Chapter 1

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The coordination chemistry of transition metal with physiologically active ligand containing nitrogen, oxygen and sulphur donors have received a great deal of attention because of the possible relationship with many biological problems and valuable catalytic applications.

Moreover, the role of chromium is a subject of much more studied but it is involved in many biological activities Chromium is associated with the glucose tolerance factor and diabetes. It plays an active role inner sphere electron transfer reactions that involve a pair of Co and Cr metalloproteins. Hetero atom of nucleoside bases of DNA forms complexes with Cr (III) ion which disrupts the gene function and most probably causes carcinogenic action.

Vanadium form oxy anion and oxycation species so it plays wide role in biological functions. It plays an important role in introbactin complexes. It also plays an important role in nitrogen fixation through nitrogenase.

Manganese has very important role in bioactivities. It takes part in ATP activation zinc figure binding saccharides extra cellular binding, transfer of glactosyl group- C-C carboxylase and
C-C carboxylation synthesis in mitochondria. Dioxygen released in plants (chloroplasts) and citric acid cycle in mitochondria.

Iron ions have played many biological activities. Such as oxygen transport in plasma, oxygen storage in muscle, iron transport plasma, iron storage in muscular, iron metabolism of hydrogen peroxide and terminal oxidation iron. Sulphur proteins ruberdoxins are participate in biological redox reactions.

Isonicotanic acid hydrazide a common plant product of Leguminosac family is a very popular antitubercular agent and contain several potential donor sites for chelating with metal ions. It is one of the simplest of the known chemotherapeutic bactericidal agent and its metal chelates are fond to an effective anticancer agent. This plant family also contains a variety of physiological active products such as nicotine (an insecticide), nicotinic acids a component of vitamin B complex and its deficiency causes pellagra, nicotinamide (a co-enzyme useful in paediatric is the rapeutic agent and hypoglycemia agent), coramine (cardiac and respiratory stimulant). In view of biological importance of metal chelates of Isonicotanic acid hydrazide, the present work embodies the various physicochemical and biochemical behavior and structural investigation using vanadium, chromium and manganese Iron ion.

The present work of this thesis is an attempt in the direction of seeking co-relation between the different physico-chemical and Bio-chemical properties of complexes with ligand having carbonyl
oxygen and nitrogen as potential donor to VO₂(I) Mn(II) Fe(II) Cr(III) & VO(IV) ions.

Moreover the ligands chosen in this study are such that the charge delocalized between oxygen and nitrogen atoms. This may lead in a semiquantitative way to have a better understanding of –

(i) The donor properties of nitrogen in general
(ii) Nature of metal phosphorus and metal nitrogen link
(iii) Position of ligand in spectrochemical series
(iv) Stereochemistry and coordination number of VO₂(I), Mn(II), Fe(II), Cr(III) and VO(IV) ions.
(v) Stability of octahedral complexes.
(vi) Antifungal activities of complexes.
(vii) Classification of antifungal active complexes and
(viii) Investigation of νMn-N, νV-N, νCr-N, νFe-N, νMn-Cl, νV=O frequencies in far infrared spectra.

The ligand may exist in keto-form as well as enol form (amidol system structure Ia and Ib) forming salt type compound (structure II), inner type complexes (structure III), dimmer (structure IV) or polymer (structure V).
Previous work in this field

A short survey of Isonicotanic acid hydrazide and its complexes of VO$_2$(I), Mn(II), Fe(II), Cr(III) and VO(IV) ions and their biological activities are given in the following paragraphs in order to throw light on the type of work already done in this field. Very recent, R.N. Sharma and coworkers$^{18-19}$ have reported some solid and air stable complexes of ditriazole-5,5′ disulphide (TTDS) with Mn(II), Cr(III), VO(III) and 4-amino-3-propyl-5-mercapto-5-
triazine with oxovanadium, dioxo vanadium and oxozirconium ions. All these complexes have been tested for their antimicrobial activities. Isonicotinic acid hydrazide is one of the simplest of known chemotherapeutics and it is a bactericidal agent that have very specific for certain strains of mycobacteria. Chlorine\textsuperscript{20} found that Isonicotinic acid hydrazide has similar carbon skeleton to that of nicotinamide (structure VI) which is weakly tuberculotatic.

