CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Introduction
The present thesis embodies the results of investigations of reactions of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone, \( \text{MoO}_2(\text{acac})_2 \), \( \text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O} \) and \( \text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O} \) 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, IR, \(^1\text{H} \) NMR, \(^{13}\text{C} \) NMR, conductivity measurements, magnetic susceptibility measurement and electronic spectral data. Accordingly, the present chapter gives a brief account of the importance of molybdenum, nickel and zinc in monometallic and heterometallic systems followed by description of bonding modes of dihydrazone ligand and literature survey on metal complexes of dihydrzones.

Molybdenum is the only element of the second transition series, being essential for life \([1, 2]\). The element molybdenum is present in two types of enzymes, one of these is nitrogenase \([3]\) 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 \([4]\) 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 \([5]\), and reduction of nitrate to molecular nitrogen \([6, 7]\). Molybdenum’s biochemical role is based on its ability to facilitate electron exchanges and to form stable complexes with oxygen, nitrogen and sulfur containing ligands \([2]\).

Mixed metal-molybdenum oxides are used as efficient and selective catalysts for partial oxidation of light alkanes in petrochemistry \([8]\).

A cobalt, nickel or platinum promoted molybdenum catalyst is used in the hydrosulfurization and hydrodenitrogenation processes \([9, 10, 11]\) whereby organo sulfur and nitrogen compounds in petroleum feed stocks are heterogeneously desulphurised and denitrogenated. Homogeneous molybdenum(VI) catalysts containing the cis-[\( \text{MoO}_2 \)]\(^{2+}\) unit are the basis of important industrial oxidation processes such as olefin epoxidation using alkyl hydroperoxides as the oxygen source \([12, 13, 14]\). The molybdenum compound [\( \text{NH}_3\text{Pr}^+\)][\( \text{Mo}_7\text{O}_{24}^-\)]\( \cdot 3\text{H}_2\text{O} \) (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 [15]. The polyoxomolybdenum anions have potential applications in catalysis, solid-state technology and medicine, including anti-tumor, anti-bacterial and anti-virus (HIV) activity [17, 18].

In 1975, Zerner discovered that nickel is present in urease enzyme. The other enzymes of nickel are urease, E. Coli glyoxalase I (E. Coli Glx I), [NiFe]-hydrogenase, methyl-CoM reductase (MCR), Co-dehydrogenase (CODH) and acetyl CoA synthase (ACS) [19].

Nickel occurs widely in bacterial hydrogenase which catalyzes the combination of hydrogen and oxygen, the reduction of sulfate ion, the production of methane and other reductive processes such as reduction of alkyl halides [20]. Nickel also occurs in urease obtained from jack beans [21]. Urease catalyses the hydrolysis of urea to ammonia and carbonic acid. Nickel complexes are also used as anti-oxidants [22] and are also used as catalysts for the oligomerization of ethylene [23].

Nickel plays a prominent role in several areas of material chemistry. Some topical interplay between nickel coordination chemistry and material science exists in the use of Ni-containing alkoxides for the synthesis of ceramic materials by MOCUD and sol-gel processes, the preparation and nanoscopic dendrimers incorporating Ni, the construction of 3D hybrid inorganic-organic porous materials with Ni coordination units and the fabrication of supported Ni catalysts and Ni nano structures through nanotechnology. Paramagnetic high spin Ni^{II} has found particular attention in the field of molecular magnetism, culminating in the recent discovery of the first single molecule magnets based on Ni^{II} centres [19].

Zinc(II) is one of the most abundant divalent metal ion occurring in living organisms (2.30 g Zn for an average person) and is the second most abundant metal in the body and is a structural or catalytic component of more than 300 enzymes. It is an essential component of many protein scaffolds (e.g., carbonic anhydrase and zinc finger protein). Zn(II) plays critical roles in gene transcription and metalloenzymes function [24].

Zinc(II) plays important role in several biological processes. Apart from enzymes with one zinc binding sites e.g., carbonic anhydrase and carboxypeptidase A, enzymes containing two or three zinc ions at the active sites are also of particular interest. Dinuclear Zn(II) cores are often seen in biological systems, such as phosphatases and aminopeptidases. In addition, some synthetic dinuclear zinc(II) complexes are found to have functions in RNA hydrolysis and dephosphorylation. In addition, the role of zinc in neuro-biology is a topic of substantial current interest [25].
Zn(II) is used extensively as an anodic inhibitor for metallic corrosion protection [26]. Zinc has been shown to be a useful metal centre in hybrid organic-inorganic framework solids, particularly with di- and tri-carboxylic acids and diphosphonates, framing a wide range of coordination polymers, many stable to the removal of included solvent [27].

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 [28] and heterogeneous catalysis [29]. 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 metals [30]. 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 [31]. They exhibit distinct reactivity pattern as compared to their monometallic and homobimetallic complexes.

The heterobimetallic complexes have been successfully used as precursors in the preparation of ceramic materials favouring an intimate mixing of the elements which enable reactions at lower temperature rather than for traditional route for the preparation of purer inaccessible solid state phases [32].

**Description of the ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone**

The present ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone has been derived from the condensation of succinoyl dihydrazine with 2-hydroxy-1-naphthaldehyde. The present ligand has several potential coordination centres such as carbonyl oxygen atoms, naphtholic oxygen atoms, secondary amine nitrogen atoms and azine group nitrogen atoms, all in duplicate which due to symmetry has equal probability of taking part in coordination. This can react with the metal ions in keto, keto-enol and enol forms.

![ligand structure](image-url)

**Fig 1.1. Bis(2-hydroxy-1-naphthaldehyde)succinoyl dihydrazone**
Thus because of the presence of as many as eight bonding sites and because of its ability to exhibit keto-enol tautomerism in the complexes, it can form bonds to metal ions in several different ways as shown below:

1. It may function as a neutral bidentate ligand coordinating either through two carbonyl oxygen atoms (I) or the two secondary amine nitrogen atoms (II), the OH groups remaining hydrogen bonded in the complexes.

![Diagram of structure I](image)

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

![Diagram of structure III](image)
3. It may function as a dibasic tetradeutate ligand coordinating through two hydroxyl oxygen atoms and the two azine group nitrogen atoms (IV), the two carbonyl oxygen atoms remains unbonded.

4. It may act as a dibasic hexadentate ligand bonding to the metal ion through the two hydroxyl atoms, two azine group nitrogen atoms and the two carbonyl oxygen atoms (V).

5. 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 atom and carbonyl oxygen atom to the same metal centre or even to different metal centres due to steric considerations and inductive effect.

