CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Introduction

The present thesis embodies the results of investigations of reactions of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones, Cu(αAc)$_2$·H$_2$O, CuCl$_2$·2H$_2$O, CuSO$_4$·5H$_2$O, MoO$_2$(acac)$_2$ and the characterization of the resulting complexes. The structural assessment of the complexes described in this thesis is based on the data obtained from elemental analyses, mass spectroscopy, IR, $^1$H NMR, ESR, conductivity measurements, magnetic susceptibility measurements, electronic and cyclic voltammetry measurements. Accordingly, the present chapter gives a brief account of the importance of copper and molybdenum in monometallic, homobimetallic and homotrimetallic systems followed by description of bonding modes of dihydrazone ligands and literature survey on metal complexes of dihydrazones.

Copper is a relatively ‘modern’ element [1, 2], having become bioavailable only about 1.7 billion years ago with the advent of an oxygen atmosphere [3]. The oxidizing environment generated by photosynthetic organisms not only allowed the conversion of Cu(I) to Cu(II), which is more soluble and bioavailable, but also led to the need for a redox-active metal with potentials between 0 and 800 mV [2]. The Cu(I)/Cu(II) redox pair fits this requirement and as a result, many copper-containing enzymes function in O$_2$ binding, activation and subsequent substrate oxidation. These enzymes include monooxygenases, dioxygenases, oxidases and play an essential role in biological processes such as peptide hormone activation, biosynthesis of melanin pigments, iron homeostasis and methane oxidation. The O$_2$-reactive centres are mononuclear (type 2), dinuclear (type 3) or trinuclear (type 2 and type 3). Copper containing enzymes that react with O$_2$ play a key role in many biological processes. Mononuclear, dinuclear and trinuclear copper centers function in O$_2$ binding, activation and subsequent substrate oxidation. In the structural biology of O$_2$ activating copper enzymes range from the identification of novel copper centres, such as that of particulate methane
monooxygenase, to the elucidation of the details of $O_2$ binding and reactivity in peptidylglycine α-hydroxylating monooxygenase.

Copper occurs in several enzymes and metalloproteins [4] like ascorbate oxidase, copper dioxygenase, copper monooxygenase, super dismutase, cytochrome oxidase and 'blue' oxidase [5-10] etc. Copper is an essential bioelement responsible for numerous catalytic processes in living organism where it is often present in di- or tri nuclear assemblies [11]. Polynuclear copper centres are widespread in biological systems, occurring in type 3 cuproproteins, such as tyrosinase and hemocyanin [12].

Molybdenum is the only element of the second transition series, being essential for life [13, 14]. The element molybdenum is present in two types of enzymes, one of these is nitrogenase [15] which is found in free living and symbiotic microorganisms and catalyses the reduction of dinitrogen to ammonia. The other category of molybdenum enzymes consists of hydroxylases or oxotransferases [16] which catalyses a variety of two electron oxidation-reduction reactions. As a constituent of enzymes, molybdenum also participates in redox reactions, viz., oxidation of aldehydes, xanthine and other purines [17], and reduction of nitrate to molecular nitrogen [18, 19]. Molybdenum’s biochemical role is based on its ability to facilitate electron exchanges and to form stable complexes with oxygen, nitrogen and sulphur containing ligands [14].

It is well-known that metalloproteins often use binuclear metal centers to perform catalytic functions. Moreover, the well-known anagonistic function of the molybdenum ion with regard to copper in ruminants [20] has raised interest in the interaction of Cu ions with ligated molybdenum species. However, most of the Mo-Cu mixed-metal complexes reported till now [21] employ mainly $(\text{MoS}_4)^{2-}$ as the source of the molybdenum component, moreover, these Mo-Cu mixed-metal complexes involve Mo-Cu(I) metal pairs in which the Mo most often exhibits a VI oxidation state. Mo(VI)-Cu(I) Schiff-base complexes having cubane-like cores of the formula $\text{Mo}_2\text{Cu}_2\text{O}_4$ in which Mo and Cu retain +6 and +2 oxidation states, respectively, have not been reported in the literature.
Mixed metal-molybdenum oxides are used as efficient and selective catalysts for partial oxidation of light alkanes in petrochemistry [22]. The molybdenum compound \([\text{NH}_3\text{Pr}']\text{[Mo}_7\text{O}_{24}]\cdot3\text{H}_2\text{O} \) (PM-8) is proved to be significant in tumor growth suppression in bearing several human tumors and has shown anti-tumour activity against human gastric cancer [23]. The polyoxomolybdenum anions have potential applications in catalysis, solid-state technology and medicine, including antitumor, antibacterial and antivirus (HIV) activity [24, 25].

The molecular complexes derived from transition and inner-transition metals having the same or different metal ions are of interest in areas like homogeneous catalysis [26] and heterogeneous catalysis [27]. In homogeneous catalysis, a heterobimetallic complex containing an electron deficient metal atom and an electron rich metal atom presents the possibility of Lewis acid activation of a substrate molecule bound to the electron rich metal centre. The heterobimetallic complexes which have such types of properties are usually derived from widely divergent metal [28]. Further, the heterobimetallic complexes have the potential to mediate certain chemical reactions of industrial relevance either more efficiently or in different manner to isolated metal centres [29]. They exhibit distinct reactivity pattern as compared to their monometallic and homobimetallic complexes.
LITERATURE SURVEY

The dihydrazones are examples of polyfunctional ligands which can bind two metals in close proximity to one another. The work on metal complexes of polyfunctional ligands has recently created much interest among chemists, because the magneto and electrochemical properties of complexes derived from them show promise in developing theories whereby electron transport phenomena can be understood [30]. Acyl-, aroyl-, and pyridoyl-, dihydrazones are some of the few examples of ligands which can yield binuclear, heteronuclear and polynuclear complexes of transition and inner-transition metals, possessing interesting magnetic and electrochemical properties [31] and which can serve as models in bioinorganic chemistry [33]. Acyl-, aroyl-, and pyridoyl-, dihydrazones derived from the condensation of o-hydroxyaromatic aldehydes and ketones and acyl- and aroyl-dihydrazines in which two hydrazone groups are separated from each other by methylene chains of varying length or phenyl group, or pyridoyl group and those derived from condensation of monohydrazines with dialdehydes, constitute a special class of molecules. This class of molecules reacts in the keto-enol forms [36] depending upon the mode of preparation of the complexes, the nature of the reaction medium, the pH of the reaction medium, the nature of the metal salt and the molar ratio of the metal salt and the ligand employed ad can act as mono-, di-, tri-, and tetrabasic hexadentate ligands and give rise to polymeric complexes through both ligand bridging due to their flexibility in three-dimensional space and oxo-bridging through the phenolic atoms.

The dihydrazones can be obtained from condensation of acyl-, aroyl-, and pyridoyl-, dihydrazines \([\text{R(CONHNH}_2\text{)}_2] \); \((\text{R} = \text{O, -(CH}_2\text{)}_n\text{, C}_6\text{H}_4\text{<, C}_6\text{H}_3\text{N<})\) with o-hydroxyaromatic aldehydes and ketones. Another category of the dihydrazones can be obtained from condensation of dialdehydes \([\text{R(CR'}\text{O)_2]} \); \((\text{R} = \text{O, -(CH}_2\text{)}_n\text{, C}_6\text{H}_4\text{<, C}_6\text{H}_3\text{N<, R'} = \text{alkyl groups})\) with monoacyl-, aroyl-, pyridoyl- and quinaldenoyl-, 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-, dihydrazines with simple and o-hydroxyaromatic aldehydes and ketones.
B) Complexes of dihydrazones derived from condensation of dialdehydes with monoacryl-, aryl-, pyridyl- and quinaldinoyl-, hydrazines.

Sacconi [34] has isolated a series of diamagnetic dinuclear 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 their enol forms with Ni(OAc)₂ in aq. alc. ammonia as bis-tridentate complexing agents.

Aggarwal and coworkers [35] isolated complexes of the compositions [VO(LH₂)₂SO₄, [VO(LH₂)₂Cl₂, [VO(LH₂)py]SO₄ from reaction of vanadyl sulphate and chloride and metal (II) chloride with bis(acetone)oxaloyldihydrazine, bis(acetone)malonyldihydrazine and bis(acetone)succinoyldihydrazines in alcoholic medium. The complexes [VO(LH₂)₂SO₄ and [VO(LH₂)₂Cl₂ were proposed to have square pyramidal stereochemistry while the remaining complexes were proposed to have octahedral stereochemistry.

Iskander and coworkers [36] isolated the metal (II) complexes of the composition M(LH₃)X.nH₂O, M₂(LH₂)X₂.nH₂O, M(LH₂).nH₂O and M(LH₃)₂.nH₂O (where M = Cu(II), Ni(II) and Co(II); X = Cl⁻, Br⁻, I⁻) from reaction of the metal(II) salts with dihydrazones (LH₄) derived from condensation of salicylaldehyde with acylhydrazines with the methylene backbone varying from 1 to 5 under different experimental conditions. They assigned a pseudo-octahedral stereochemistry for the nickel(II) complexes [Ni(LH₃)X].nH₂O (X = Cl⁻, Br⁻, I⁻) and [Ni₂(LH₂)Cl₂].2H₂O on the basis of magnetic moment data and spectral studies. The latter complexes change to pentacoordinated state on dehydration. However, five coordinate structure was proposed for the nickel(II) complexes Ni(LH₂).nH₂O as against a distorted octahedral structure for the corresponding cobalt(II) analogues. On the other hand, Kapoor and coworkers [37] suggested that the nickel(II) complexes Ni(LH₂).nH₂O have octahedral stereochemistry. Anomalous magnetic behaviour of the nickel complexes Ni₃(L).nH₂O (μₚeff values lying in the range 1.65-1.70 BM) is ascribed to arise due to the presence of two magnetically non-equivalent sites in the same unit cell. This is confirmed from electronic spectral study of the complexes as well which show bands characteristic of octahedral and square planar nickel(II) sites in the complexes. All the cobalt(II) complexes are proposed to have
octahedral stereochemistry. The copper complexes \( \text{Cu}(LH_3)X_nH_2O \) and \( \text{Cu}_2(LH_2)X_2.nH_2O \) are proposed to have square pyramidal stereochemistry. The low magnetic moment values than the spin only value is attributed to superexchange interactions through the oxygen bridges. The complex \( \text{Cu}(LH_2).nH_2O \) has been suggested to have square planar stereochemistry.

