INTRODUCTION

The present thesis is an embodiment of the development of heterobimetallic chemistry of manganese and ruthenium. Hence, it appears pertinent to mention the importance of manganese and ruthenium in general and to describe the characteristic features of bonding properties of dihydrazones and then literature survey on dihydrazones metal complexes.

Manganese is an essential cofactor of green plant photosynthesis in photosystem II for the oxidation of water to dioxygen. Another important role of manganese is as the active catalytic centre in mitochondrial and several bacterial superoxide dismutases [1]. Manganese also plays a central role in an azide sensitive catalase [2]. Besides this, it occurs in some enzymes. Some multinuclear enzymes like arginase also require manganese to show their biological activity [3].

The role of manganese in our natural ecosystem is far more important. Manganese is known to be a key player of water-oxidation, a process that occurs during the natural photosynthesis [4]. Plants use an extensive array of photopigments in photosystem-II, 4 manganese ions, calcium and chloride. In photosystem-II, the water oxidizing enzyme uses water as an electron source. Therefore, it provides an unlimited source of electron to the entire biosphere.

The key player in water oxidation is a triad composed of a multimer of chlorophyll, (named P₆₈₀), a redox-active aminoacid (named tyrosine) and a Mn cluster composed of 4 Mn ions of high valence (the oxygen evolving complex, OEC). In the PSII, the tetramanganese complex serves as an electron donor.
Upon the absorption of photon, $P_{680}$ is excited and loses an electron leading to formation of $P'_{680}$. This is the first step of the conversion of light into chemical energy. $P'_{680}$ is transformed reversibly into the original photosynthesizer $P_{680}$ by receiving an electron from the tetramanganese complex. Further it has been established that $O_2$ evolution continues even when some of the manganese atoms are replaced with other divalent metal ions which restore electron transportation in PSII [5].

Our entire ecosystem is dependent on this process for the harvesting of the solar energy. Solar energy emerges as one of the most promising source for future sustainable production of fuel and electricity. The concept of natural photosynthesis can be used to build an artificial system which can harvest solar energy. This system should convert solar energy into fuel, such as hydrogen which could be stored in a chemical form. However, at present no system is known which operates on the principle of the photosynthesis of green plants. Fundamental research work is clearly required in this area. In nature, the solar energy is converted into chemical energy with water as electron source. The efficiency in the crucial steps is remarkably high. The construction of artificial system that exactly mimics these reactions remains a great challenge to chemists.

If a successful mimetic system could be made, much would be learnt at the fundamental level. Furthermore and potentially very importantly, we would have new tools to better exploit solar energy for the generation of fuels and electricity.

Ruthenium exhibits a wide range of oxidation states in its compounds and complexes stabilized by a wide variety of co-ordinating ligands. These varying oxidation states control the chemistry of the metal. Ruthenium-Schiff base complexes, particularly those containing oxygen and nitrogen as donor atoms, are found to be very efficient catalysts in oxidation reactions. High
valent polypyridyl ruthenium oxo-complexes have been found to be stoichiometric or catalytic oxidants.

Thus, the complexes of ruthenium have been widely explored because of their potential in electron transfer reactions [6] and excited state redox properties that renders their potential application in areas as diverse as solar energy conversion [7], artificial photosynthesis and test theories of photophysics.

Further, because of photophysical and photochemical properties of ruthenium complexes, it has been suggested that they might find applications in many fields, like use as semiconductors in solar energy conversion [8].

Ruthenium complexes have attracted much attention not only because of their favourable photophysical and photochemical properties but also because of their potential ability as molecular switches [9] in photodynamics, chemotherapy and for charge transport through DNA [10, 11]. The luminescent properties [12] of ruthenium complexes have rendered their applications as bioanalytical species [13]. The rational design of Ru(II) complexes containing a biotin moiety have been characterized recently as a new class of species.

Bimetallic ruthenium complexes present, perhaps, the best functional model for the chemistry associated with the manganese proteins. In this scheme, a ruthenium(III) dimer undergoes oxidation by either chemical or electrochemical means to produce dioxygen from two coordinated water molecules. During this process, the ruthenium atoms cycle reversibly between d⁵ and d³ configurations. The same is, probably true of the photosynthetic manganese centres. The ruthenium complex draws particularly more attention because it presents the oxidative portion of the popular [Ru(bpy)₃]²⁺ sensitized photosystem [14]. The significance of ruthenium complex is that they can form the core of new
polymetallic systems that may have applications in excited state energy and
electron transfer reactions [15].

If some complex systems containing manganese and photosensitizer
ruthenium could be prepared, this may undergo an intermolecular electron
transfer in the presence of an electron acceptor, in solution from photoexcited
state of Ru$^{II}$ to an acceptor followed by an intermolecular electron transfer from
coordinated Mn complexes. This will lead to regeneration of the Ru$^{II}$ and
oxidation of Mn centre in the complex. The manganese centre then may receive
electron from coordinated water molecules leading to its oxidation to molecular
dioxygen and production of H$^+$ ions which could be restored in the chemical form.

In view of the above stated importance of manganese and ruthenium and
absence of work on ruthenium complexes derived from dihydrazones, present
study has been undertaken, as a part of the training programme. Further, as the
monometallic complexes serve as precursor in the synthesis of heterobimetallic
complexes, it was imperative to synthesize and characterize them as well.
Accordingly, the study of monometallic and heterobimetallic manganese and
ruthenium complexes of the polyfunctional dihydrazones has been undertaken and
the present thesis embodies the results of such an investigation.

The study could develop into a very wide field. The present investigation is
restricted to only manganese and ruthenium and specific dihydrazones,
disalicylaldehyde adipoyldihydrazone (slah$H_4$) and bis(2-hydroxy-1-
naphthaldehyde)adipoyldihydrazone (npah$H_4$).

The reactions have been carried out in neutral and alkaline methanol media
at room temperature, higher temperature or under reflux. A number of
monometallic complexes of manganese and ruthenium from slah$H_4$ and npah$H_4$
have been synthesized under different experimental conditions. The
compositions of the complexes have been established based on data obtained
from analytical studies. The structural assessment of the complexes have been carried out on the basis of molar conductance, magnetic moment data, EPR, electronic, infrared and \(^1\)H NMR spectroscopic studies. Electrochemical studies of some complexes have also been done. These results are presented in chapter III to VI.

A chapter-wise summary of the work and references have also been given at the end.

DESCRIPTION OF LIGANDS

The ligands disalicylaldehyde adipoyldihydrazone (slahl\(_4\)) and bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (npah\(_4\)) selected in the present study have been derived from condensation of adipoyldihydrazone with salicylaldehyde and 2-hydroxy-1-naphthaldehyde. These contain four methylene flanked by keto groups in addition to other functional groups like amide, azomethine and phenol functions, each in duplicate. All of the donor atoms because of their symmetrical character have equal probability of taking part in coordination. The ligands can react with the metal ions in keto, keto–enol and enol forms respectively.

Thus because of the presence of as many as eight bonding sites, its ability to exhibit keto-enol tautomerism in the complexes and its ability to offer chemically flexible ligand framework due to free rotation of the two hydrazone groupings about C-C single bond, it can bound to metal ions in several different ways as under:
i) It may function as a neutral bidentate ligand coordinating either through two carbonyl oxygen atoms (I) or the two secondary amine nitrogen atoms (II), OH groups remaining hydrogen bonded in the complexes.

(ii) It may function as monobasic tridentate ligand coordinating through one hydroxyl oxygen, one azine group nitrogen and one >C=O group oxygen atom (III) while the other half portion of the molecule remaining unbonded.

(iii) It may function as a dibasic tetradentate ligand coordinating through the two hydroxyl oxygen atoms and the azine group nitrogen atoms (IV), the two carbonyl atoms remaining unbonded.
It may act as a dibasic hexadentate ligand bonding to the same metal ion through two hydroxyl oxygen, two azine nitrogen and two carbonyl oxygen atoms (V).

It may function as a dibasic octadentate ligand bonding to the same metal ion through all the available bonding sites (VI) but such a probability is ruled out on account of the simultaneous coordination of the secondary amine nitrogen and carbonyl oxygen to the same metal or even different metal atoms due to the steric considerations and inductive effect.

When the ligand undergoes enolization as shown below it may afford newer bonding possibilities. In this form it can act as dibasic tridentate (VII), dibasic tetradentate (VIII), dibasic pentadentate (IX) and tetrabasic hexadentate (X) ligand bonding to the same or different metal ions. In the enolized form it can also act as a binucleating or polynucleating ligand.
It may also coordinate to the metal ion in keto-enol (XI) and enol (XII) forms involving active methylene proton in enolization.
(viii) It may function as a tetrabasic octadentate ligand bonding to the same metal ion through all the available bonding sites (XII), but such a probability is also ruled out on account of the reason cited above at (v).

The dihydrazone can exist in the metal complexes either in the staggered-configuration (XIII) or cis-configuration. In cis-configuration, the dihydrazone can adopt either syn-cis configuration (XIV) or anti-cis configuration (XV).

All these possibilities can actually be realized in practice if the nature of the metal salt, mole ratio of the metal ion and the ligand, the nature of the counter cation and anion, reaction medium, pH and temperature are varied.
LITERATURE SURVEY

Hydrazine is a potential ligand which functions in metal complexes as monodentate, bidentate chelating and bridging ligand. The coordination behaviour of hydrazine is modified by substitution of one of the hydrogen in hydrazine by an acyl group, which provides additional bonding sites of carbonyl oxygen atoms, the resulting -CONH- group is capable of existing in keto-enol equilibrium. In such monoacyl hydrazines, the bridging character of hydrazine is lost and the studies have revealed that such derivatives act as bidentate ligands coordinating through carbonyl oxygen and -NH₂ groups.

