Chapter 1

Introduction

1.1. Abstract

In this chapter, the importance of diazine and oxime/dioxime ligands has been briefly discussed. The aim of present investigation in the background of known metal complexes with these ligands has been stated.

1.2. Overview

Modern coordination chemistry started with the groundbreaking work of Alfred Werner in the 19th century. Basic knowledge of the three-dimensional arrangement of ligands coordinated to the metal ions was provided at that time. From the beginning, coordination chemists have been fascinated by the ability of organic molecules those sequester metal ions, and impart unusual properties like, colorimetric, electrochemical, magnetic and catalytic. As a result extension of this simple coordination chemistry towards more complex and widely spread fields such as polymers, oligomers, dendrimers, catalysis, organometallics etc. has occurred.

In this respect, the transition metal complexes with N and O donor polydentate Schiff bases were studied extensively due to their important role in the development of coordination chemistry. Among these N,O donor polydentate Schiff bases, molecules having diazine (=N=N=) and oxime (=C=N=OH) back bone have drawn immense attention in the recent years due to their versatile coordination chemistry with novel features. The research field dealing with
diazine (open-chain) and oxime metal complexes is very broad due in part to their potential interest for a number of interdisciplinary areas that includes bioinorganic, supramolecular, magnetochemistry and catalysis.\textsuperscript{3,4} The most interesting feature of this class of ligands, containing high oxidation state promoting (L $\rightarrow$ M donating) $\sigma$-basic phenolate-O or deprotonated amide–O or alkoxide functionalities as different terminals on diazine (=N–N=)\textsuperscript{5a-c} moiety and deprotonated =N=O\textsuperscript{−}, group in dioxime (C=N-OH)\textsuperscript{5d-e} moiety is to produce higher-valent metal complexes. The higher valent (> ca. +3) Mn, Fe and Co complexes are of considerable interest in the area of bioinorganic chemistry, because of important roles played by these metal ions in the functions of several metalloenzymes. Oxygen evolving center in photosystem II (tetravalent manganese); heme-monoxygenases, -peroxidases (tetra and pentavalent iron) vitamin B\textsubscript{12}-cyanocobalamine (trivalent cobalt) are few examples of these types of metalloenzymes.\textsuperscript{6}

In addition, these polydentate ligands that can serve as molecular bridges between metal centers. As they contain delocalized $\pi$-electron\textsuperscript{7} system, they can also mediate strong magnetic spin coupling between paramagnetic centers.\textsuperscript{8} Thus they can be provided a base for the understanding of new molecular magnets. Due to such possibilities intensive efforts in terms of design and synthesis of new bridging systems have been devoted.

The diazine ligands contain rotationally flexible N-N single bond and produce several $\mu$(N–N) bridged complexes readily. These complexes are subjected to a number of studies related to magnetic and structural features (from molecular to supramolecular level). Similarly in oxime containing ligands, the terminal =NO\textsuperscript{−} moiety acts as a bridging unit to bring the two metal ions into
close proximity and provides an easily communicating intramolecular pathway for spin exchange interactions. Such polyfunctional diazine and dioxime ligands have been shown to form various mono-, homo- and hetero-dinuclear, tri and polynuclear metal complexes depending upon the reaction conditions.

Due to their unique properties and wide range of applications there is a continuous quest for novel complexes derived with diazine and dioxime based Schiff bases.

1.3. Some aspects of the diazine chemistry

Azines/diazines represent a well-known class of organic compounds, which exhibits rich coordination chemistry that has emerged over last three decades. These ligands were derived by the condensation two mole equivalents of an aldehyde or a ketone with one mole equivalent of hydrazine and there is a possibility to obtain symmetrical and unsymmetrical systems by using two identical or different carbonyl compounds. Even though the diazine moiety has been found in some conjugated aromatic heterocyclic polyfunctional systems like pyrazole, triazole, pyridazine and pthalazines, but they are rigidly fixed. On the other hand, open chain diazine (dipyrindyl etc.) systems are much more flexible, and provide several possible mono and dinucleating coordination modes. Such open chain systems appealing due to various applications of them and their complexes in number of areas. These include molecular electronics, salicylaldazine shows a strongly luminescent and thermochromic properties in the solid state; analytical, the syringaldazine has been used for determination of chlorine in water by colorimetry; NLO active materials, 4-bromo-4′-methoxyacetophenone azine and some macroyclic bis(azines) show strong
second harmonic generation. Some ferroelectric liquid crystals containing ortho-palladated azines were also reported.\textsuperscript{14} Due to its unique coordination modes the diazine class of ligands have been found to form monometallic, homo/hetero di to poly-metallic complexes, with interesting properties in the fields of metallo-supramolecular and magnetochemistry.\textsuperscript{15a} On the other hand such diazine based amide-containing hydrazones and its derivatives display wide range of bioactivities. These have found extensive applications in pharmacology.\textsuperscript{15b}