Narang and Lal [38] have described complexes of disalicyaldiminesuccinamide (\( H_2L \)) and \( \text{N,N-Bis(o-hydroxyacetophenoneimine)succinamide} \) (\( H_2J \)) of the types \( \text{ML, MJ, M(HL)Cl, M(HJ)Cl} \) and \( \text{M'}(HL)_2 \) \( (\text{where } M = \text{Cu(II), Ni(II), or Co(II)} \) and \( M' = \text{Ni(II) or Co(II)} \). The complexes are proposed to have either octahedral stereochemistry or square planar stereochemistry.

Narang and Lal [39] have reported mono and binuclear zinc(II) complexes \( \text{Zn(HL)Cl} \) and \( \text{Zn}_2(L-2H) \) derived from multidentate acyldihydrazone ligands. 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 [40] of the type \( \text{M}_2L \) derived from dihydrazones obtained from condensation of oxaloyldihydrazone, succinoyldihydrazone and phthaloyldihydrazone with salicylaldehyde or o-hydroxyacetophenone have been described by the above authors. Copper complexes and few nickel and cobalt complexes are proposed to have square planar stereochemistry while other nickel and cobalt complexes are proposed to have distorted octahedral and square pyramidal stereochemistry. The anomalously low magnetic moments of some complexes are related to M-M interactions via oxo-bridge structure.

Narang and Lal [41] have prepared and characterized the metal(II) complexes \( \text{M}(H_2J) \), \( \text{M}(H_2K) \), \( \text{M}(H_3J)\text{Cl} \), \( \text{M}(H_3K)\text{Cl} \); \( \text{M}_2J \), \( \text{M}_2K \) and \( \text{M}_2 \) \( (\text{HK}) \) \( (\text{CH}_3\text{COO}) \) \( (\text{where } M = \text{Cu(II)} \), \( \text{Ni} \) (II) and \( \text{Co(II)} \)) derived from \( \text{di(salicylaldimine)malonamide}(H_4J) \) and \( \text{di(o-hydroxyacetophenoneimine)malonamide}(H_4K) \) and the zinc(II) complexes \( \text{ZnH}_2L \) and \( \text{Zn}_2L \) from a number of multidentate acyldihydrazones \( (H_4L) \). The copper complexes are shown to have square pyramidal and pseudo-octahedral stereochemistry. The cobalt complexes are shown to have square planar, square pyramidal, mixed octahedral and
tetrahedral and distorted octahedral stereochemistry in the solid state whereas zinc complexes have octahedral and tetrahedral stereochemistry.

Narang and coworkers [42] synthesized new series of polymeric cobalt (II) complex of the type $\text{Co}_2(L) \cdot n\text{H}_2\text{O}$ from reaction of metal(II) acetate and dihydrazone ($\text{LH}_2$) where $\text{LH}_4$ is $\text{bis(o-hydroxyacetophenone)}\text{oxaloyldihydrazone}$, $\text{bis(salicylaldehyde)}\text{oxaloyldihydrazone}$, $\text{bis(o-hydroxyacetophenone)}\text{succinoyldihydrazone}$ in the ratio 4:1 (metal:ligand) in ethanol under reflux. The complexes have been proposed to have polymeric structure with strong Co-Co interactions with planar disposition of donor atoms around metal centres.

Sahni and coworkers [43] synthesized and characterized complexes of the type $[\text{M(LH}_2)]\text{X}_3$ (where $\text{M} = \text{Cr(III)}, \text{Mn(III)}, \text{Fe(III)}$ or $\text{Co(III)}$; $\text{X} = \text{Cl}^-, \text{NO}_3$ or $\text{OAc}$) from reaction of metal (III) salts with $\text{N-N-dibenzylidene dipicolinic acid hydrazone}$ ($\text{LH}_2$) in ethanol medium. The ligand acts as a pentadentate unit having coordination sites at pyridine nitrogen, amide oxygen and hydrazinic nitrogens or azomethine nitrogens. In this context, it is important to mention that these authors [44] have also claimed that dipicolinic acid dihydrazine behaves as pentadentate ligand. On the other hand, Dutta and Sarkar [45] have argued in favour of neutral tridentate behaviour of this ligand in which it can function either as a (NNN) or as a (ONO) donor.

Kapoor and coworkers [46] have studied reaction of vanadyl chloride and dipicolinic acid dihydrazone in presence of acetylacetone or other $\beta$-diketones in ethanol and acetic acid. They isolated brown solid complexes of macrocyclic ligand $\text{bis(\beta-diketone)}\text{dipicolinoyldihydrazones}$. On the other hand they isolated a non-macrocyclic pyrazole derivative when reaction of vanadyl chloride was carried out with the preformed $\text{bis(\beta-diketone)}\text{dipicolinic acid dihydrazone}$. Similar products [47] were isolated in case of zirconium(IV) also.

Teotia and Rana [48] synthesized complexes $[\text{M(L)} \cdot 2\text{H}_2\text{O}]$ (where $\text{M} = \text{Cu(II)}, \text{Ni(II)}$ and $\text{Co(II)}$) of the above macrocyclic ligands by treating a methanol solution containing a mixture of 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 [49] synthesized a number of metal (II) and metal (III) complexes from reaction of metal (II) and metal (III) salts with dihydrazones obtained from condensation of salicylaldehyde with oxaloyldihydrazine, malonoyldihydrazine and succinoyldihydrazine under different experimental conditions. The trivalent metal ions are found to yield complexes having compositions \([M_2LX_2]_nH_2O\) and \([M_3(LH_2)X_4]_nH_2O\) (\(M=\text{Cr(III)}, \text{Fe (III)}\) and \(\text{Mn(III)}\)) \((X=\text{Cl, NO}_3^-, \text{OAc, OH})\) while the bivalent metal ions were found to form complexes having compositions \([M(LH_2)]\) and \([ML(H_2O)_4]\) \((M=\text{Mn(II)}\) and \(\text{Fe(II)}\)). The dihydrazones are suggested to function as dibasic and tetrabasic hexadentate binucleating ligands. Iron(III) complexes were characterized by Mossbauer spectroscopy as well. The complexes have been suggested to have distorted octahedral stereochemistry.

Narang and Yadav [50] studied reaction of aluminium(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 [51] 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 light of magnetic moment, electronic and IR spectral studies.

Yacouta and coworkers [52] studied the complexation behaviour of uranyl ion with various dihydrazides and their diydrazones obtained from condensation of simple and \(\sigma\)-hydroxyaromatic aldehydes and ketones with dihydrazides. They isolated several monometallic and bimetallic uranyl complexes and characterised by various physicochemical data and spectroscopic studies. They also studied the effect of excess acetate ion on complex formation.

Lal and coworkers [53], have prepared several homotrinuclear complexes having general formula \([M_3LCl_2(H_2O)_3]\) \((M=\text{Mn(II)}, \text{Co(II)}\) or \(\text{Ni(II)}\)) from bis(acetophenone)-2,6-dipicolinoyldihydrazone\((LH_2)\) in alcoholic medium by adjusting pH to \(\sim 8\) by KOH. The
complexes show low $\mu_{\text{eff}}$ values much less than those expected for the high-spin metal ions possibly due to metal-metal interaction and anti-ferromagnetic exchange. The complexes are proposed to have mixed six-coordinate octahedral and five coordinate square pyramidal stereochemistry.

Narang and Singh [54] have synthesized polymeric complexes $\text{M(L-2H)}:n\text{H}_2\text{O}$ (where $\text{M} = \text{Fe(II)}, \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}$ and $\text{Hg(II)}, L=A,B$) 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 [55] studied reaction of uranyl acetate with the above dihydrazones ($\text{H}_4\text{L}$) in aqueous-alcoholic media and isolated complexes of the type $(\text{UO}_2\text{L}):6\text{H}_2\text{O}$. The dihydrazones coordinate to the metal centre in enol form. They have studied the effect of complexation on the coupling of $>\text{C}=\text{O}$ vibrations, in an enolized form and of ligand coordination to the uranyl ion as a function of the number of methylene groups by comparing the asymmetric stretching vibrations of the uranyl ion in various complexes recorded under identical conditions.