Further, condensation of N-acyl hydrazines with aldehyde and ketones give acyl-hydrazones (Schiff bases). In such ligands basicity of nitrogen atoms in hydrazine residue is considerably reduced by substitution on either side. A variety of such hydrazones can be prepared in which the number of bonding sites can be increased as desired by changing acyl groups. Condensation of acylhydrazines with an o-hydroxy aromatic aldehyde and ketones enhances chelating tendencies of the acylhydrazones. The Schiff bases derived from monoacyl and aroylhydrazines with hydroxyaldehydes and ketones form 1:1 and 1:2 (metal:ligand) complexes can function either as a monobasic bidentate [16], monobasic tridentate [17] in keto form [17, 18] or dibasic tridentate in enol form [19, 20] and yield dimeric or polymeric chelates in which they coordinate to metal ion through >C=O and >C=N groups besides bonding through -OH group. Closely related to monoacyl, aroyl-, and pyridoyl-, hydrazones are acyl-, aroyl- and pyridoyl, dihydrazones containing same donor group but each in duplicate, which increases their bonding potentialities. In such dihydrazones, the two hydrazone parts may be linked to one another either directly or by methylene chains of varying length or phenyl or pyridyl groups.
The dihydrazones can be obtained from condensation of acyl-, aroyl- and pyridoyl- dihydrazines [R(CONHNH₂)₂; R = O, -(CH₂)ₙ, –C₆H₄<, C₃H₃N<] with o-hydroxy aromatic aldehydes and ketones. Another category of the dihydrazones can be obtained from condensation of dialdehydes [R(CR₁O)₂, R = O, -(CH₂)ₙ, -C₅H₃N<, R₁ = alkyl groups] with mono acyl-, aroyl-, pyridoyl- and quinaldinoyl- hydrazines. Accordingly, the literature survey is presented under the following two major sections.

A) Complexes of dihydrazones derived from condensation of acyl-, aroyl-, and pyridoyl- dihydrazones with simple and o-hydroxy aromatic aldehydes and ketones.

B) Complexes of dihydrazones derived from condensation of dialdehydes with mono acyl-, aroyl-, pyridoyl- and quinaldinoyl- hydrazines.

Sacconi [21] has isolated a series of diamagnetic nickel(II) complexes of dihydrazones obtained from condensation of aliphatic dicarboxylic acid dihydrazides with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, o-aminobenzaldehyde and o-hydroxyacetophenone. He showed that the hydrazones react in the enol form with Ni(OAc)₂ in aqueous alcoholic ammonia as bis tridentate complexing agents.

Aggarwal and Singh [22] isolated complexes of the compositions [VO(LH₂)SO₄], [VO(LH₂)Cl₂], [VO(LH₂)py]SO₄ and M(LH₂)Cl₂ (where M = Zn(II), Cu(II), Ni(II) and Co(II)) from reaction of vanadyl sulphate and chloride and metal(II) chloride with bis(acetone)oxaloyldihydrazone, bis(acetone)malonoyldihydrazone and bis(acetone)succinoyldihydrazone in alcoholic medium. The complexes [VO(LH₂)]SO₄, [VO(LH₂)]Cl₂ were proposed to have square pyramidal stereochemistry while the remaining complexes were proposed to have octahedral stereochemistry.
Iskander and coworkers [23] isolated the metal(II) complexes of the composition \( \text{M}(\text{LH}_3)\text{X}.\text{nH}_2\text{O}, \text{M}_2(\text{LH}_2)\text{X}_2.\text{nH}_2\text{O}, \text{M}(\text{LH}_2).\text{nH}_2\text{O} \) and \( \text{M}(\text{LH}_2).\text{nH}_2\text{O} \) (where \( \text{M} = \text{Cu}(\text{II}), \text{Ni} (\text{II}), \) and \( \text{Co}(\text{II}); \text{X} = \text{Cl}, \text{Br}, \text{I} ) \) from reaction of the metal (II) salts with dihydrazones \( (\text{LH}_2) \) derived from condensation of salicylaldehyde with acyldihydrazines containing methylene backbone varying from (1) to (5) under different experimental conditions. They assigned a pseudo-octahedral stereochemistry for the nickel(II) complexes \([\text{Ni}(\text{LH}_3)\text{X}].\text{nH}_2\text{O}\) (\( \text{X} = \text{Cl}, \text{Br}, \text{I}) \) and \([\text{Ni}_2(\text{LH}_2)\text{Cl}_2].2\text{H}_2\text{O}\) on the basis of magnetic moment data and spectral studies. The latter complexes change to penta-coordinated state on dehydration. However, five coordinate structure was proposed for the nickel(II) complexes \([\text{Ni}(\text{LH}_2)]\text{nH}_2\text{O}\) as against a distorted octahedral structure for the corresponding cobalt(II) analogues. On the other hand, Kapoor and coworkers [24] suggested that the nickel(II) complexes \([\text{Ni}(\text{LH}_2)].\text{nH}_2\text{O}\) have octahedral stereochemistry. Anomalous magnetic behaviour of the nickel complexes \([\text{Ni}(\text{L})].\text{nH}_2\text{O}\) (\( \mu_{\text{eff}} \) values lying in the range 1.65-1.70 B.M) is ascribed to arise due to the presence of two magnetically non-equivalent sites in the same unit cell. All the cobalt(II) complexes are proposed to have octahedral stereochemistry. The copper complexes \([\text{Cu}(\text{LH}_3)\text{X}].\text{nH}_2\text{O}\) and \([\text{Cu}_2(\text{LH}_2).\text{X}_2].\text{nH}_2\text{O}\) are proposed to have square pyramidal stereochemistry. The low magnetic moment values than spin-only values attributed to superexchange interactions through the oxygen bridges.

Narang and Lal [25] have described complexes of disalicyldiminesuccinamide \((\text{H}_2\text{L})\) and \( \text{N}, \text{N}-\text{Bis(o-hydroxyacetophenone-imine)succinamide} \) \((\text{H}_2\text{J})\) of the types \( \text{ML}, \text{MJ}', \text{M(HL)Cl}, \text{M(HJ)Cl} \) and \( \text{M'(HL)}_2 \) (where \( \text{M} = \text{Cu}(\text{II}), \text{Ni}(\text{II}) \) or \( \text{Co}(\text{II}) \) and \( \text{M}' = \text{Ni}(\text{II}) \) or \( \text{Co}(\text{II}) \)). The complexes are proposed to have either octahedral stereochemistry or square planar stereochemistry.
Narang and Lal [26] have reported mono and binuclear zinc(II) complexes $\text{Zn(HL)Cl}$ and $\text{Zn}_2(\text{L-2H})$ derived from multidentate acyldihydrazone ligands ($\text{H}_2\text{L}$). The reaction medium, zinc salts and ligand geometry are shown to influence the composition and stereochemistry of the complexes. The zinc centres were proposed to have octahedral as well as tetrahedral stereochemistry.

Polymeric metal (II) complexes [27] of the type $\text{M}_2\text{L}$, derived from dihydrazones obtained from condensation of oxaloyldihydrazone, succinoyldihydrazone and phthaloyldihydrazone with salicylaldehyde or o-hydroxyacetophenone have been described by the above authors. The anomalously low magnetic moments of some complexes are related to M-M interactions via oxo-bridge structure.

Narang and Lal [28] have prepared and characterized the metal(II) complexes $\text{M(H}_2\text{J)}$, $\text{M(H}_2\text{K)}$, $\text{M(H}_3\text{J)}\text{Cl}$, $\text{M(H}_3\text{K)}\text{Cl}$; $\text{M}_2\text{J}$, $\text{M}_2\text{K}$ and $\text{M}_2(\text{HK})(\text{CH}_3\text{COO})$ (where $\text{M} = \text{Cu(II)}, \text{Ni(II)}$ and $\text{Co(II)}$) derived from di(salicylaldimine)malonamide ($\text{H}_4\text{K}$) and the zinc(II) complexes $\text{Zn(H}_2\text{L)}$ and $\text{Zn}_2(\text{L})$ from a number of multidentate acyldihydrazones ($\text{H}_4\text{L}$).

Narang and coworkers [29] synthesized new series of polymeric cobalt(II) complexes of the type $\text{Co}_2(\text{L}).n\text{H}_2\text{O}$ from reaction of metal(II) acetate and dihydrazone ($\text{LH}_4$) where $\text{LH}_4$ is bis(o-hydroxyacetophenone)-oxaloyldihydrazone or bis(salicylaldehyde)oxaloyldihydrazone, bis(o-hydroxyacetophenone)succinoyldihydrazone in the ratio 4:1 (metal:ligand) in ethanol under reflux. The complexes have been proposed to possess polymeric structure with strong Co-Co interactions with planar dispositions of donor atoms around metal centres.

Sahni and coworkers [30] synthesized and characterized complexes of the type $[\text{M(}\text{LH}_2\text{)]X}_3$ (where $\text{M} = \text{Cr(III)}, \text{Mn(III)}, \text{Fe(III)}$ or $\text{Co(III)}$; $\text{X} = \text{Cl}, \text{NO}_3$ or
(OAc)) from reaction of metal(III) salt with N, N-dibenzylidene dipicoline acid hydrazone \((LH_2)\) in ethanol medium. The ligand acts as a pentadentate unit having coordination sites at pyridine nitrogen, amide oxygens and hydrazinic nitrogens or azomethine nitrogens. In this context, it is important to mention that these authors [31] have also claimed that dipicolinic acid dihydrazine behaves as pentadentate ligand. On the other hand, Dutta and Sarkar [32] have argued in favour of neutral tridentate behaviour of this ligand in which it can function either as a \((NNN)\) or as \((ONO)\) donor.

Kapoor and coworkers [33] have studied reaction of vanadyl chloride and dipicolinic acid dihydrazine in presence of acetylacetone or other \(\beta\)-diketones in ethanol and acetic acid. They isolated brown solid complexes of macrocyclic ligand \(\text{bis}(\beta\text{-diketone})\text{dipicolinoyldihydrazone}\). On the other hand, they isolated a non-macrocyclic pyrazole derivative when reaction of vanadyl chloride was carried out with the preformed \(\text{bis}(\beta\text{-diketone})\text{dipicolinic acid dihydrazine}\). Similar products [34] were also isolated in case of zirconium(IV).

Teotia and Rana [35] synthesized complexes \([M(L)(H_2O)_2]\) \((M = \text{Cu(II)}, \text{Ni(II)} \text{and Co(II)}\) of the above macrocyclic ligands by treating a methanol solution containing acetylacetone and 2, 6-dipicolinic acid hydrazide and the appropriate metal chloride. The IR spectra indicated condensation of both the oxygen atoms of acetylacetone with NH groups of dihydrazine. The electronic spectral bands agree reasonably well with five coordinate geometry.

