INTRODUCTION

A. GENERAL

After Chugaev's\(^1\) initial work on reaction between Ni(II) salts and dimethyl glyoxime, the developments in this area of research have been expanding at an exponential rate in many directions\(^2\)-\(^37\). Traditionally, oximes have been extensively used in analytical chemistry and metallurgy as very effective complexing agents for the purposes of isolation, separation and extraction of different metal ions. Molecular design of multidonor ligands containing other strong donor groups along with the oxime function may lead to new, very effective complexing agents. The example of such approach is the modification of poorly coordinating carboxylic group into a hydroxamine moiety which leads to one of the most powerful donors found in biological systems\(^31\). The coordinated oxime groups appear to be suitable matrices in which to conduct versatile organometallic reactions, resulting in different heterocyclic compounds thus much effort has been made in recent years studying the reactivity of the coordinated oxime
groups. The capacity of the oximato group to coordinate metal ions via the bridging N and O functions and the fact that the oxime bridges were established to mediate exchange interactions between paramagnetic centers very effectively provoked the start of a wide usage of oxime ligands in molecular magnetism for the design and synthesis of polynuclear assemblies.

Oximes have been widely used as versatile reaction intermediates in organic synthesis and also as carbonyl protecting groups. In recent years, the interest in oxime containing coordination compounds is constantly increasing in connection with the biological implication of the oximes. It is also interesting to note that the realization of the biological function of oximes and the mechanism of their metabolism in living systems are evidently connected with their complexation by metal ions.

The oxime group >C=NOH is amphiprotic with slightly basic nitrogen atom and mildly acidic hydroxyl group. Oximes are prepared by (i) the action of hydroxylamine on aldehyde or ketone (ii) the action of nitrous acid, ester of nitrous acid or nitrosyl chloride on compound containing reactive methylene groups (iii) the oxidation of primary amine
with Caro's acid\textsuperscript{73} (iv) the reduction of nitro olefin with zinc and acetic acid\textsuperscript{74} (v) the reduction of pseudonitrile with hydroxylamine\textsuperscript{75} etc.

The oxime group may be present in ligand as sole coordinating group or in combination with another donor group\textsuperscript{30}. On these basis the oximes may be grouped into the following main classes\textsuperscript{30,55}:

Simple oximes i.e. ligands which have only one oxime group as sole coordination site, \textit{vic}-oximes, carbonyl oximes, imino oximes, hydroxy oximes, azo oximes, amino oximes, amido oximes, pyridine oximes, oxime hydrazones, oxime phenols, oxime semicarbazones, oxime thiosemicarbazones, dioximes etc.

Oximes are commonly characterized on the basis of their spectral studies. Detailed studies on ultraviolet absorption spectra\textsuperscript{76-85}, on electric dipole moments\textsuperscript{86-89}, on electron spin resonance\textsuperscript{90}, on infrared spectra\textsuperscript{91-97}, on Raman spectra\textsuperscript{98}, on PMR spectra\textsuperscript{99-102}, on \textsuperscript{13}C NMR spectra\textsuperscript{103-105} of oximes have been made by various workers.
In infrared spectra, oximes show characteristic absorption due to $\nu_{O-H}$, $\nu_{N-O}$ and $\nu_{C=N}$ bands in $>\text{C}=\text{NOH}$. The general regions of absorption are\(^{106}\): free $\nu_{O-H} \rightarrow 3600-3500$ cm\(^{-1}\), bonded $\nu_{O-H} \rightarrow 3400-3100$ cm\(^{-1}\), $\nu_{C=N}$ (in saturated oximes) $\rightarrow 1685-1650$ cm\(^{-1}\), $\nu_{C=N}$ (unsaturated oximes) $\rightarrow 1670-1620$ cm\(^{-1}\) and $\nu_{N-O} \rightarrow 900-1050$ cm\(^{-1}\).

It is well known that oximes can form complexes with many metal ions easily. Donohue\(^{107}\) proposed following two tautomers for oximes.

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\begin{align*}
\text{[I]} & \quad \text{[II]} \\
\text{[I]} & \quad \text{[II]}
\end{align*}
\]

**Tautomeric Forms of Oximes**

It has been generally agreed that the oxime has structure I. Oximes are associated\(^{14}\) in the solid state via $\text{H}---\text{O}---\text{N}$ hydrogen bond.

**Coordination modes of oxime and oximato ligands in the metal complexes:** The oximes are ambidentate ligands\(^{16}\), capable of coordinating through either oxygen atom by
replacement of proton of hydroxyl group and/or through nitrogen donors.

The various known modes of possible metal-oxime linking are shown in structures III-VI (electrical charges are not shown).

Coordination Modes of Oximes and Oximato Species

Oximes can react in a neutral manner or in the form of conjugate base. This is what is meant by putting the hydrogen
atom in structure III, in parenthesis it may or may not be present. In structure IV, one oxime group is present as such while the second group is present as the conjugate base, the single hydrogen atom is then shared in the O—H—O bridge. The structure types III and IV are common. Several polynuclear species containing structure V are also known. In structure VI the oximate anion is linked to the metal through oxygen, is found in a limited number of complexes. The binding mode of the oxime group depends to a great extent not only the nature of the metal ion but also on the presence of a neighbouring donor group in the same ligand. The combination of these two moieties results in a stable complex rings upon coordination to a metal ion\textsuperscript{108-110}.

B. STRUCTURAL STUDIES ON MEAL COMPLEXES OF THE OXIMES

The ligand having only one oxime group as the sole coordination site as in acetaldoxime and acetoxime are reported by Hieber and Leutert\textsuperscript{111}. These oximes react with Cu(II), Ni(II) and Co(II) salts, giving complexes of the type $M(L)_nX_2$ where $n = 2$ or $4$ and $X$ is auxiliary ligand like halogen. They are used in the detection of metal ions. A few Co(II) complexes of them are found to be high-spin\textsuperscript{112}. Stone et al.\textsuperscript{113} have studied
Ni(acetaldoxime)\textsubscript{4}Cl\textsubscript{2} complex by X-ray crystallography and established that the coordination polyhedron is \textit{trans}-octahedral NiN\textsubscript{4}Cl\textsubscript{2} in which NiN\textsubscript{4} fragment is planar. The oxime protons are involved in intramolecular hydrogen bonding with the coordinated chloride ions. The electronic, vibrational and PMR spectra of the complex are reported to be in agreement with the above structures\textsuperscript{114}. Babaeva et al.\textsuperscript{115} have studied Pt(II) monoxime complexes, Pt(acetoxime)\textsubscript{X} where X is halogen. They have also prepared a series of Pt(acetoxime)\textsubscript{n}-(thiourea)\textsubscript{2}X\textsubscript{m} where n = 1, 2 or 3 and m = 1 or 2, in which halogen may or may not be coordinated to metal ion. They have attempted to prepare similar type of metal complexes with Co(II), Ni(II) and Cu(II) with monoxime but largely unsuccessful as the compound are decomposed even with a trace of moisture. The metal complexes of monoxime with group III elements contain a six-membered complex ring "MON-MON"\textsuperscript{116}. Menard et al.\textsuperscript{117} and Coates et al.\textsuperscript{118} have studied formation of zinc complexes of the type (Me\textsubscript{2}C:NOH)\textsubscript{2}Zn or tetrameric (Me\textsubscript{2}C:NOZnMe)\textsubscript{4}, the latter having a cage-like structure in the crystalline state, consisting of zinc-oxygen-nitrogen rings. A number of tetracoordinated planar Pt(II) complexes of acetaldoxime and acetoxime such as \textit{cis}- and \textit{trans}-[Pt(NH\textsubscript{3})\textsubscript{2}(acetoxime)\textsubscript{2}]Cl\textsubscript{2} and \textit{trans}-[Pt(NH\textsubscript{3})\textsubscript{2}(acetaldoxime)\textsubscript{2}]Cl\textsubscript{2} etc. are reported\textsuperscript{119-122}. Anne and
Pringle\textsuperscript{123} have determined structure of Pd(CH$_3$COO)$_2$acetoxime by X-ray crystallographic method. Toshio et al.\textsuperscript{124} have isolated (RR'C=NOH)$_2$PdCl$_2$ from the reaction of PdCl$_4$$^{2-}$ with ketoximes and aldoximes. Onoue et al.\textsuperscript{125} have reported metalation reactions with Pt(II) and Pd(II) on aromatic aldoximes and ketoximes and assigned a bridged structure to dimeric metal complexes. Imamura et al.\textsuperscript{126} have studied ligand-exchange reactions of Pd(II) complexes having $\pi$-allyl and acetylacetoneate as ligands with cyclohexanone oxime.