Lal and Das [56] studied reaction of uranyl nitrate and acetate with dihydrazones ($\text{H}_4\text{L}$) (where $\text{H}_4\text{L} = \text{disalicylaldehydeoxtaloyldihydrazone(H}_4\text{A}), \text{-malonoyldihydrazone(H}_4\text{B}), \text{-succinoylijhydrazone(H}_4\text{C)}, \text{-glutoylidihydrazone(H}_4\text{D)}, \text{-adipoyldihydrazone (H}_4\text{E), and phthaloyldihydrazone (H}_4\text{F})$ in 3:1 molar ratio in alcoholic medium. The complexes $[(\text{UO}_2\text{L})(\text{H}_2\text{L})\text{(NO}_3\text{)}_2(\text{H}_2\text{O})_4]\text{.2H}_2\text{O}$ and $[(\text{UO}_2\text{L})(\text{H}_2\text{L})(\text{CH}_3\text{COO})_2(\text{C}_2\text{H}_5\text{OH})_2]\text{.C}_2\text{H}_5\text{OH}$ have been isolated and characterized.

Lal and coworkers [57] synthesized copper(II) complexes $\text{Cu}_2(\text{L})\text{nH}_2\text{O}$ and dioxouranium(VI) complexes $[(\text{UO}_2\text{L})(\text{H}_2\text{L})(\text{C}_2\text{O}_4)]\text{2nH}_2\text{O}$ of the above dihydrazones. The $\text{C}_2\text{O}_4^{2-}$ group is suggested to coordinate to the uranium centre retaining its $\text{D}_{2h}$ symmetry.

Lal and coworkers [58] synthesized a series of uranyl complexes of the composition $[\text{UO}_2(\text{H}_3\text{L})_2]\text{nH}_2\text{O}$ from above dihydrazones from reaction of uranyl nitrate with salicylaldehyde and acyl- and aroyl- dihydrazines in 1:4:2 molar ratio in ethanol medium.
Lal and coworkers [59] studied reactions of disalicylaldehyde adipoyldihydrazine with uranyl nitrato and uranyl acetate in aqueous and ethanol media under different experimental conditions. The resulting complexes of the compositions \([\text{UO}_2(\text{H}_2\text{L})(\text{H}_2\text{O})]_{\text{n}}\), \([\text{UO}_2(\text{H}_2\text{L})_2]_{\text{n}}.3\text{nH}_2\text{O}\), \([\text{UO}_2(\text{H}_2\text{L})(\text{CH}_3\text{COO})]_{\text{n}}.3\text{nH}_2\text{O}\), \([\text{UO}_2\text{Zn}(\text{H}_2\text{L})(\text{H}_2\text{O})]_{\text{n}}.2\text{nH}_2\text{O}\), \([(\text{UO}_2)_2(\text{H}_2\text{L})(\text{C}_2\text{O}_4)]_{\text{n}}.\text{nH}_2\text{O}\), \([(\text{UO}_2)_2(\text{L})(\text{py})_{\text{2}}(\text{H}_2\text{O})_{\text{4}})]_{\text{n}}.\text{nH}_2\text{O}\), \([(\text{UO}_2)_3(\text{L})(\text{CH}_3\text{COO})_{\text{2}}(\text{H}_2\text{O})_2]_{\text{n}}.2\text{nH}_2\text{O}\), \([(\text{UO}_2)_2(\text{L})(\text{py})_{\text{2}}(\text{H}_2\text{O})_{\text{2}}]_{\text{n}}.\text{xnH}_2\text{O}\), (where \(\text{py} = \text{pyridine or } \alpha-, \beta-, \gamma\)-picoline, \(X=0, 1\)) have been isolated and characterized. In the complexes the ligand functions as a bridging monobasic tetradentate, dibasic hexadentate and tetrabasic hexadentate ligand and exhibits keto-enol tautomerism. In the heterobimetallic complexes \([\text{UO}_2\text{Zn}(\text{L})(\text{H}_2\text{O})_2]_{\text{n}}.2\text{nH}_2\text{O}\), the uranium and zinc atoms are considered to have hexagonal bipyramidal and tetrahedral stereochemistry respectively.

Lal and coworkers [60] have described dioxouranium(VI) and Zn(II) complexes \([\text{M}(\text{H}_2\text{L})(\text{H}_2\text{O})_2]_{\text{2}}.2\text{nH}_2\text{O}\) (where \(\text{M} = \text{UO}_2^{2+}, \text{Zn}^{2+}\)) of bis(o-hydroxynaphthaldehyde) oxaloyldihydrazine(\(\text{H}_4\text{L}\)). The complexes are obtained from reaction of metal acetate with oxaloyldihydrazine in 1:1 molar ratio in ethanol followed by reaction of excess o-hydroxynaphthaldehyde under reflux. 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-\(\text{OH}\) are proposed to be non-coordinated. They [61] have, further, synthesized dioxouranium(VI) complexes \([\text{UO}_2(\text{H}_2\text{L})]_{\text{n}}.2\text{nH}_2\text{O}\) and \([(\text{UO}_2)_2(\text{L})(\text{H}_2\text{O})_6]_{\text{n}}\) from reaction of uranyl nitrate with preformed dihydrazone bis (o-hydroxynaphthaldehyde)oxaloyldihydrazine in a 3:1 molar ratio in aqueous and ethanol media, respectively, under reflux. Based on the splitting of the \(\delta \text{NH}\) signal in monometallic complex and \(\delta \text{CH=N}\) in both complexes into quartet as compared to the singlet in free dihydrazone, the complexes are proposed to exist in chair formation with the anti-cis-configuration of dihydrazone involving eight and nine coordinated uranium atoms, respectively.

The complexes [62] \(\text{Na}_4[(\text{UO}_2)_4(\text{L})_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_4].4\text{H}_2\text{O}\) and \(\text{Na}_4[(\text{UO}_2)_4(\text{L})_2\text{F}_4(\text{H}_2\text{O})_4]\) have been obtained from the same ligand and have also been described by them.
Patil and Kulkarni [63] and others [64] obtained complexes of the type \([\text{UO}_2\text{L}]\cdot n\text{H}_2\text{O}\) from interaction of uranyl acetate disalicylaldehyde thiocarboxydradizaone\((\text{H}_2\text{L})\) and established their structure by \(^1\text{H}\) NMR and IR spectroscopic studies.

Kapoor and coworkers [65] studied reaction of malonooyldihydrazine and phthaloyldihydrazine with β-diketones in presence of the dioxouraninum\((\text{VI})\) cation which appears to function as a metal template. This facilitates condensation of dihydrazide with diketones resulting in the formation of several dioxouranium\((\text{VI})\) complexes of macrocyclic ligands. The formation of a macrocyclic ring was confirmed from infrared spectroscopic studies. However, when dioxouraninum\((\text{VI})\) nitrate is treated with the condensation product of phthaloyldihydrazine and acetylacetone, an entirely different pyrazole derivative is formed.

Sahoo and coworkers [66] have synthesized several first series transition metal complexes from several dihydrazones. The complexes were characterized by elemental analyses, physico-chemical data and spectral studies.

Pandey [67] reported a number of organometallic complexes derived from pyridooyldihydrozones. In this study, he showed from IR spectral data that dihydrazones coordinate to the metal centre in keto form through both >C=O and >C=N groups.

Mahale and Havanur [68] studied dioxomolybdenum\((\text{VI})\) complexes of the composition \((\text{MoO}_2)_2(\text{L})(\text{py})_2\) synthesized from dihydrazones\((\text{H}_4\text{L})\) obtained from condensation of the several acyl dihydrazines and substituted salicylaldehyde.

Panda and coworkers [69] synthesized heterobimetallic complexes [M\(\text{NiM}(\text{BTDO})_2\text{X}_2(\text{H}_2\text{O})_n\)]\(\cdot n\text{H}_2\text{O}\) (where M = Ni\((\text{II})\), Co\((\text{II})\) and Cu\((\text{II})\); \(X = \text{Cl}^-, \text{NO}_3^-, n = 0\) or 0.5 and 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\([\text{bis(diacylhydrazone})]\). The metal centres have been proposed to have octahedral stereochemistry.

Gopinathan and coworkers [70] synthesized a tin complex of disalicylaldehyde malonoyldihydrazone and studied its structure by X-ray crystallography.

Sacconi [71] studied reactions of biacetyl-bis(benzoylhydrazone) with nickel\((\text{II})\) acetate in alcohol in the presence of concentrated ammonia and isolated orange coloured
biacetylbenzoylhydrazonato)nickel(II) complex and studied its reaction with pyridine [72]. The formation constant of complexes formed between biacetylbenzoylhydrazonato)nickel(II) and various alkyl amines [73] have been studied. Complexes of lead(II), lead(IV) and tin(IV) of the types [Pb(L)], [Pb₂L], [SnL₂], [SnClL] and [Sn₂L] have been obtained by mixing methanol solutions of the appropriate metal salts and the ligand [74].

Pelizzi and coworkers [75] have studied reaction of copper(II) chloride dihydrate with 2,6-diacetylpyridinebis(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 ligand behaves 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 a basal plane consisting of a chloride, two nitrogen atoms from the ligand (LH₂), an oxygen atom from second adjacent ligand molecule and another nitrogen 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 chlorine ion takes up the apical site. Same authors [76] 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(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 [77]. 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 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 [78] and others [79] studied Cu(II) and Ni(II) complexes of acetylacetonebis(picoloylhydrazone) 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 acetyl acetone and confirmed the square pyramidal stereochemistry.

Giordano and coworkers [80] isolated cobalt(II) and nickel(II) complexes of compositions [Co(LH₂)(H₂O)(NO₃)]NO₃ and [Ni(LH₂)(H₂O)₂](NO₃)₂·2H₂O from reaction of metal nitrates with 2,6-diacetylpyridine bis(benzoylhydrazone) (LH₂) in 95% ethanol. The X-ray crystallographic study confirmed that the metal atoms are in a pentagonal bipyramidal arrangement in the structural unit of the complexes.