6. When the ligand undergoes enolization as shown below, it may afford newer bonding sites. In this form, it can act as dibasic tridentate (VII), dibasic tetradeutate (VIII), dibasic pentadentate (IX), and tetrabasic hexadentate (X) ligand bonding to
the same or different metal ions. In the enolized form it can act as a binucleating or a polynucleating ligand.

The most essential characteristic feature of the ligand skeleton is that, it possesses the group \(-\text{CH}_2\text{-CH}_2\) which offers high flexibility to the ligand whereas naphthaldimine fragment is associated with bulky characteristic which may introduce steric crowding in the molecule. The present dihydrazone can exist in the staggered configuration (XI) or cis-configuration in the uncoordinated state and as well as in the metal complexes. In cis-configuration the dihydrazone can adopt either syn-cis configuration (XII) or anti-cis configuration (XIII).
All these possibilities can actually be realized in practice if the nature of the metal salt, molar ratio of the metal ion and the ligand, the nature of the counter cation and anion, reaction medium, pH and temperature of the reaction medium are varied.
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 electro chemical properties of complexes derived from them show promise in developing theories whereby electron transport phenomena can be understood [33]. 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 [34] and which can serve as models in bioinorganic chemistry [35]. 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, the present ligand can act as mono-, di-, tri-, and tetrabasic hexadentate ligand 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 \([R(CONHNH_2)_2]; (R = O, -(CH_2)_n-, C_6H_4<, C_6H_3N<)\) with o-hydroxyaromatic aldehydes and ketones. Another category of the dihydrazones can be obtained from condensation of dialdehydes \([R(CR'O)_2]; (R = O, -(CH_2)_n-, C_6H_4<, C_6H_3N<, R' = alkyl groups)\) with monoacetyl-, aroyl-, pyridoyl- and quinaldinooyl-, hydrazines. Accordingly, the literature survey is presented under the following two major sections.

1. Complexes of dihydrazones derived from condensation of acyl-, aroyl-, and pyridoyl-, dihydrazines with simple o-hydroxyaromatic aldehydes and ketones.

2. Complexes of dihydrazones derived from condensation of dialdehydes with monoacetyl-, aroyl-, pyridoyl- and quinaldinooyl-, hydrazines.

Sacconi [37] 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 co-workers [38] isolated complexes of the compositions [VO(LH$_2$)]SO$_4$, [VO(LH$_2$)]Cl$_2$, [VO(LH$_2$)py]SO$_4$ from reaction of vanadyl sulfate and chloride and metal(II) chloride with bis(acetone)oxaloyldihydrazone, bis(acetone)malonoyldihydrazone and bis(acetone)succinoyldihydrazones in alcoholic medium. The complexes [VO(LH$_2$)]SO$_4$ and [VO(LH$_2$)]Cl$_2$ were proposed to have square-pyramidal stereochemistry while the remaining complexes were proposed to have octahedral stereochemistry.

Iskander and co-workers [39] isolated the metal (II) complexes of the composition $\text{M(LH}_3\text{X}_n\text{H}_2\text{O)}$, $\text{M}_2(\text{LH}_2\text{X}_2\text{H}_2\text{O})$, $\text{M(}\text{LH}_2\text{H}_2\text{O)}$ and $\text{M(LH}_3\text{H}_2\text{O)}$ (where $\text{M} = \text{Cu(II)}, \text{Ni(II)}$ and Co(II); $\text{X} = \text{Cl}, \text{Br}, \Gamma$) from reaction of the metal(II) salts with dihydrazones (L$_4$) derived from condensation of salicyaldehyde with acylidihydrazines 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(LH$_3$)X]$_n$H$_2$O (X = Cl, Br, $\Gamma$) and [Ni$_2$(LH$_2$)Cl$_2$]$_2$H$_2$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 Ni(LH$_2$)$_n$H$_2$O as against a distorted octahedral structure for the corresponding cobalt(II) analogues. On the other hand, Kapoor and co-workers [40] suggested that the nickel(II) complexes Ni(LH$_2$)$_n$H$_2$O have octahedral stereochemistry. Anomalous magnetic behaviour of the nickel complexes Ni$_2$(L)$_n$H$_2$O ($\mu_{\text{eff}}$ 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 Cu(LH$_3$)$_X$H$_2$O and Cu$_2$(LH$_2$)$_X_2$H$_2$O 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 Cu(LH$_2$)H$_2$O has been suggested to have square planar stereochemistry.

Narang and Lal [41] have described complexes of disalicyaldiminesuccinamide (H$_2$L) and N,N-bis(o-hydroxyacetophenoneimine)succinamide (H$_2$J) of the types ML, MJ, M(HL)Cl,
M(HJ)Cl and M'(HL)₂ (where M = Cu(II), Ni(II), or Co(II)). The complexes are proposed to have either octahedral stereochemistry or square planar stereochemistry.

Narang and Lal [42] have reported mono and binuclear zinc(II) complexes Zn(HL)Cl and Zn₂(L-2H) derived from multidentate acylidihydrazide 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 [43] of the type M₂L derived from dihydrazones obtained from condensation of oxaloyldihydrazide, succinoyldihydrazide and phthaloyldihydrazide 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-bridged structure.

Narang and Lal [44] have prepared and characterized the metal(II) complexes M(H₂J), M(H₂K), M(H₃J)Cl, M(H₃K)Cl, M₂J, M₂K and M₂(HK)(CH₃COO) (where M = Cu(II), Ni(II) and Co(II)) derived from di(salicylaldimine)malonamide (H₄J) and di(o-hydroxyacetophenoneimine)malonamide (H₄K) and the zinc(II) complexes ZnH₂L and Zn₂L from a number of multidentate acylidihydrazones (H₄L). 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 co-workers [45] synthesized a new series of polymeric cobalt (II) complex of the type Co₂(L):nH₂O from reaction of metal(II) acetate and dihydrazone (LH₄) where LH₄ is bis(o-hydroxyacetophenone)oxaloyldihydrazone, bis(salicylaldehyde)oxaloyldihydrazone, bis(salicylaldehyde)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 co-workers [46] synthesized and characterized complexes of the type [M(LH₂)]X₃ (where M = Cr(III), Mn(III), Fe(III) or Co(III); X =Cl⁻, NO₃⁻ or OAc) from
reaction of metal (III) salts with N-N-dibenzyldiene dipicolinic acid hydrazone (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 [47] have also claimed that dipicolinic acid dihydrazine behaves as pentadentate ligand. On the other hand, Dutta and Sarkar [48] 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 co-workers [49] have studied reaction of vanadyl chloride and dipicolinic acid dihydrazine in presence of acetylacetone or other β-diketones in ethanol and acetic acid. They isolated brown solid complexes of macrocyclic ligand bis(β-diketone) dipicolinoyldihydrazones. On the other hand they isolated a non-macrocyclic pyrazole derivative when reaction of vanadyl chloride was carried out with the preformed bis(β-diketone)dipicolinic acid dihydrazine. Similar products [50] were also isolated in case of zirconium(IV).