In the following section, we have described few types of dinucleating open chain diazine ligands and their complexes with a general discussion on their synthesis, structure, properties and applications.

\textbf{1.3.1. Types of ligands and their modes of coordination}

The flexible diazine ligands provide very interesting topological arrangements due to the presence of terminal main donor groups as pyridyl, pyrazyl, salicyl, etc., and additional donor groups as OH, SH, NH\textsubscript{2}, etc. A number of open chain diazine ligands with such fragments have been reported. We have restricted our discussion to:

1) Dinucleating hydrazides having picolinylidene or salicylidene chelating groups with NH\textsubscript{2} or OH as additional donor groups.

2) Aroyl or acyl hydrazones, which contain deprotonable amide functionality. The pictorial representations of such polydentate hydrazides and hydrazones are shown below.
L^1: R = H, L^2: R = Me

L^3

L^4: R^1 = R^2 = NH_2, L^5: R^1 = NH_2, R^2 = H
L^6: R^1 = NH_2, R^2 = CH_3
$L^7: R = H, L^8: R = 3\text{-OH}$
$L^9: R = 6\text{-OH}, L^{10}: R = 6\text{-Me}$

$L^{12}$

$L^{13}: R = H, \text{CH}_3, \text{OH}, \text{OCH}_3, \text{N(CH}_3)_2 \text{NH}_2 \text{ Cl, Br, NO}_2$
L^{14}: R = H, CH₃, OH, OCH₃, N(CH₃)₂, NH₂, Cl, NO₂

L^{15}

L^{16}

L^{17}

L^{18}

L^{19}: R = H, CH₃, Ph, NH₂, C₅H₈O, C₆H₅C₄H₅O
For these types of hydrazides Thompson and coworkers have proposed possible coordination modes, through a series of topological operations.\textsuperscript{16a} Depending upon the donor groups and the assembled metal ions, the coordination modes of the ligands will vary with the changes at azine moiety by two types of angles, namely the torsion angle ($\alpha$) about the N–N single bond and the bending angle at two N atoms ($\beta$, $\beta'$).

![Diagram](image)

\textbf{Figure 1.1}
The simple N,N'-bis(pi/colinilydene)hydrazine ligand have show at least five possible coordination modes due to the changes in the α and β planes (Figure 1.1).\textsuperscript{9a} Most of the remaining hydrazine systems adopt a typical dinucleating mode \textit{via} bridging N–N single bond due to terminal chelating sites (Figure 1.2).\textsuperscript{16b} In all these dinucleating modes the N–N fragments are found to be in \textit{cis}, \textit{trans} or in between manner, depending upon the terminal and additional-donor groups and the ancillary ligands coordinated to the metal ions. The ligand having an alkoxide group as an additional coordinating site, adopts two types of binding modes.\textsuperscript{16c} The dominating mode provides alkoxy bridge in addition to the N–N bridge between the metal ions. This was demonstrated by a number of polynuclear complexes. The minor is a non-bridging mode (Figure 1.2).\textsuperscript{16d}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig1.2.png}
\caption{Figure 1.2}
\end{figure}
1.3.2. **A brief survey on diazine based metal complexes**

Self-assembly of molecules *via* metal–ligand interactions leads various supramolecular architectures such as helicates, grids, cylinders and boxes.\textsuperscript{17,18,19} Due to the arrangement of donor sites and high flexibility, these polydentate hydrazides can coordinate in a variety of ways leading to such diverse molecular structures. The studies on such species have attracted great attention due to their potential applications in magnetism, molecular selection, ion exchange, catalysis, medicine, electrical conductivity and enantioselectivity.\textsuperscript{20}

Due to such a wide range of applications a large literature is now available in this area, out of which, some recent and interesting examples are briefly presented.