Palenik and coworkers [81] isolated lanthanum complex of composition [La(LH₂)(NO₃)₃] from reaction of lanthanum nitrate and the ligand in ethanol at 55 °C in the presence of water. The complex was studied 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 [82] prepared a series of dioxouranium(VI) complexes of 2,6-acetylpyridine bis(4-methoxy benzoylhydrazone)(H₂dapmb). The neutral compound of the composition UO₂(dapmb) was formed in two different crystalline forms, α and β depending upon the experimental conditions. The geometry of [UO₂(dapmb)] which was formed in two forms is 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 [83] isolated tin(IV) complexes of the composition [Snpr₂(LH₂)] from reaction of n-propyltinchloride in anhydrous acetone, under nitrogen atmosphere with boiling suspension of 2, 6-diacylpyridinebis(salicylhydrazone) (LH₄) in dry methanol. X-ray crystal structure study has established that tin atom is seven coordinated in the complex with pentagonal bipyramidal arrangement of ligand atoms. The -OH groups remain uncoordinated.
Teotia and coworkers [84] have studied reactions of metal(II) salts ($M = \text{Cu(II)}, \text{Ni(II)}$) with picolinoyl/isonicotinoylhydrazine in presence of acetylacetone. They isolated complexes of the compositions $[M(LH)X]$ ($M = \text{Ni(II)}, \text{Cu(II)}$, $X = \text{Cl}^-, \text{Br}^- \text{NO}_3^-$ and \text{NCS}$, \text{LH}_2 = \text{acetylacetonebis(picolinoylhydrazone)}$ or acetylacetonebis(isonicotinoylhydrazone). All the complexes have been established to have square pyramidal stereochemistry. Complexes $[M(LH)X_2]$ ($X = \text{Cl}^-, \text{Br}^- \text{NO}_3^-$ and \text{NCS}$ for $M = \text{Cu(III)}$; $X = \text{OAc}, \text{Cl}^-, \text{Br}^-, \text{NCS}$ for $\text{Mn(III)}$ and $\text{OH}$ for $\text{Co(III)}$) were also prepared similarly [85] by them. The complexes have been suggested to have six-coordinate tetragonal structure.

Paolucci and coworkers [86] synthesized several complexes of 2, 6-diformylphenolbis(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 physicochemical techniques. A fascinating aspect of these ligands is the coordinating and bridging ability of phenolic-OH of the 2, 6-formylphenol moiety plus the very subtle behaviour of acidic protons.

Dutta and coworkers [87] isolated complexes of the composition $[\text{VO(L)}]$ from reaction of $\text{VO(acac)}_2$ with acetylacetonebis(benzoylhydrazone) ($\text{LH}_2$) in acetone. The same ligand on reaction with $\text{CoX}_2$ ($X = \text{Cl}^-, \text{Br}^-$) in anhydrous medium yield blue coloured tetrahedral polymeric complexes $[\text{Co(LH}_2\text{X}_2]$ [88]. However, in the presence of lattice water, bromide salt yields pink coloured pseudo-octahedral $[\text{Co(LH}_2\text{Br}_2]$ complexes.

The dihydrazone reacts with nickel(II) chloride in rectified spirit and yields diamagnetic, orange yellow complex $[\text{Ni(L)}]$ [89]. However reaction with anhydrous $\text{NiCl}_2$ in warm anhydrous methanol gives a paramagnetic complex $[\text{Ni(LH}_2\text{Cl}_2]$ having a $\text{trans}$-dichloro pseudo-octahedral structure. When this complex is exposed to moist atmosphere and over KOH, the partial dechlorination occurs giving the complex $[\text{Ni(LH)Cl}]$. This complex is proposed to have a five-coordinate structure. They also isolated complexes $[\text{Zn(L)}]$, $[\text{Cd(L)}].2\text{H}_2\text{O}$ and $[\text{Pb(L)}]$ from the interaction of appropriate metal acetate with the ligand in ethanol.
Snow and coworkers [90] studied the reaction of bis(acetylacetonato)oxovanadium(IV) with benzoylhydrazine in dry ethanol under dry nitrogen. They isolated bis(acetylacetone benzoylhydrazonato)vanadium(IV). A trigonal prismatic geometry was verified for this complex.

Dutta and coworkers [91] 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 or methylethylketone yielded (acetylacetonebenzoylhydrazonato)oxovanadium(IV). While in the former complex, the abstraction of oxo-group has been suggested to occur, in the latter complex it is retained.

Lanthanide complexes [92] 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 biacetyl, benzoylhydrazine and the 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 [93] have isolated a new series of metal(II) complexes of the type [M(LH₂)(OH₂)Cl] (M = Co(II), Ni(II), Mn(II), Cu(II) and Zn(II)) by mixing ethanol solutions of LH₂ with ethanol solutions of metal(II) chloride 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 [MLH₂(OH₂)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 [94] have studied the reaction of MoO₂(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 complexes (acetylacetonato) (cis-dioxo)molybdenum(VI)-μ-diol-(benzoylhydrazino) (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 above, but they give complexes of the \([\text{UO}_2\text{L}]\text{Cl}\) (where \(\text{LH} = \text{Schiff base}\), in which Schiff bases coordinate through both azomethine nitrogen and pyridine nitrogen (in the case of 2-picolinoylhydrazone) or carbonyl oxygen (in the case of isonicotinoylhydrazone) [95].

On the basis of IR and conductivity data Day et al [96] have reported the formation of \([\text{UO}_2(\text{LH}_2)](\text{NO}_3)_2\) (where \(\text{LH}_2\) represents \(1,2\)-dimethyl bis(4-methoxybenzoylhydrazone)). Similarly they have reported the formation of \([\text{UO}_2(\text{LH}_2)(\text{NO}_3)]\text{NO}_3\) upon acidification of \([\text{UO}_2\text{L}]\) 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 \([\text{UO}_2\text{L}(\text{AA})]\) (where \(\text{A} = \text{pyridine, picoline, methylamine, aniline, ph}_3\text{PO}; \text{AA} = \text{en, ph, phen}\)).

Marangoni and coworkers [97] synthesized mercury(II) complex with 2,6-diacetylpyridine bis(2-pyridoylhydrazone). They carried out X-ray structural analysis of the complex, and confirmed its pentagonal bipyramidal stereochemistry.

Pelizzi and coworkers [98] synthesized nickel(II) complex \([\{\text{Ni}(\text{H}_2\text{apsh})(\text{OH}_2)(\text{I})\}_2\text{Cl}_2\} \cdot \text{2dmf.5H}_2\text{O}, \text{and cobalt(II) and copper(II) complexes, viz.,}\ [\text{Co}(\text{H}_2\text{dpsah})(\text{OH}_2)_2\text{Cl}4\text{H}_2\text{O} \text{of 2,6-diacetylpyridinebis[2-(semicarbozono)propionylhydrazone]} (\text{H}_4\text{apsh}) \text{and H}_2\text{dpsah = 2,6-diacetylpyridinebis[2-(semicarbazono)acetophenoylhydrazone]} (\text{H}_2\text{dpsah}) \text{respectively. In the nickel complex, the four atoms of the semicarbazone system are involved in coordination while in the cobalt complex, semicarbazone system does not participate in coordination. They established the structure of the complexes by IR spectroscopy and X-ray crystallography.}\]

Pelizzi and coworkers [99] studied the structure of a tetranuclear copper(II) complex \([\text{Cu}_2(\text{dappc})(\text{OH}_2)_3]_2\), \([\text{Cu}_2(\text{dappc})(\text{OH}_2)_2(\text{ClO}_4)]_2(\text{ClO}_4)_6\cdot 2\text{H}_2\text{O} \text{(I) and} \ [\{\text{Cu}_2(\text{dapip})\text{Br}\}_2 \text{(II) derived from the polyfunctional ligand 2, 6-diacetylpyridinebis(2-pyridine carbonylhydrazone)} (\text{H}_2\text{dappc}) \text{and 2,6'-diacetylpyridinebis(2-(2-pyridine-carbonyl)phenylacetohydrazone}} (\text{H}_4\text{dapip}) \text{respectively. The structure of compound (I) is built up of complex cations of formula } [\text{Cu}_2(\text{dappc})(\text{OH}_2)_3]_2 \text{and} [\text{Cu}_2(\text{dappc})(\text{OH}_2)_2\text{ClO}_4]^2^-\text{. ClO}_4^-\text{anions and uncoordinated H}_2\text{O molecule while that of} \]
the compound (II) consists of neutral unit of formula \([\text{Cu}_2(\text{dapip})\text{Br}]_2\) and solvating \(\text{H}_2\text{O}\) molecules. In both compounds, two metal atoms for one hydrazone molecule are present and the ligand is bideprotonated in complex (I) and trideprotonated in complex (II).

A monoperoxo complex of Schiff base \((\text{H}_5\text{C}_6\text{C}=\text{N}-\text{NH}(\text{S})\text{SCH}_2\text{C}_6\text{H}_5)_2, \text{(LH}_2)\) has been reported by Tarafder et al \[100\]. The complex \([\text{UO}_2(\text{O}_2)\text{L}]\) was prepared by treating uranyl nitrate with the Schiff base dissolved in a solution of \(\text{KOH}\) in 30\% \(\text{H}_2\text{O}_2\). 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 \[101\] reported the dioxouranium complex of diacetyl~bis(thiobenzoilhydrazone) in which uranium has a distorted pentagonal bipyramidal structure with the uranyl oxygen atoms at the axial positions.