Ramaswami et al.\textsuperscript{127} studied IR spectra of salicylaldoxime and its metal complexes and observed that complexation cause the $\nu_{C=O}$ stretching frequency to shift towards the higher frequency range. They also studied the reactions of a number of other ortho-hydroxy oximes, which contains same reactive groups as salicylaldoxime. These include o-hydroxyacetophenone oxime, o-hydroxybenzophenone oxime, 1-naphthol-2-aldoxime, quinacetophenone oxime, resacetophenone oxime. However, it was observed that none of these had any special advantage over the more readily available salicylaldoxime.
Burger et al.\textsuperscript{128} investigated the properties of hydrogen bonding and $\pi$-donor bonds in transition metal complexes of salicylaldoxime and its derivatives. The Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of salicylaldoxime and its 5-Methyl, 5-Chloro and 5-Nitro derivatives were prepared and their structural properties were evaluated by infrared and ultraviolet spectral studies.

Cyclohexane-1,2-dione monoxime produces polymeric Cu(II), Ni(II) and Co(II) complexes with composition ML$_2$. Spectral and magnetic data revealed that the metal(II) environment is grossly octahedral\textsuperscript{129}.

2-Hydroxy-4-methyl-5-chloroacetophenone oxime has been prepared, purified and used as complexometric reagent for copper and nickel\textsuperscript{130}. The structures of complexes have been established by conductometric methods and by elemental analyses. Infrared study of the complexes have been done with a view to study how far the IR spectra help in establishing the complexation and structure of the complexes.

B.C.Haldar\textsuperscript{131} studied the Ni(II) complexes of isonitroso ketones. The structures of the complexes were established on the basis of analytical, magnetic and spectral
studies. B.C. Haldar\textsuperscript{132} also reported a review article on the structural studies on transition metal complexes of isonitroso ketones and $\alpha$-benzil monoxime. Bose and Patel\textsuperscript{133} published a review article on the coordination properties of $\beta$-isonitroso-imine ligands.

Biradar et al.\textsuperscript{134} synthesized the metal complexes of oxovanadium(IV) of the type $\text{VOL}_2$ ($\text{HL} = 2\text{-HOC}_6\text{H}_4\text{CMe}:\text{NOH}$ and its 5-Chloro, 3-Methyl, 4-Methyl and 5-Methyl derivatives). They characterized the complexes by chemical analysis, magnetic susceptibility data, infrared and electronic spectral studies.

Lumme and Korvola\textsuperscript{135} prepared and studied the thermal behaviour of the metal complexes of Co(II), Ni(II) and Cu(II) with salicylaldoxime by thermogravimetric analysis (TGA), differential thermogravimetric (DTG), differential thermal analysis (DTA) and mass spectral studies. The decomposition process is also reported and discussed.

Biradar and Angadi\textsuperscript{136} prepared the complexes of oxovanadium(IV) with the following ligands, $\text{R-2-HOC}_6\text{H}_3\text{CH}:\text{NOH}$ (HL) where $\text{R} = \text{H, 3-Methyl, 5-Methyl and 5-Chloro}$ and 2-hydroxynaphthaldoxime. The magnetic
moment data for the complexes are agreed with the spin-only value of oxovanadium(IV) complexes and suggesting that the oxovanadium(IV) was not oxidized to vanadium(V) during the reaction. Square-pyramidal structures are proposed for the complexes. The IR spectral data for the investigated compounds are reported.

Khariton et al.\textsuperscript{137} reported the mass spectral studies of salicylaldoxime, 5-chlorosalicylaldoxime and their nickel and palladium complexes. They presented the probable fragmentation scheme and mechanism of formation of the organic fragments. The investigation also revealed that the intramolecular hydrogen bond is non-symmetric and the hydrogen atom is displaced toward the phenol oxygen atom.

Dixit and Patel\textsuperscript{138} presented a review article on the metal complexes formed by the reaction of isonitroso-\(\beta\)-ketoimines and some transition metal(II) ions.

Thermal studies of 2-hydroxy-1-naphthaldoxime and its copper(II), nickel(II) and palladium(II) complexes have been reported by Naidu et al.\textsuperscript{139}. 
Magnetic and spectral data of the cobalt and rhodium complexes are reported by Haidar et al.\textsuperscript{140} and it suggests that [CoL\textsubscript{3}] and [RhL\textsubscript{3}] (HL = α-benzil monoxime) are octahedral and have 5-membered complex ring structures involving bonding through O and N donor atoms. Copper complexes of CH\textsubscript{3}COC(:NOH)COCH\textsubscript{3} (HL) with the composition [CuL\textsubscript{2}] and [CuL(OAc)(H\textsubscript{2}O)] were prepared by Khataukar and Haidar\textsuperscript{141}. They investigated the structures of the complexes by magnetic and spectral measurements. The magnetic moments can be explained by the assumption that each composition is a mixture of a monomeric and a dimeric complex. Complexes formed by α-benzil monoxime with Ni(II), Pd(II) and Pt(II) have been synthesized and characterized by Dhadke and Haldar\textsuperscript{142}. They elucidated the structures of the complexes by analytical and spectral studies.

Complexes of Co(II), Ni(II) and Cu(II) salts with acetaldoxime and α-benzaldoxime have been prepared by Patel et al.\textsuperscript{143} and characterized on the basis of elemental analyses, conductivity, magnetic moment, infrared and electronic spectral data. Various ligand field and nephelauxetic parameters are reported for the nickel(II) and cobalt(II) complexes of the type ML\textsubscript{4}X\textsubscript{2} and values are found to be consistent with six-coordinate structure. The infrared spectra suggest that nitrogen
atom of the ligand molecule acts as the coordination site. Cu(II) and Co(II) complexes of the type $ML_2X_2$ show sub-normal magnetic moments. Electronic spectra of Cu(II) complexes indicate tetragonally distorted structure. All complexes are found to be non-electrolytes.

Preparation and characterization of manganese(II) complexes with some ortho-hydroxy aldoxime, viz. (i) salicylaldoxime ($salH_2$) and (ii) o-vanilinoxime ($vanH_2$) have been reported by Rani et al.\textsuperscript{144}. They proposed square-planar geometry for bis-complexes of manganese(II) with rare spin state $S = 3/2$ and following structural formula has been suggested.

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\text{Suggested Structure of the Metal Complexes} \\
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Coakley and Casey\textsuperscript{145} isolated and studied the Co(II), Ni(II), Cu(II) and Cu(I) complexes of syn-thiophene-2-
aldoxime. Gilles et al.\textsuperscript{146} studied the Co(II), Ni(II) and Cu(II) complexes of 3-(2-furyl)-2-propenaldoxime. The infrared spectra indicate that the ligand is bidentate.

D'yachenko et al.\textsuperscript{147} reported the complexes of cobalt(II) with \(\alpha\)-hydroxylamino oximes. These complexes were characterized by electrical conductivity and electronic spectral studies.

Dubiniva et al.\textsuperscript{148} determined the stoichiometric composition of the complexes of Co(II), Ni(II) and Cu(II) with alkyl(aryl) benzimidazolyl azoketoximes.

Voiculescu and Dominte\textsuperscript{149} reported a review article on the configuration and reactivity of the complexes of copper(II), nickel(II) and palladium(II) with salicylaldoxime.

Lal and Malhotra\textsuperscript{150} synthesized the complexes of 3-bromo-2-hydroxy-5-methylacetophenone oxime of the type \([ML_2]\) (\(M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}\) and \(\text{Pd(II)}\)), \([M'L_2\cdot\text{OH}]\) (\(M = \text{Ti, V}\)), \([VOL_2]\), \([\text{MoO}_2L_2]\) and \([\text{FeL}_3]\). The geometry of the complexes were established by magnetic moment, elemental analyses, conductivity, electronic, ESR and
Mossbauer spectral studies. All the complexes are non-electrolytes in DMF.