Teotia and Rana [51] synthesized complexes [M(L)-2H$_2$O] (M = Cu(II), Ni(II) and 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 the five coordinate geometry.

Kapoor and co-workers [52] 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, malonyldihydrazine and succinoyldihydrazine under different experimental conditions. The trivalent metal ions are found to yield complexes having compositions [M$_2$LX$_2$]·nH$_2$O and [M$_2$(LH$_2$)X]·nH$_2$O (M= Cr(III), Fe (III) and Mn (III)) (X= Cl, NO$_3$, OAc, OH) while the bivalent metal ions were found to form complexes having compositions [M(LH$_2$)] and [ML(H$_2$O)$_4$] (M= Mn(II) and 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 [53] 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 [54] 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 co-workers [55] studied the complexation behaviour of uranyl ion with various dihydrazides and their diydrazones 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 the effect of excess acetate ion on complex formation.

Lal and co-workers [56], have prepared several homotrinuclear complexes having general formula \[ [M_3LCl_2(H_2O)_3] (M=Mn(II), Co(II) or Ni(II)) \] from bis(acetophenone)-2,6-dipicolinoyldihydrazone (LH₂₄) in alcoholic medium by adjusting pH to ~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 [57] have synthesized polymeric complexes \( M(L-2H)\cdot nH_2O \) (where \( M = \text{Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L=A,B} \) 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 co-workers [58] studied the reaction of uranyl acetate with the above dihydrazones (H₄L) in aqueous-alcoholic media and isolated complexes of the type \( (UO_2)_2L\cdot 6H_2O \). 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 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 [59] studied reaction of uranyl nitrate and acetate with dihydrazones (H₄L) (where H₄L = disalicylaldehydeoxaloyldihydrazone (H₄A), -malonyldihydrazone (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 co-workers [60] synthesized copper(II) complexes Cu₂(L)·nH₂O and dioxouranium(VI) complexes [(UO₂)₂(H₂L)(C₂O₄)]·2nH₂O of the above dihydrazones. The C₂O₄²⁻ group is suggested to coordinate to the uranium centre retaining its D₂h symmetry.

Lal and co-workers [61] synthesized a series of uranyl complexes of the composition [UO₂(H₃L)]·nH₂O 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 [62] studied reactions of disalicylaldehyde adipoyldihydrazone with uranyl nitrate and uranyl acetate in aqueous and ethanol media under different experimental conditions. The resulting complexes of the compositions [UO₂(H₃L)(H₂O)]ₙ, [UO₂(H₂L)]ₙ·3nH₂O, [UO₂(H₃L)(CH₃COO)]ₙ·3nH₂O, [UO₂Zn(L)(H₂O)]ₙ·2nH₂O, [(UO₂)₂(H₂L)(C₂O₄)]·nH₂O, [(UO₂)₂(L)(py)₂(H₂O)]ₙ·4H₂O, [(UO₂)₂(HL)(CH₃COO)(H₂O)]ₙ·nH₂O, [(UO₂)₃(L)(CH₃COO)₂(H₂O)₂]·2nH₂O, [(UO₂)₂(L)(py)₂(H₂O)]ₙ·XnH₂O, (where py = pyridine or α-, β-, γ-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 [UO₂Zn(L)(H₂O)]ₙ·2nH₂O, the uranium and zinc atoms are considered to have hexagonal bipyramidal and tetrahedral stereochemistry respectively.

Lal and co-workers [63] have described dioxouranium(VI) and Zn(II) complexes [M(H₂L)(H₂O)]₂·2nH₂O (where M= UO₂²⁺, Zn²⁺) of bis(o-hydroxynaphthaldehyde) oxaloyldihydrazone (H₄L). 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 -OH groups are
proposed to be non-coordinated. They [64] have, further, synthesized dioxouraninum(VI) complexes \([\text{UO}_2(\text{H}_2\text{L})_2\cdot 2n\text{H}_2\text{O}}\) and \(\text{[UO}_2(\text{L})(\text{H}_2\text{O})_2\text{n}]_n\) from reaction of uranyl nitrate with preformed dihydrazone bis(o-hydroxynaphthaldehyde)oxaloyldihydrazone in 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 \(\delta \text{CH} = \text{N}\) in both complexes into quartet as compared to the singlet in free dihydrazone, the complexes are proposed to exist in chair formation with the \textit{anti-cis}-configuration of dihydrazone involving eight and nine coordinated uranium atoms, respectively. The complexes [65] \(\text{Na}_4[\text{UO}_2(\text{L})_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}\) and \(\text{Na}_4[\text{UO}_2(\text{L})_2\text{F}_4(\text{H}_2\text{O})_4]\) obtained from the same ligand have also been described by them.

Patil and Kulkarni [66] and others [67] obtained complexes of the type \([\text{UO}_2\text{L}]_n\text{H}_2\text{O}\) from interaction of uranyl acetate disalicylaldehyde thiocarbohydrrazone \((\text{H}_2\text{L})\) and established their structure by \(^1\text{H} \text{NMR}\) and IR spectroscopic studies.

Kapoor and co-workers [68] studied reaction of malonyldihydrazone and phthaloyldihydrazone with \(\beta\)-diketones in presence of the dioxouraninum(VI) cation which appears to function as a metal template. This facilitates condensation of dihydrazone with diketones resulting in the formation of several dioxouranium(VI) complexes of macrocyclic ligands. The formation of a macrocyclic ring was confirmed from infrared spectroscopic studies. However, when dioxouranium(VI) nitrate was treated with the condensation product of phthaloyldihydrazone and acetylacetone, an entirely different pyrazole derivative was formed.

Sahoo and co-workers [69] have synthesized several first series transition metal complexes from several dihydrazones. The complexes were characterized by elemental analyses, physic-chemical data and spectral studies.

Pandey [70] 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 >C=O and >C=N groups.

Mahale and Havanur [71] studied dioxomolybdenum(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 salicylaldehydes.

Panda and co-workers [72] synthesized heterobimetallic complexes \([\text{MNiM}(\text{BTDO})_2\text{X}_2(\text{H}_2\text{O})_4]\cdot n\text{H}_2\text{O}\) (where M = Ni(II), Co(II) and Cu(II); X = Cl, NO$_3$; n =
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[bis(diacetyldihydrazone)]. The metal centres have been proposed to have octahedral stereochemistry.