Pelizzi and coworkers \[102\] synthesized copper complexes of di-2-pyridylketone(phenylsemicarbazone)acetylhydrazone \((\text{H}_2\text{psah})\) and studied their structure by X-ray crystallography. They showed that the copper complex \([\text{Cu}_2(\text{psah})\text{Cl}].\text{H}_2\text{O}\) consists of a pair of structurally distinct metal centres with different environments bound to the heptadentate hydrazone ligand and held together by a \(-\text{N-N-}\) bridge.

Katti and coworkers \[103\] synthesized a number of Palladium(II) complexes from series of phosphorous hydrazide and hydrazones. The complexes were characterized by elemental analyses. The structural assessment was carried out by NMR and IR spectroscopic studies. They established the structure of one complex by X-ray crystallography as well.

Lukyanenko and coworkers \[104\] have determined complex stability of \(\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+\) 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. The studied bis-crown 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 [105] studied several dinuclear yttrium(III) and lanthanide(III) picrate complexes derived from acetylferrocenepyridine-2,6-diformylhydrazone having the stoichiometric formula \( \text{Ln}_2L_2\text{pic}_n\cdot n(\text{C}_3\text{H}_7\text{OH})\cdot m\text{H}_2\text{O} \) (pic = picrate anion, \( \text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, n = 2, m = 4; Ln} = \text{Er, Tm, Yb, n = 0, m = 2} \)). These complexes were characterized by EA, 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.

Xianzeng and coworkers [106] synthesized zinc(II) complex \([\text{Zn}_2L(\text{CH}_3\text{COO})_2]\cdot \text{CH}_3\text{CH}_2\text{OH}, \) from binucleating ligand \( L, 2,6\)-diformylpyridine N-oxidebis(benzoylhydrazone) via template reaction in alcohol. They characterized the complex by X-ray crystallographic studies. The dihydrazone ligand was found to be present in doubly deprotonated form. They established that all the coordinated atoms of the Schiff base ligand and two zinc atoms with the same bond length of 2.24(1) \( \text{Å} \). The two acedtato ions act as bidentate ligands linking two zinc atoms. Both the zinc atoms have a distorted trigonal-bipyramidal environment. The complex crystallizes in the triclinic space group P1.

Pelizzi and coworkers [107] synthesized six complexes of copper(II), nickel (II), and iron(II) from a chiral ligand 2,6-diacetyl pyridinebis([DL-hydroxy-(phenyl)acetic]hydrazone (H\textsubscript{4}dapm) and characterized them by spectroscopic studies. They established the structure of the nickel complex \([\text{Ni}(\text{H}_4\text{dapm})- (\text{H}_2\text{dapm})]\cdot 13\text{H}_2\text{O} \) by X-ray diffraction methods. The complex crystallizes in the monoclinic space group C2/c. The complex has a two fold crystallography imposed symmetry with the nickel atom in a distorted octahedral environment consisting of six nitrogen atoms from two ligand molecules. With the help of \(^1\text{H} \) NMR spectroscopic studies, the existence of the ligand in therr forms i.e the meso DL and the two enantiomeric DD and LL ones were established. They attributed the doublets at 6.40 and 5.58ppm to the OH groups. The \(^1\text{H} \) NMR spectrum of the complex \([\text{Ni}(\text{H}_4\text{dapm})(\text{H}_2\text{dapm})]\cdot 13\text{H}_2\text{O} \) showed the presence of two inequivalent ligand molecules i.e. one in meso form and the other in the DD or LL form. The complexes were characterized by IR spectroscopic studies.

Rana and coworkers [108] synthesized several manganese(II), iron(II), cobalt(II), nickel (II), and copper(II) complexes of 2, 6-diacetylpyridine(benzylacetone)hydrazone (H\textsubscript{2}L).
The complexes have been shown to have composition \([M(H_2L)X_2]\) (where \(M = \text{Mn, Fe, Co, Ni and Cu; } X = \text{Cl, Br, NO}_3, \text{SCN}\)) and have been characterized by molar conductance, magnetic moment data, infrared, and electronic spectroscopy. The dihydrazone has been shown to function as a tridentate ligand bonding to the metal centre through pyridyl nitrogen and azomethine nitrogen atoms. All the complexes have been proposed to be five coordinate having trigonal bipyramidal stereochemistry in which the dihydrazone donor atoms occupy equatorial position while the anions occupy axial positions.

Paolucci and coworkers [109] studied the interactions of potentially binucleating ligand, 2, 6-diacetylpyridine-bis(1-phthalazinylhydrazone) \((H_2\text{dapz})\), 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, \(\text{Ni(II)}\) and \(\text{Cu(II)}\) ions, selectively enter in one of the two compartments present in the ligand. They isolated five series of mononuclear complexes \([\text{dapzM}], [H_2\text{dapzMCl}_2], [\text{HdapzMCl}], [(H_2\text{dapz})_2\text{M}][\text{ClO}_4]_2, [\text{HdapzM}][\text{ClO}_4]\), from reactions of metal acetates, metal chlorides and metal perchlorates, respectively and the ligand. They established that the dihydrazone is present in the bisdeprotonated, monodeprotonated and undeprotonated forms, respectively in the complexes. They also studied some interconversion reactions. The complexes were characterized by analytical techniques and spectroscopic methods. Some tentative stereochemical assignments of these compounds are reported on the basis of their physico-chemical properties. Different behaviour has been observed in the case of \(\text{zinc(II)}\) chloride and perchlorate. Crystal structure analysis on the bisdeprotonated complex \([\text{dapzNI}]_2\) 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 [110] synthesized binuclear dioxotungsten(VI) complexes of the type \([(\text{WO}_2)\_2\text{L}], \text{where } L \text{ is a flexibly bridged hexadentate tetra anionic Schff base derived from the condensation of methylene or dithiobissalicylaldehyde with isonicotinoylhydrazone, benzoilhydrazone, } p\text{-nitrobenzoylhydrazone and furoylhydrazone are reported. The IR and NMR spectral data suggest an oligomeric structure for these complexes in which each tungsten atom achieves a pseudo-octahedral structure via } W - O - W \text{ bridging. Cyclic voltammetric measurements indicate irreversible to} \)
quasireversible reduction of the dioxotungsten(VI) complexes to oxotungsten(V) with a cathodic reduction potential of -1.0 to -1.1 V vs SCE at the scan rate of 500 mV/s. The bridging methylene (-CH$_2$) or dithio (-S-S-) group has very little effect on the thermodynamic stability of the complexes.

Lal and coworkers [111] synthesized the bimetallic manganese(II, III) and dioxouranium(VI) complexes [Mn$_4$(H$_2$L)(OAc)$_4$.4H$_2$O, [Mn$_4$(L)$_2$(H$_2$O)$_8$].4H$_2$O, K$_4$[Mn$_4$(L)$_2$F$_6$(H$_2$O)$_2$].2H$_2$O, [UO$_2$(H$_2$O)$_4$[Mn$_4$(L)$_2$(OAc)$_4$].4H$_2$O, and K$_4$[(UO$_2$)Mn$_3$(L)$_2$F$_5$(H$_2$O)$_3$] from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H$_4$L). 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 in enol forms in the anti-cis-configuration in all of the complexes.

Lal and Adhikari [112] synthesized the compound [(MoO$_2$)$_2$(L)(H$_2$O)].2H$_2$O from the reaction of MoO$_2$(acac)$_2$ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H$_4$L) in ethanol-acetonitrile in 3:1 molar ratio under reflux. The complex is proposed to be a hexamer in which ligands are arranged in sets of three in two parallel planes one above the other. The intra-planer metal atoms are bonded to each other by naphthoxo-bridges whereas the inter-planer metal atoms are bonded to each other by M = O...Mo type bridging. The anti-cis-configuration of the dihydrazone moieties leads to the chair conformation of the complexes.

Lal and coworkers [113] isolated the homobimetallic complex [(MoO$_2$)$_2$(L)].4H$_2$O from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H$_4$L) in the solid state. It reacts with Lewis bases pyridine and 3-picoline to form the complexes [{$\mu_2$-O}MoO$_2$]MoO$_2$(H$_2$L)].2D.4H$_2$O (where D = pyridine(py) (2), 3-picoline(3-pic) (3) and with proton bases salicyloyldihydrazone (sylshH$_3$) and isonicotinoylhydrazine (inhH$_3$) to yield the Mo(V) compounds [Mo$_2$(L)(sylsh)$_2$]. 5H$_2$O (4), and [Mo$_2$(L)(inh)$_2$(H$_2$O)$_2$]. 3H$_2$O (5), respectively. The complexes have been characterized by elemental analysis, molecular weight determinations, molar conductance, magnetic moment, ESR, electronic, infrared, and $^1$H NMR spectral studies. IR and $^1$H NMR data indicate that the dihydrazone coordinates to the metal centre in and anti-cis-configuration in all the complexes. The dihydrazone is present in the enol form in the complexes (1), (4), and (5)
but in the keto form in the complexes (2) and (3). The complexes (4) and (5) are paramagnetic to the extent of 3.02 and 3.16 \( \mu_B \) respectively.