Goswami et al.\textsuperscript{151} studied the metal complexes of Fe(II), Ni(II) and Cu(II) with 2,4'-dihydroxy-3',5'-dinitroacetophenone oxime. Studies on complex compounds of Co(II) and Ni(II) with 2'-hydroxy-2,5'-dichloro-4'-methylbenzalacetophenone oxime have been made by Bhardwaj and Singh\textsuperscript{152}.

Kuma and Yamada\textsuperscript{153} studied the iron(II) complexes of 2-furancarboxaldehyde oxime and 2-thiophene aldehyde oxime (L) of the type $\text{trans-FeL}_4X_2$, $X = \text{Cl, Br}$. In these high spin Fe(II) complexes, L is monodentately coordinated to metal ion through nitrogen atom.

Binuclear complexes of silicon(IV) chloride with nickel(II)salicylaldoximates have been reported by Biradar et al.\textsuperscript{154}. $[\text{NiL}_2]$, $\text{HL} = \text{R-2-HOC}_6\text{H}_3\text{CH:NOH}$ where R = H-, 3-Methyl, 4-Methyl, 5-Methyl and 5-Chloro; reacted with SiCl$_4$ in benzene to give $\text{NiL}_2\text{SiCl}_4$, which were characterized by elemental analyses, conductivity measurements, magnetic and spectral data. $\text{NiL}_2\text{SiCl}_4$ are amorphous electrolytes in DMF. IR spectra indicates a Si-OH bond and bonding of oxime oxygen to silicon; Ni is bonded through nitrogen and oxygen atoms.
Abdul et al.\textsuperscript{155} isolated the metal complexes of the types 
[\text{VOL}_2], [\text{CrL}_2(\text{OH})(\text{H}_2\text{O})], [\text{FeL}_3], [\text{CoL}_3], [\text{CuL}_2] \text{ and } [\text{NiL}_2] 
(\text{HL} = \text{phenanethrenequinone monoxime}) \text{ and characterized by methods such as magnetic moment measurements, thermal analysis, IR, electronic and ESR spectral studies. They also reported the crystal field parameters for the chromium(III), cobalt(III) and nickel(II) complexes.}

Synthesis and structural studies of copper and silver complexes with 1-azafluorenone oxime have been reported by Zaitsev et al.\textsuperscript{156}. The compounds were characterized by IR and electronic spectral studies. They reported that the ligand is coordinated to metal ion through the cyclic and oxime nitrogen atoms.

Mostafa et al.\textsuperscript{157} prepared the complexes of the types 
[M(H\text{L}_2)\text{Cl}_2\cdot n\text{H}_2\text{O}] (M = \text{Cu, Cd, Hg, Zn, Ni}, n = 0-3), 
[M^{1}(\text{HL})_2\cdot \text{H}_2\text{O}] (M^{1} = \text{Co, Cd}), [\text{UO}_2(\text{HL})_2], [M^{2}\text{L}(\text{H}_2\text{O})\text{H}_2\text{O}] 
(M^{2} = \text{Cu, Ni}) \text{ and } [\text{Cu(HL)Br}_2\text{H}_2\text{O}]; \text{H}_2\text{L} = \text{biacetyl-2-oxime-3-p-nitrobenzoyl hydrazone}. \text{ The structure of the complexes have been established by known methods such as elemental analyses, magnetic moment, IR, Visible and NMR spectral studies. They proposed that ligand acts in a bidentate/tridentate manner depending on the nature of the metal ion.}

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intramolecular hydrogen bonding in the ligand and its metal complexes is discussed. They also reported the stereochemistry of the Co(II), Ni(II) and Cu(II) complexes.

Yousif et al.\textsuperscript{158} studied the copper(III) complex of an imine-oxime ligand. They reported the complex \([\text{Cu(HL)ClO}_4\cdot2\text{H}_2\text{O}],\) where \(\text{H}_2\text{L} = \text{HON:C(CH}_3\text{)C(CH}_3\text{):N(CH}_3\text{)}_3\text{N:C(CH}_3\text{)(CH}_3\text{)C:NOH},\) which was oxidized by \(\text{PbO}_2,\) \(\text{S}_2\text{O}_8^{2-}\) or \(\text{IO}_4^-\) in aqueous acidic solution to give \([(\text{CuL})\text{ClO}_4\cdot2\text{H}_2\text{O}].\) They characterized the Cu(III) complex by elemental analyses, electrochemical, electronic spectral and redox reactivity methods.

Aggarwal et al.\textsuperscript{159} investigated the complexes of salicylaldoxime (\(\text{H}_2\text{Salox}\)) and o-hydroxy naphthaldoxime (\(\text{H}_2\text{Nolox}\)) having the compositions \([\text{M(HNolox)}_2] [\text{M} = \text{VO(II), Mn(II), Fe(II), Co(II), Ni(II) or Cu(II)}], [\text{M(Nolox)}\cdot2\text{H}_2\text{O}]\) and \([\text{M(Salox)}\cdot2\text{H}_2\text{O}] [\text{M} = \text{Mn(II), Co(II), Ni(II), Cu(II) or Zn(II)}].\) The structures of the complexes have been established by molar conductance, magnetic susceptibility and electronic spectral measurements. Magnetic and electronic spectral studies suggest the square-pyramidal geometry for \([\text{VO(HNolox)}_2],\) square-planar geometry for the other 1:2 complexes and octahedral geometry for 1:1 Co(II), Ni(II) and Cu(II) complexes. The
infrared spectral studies show that H$_2$Nolox acts as mononegative bidentate ligand in 1:2 complexes, the bonding sites being nitrogen and phenolate oxygen and as binegative tetradebate ligands in 1:1 complexes bonding through phenolate and iminoximate oxygen bridging in addition to the bonding sites indicated in the 1:2 complexes.

Keeney et al.$^{160}$ reviewed the transition metal complexes of hydroxy oximes. This review covers 313 references. Wan et al.$^{161}$ synthesized and characterized the Ni(II) complexes with imine-oxime ligands. They examined the substituent effect of ligands on the structure of the metal complexes.

Mohan and Kumar$^{162}$ reported the complexes of the types [Ni(HL)$_2$(X)$_2$] (HL = quinoline-2-aldoxime (Hqox) or isoquinoline-3-aldoxime (Hiqox) and X = Cl$^-$, Br$^-$, I$^-$, NCS$^-$, OAc$^-$) and [Ni(HL)$_2$(NO$_3$)](NO$_3$). The complexes were characterized on the basis of elemental analyses, molar conductance, molecular weight determinations, X-ray powder diffraction patterns, magnetic susceptibility data and infrared spectral measurements. All these physical studies suggest a dimeric halobridged cis-octahedral structure for halo complexes and a monomeric cis-octahedral structure for the remaining complexes.
Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions with the bidentate ligands 2,3-butanedione monoxime (BDMOH), 2,4-pentanediione monoxime (PDMOH) and 1-phenyl-1,2-propanedione-2-oxime (PPDMOH) have been prepared and characterized by Bhargava and Tyagi\textsuperscript{163}. The magnetic moment studies provide evidence for square-planar Co(II), Ni(II) and Cu(II) complexes.

Kariya and Bhave\textsuperscript{164} prepared and characterized the complexes of uranyl thiocyanate and thorium thiocyanate of the types $[\text{UO}_2\cdot\text{L}_2]\cdot3\text{H}_2\text{O}$ and $[\text{UO}_2\cdot\text{L}_2\cdot\text{B}_2]\cdot2\text{H}_2\text{O}$ and $[\text{Th}\cdot\text{X}_2\cdot\text{L}_2\cdot\text{B}_2]\cdot2\text{H}_2\text{O}$ where $X = \text{SCN}$, $B = \text{pyridine}$ and $L = \text{chalkones and their oximes}$. Chalkones and their oximes act as O, O and N, O donors respectively.