1.3.2.1. **Helicates and twisted complexes and their magnetic properties**

With obvious parallels to the structure of DNA, metal complexes that spontaneously adopt helical structures have a long held fascination.\textsuperscript{19} Helicates based on imine ligands or particularly diazine ligands are synthetically versatile and inexpensive.\textsuperscript{21} Studies on the helicates formation have elucidated many supramolecular coordination chemistry principles. Flexibility of the polydentate ligand and how it is partitioned into distinct metal binding sites, are the two crucial factors to be considered for the fabrication of helicates. In many cases, ligands have been constructed as a polyfunctional system, which contain bis bidentate or terdentine domains. These bis chelating ligands are separated by a spacer or connected directly, to bind two metal ions separately rather than chelating to a single metal ion (essential for helication).\textsuperscript{22}
The coordination chemistry of the simplest Schiff bases $L^1$ and $L^2$ was reported by Stratton and Bush\textsuperscript{23a-c} in 1950’s. Based on the magnetic studies they have concluded the dinuclear structures of the $[M_2L^1_3]^4^+$ cations ($M = \text{Fe(II)}$ Co(II) and Ni(II)). Subsequent variable temperature magnetic studies of $[\text{Ni}_2L^1_3]^4^+$ (by Blake)\textsuperscript{23d} and $[M_2L^2_3]^4^+$ ($M = \text{Fe(II)}$ Co(II) and Ni(II)) by Stratton\textsuperscript{23e} supported the dinuclear nature and spiral structures of this class of complexes. Although none of the structures were confirmed by X-ray crystallographic studies, but these studies are of particular historic importance to the field of metallo-supramolecular chemistry and in particular to helicate formation.

The X-ray structure of one of these complexes was first reported by Sheldrick.\textsuperscript{24} In the dicobalt(II) $[\text{Co}_2(L^2)^3][\text{ZnCl}_4][\text{ZnCl}_3(\text{H}_2\text{O})]_2\cdot4\text{H}_2\text{O}$, the distorted octahedral Co(II) centers are bridged by three ligand molecules in a twisted manner with an average ($\text{Co--N--N--Co}$) angle 44° (Figure 1.4). Recently Hannon and coworkers have also reported the similar triple helicate X-ray structures of hexafluorophosphahte salts of Stratton and Busch’s original iron(II) complex with $L^1$ and Zn(II) complex with $L^2$ (Figure 1.4).\textsuperscript{25} Further, the Schiff
base $L^2$ with $\text{AgClO}_4$ (in 1:1 mole ratio) produced double helical complex cation\textsuperscript{26} $[\text{Ag}_2L^2_2](\text{ClO}_4)_2$. However, in presence of $\text{NaClO}_4$ the triple-helical $[\text{Ag}_2L^2_3]^2^-$ structure was generated, with crystallographic $C_3$ symmetry passing through the Ag(I) ions.

![Figure 1.4](image)

Thompson et al. have reported a systematic study on structural and magnetic properties\textsuperscript{2} of the first row transition metal complexes with open chain diazine ligands like amidrazones, hydrazones, dihydrazones etc. They have reported a series of dicopper(II) systems by using the mono ligand $L^4$ and various co-ligands (Cl\textsuperscript{−}, Br\textsuperscript{−} and NO\textsubscript{3}−).\textsuperscript{17a} In these complexes two copper(II) centers are bridged by a single N–N bond. In $[\text{Cu}_2L^4(\text{NO}_3)_2(\text{H}_2\text{O})_6]^\cdot(\text{NO}_3)_2$ (Figure 1.5a), the two metal centers are in distorted octahedral coordination geometry, with an 100.2° dihedral angle between the magnetic planes. This compound exhibits antiferromagnetic spin exchange. In contrast, the complex $[\text{Cu}_2L^4\text{Br}_4]\cdot\text{H}_2\text{O}$ (Figure 1.5b) with the same ligand has a much smaller rotational angle between the metal magnetic planes (75.08°) and exhibits significant intramolecular ferromagnetic spin coupling.
Figure 1.5