\begin{center}
\begin{align*}
&\begin{array}{c}
\text{(Isonicotinic acid hydrazide)} \\
\text{Structure (VI)}
\end{array} \\
&\begin{array}{c}
\text{(Nicotinic amide)}
\end{array}
\end{align*}
\end{center}

The lethal action of any antibiotic must depends upon the events occurring before to the viability of the organisms exposed to the antibiotic declines and it was systematically studied by a number of workers\textsuperscript{21-31}.

Mcclatchy\textsuperscript{32} and Takayam et al\textsuperscript{33} studied the viability of mycobacterium B.C.G. and H\textsubscript{37} Ra respectively are found that Isonicotinic acid hydrazide is so effective which begins to decline these just after 60 minutes of exposure at concentration 0.05 µg/ml and 0.51 µg/ml respectively. The structural change of the bacilli
has been observed by Takayama et al\textsuperscript{34} scanning electron microscopy (SEM) after exposure to Isonicotanic acid hydrazide (0.5 µg/ml) for three hours.

The turbidity of mycobacterial cultures continues to increase after the addition of Isonicotanic acid hydrazide. The observation of Schaefer\textsuperscript{35} on tuberculosis suggest that growth continues for 1-1.5 generation after the addition of Isonicotanic acid hydrazide. Takayama et al used the high sensitive method of Keith and coworkers\textsuperscript{36} to measure the protoplasmic velocity of M. Tuberculosis H 37 Ra during incubation with Isonicotanic acid hydrazide (0.5 µg/ml). In protoplasmic velocity increased during the first 15 hours of exposure from a rotational correlation time value of $2.4 \times 10^{-10}$ sec to $3.4 \times 10^{-10}$ sec then decreased linearly to the control level over next 12 hours. These results may indicate that INTAH allows continued synthesis of protoplasmic components while lowering the rate of increase in cell volume.\textsuperscript{37}

Moreover, observation of Isonicotanic acid hydrazide sensitive strain of M. Tuberculosis readily take up leble from extra cellular \textsuperscript{14}C-INTAH and it has been assumed that the most of take up is the results of an aerobic process\textsuperscript{38-40}. The take up is inhibited by $10^{-2}$ M – $10^{-3}$ M. NaCN by other hyrazide (in order of decreasing efficiency as inhibitors: cyanoacetic acid hydrazide > benzoic acid hydrazide > p-amino benzoic acid hydrazide > m-aminobenzoic acid hydrazide > Nicotinic acid hydrazide, picolinic acid hydrazides.\textsuperscript{41-42}
Boone et al\textsuperscript{43} and Winder\textsuperscript{44} were studied the metabolic product analysis of M. Tuberculosis and INTAH interaction and found the rapid production of Isonicotanic acid and 4-pyridyl methanol\textsuperscript{45-47}. The path map has been shown in structure-VII.

\textbf{\begin{center}
\begin{tikzpicture}
\node at (0,0) (i) {\textbf{I}};
\node at (2,0) (ii) {\textbf{II}};
\node at (0,-2) (iii) {\textbf{III}};
\node at (2,-2) (iv) {\textbf{IV}};
\draw[->] (i) -- (ii);
\draw[->] (i) -- (iii);
\draw[->] (ii) -- (iv);
\draw[->] (iii) -- (iv);
\end{tikzpicture}
\end{center}}

The nature of nitrogenous products of INTAH degradation by M. Tuberculosis, other than the hydrazones is unknown. Neither ammonia nor hydrazine have detected.\textsuperscript{48}