Kapoor and coworkers [36] synthesized a number of metal(II) and metal(III) complexes from the reaction of metal(II) and metal(III) salts with dihydrazones obtained from condensation of salicylaldehyde with oxaloyldihydrazone, malonoyldihydrazine and succinoyldihydrazine under different experimental conditions. The trivalent metal ions are found to yield complexes having compositions \([M_2LX_2].nH_2O\) and \([M_2(LH_2)X_4].nH_2O\) \((M =\)
Cr(III), Fe(III) and Mn(III); X= Cl, NO₃, OAc, OH) while the bivalent metal ions were found to form complexes having compositions [M(LH₂)] and [ML(H₂O)₄] (M = Mn(II) and Fe(II)). The dihydrazones are suggested function as dibasic and tetrabasic hexadentate binucleating ligands. In Cr(III) complexes were characterized by Mossbauer spectroscopy as well.

Narang and Yadav [37] studied reaction of aluminum(III) salts with several dihydrazone ligands in aqueous medium at controlled pH and characterized the resulting complexes by infrared spectroscopy. The complexes are suggested to be polymeric with dihydrazones coordinated in the keto form.

Narang and Dubey [38] have described Zn(II), Cu(II), Ni(II) and Co(II) complexes of solid polymers derived from glyoxal and organic acid dihydrazides. They have discussed the structure of the complexes in the light of magnetic moment, electronic and IR spectral studies.

Yacouta and coworkers [39] studied the complexation behaviour of uranyl ion with various dihydrazides and their dihydrazones obtained from condensation of simple o-hydroxyaromatic aldehydes and ketones with dihydrazides. They isolated several monometallic and bimetallic uranyl complexes and characterized them by various physico-chemical data and spectroscopic studies. They also studied effect of excess acetate ion on complex formation.

Lal and coworkers [40] have prepared several homotrinuclear complexes having general formula [M₃LCl₂(H₂O)₃] (where M = Mn(II), Co(II) or Ni(II) from bis(acetophenone)-2, 6-dipicolinoylidihydrazone (LH₄) in alcoholic medium by adjusting pH to ~8 by KOH. The complexes show \( \mu_{\text{eff}} \) values much less than those expected for the high-spin metal ions possibly due to metal-metal interaction and antiferromagnetic exchange. The complexes are proposed to have mixed six-coordinate octahedral and five coordinate square...
pyramidal stereochemistry.

Narang and Singh [41] have synthesized polymeric complexes M(L2H)nH2O (where M = Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); L = A, B) from bis(2-hydroxy-1-naphthaldehyde)-oxaloyldihydrazone (A) and bis(2-hydroxy-1-naphthaldehyde)-malonoyldihydrazone (B) by solid-solution reaction. All of the complexes were suggested to have distorted octahedral stereochemistry.

Lal and coworkers [42] studied reaction of uranyl acetate with the above dihydrazones (H4L) in aqueous–alcoholic media and isolated complexes of the type (UO2)2L6H2O. The dihydrazones coordinate to the metal centre in enol form. They have studied the effect of complexation on the coupling of >C=O vibrations, in enolized form and of ligand coordination to the uranyl ion as a function of the number of methylene group by comparing the asymmetric stretching vibrations of the uranyl ion in various complexes recorded under identical conditions.

Lal and Das [43] studied reaction of uranyl nitrate and acetate with dihydrazones (H4L) (where H4L = disalicylaldehyde-oxaloyldihydrazone (H2L), -malonoyldihydrazone (H4B), -succinoyldihydrazone (H4C), -glutoyldihydrazone (H4D), -adipoyldihydrazone (H4E) and phthaloyldihydrazone (H4F) in 3:1 molar ratio in alcoholic medium. The complexes [(UO2)2(H2L)(NO3)2(H2O)4].2H2O and [(UO2)2(H2L)(CH3COO)2-(C2H5OH)2].C2H5OH have been isolated and characterized.

Lal and coworkers [44] synthesized copper(II) complexes Cu2(L)nH2O and dioxouranium(VI) complexes [(UO2)2(H2L)(C2O4)]n.2nH2O of the above dihydrazones. The C2O42− group is suggested to coordinate to the uranium centre retaining its D2h symmetry.

Lal [45] synthesized a series of uranyl complexes of the composition
[UO₂(LH₃)₂]nH₂O from above reaction of uranyl nitrate with salicylaldehyde and acyl- and aroyl-dihydrazines in 1: 4: 2 molar ratio in ethanol medium.

Lal and coworkers [46] studied reactions of disalicylaldehyde adipoyldihydrazone with uranyl nitrate and uranyl acetate in aqueous and ethanol media under different experimental conditions. The complexes of the compositions

[UO₂(H₂L)(H₂O)]ₙ, [UO₂(H₂L)₂]ₙ.3nH₂O,
[UO₂(H₂L)(CH₃COO)]ₙ.3nH₂O,
[UO₂Zn(L)(H₂O)]ₙ.2nH₂O,
[(UO₂)₂(H₂L)(C₂O₄)]ₙ.2nH₂O,
[[UO₂]₃(L)(py)₂(H₂O)₄],
[(UO₂)₂(HL)(OAc)(H₂O)]ₙ.nH₂O,
[(UO₂)₃(L)(CH₃COO)₂(H₂O)₂]ₙ.2H₂O,
[(UO₂)₂(L)(py)₂(H₂O)₂]ₙ.xnH₂O (where py = pyridine or α-, β-, γ- picoline; x = 0, 1) have been isolated and characterized. In these complexes the ligand functions as a bridging monobasic tetradeinate, dibasic hexadentate and tetrabasic hexadentate ligand and exhibits keto-enol tautomerism.

Lal and coworkers [47] have described dioxouranium(VI) and zinc(II) complexes [M(H₂L)(H₂O)₂]n.2nH₂O (where M = UO₂²⁺, Zn²⁺) of bis(o-hydroxynaphthaldehyde)oxaloyldihydrazone (H₂L). Dioxouranium(VI) complex is proposed to be eight coordinate involving coordination of dihydrazone in the enolic form with cis-configuration while the zinc complex is proposed to be octahedral involving coordinated dihydrazone in enolic form in the staggered-configuration. The naphtholic -OH groups are shown to be non-coordinated. They have, further, synthesized dioxouranium(VI) complexes [UO₂(H₂L)]ₙ.2nH₂O and [(UO₂)₂(L)(H₂O)₆]ₙ [48] from reaction of uranyl nitrate with preformed bis(o-hydroxynaphthaldehyde)oxaloyldihydrazone in a 3:1 molar ratio in aqueous and ethanol media, respectively, under reflux. Based on the splitting of the δ-NH- signal in monometallic complex and δ-CH=N signal in both the complexes into quartet as compared to the singlet in free
dihydrazones, the complexes are proposed to exist in chair conformation with
the anti-cis-configuration of dihydrazones involving eight coordinated uranium
atoms, respectively.

The complexes $\text{Na_4[(UO_2)_6(L)_2(OAc)_4(H_2O)_4]}\cdot4\text{H_2O}$ and
$\text{Na_4[(UO_2)_6(L)_2F_4(H_2O)_4]}$ [49] obtained from the same ligand have also been
described by them.

Patil and Kulkarni [50] and others [51] obtained complexes of the type
$[\text{UO}_2\text{L}_n\cdot\text{nH}_2\text{O}]$ from interaction of uranyl acetate and disalicylaldehyde
thiocarbohydrazones (H$_2$L) and established their structure by $^1$H NMR and IR
spectroscopic studies.

Kapoor and coworkers [52] studied reactions of malonoyldihydrazine and
phthaloyldihydrazine with $\beta$-diketones in the presence of dioxouranium(VI)
cation which appears to function as a metal template. This facilitates
condensation of dihydrazides with diketones giving macrocyclic ligands which
coordinate to the metal centre leading to the formation of several
dioxouranium(VI) complexes. The formation of a macrocyclic ring was
confirmed from infrared spectroscopic studies. However, when
dioxouranium(VI) nitrates is treated with the condensation product of
phthaloyldihydrazine and acetophenone, an entirely different pyrazole
derivative is formed.

Sahoo and coworkers [53] have synthesized several first series transition
metal complexes from several dihydrazones. The complexes were characterized
by elemental analysis, physico-chemical data and spectral studies.

Pandey [54] reported a number of organometallic complexes derived from
pyridoyldihydrazones. In this study, he showed from IR spectral data that
dihydrazones coordinate to the metal centre in keto form through both $>\text{C=O}$ and
$>\text{C=N}$ groups.
Mahale and Havanur [55] studied dioxomolybdenum(VI) complexes of the composition \((\text{MoO}_2)_2(L)(\text{py})_2\) synthesized from dihydrazones \((\text{H}_4\text{L})\) obtained from condensation of several acyl-dihydrazines and substituted salicylaldehydes.

Panda and coworkers [56] synthesized heterobimetallic complexes \([\text{MNiM(BTDO)}_2\text{X}_2(\text{H}_2\text{O})_4].\text{nH}_2\text{O}\) (where \(\text{M} = \text{Ni(II)}, \text{Co(II)}\) and \(\text{Cu(II)}\); \(\text{X} = \text{Cl}, \text{NO}_3\); \(\text{n} = 0\) or \(0.5\) and \(\text{BTDO} = 1\), 8-Bis(2-oxophenyl)-2, 3, 6, 7-tetraza-4, 5-dimethyl-1, 3, 5, 7-octatetraene) from the precursor nickel complex nickel \([\text{bis(diacyclidihydrazone})\). The metal centres have been proposed to have octahedral stereochemistry.

