The study of the synthesis, structures and properties of transition metal complexes is a key line of research in modern coordination chemistry. Hydrazones are an interesting class of ligands in coordination chemistry, and they are obtained by the condensation reaction between a carbonyl compound and a hydrazide. Their coordination capability and binding modes can be altered by the use of suitable substituents both in the carbonyl and hydrazide part. Acting as ligands they easily form mono, bi and polynuclear coordination compounds. The metal complexes derived from hydrazones find applications in many areas such as medicine, biology, catalysis, optics and analytical chemistry. Hence, the knowledge of characteristics of deprotonation, tautomerization and complexation in solution as well as the structural details of coordination with metal ions in solid state is fundamental for forecasting the properties of this class of azomethine compounds.

To explore the coordination properties of acylhydrazones, in this work we have synthesized four different acylhydrazones by the condensation of $o$-hydroxy aromatic aldehyde and ketone with benzhydrazide and nicotinic acid hydrazide. The thesis is divided into seven chapters and Chapter 1 gives an introduction to acylhydrazones, their mode of bonding in complexes and applications in different areas. The objectives of the present work and the details of different analytical techniques used for characterization are also presented in this chapter. Chapter 2
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deals with the syntheses and characterization of four different acylhydrazones and they are

1. 2-Hydroxy-4-methoxybenzaldehyde nicotinoylhydrazone monohydrate ($H_2hmbn\cdot H_2O$)
2. 2-Hydroxy-4-methoxyacetophenone nicotinoylhydrazone ($H_2hman$)
3. 2-Hydroxy-4-methoxybenzaldehyde benzoylhydrazone ($H_2hmbb$)
4. 2-Hydroxy-4-methoxyacetophenone benzoylhydrazone ($H_2hmab$).

The acylhydrazones were characterized by elemental analyses, FTIR, $^1$H NMR and UV–Vis spectral studies. Single crystal X-ray diffraction studies of one of the hydrazones $H_2hmbn\cdot H_2O$ revealed that the compound is non planar and exist in amido form in solid state. The novelty about this crystal lies in the packing; three molecules are involved in intermolecular hydrogen bonding interactions with one water molecule. The $^1$H NMR studies indicate the enolization of these compounds in solution state.

Chapter 3 describes the syntheses and structural characterization of twelve oxovanadium complexes of acylhydrazones. Magnetic susceptibility measurements clearly indicate that, all the compounds except one, are paramagnetic compounds with vanadium is in +4 oxidation state. Some compounds exhibit subnormal magnetic moments due to the strong antiferromagnetic exchange, suggesting dimeric nature to these complexes. The molar conductivity values for all the complexes in $10^{-3}$ M DMF solution are found to be less than the value of 65-90 ohm$^{-1}$ cm$^2$ mol$^{-1}$ obtained for a 1:1 electrolyte in the same solvent confirmed the non-electrolytic nature of the complexes. IR spectroscopy gives evidence for the coordination of hydrazones to the metal centre in enolic form and hence act as dideprotonated tridentate ligands. EPR spectra of the compounds in DMF at 77 K displayed axial features with eight
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Hyperfine splitting and in all complexes except one follows the $g_{||} < g_{\perp}$ and $A_{||} > A_{\perp}$ relationship, is characteristic of an axially compressed $d_{xy}^1$ configuration. One of the oxovanadium compound is crystallized from methanol and single crystal X-ray diffraction studies showed that the compound is a centrosymmetric bis(µ-methoxy) bridged vanadium(V) dimeric complex.

Chapter 4 depicts the syntheses and characterization of some manganese and iron complexes of acylhydrazones. Two manganese and five iron complexes were prepared by refluxing 1:1 mixture of metal salt and corresponding acylhydrazones in methanol/ethanol for about 4-6 hours. The prepared complexes were characterized by elemental analyses, IR, electronic and EPR spectral studies, thermogravimetric analyses, conductance and magnetic susceptibility measurements. The non-electrolytic nature of the complexes is evident from their low conductivity values. Magnetic susceptibility measurements suggest that all the compounds are paramagnetic with central metal atom has a $d^5$ high spin configuration. Infrared spectral data suggest that the ligands are coordinated in amido form in complexes. In the EPR spectra of manganese complexes only one sextet is observed due to electron spin-nuclear spin coupling and the $g$ values are close to the $g$ value of a free electron. And the values of hyperfine coupling constants are consistent with an octahedral environment. Single crystals of one of the iron complexes were isolated from ethanol and it is found that in the compound iron is in a distorted octahedral environment.

Chapter 5 deals with the syntheses of six Cu(II) complexes and their characterization by different physicochemical techniques. The magnetic susceptibility measurements suggest that the compounds are paramagnetic and in close agreement with the spin only value for a $d^9$ copper system. Some complexes show substantial low magnetic moment may be due to the coupling of two magnetic centers suggesting dimeric nature to these complexes. In the IR spectra
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of the free ligands, the carbonyl and azomethine bands are observed in the region 1630-1650 cm\(^{-1}\) and 1600-1605 cm\(^{-1}\) respectively. In the infrared spectra of the all six complexes there are no bands due to carbonyl group. Upon complexation, the stretching vibrations of azomethine bond are found to be weakened due to coordination with copper centre, *ie.* the ligands were coordinated in iminol form. In the electronic spectra of the complexes weak *d*-*d* bands are observed. EPR spectra of the complexes were taken in polycrystalline state at 298 K, DMF at 298 K and 77 K. The *g* value obtained from EPR spectral assignments are consistent with the single unpaired electron is in the *d*\(_{x^2-y^2}\) orbital. Single crystals of one of the complexes are separated from methanol and the X-ray diffraction studies showed that in the compound, Cu is in a distorted square pyramidal environment. Packing of the compound is stabilized by strong π–π stacking interactions. In addition to the π–π stacking interactions, significant C–H···π interactions and hydrogen bonding are also present.

**Chapter 6** describes the syntheses and characterization of four zinc complexes. All the complexes are non-electrolytic as well as diamagnetic compounds. In all the complexes except one, ligands are coordinated in the iminol form.

**Chapter 7** explains the syntheses and characterization four dioxomolybdenum complexes. The \(^1\)H NMR and IR spectral data indicate tridentate nature of the ligands through enolization. IR spectra provide information about the dimeric nature of the complexes. The thermal analyses of the complexes showed the presence of lattice water in some of the complexes.