Gopinathan and co-workers [73] have shown that the Schiff base, (HOCH\(_2\)CH=NNCO\(_2\)CH\(_2\)) \((H\_4L)\) derived from the condensation of salicylaldehyde and malonoylethylnhydrazone reacts with organotin chlorides to yield binuclear complexes of the type R\(_2\)Sn(L)SnR\(_2\), where R = CH\(_3\), C\(_2\)H\(_5\), C\(_4\)H\(_9\), C\(_6\)H\(_5\), CH\(_3\)CO\(_2\)CH\(_2\)CH\(_2\), and C\(_6\)H\(_5\)CH\(_2\). The complexes have been characterized and the structures were assigned on the basis of their elemental analyses, IR, \(^1\)H, \(^{13}\)C, \(^{119}\)Sn NMR spectra and X-ray crystallographic data. They studied the structure of the complex [\((C\(_2\)H\(_5\))\(_2\)Sn\]\(_2\)(OC\(_4\)H\(_4\)CH=NNCO\(_2\)CH\(_2\) by X-ray crystallography.

Sacconi [74] studied the 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 [75]. The formation constant of the complexes formed between biacetyl-bis(benzylhydrazonato)nickel(II) and various alkyl amines [76] have been studied. Complexes of lead(II), lead(IV) and tin(IV) of the types [Pb(L)], [Pb\(_2\)Pb(L)], [Sn(L)_2], [PhSn(L)Cl] and [Ph\(_2\)Sn(L)] have been obtained by mixing methanol solutions of the appropriate metal salts and the ligand [77].

Pelizzi and co-workers [78] have studied reaction of copper(II) chloride dihydrate with 2,6-diacetylpyridine-bis(picoloylhydrazone) \((LH\_2)\) in refluxing ethanol yielding a dark green crystal of Cu\(_2\)(L)Cl\(_2\)-H\(_2\)O. 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 around one Cu(II) is made up of a basal plane consisting of a chloride, two nitrogen atoms from the ligand \((LH\_2)\), 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 chloride ion takes up the apical site. Same authors [79] have isolated another series of complexes of the type M(LH\(_2\))Cl\(_2\)-nH\(_2\)O (M=Mn(II), Co(II), Ni(II) and Cu(II)) by mixing chloroform solution of LH\(_2\) and ethanolic solution of the metal chlorides in 1:1 molar ratio. Another Mn(II) compound MnL\(_2\)-9H\(_2\)O was obtained by adding dropwise, a dilute NaOH solution to a warm ethanol-water solution containing LH\(_2\) and MnCl\(_2\)-4H\(_2\)O 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 [80]. 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 also proposed for them 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 was shown to have pentagonal bipyramidal stereochemistry.

Curtis and co-workers [81] and others [82] studied Cu(II) and Ni(II) complexes of acetylacetonebis(picoloylhydrazone) and acetylacetonebis(isonicotinoylhydrazone). They carried out X-ray structural analysis of the copper(II) complex of acetylacetonebis(isonicotinoylhydrazone) obtained from reaction of metal(II) salt, isonicotinoylhydrazone and acetyl acetone and confirmed the square-pyramidal stereochemistry.

Giordano and co-workers [83] isolated cobalt(II) and nickel(II) complexes of compositions [Co(LH2)(H2O)(NO3)]NO3 and [Ni(LH2)(H2O)2](NO3)2·2H2O from the 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 co-workers [84] isolated lanthanum complex of composition [La(LH2)(NO3)3] from the 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 co-workers [85] prepared a series of dioxouranium(VI) complexes of 2,6-acetylpyridinebis(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 co-workers [86] isolated tin(IV) complexes of the composition [Snpr\textsubscript{2}(LH\textsubscript{2})] from reaction of n-propyltinchloride in anhydrous acetone, under nitrogen atmosphere with boiling suspension of 2,6-diacylpyridinebis(salicylhydrazone) (LH\textsubscript{i}) 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 co-workers [87] have studied reactions of metal(II) salts (M=Cu(II), Ni(II)) with picolinoyl/isonicotinoylhydrazine in presence of acetylacetone. They isolated complexes of the compositions [M(LH)X] (M = Ni(II), Cu(II), X = Cl\textsuperscript{-}, Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-} and NCS, L\textsubscript{H\textsubscript{2}} = acetylacetonebis(picolinoylhydrazone) or acetylacetonebis(isonicotinoylhydrazone). All the complexes have been established to have square-pyramidal stereochemistry. The complexes [M(LH)X\textsubscript{2}] [X= Cl\textsuperscript{-}, Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-} and NCS for M=Cu(III); X = OAc, Cl\textsuperscript{-}, Br\textsuperscript{-}, NCS for Mn(III) and OH for Co(III)] were also prepared similarly [88] by them. These complexes have been suggested to have six-coordinate tetragonal structure.

Paolucci and co-workers [89] synthesized several complexes of 2,6-diformylphenolbis(benzoylhydrazone) and its substituted derivatives with the bivalent metal ions (M = Co (II), Ni (II), Cu(II) and Zn(II) and established their molecular structure by various physico-chemical 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 co-workers [90] isolated complexes of the composition [VO(L)] from reaction of VO(acac\textsubscript{2}) with acetylacetonebis(benzoylhydrazone) (L\textsubscript{H\textsubscript{2}}) in acetone. The same ligand on reaction with CoX\textsubscript{2} (X = Cl\textsuperscript{-}, Br\textsuperscript{-}) in anhydrous medium yield blue coloured tetrahedral polymeric complexes [Co(L\textsubscript{H\textsubscript{2}})X\textsubscript{2}] [91]. However, in the presence of lattice water, bromide salt yields pink coloured pseudo-octahedral [Co(L\textsubscript{H\textsubscript{2}})Br\textsubscript{2}] complexes. The dihydrazone reacts with nickel(II) chloride in rectified spirit and yields diamagnetic, orange yellow complex [Ni(L)] [92]. However the reaction with anhydrous NiCl\textsubscript{2} in warm anhydrous methanol gives a paramagnetic complex [Ni(L\textsubscript{H\textsubscript{2}})Cl\textsubscript{2}] having a 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]. This complex is proposed to have a five-coordinate structure. They have also isolated the complexes [Zn(L)], [Cd(L)\textsubscript{2}H\textsubscript{2}O and [Pb(L)] from the interaction of appropriate metal acetate with the ligand in ethanol.
Snow and co-workers [93] 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 co-workers [94] 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 methyl ethyl ketone 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 [95] 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 co-workers [96] 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 co-workers [97] 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 [UO₂L]Cl (where LH = Schiff base), in which Schiff bases coordinate through both azomethine nitrogen and pyidine nitrogen (in
the case of 2-picolinoylhydrazone) or carbonyl oxygen (in the case of isonicotinoylhydrazone) [98].

