\text{Cl}_2\cdot\text{Cl} \quad \text{M} = \text{Cr(III)} , \text{Fe(III)} , \text{Ru(III)} \) and \( \text{Rh(III)} \);

\( \text{HL} = \text{HafH}, \text{Hatfh}, \text{Hapfh} \) and \( \text{Hafth} \).

The complexes are stable in normal atmospheric condition. The complexes are insoluble in common organic solvents while most of them are slightly or fairly soluble in DMF and DMSO. Some complexes melt in the 215-315 °C temperature range. The remaining complexes are either non-melting or decomposing below 350 °C. A few complexes are 1:1 electrolyte in solution and the remaining complexes are non-ionic. Some complexes, however, give conductance values too low for their ionic nature presumably due to solvolysis. The water molecules in the hydrated complexes are coordinated to the metal ions.

**INFRARED SPECTRA:**

Haff, Hatfh, Hapfh and Hafth coordinate to the metal ions through the carbonyl oxygen and the azomethine nitrogen in the adducts. In deprotonated complexes the Schiff bases behave as the uninegative bidentate, bonding sites being the imidol oxygen and the azomethine nitrogen.
The non-ligand bonds observed in 350-410, 310-340 and 260-305 cm⁻¹ regions are tentatively aligned to ν(M-O), ν(M-N) and ν(M-X) modes respectively, in all the complexes.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS:

The magnetic moments of the iron (III) complexes indicate presence of five unpaired electrons. The anomalous μeff values of some Fe(III) complexes may be attributed to metal – metal and/or antiferromagnetic interaction. The μeff values of Cr(III) complexes indicate spin free octahedral geometry except some Cr(III) complexes with the anomalous μeff values which can be explained on the basis of spin orbit coupling and/or through oxo-bridging or coupling between to paramagnetic chromium (III) center. Rh(III) complexes show normal magnetic moment corresponding to one unpaired electron.

ELECTRONIC SPECTRAL STUDIES:

The electronic spectra of the Cr(III) complexes yield two d-d transition bands characteristic of an octahedral ligand field around the metal ion. The spectral profiles of Fe(III) complexes are indicative of an octahedral geometry exhibiting one to two d-d
bands in their electronic spectra. The Mössbauer spectra also support the octahedral stereochemistry around Fe(III).

MÖSSBAUER SPECTRAL STUDIES:

The Mössbauer spectra of Fe(III) complexes show quadrupole splitting in the range of 0.32-0.42 mm/sec. and chemical isomer shift in the range of 0.68-0.88 mm/sec.; which are indicative of high spin Fe(III) complexes possessing octahedral or distorted octahedral geometry. Thus octahedral geometry around Fe(III) adduced from magnetic and electronic spectral studies is further supported from Mössbauer studies.

Based on these studies an octahedral stereochemistry for the complexes have been proposed. It may be mentioned that in the absence of X-ray single crystal data the structures proposed for the complexes are only tentative.