Kruger-Thiemer\textsuperscript{49} further proposed that the Isonicotanic acid cannot leave the bacilli as rapidly as Isonicotanic acid hydrazide enters. It is due to completely ionization at intra cellular pH (pka = 4.84).
It has been observed that Isonicotanic acid hydrazide was converted to Isonicotanic acid was incorporated into analogues of NAD$^+$ and NADP$^+$. It was suggested that the analogues inhibited the cytochrome electron transport system causing on accumulation of potential electron donors. Oxidation of these compounds by Flavin enzymes would results in the over production of more Isonicotanic acid by the myobacterial peroxidase.$^{50}$

Ellard and other$^{51-52}$ have reported that hydrazine may be one of the metabolic product in mammals. It is due to mutagenic nature of hydrazine and Isonicotanic acid hydrazide has been suspected to having mutagenic properties.

Raghuwanshi et al$^{53}$ have prepared a number of 1,3-Thiazine derivatives and found that these are very microbial active against both fungal and bacterial species, would be applicable in therapeutic purpose in human disease as well as helpful in controlling plant disease providing a non-toxic to human and plant body. Desai and coworkers$^{54}$ have synthesized a number of nitrogen containing heterocyclic derivatives and these are screened for antimicrobial activity against S. Aureus, B. Subtilis, E. Coli and S. Paratyphi using agar diffusion technique. The evolution of antibacterial activity and comparison of the results against standard Ampicillin and Erythromycin are found that the compounds having chloro-substitution in meta and para position in thioureidophanyl ring exhibit maximum activity.
A. Kumar and L.K. Mishra\textsuperscript{55} have been reported the preparation and characterization of some oxomolybdenum (V) and oxo-vanadium (IV) complexes with morpholin-N-thiohydrazide and morpholin-N-thiohydrazones.

They reported the complexes [M\textsubscript{0}OCl\textsubscript{3}(LH)] displayed the magnetic moment values of 1.63-1.69 BM which fall in the range of values of shown by mononuclear oxomolybdenum (V) complexes. The oxovanadium (IV) shows the magnetic moment values between 1.43-1.79 B.M.

S.K. Roy and coworkers\textsuperscript{56} have been reported the synthesis and characterization of polynuclear oxometallates of Molybedenum, Vanadium and Silicon. They studied the two new series of triheteropolyoxometallates of M\textsubscript{0}, V & Si as 11:1:1 and 10:2:1. Infrared spectrum of sodium salt of the hydrated anion [SiV M\textsubscript{011}O\textsubscript{40}]\textsuperscript{5–} shows peak at 34575b, 1605b, 980s, 946b, 700s and 600s. Sodium salt of hydrated anion [SiV\textsubscript{2}M\textsubscript{010}O\textsubscript{40}]\textsuperscript{6–} shows peaks at 3400b, 1650m, 965s, 920b, 720s and 610s while the ammonium salt shows peaks at 3425b, 3180b, 1635m, 1405s, 960s, 925b and 605s. The broad peaks at 3400-3500 and 3150-3180 cm\textsuperscript{-1} are assignable to ν OH sym + ν OH asym and lattice water and that at 1600-1650 cm\textsuperscript{-1} are for δH-O-H bending modes of lattice water.

Vanadium (V) complexes with hydrazone based ONO and ONN donor ligands that partly model active-site structures of vanadate dependent haloperoxidases has been reported by mannar R. Maurya\textsuperscript{57}. On reaction with [VO(acac)\textsubscript{2}] (i.e. acac =
acetyl acetone) under nitrogen, these ligands generally provide oxovanadium (IV) complexes [VO(ONO)X]. (x = solvent or nothing) and [VO(acc)(ONN)] respectively. Under aerobic conditions these oxovanadium (IV) species undergo oxidation to give oxovanadium (V), dioxovanadium (V) or µ-oxobis {oxovanadium(V)} species depending upon the nature of the ligand. Anion and neutral dioxo-vanadium(V) complexes slowly deoxygenate in methanol to give monooxo complexes [VO(OMe)(MeOH)(ONO)].