Gopinathan and coworkers [57] have shown that the Schiff base, \((\text{HOC}_6\text{H}_4\text{CH}=\text{NNCO})_2\text{CH}_2(\text{H}_4\text{L})\) derived from the condensation of salicylaldehyde and malonyldihydrazine reacts with organotin chlorides to yield binuclear complexes of the type \(\text{R}_2\text{Sn}(\text{L})\text{SnR}_2\), where \(\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_6\text{H}_5, \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\) and \(\text{C}_6\text{H}_5\text{CH}_2\). The complexes have been characterized and the structures assigned on the basis of their elemental analyses, IR, \(^1\text{H}, ^{13}\text{C}, ^{119}\text{Sn}\) NMR spectra and X-ray crystallographic data. They studied the structure of the complex \([(\text{C}_2\text{H}_5)_2\text{Sn}(\text{OC}_6\text{H}_4\text{CH}=\text{NNCO})_2\text{CH}_2\) by X-ray crystallography. The crystal belongs to monoclinic space group 12/a.

Sacconi [58] studied reactions of biacetyl-bis(benzoylhydrazone) with nickel(II) acetate in alcohol in the presence of concentrated ammonia and isolated orange coloured biacetyl-bis(benzoylhydrazonato)nickel(II) complex and studied its reaction with pyridine [59]. The formation constant of complexes formed between biacetyl-bis(bezoylhydrazonato)nickel(II) and various alkyl amines [60] have been studied. Complexes of lead(II), lead(IV) and tin(IV) of the types \([\text{Pb}(\text{L})]\), \([\text{Pb}_2\text{Pb}(\text{L})]\), \([\text{Sn}(\text{L})_2]\), \([\text{phSn}(\text{L})\text{Cl}]\) and \([\text{ph}_2\text{Sn}(\text{L})]\) have been obtained by mixing methanol solutions of the appropriate metal salts and the
Pelizzi and coworkers [62] have studied reaction of copper(II) chloride dihydrate with 2, 6-diacetylpyridine-bis(picoloylhydrazone) (LH₂) in refluxing ethanol yielding dark green crystal of Cu₂(L)Cl₂·H₂O. IR spectral data indicate coordination of all the three pyridine nitrogens. The ligands behave as an octadentate bridging (NONNNNNN) donor. The authors have established the square pyramidal structure of the complex unequivocally by X-ray crystallography. The environment about one Cu(II) is made up of basal plane consisting of a chloride, two nitrogen atoms from the ligand (LH₂), an oxygen atom from second adjacent ligand molecule and another nitrogen atom from the same adjacent ligand molecule taking up the axial position. The environment around the second Cu(II) is made up of four nitrogen atoms from the first ligand molecule, while a chloride ion takes up apical site. Some authors [63] have isolated another series of complexes of the type M(LH₂)Cl₂·nH₂O (M = Mn(II), Co(II), Ni(II) and Cu(II)), by mixing chloroform solution of LH₂ and ethanolic solution of the metal chlorides in 1:1 molar ratio. Another Mn(II) compound MnL·9H₂O was obtained by adding, dropwise, a dilute NaOH solution to a warm ethanol–water solution containing LH₂ and MnCl₂·4H₂O in (1:1) molar ratio until pH~ 8.0. The compounds were characterized by magnetic moment data, electronic and IR spectroscopic studies.

The complex Mn(LH₂)Cl₂·5H₂O was shown to have pentagonal bipyramidal stereochemistry by X-ray crystallography [64]. On the basis of similarity of IR spectra of Cu(II), Ni(II) and Zn(II) complexes with that of Mn(II) complexes, a similar pentagonal bipyramidal stereochemistry was proposed for them also with ligand acting as a ONNNO donor and chloride or water molecules occupying apical positions. The complex MnL·9H₂O was also characterized by X-ray crystallography and shown to have pentagonal
bipyramidal stereochemistry.

Curtis and coworkers [65] and others [66] studied Cu(II) and Ni(II) complexes of acetylacetonebis(picolinoylhydrazone) and acetylacetonebis(isonicotinoylhydrazone). They carried out X-ray structural analysis of copper(II) complex of acetylacetonebis(isonicotinoylhydrazone) obtained from reaction of metal(II) salt, isonicotinoylhydrazine and acetylacetone and confirmed the square pyramidal stereochemistry.

Giordano and coworkers [67] isolated cobalt(II) and nickel(II) complexes of compositions $[\text{Co(LH}_2\text{(H}_2\text{O})(\text{NO}_3)\text{]}_2\text{NO}_3$ and $[\text{Ni(LH}_2\text{(H}_2\text{O})_2\text{]}(\text{NO}_3)_2\text{.2H}_2\text{O}$ from reaction of metal nitrates with 2, 6-diacetylpyridinebis(benzoylhydrazone) ($\text{LH}_2$) in 95% ethanol. The X-ray crystallographic study confirmed that the metal atoms are in pentagonal bipyramidal arrangement in the structural unit of the complexes.

Palenik and coworkers [68] isolated lanthanum complexes of composition $[\text{La(LH}_2\text{(H}_2\text{O})_3\text{]}$ from reaction of lanthanum nitrate and ligand in ethanol at 55 °C in the presence of water. The complex was characterized by infrared spectroscopy and X-ray crystallographic studies. They showed lanthanum to be eleven coordinated in these complexes. A decahedral arrangement of the donor atoms of the ligand is proposed around the lanthanum atom in the complexes.

Paolucci and coworkers [69] prepared a series of dioxidouranium(VI) complexes of 2, 6-diacetylpyridinebis(4-methoxybenzoylhydrazone) ($\text{H}_2\text{dapmb}$). The neutral compound of the composition $[\text{UO}_2\text{(dapmb)}]$ was formed in two different crystalline forms $\alpha$ and $\beta$, depending upon the experimental conditions. The geometries of the two forms of $[\text{UO}_2\text{(dapmb)}]$ are very similar, the only significant difference being the difference in the conformation of carbon atoms in a methoxy group. Seven fold coordination of uranium (VI) was established with the five donor nitrogen atoms in the equatorial plane.
Pelizzi and coworkers [70] isolated tin(IV) complexes of the composition \([\text{Snpr}_2(LH_2)]\) from reaction of \(n\)-propyltinchloride in anhydrous acetone under nitrogen atmosphere with boiling suspension of 2, 6-diacylpyridinebis(salicylhydrazone) \((LH_2)\) in dry methanol. The X-ray crystal structure study has established that tin atoms is seven coordinated in the complex with pentagonal bipyramidal arrangement of ligands atoms. The \(-\text{OH}\) groups remain uncoordinated.

Teotia and coworkers [71] have studied reaction of metal(II) salts \([M = \text{Cu(II)}\) and \(\text{Ni(II)}\)] with picolinoyl/isonicotinoyl-hydrazine in presence of acetylacetone. They isolated complexes of the compositions \([M(LH)X]\) \((M = \text{Ni(II)}, \text{Cu(II)}; X = \text{Cl, Br, NO}_3, \text{and NCS}, LH_2 = \text{acetylacetonebis(picolinoylhydrazone) or acetylacetonebis(isonicotinoylhydrazen})\). All the complexes have been established to have square pyramidal stereochemistry. Complexes \([M(LH)X_2]\) \((X = \text{Cl, Br, NO}_3, \text{NCS for M = Cu(II)}; X = \text{OAc, Cl, Br, NCS for Mn(III) and OH for Co(III)}\) were also prepared similarly [72] by them. The complexes have been suggested to have six-coordinated tetragonal structure.

Paolucci and coworkers [73] synthesized several complexes of 2, 6-diformylphenol bis(benzoylhydrazone) and its substituted derivatives with the bivalent metal ions \((M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}\) and \(\text{Zn(II)}\) and established their molecular structure by various physico-chemical techniques.

Dutta and coworker [74] isolated complex of the composition \([\text{VO(L)}]\) from reaction of \(\text{VO(acac)}_2\) with acetylacetonebis(benzoylhydrazone) \((LH_2)\) in acetone. The same ligand on reaction with \(\text{CoX}_2\) \((X = \text{Cl, Br})\) in anhydrous medium yielded blue coloured tetrahedral polymeric complexes \([\text{Co(LH)}_2X_2]\) [75]. However, in the presence of water, bromide salt yields pink coloured pseudo-octahedral \([\text{Co(LH)}_2\text{Br}_2(\text{H}_2\text{O})_2]\) complex. The dihydrazone
reacts with nickel(II) chloride in rectified spirit and yields diamagnetic, orange, yellow complex [Ni(L)] [76]. However, reaction with anhydrous NiCl₂ in warm anhydrous methanol gives a paramagnetic complex [Ni(LH₂)Cl₂] having trans-dichloro pseudo-octahedral structure. When this complex is exposed to moist atmosphere and over KOH, the partial dechlorination occurs giving the complex [Ni(LH)Cl]. The complex is proposed to have five coordinate structure. They also isolated complex [Zn(L)], [Cd(L).2H₂O] and [Pb(L)] from the interaction of appropriate metal acetate with the ligand in ethanol.

Snow and coworkers [77] studied the reaction of bis(acetylacetonato)-oxovanadium(IV) with benzoylhydrazine in dry methanol under dry nitrogen. They isolated bis(acetylacetonebenzoylhydrazonato)vanadium(IV). A trigonal prismatic geometry was verified for this complex.

Dutta and coworkers [78] showed that the reaction of VO(acac)₂ with benzoylhydrazine and related ligands in methanol, ethanol and methyl acetate yielded violet or almost black coloured bis(acetylacetonebenzoylhydrazonato)vanadium(IV) whereas reaction in acetone and ethyl methyl ketone yielded (acetylacetonebenzoylhydrazonato)oxovanadium(IV). While in the former complex, the abstraction of oxo-group has been suggested to occur, in the latter complex is retained.

Lanthanide complexes [79] of the type [Ln(L)(OH)(H₂O)] (Ln = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Ho(III), Er(III)) have been obtained in situ by refluxing biacetylbenzoylhydrazine and appropriate metal chloride in ethanol in the presence of a regulated quantity of NH₄OH. The ligand acts as a quadridentate ONNO donor in its enol form.

Pelizzi and coworkers [80] have isolated a new series of metal(II) complexes of type [M(LH₂)(H₂O)Cl] (M = Co(II), Ni(II), Mn(II), Cu(II) and
Zn(II) by mixing LH$_2$ and metal(II) chloride in ethanol in 1:1 molar ratio. With metal(II) acetates, the compounds of the type [ML] are obtained. The ligand reacts with metal centres in keto form in complexes [M(LH$_2$(OH)$_2$)Cl]Cl and enol form in complexes [ML]. Some of the complexes are characterized by X-ray crystallographic method as well. The complexes are shown to have pentagonal bipyramidal stereochemistry.