Spectral, thermal and magnetic studies on metal complexes of the types $\text{M}(\text{H}_2\text{L})\text{X}_2\cdot\text{nQ}$ ($\text{M} = \text{Ni, Cu, Cd, Mn}$; $\text{X} = \text{Br, Cl}$; $\text{H}_2\text{L} = \text{biaacetilmonoxime isonicotinoyl hydrazone}$, $\text{Q} = \text{EtOH, H}_2\text{O}$, $\text{n} = 0-2$), $[(\text{Zn}(\text{HL})\text{Br})\text{H}_2\text{O}]$, $[\text{NiL}(\text{H}_2\text{O})_2(\text{EtOH})]$, $[\text{CdL}_2]$, $[\text{Co}(\text{HL})(\text{OAc})]\cdot4\text{H}_2\text{O}$, $[\text{CuL}(\text{H}_2\text{O})_2]\cdot2\text{H}_2\text{O}$ and $[\text{UO}_2\text{L}_2]$ are reported by Ibrahim et al.$\textsuperscript{165}$. IR spectral data show that the ligand behaves in a bidentate and/or tridentate manner. An octahedral structure is proposed for the nickel complexes while a square-planar structure is proposed for both cobalt and
copper complexes on the basis of magnetic and spectral measurements.

Synthesis and characterization of hafnium(IV) isopropoxide complexes with cyclohexanone oxime, dimethyl glyoxime, benzophenone oxime, α-benzoin oxime and salicylaldoxime have been studied by Tyagi et al.\textsuperscript{166}.

Jayashankar and Indrasenan\textsuperscript{167} synthesized and characterized the some lanthanide perchlorate complexes of 4-nitroso antipyrine. The ligand 4-nitroso antipyrine has two donor sites, namely ring carbonyl group and the nitroso group and therefore ligand behaves like a bidentate manner and forming a stable six-membered ring with metal ion.

Dhar et al.\textsuperscript{168} studied the nature and compositions of ten solid lanthanide complexes of o-vanillin oxime. Khalil et al.\textsuperscript{169} reported the metal complexes of 8-hydroxy-5-quinolyl-ketone oxime. They also examined the structure activity relationship to evaluate bactericidal activity of the synthesized compounds. Rao\textsuperscript{170} prepared and characterized the lanthanide complexes of the type [DyL·Cl\textsubscript{3}·nH\textsubscript{2}O] (L= diacetyl monoxime). The mechanisms of the thermal decompositions of these complexes are discussed.
Sanyal and Modak\textsuperscript{171} prepared the metal complexes of cobalt(II) and nickel(II) with pyridine-4-amidoxime and characterized on the basis of elemental analyses, conductance, magnetic and spectral measurements. The ligand is bonded through its ring nitrogen only.

Revankar and Mahale\textsuperscript{172} synthesized and characterized thirteen new non-ionic Co(II), Ni(II) and Cu(II) complexes with 2-acetyl-benzimidazole oxime or 2-benzoyl-benzimidazole oxime. They suggested that in the present complexes the oxime ligands exhibit five different coordination modes using different combinations of oximino nitrogen, pyrrole nitrogen and pyridine nitrogen as donor atoms. The antibacterial and antifungal activities of ligands and their metal complexes have also been reported.

Singh et al.\textsuperscript{173} prepared and characterized a series of mono, bi and trinuclear UO$_2$(VI) metal complexes with furfuraldoxime (FDH), salicylaldoxime (H$_2$Salo) and series of polydentate Schiff bases obtained by condensation of diacetyl monoxime with ethylenediamine (DMED), diethylenetriamine (DMDT) and diethylenetetramine (DMTT) respectively to form a series of mono, bi and trinuclear complexes. Bi and trinuclear metal complexes contain hydroxo bridge.
Meyer and Werner\textsuperscript{174} reacted $\text{MHCl(CO)}[\text{PMe(CMe}_3\text{)}_2]_2$ ($M = \text{Ru, Os}$) with aldoxime and ketoxime and obtained the octahedral $\text{MHCl(CO)[N(OH):CRR',][PMe(CMe}_3\text{)}_2]_2$ ($R = R' = \text{Me} ; R = \text{H}, R' = \text{Me} ; R+R' = \text{cyclohexyl}$). They suggested that the oximato ligand coordinates \textit{via} N and O atoms.

The modifications of molecular geometry and electronic structure of CF$_3$NO and CH$_3$NO caused by coordination to a Pt(0) center have been studied\textsuperscript{175} by means of non-empirical MO-LCAO theoretical calculations on the model complexes Pt(PH$_3$)$_2$(RNO). Fantucci et al.\textsuperscript{175} reported the $\eta^2$ coordination mode of RNO, in which the N-O group acts as a side-on $\sigma$-donor and $\pi$-acceptor, is found to be more favourable than the $\eta^1$ mode, in which only the N atom directly interacts with the metal center. The bonding characteristics of the RNO ligands are compared with those of the isoelectronic dioxygen ligand by investigating the electronic structure of the Pt(PH$_3$)$_2$(\textit{$\eta^2$}-O$_2$) complex.

Ligational behaviour of biacetylmonoxime-$\alpha$-naphthylacetylhydrazone ($\text{H}_2\text{BNAH}$) towards some transition metal ions have been reported by Bekheit\textsuperscript{176}. $\text{H}_2\text{BNAH}$ behaves as an oxidizing agent towards Co(II) forming a diamagnetic Co(III) complex. An octahedral structure is proposed for
[Ni(HBNAH)₂(H₂O)₂] and [Co(HBNAH)₂OAc] while square-planar one is suggested for [M(BNAH)]₂ (M = Cu or Ni) and Pd complexes according to the data of magnetic moments and electronic spectra.

Havanur et al. studied the complexes of 2-acetyl-benzimidazole oxime and 2-benzoyl-benzimidazole oxime with MoO₂(II), UO₂(II), VO(II), Zn(II), Cd(II), Hg(II), Mn(III), Co(III) and Fe(III). They reported that the oxime ligands exhibit three different coordination modes, using different combinations of oximino nitrogen, pyrrole nitrogen and pyridine nitrogen as donor atoms. The complexes have been characterized on the basis of their magnetic, IR, electronic, EPR, Mossbauer and thermal studies.

Hassan et al. synthesized and characterized a new technetium(V) complex with butane-2,3-dione monoxime. IR, UV-visible spectra, electrophoresis and HPLC data of the complex are reported and discussed.

Oliviero et al. examined the crystal structures of the ortho-benzoquinone monoxime complexes with d-metals. They reported that the ligand o-benzoquinone monoxime can, in principle be present as o-benzoquinone monoximes (I) or
o-nitroso phenols (II). They suggested from the available data that the ligands are always intermediate between these limiting forms [(I) and (II)]. Moreover, a comparison between the structures of the free ligands and those of their d-metal complexes show that complexation to a d-metal influence the mesomorphic equilibrium between form I and II, causing shift towards (II). They discussed this features in terms of the interaction of the ligands with d orbitals of the metal.

Basu and Chakravorty\(^{180}\) reported the synthesis, isomerism and equilibria of the low-spin Mn(II and III) complexes with substituted 1,2-quinone oximes.

M.I.DeFrutos et al.\(^{181}\) prepared and characterized the complexes of oxovanadium(V) with 2-hydroxyacetophenone oxime (L\(^1\)H) and 2-hydroxybenzophenone oxime (L\(^2\)H). The following two general formulae have been proposed [VO(X)\(_2\)L] and [VO(X)L\(_2\)] with 5 and 6 coordinate vanadium respectively. The hydrogen atom of the phenolic group is replaced by vanadium metal ion on complexation and nitrogen atom of the oxime group is also coordinated to the metal ion on complexation.
Djebbar-Sid and Benali-Baitich\textsuperscript{182} isolated the vanadium(V), molybdenum(VI) and tungsten(VI) complexes of salicylaldoxime (H\textsubscript{2}SAL) and 2-hydroxybenzophenone oxime (H\textsubscript{2}BPO) of the composition 1:2 (metal:ligand) and characterized by methods such as elemental analyses, UV-visible, IR and NMR spectrometry. They proposed following hypothesis for every complex. The coordination number of the central metal atom is six. The two ligands are bonded bidentately by the nitrogen of the oxime function and oxygen of the phenolic group.

The thermal stability and mode of decomposition of Cu(II), Ni(II) and Pd(II) complexes with 2-hydroxyaryl oximes have been studied\textsuperscript{183} in air atmosphere using the TG or DTA techniques. For copper complexes, their thermal behaviour was also studied in nitrogen atmosphere by TG or DTG techniques. They performed kinetic analysis of the complexes using the Coats-Redferm method to determine apparent activation energy and the pre-exponential factor of the Arhenious equation. They also reported and discussed possible fragmentation of the complexes on the basis of mass spectral studies.