On the basis of IR and conductivity data Dey et al [99] have reported the formation of [UO₂(LH₂)][NO₃]₂ (where LH₂ represents 1,2-dimethylbibis(4-methoxybenzoylhydrazone)). Similarly they have reported the formation of [UO₂(LH₂)(NO₃)]NO₃ upon acidification of [UO₂L] with HNO₃. 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 [UO₂L(A)₂] and [UO₂L(AA)] (where A = pyridine, picoline, methylamine, aniline, Ph₃PO; AA = en, ph, phen).

Marangoni and co-workers [100] synthesized mercury (II) complex with 2,6-diacytelylpyridinebis(2-pyridylhydrazone). They carried out X-ray structural analysis of the complex, and confirmed its pentagonal bipyramidal stereochemistry.

Pelizzi and co-workers [101] synthesized nickel(II) complex [{Ni(H₂apsh)(OH₂)(I)}₂Cl₂]-2dmf·5H₂O, and cobalt(II) and copper(II) complexes, viz. [Co(H₂dpash)(OH₂)]Cl·4H₂O of 2,6-diacytelylpyridinebis[2-(semicarbozono)propionylhydrazone] (H₂apsh) and 2,6-diacytelylpyridinebis[2-(semicarbozono)acetophenoylhydrazone] (H₂dpash) respectively. In the nickel complex, the four atoms of the semicarbozono system are involved in coordination while in the cobalt complex, semicarbozono system does not participate in coordination. They established the structure of the complexes by IR spectroscopy and X-ray crystallography.

Pelizzi and co-workers [102] studied the structure of a tetranuclear copper(II) complex [Cu₂(dappc)(OH₂)₃]₂[Cu₂(dappc)(OH₂)₂(ClO₄)]₂(ClO₄)₆·2H₂O (I) and [{Cu₂(dapip)Br}₂ (II) derived from the polyfunctional ligand 2,6-diacytelylpyridinebis(2-pyridine carboxylhydrazone) (H₂dappc) and 2,6-diacytelylpyridinebis(2-(2-pyridinecarboxylhydrazone phenylacetohydrazone) (H₂dapip) respectively. The structure of compound (I) is built up of complex cations of formula [Cu₂(dappc)(OH₂)₃]⁴⁺ and [Cu₂(dappc)(OH₂)₂ClO₄]²⁻·ClO₄ anions and uncoordinated H₂O molecule while that of the compound (II) consists of neutral unit of formula [Cu₂(dapip)Br]₂ and solvating H₂O 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 monoperxoo complex of Schiff base (H₂C₆C=N-NHC(S)SCH₂C₆H₃)₂, (LH₂) has been reported by Tarafder et al [103]. The complex [UO₂(O₂)L] was prepared by treating uranyl nitrate with the Schiff base dissolved in a solution of KOH in 30% H₂O₂. The Schiff base
behaves as dibasic NNSS tetradentate ligand, while peroxy group is bonded to the metal centre as a bidentate chelating ligand.

Toshev and co-workers [104] reported the dioxouranium complex of diacetyl-bis(thiobenzoylhydrazone) in which uranium has a distorted pentagonal bipyramidal structure with the uranyl oxygen atoms at the axial positions.

Pelizzi and co-workers [105] synthesized copper complexes of di-2-pyridylketone(phenylsemicarbazone)acetylhydrazone (H₂psah) and studied their structure by X-ray crystallography. They showed that the copper complex [Cu₂(psah)Cl]·H₂O consists of a 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 [106] synthesized a number of palladium(II) complexes from a 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 co-workers [107] have determined the 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. 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. Bis-crown 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 co-workers [108] studied several dinuclear yttrium(III) and lanthanide(III) picrate complexes derived from acetylferrocenepyridine-2,6-diformylhydrazone having the stoichiometric formula Ln₂L₂pic₉·n(C₃H₇OH)·mH₂O (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, ¹H NMR spectra and molar conductance data. It was found that the ligand coordinates in keto form to the lanthanide ions. All the complexes described were found to be 1:6 electrolytes in methanol.
Xianzeng and co-workers [109] synthesized zinc(II) complex [Zn2L(CH3COO)2]·C2H5OH, from a binucleating ligand 2,6-diformylpyridine N-oxidebis(benzoylhydrazone) (L) 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) Å. The two acetato 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 co-workers [110] synthesized six complexes of copper(II), nickel(II), and iron(II) from a chiral ligand 2,6-diacetylpyridinebis[DL-hydroxyphenyl]acetic|hydrazone (H4dapm) and characterized them by spectroscopic studies. They established the structure of the nickel complex [Ni(H4dapm)-(H2dapm)]·13H2O by X-ray diffraction methods. The complex crystallizes in the monoclinic space group C2/c. The complex has 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 1H NMR spectroscopic studies, the existence of the ligand in three forms i.e the meso DL and the two enantiomeric DD and LL ones were established.

Rana and co-workers [111] 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, Br, NO3, 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 co-workers [112] studied the interactions of potentially binucleating ligand, 2,6-diacetylpyridine-bis(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 the
reaction of metal acetates, metal chlorides and metal perchlorates, respectively and the ligand. 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 zinc(II) chloride and perchlorate. 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 co-workers [113] synthesized binuclear dioxotungsten(VI) complexes of the type [(WO₂)₂L], where L is a flexibly bridged hexadentate tetra anionic Schiff base derived from the condensation of methylene or dithiobissalicylaldehyde with isonicotinoylhydrazine, benzoylhydrazine, p-nitrobenzoylhydrazine and furoylhydrazine 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 bridging. They have shown that the bridging methylene (-CH₂) or dithio (-S-S-) group has very little effect on the thermodynamic stability of the complexes.

Lal and co-workers [114] synthesized the bimetallic manganese (II, III) and dioxouranium(VI) complexes [M₁₄(H₂L)(OAc)₄]·4H₂O, [M₁₄(L)₂(H₂O)₈]·4H₂O, K₄[M₁₄(L)₂F₆(H₂O)₂]·2H₂O, [UO₂(H₂O)₄][M₁₄(L)₂(OAc)₄]·4H₂O, and K₄[(UO₂)Mn₃(L)₂F₆(H₂O)₃] from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (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 in enol forms in the anti-cis-configuration in all of the complexes.