Dutta and coworkers [81] have studied the reaction of MoO$_2$(acac)$_2$ with benzoylhydrazine and related ligands in different solvents. They isolated the complex (benzoylhydrazine)(benzoylhydrazido)(acetylacetonato)molybdenum (VI) in dry methanol while in ordinary methanol, the complex (acetylacetonato)(cis-dioxo)molybdenum(VI)-μ-diol-(benzoylhydrazinato)(cis-dioxo)molybdenum(VI) dihydrate was isolated. They have shown that in dry methanol acetylacetone and hydrazines condense to give Schiff base complexes whereas no Schiff base formation occurs in ordinary methanol.

The Schiff bases derived from acetylacetone and 2-picolinoylhydrazide or isonicotinoylhydrazide are similar to one another and gave complexes of the type [UO$_2$L]Cl (where LH = Schiff base) with UO$_2$Cl$_2$. However, in 2-picolinoylhydrazone complex, the Schiff base coordinates through both azomethine nitrogen atom and pyridine nitrogen atoms while in the case of isonicotinoylhydrazone complex, the Schiff base coordinates through azomethine nitrogen atom and carbonyl oxygen atom [82].

On the basis of IR and conductivity data Dey et al [83] have reported the formation of [UO$_2$(LH$_2$)](NO$_3$)$_2$ (where LH$_2$ represents 1, 2-dimethylbis(4-methoxybenzoylhydrazone)). Similarly, they have reported the formation of [UO$_2$(LH$_2$)(NH$_3$)]NO$_3$ on acidification of [UO$_2$L] with HNO$_3$. Ligands are proposed to coordinate to the metal centres in keto as well as enol forms. Interaction of these complexes with neutral mono and bidentate ligands lead to the
formation of \([\text{UO}_2\text{L}(\text{A})_2]\) and \([\text{UO}_2\text{L}(	ext{AA})]\) (where, A = pyridine, picolines, methylamine, aniline, OPph; AA = en, ph, phen), respectively.

Marangoni and coworkers [84] synthesized mercury(II) complex with 2, 6-diacetylpyridinebis(2-pyridoylhydrazone). They carried out X-ray structural analysis of the complex and confirmed its pentagonal bipyramidal stereochemistry.

Pelizzi and coworkers [85] synthesized nickel(II) complex \([\{\text{Ni}(\text{H}_2\text{aps})\text{(OH)}_2\}_2\text{Cl}_2\}2\text{dmf.5H}_2\text{O}\) and cobalt(II) and copper(II) complexes, viz., \([\text{Co}(\text{H}_2\text{dps})\text{(OH)}_2\}_2\text{Cl.4H}_2\text{O}\) of 2, 6-diacetylpyridinebis[2-semicarbazono]-propionylhydrazone] \((\text{H}_2\text{aps})\) and 2, 6-diacetylpyridinebis[2-semicarbazono]-acetophenoxyhydrazone] \((\text{H}_2\text{dps})\), respectively. In the nickel complex, the four atoms of semicarbazone system are not involved in coordination while in the cobalt complex, semicarbazone system does not participate in coordination. They established structure of the complexes by IR spectroscopy and X-ray crystallography.

Pelizzi and coworkers [86] studied the structure of a tetranuclear copper(II) complex \([\text{C}_{2}\text{z}(\text{dappc})(\text{OH})_2\}_2\{\text{Cu}_{2}\text{z}(\text{dappc})(\text{OH})_2\}_2\text{ClO}_4\}_2\cdot\text{ClO}_4\cdot2\text{H}_2\text{O}\) (I) and \([\text{Cu}_{2}\text{z}(\text{dapi})\text{Br}_2\}_2\) (II) derived from the polyfunctional ligand 2, 6-diacetylpyridinebis-(2-pyridinecarbonylhydrazone) \((\text{H}_2\text{dappc})\) and 2, 6-diacetylpyridinebis(2-(2-pyridine carbonylhydrazone)(phenylacetoxyhydrazone) \((\text{H}_2\text{dapi})\), respectively. The structure of compound (I) is built up of complex cations of formula \([\text{Cu}_{z}\text{z}(\text{dappc})(\text{OH})_2\}_2\text{ClO}_4\] and \([\text{Cu}_{2}\text{z}(\text{dappc})(\text{OH})_2\}_2\text{ClO}_4\] anions and uncoordinated \(\text{H}_2\text{O}\) molecules while that of the compound (II) consists of neutral unit of formula \([\text{Cu}_{2}\text{z}(\text{dapi})\text{Br}_2\}_2\) and solvating \(\text{H}_2\text{O}\) molecules. In both compounds two metal atoms are present for one hydrazone and the ligand is bideprotonated in complex (I) and trideprotonated in complex (II).

A monoperoxo complex of Schiff base \((\text{H}_2\text{C}_6\text{N} = \text{NHC}(\text{S})\text{CH}_2\text{C}_6\text{H}_3\}_2\text{LH}_2\),
has been reported by Tarafder et al. [87]. The complex \([\text{UO}_2\text{(O}_2\text{)}\text{L}]\) was prepared by treating uranyl nitrate with the Schiff base dissolved in a solution of KOH in 30 % H\(_2\)O\(_2\). The Schiff base behaves as dibasic NNSS tetradentate ligand, while peroxo group is bonded to the metal centre as bidentate chelating ligand.

Toshev and coworkers [88] reported the dioxouranium complex of diacetylbis(thiobenzoylhydrazone) in which uranium has a distorted pentagonal bipyramidal structure with the uranyl oxygen atoms at the axial positions.

Pelizzi and coworkers [89] synthesized copper complex of di-2-pyridyl ketone(phenylsemicarbazone)acetylhydrazone (H\(_2\text{psah}\)) and studied their structure by X-ray crystallography. They showed that the copper complex \([\text{Cu}_2(\text{psah})\text{Cl}]\cdot\text{H}_2\text{O}\) consists of pair of structurally distinct metal centres with different environments bound to the heptadentate hydrazone ligand and held together by a -N-N- bridge.

Katti and coworkers [90] synthesized a number of palladium(II) complexes from a series of phosphorous hydrazide and hydrazones. The complexes were characterized by elemental analysis. The structural assessment was carried out by NMR and IR spectroscopic studies. The structure of one complex was established by X-ray crystallography as well.

Lukyanenko and coworkers [91] have determined complex stability of Na\(^+\), K\(^+\), Rb\(^+\) and Cs\(^+\) ions with bis(benzo-15-crown-5) with acylhydrazide fragments in the linking chain in 95 % aqueous methanol. In all cases, the formation of 1:1 complex was observed. They studied biscrown ethers form more stable complexes than benzo-15-crown-5. The stability of biscrown ether complexes is substantially determined by the length of the linking chain. Biscrown ether with a glutaric acid residue in the linking chain exhibits striking potassium selectivity. High selectivity and stability of the
complexes are due to the increase of their sandwich structure rigidity resulting from the formation of H-bonds between acylhydrazide fragments.

Ji and coworkers [92] studied several dinuclear yttrium(III) and lanthanide(III) picrate complexes derived from acetylferrocenepyridine-2, 6-diformylhydrazone having the stoichiometric formula $\text{Ln}_2\text{L}_2\text{pic}_6.n(1\text{-C}_3\text{H}_7\text{OH}).m\text{H}_2\text{O}$ (pic = picrate anion, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, n = 2, m = 4; Ln = Er, Tm, Yb, n = 0, m = 2). These complexes were characterized by EPR, IR, UV, $^1\text{H}$ NMR spectra and molar conductance data. It was found that the ligand coordinates in keto form to the lanthanide ions. All the complexes described in the present study are 1:6 electrolyte in methanol.

Xiaozeng and coworkers [93] synthesized binuclear zinc(II) complex $[\text{Zn}_2\text{L}(\text{OAc})_2].\text{EtOH}$, from binucleating ligand 2, 6-diformylpyridine N-oxide bis(benzoylhydrazone) (L) via template reaction in alcohol. They characterized the complex by X-ray crystallographic studies.

Pelizzi and coworkers [94] synthesized six complexes of copper(II), nickel(II) and iron(II) from a chiral ligand 2, 6-diacetylpyridinebis[DL-hydroxy(phenyl)acetic]hydrazone ($\text{H}_4\text{dapm}$) and characterized them by spectroscopic studies. They established the structure of the nickel complex $[\text{Ni}(\text{H}_4\text{dapm})(\text{H}_2\text{dapm})].13\text{H}_2\text{O}$ by X-ray diffraction methods. The complex crystallized in the monoclinic space group C2/c. With the help of $^1\text{H}$ NMR spectroscopic studies, the existence of ligand in three forms i.e., meso DL and two enantiomeric DD and LL was established. The $^1\text{H}$ NMR spectrum of the complex $[\text{Ni}(\text{H}_4\text{dapm})(\text{H}_2\text{dapm})].13\text{H}_2\text{O}$ showed the presence of two inequivalent ligand molecules i.e., one in meso form and the other in DD or LL form.

Rana and coworkers [95] synthesized several manganese(II), iron(II),
cobalt(II), nickel(II) and copper(II) complexes of 2, 6-diacetylpyridine (benzylacetone)hydrazone (H₂L). The complexes have been shown to have composition [M(H₂L)X₂] (where M = Mn, Fe, Co, Ni and Cu; X = Cl, NO₃, SCN) and have been characterized by molar conductance, magnetic moment data, infrared and electronic spectroscopy.

Paolucci and coworkers [96] studied the interaction of potentially binucleating ligand 2, 6-diacetylpyridine(1-phthalazinylhydrazone) (H₂dapz), containing only nitrogen donor atoms, with nickel(II) copper(II) and zinc(II) salts. They showed that depending on the nature of the counter ions, Ni(II) and Cu(II) ions, selectively, enter in one of the two compartments present in the ligand. They isolated five series of mononuclear complexes [dapzM], [H₂dapzMCl₂], [HdapzMCl], [(H₂dapz)₂M][ClO₄]₂, [HdapzM][ClO₄], from reactions of metals acetates, metal chlorides and metal perchlorates respectively and the ligand. The complexes were characterized by analytical techniques and spectroscopic methods. Crystal structure analysis on the bisdeprotonated complex [dapzNi]₂ shows that the compound is dimeric with the metal ions octahedrally coordinated into the upper compartment and the pyridine nitrogens bridging the two nickel atoms.