The anionic complexes [VO₂(ONO)]⁻ can also be converted in situ on acidification to oxohydroxo complexes [VO(OH) (HONO)]⁺ and to peroxo complexes [VO(O₂)(ONO)] and thus to the species assumed to be intermediates in the haloperoxidases activity of the enzymes. In the presence of catechol (H₂Ca⁺) and benzohydroxamic acid (H₂bha), oxovanadium (IV) complexes, [VO(acac)(ONN)] gave mixed chelate oxovanadium (V) complexes [VO(cat)(ONN) and VO(bha)(ONN)] respectively. These complexes are not very stable in solution and slowly convert to the corresponding dioxo species [VO₂(ONN) as observed by ⁵¹V NMR and electronic absorption spectroscopic studies.

Recent interest in vanadium complexes stems from their potential therapeutic⁵⁸-⁶⁰ and catalytic application⁶¹-⁶². Modelling the structure and properties of vanadium-containing molecules have also influenced research on vanadium chemistry. Vanadate dependent haloperoxidase enzymes eg. Ascophyllum nodosum
(isolated from brown alga)\textsuperscript{63}, coralline officinalis (from red alga)\textsuperscript{64} and Curvularia inaequalis (from fungi)\textsuperscript{65} have been structurally characterized and all of these show a high degree of amino acid homology in their active centres and thus have almost identical active site structures for Ascophyllum nodosum.

Preparation of sodium, ammonium and Guanidium salts of the anion of the type $[\text{ZyV}_{11}\text{O}_{36}]^{9-}$, (where $z = \text{Co, Ni}$, $Y = \text{Te}$) by Sinha and coworkers\textsuperscript{66}. The metal constituents were estimated by standard gravimetric methods and the results were corroborate by inductively coupled plasma atomic emission spectroscopy, calorimetry and atomic adsorption spectra.

Taylor et al\textsuperscript{67} reported that the reaction of $[\text{V}_{2}\mu - \text{S}_{2}]_{2}(\text{S}_{2}\text{CN R}_{2})_{4}$ (where $R = \text{Et, iPr, iBu}$) with NOBF$_4$ produce highly oxidized S-rich, V(IV/V) complexes $[\text{V}_{2}\mu - \text{S}_{2}]_{2} \text{S}_{2}(\text{NR}_{2})_{4}]$ BF$_4$ that exhibit 15-line EPR spectra and structures consistent with class III mixed-valence behavior.

A vanadium (V) cerium (IV) trinuclear complexes $[\{\text{VO}_{2}(\text{L})_{2}\text{Ce}\}]$ (L, $\text{H}_{3}\text{L}$: N-N’-bis (3-Ethoxy salicylidene)-2-hydroxy-1,3-propane diamine) was prepared by the reaction of $[\text{VIVO(acac)}_{2}]$ and $[\text{CeIII(acac}_{3}]$.3H$_2$O with $\text{H}_{3}\text{L}$ in CH$_3$CN followed by oxidation of the product in air this work had been done by Tsuchimoto et al\textsuperscript{68}.

Singh\textsuperscript{69} has been worked on the tridentate amino acid viz. aspartic acid and glutamic acid with VO$^{2+}$ ion in 1:1 molar ratio in
aqueous solution ion, amino acid and imidazole in 1:1:1 molar ratio in aqueous solution yields [VO(aspa'/gluta) ImH] (monomer). In addition to synthesis, he reports the magnetic IR, EPR and optical absorption data to these compounds. [VO(aspa gluta)H₂O] exhibit a band in the range 3400-3100 cm⁻¹ which is assigned to the ν(OH) of coordinated water molecule the compounds are [VO(Aspa)H₂O], [VO(Aspa)(ImH)], [VO(Gluta) H₂O] and [VO(Gluta)(ImH)].

Nelson and coworker⁷⁰ have been reported the reaction of [V₃⁺(CN)₆]·4MeCN and studied their structure by using X-ray crystallography. The reaction of (NEt₄)₄[V₃⁺(CN)₆] 4MeCN with [Cr₃⁺(NCMe)₄(BF₄)] occurs in via internal electro transfer and form Cr₃⁺₀.₅Cr₃⁺ [V₃⁺(CN)₆].2.MeCN whose structure and magnetic properties are dependent on the degree of salvation.