Lal and coworkers \cite{114} have synthesized the complexes of the type [(UO\(_2\))\(_4\)(L\(_2\)(H\(_2\)O)\(_8\)].4H\(_2\)O (1), K\(_4\)[(UO\(_2\))\(_4\)(L\(_2\))(OAc)\(_4\)(H\(_2\)O)\(_4\)].4H\(_2\)O (2), and K\(_4\)[(UO\(_2\))\(_4\)(L\(_2\))F\(_4\)(H\(_2\)O)\(_4\)] (3), from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H\(_4\)L) and characterized by elemental analyses, molecular weight determinations, molar conductance, electronic, IR and \(^1\)H NMR spectroscopic studies. The dihydrazone coordinates to the metal centre in the \emph{anti-cis}-configuration in enol form in the complexes (1) and (3) which contain water and fluoro groups as co-ligands in the coordination sphere functioning as terminal monodentate ligand. The dihydrazone isomerizes to \emph{syn-cis}-configuration when the bridging bidentate acetate group is introduced into the first coordination sphere in the complex (2). The coordination of both azomethine groups of the dihydrazone to the same metal centre in \emph{anti-cis-} configuration in complexes (1) and (3) leads to coupling between azomethine protons suggesting their chair conformation. However, no such coupling occurs when different hydrazone parts of the dihydrazone coordinates to different metal centres in \emph{syn-cis}-configuration in complex (2) eliminating the possibility of its existence in chair conformation.

Lal and Kumar \cite{115} have synthesized an unstable monomeric yellow complex of the type [(MoO\(_2\))\(_2\)(CHsalmlhH\(_4\))(H\(_2\)O)\(_2\)].H\(_2\)O \{complex (A)} from the reaction between bis(acetylacetonato)dioxomolybdenum(VI) and disalicylaldehyde malonoyldihydrazone (CH\(_2\)salmlhH) in ethanol. This is transformed into an intermediate complex [(MoO\(_2\))\(_2\)(CHsalmlhH)(H\(_2\)O)]\(_2\).4H\(_2\)O \{complex (AB)} after sometime. Ultimately a stable brown isomer complex [(MoO\(_2\))\(_2\)(CH\(_2\)salmlh)(H\(_2\)O)\(_2\)].4H\(_2\)O \{complex (AB)} is obtained. All the products have been characterized by various physico-chemical techniques and IR and \(^1\)H NMR spectroscopic studies.

Lal and coworkers \cite{116} isolated the complexes of the composition [UO\(_2\)(H\(_3\)salligh)(OAc)].3H\(_2\)O and [UO\(_2\)Zn(salligh)(H\(_2\)O)\(_2\)].2H\(_2\)O, where H\(_3\)salligh refers to disalicylaldehydeoxaloyldihydrazone (H\(_4\)saloxlh), malonoyldihydrazone (H\(_4\)salmlh), succinoyldihydrazone (H\(_4\)salsuch), glutaroyldihydrazone (H\(_4\)salgluth), and phthaloyldihydrazone (H\(_4\)salphth). The complexes have been characterized by molar conductance and spectral data.
Lal and coworkers [117] have synthesized the complexes, 
Na₄[(UO₂)₄(L)₂(OAc)₄(H₂O)₄].4H₂O (1) and Na₄[(UO₂)₄(LhF₄(H₂O)₄] (2) from bis(o-hydroxynaphthaldehyde)oxaloyldihydrazone (napoxH₄) and characterized by elemental analysis, molar conductance, electronic, IR and ¹H 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 the acetato complex, the coordination of two hydrazone parts of the dihydrazone even in cis-configuration to different metal centres eliminates the possibility of azomethine proton coupling and thus, its existence in chair conformation. All the complexes involves eight-coordinated uranium atom with the dihydrazone in the enol form.

Lal and coworkers [118] have synthesized the monometallic complexes of the type [Zn₂(H₂L)₂(SO₄)₂] (1), [Zn₂(H₂L)₂(H₂O)₂] (2), K₂[Zn₂(H₂L)₂F₂] (2a), and the heterometallic complexes of the type compound [(UO₂)₂Zn₂(H₂O)₆] (3), [(UO₂)₂Zn₂(L)₂F₄(H₂O)₂] (3a), [Cu₂Zn₂(L)₂(H₂O)₄] (4), K₄[Cu₂Zn₂(L)₂F₄(H₂O)₂] (4a), and characterized by analytical, molar conductance and magnetic moment data and electronic, ESR, IR, and ¹H NMR spectroscopic studies. All of the complexes have been proposed to be dimmer 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 contain the coordinated dihydrazone in the anti-cis-configuration. In these complexes, copper and zine metal centres have been shown to be five coordinate square-pyramidal whereas uraniumcentres have been shown to be eight-coordinate hexagonal bipyramidal.

Ma Yongxiang and coworkers [119] synthesized the chelates Na₂[Ln(C₃₄H₂₈N₆O₈)Cl].nH₂O of the malonoyl dihydrazone of salicylaldehyde with the lanthanides and characterized them by elemental analysis, IR, UV, molar conductance and TGA. They showed that the ligand coordinates to the central ion with one hydrazone unit in the keto form and one chloride ion participates in coordination to the metal ion. These chelates are 1:2 electrolytes in DMF and are more thermostable than their ligand due to the formation of chelate rings.
Bolgar and coworkers [120] synthesized a series of dihydrazone and substituted dihydrazone derivatives of biacetyl and of hydrazine and phenylhydrazine derivatives of 2-acetylpyridine. They studied the reactions of those dihydrazones with \([\text{Ru(bipy)}_2\text{Cl}_2]\) and isolated the products of the composition \([\text{Ru(bipy)}_2(L-\text{L})][\text{PF}_6]_2\) \(\text{bipy} = 2,2'\)-bipyridine; \(L-\text{L} = \) biacetyl di(phenylhydrazone) \(1a\), biacetyl di[methyl(phenyl)hydrazone] \(1b\), biacetyl di(o-tolylhydrazone) \(1c\), biacetyl di(methylhydrazone) \(1d\), biacetyl di(benzaldehyde azine) \(1f\), 2-acetylpyridinephenylhydrazone \(1g\), or 2-acetylpyridinehydrazone \(1h\). The structures of all complexes were determined using IR, UV/Vis, \(^1H\) NMR and microanalysis. The proton NMR spectra of \(1a-1c\) showed an unusual dependence on probe temperature with broadened aromatic resonances, sharpening at both high and low temperatures in the case of \(1b\) and \(1c\). No emission was observed for complexes with two hydrazone moieties, whereas it was observed for \(1g\) and \(1h\) with one hydrazone. The molecular structure of \(1a\) was determined and it was shown that a hydrazone phenyl group lies over each of the bipyridyl rings: space group C2/c, \(a = 25.895(3)\), \(b = 10.505 (1)\), \(c = 17.431(2)\) Å, \(\beta = 106.03 (2)\)° and \(Z = 4\).

Khan and coworkers [121] synthesized a new class of tetraiminetetraamide macrocyclic \(\text{Ph}_4[20]\text{tetraene, N}_8\text{O}_4\), and \(\text{Ph}_6[20]\text{tetraene, N}_8\text{O}_4\) complexes through the metal ion controlled reaction of 1,2-diphenylethane-1,2-dione dihydrazone (DPEDDH) with succinic acid \([\text{ML}_1\text{X}_2]\) or phthalic acid \([\text{ML}_2\text{X}_3]\) \([\text{M} = \text{Co, Ni, Cu or Zn}; \text{X} = \text{Cl or NO}_3]\). They elucidated the structure 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 the imine nitrogens.

Labib and coworkers [122] synthesized a series of polyaclyhydrazones by condensing diacetyl with oxalic, malonic, succinic, glutaric and adipic dihydrazides and characterized them by conventional spectroscopic studies. They reacted these dihydrazones of general formula \{\{[\text{Cu}_2(L)(\text{OAc})_2(\text{OH})(\text{H}_2\text{O})_2].y\text{H}_2\text{O}\}_n, \{[\text{Cu}(L)(\text{AcO})_2(\text{HO})(\text{H}_2\text{O})].y\text{H}_2\text{O}\}_n, \{[\text{Ni}_2(L)(\text{AcO})_2(\text{HO})_2].y\text{H}_2\text{O}\}_n, \{[\text{Ni}(L)(\text{AcO})(\text{HO})].y\text{H}_2\text{O}\}_n, \} \), where \(L\) refers to the neutral dihydrazone unit. Magnetic susceptibility measurements in the 4.2-300 K range indicated significant antiferromagnetic coupling between the Cu\(^{II}\) centers in the
metallopolymers. The results might 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 Cu\textsuperscript{II} and Ni\textsuperscript{II} metallopolymers were proposed. The dihydrazine units in these polymers were found to be coordinated to the metal(II) via the azomethine nitrogen(s) whereas the amide group was found to remain uncoordinated. Each Cu\textsuperscript{II} is penta-coordinated in a distorted square pyramidal environment and is neutralized by one bridged acetate and a hydroxide ion, while the fifth coordination site is occupied by a 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\textsuperscript{[123]} synthesized the dinuclear copper(II) complexes with 2-hydroxypropiophenone, 2-hydroxy-5-methyl and 5-chloro-2-hydroxyacetophenone acyldihydrazones (H\textsubscript{L}) having the composition [Cu\textsubscript{2}L.mPy], where L ligand contains the polymethylene chain with different lengths (from two to five units). The crystal and molecular structure of the 2-hydroxypropiophenone adipoyldihydrazone complex [Cu\textsubscript{2}L.4Py].Py were established by X-ray diffraction analysis. Copper atoms were found to be separated from one another by a distance of 8.212Å. Their nearest environment were found to have tetragonal pyramidal geometry. The ESR spectra of solutions of the complexes based on acyldihydrazones of succinic, malonic, glutaric, and adipic acids contain seven HFS lines with the constant $\sim 40 \times 10^{-4}$ cm\textsuperscript{-1} from two equivalent copper atoms. The spectra were interpreted as a result of the spin-spin exchange interaction of two unpaired electrons. An increase in the polymethylene chain length of five units prevents exchange interactions. The ESR spectrum of the complex with acyldihydrazone of pimelic acid contains a signal of four HFS lines with $A_{Cu} = 73.4 \times 10^{-4}$ cm\textsuperscript{-1}, which is typical of mononuclear copper(II) complexes.