An expanded study related to the extent and type of metal ion spin-exchange as a function of twist of the copper magnetic planes about \( N-N \) single bond, shows a linear correlation between the exchange integral and rotational angles.\(^{17c}\) This observation was supported by the extended Hückel calculations. The orthogonality between the nitrogen p-orbitals and copper magnetic (\( d_{x^2-y^2} \)) orbitals, is attained at \( \sim 70^\circ \). Below this angle ferromagnetic coupling and above this angle antiferromagnetic coupling occur.\(^{27a}\) They have also studied few more dinuclear triple helicate structures of general formula \([M_2L_3]\) \([M = Mn(II), Fe(II), Fe(III), Co(II) and Ni(II)]\) with \( L^4 \). In each complex, the hexa-coordinated metal centers are bridged by three \( N-N \) single bonds as shown in Figure 1.6. In this series, the dimanganese(II) complex shows a weak ferromagnetic spin exchange, which is consistent with the average twist angle \( (67.8^\circ) \) of the three ligands. However, an isostructural Ni(II) complex does not show any such spin exchange.\(^{27b}\)
Cationic $[{{\text{M}}_2}{{\text{L}}_3}]^+$ triple helicates were produced by the reaction of ${{\text{L}}^3}$ with Cu(II) and Zn(II) salts. Similarly Meng and coworkers generated ferrocene containing double helical$^{28}$ (${{\text{Cu}}_2}{{\text{L}}_2}^{12b}$) copper(II) complex with ${{\text{L}}^{12b}}$ and mononuclear Ag(I) and Cu(II) complexes with ${{\text{L}}^{12a}}$.

### 1.3.2.2. Supramolecular species

#### (a) Self-assembled Grids and Clusters

Self-assembly strategies for the formation of metal ion containing advanced materials with predetermined topological architectures are limited. Significant success has been achieved by using polytopic hydrazides with contiguous coordinating packets separated by pyridazine, pyrimidine, phenoxide, and alkoxide bridging fragments,$^{29a}$ that allow the metal ions in a roughly linear fashion. Essentially self-assembled rectangular tetranuclear [2x2] grids, square [3x3] nine metal grids, and high-nuclearity [4x4] grids have been produced in high yield.$^{29}$

Mathews et al. reported self assembled [2x2] square tetranuclear homometallic$^{29b,30a}$ M(II) (M = Mn, Co, Ni, Cu, Zn) and heterometallic$^{30b}$
(Co$^{II}_{2}$Fe$^{III}_{2}$, and Fe$^{III}_{3}$Cu$^{II}_{3}$) grid complexes (Figure 1.7) with the hydrazides like L$^7$. In these square tetranuclear homometallic clusters, the antiferromagnetic spin coupling within the structure is dominated for the Mn(II), Co(II) and Ni(II) systems, due to large M–O–M bridge angles.

However in the case of Cu(II), the strictly orthogonal bridging arrangement between the adjacent copper magnetic orbitals and the close proximity of the Cu centers lead to intramolecular ferromagnetic spin exchange.

By a controlled self assembly process the L$^7$ ligand yields, homoleptic pentanuclear trigonal-bipyramidal M(II) (M = Mn, Co, and Zn)$^{31}$ clusters (Figure 1.8). In both the Mn(II) and Co(II) complexes an antiferromagnetic interaction is operative between the metal centers.
In addition to the spiral $[\text{M}_2\text{L}^3]^{+}$ complexes, the $\text{L}^3$ ligand has also provided a trinuclear species $[\text{Cu}_3(\text{L}^3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Figure 1.9), which exhibits moderately strong antiferromagnetic exchange as a result of super exchange via N–N bridges.

(b) Metallacrown compounds

The new class of polynuclear clusters that are analogous to crown ethers with respect to both structure and function are described as metallacrown
compounds (Figure 1.10). The studies on crown ethers and metallacrowns, fall in the new branch of chemistry known as “host–guest” or supramolecular chemistry. Self-assembly is one of the most efficient method for the synthesis of such variety of supramolecular species. Before these species, most of the studies were focused on organic host molecules. Inorganic metallacrown cluster can also mimic the macrocyclic organic host molecules. The interest in metallacrown system is not only from their high symmetry and aesthetic molecular frameworks, but also from the potential applications as chemically modified electrodes, anion-selective separation agents, liquid crystal precursors and magnetic materials.