Lal and Adhikari [115] synthesized the 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 complex is proposed to be a hexamer in which the ligand is arranged in sets of three 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 co-workers [116] isolated the homobimetallic complex [(MoO₂)₂(L)]·4H₂O from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H₄L) in the solid state. It reacts
with Lewis bases pyridine and 3-picoline to form the complexes \([\{\mu_2-O\}MoO_2\}MoO_2(H_2L)]2D\cdot4H_2O\) (where D = pyridine (py) (2), 3-picoline (3-pic) (3) and with proton bases salicyloylhydrazine (sylshH_3) and isonicotinoylhydrazine (inhH_3) to yield the Mo(V) complexes \([Mo_2(L)(sylsh)_2]5H_2O\) (4), and \([Mo_2(L)(inh)_2(H_2O)_2]3H_2O\) (5), respectively. The complexes have been characterized by elemental analyses, molecular weight determinations, molar conductance, magnetic moment, ESR, electronic, infrared, and \(^1H\) NMR spectral studies. IR and \(^1H\) NMR data indicate that the dihydrazone coordinates to the metal centre in 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 co-workers [117] have synthesized the complexes of the type \([\{(UO_2)\}_2(L)(H_2O)_2]4H_2O\) (1), \(K_4[(UO_2)\_4(L)(OAc)_4(H_2O)_4]4H_2O\) (2), and \(K_4[(UO_2)\_4(L)F_4(H_2O)_4]\) (3), from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) and characterized them by elemental analyses, molecular weight determinations, molar conductance, electronic, IR and \(^1H\) NMR spectroscopic studies. The dihydrazone coordinates to the metal centre in the 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 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 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 syn-cis-configuration in complex (2) eliminating the possibility of its existence in chair conformation.

Lal and Kumar [118] have synthesized an unstable monomeric yellow complex of the type \([(MoO_2)_2(CH_2salmlhhH)\_2(H_2O)_2]H_2O\) \{complex (A)\} from the reaction between bis(acetylacetonato)dioxomolybdenum(VI) and disalicylaldehyde malonoyldihydrazone (CH_2salmlhhH) in ethanol. This is transformed into an intermediate complex \([(MoO_2)_2(CH_2salmlhhH)(H_2O)\_2]4H_2O\) \{complex (AB)\} after sometime. Ultimately a stable brown isomer complex \([(MoO_2)_2(CH_2salmlhh)(H_2O)_2]4H_2O\) \{complex (AB)\} is obtained. All the products have been characterized by various physico-chemical techniques, IR and \(^1H\) NMR spectroscopic studies.
Lal and co-workers [119] isolated the complexes of the composition 
\[\text{[UO}_2\text{(H}_3\text{salligh})(\text{OAc})] \cdot 3\text{H}_2\text{O}\] and \[\text{[UO}_2\text{Zn(salligh)(H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\], where H\text{salligh refers to disalicylaldehydeoxaloyldihydrazone (H\text{salo})}, malonoyldihydrazone (H\text{sal}), succinoyldihydrazone (H\text{salsu}), glutaroyldihydrazone (H\text{salglu}), and phthaloyldihydrazone (H\text{salph}). The complexes have been characterized by molar conductance and spectral data.

Lal and co-workers [120] have synthesized the complexes, 
\[\text{Na}_4\text{[(UO}_2\text{)}_4\text{(L)}_2\text{(OAc)}_4\text{(H}_2\text{O})_4] \cdot 4\text{H}_2\text{O (1) and Na}_4\text{[(UO}_2\text{)}_4\text{(L)}_2\text{F}_4\text{(H}_2\text{O})_4] (2) from bis(o-}

hydroxynaphthaldehyde)oxaloyldihydrazone (napoxH\text{a}) and characterized by elemental analyses, molar conductance, electronic, IR and \text{^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 co-workers [121] have synthesized the monometallic complexes of the type 
\[\text{[Zn}_2\text{(H}_4\text{L})_2\text{(SO}_4)_2] (1), \text{[Zn}_2\text{(H}_2\text{L})_2\text{(H}_2\text{O})_2] (2), \text{K}_2\text{[Zn}_2\text{(H}_2\text{L})_2\text{F}_2] (2a), and the heterometallic complexes of the type compound \{(\text{UO}_2\text{)}_2\text{Zn}_2\text{(H}_2\text{O})_6\} (3), \{(\text{UO}_2\text{)}_2\text{Zn}_2\text{(L)}_2\text{F}_4\text{(H}_2\text{O})_2\} (3a), \text{[Cu}_2\text{Zn}_2\text{(L)}_2\text{(H}_2\text{O})_4] (4), \text{K}_4\text{[Cu}_2\text{Zn}_2\text{(L)}_2\text{F}_4\text{(H}_2\text{O})_2] (4a), and characterized them by analytical, molar conductance, magnetic moment data, electronic, ESR, IR and \text{^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 contain the coordinated dihydrazone in the anti-cis-configuration. In these complexes, copper and zinc metal centres have been shown to be five coordinate square-pyramidal whereas uranium centres have been shown to be eight-coordinate hexagonal bipyramidal.

Ma Yongxiang and co-workers [122] synthesized the chelates 
\[\text{Na}_2\text{[Ln(C}_3\text{H}_2\text{N}_4\text{O}_8}\text{Cl}] \cdot \text{nH}_2\text{O of malonyl dihydrazone of salicylaldehyde with the lanthanides and characterized them by elemental analyses, 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 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 co-workers [123] 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 \([\text{Ru(bipy)}_2(L-L)]\text{[PF}_6\text{]}_2\) (bipy = 2,2'-bipyridine; \(L-L = \text{biacetyldi(phenylhydrazone)}\) 1a, biacetylidi[methyl(phenyl)hydrazone] 1b, biacetylidi(o-tolylhydrazone) 1c, biacetylidi(methylhydrazone) 1d, biacetyl dihydrazone) 1e, biacetylidi(benzaldehyde azine) 1f, 2-acetylpyridinephenylhydrazone 1g, or 2-acetylpyridinehydrazone 1h). The structures of all the complexes were determined using IR, UV/VIS, 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 by X-ray crystallography and it was shown that a hydrazone phenyl group lies over each of the bipyridyl rings: space group \(C2/c\), \(a = 25.895(3)\) Å, \(b = 10.505(1)\) Å, \(c = 17.431(2)\) Å, \(\beta = 106.03(2)^\circ\) and \(Z = 4\).