Maurya and coworkers [97] synthesized binuclear dioxotungsten (VI) complexes of the type [(WO₂)₂L], where L is a flexibly bridged hexadentate tetra anionic Schiff base derived from condensation of methylene or dithiobissalicylaldehyde with isonicotinoylhydrazine, bezoylhydrazine, p-nitrobenzoylhydrazine and furoylhydrazine are reported. The IR and NMR spectral data suggests an oligomeric structure for these complexes in which each tungsten atom achieves a pseudo-octahedral structure via W=O→W bridging.

Lal and coworkers [98] synthesized the bimetallic manganese (II, III) and dioxouranium(VI) complexes [Mn₄(H₂L)₂(OAc)₄].4H₂O, [Mn₄(L)₂(H₂O)₈].4H₂O,
K₄[Mn₄(L)₂F₆(H₂O)]₂H₂O, [UO₂(H₂O)₄]₂[Mn₄(L)₂(OAc)₄].4H₂O and K₄[UO₂Mn₃(L)₂F₃(H₂O)₃] from bis(2-hydroxy-1-naphthaldehyde)oxaloyl-dihydrazone (H₄L). The complexes have been characterized by physical and spectral data. IR spectral data indicate that the dihydrazone coordinates to the metal centres in keto as well as enol forms in the anti-cis-configuration in all of the complexes.

Lal and Adhikari [99] synthesized the hexamer compound [(MoO₂)₂(L)H₂O].2H₂O from the reaction of MoO₂(acac)₂ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H₄L) in ethanol-acetonitrile in 3:1 molar ratio under reflux. The anti-cis-configuration of the dihydrazone moieties leads to the chair conformation of the complex.

Lal and coworkers [100] isolated the homobimetallic complex [(MoO₂)₂(L)].4H₂O (1) from bis(2-hydroxy-1-naphthaldehyde)oxaloyl-dihydrazone (H₄L) in the solid state. It reacts with Lewis bases pyridine and 3-picoline to form the complexes [{(μ₂-O)MoO₂}₂MoO₂(H₂L)].2D.4H₂O (where D = pyridine (py, 2); 3-picoline (3-pic, 3)) and with proton bases salicyloylhydrazine (sylshH₃) and isonicotinoylhydrazine (inhH₃) to yield the Mo(V) compounds [Mo₂(L)(sylsh)₂].5H₂O (4) and [Mo₂(L)(inh)₂(H₂O)₂].5H₂O (5), respectively. The complexes have been characterized by elemental analyses, molecular weight determinations, molar conductance, magnetic moment, EPR, electronic, infrared and ¹H NMR spectral studies. The complexes (4) and (5) are paramagnetic to the extent of 3.02 and 3.16 B.M. respectively.

Lal and coworkers [101] have synthesized the complexes of the type [(UO₂)₄(L)₂(H₂O)₈].4H₂O (1), K₄[(UO₂)₄(L)₂(OAc)₄(H₂O)₄].4H₂O (2) and K₄[(UO₂)₄(L)₂F₄(H₂O)₄] (3) from bis(o-hydroxynaphthaldehyde)oxaloyl-dihydrazone (H₄L) and characterized by elemental analysis, molecular weight determination, molar conductance data and electronic, IR and ¹H NMR
Lal and Kumar [102] have synthesized an unstable monomeric yellow complex of type \([(\text{MoO}_2)_2(\text{CHsalmlhH}_4)(\text{H}_2\text{O})_2]_{\cdot}\text{H}_2\text{O}\) \{complex (A)\} from the reaction between bis(acetylacetonato)dioxomolybdenum(VI) and disalicylaldehyde malonyldihydrazone \((\text{CH}_2\text{salmlhH}_4)\) in ethanol. This is transformed into an intermediate complex \([(\text{MoO}_2)(\text{CHsalmlhH})(\text{H}_2\text{O})]_2\cdot4\text{H}_2\text{O}\) \{complex (AB)\} after sometime. Ultimately a stable brown isomer complex \([(\text{MoO}_2)_2(\text{CH}_2\text{salmlh})(\text{H}_2\text{O})]_2\cdot4\text{H}_2\text{O}\) \{complex (B)\} is obtained. All the products have been characterized by various physico-chemical techniques and IR and \(^1\text{H}\) NMR spectroscopic studies.

Lal and coworkers [103] isolated the complexes of the composition \([\text{UO}_2((\text{H}_4\text{salligh})(\text{OAc}))_3\cdot\text{H}_2\text{O}\) and \([\text{UO}_2\text{Zn(salligh})(\text{H}_2\text{O})_2]\cdot2\text{H}_2\text{O}\) where \(\text{H}_4\text{salligh}\) refers to disalicylaldehyde oxaloyldihydrazone \((\text{H}_4\text{saloxlh})\), malonyldihydrazone \((\text{H}_4\text{salmlh})\), succinoyldihydrazone \((\text{H}_4\text{salmlsh})\), glutaroyldihydrazone \((\text{H}_4\text{salguth})\) and phthaloyldihydrazone \((\text{H}_4\text{salphth})\). The complexes have been characterized by molar conductance and spectral data.

Lal and coworkers [104] have synthesized the complexes \(\text{Na}_4[(\text{UO}_2)_4(\text{L})_2(\text{OAc})_4(\text{H}_2\text{O})_4]\cdot4\text{H}_2\text{O}\) (1) and \(\text{Na}_4[(\text{UO}_2)_4(\text{L})_2\text{F}_4(\text{H}_2\text{O})_4]\) (2) from bis(o-hydroxynaphthaldehyde)oxalodihydrazone \((\text{H}_4\text{L})\) and characterized by elemental analysis, molar conductance, electronic, IR and \(^1\text{H}\) NMR spectroscopic studies. On the basis of these studies, it is suggested that the fluoro complex exists in chair conformation in which coordination of both azomethine nitrogen atoms of the dihydrazone in cis-configuration to the same metal centre leads to coupling between azomethine protons. In acetato complex, the coordination of two hydrazone parts of the dihydrazone even in cis-configuration to different metal centres eliminates the possibility of coupling between azomethine protons and thus, its existence in chair conformation.
Lal and coworkers [105] have synthesized the monometallic complexes of the type [Zn₂(H₄L)₂(SO₄)₂], [Zn₂(H₂L)₂(H₂O)₂], K₂[Zn₂(H₂L)₂F₂] and the heterobimetallic complexes of the type [(UO₂)₂Zn₂(L)₂(H₂O)₆], K₄[(UO₂)₂Zn₂(L)₂F₄(H₂O)₂], [Cu₂Zn₂(L)₂(H₂O)₄] and K₄[Ca₄(Zn₂(L)₂F₄(H₂O)₂] and characterized by analytical, molar conductance, magnetic moment data, and electronic, EPR, IR and ¹H NMR spectroscopic studies. All of the complexes have been proposed to be dimer on the basis of molecular weight determinations. Monometallic complexes have been shown to contain the coordinated dihydrazone in syn-cis-configuration while the heterobimetallic complexes have been shown to contain the coordinated dihydrazone in the anti-cis configuration.

Fenton and coworkers [106] prepared green coloured nitrato complex of copper Cu₃(HL)(NO₃)₂.2CH₂OH.2H₂O from reaction of cupric nitrate with bis(salicylhydrazone) derived from the diethyl ester of iminodiacetic acid in methanol-chloroform solution. They also prepared dark green perchlorato complex [Cu₃(HL)(ClO₄)₂] from reaction of Cu(ClO₄)₂.6H₂O with the title ligand in absolute ethanol. The compound crystallized from DMSO solution was found to have the composition of [Cu₆(HL)₃(dms)₃(EtOH)(H₂O)₂].(ClO₄)₄.2H₂O. The structure of the perchlorato complex established that a coordination polymer has formed in which the repeat unit was based on six copper(II) atoms with an alternating mononuclear-dinuclear motive with the help of X-ray crystallography. All of the copper atoms were found to have the square pyramidal structure.

Lal and coworkers [107] synthesized homobimetallic and heterobimetallic complexes [Zn₄(LH)₂(OAc)₄].2H₂O (1), [Zn₄(L)₂(H₂O)₄].4H₂O (2), M₄[Zn₄(L)₂F₄(H₂O)₄] (where M = K for (3) and Na for (4), [UO₂(H₂O)₄]₂[Zn₄(L)₂(OAc)₄].2H₂O (5), M₄[Ca₄(UO₂Zn₃(L)₂F₄(H₂O)₄].4H₂O (where M = K for (6) and Na for (7)) from bis(2-hydroxy-1-naphthaldehyde)-oxaloyldihydrazone (LH₄). The structural assessment of the complexes was done.
by molecular weight determinations, molar conductance data, electronic, IR and 
$^1$H NMR spectral data. In the complexes, the dihydrazones has been suggested to 
coordinate to the metal centre in anti-cis-configuration in the keto as well as in 
enol forms.

Lal and coworkers [108] synthesized and characterized manganese(IV) and 
manganese(II) complexes $[\text{Mn}^{IV}(\text{L})(\text{H}_2\text{O})_2] \ (1)$ and $[\text{Mn}(\text{II})(\text{LH}_2)(\text{A}_2)] \ (\text{where A} = \text{H}_2\text{O} \ (2), \text{pyridine (py, 3), 3-picoline (3-pic, 4) and 4-picoline (4-pic, 5)}$ from 
$\text{bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone}$. The complex (1) has $\mu_B$
value equal 4.02 B.M which is in good agreement with the moments of the 
characterized manganese(IV) complexes. For the remaining complexes, the $\mu_B$
value falls in the range 5.90-5.85 B.M, a region characteristic of Mn(II)
complexes. The electronic spectra of the complexes show LMCT bands in 
the visible region and UV-visible border region. The Mn$^{IV}$ complex (1)
shows two resonances, a strong one near $g \approx 2.0$ and a weak one near $g \approx 4.9$
in its EPR spectrum. The $^{55}\text{Mn}$ hyperfine coupling constant for $g \approx 2.0$
signal is equal to 78 G which is closer to the values observed for Mn(IV) than for 
Mn(II). The EPR spectral features for the remaining complexes are characteristic
for Mn(II). In all of the complexes, the dihydrazone is suggested to 
coordinate to the metal centres in enol form.