In 1989 Pecoraro and coworkers reported the first metallacrown compound and described a synthetic strategy by using a metal salt and a bifunctional hydroxamic acid. Latter a rich variety of structural types, e.g. [9]metallacrown-3, [12]metallacrown-4, [15]metallacrown-5 and [18]metallacrowns-6 were reported with a [M–N–O] repeat unit. However Lah and coworkers have described Mn(III) [18]metallacrown-6 complexes with a triply deprotonated diazine based hydrazides L. In each complex, the ligands bridge the metal ions using the hydrazide N–N group with [M–N–N] repeat unit as shown in Figure 1.11. After that several metallacrowns like
Fe(III)/Co(III)[18]metallacrown-6 and Mn(III)/Fe(III)[30]metallacrown-10 compounds\textsuperscript{36c,d} have been synthesized using L\textsuperscript{13} ligand system.

\[ R = \text{CH}_3, \text{CH}_2\text{CH}_3, (\text{CH}_2)_4\text{CH}_3 \text{ and } (\text{CH}_2)_{10}\text{CH}_3, \text{ S = Solvent} \]

\textbf{Figure 1.11}

\textbf{1.3.2.3. Pharmacologically versatile metal–hydrazone complexes}

Hydrazones and their transition metal complexes are known to provide useful models for elucidation of the mechanism of enzyme inhibition. Due to the chemistry and pharmacological applications hydrazones have been extensively investigated.\textsuperscript{37a-g} The biological properties of hydrazones are often related to metal ion coordination. The lipophilicity, which controls the rate of entry into the cell, was less to the metal complexes rather than free ligand.\textsuperscript{37h} Moreover some side effects may decrease upon complexation. In some cases the complex can exhibit bioactivities, where the free ligands dose not show any such activity. The mechanism of action can involve binding to a metal ion \textit{in vivo} or the metal
complex may be a vehicle for activation of the ligand as the cytotoxic agent. In addition, coordination may lead to significant reduction of drug-resistance.\textsuperscript{37i}

These hydrazones are good chelating agents by coordinating the metal ions through the phenolic or acylic or alkoxy or amide oxygen and pyridyl or imine nitrogen atoms.

Several research groups reported bioactive copper(II) complexes with salicylaldehyde bezoylhydrazones (L\textsuperscript{13}), which were shown as potent inhibitors of DNA synthesis and cell growth.\textsuperscript{38} The analogues have been also investigated as potential oral iron chelating drugs. Recently Kurup \textit{et al}. synthesized [CuL\textsuperscript{13}(bipy)] (R = OH) complex (Figure 1.12a) and studied their bioactivity against Gram-positive \textit{Bacillus sp}. and Gram negative \textit{V. cholerae}.\textsuperscript{39a} Similarly the hydrazones in combination with cholesterol\textsuperscript{39b} have also shown promising antimicrobial activity against the \textit{C. abicans} and \textit{S. Aureus}.

A pioneering work of Richards on in synthesis and studies (\textit{in vitro} and \textit{in vivo}) of orally effective high Fe chelating hydrazones in place of DFO therapy are came into light recently.\textsuperscript{40} DFO (desferrioxamine) is a Fe chelator that has been extensively used for the treatment of Fe overload disease (e.g. \textit{thalassemia}). He has successfully screened several aroylhydrazones, like L\textsuperscript{15}, L\textsuperscript{16} and salicylaldehyde isonicotinoyl hydrazones etc. having greater activity than DFO as anti-malarial agents against chloroquine-resistance and -sensitive parasite. In further investigations on anti malarial hydrazones, Bernhardt \textit{et al}. has reported the results on pyridoxal isonicotinoyl hydrazones (L\textsuperscript{17}) and its analogues (L\textsuperscript{18}) having clinically useful Fe chelator properties (Figure 1.12b).\textsuperscript{41} Moreover these chelators have shown low toxicity (\textit{in vitro}) in cultured cells and they are simple and economical to prepare. They have also prepared Mn(II), Co(II), and Cu(II)
bis-complexes with these hydrazones and studied them systematically. The recent reports on the antibacterial and antifungal active bis acylhydrazones ($L^{19}$) ($R = \text{CH}_3$) and their complexes with some first row transition metal salts, revealed good activity against *Gram positive* bacteria.