Khan and co-workers [124] synthesized a new class of tetraiminetetraamide macrocyclic (Ph₄[20]tetraene, N₈O₄, and Ph₆[20]tetraene, N₆O₄) 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 of the composition \([\text{ML}_2\text{X}_2]\) \([M = \text{Co, Ni, Cu or Zn; X = Cl or NO}_3\text{]}\). They elucidated the structure of the complexes on the basis of IR, \(^1\text{H 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 co-workers [125] synthesized a series of polyacylhydrazones by condensing diacetyl with oxalic, malonic, succinic, glutaric and adipic dihydrazides and characterized them by conventional spectroscopic studies. They reacted these dihydrazones with copper (II) and nickel(II) acetate to give metallopolymers 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 range 4.2-300 K indicated significant antiferromagnetic coupling between the \(\text{Cu}^{II}\) 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 dihydrazone 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 co-workers \cite{126} synthesized the dinuclear copper(II) complexes with 2-hydroxypropiophenone, acyldihydrazones (H\textsubscript{2}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 adipoylhydrazone 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 8.212 Å. Their nearest environment was found to have tetragonal pyramidal geometry. The ESR spectra of solutions of the complexes based on acyldihydrazones of succinic, malonic, glutaric, and adipic acids were found to contain seven HFS lines with the constant \( \sim 40 \times 10^{-4} \text{ cm}^{-1} \) 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 was found to contain a signal of four HFS lines with \( A_{Cu} = 73.4 \times 10^{-4} \text{ cm}^{-1} \), which is typical of mononuclear copper(II) complexes.

Andelkovic and co-workers \cite{127} 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 \( \alpha \)-oxyazine, forming an octahedral geometry around Zn(II), and a square-planar one around Pd(II) and Pt(II). The structure determination was performed by IR, \(^{1}\text{H} \text{NMR} \) and \(^{13}\text{C} \text{NMR} \) spectroscopy, and for the Zn(II) complex by X-ray structure analysis.
Para et al [128] synthesized dialdehyde starch dihydrazone DASHZ from the reaction of dialdehyde starch with hydrazine. The metal complexes of Ca, Cd, Co(II), Cu(II), Fe(II), Mg, Mn(II), Ni(II), Pb(II), and Zn ions with the dihydrazone ligand DASHZ were isolated. It was found that the nitrogen atoms of the $\text{C}=$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 co-workers [129] 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 $[\text{Ni}_2(2\text{poap})_2(\text{H}_2\text{O})_2](\text{NO}_3)_{2.5}\cdot 2\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O}$ (1), $[\text{Mn}_2(\text{pttp})_2(\text{NO}_3)_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_{2.2}\cdot 2\text{H}_2\text{O}$ (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 $[\text{Ni}_4(\text{pttp})_6](\text{BF}_4)_6\text{F}_2\cdot 14\text{H}_2\text{O}$ (7), and a mixed spin state tetranuclear Ni(II) complex $[(2\text{pyoap})_2\text{Ni}_4(\text{CH}_3\text{OH})_4]\cdot 1.5\text{CH}_3\text{OH}$ (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 co-workers [130] 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 Cd(ClO$_4$)$_2\cdot \text{H}_2\text{O}$ 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 centre.

Carcelli and co-workers [131] 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 NN'N''N", respectively. These hydrazones, (2,9-diformylphenanthroline)bis(benzoyl)hydrazone ($\text{H}_2\text{L}^1$), (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone ($\text{H}_2\text{L}^2$). They prepared and fully characterized both nitrate and acetate complexes of $\text{H}_2\text{L}^1$ with La, Eu, Gd, and Tb.
They presented the X-ray crystal structure of the complex \([\text{Eu(HL}^1\text{)(CH}_3\text{COO)}_2\text{]}\cdot\text{SH}_2\text{O}\). The stability constants of the equilibria \(\text{Ln}^{3+} + \text{H}_2\text{L}^1 = [\text{Ln(H}_2\text{L}^1\text{)}^3^+\text{ and } \text{Ln}^{3+} + (\text{L}^1)^2^- = [\text{Ln(L}^1\text{)}^+]\) (\(\text{Ln} = \text{La(III), Eu(III), Gd(III), and Tb(III)}\)) were determined by UV spectrophotometric titrations in DMSO at \(t = 25^\circ\text{C}\). They also synthesized the nitrate complex of \(\text{H}_2\text{L}^2\) with \(\text{La, Eu, Gd and Tb}\). The X-ray crystal structure of the complexes \([\text{La(H}_2\text{L}^2\text{)}(\text{NO}_3\text{)}_2\text{]}(\text{H}_2\text{O})\)(\(\text{NO}_3\))\], \([\text{Eu (H}_2\text{L}^2\text{)}(\text{NO}_3\text{)}_2\text{]}(\text{NO}_3)\) \] and \([\text{Tb(H}_2\text{L}^2\text{)}(\text{NO}_3\text{)}_2\text{]}(\text{NO}_3)\) were also established.

Salem [132] synthesized a series of acyldihydrazones, \(\text{H}_2\text{L}^n\) from the condensation of ethylpyruvate with oxalic, malonic, succinic, and glutaric and adipic dihydrazides. The author isolated dicopper(II) complexes of the general formula \([\text{Cu(L}^n\text{)}\cdot\text{H}_2\text{O)}\cdot\text{xH}_2\text{O}\), where \(\text{L}^n\) refers to the quadruply deprotonated pyruvic acid dihydrazone ligand and \(\text{n}\) 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 range 4.2-298 K indicate significant antiferromagnetic coupling between copper(II) centers and suggest association of the coordinated copper(II) units \(\text{Cu(ONO)}\) 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 (\(\rho\)), the degree of association in these polynuclear copper(II) complexes were also estimated.

Elengoz et al [133] synthesized the zinc complex tris(biacetyldihydrazone-x\(2^N,N^\prime\))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 centre. 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 Zn\(\text{II}\) 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=\(\text{N}\) 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)\(^\circ\). In the free form of
the ligand, the N=N=C=C=N backbone was found to adopt a planar *anti* conformation (Hauer et al., 1987).

V. P. Singh and P. Gupta [134] synthesized and characterized the complexes of dicarboxylaldehydesalicylaldehydic acid dihydrazone, CH$_3$COC(CH$_3$)=NNHCOCONHN=CHC$_6$H$_4$(OH), (dsodh) and 

\[ \text{dicarboxylsalicylaldehydemalonaticid dihydrazone} \]

CH$_3$COC(CH$_3$)=NNHCOCH$_2$CONHN=CHC$_6$H$_4$(OH), (dsmdh) by elemental analyses, molar conductance, magnetic moment, electronic, ESR and infrared spectra and X-ray diffraction data and were found to have the 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). With the help of magnetic moments and electronic spectral data they predicted a six-coordinate octahedral geometry for Co(II) and square-planar geometry for Ni(II) complexes. They also found that the ESR spectral data of Cu(II) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through >C=O, >C=N and deprotonated phenolate groups in all octahedral complexes and through >C=N and deprotonated phenolate groups in Ni(II) square-planar complexes.