Patel et al.\textsuperscript{184} isolated and characterized the metal complexes of Mn(II), Co(II), Ni(II), Zn(II), Hg(II), Cd(II), and
UO₂(II) with α-oximinoacetoacet-o-anisidide thiosemicarbazone and α-oximinoacetoacet-p-anisidide thiosemicarbazone. The isolated compounds have also been tested for their antimicrobial activities.

Shetti et al.¹⁸⁵ reported the complexes having the formulae [MLCl₃]Cl, [ML'Cl₃]Cl (M = Ti); [ML₂], where M = Mn(II), Co(II), Ni(II) and Zn(II); L = isonitrosoacetophenone thiosemicarbazone and L' = isonitroso-4-chloroacetophenone thiosemicarbazone. Structures of the complexes have been established by known methods. In all the complexes the ligand is coordinated to the central metal ion through 'S' (¿C=S ), 'N' (¿N-OH ) after deprotonation and 'N' (¿C=N ) as shown by IR and NMR spectral studies.

Synthesis, spectral and magnetic properties of the complex of chromium(III) with chrysenesemiquinone monoxime having the formula [Cr(ChrySQM)₃] (HChrySQM = chrysenesemiquinone monoxime) have been investigated by Ramadan et al.¹⁸⁶ Spectroscopic studies of the complex suggest that the HChrySQM is attached to the metal in both nitroso and oxime forms.
Thakkar and Deshmukh\textsuperscript{187} studied the Co(III), Ni(II) and Cu(II) complexes of alkylimino derivatives of isonitrosopropiophenone. They reported octahedral Co(III) and square-planar Ni(II) complexes and square-planar or elongated octahedral Cu(II) complexes on the basis of various findings. The infrared spectral studies reveal a Co-N_2O chromophore for the Co(III) complexes in which two five membered rings, involving bonding through oximino nitrogen and alkylimino nitrogen atoms, coexist along with a six-membered ring involving bonding between the Co(III) ion and oximino oxygen and alkylimino nitrogen atoms. In the case of the Ni(II) and Cu(II) complexes presence of M-N_3O chromophore is suggested.

Daniel et al.\textsuperscript{188} studied the half-sandwich type osmium complexes with oximes HON:CRR' (CRR' = CPh_2, CMePh, CMe_2, cyclohexyl). Kumbhar et al.\textsuperscript{189} synthesized the complexes of Cu(II), Ni(II) and Fe(II) with 2-acetylpyridine oxime and characterized by elemental analyses, infrared and UV-visible spectroscopy, magnetic moments and cyclic voltammetry. They also investigated the interactions of metal complexes with plasmid DNA.
Reddy et al.\textsuperscript{190} prepared cobalt(II) and nickel(II) metal complexes of benzil-\(\alpha\)-monoxime-2-iminoethanethiol (BMET\(\text{H}_2\)), benzil-\(\alpha\)-monoxime-2-iminobenzenethiol (BMBTH\(\text{H}_2\)), benzil-\(\alpha\)-monoxime thiosemicarbazone (BMTH\(\text{H}_2\)), benzil-\(\alpha\)-monoxime semicarbazone (BMSH\(\text{H}_2\)) and characterized on the basis of elemental analyses, conductivity, magnetic moment, IR and electronic spectral data. They reported that all dimeric complexes are non electrolytes and dimeric structure is bridged through oxime groups. They also calculated various electronic spectral parameters.

Karmakar et al.\textsuperscript{191} reported that the ligand HON=C(Ph)N=N-C\(_6\)H\(_4\)COOH (H\(_2\)L) forms the low-spin (\(S = 1/2\)) iron(III) complex Et\(_4\)N[Fe(PhL)\(_2\)]. The complex shows the presence of \textit{cis}-FeN\(_4\)O\(_2\) coordination sphere. They also reported that carboxyl bonded low-spin iron(III) species are very rare and spin-pairing contracts metal radius. They found that the Fe-N and Fe-O lengths are significantly shorter than those in representative high-spin complexes.

Gaikwad et al.\textsuperscript{192} synthesized six new complexes of beryllium(II) and magnesium(II) with 3-Chloro, 3-Bromo and 3-Iodo derivatives of lawsone monoxime (2-hydroxy-1,4-naphthalenedione-1-oxime) of the types [BeL\(_2\)(OH\(_2\))\(_2\)\cdot2\text{H}_2\text{O}]}
and \([\text{Mg}(L)_2(H_2O)_2]\), where \(L\) = anion of 3-halolawsone monoxime and characterized on the basis of elemental analyses, molar conductance, infrared spectra, electronic spectra and TGA data. They suggested an octahedral geometry for the Mg(II) complexes.

Stoyanov et al.\(^{193}\) prepared Co(II), Ni(II) and Cu(II) complexes of 2-nitroso-2,3-dihydrophenalene-1,3-dione and their structures and coordination modes of the ligand were studied using spectroscopic and magnetochemical methods.

Hasan et al.\(^{194}\) isolated the oxovanadium(IV) complexes of arylazobenzaldoximes of the general formula \([\text{VO}(L)_2] \cdot nH_2O\), where \(n = 1, 2\). These complexes were characterized on the basis of elemental analyses, conductivity measurements, magnetic susceptibility, IR and \(^1\text{H}\) NMR data. They propose dimeric structures with strong vanadium-vanadium interaction for the complexes.

Charalambous et al.\(^{195}\) isolated the palladium(II) and platinum(II) complexes of 5-acyl and 5-alkylamino-1,2-benzoquinone-2-oximes. These complexes were identified by elemental analyses, IR, NMR (\(^1\text{H}\) and \(^{195}\text{Pt}\)) spectroscopy. They reported that the ligands are bonded to metal ion via the oxime
nitrogen and the quinonoid carbonyl oxygen. The mass spectral data indicate that the complexes are monomeric in nature.

A number of mixed ligand complexes of the type \( \text{trans-}[\text{Co(DH)}_2(\text{AM})X] \) where DH = dimethylglyoxime, AM = dodecylamine or butylamine and X = Cl\(^-\), I\(^-\), N\(_3\)\(^-\), NO\(_2\)\(^-\) and SCN\(^-\) have been synthesized and characterized by Arumugam and Arunachalam\(^{196}\). They proposed the trans-configuration for the isolated complexes.

Fe(II) complex of 2-nitroso-2,3-dihydrophenalene-1,3-dione has been obtained as a result of Fe(III) interaction with ligand by Mitewa et al.\(^{197}\). The analytical data of the complex show that complexation occurred with metal to ligand ratio of 1:2, thus suggesting the proceeding of a redox process. The excess of N=O containing ligand reduces Fe(III) to Fe(II) and then stabilize it through complexation. This was confirmed by Mossbauer data. The magnetochemical and EPR data obtained are in agreement with the assumption for planar structure of the complex studied. The coordination modes of the ligand are discussed on the basis of the IR spectral data. The following two possible structures have been proposed for the investigated complex.
Suggested Structures of the Metal Complex

Cukurovali et al.\textsuperscript{198} studied the metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with p-tolyl-N-imidazolylmethyl ketoxime. The compounds were identified by analytical, spectral, thermal and magnetic studies. Synthesis, spectral (IR, electronic) and thermal studies of some divalent metal complexes with 8-acetyl-7-hydroxy-4-methylcoumarin oxime have been reported by Pokhariyal et al.\textsuperscript{199}.

El-Asmy et al.\textsuperscript{200} reported the transition metal complexes of 3-oximino-3-(2-pyridylcarbomyl)-propane-2-one (H\textsubscript{2}OPP). The conductivity data of the complexes in DMSO as well as in aqueous solution was reported. The geometries of the studied complexes have been elucidated on the basis of magnetic, spectral and TGA studies.