Lal and coworkers [109] prepared manganese(IV) complexes
$[\text{Mn}^{IV}(\text{L})(\text{A})_2].2\text{H}_2\text{O} \ (\text{where LH}_4 = \text{bis(2-hydroxy-1-napthaldehyde)oxaloyl-}
dihydrazone and A = \text{H}_2\text{O} \ (1), \text{pyridine (py, 2), 2-picoline (2-pic, 3), 3-picoline}
(3-pic, 4), 4-picoline (4-pic, 5)}$ in ethanol by the template method directly 
from manganese(II) acetate, oxaloyldihydrazone $(\text{H}_2\text{oxh})$ and 2-hydroxy-1-
napthaldehyde. All of the complexes have $\mu_B$ values in the range 3.96-4.08
B.M. which are in good agreement with manganese(IV) complexes. Electronic
spectra of the complexes are dominated by ligand-to-metal charge
transfer (LMCT) transitions. In the polycrystalline phase at LNT, two resonances at $g \geq 2.0$ (strong) and $g \geq 4.9$ (weak) are observed. In the magnetically dilute glassy state, the $^{55}\text{Mn}$ hyperfine structure is well resolved for the resonance near $g \geq 2.0$. Between every pair of the six hyperfine line of the $g \geq 2.0$ resonance, there is a pair of relatively weak forbidden transition. The $^{55}\text{Mn}$ hyperfine coupling constant for the $g \geq 2.0$ signal is 78 G. The dihydrazone is coordinated to the metal centre in keto form through deprotonated secondary amine nitrogen atom and deprotonated naptholate oxygen atoms in atoms in anti-cis-configuration.

Monometallic copper(II) complex $[\text{Cu(LH}_2\text{)(H}_2\text{O})_2]$ (1) and heterobimetallic complexes $[\text{MCu(L)(H}_2\text{O})_3]$ (where $\text{M} = \text{UO}_2$ (2) and $\text{Zn}$ (4) and $[\text{MCu(L)(H}_2\text{O})_4]$ (where $\text{M} = \text{MoO}_2(3)$, $\text{Ni}$ (5), $\text{Co}$ (6) and $\text{Mn}(7)$) and homobimetallic copper(II) complex $[\text{Cu}_2\text{(L)(H}_2\text{O})_4].2\text{H}_2\text{O}$ (8) have been isolated and characterized by Lal and coworkers [110] by analytical, molecular weight, magnetic moment, electrical conductance, electronic, IR and EPR spectral data. IR spectral evidences indicate that dihydrazone coordinates to the metal centres in enol forms. The monometallic copper(II) complex (1) and the heterobimetallic complexes $\text{UO}_2\text{Cu}$ (2) and $\text{MoO}_2\text{Cu}$ (3) and $\text{Zn-Cu}$ (4) are normal paramagnetic indicating absence of metal–metal interaction in the structural unit of the complexes while the remaining heterobimetallic complexes $\text{Ni-Cu}$ (5), $\text{Co-Cu}$ (6) and $\text{Mn-Cu}$ (7) have much less $\mu_{\text{eff}}$ values than those required for 3, 4 and unpaired electrons indicating considerable metal-metal interactions. The monometallic copper(II) complex (1) shows an anisotropic EPR spectrum at LNT (77K). The parallel and perpendicular features are resolved. The essential feature of the spectrum are consistent with octahedral stereochemistry. The EPR spectral feature of homobimetallic copper(II) complex (8) suggest square pyramidal stereochemistry of the complex. The heterobimetallic complexes
have also been characterized by EPR spectral studies. The EPR spectral data indicate that either there is no interaction or very weak interaction between metal centres in the structural unit of the heterobimetallic complexes. The complexes have been characterized by electronic and IR spectral data also. Copper has distorted octahedral geometry in monometallic complexes and heterobimetallic complexes. Uranium has pentagonal bipyramidal stereochemistry while zinc has square pyramidal stereochemistry.

The monometallic uranium(VI) complex \([\text{UO}_2(\text{CH}_2\text{LH}_2)(\text{H}_2\text{O})]\) has been synthesized by Lal and coworkers [112] from bis(2-hydroxy-1-naphthaldehyde)-malonoyldihydrazone \((\text{CH}_2\text{LH}_4)\) in ethanol. The reaction of this complex with bis(acetylacetonate)dioxomolybdenum(VI) and metal acetates \((M = \text{Zn, Cu, Ni, Co, and Mn})\) in \((1:1)\) molar ratio in ethanol (methanol in the case of copper) under reflux yields heterobimetallic complexes \([\text{MUO}_2(\text{CH}_2\text{L})(\text{H}_2\text{O})_2]\) \((M = \text{Zn and Cu})\) and \([\text{MUO}_2(\text{CH}_2\text{L})(\text{H}_2\text{O})_3]\) \((M = \text{MoO}_2, \text{Ni, Co and Mn})\), respectively. The complexes have been characterized by analytical, molecular weight, molar conductance, magnetic moment data and spectral studies. In all the complexes, the dihydrazones coordinates to the metal centres in an \textit{anti-cis} configuration.

The complexes \([\text{[UO}_2(\text{CH}_2\text{L})(\text{H}_2\text{O})_4].4\text{H}_2\text{O}}\) \((1), [\text{M}_4(\text{CH}_2\text{L}_2)(\text{H}_2\text{O})_4].4\text{H}_2\text{O} (M = \text{Zn(2) and Cu(3)}), (M')_2[(\text{UO}_2\text{F})_2(\text{CH}_2\text{L})(\text{H}_2\text{O})_2] [M = \text{K(4), Na(6)}, M'[\text{[UO}_2\text{F}_2(\text{CH}_2\text{L})(\text{OAc})(\text{H}_2\text{O})_2] [M = \text{K(5), Na(7)}, K_4[(\text{MF})_2(\text{CH}_2\text{L}_2)].4\text{H}_2\text{O} [M = \text{Zn(8) and Cu(9)}]\] have been synthesized by Lal and coworkers [113] from reaction of appropriate metal salts with bis(2-hydroxy-1-naphthaldehyde)-adipoyldihydrazone \((\text{CH}_2\text{LH}_4)\) in different experimental conditions in ethanol/methanol media. The complexes have been characterized by elemental analyses, molecular weight, molar conductance, magnetic moment and EPR data. The structural assessments of the complexes have been carried out on the basis of electronic, infrared, \(^1\text{H} \text{NMR} \) and \(^{13}\text{C} \text{NMR} \) spectral studies.
Gang et al. [114] synthesized the lanthanide chelates Na$_2$[Ln(C$_{32}$H$_{28}$N$_8$O$_8$)Cl]$_n$H$_2$O from malonoyl dihydrazone salicylaldehyde and characterized them by elemental analysis, IR, UV, molar conductance and TGA. They showed that the ligand coordinates to the central metal ion with one hydrazone unit in the keto form with one chloride ion in the coordination sphere. These chelates are 1:2 electrolyte in DMF and are more thermostable than the ligand due to the formation of chelate rings.

Bolger and coworkers [115] synthesized a series of dihydrazone and substituted dihydrazone derivatives of biacetyl and of hydrazone and phenylhydrazone derivatives of 2-acetylpyridine like biacetyl di(phenylhydrazone) (1a), biacetyl di[methyl(phenyl)hydrazone] (1b), biacetyl di(o-tolylhydrazone) (1c), biacetyl di(dimethylhydrazone) (1d), biacetyl dihydrazone (1e), biacetyl di(benzaldehyde azine) (1f), 2-acetylpyridine phenylhydrazone (1g) or 2-acetylpyridine hydrazone or 2-acetylpyridine hydrazone (1h). Subsequently, they studied the reactions of these dihydrazones with [Ru(bpy)$_2$Cl$_2$] (where bpy = bipyridine) and isolated the complexes of the composition [Ru(bpy)(L-L)](PF$_6$)$_2$ where L-L represents dihydrazone. The structures of all complexes were determined using IR, UV-vis, NMR and microanalysis. The proton NMR spectra of the complexes derived from dihydrazones (1a-1c) showed an unusual dependence on probe temperature with broadened aromatic resonances. The signals sharpened at both high and low temperature in the complexes derived from dihydrazone 1b and 1c. Emission was observed for the complexes with two hydrazones and 1g and 1h containing only one hydrazone moiety. The molecular structure of 1a was determined and it was shown that a hydrazone phenyl group lies over each of the bipyridyl rings.

N₈O₄) complexes through the metal ion controlled reaction of 1, 2-diphenylethane-1, 2-dione dihydrazone (DPEDDH) with succinic acid [ML₁X₂] or phthalic acid [ML₂X₂] [M = Mn, Co, Ni, Cu or Zn; X = Cl or NO₃]. They elucidated the structures of the complexes on the basis of IR, ¹H NMR, EPR and electronic spectral data and conductance as well as magnetic properties. An octahedral geometry was assigned for all the complexes involving coordination of all imine nitrogens.

Labib and coworkers [117] synthesized a series of polyacylhydrazones by condensing diacetyl with oxalic, malonic, succinic, glutaric and adipic dihydrazides and characterized them by conventional spectroscopic studies. The complexes of the compositions \{[Cu₂(L)(AcO)₂(OH)(H₂O)₂]yH₂O\}ₙ, \{[Cu(L)(AcO)(HO)₂]yH₂O\}ₙ, \{[Ni₂(L)(AcO)₂(OH)₂]yH₂O\}ₙ and \{[Ni(L)(AcO)(HO)]yH₂O\}ₙ, were isolated where L refers to the neutral dihydrazone unit. Magnetic susceptibility measurements in the 4.2 - 300 K range indicated significant antiferromagnetic coupling between the CuⅡ centres in the metallopolymers. The results indicate the presence of two polymer chains crosslinked by bis-μ-acetatocopper(II) bridges. Based on IR, spectral and magnetic measurements tentative structures of the CuⅡ and NiⅡ metallopolymers were proposed. The dihydrazone units in these polymers were found to be coordinated to the metal(II) via the azomethine nitroen(s) whereas the amide group was found to be uncoordinated. Each CuⅡ is penta coordinated in a distorted square pyramidal environment and bridged by one acetate group. A hydroxide ion is also coordinated to the CuⅡ centre. The fifth coordination site is occupied by water molecule. In the nickel(II) metallopolymers, the metal ions were in a tetrahedral environment and were coordinated to azomethine nitrogen, two bridged acetate oxygens and to the hydroxide ion.