C. T. Yang and co-workers [135] synthesized the complexes of dioxouranium(VI) with four dipyridoxal hydrazone ligands H$_4$PL$_n$ and characterized them by various analytical and spectroscopic methods including X-ray crystallography. The ligands and the UO$_2$ 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 co-workers [136] synthesized and characterized two series of dicopper(II) complexes derived from bis(N-salicylidine)dicarboxylvicacid dihydrazones (H$_4$L$_n$) of general formula [Cu$_2$(L$_n$)·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-salicylideneacetylhydrazine units. Magnetic susceptibility measurements for neutral dicopper(II) complexes [Cu$_2$(L$_n$)·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) 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 were estimated. The chloro
dicopper(II) complexes [Cu₂(H₂Lⁿ)Cl₂·xH₂O]·yH₂O 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 were found to show weak antiferromagnetic exchange coupling (-2J=16–
20 cm⁻¹).

N. R. Filipovic et al [137] synthesized a new dinuclear complex of Cd(II) with N',N²-
bis[(1E)-1-(2-pyridyl)ethylidene]propanedihyrazide (H₂L) and its crystal structure was
determined. The basic structural unit of the complex was found to be the binuclear
[Cd₂(H₂O)₂(H₂L)₂]⁴⁺ cation, where each cadmium atom was hepta coordinated by two
tridentate H₂L ligands, by means of the NNO chelating system, and one water molecule. A
12-membered macrocycle is defined at the core of the binuclear cation. The complex
showed a pronounced cytotoxic activity to murine melanoma B16 cells and human
cervical cancer HeLa cells.

V. P. Singh and co-workers [138] isolated the metal (II) complexes of the general formula
[M(Bsodh)]Cl and [(MBsmdh)]Cl where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)
(HBsodh = benzyl salicylaldehyde oxalic acid dihydrazone and HBsmdh = benzyl
salicylaldehyde malonic acid dihydrazone) 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 fluorescens.

L. D. Popov and co-workers [139] synthesized the dihydrazone ligand 2,6-diformyl-4-tert-
butylyphenolbis(8-quinolylhydrazone) and its transition metal complexes of the
composition [Cu₂(H₂L)Cl]Cl₂, [Ni₂(H₂L)Cl₂] and [Mn₂(H₂L)Cl₂], where H₂L 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 physico-chemical study of the complexes.
S. Naskar and D. Mishra \[140\] synthesized a Ni(II) complex of 2,6-diacetylpyridine bis(anthraniloylhydrazone) 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 \[141\] 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 \[142\] synthesized and characterized dinuclear copper(II) complexes with acyldihydrazones of 2-hydroxy-5-nitroacetophenone (H\(_4\)L) of the composition Cu\(_2\)(py)\(_3\)L·mEtOH. 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 of [Cu\(_2\)L·4Mrf] complex (where Mrf is morpholine) based on acyldihydrazone of malonic acid by X-ray diffraction.

M. Salavati-Niasari and A. Sobhani \[143\] 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)oxaloyldihydrazine (H\(_2\)L) 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 \textit{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 analyses and spectroscopic methods. They also reported the catalytic activities for the oxidation of cyclohexane with HGNM.

Da-Yu Wu and co-workers \[144\] isolated three ligands, di(2-pyridylcarbaldehyde)-6,6'-dicarboxylicacidhydrazone-2,2'-bipyrindine (H\(_2\)L\(_1\)), di(2-acetylpyridyl)-6,6'-dicarboxylic acidhydrazone-2,2'-bipyrindine (H\(_2\)L\(_2\)) and di(2-pyridylketone)-6,6'-dicarboxylicacid hydrazone-2,2'-bipyrindine (H\(_2\)L\(_3\)) with flexible bis-terdentate coordination sites and their cobalt complexes. The complexes were obtained via self-assembly and their structures were determined by FT-IR, elemental analyses, ESI-MS and X-ray diffraction method.

Lal and co-workers \[145\] synthesized the complexes [(UO\(_2\))(CH\(_2\)L)(H\(_2\)O)\(_4\)]·4H\(_2\)O, [M\(_4\)(H\(_2\)L)\(_2\)(H\(_2\)O)\(_4\)]·4H\(_2\)O (M = Zn, Cu), (M')\(_2\)[(UO\(_2\)F)(CH\(_2\)L)(H\(_2\)O)\(_2\)] [M' = K, Na], M'[(UO\(_2\))\(_2\)(CH\(_2\)L)(OAc)(H\(_2\)O)\(_2\)] [M' = K, Na], K\(_4\)[(MF)\(_2\)(CH\(_2\)L)\(_2\)]·4H\(_2\)O [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 has been carried out on the basis of electronic, infrared, $^1$H NMR and $^{13}$C NMR spectral studies.

Lal and co-workers [146] 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) sulfate 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) sulfate 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 structures of the complexes have been established by spectroscopic studies.

Lal and co-workers [147] synthesized the monomer molybdenum(VI) complex [MoO$_2$(napoxlh$_2$)]-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 dimer molybdenum(VI) complex [Mo$_2$O$_4$(napoxlh$_2$)(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(napoxlh$_2$)(hzid)$_2$]H$_2$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.

M. K. Singh and co-workers [148] studied the reaction of bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (naohH$_4$) with manganese(II) acetate in methanol followed by addition of KOH to get the complex [Mn$^{IV}$(naoh)(H$_2$O)$_2$]. They also studied the reaction of activated ruthenium(III) chloride with naohH$_4$ in methanol to get the complex [Ru$^{III}$(naohH$_4$)(H$_2$O)Cl$_2$] and characterized them by elemental analyses, IR,
electronic, ESR and cyclic voltammetric studies. They observed the replacement of aquo by heterocyclic nitrogen donor in these complexes when the reaction was carried out in presence of heterocyclic nitrogen donors such as pyridine, 3-picoline or 4-picoline.

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. Further, the heterobimetallic complexes of such dihydrazones are almost non-existent. 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, homobimetallic and heterobimetallic complexes of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone with zinc(II), nickel(II) and molybdenum(VI). Part of the work is under consideration for publications.
References


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