Pavani et al.⁷¹ were described two new fully oxidized polyoxovanadium cluster-based solids (C₄N₂S₂H₁₄)₂ (H₂V₁₀O₂₈). 4H₂O and (C₄N₂S₂H₁₄)₅ [H₄V₁₅O₄₂].10H₂O. These are crystallized under self assembly process in the presence of cysteamine. In above both compounds cysteamines are oxidized forming disulphide linkage and occur as counter cations. The organic cations assemble around V₁₀O₂₈ cluster anions in complex (C₄N₂S₂H₁₄)₂ [H₂V₁₀O₂₈]. 4H₂O whereas they aggregate around V₁₅O₄₂ cluster (C₄N₂S₂H₁₄)₅ [H₄V₁₅O₄₂]₂. 10H₂O. pH appears to be structure determinant in occurrence of decavanadate cluster in first and pentadecavanadate in second complex with the same counter cation.
The crystal structure\textsuperscript{72} of \((C_4N_2S_2H_{14})_2\ [H_2V_{10}O_{28}].4H_2O\) reveals the presence of a discrete cluster anion \([H_2V_{10}O_{28}]\) and the crystal structure of \((C_4N_2S_2H_{14})_5[H_4V_{15}O_{42}]_2.10H_2O\) reveals the presence of a discrete molecular anion \(V_{15}O_{46}^{6-}\) cluster that has a central cavity encapsulating an almost regular \(VO_4\) tetrahedron.\textsuperscript{73}

Verma et al.\textsuperscript{74} have reported the preparation and characterization of oxovanadium(IV) oxomolybdenenum(V) and manganese(II) complexes of Schiff bases derived from condensation of 5-methyl salicylaldehyde, 5-bromosalicylaldehyde, 3-methyl salicylaldehyde with thio-semicarbazide. The complexes have been characterized by IR electronic spectra, ESR spectra, TGA, molar conductance and magnetic moment. These studies indicate octahedral geometry around the metal ion complexes were also screen for biological activities. All the oxovanadium (IV) complexes and oxomolybdenenum 1.62-1.73 and for manganese (II) complexes shows in the range of 5.76 to 5.92 BM.

Awadallah et al\textsuperscript{75} have reported the conductometric and spectrophotometric studies of V(V), Nb(V) and Ta(V) complexes with Erichrome Cyanine (ECR) and Methylene blue (MB). The determination of their composition \(K_f; \Delta G^\circ, \Delta H, \Delta S\) and in analytical chemistry for the microdetermination of the elements. Effect of pH on the absorption spectra of complexes, effect of time and temperature of the stability of metal chelates were also studied.
Vanadium, Niobium and Tantalum form complexes at pH = 8.0 (\(\lambda = 660 \text{ nm}\)) 3 (\(\lambda = 665 \text{ nm}\)) and 7 (\(\lambda = 670 \text{ nm}\)) with methylene blue at 3.5 (\(\lambda = 540 \text{ nm}\)) 4.53 (\(\lambda = 520 \text{ nm}\)) and 4.5 (\(\lambda = 520 \text{ nm}\)) with ECR for V(V) Nb(V) and Ta(V) complexes. The complexes reach maximum development immediately and at 60° in the case of V(V) M.B. immediately and at 50° in the case of Nb(V)-M.B., immediately and at 80° in the case of Ta(V) M.B. after 30 minutes and at 30° in the case of Ta(V) ECR complexes.