**Figure 1.12**

Apart from the bioactive complexes, hydrazones have been used to prepare NLO active$^{42}$ materials like penta coordinated Cu(II) and tetra coordinated square-planar Cu(II) and Pd(II) complexes (Figure 1.13) by using hydrazine-based donor-acceptor $L^{13}$ type Schiff bases and their derivatives.

**Figure 1.13**
Over the past decade, a wide variety of mono and dinuclear transition metal (V, Mn, Fe, Ni, Cu, and Ru) complexes (Figure 1.14) with amide containing aroyl hydrazones (L$^{14}$) have been reported from our laboratory.$^{43}$ We have also isolated some square-planar Ni(II) and Cu(II) complexes with L$^{19}$ (R = acac) and ruthenium(III) bis-complex by using L$^{19}$ (R = CH$_3$) Schiff bases. In all the cases, the ligands coordinate the metal ion via deprotonated amide-O, imine-N and pyridine-N/phenolate-O/alkoxy-O atoms.

1.4. A short note on oximes and their metal complexes

Chemistry of oxime/oximate metal complexes have been investigated actively since 1890, when Schugaeff first introduced dimethylglyoxime as a reagent for nickel. Later Chugaev recognized its five-memberd chelating character$^{44}$. These oxime ligands have played an important role for the continuing progress in the coordination chemistry. A vast amount of fascinating oxime
chemistry has been accumulated from various research works on structure, stability and reactivity of transition metal complexes. Extensive applications of these complexes have been found for their unusual electronic properties and as biochemical models. A. Chakravorty’s excellent treatises and reviews in 1974 and 1980 described the synthesis and electron transfer studies of higher valent complexes with \( \text{L}^7 \) and \( \text{L}^8 \) oxime containing ligands.\(^{45a,b}\) After that, few more review articles have been published on synthesis and reactivity of oxime/oximate complexes.\(^{45c-f}\)

Both diazine and dioxime ligand systems are known to act as molecular bridges between metal centers in polynuclear metal complexes. Additionally deprotonated oximes have been demonstrated to stabilize the metal centers in high oxidation states through strong \( \text{L} \rightarrow \text{M} \sigma \) donation.\(^{5d,e}\) In such higher-valent polynuclear (both homo- and hetero- nuclear) metal-oximates, the \((\equiv \text{N}=\text{O})\) oxime function acts as a bridging\(^{46}\) unit to yield several varieties of compounds. Such complexes are specially interesting with respect to new molecule based magnetic materials and bioinspired and/or biomimic materials. Dimethylglyoxime has been widely used for preparation of linear homo- and heterometallic oligonuclear complexes. Similarly oximes containing additional nitrogen, phenolate oxygen or thioether donors, such as those Schiff bases formed by condensation of diamines with diacetyl monooxime, 2,6-diacetylphenol dioximes and the dioxime of 4,7-dithiadecane-2,9-dione, have also found applications in the preparation of various polynuclear complexes.\(^{47}\) To date, several varieties of oxime-ligands are known for synthesizing high nuclearity clusters. A few of them are shown below.
\[ R = \begin{align*} \text{H}_2\text{N} & \quad \text{N} \\ \text{HO} & \quad \text{N} \\ \text{NH}_2 & \quad \text{N} \end{align*} \]

\[ L^1 \quad L^2 \quad L^3 \quad L^4 \]

\[ \text{R} = \begin{array}{c} \text{N} \\ \text{C} \end{array} \quad \text{OH} \quad \text{R} \]

\[ L^5 \quad L^6 \]

\[ \begin{align*} \text{H}_3\text{C} & \quad \text{N} \\ \text{N} & \quad \text{H} \\ \text{H}_2\text{N} & \quad \text{N} \\ \text{CH}_3 & \quad \text{N} \end{align*} \]

\[ L^7 \quad L^8 \]

\[ \begin{align*} \text{H}_3\text{C} & \quad \text{N} \\ \text{N} & \quad \text{N} \\ \text{R} & \quad \text{N} \\ \text{CH}_3 & \quad \text{N} \end{align*} \]