Boutamine et al.\textsuperscript{201} isolated the metal complexes of vanadium(V, IV or III) with α-benzoin oxime (H\textsubscript{2}L\textsuperscript{1}) by
different experimental conditions. The isolated complexes are of the types, (i) \([V_2O_4(H_2L^1)_2(L^2)_2] \cdot 3H_2O\), where, \(L^2 = C_6H_5(C=O)(C=NO)C_6H_5\), deprotonated oxidized form of \(\alpha\)-benzoin oxime. (ii) \(Na_5[HV_{10}O_{28}(H_2L^1)_2(HL^2)_2] \cdot 6H_2O\) (iii) \(Na_6[H_5V_{10}O_{28}(HL^2)_6] \cdot 10H_2O\). In all metal complexes, ligand-metal redox reaction takes place at room temperature, which progressively leads to a reduction of vanadium(V) to vanadium(IV). The reaction of \(\alpha\)-benzoin oxime with vanadium(III) leads to dimeric coordination compound of vanadium(IV) of the formula \([V_2O_4(H_2O)_2(L^4)_4]\) in which \(\alpha\)-benzoin oxime was transformed to dibenzil (\(L^4\)) after hydrolysis and oxidation. Under inert atmosphere (nitrogen) \(\alpha\)-benzoin oxime does not form any complex with vanadium(III). It was hydrolyzed to benzoin (\(HL^3\)), vanadium(III) being the catalyst of the reaction.

Kelkar et al.\(^{202}\) synthesized Co(III) complexes of lawsone, \(HL\) (2-hydroxy-1,4-napthalenedione), 3-chloro lawsone, pthiocol (3-methyl lawsone) and their 1-oximes from chloropentaminecobalt(III) chloride via ligand replacement reactions. The spectral data reveal that lawsones bonded through O atoms and lawsone monoximes bonded via N and O atoms with Co(III). They suggested an octahedral geometry for the complexes.
Ghoshal and Chawan synthesized and characterized the mixed ligand complexes of rare earth ions La(III), Pr(III), Nd(III) Sm(III), Gd(III) and Dy(III) with ortho-vanilin monoxime as primary ligand and N-phenylurea and N,N'-diphenylurea as secondary ligands. Their structures have been established on the basis of analytical, spectral and thermal studies.

Das et al. reported the synthesis and characterization of tris(1-nitroso-2-naphtholate)ruthenium(II) and its utilization as an efficient building unit to form heterometallic trinuclear complexes. They reported that anionic ligand is known to coordinate metal ions as a bidentate N, O donor forming a five-membered complex ring (Structure I) having the oximato oxygen available for further coordination to second metal ion (Structure II) and thus it can act as a bridging ligand.

\[ \text{[I]} \quad \equiv \quad \text{[II]} \]

**Suggested Structures of the Metal Complex**
Jayaramudu and Reddy\textsuperscript{205} prepared complexes of Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) with diacetylmonoxime isonicotinoylhydrazone. The structures of the complexes have been elucidated by analytical, spectral and magnetic studies. The molar conductivities data revealed that the metal complexes are electrolytes. They reported that the ligand behaves as a tetradeutate ligand in all cases. They established octahedral geometry for all the complexes [except Cu(II) complex] from IR, electronic and magnetic studies. In all these complexes, the oxime (=N-OH) group acts as a bridging function to give dimeric structures.

Thamizharasi et al.\textsuperscript{206} synthesized and characterized polymer metal complexes of Cu(II) and Ni(II) derived from poly[2-hydroxy-4-(methacryloyloxy)acetophenone oxime] and poly[2-hydroxy-4-(acryloyloxy)acetophenone oxime].

Mokhir et al.\textsuperscript{207} prepared multidentate 2-hetaryl-cyanoximes of general formula HO-N:C(CN)R, where R = heterocyclic group, 2-pyridyl, 2-quinolyl, 2-benzothiazolyl. They synthesized the intensely coloured Fe(II) and Cu(I) complexes of 2-hetarylcyanoximes and described detailed crystal structures. They also reviewed the synthesis and
coordination modes for 2-heteroarylcyanoximes in various complexes with s, p and d metals.

Singh et al.\textsuperscript{208} synthesized some di- and triorganotin(IV) complexes of benzil monoxime and benzil dioxime by the reactions of the corresponding di- and triorganotin(IV) chlorides with the sodium salt of oximes in different stoichiometric ratio in dry benzene. They characterized all the metal complexes by elemental analyses, molecular weights, conductivity measurements, IR and NMR (\textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{119}Sn) spectral studies.

Rakha et al.\textsuperscript{209} investigated the complexes of biacetylmonoxime phenylacetylhydrazone [H\textsubscript{2}BMPH] with Co(II), Co(III), Ni(II), Cu(II), Pd(II) and UO\textsubscript{2}(VI). They proposed an octahedral structure for [Co(H\textsubscript{2}BMPH)\textsubscript{2}(OAc)] and [Ni(HBMPH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}], tetrahedral for [Co(H\textsubscript{2}BMPH)Cl\textsubscript{2}], square-planar for [Cu(HBMPH)Cl(H\textsubscript{2}O)], [Cu(HBMPH)]\textsubscript{2}, [Ni(BMPH)]\textsubscript{2} and Pd(II) complexes on the basis of chemical analysis, thermal analysis (TG, DTG, DTA), molar conductivities, spectral (IR, NMR, UV, Visible) and magnetic measurements.
Reddy et al.\textsuperscript{210} isolated the complexes of cobalt(III), nickel(II) and copper(II) with benzil-\(\alpha\)-monoxime (BMO), the molar conductivity data show them to be non-electrolytes. The monoanionic bidentate behaviour of BMO ligand is inferred from infrared spectra. They proposed square-planar geometry for nickel(II) and copper(II) complexes and an octahedral geometry for nickel(II) in coordinating solvent DMF. Reddy et al.\textsuperscript{210} isolated single crystal of \([\text{Co(BMO)}_3]\) complex and confirmed its structure by x-ray diffraction studies and showed the presence of a \textit{fac}-octahedral configuration for this complex. Electrochemical studies suggest that the cobalt complex undergoes two single 1-electron reduction steps corresponding to \(\text{Co(III)} \rightarrow \text{Co(II)}\) and \(\text{Co(II)} \rightarrow \text{Co(I)}\).

Singh and Narayan\textsuperscript{211} isolated the mono nuclear titanium(IV) complex of salicylidene anthranilic acid and \(-o\)-vanilinoxime in good yield with an excellent purity. Singh and Tawade\textsuperscript{212} synthesized the complexes of some di- and triorganotin(IV) with \(\alpha\)-benzoin oxime. Singh and Tawade\textsuperscript{213} also synthesized the complexes of some di- and triorganotin(IV) with benzil-\(\alpha\)-monoxime thiosemicarbazone by the reaction of di- and triorganotin(IV) chlorides and sodium salts of benzil-\(\alpha\)-monoxime thiosemicarbazone in desired molar ratios. They
characterized all the synthesized compounds by elemental analyses, IR and NMR (\(^1\text{H}, \, ^{13}\text{C} \) and \(^{119}\text{Sn}\)) spectral studies.

The chloroalumino-organic compounds of coordinated salicylaldoxime, which was resulted from the reaction of Pd(II), Ni(II) and Cu(II)bis(salicylaldoximates) with diethylaluminium chloride were isolated by Voiculescu\(^{214}\). These compounds were characterized by elemental analyses, magnetic measurements, infrared absorption and x-ray diffraction spectra.

Zekri et al.\(^{215}\) presented various aspect of the reactivity of \(\alpha\)-benzoin oxime with tungsten(VI) by altering the \(p^H\) of the aqueous tungsten salt solution and metal:ligand ratio. Zekri et al.\(^{216}\) also reported the metal complexes of uranium(VI) with acetone oxime and \(\alpha\)-benzoin oxime. They characterized the metal complexes on the basis of elemental analyses, infrared, UV-visible absorption and \(^1\text{H}\) NMR spectral studies.

Hierso et al.\(^{217}\) synthesized and characterized the complexes of the types, \([\text{Co}(L)_4X_2] \) (\(L = \text{acetaldoxime (aax) or butraldoxime (bax)} \); \(X = \text{Cl or Br}\)) and \([\text{Mn(bax)}_4\text{Cl}_2]\). They characterized all cobalt complexes by single crystal x-ray diffraction studies and suggested a mononuclear octahedral
geometry for all cobalt complexes. They suggested that spectroscopic studies of manganese complexes with aax and bax ligands are similar to cobalt analogs. The isolated coordination complexes are all highly reactive towards atmospheric H₂O and readily decomposed to yield metal hydrates.