Equimolar interaction of VO(OPr\(^i\))\(_3\) with N-Phenyldiethanolamine (H\(_2\)L) affords the dimeric complexes [VO(L)(\(\mu-\text{OPr}^i\))]\(_2\) has been reported by Rajendra S. Ghadwal et al\(^{76}\) which on reaction with different glycols yields a new class of oxovanadium (V) complexes of the type: [VO(L)(O\(\text{G}^\theta\)OH)] (where L = C\(_6\)H\(_5\)N(CH\(_2\)CH\(_2\)O)\(_2\) and \(\text{G} = \text{G}^1\) (C Me\(_2\)CH\(_2\)CH\(_2\)C.Me\(_2\)), \(\text{G}^2\) (CHMeCHMe\(_2\)), \(\text{G}^3\) (CH\(_2\)C.Me\(_2\)CH\(_2\)), \(\text{G}^4\) (CH\(_2\)CEt\(_2\)CH\(_2\)), \(\text{G}^5\) (CHMeCHMe) and \(\text{G}^6\) (CMe\(_2\)CMe\(_2\)), featuring N-phenyldiethanolaminate and glycolate moieties. Complexes from \(\text{G}^1 - \text{G}^6\) react will Al(OPr\(^i\))\(_3\) to afford novel heterobimetallic coordination complexes of the type: VO(L) \{O\(\text{G}^\theta\)Al(OPr\(^i\))\(_2\}\} (\(\text{G} = \text{G}^1 - \text{G}^6\)).

All these complexes have been characterized by elemental analysis and molecular weight measurements. Spectroscopic (IR, UV-vis) and (\(^1\)H, \(^{27}\)Al, \(^{51}\)V, NMR) properties of the new complexes have been investigated and their plausible structures suggested.

\(^{51}\)V NMR spectra of the complexes [VO(L)(O\(\text{G}^\theta\)OH)], [VO(L)(O\(\text{G}^2\)OH)], [VO(L)(O\(\text{G}^3\)OH)], [VO(L)(O\(\text{G}^4\)H)], [VO(L)
(OG₅H)], [VO(L)(OG₆H)], [VO(L){OG₅O}Al(OPrᵢ)₂], [VO(L) {OG₂O} Al(OPrᵢ)₂]], [VO(L){(OG₃O)Al(OPrᵢ)₂}], [VO(L) {OG₄O}Al (OPrᵢ)₂]], [VO(L){(OG₅O)Al(OPrᵢ)₂}] and [VO(L){(OG₆O)Al(OPrᵢ)₂}] exhibit sharp signals at f-544 ± 16 ppm, consistent with vanadium in six-coordinate⁷⁷-⁸⁰ environment. All NMR spectra last. Six complexes show broad (w ½ = 160 ± 20 Hz) signals at δ50.76 ± 3.55 ppm consistent with four coordinate⁸¹-⁸² aluminium complexes.

A contribution to development of novel vanadium complexes with pharmacologically interesting properties, two neutral dioxovanadium(V) complexes (VO₂(Hpydx – Sbdt]) and [VO₂(Hpydx – Smdt)] recently reported by Mannar R. Maurya and coworkers⁸³ (H₂ Pydx – Sbdt) and [H₂Pydx – Smdt] are the Schiff based derived from pyridoxal and S-benzyl or S-methyl dithiocarbazate) have been synthesized by the reaction of [VO(acac)] and the potassium salts of the ligands in methanol followed by aerial oxidation.

Heating of the methanolic solutions of the complexes yields the oxobridge binuclear complexes [(VO(Pydx – Sbdt)]₂ µ – O] and [(Vo(Pydx – Smdt)]₂. In vitro antimoebic activity (against HM – 1:1 MSS strain) of Entamoeba histolytica) were established for all of the dioxo and oxovanadium(V) complexes. All above complexes were more effective than metronidazole, a commonly used drug against amoebiasis, suggesting that oxovanadium(V) complexes derived from thiohyrazones may open a new dimension in therapy of amoebiasis.
Laurent Lishard et al\textsuperscript{84} have been reported the hydrothermal reaction of Na\textsubscript{2}WO\textsubscript{4}, VOSO\textsubscript{4}, 2,2'-bpy and H\textsubscript{3}PO\textsubscript{4} has afforded in high yield the compound [V\textsuperscript{2IV} V\textsubscript{6}VO\textsubscript{14} (bpy)\textsubscript{8} (PO\textsubscript{4})\textsubscript{2}] and (PW\textsubscript{11}V\textsuperscript{V} O\textsubscript{40}] (bpy).\textsubscript{12}H\textsubscript{2}O. thermodiffractometry experiments indicate that the second instable upto 360°C. The magnetic measurements performed on first has shown the occurrence of weak ferromagnetic interactions between V(IV) centers (J = 0.34 cm\textsuperscript{-1}, H\textsubscript{ex} = -JS\textsubscript{1}) and combined DFT calculations have allowed to propose a localization of the two V(IV) centre on two of the four equivalent crystallographic sites. Finally high field electron paramagnetic resonance has evidenced the magnetic axial anisotropic of the paramagnetic centre (g\textsubscript{x} = g\textsubscript{y} = 1.975, g\textsubscript{z} = 1.939).