Andelkovic and coworkers\textsuperscript{[124]} synthesized complexes of Zn(II), Pd(II) and Pt(II) with 2'-[1-(2-pyridinyl)ethylidene]oxamohydrazide (Hapsox). The complexes were characterized and their structures were determined. All the complexes were found to be neutral type with two apsox ligands coordinating to Zn(II) and one apsox ligand coordinating to Pd(II) or Pt(II). In each case, the polydentate ligand was coordinated via pyridine and hydrazone nitrogens and α-oxyazine, forming an octahedral geometry.
around Zn(II), and a square planer one around Pd(II) and Pt(II). The structure determination was performed by IR, $^1$H NMR and $^{13}$C NMR spectroscopy, and for the Zn (II) complex by X-ray structure analysis.

Para et al [125] synthesized dialdehyde starch dihydrazone DASHZ from reaction of dialdehyde starch with hydrazine. 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 $>\text{C}=\text{N}$ moiety in dihydrazone as well as the oxygen atom of the former pyranose ring were the coordination sites. Metal ions were chelated to a different extent. One mole of a metal ion could coordinate with 3 [Cu(II)] to 50 [Mn(II)] mole 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. Except the complex with Mg, these rates for complexes were lower.

Zhao and coworkers [126] 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 $[\text{Ni}_2(2\text{poap})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2.2\text{CH}_3\text{OH}.2\text{H}_2\text{O}(1)$, $[\text{Mn}_2(\text{pttp})_2(\text{NO}_3)_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2.2\text{H}_2\text{O}(2)$, and $[\text{Mn}_2(\text{mapttp})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2.10\text{H}_2\text{O}(3)$, a square tetranuclear complex $[\text{Co}_4(\text{pttp})_4]\text{Br}_6.9\text{H}_2\text{O}$, a tetranuclear tetrahedral complex $[\text{Ni}_4(\text{pttp})_6](\text{BF}_4)_6\text{F}_2.14\text{H}_2\text{O}(7)$, and a mixed spin state tetranuclear Ni(II) complex $[2\text{pyoap}_2\text{Ni}_4(\text{CH}_3\text{OH})_4].1.5\text{CH}_3\text{OH}(10)$, with a diamond-like arrangement of metal ions. The paramagnetic metal centres are well separated in each case, leading to weak antiferromagnetic coupling or non-existent spin exchange.

Tirosh and coworkers [127] synthesized the cadmium (II) complex $[\text{Cd}(\text{C}_4\text{H}_{10}\text{N}_4)_3(\text{ClO}_4)_2]$ from the reaction of $\text{Cd}(\text{ClO}_4)_2.\text{H}_2\text{O}$ with biacetyl dihydrazone in methanol. They established the structure of the compound with the help of X-ray crystallography. The cation was found to be located on a 3 axis and was characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal.
Carcelli and coworkers [128] synthesized a novel series of lanthanide (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”), respectively. These hydrazones, (2,9-diformylphenanthroline)bis(benzoyl)hydrazone (H₂L¹), (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone (H₂L²). They prepared both nitrate and acetate complexes of H₂L¹ with La, Eu, Gd, and Tb and fully characterized. They presented the X-ray crystal structure of the complex [Eu(HL¹(CH₃COO))₂].5H₂O. The stability constants of the equilibria Ln³⁺ + H₂L¹ = [Ln(H₂L¹)³⁺] and Ln³⁺ + (L¹)²⁻ = [Ln(L¹)⁺] (Ln = La(III), Eu(III), Gd(III), and Tb(III)) were determined by UV spectrophotometric titrations in DMSO at t = 25°C. They also synthesized the nitrate complex of H₂L² with La, Eu, Gd and Tb. The X-ray crystal structure of the complex [La(H₂L²)(NO₃)₂(H₂O)](NO₃), [Eu(H₂L²)(NO₃)₂](NO₃) and [Tb(H₂L²)(NO₃)₂](NO₃) were also established.

Salem [129] synthesized a series of acyldihyrazones, H₂Lⁿ from condensation of ethylpyruvate with oxalic, malonic, succinic, glutaric and adipic dihydrazides. The author isolated dicopper(II) complexes of the general formula [Cu(Lⁿ⁺).H₂O].xH₂O, where Lⁿ 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 and variable temperature magnetic susceptibility measurements. Magnetic susceptibility measurements in the 4.2-298 K range indicate significant antiferromagnetic coupling between copper(II) centers and suggest association of the coordinated copper(II) units Cu(ONO) via oxazine oxygen bridges. This leads 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) centers (p), the degree of association in these polynuclear copper(II) complexes were estimated.

Elengoz et al [130] synthesized the zinc complex tris(biacetyl dihydrazone-κ²N,N')zinc(II) bis(perchlorate) at 110 K and determined its crystal structure precisely. The metal-organic cation, which is located on a 3 axis, is characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal. The title compound, crystallizes in the trigonal space group P3c1.
with two units of the \([\text{Zn(C}_4\text{H}_10\text{N}_4\text{)}_3\text{]}^{2+}\) cationic complex and four \(\text{ClO}_4^-\) anions in the unit cell. The \(\text{Zn}^{II}\) atom is located on a 3-axis, while the perchlorate anion is located on a threefold rotation axis. The cation is characterized by perfect 3 symmetry, in which three chelating ligands occupy the octahedral coordination sites of the zinc metal ion. 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 coordinating 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 ligand, the \(\text{N}—\text{C}—\text{C}—\text{N}—\text{N}\) backbone adopts a planar anti conformation (Hauer et al, 1987).

V. P. Singh and P. Gupta [131] synthesized and characterized the Complexes of diacetyl salicylaldehyde oxalic acid dihydrazone, \(\text{CH}_3\text{COC(CH}_3\text{)}=\text{NNHCOCONHN}=\text{CHC}_6\text{H}_4\text{(OH)}\) (dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone \(\text{CH}_3\text{COC(CH}_3\text{)}=\text{NNHCOCH}_2\text{CONHN}=\text{CHC}_6\text{H}_4\text{(OH)}\), (dsmdh) by elemental analyses, molar conductance, magnetic moments, electronic, ESR and infrared spectra and X-ray diffraction data and were found to have the general compositions \([\text{M(L)}\text{Cl}], [\text{M}'(\text{L})\text{Cl}], [\text{M}(\text{L'})\text{Cl}]\) and \([\text{M}'(\text{L'})\text{Cl}]\) (where \(\text{M} = \text{Co(II)}, \text{Cu (II)}, \text{Zn (II)}, \text{Cd (II)}\) and \(\text{M}' = \text{Ni(II)}\); \(\text{HL}=\text{dsodh}\) and \(\text{HL'} =\text{dsmdh}\). With the help of magnetic moments and electronic spectral data they predicted a six-coordinate octahedral geometry for \(\text{Co(II)}\) and square planar geometry for \(\text{Ni(II)}\) complexes. They also found that the ESR spectral data of \(\text{Cu(II)}\) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through \(>\text{C}=\text{O}, >\text{C}=\text{N}\) and deprotonated phenolate groups in all octahedral complexes and through \(>\text{C}=\text{N}\) and deprotonated phenolate groups in \(\text{Ni(II)}\) square planar complexes. The lattice parameters for \(\text{Cu(dsodh)}\) and \(\text{Co(dsmdh)}\) correspond to an orthorhombic and \(\text{Ni(dsodh)}\) corresponds to a tetragonal crystal lattice. The complexes were found to exhibit significant antifungal activity against a number of pathogenic fungi viz. Stemphylium, Myrothecium and Alternaria. The antibacterial activity was studied against Pseudomonas fluorescence (gram -ve) and Clostridium thermocellum (gram +ve).

C. T. Yang and coworkers [132] synthesized the complexes of dioxouranium(VI) with four dipyridoxal hydrazone ligands \(\text{H}_4\text{PL}^n\) and characterized them by various analytical
and spectroscopic methods including X-ray crystallography. The ligands and the UO$_2^{VI}$ complexes were also tested for cytotoxicity. They found that the solid-state structure of [(UO$_2$)$_4$(PL')$_2$(H$_2$O)$_4$].12H$_2$O is a cyclic tetramer.

M. F. Iskander and coworkers [133] synthesized and characterized two series of dicopper(II) complexes derived from bis(N-salicylidine)dicarboxylic acid dihydrazides (H$_4$L$^n$) of general formula [Cu$_2$(L$_n$)$_x$.xH$_2$O].yH$_2$O and [Cu$_2$(H$_2$L$^n$)Cl$_2$.xH$_2$O].yH$_2$O where $n$ refers to the number of carbon atoms in the aliphatic spacer between the two N-salicylideneacylhydrazine units. Magnetic susceptibility measurements for neutral dicopper(II) complexes [Cu$_2$(L$_n$)$_x$.xH$_2$O].yH$_2$O indicate significant antiferromagnetic coupling between copper(II) centers. The $-2J$ values obtained from the Bleany–Bowers equation are within the range 121–223 cm$^{-1}$, suggesting association of the coordinated copper(II) units Cu(ONO)$_2$ via phenoxy bridges. This leads to a polynuclear structure in which the dimeric units are connected with the aliphatic spacer. From the best-fit values of the mole fraction of paramagnetic uncoupled copper(II) centers ($p$), the degree of association in these polynuclear copper(II) complexes has been estimated. The chloro dicopper(II) complexes [Cu$_2$(H$_2$L$^n$)Cl$_2$. xH$_2$O].yH$_2$O with $n= 0$, 2 and 3 also show strong antiferromagnetic exchange coupling ($-2J$=215–423 cm$^{-1}$), suggesting a polynuclear structure in which the copper(II) is in a distorted square-pyramidal environment, bound in the equatorial plane with a monoanionic ONO tridentate acylhydrazone unit and the µ-phenoxy oxygen and the axial site occupied by a chloride. The dicopper(II) complexes with $n=1$ and 4 show weak antiferromagnetic exchange coupling ($-2J$=16–20 cm$^{-1}$). In these complexes the chloride ion may occupy the fourth equatorial site while the µ-phenoxy is in the apical position.