\[ L^9 \quad L^{10} \quad L^{11} \]
Okawa et al. reported the linear trinuclear Cu(II) complexes bridged by dimethylglyoximates showing very strong antiferromagnetic interactions between the copper centers. Later, a related butterfly shaped trinuclear copper(II) complex (Figure 1.15a) and the homo (Cu, Cu and Ni, Ni) and hetero (Cu, Ni) dinuclear complexes with $L^9$ have been reported. A. Chakravorty and coworkers synthesized and studied various homo- and hetero-metallic dinuclear and linear trinuclear complexes (Figure 1.15c) containing oximate bridges with arylazo oximes and nitroso phenols. Later Chauduri et al. reported some similar oximato ($=\text{N}-\overline{\text{O}}$) bridged homo- and hetero- dinuclear ($M^{II}M^{III}$ and $Cu^{II}M^{III}$) transition metal complexes (Figure 1.16a.). These complexes exhibit weak to strong antiferromagnetic and also ferromagnetic coupling between the metal centers. A number of asymmetric dinuclear $[\text{Cr}^{III}_\mu(\text{O--N})_3M^{II}]$ transition metal complexes $[\text{LCr}^{III}_\mu(\text{PyA})_3M^{II}]^{2+/3+}$ $M = \text{Fe}, \text{Ni}, \text{Cu}, \text{Zn}$ and Co(III) (Figure 1.16b) have been produced by using pyridine-2-aldoxime ($L^{10}$). Earlier to these dimetallic complexes, a triangular $\mu_3$-oxo bridged copper(II) complex with this same ligand $L^{10}$ (Figure 1.15b) has been reported. In this triangular complex, each copper center is in square-pryamidal geometry with sulfate–O group in the
axial position. The magnetic moment of the compound reveals strong antiferromagnetic interaction.

![Diagram](a) ![Diagram](b) ![Diagram](c)

**Figure 1.15**

The hexanuclear M$^{\text{III}}$ complexes containing $[\text{M}^{\text{III}}_6(\mu_3\text{-O})_2]$ (M = V, Cr, Mn and Fe) structural core by using salicylaldoxime ($L^{11}$) ligand systems have been reported (Figure 1.17a).$^{51c}$ These complexes having the general formula $[\text{M}^{\text{III}}_6(\mu_3\text{-O})_2(L^{11})_6(\mu_2\text{OOOCR})_2(\text{OH})_2(\text{RCN})_2]$, $\text{RCOO}^- = $ pivalate, benzylate, benzoate or propionate, and $\text{RCN} = $ acetonitrile, propionitrile or butyronitrile, have been structurally characterized and found to be isotypic.
A significant number of metallacrown and inverse metallacrown compounds synthesized using salicylhydroxamic acid and its analogous ligand systems, with an additional ($-\text{C}=\text{O} \leftrightarrow =\text{C}−\text{O}$) bridging O$^-$ atom in compared to the $L^{11}$ ligands. There is an enormous growth of pendent-arm derivatives of azamacrocyclic ligands. Pavlishchuk et al. synthesized the 1,4,7-
(acetophenone oxime)-1,4,7-triazacyclononane ligand (L\textsuperscript{12}), a new member of the \textit{N}-functionalised TACN series\textsuperscript{51d} derived by the combination of azamacrocycle and strong ligand field oxime group. Polynuclear Mn, Co and Ni complexes (Figure 1.17b) with high-spin ground states, having ferro and antiferromagnetic spin-exchange interactions between the metal centers have been synthesized with this ligand.

**1.5. About the present investigation**

In the previous sections we have discussed briefly about the different types of diazine and oxime/dioxime ligands and their coordination modes. A brief survey of the known first row transition metal complexes of these ligands with unique properties is outlined.

In the present investigation, we have used two diazine compounds (1 and 2), aroylhydrazones of 2-pyridinecarboxaldehyde (3) and a dioxime compound (4) to explore the chemistry of the Mn, Fe and Co.
The diazine compounds (1 and 2) have been selected with the aim of synthesizing dinuclear helical species. New higher-valent and polynuclear complexes have been targeted with the aroylhydrazones (3) and the dioxime (4) compounds. In the following chapters we have described our observations in the above efforts. With special reference to (i) synthesis and characterization, (ii) structure and bonding and (iii) chemical, spectroscopic and electrochemical properties.

1.6. References


34 Chapter 1