Studies on spectral properties of Co(II), Ni(II) and Cu(II) complexes with ninhydrine and ninhydrine oximes have been reported by Rai et al. They characterized metal complexes by elemental analyses, molar conductivity, electronic absorption and IR spectra. They proposed square-planar structures for all ML' Cl₂ and octahedral structures for all ML'3Cl₂Y₂, where L₁ = ninhydrine, L₂ = ninhydrine monoxime, L₃ = ninhydrine dioxime and Y = NH₃ or pyridine. All metal complexes are non-electrolytes.

Raut and Patil reported the synthesis and characterization of Cr(III), Fe(II) and Pd(II) complexes with 4-methylisonitroso acetophenone [HIMAP]. They assigned the formula of the complexes as [Cr(IMAP)₃], [Fe(IMAP)₂] and [Pd(IMAP)₂]. The probable geometries of the complexes have been assigned on the basis of magnetic, electronic and IR spectral data. Raut and Patil also synthesized and
characterized the Co(II), Ni(II) and Cu(II) complexes with the same ligand 4-methylisonitroso acetophenone.

A series of complexes having the formulae, \([\text{Co}(\text{HL})_2]\), \([\text{Co}(\text{HL})_2\text{X}_2]\) and \([\text{Co}(\text{HL})_2\text{Y}_2]\), where \(\text{HL}=3\)-phenyl-quinazolone-4(3H)-one-2-carboxaldehyde oxime, \(\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{and ClO}_4^-\) and \(\text{Y} = \text{NH}_3\) or pyridine have been synthesized and characterized by Rai et al.\(^{221}\). On the basis of experimental data Rai et al.\(^{221}\) proposed square-planar structure for \([\text{Co}(\text{HL})_2]\), an octahedral structure for \([\text{Co}(\text{HL})_2\text{X}_2]\) and \([\text{Co}(\text{HL})_2\text{Y}_2]\) complexes. All complexes are non-electrolyte in nature.

X-ray crystallographic studies of nickel(II) and palladium(II) complexes of o-hydroxyacetophenone oxime have been made by Mehta and Swar\(^{222}\). They indicated that the compound has orthorhombic system with space group \(P_{mmm}\) or \(P_{222}\) from XRD data.

Cobalt(II) complexes of 2-hydroxy-1-naphthaldoxime and 2,4-dihydroxyacetophenone oxime have been prepared and characterized by Kelkar and Mehta\(^{223}\). Geometry of the complexes were assigned on the basis of electronic absorption
and magnetic moment data. Using X-ray powder diffraction, they calculated the lattice parameters for the complexes.

Synthesis and characterization of some transition metal complexes of 2-naphthoinoxime have been reported by Mehta and Nagarkoti\textsuperscript{224}. They presented various bonding features of the metal complexes on the basis of infrared spectral studies. Probable geometries of the complexes have been assigned on the basis of various spectral findings. Electronic spectral data of the complexes are also calculated.

X-ray crystallographic studies of dioxouranium(VI), dioxomolybdenum(VI) and oxovanadium(IV) complexes of o-hydroxyacetophenone oxime have been made by Mehta and Syed\textsuperscript{225}. They proposed monoclinic system for the complexes with space group P\textsubscript{2}/m, B\textsubscript{2}/m and C\textsubscript{2}/m.

Transition metal complexes of α-benzoin oxime have been synthesized by Attia et al.\textsuperscript{226}. These complexes were characterized on the basis of spectral, thermal and magnetic studies.

A great number of publications on the oxime containing complexes have appeared in literature, which covers the areas
viz. organic solution and analytical, general inorganic and organometallic chemistry of the oximes and their complexes have been extensively explored as shown by following review articles:

1. The analytical properties of the various type of the oximes are briefly reviewed by Diehl.

2. Singh et al. published a review article on the use of oximes as a spectrophotometric reagents.

3. A review with 220 references on extraction of Cu, Fe, Co, Ni, Ge, Pt-group metals, Mo, V and other metals with the hydroxy oximes have been reported by Whewell and Hanson.

4. A review on application of the hydroxy oxime extractants in the separation of the metal ions have been reported by J.Yu. The following topics are covered in this review article (i) structure and classification of the title extractants (ii) complexation of actinides and transition metals by the extractants (iii) use of the extractants for the separation of metals.

5. Szymanowski presented a review on kinetics and mechanism of copper extraction by the hydroxy oximes. This article has content of papers published between 1972 and 1983 with 106 references.
6. R.P. Singh and N.K. Singh\textsuperscript{232} presented a review article with 130 references on first row transition metal complexes of aromatic o-hydroxy aldimines.

7. Kukushkin et al.\textsuperscript{233} reported a review article with 165 references, focusing on metal-ion assisted reactions of oximes and reactivity of oxime-containing metal complexes.

8. Kukushkin and Pombeiro\textsuperscript{234} published a review article with content of 135 references, which explores the unconventional synthesis and reactivity of oxime and oximate metal complexes.

Brady and Porter\textsuperscript{235} have prepared the coordination compounds of alkali metals, nickel(II) and thallium(I) with 4-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one. These compounds are practically insoluble in water, but when boiled with it, suffer partial decomposition and the ligand separates from the solution on cooling.

Hovorka and Sykora\textsuperscript{236} studied the reactions of 4-oximino-3-methyl-2-pyrazolin-5-one with different metal salts and have assigned the following structure for the internal complex salts.
Suggested Structure of the Complex Salts

Shah et al.\textsuperscript{237,238} studied the complexes of 4-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one with divalent metal ions. They have also investigated the nature of the Cu(II) complex by extraction studies\textsuperscript{239}.

Eighteen complexes have been synthesized\textsuperscript{240} having the composition $[\text{M}(L \text{ or } L')_2\text{X}_2]$ and $[\text{M}'\text{L}_2\text{Y}_2]$, where $\text{M} = \text{Co(II)}$, $\text{Ni(II)}$, $\text{Cu(II)}$ and $\text{Zn(II)}$; $\text{M}' = \text{Co(II)}$, $\text{Ni(II)}$; $\text{X} = \text{Cl}^-$, $\text{Br}^-$, $\text{NO}_3^-$; $\text{Y} = \text{ClO}_4^-$ and $L = 4$-nitroso-3-methyl-1-phenyl-2-pyrazolin-5-one and $L' = 4$-nitroso-3-methyl-2-pyrazolin-5-one. They reported that the complexes of the type $[\text{M}(L \text{ or } L')_2\text{X}_2]$ have either an octahedral or distorted-octahedral configuration and complexes of the type $[\text{M}'\text{L}_2\text{Y}_2]$ have either tetrahedral or planar geometry. The synthesized compounds have also been screened for their antifungal activities.
Structural studies on the VO(II), Mn(II), Fe(II), Zn(II) and UO₂(II) complexes of some 4-oximino-2-pyrazolin-5-ones have been reported. All complexes except UO₂(II) complexes are octahedral. They reported that UO₂(II) complexes possess higher coordination number.

Rana and Shah investigated the transition metal complexes of 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one. All complexes are found to be non-electrolyte in nature. The probable geometries of the complexes have been assigned on the basis of elemental analyses, magnetic moment, IR and diffuse reflectance spectral studies. Various ligand field parameters for some of the distorted complexes are evaluated.

Shah et al. reported the pyridine and 3-picoline adducts of Ni(II) and Zn(II) complexes with some 4-oximino-2-pyrazolin-5-ones. They suggested an octahedral structure for all metal complexes on the basis of analytical, spectral, thermal and magnetic studies.

Complexes of Cr(III), Co(II) and Ni(II) with 4-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one, 4-oximino-3-methyl-2-pyrazolin-5-one, 4-oximino-3-phenyl-2-pyrazolin-5-one, 4-oximino-1,3-diphenyl-2-pyrazolin-5-one have been prepared.
and characterized by Shah et al.\textsuperscript{244}. Various ligand field parameters have been evaluated for all the complexes.