Larin and coworkers [118] synthesized the dinuclear copper(II) complexes
with 2-hydroxypropiophenone, 2-hydroxy-5-methyl and 5-chloro-2-hydroxy-acetophenone, acyldihydrazones (H,L) having the compositions [Cu2L.mPy], where the L ligand contains the polymethylene chain with different lengths from two to five units. The crystal and molecular structures of the 2-hydroxy propiophenone adipoyldihydrazone complex [Cu2L.4Py]Py were established by X-ray diffraction analysis. Each copper(II) atom was found to have the tetragonal pyramidal geometry. The EPR spectra of solutions of the complexes derived from acyldihydrazones of succinic, glutaric and adipic acids contain seven HFS lines with the constant $\sim 40.10^{-4}$ cm$^{-1}$. Such a value of HFS constant indicated that the two copper atoms are coupled to one another as a result of the spin–spin exchange interaction between unpaired electrons. An increase in the polymethylene chain length to five units prevents exchange interactions. The EPR spectrum of the complex with pimelic acid dihydrazone contains a signal of four HFS lines with $\Delta_{\text{Cu}} = 73.4.10^{-4}$ cm$^{-1}$, which is typical of mononuclear copper(II) complexes.

Andelkovic and coworkers [119] synthesized Zn(II), Pd(II) and Pt(II) complexes with 2'-[1-(2-pyridinyl)ethylidene]oxamohydrazide (Hapsox). The Zn(II) complexes was found to contain two coordinated apsox ligands to Zn(II) while Pd(II) and Pt(II) complexes were found to contain one coordinated apsox ligand to the metal centres. In each case, the polydentate ligand was coordinated via pyridine and hydrazone introgens and $\alpha$-oxyazine oxygen. An octahedral geometry around Zn(II) and a square planar geometry around Pd(II) and Pt(II) were established. The structure determination was performed by IR, $^1$H NMR and $^{13}$C NMR spectroscopy. The structure of Zn(II) complex was established unequivocally by X-ray diffraction analysis.

Para et al [120] synthesized dialdehyde starch dihydrazone from reaction of dialdehyde starch (32 %) from periodate oxidized potato starch with hydrazine DASHZ. The dihydrazone (DASHZ) coordinated to Ca, Cd, Co(II), Cu(II),
Fe(II), Mg, Mn(II), Ni(II), Pb(II) and Zn ions. The nitrogen atoms of the C=N moiety in dihydrazone as well as the oxygen atom of the pyranose ring of starch moiety were the coordination sites. Metal ions were chelated to a different extent while Cu(II) could coordinate with three moles of DASH while Mn(II) could coordinate with 50 moles of the DASHZ units. The ligand DASHZ and the metal complexes decomposed, thermally in four steps but the rates of decomposition of the ligand and chelates in relevant steps were different. Mg complex has a very high rate of decomposition while complexes of other metals have low rates of decomposition.

Zhao and coworkers [121] synthesized polynuclear manganese(II), cobalt(II)/(III), iron(II)/(III) and nickel(II) complexes of a group of flexible polydentate dihydrazone ligands, based on pyridine-2, 6-dipicolinic (A), oxalic (B) and malonic (C) subunits. They reported the structural details for the linear dinuclear complexes \([\text{Ni}_2(\text{2poap})_2(\text{H}_2\text{O})_2]\text{(NO}_3\text{)}_4\cdot\text{2CH}_3\text{OH}\cdot\text{2.5H}_2\text{O} \) (1), \([\text{Mn}_2(\text{pttp})(\text{NO}_3)_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2]\text{(NO}_3\text{)}_2\cdot\text{H}_2\text{O} \) (2) and \([\text{Mn}_2(\text{mapttpp})(\text{NO}_3)_2(\text{H}_2\text{O})_2]\text{(NO}_3\text{)}_2\cdot\text{H}_2\text{O}_2 \) (3), a square tetranuclear complex \([\text{Co}_4(\text{pttp})_4]{\text{Br}_6}\cdot\text{9H}_2\text{O} \) (4), a tetranuclear tetrahedral complex \([\text{Ni}_4(\text{pttp})_6]{\text{(BF}_4\text{)}}\text{6F}_2\cdot\text{14H}_2\text{O} \) (7) and a mixed spin state tetranuclear Ni(II) complex \([\text{2pyoap})_2\text{Ni}_4(\text{CH}_3\text{OH})_4\cdot\text{1.5CH}_3\text{COH} \) (10), with a diamond-like arrangement of metal ions. The paramagnetic metal centres are well separated in each case, leading to weak antiferromagnetic coupling or nonexistent spin exchange.

Tirosh and coworkers [122] synthesized cadmium complex \([\text{Cd}(\text{C}_4\text{H}_{10}\text{N}_4)_3]\text{(ClO}_4\text{)}_2 \) from reaction of \(\text{Cd(ClO}_4\text{)}_2\cdot\text{H}_2\text{O} \) with biacetyl dihydrazone in methanol. They established the crystal structure of the compound at ca. 110 K with the help X-ray crystallography. The cation was found to be located on a \(\frac{1}{3} \) axis. The complexes were characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal.
Carcelli and coworkers [123] synthesized a series of lanthanides (III) complexes with two potentially hexadentate ligands containing a rigid phenanthroline moiety and two flexible hydrazonic arms with different donor atom sets (NNN'N'OO and NNN'N'N''N") respectively. These hydrazones are (diformylphenanthroline)bis(benzoyl)hydrazone (H$_2$L), (2, 9-diformyl phenanthroline)bis(2-pyridyl)hydrazone (HL$_2$). They prepared complexes of H$_2$L$^1$ with La, Eu, Gd and Tb and characterized them fully. They presented the X-ray crystal structure of the complex [Eu(HL$^1$)(CH$_3$COO)$_2$].5H$_2$O. The stability constants of the equilibria regarding synthesis of the complexes were determined by UV spectrophotometric titrations in DMSO at 25 °C. They also synthesized nitrate complexes of H$_2$L$^2$ with La, Eu, Gd and Tb. The X-ray crystal structures of the complexes [La(H$_2$L$^2$)(NO$_3$)$_2$(H$_2$O)](NO$_3$), [Eu(H$_2$L$^2$)(NO$_3$)$_2$](NO$_3$) and [Tb(H$_2$L$^2$)(NO$_3$)$_2$](NO$_3$) were also established.

Salen [124] synthesized a series of new acyldihydrazones, H$_2$L$^n$ from condensation of ethylpyruvate with oxalic, malonic, succinic, glutaric and adipic acid dihydrazides. They synthesized copper(II) complexes [Cu$_2$(L$^n$)$_2$H$_2$O].xH$_2$O where L$^n$ refers to the quadruply deprotonated pyruvic acid dihydrazone ligand and $n$ refers to the number of carbon atoms of the aliphatic spacer between the two acylhydrazone units. The isolated complexes were characterized by elemental analyses, infrared spectra, mass spectra as well as variable temperature magnetic susceptibility measurements. Magnetic susceptibility measurements in the 4.2 - 298 K range indicated significant antiferromagnetic coupling between Copper(II) centres and suggested association of the coordinated copper(II) units Cu(ONO) via oxazine oxygen bridges. This led to a polymeric structure where the dimeric units are connected together with aliphatic spacer. From the best fit values of the mole fraction of paramagnetic uncoupled copper(II) centres ($\rho$), the degree of association in these polynuclear copper (II) complexes was estimated.
Elengoz et al [125] synthesized zinc(II) complex tris(biacetyl- dihydrazine- k^2 N, N’ zinc(II)bis(perchlorate), [Zn(C_4H_{10}N_4)_3][ClO_4]_2 and determined its crystal structure at 110 K. The metal-organic cation is located on a \( \overline{3} \) axis and is characterized by an approximate octahedral geometry in which each of the ligands occupies two coordination sites around the metal. The compound crystallizes in the trigonal space group \( P\overline{3}c1 \) with two units of the \([Zn(C_4H_{10}N_4)_3]^{2+}\) cationic complex and four ClO_4\(^-\) anions in the unit cell. The zinc(II) atom is located on a \( \overline{3} \) axis, while the perchlorate anion is located on a threefold rotation axis. The cation is characterized by perfect \( \overline{3} \) symmetry, in which three chelating ligands occupy the octahedral coordination sites of the zinc metal ions. The imine N atoms of the ligand provide the coordination sites to the central metal ion.

The conformation about the central C-C bond of the ligand is cis with the two C= N bonds being nearly coplanar, to direct the two imine coordination sites towards the metal centre. The N-Zn-N bond angle involving two coordinating N-atoms of a given ligand is 74.33 (11)°. In the free form of the ligands, the N-N=C-C=N-N backbone adopts a planar anti-conformation [126].

From the survey of literature presented above, it is evident that although mono and bimetallic complexes of various types of dihydrazones have been synthesized and characterized, in some detail, those derived from dihydrazones containing methylene function and bulky fragments in their molecular skeleton have scarcely been studied. Further the heterobimetallic complexes of such dihydrazones are almost non-existent. In view of limited investigations on metal complexes of dihydrazones containing methylene function and bulky fragments in their molecular skeleton, the present project has been undertaken. It is quite possible to extend and develop such a study, with the help of variety of metal ions into a major field, but because of time factor, it has been
restricted to monometallic and heterobimetallic complexes of disalicylaldehyde adipoyldihydrazone ($\text{slahH}_4$) and bis(2-hydroxy-1-naphthaldehyde)-adipoyldihydrazone ($\text{npahH}_4$) with manganese and ruthenium metal ions.