V. P. Singh and P. Gupta [134] synthesized and characterized the Complexes of diacetyl salicylaldehyde oxalic acid dihydrazone, CH$_3$COC(CH$_3$)=NNHCOCONHN=CHC$_6$H$_4$(OH), (dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone CH$_3$COC(CH$_3$)=NNHCOC(CH$_3$)=NNHCOCH$_2$CONHN=CHC$_6$H$_4$(OH), (dsmdh) of general compositions[M(L)]Cl, [M'$(L')$]Cl, [M(L')]Cl and [M'$(L')$]Cl (where M= Co(II), Cu(II), Zn(II), Cd(II) and M' = Ni(II); HL = dsodh and HL' = dsmdh) were prepared and characterized by elemental analyses, molar conductance, magnetic moments, electronic, ESR and infrared spectra and X-ray diffraction data. The magnetic moments and
electronic spectra indicate six-coordinate octahedral geometry for Co(II) and square planar geometry for Ni(II) complexes. The ESR spectral data of Cu(II) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through $\text{>C=O}$, $\text{>C=N}$ and deprotonated phenolate groups in all octahedral complexes and through $\text{>C=N}$ and deprotonated phenolate groups in Ni(II) square-planar complexes. The lattice parameters for Cu(dsodh) and Co(dsmdh) correspond to an orthorhombic and Ni(dsodh) corresponds to a tetragonal crystal lattice. The complexes were found to exhibit significant antifungal activity against a number of pathogenic fungi viz. *Stemphylium, Myrothecium and Alternaria*. The antibacterial activity was studied against *Pseudomonas fluorescens* (gram -ve) and *Clostridium thermocellum* (gram +ve)

V. P. Singh and co-workers [135] isolated the metal(II) complexes of the general formula $\left[M(H_{2}B_{sodh})\right]Cl$ and $\left[MB_{smdh}\right]Cl$ where $M = \text{Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)}$ ($HB_{sodh} = \text{benzyl salicylaldehyde oxalic acid dihydrazone and HB}_{smdh} = \text{benzyl salicylaldehyde malonic acid dihydrazide}$) and characterized them by elemental analyses, molar conductance, magnetic moment, ESR, IR and X-ray diffraction studies. The ligands and their metal complexes were found to exhibit significant antibacterial activity against Bacillus subtilis and Pseudomonas fluoescens.

L. D. Popov and co-workers [136] synthesized the dihydrazone ligand 2, 6-diformyl-4-tert-butylphenol bis(8-quinolylhydrazone) and its transition meta complexes of the compositions $\left[Cu_{2}(H_{2}L)Cl\right]Cl$, $\left[Ni_{2}(H_{2}L)Cl\right]Cl$ and $\left[Mn_{2}(H_{2}L)Cl\right]Cl$, where $H_{2}L$ is the monodeprotonated form of the hydrazone. They studied the conformations of the bis-hydrazone, geometries of the complexes, and parameters of exchange coupling between the ferromagnetic centres using quantum-chemical calculations. They also compared the calculated results with the results of the physicochemical study of the complexes.

S. Naskar and D. Mishra [137] synthesized a Ni(II) complex of 2, 6-diacetylpyridine bis(anthraniloyl hydrazone) and characterized it by various physico-chemical methods. The structure of the complex was determined by X-ray crystallography. They also found that, in the solid state, the compound exist as a dimer and two coordinated ligand moieties form a double helix around the two metal ions.
R. M. Issa and co-workers [138] studied the thermal stabilities of bis salicylidine adipic dihydrazone derivatives and their complexes with divalent Mn, Ni, Cu and Zn ions and discussed them in terms of structure and type of metal ions. They also found that, the TG curves display mostly four steps of thermal decomposition.

V. F. Shulgin and co-workers [139] synthesized and characterized dinuclear copper(II) complexes with acyldihydrazones of 2-hydroxy-5-nitroacetophenone (H₄L) of the composition Cu₂(py)₄LₘEtOH. It was found that, in the complexes, the coordination polyhedra of the copper atoms are linked to each other by a polymethylene chain of different lengths, from one to five monomer units. They also established the structure for [Cu₂L₄Mrf] complex (where Mrf is morpholine) based on acyldihydrazone of malonic acid by X-ray diffraction.

M. Salavati-Niasari and A. Sobhani [140] isolated the monomer transition metal complexes, [ML] (M = Mn(II), Co(II), Ni(II) and Cu(II)) from the reaction of metal acetates with bis(salicylaldehyde)oxaloyldihydrazone (H₂L) in 1:1 molar ratio in ethanol under reflux. It was suggested that, in all of the complexes, the principal dihydrazone ligand coordinate to the metal centres in the anti-cis configuration. These metal complexes were entrapped in the nano cavity of zeolite-Y. The new Host-Guest Nano Composite Materials (HGNM) were characterized by chemical analysis and spectroscopic methods. They also reported the catalytic activities for the oxidation of cyclohexane with HGNM.

Da-Yu Wu and co-workers [141] isolated three ligands, di(2-pyridylcarbaldehyde)-6',6'-dicarboxylic acid hydrazone-2, 2'-bipyridine (H₂L¹), di(2-acetylpyridyl)-6',6'-dicarboxylic acid hydrazone-2, 2'-bipyridine (H₂L²) and di(2-pyridyketone)-6',6'-dicarboxylic acid hydrazone-2, 2'-bipyridine (H₂L³) with flexible bis-terdentate coordination sites and their cobalt complexes. The complexes were obtaine via self-assembly and their structures were determined by FT-IR, elemental analyses, ESI-MS and X-ray diffraction method.

Lal and coworkers [142] synthesized the complexes [(UO₂)(CH₂L)(H₂O)₄].4H₂O, [M₄(H₂L)₂(H₂O)₄].4H₂O (M = Zn, Cu), (M')₂[(UO₂F)(CH₂L)(H₂O)₂] [M' = K, Na], M'[(UO₂)₂(CH₂L)(OAc)(H₂O)₂] [M' = K, Na], K₄[(MF)₂(CH₂L)₂].4H₂O [M Zn, Cu]
from the reaction of appropriate metal salts with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (CH$_2$LH$_4$) under different experimental conditions in ethanol/methanol media. The complexes have been characterized by elemental analyses, molecular weight, molar conductance, magnetic and EPR data. The structural assessment of the complexes have been carried out on the basis of electronic, infrared, $^1$H NMR and $^{13}$C NMR spectral studies.

Lal and coworkers [143] synthesized and characterized zinc(II), copper(II), nickel(II) and manganese(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone. In their study, they have shown that the reaction of different salts of the same metal with sterically crowded dihydrazone bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH$_2$LH$_4$) in ethanol/aqueous media gives complexes of different stereochemistry. While the reaction of Zn(II) and copper(II) sulphate with dihydrazone yields tetrahedral complexes, the zinc(II) and copper(II) chlorides give square-pyramidal and distorted octahedral complexes respectively. On the other hand, nickel(II) sulphate and chloride, both gave high-spin octahedral complexes. They also investigated the reaction of these complexes with KF. All of the products were characterized by analytical, magnetic moment and molar conductance data. The structure of the complexes have been established by spectroscopic studies.

Lal and coworkers [144] synthesized the monomer molybdenum(VI) complex [MoO$_2$(napoxlhH$_2$)].2H$_2$O (1) from the reaction of MoO$_2$(acac)$_2$ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (napoxlhH$_4$) in 1:1 molar ratio in ethanol under reflux. This complex on reaction with pyridine/3-picoline/4-picoline yielded the dimmer molybdenum(VI) complex [Mo$_2$O$_4$(napoxlhH$_2$)(A)$_2$].2H$_2$O (A = py (2), 3-pic(3), 4-pic(4)), whereas the reaction with isonicotinoyl hydrazine (inhH$_3$) and salicyloyl hydrazine (sylshH$_3$) led to the reduction of the metal centre yielding monomeric molybdenum(V) complexes [Mo(napoxlhH$_2$)(hzid)].2H$_2$O (where hzidH$_3$ = inhH$_3$ (5) and (sylshH$_3$ (6)). The complexes have been characterized by elemental analyses, molecular weight determinations, molar conductance data, magnetic moment data, electronic, IR, ESR and $^1$H NMR spectroscopic data.

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
characterised, in some detail, those derived from dihydrazones containing bulky fragments in their molecular skeleton have much less been studied. In view of limited number of investigations on metal complexes of dihydrazones containing bulky fragments in their molecular skeleton, the 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 homobimetallic complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones with copper(II) and molybdenum(VI). Part of the work is under consideration for publications.
References


26: C. P. Casey, J. Organomet., 205, 400 (1992)