Structural studies on the oxovanadium(IV), chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and Zinc(II) complexes of 4-formyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one have been reported by Patel et al.\textsuperscript{245}. They isolated the solid metal complexes and characterized them by analytical, magnetic and spectral studies. They assigned an octahedral geometry to all metal complexes (except oxovanadium(IV) complex) and square-pyramidal geometry for the oxovanadium(IV) complex.

The ligating properties of the 4-acyloxime-3-methyl-1-phenyl-2-pyrazolin-5-ones [acyl = acetyl, propionyl, butyryl, chloroacetyl] and 4-acyloxime-3-methyl-1-(3' Chlorophenyl)-2-pyrazolin-5-ones [acyl = formyl, acetyl, benzoyl and propionyl] with chromium(III) have been investigated by Patel et al.\textsuperscript{246}. They synthesized and characterized all Cr(III) complexes of 4-acyloxime-2-pyrazolin-5-ones (L) and formulated them as [CrL\textsubscript{3}] on the basis of elemental analyses, electrical conductance, electronic and IR spectral and magnetic susceptibility measurements. They determined the coordination sites of the ligands from $\nu_{\text{C=N}}$ (oxime) and $\nu_{\text{C-O}}$ (pyrazole ring).
They suggested that oximino proton is not involved in complexation.

Patel and Shah$^{247}$ studied the several six-coordinated, spin-paired complexes of the type $[\text{CoL}_2\cdot\text{NO}_3\cdot\text{H}_2\text{O}]$, where $\text{HL} = 4$-acyloxime-3-methyl-1-aryl-2-pyrazolin-5-ones ($\text{Ar}$ is phenyl or 3-chlorophenyl; in the acyloxime $\text{R}-\text{C}=\text{N}-\text{OH}$, $\text{R}$ may be H, Me, Et, Pr, $\text{CH}_2\text{Cl}$ or phenyl).

Nine new complexes of thorium(IV) nitrate with some pyrazol-5-one derivatives such as 3-methyl-1-phenylpyrazol-5-one, 3-methyl-4-phenacyl-1-phenylpyrazol-5-one, 4-benzoyl-3-methyl-1-phenylpyrazol-5-one, 3-methyl-4-nitroso-1-phenyl pyrazol-5-one, 3-methyl-4-nitrosopyrazol-5-one, 2,3-dimethyl-4-nitroso-1-phenylpyrazol-5-one, 1-carbimido-3-methylpyrazol-5-one, 2,3-dimethyl-1-phenyl-4-(2,4-dihydroxyphenylazo) pyrazol-5-one, 2,3-dimethyl-1-phenyl-4-(2-hydroxynaphthylazo)pyrazol-5-one have been synthesized and characterized on the basis of elemental analyses, IR spectra, conductance, magnetic moment and molecular weight data by Kuncheria and Indrasenan$^{248}$.

The synthesis and characterization of $\text{ThL}_n\text{X}_4$ ( $\text{L} = 3$-methyl-5-pyrazolone, 3-methyl-1-phenyl-5-pyrazolone, 4-
nitroso-3-methyl-5-pyrazolone; n = 4, X = Cl\(^-\), Br\(^-\), NCS\(^-\), I\(^-\); n = 6, X = ClO\(_4\)^-; n = 2, X = NO\(_3\)^- ) are reported by Agarwal and Arora\(^{249}\). They suggested that all adducts are diamagnetic or weakly paramagnetic. They reported that the coordination number of Th(IV) is 6, 8 or 10 in these adducts and it depends on the nature of anion. They suggested that the ligand coordinates to the metal ion through oxygen atom. The thermal properties and X-ray powder diffraction studies on some of the complexes were also reported.

Eighteen UO\(_2\)X\(_2\)L ( X = NO\(_3\)^-, Br\(^-\), I\(^-\), NCS\(^-\) and OAc\(^-\) ) or UO\(_2\)(ClO\(_4\))\(_2\)4L (L = 3-methyl-5-pyrazolone, 3-methyl-1-phenyl-5-pyrazolone, 4-nitroso-3-methyl-5-pyrazolone) were prepared in non-aqueous media and characterized from elemental analyses, electrical conductivity, IR and electronic spectral studies by Agarwal and Arora\(^{250}\). TGA and X-ray diffraction studies on some of the complexes were also reported. The probable coordination number of the synthesized complexes have tentatively been assigned as 6 or 8 depending upon the nature of anions.

4-oximino-2-pyrazolin-5-ones are reported for identification of the metal ions\(^{251}\). The use of these compounds
as the reagent in quantitative analysis have also been proposed.252

C. PRESENT WORK

The survey of the literature cited above showed that the different oxime systems have been extensively studied.

The 2,4-Dihydro-3H-pyrazol-3-ones constitutes an interesting class of reagents because of their varied medicinal, analytical and commercial applications, viz. potential antituberculotic253, antineoplastic254, antidiabetic255, antifertility256, antibacterial257, antiviral258 and antifungal259 agents. Moreover, it has been demonstrated that they are potential extractants260-262 and powerful drugs263. The chemistry of 2,4-dihydro-3H-pyrazol-3-ones have assumed considerable importance because of their practical use as potential laser materials264,265 and also as NMR shift reagents266-270.

Several investigations regarding the synthesis and characterizations of the metal complexes derived from different derivatives of 4-substituted-2,4-dihydro-3H-pyrazol-3-ones have also been made271-288.
But to the best of our knowledge no work has been reported on the synthesis and complexation studies of the following heterocyclic ketoxime ligands.

(I) 4-Formyloxime-2,4-dihydro-2,5-diphenyl-3H-pyrazol-3-one, i.e. 4-Formyloxime-1,3-diphenyl-2-pyrazolin-5-one.

(II) 4-Formyloxime-2,4-dihydro-5-phenyl-2-(2',4'-dinitrophenyl)-3H-pyrazol-3-one, i.e. 4-Formyloxime-3-phenyl-1-(2',4'-dinitrophenyl)-2-pyrazolin-5-one.

(III) 4-Formyloxime-2,4-dihydro-5-methyl-2-(2',4'-dinitrophenyl)-3H-pyrazol-3-one, i.e. 4-Formyloxime-3-methyl-1-(2',4'-dinitrophenyl)-2-pyrazolin-5-one.

(IV) 4-Acetyloxime-2,4-dihydro-5-phenyl-2-(2',4'-dinitrophenyl)-3H-pyrazol-3-one, i.e. 4-Acetyloxime-3-phenyl-1-(2',4'-dinitrophenyl)-2-pyrazolin-5-one.

(V) 4-Benzoyloxime-2,4-dihydro-5-methyl-2-(2',4'-dinitrophenyl)-3H-pyrazol-3-one, i.e. 4-Benzoyloxime-3-methyl-1-(2',4'-dinitrophenyl)-2-pyrazolin-5-one.

(VI) 4-Oximino-2,4-dihydro-5-phenyl-2-(2',4'-dinitrophenyl)-3H-pyrazol-3-one, i.e. 4-Oximino-3-phenyl-1-(2',4'-dinitrophenyl)-2-pyrazolin-5-one.
4-Oximino-2,4-dihydro-5-methyl-2-(2',4'-dinitrophenyl)-3H-pyrazol-3-one, i.e. 4-Oximino-3-methyl-1-(2',4'-dinitro phenyl)-2-pyrazolin-5-one.

It is therefore thought worthwhile to study structure and properties of Oxovanadium(IV), Chromium(III), Manganese(II), Iron(II), Iron(III), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes with the heterocyclic ketoxime ligand I, II, III, IV, V, VI and VII.

These metal complexes were characterized by colour, elemental analyses, conductivity measurements and by infrared spectral studies. The electronic spectral and magnetic studies have been made to assign the probable structure to the metal complexes. The $^{13}$C NMR and mass spectra of all ligands (I-VII) studied in the present work are also recorded.

The results of these investigations are presented in three chapters as outlined below:

Chapter II describes the synthesis and characterization of the seven heterocyclic ketoxime ligands I-VII.
Chapter III describes the synthesis and characterization of the metal complexes of all the above hetercyclic ketoxime ligands I-VII. This chapter is divided into two sections. The results of the studies are analyzed with a view to correlate structures with various properties.

Chapter IV describes the studies on antimicrobial activities of the heterocyclic ketoxime ligands (I-VII) and their metal complexes.
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