Kwiat Kowski and coworkers\textsuperscript{85} have been prepared the ten new dioxovanadium(V) complexes incorporating Schiff bases derived from (S) – (+) – 2 – (aminoethyl) pyrrolidone and arom-o-hydroxy carbonyl compounds were synthesized and studied by spectroscopic methods. The x-ray experiment on N-(methyl salicylidene)-(S)-(2-pyrollidinyl methyl amine) dioxovanadium(V) monohydrate shows that the crystal of that compound is a solid solution of two diastereomers, which differ in conformation of five membered rings and in absolute configuration of the chiral center containing the asymmetrical C-atom.

The weak predominance in content of S-diastereomer over R. distereomer in the crystal (55:45) increases strong in DMSO solution (75:25) as evidenced by \textsuperscript{1}H and \textsuperscript{51}V NMR studies
indicating that the crystals induces the asymmetrical transformation of S-diastereomer. The free energy of transformation of S. diastereomer into its R. analog in DMSO solution in particularly low for complexes containing ethylidene substituent attached to the aromatic ring.

The studies of the oxidation of the cyclohexanone by vanadium(V) in sulphuric acid medium is catalysed marginally in presence of CTAB and NDPC reaches a maximum and the decreases. The oxidation rate (micelle) profile in rationalized by Berzein model and binding constants of both the reactants with the micelle have been computed using the model. The data also fit into Piszkieiewiez model. The study of above analysis has been reported by Panda and Panigrahi.86

Grandhi et al87 have studied on the complexation equilibria of succinyl sulphathiazole (SSIZ) with proton and different metals VO(II), VO₂(II), Cu(II), Ni(II) and Mn(II) ions in aqueous DMF and aqueous DMF 50 mixture at 25±0.1°C and 0.15M ionic strength using potentiometric technique.

Jejurkar et al88 have reported the synthesis and characterization of Schiff base on complexes of Cu(II), Ni(II). The isolated ligand and metal complexes are characterized by elementals analysis reflectance and IR spectral studies. The Schiff base ligands and their metal complexes were tested for their antibacterial behavior using E. coli as a tested organism. Uranium and vanadium complexes were found to be excellent antibacterial
agents. The analytical data shows that the composition of the complex is $ML_2(H_2O)_2$. (where $M = Cu(II)$, $Ni(II)$) complexes show recognizable spectral bands at $Ca\ 16200\ cm^{-1}$ and $Ca\ 26000\ cm^{-1}$. The broad band (unasymmetrical) at $Ca-16200\ cm$ may be due to $3E_g \rightarrow 3T_{2g}$ transitions in octahedral geometry at the band at $26000\ cm^{-1}$ may be due to ligand metal charge transfer. The magnetic measurements for $Cu(II)$ complexes are 1.6-1.9 BM which suggest an octahedral geometry for $Cu(II)$ complexes.

Reflectance spectra of vanadium(IV) shows three bands at $12050cm^{-1}$, $15380cm^{-1}$ and $17860cm^{-1}$ which can be assigned to the following d-d-transitions, $d_{xy} \rightarrow d_{xz}, d_{yz} \rightarrow d_{xy} \rightarrow dx^2 - y^2$ and $d_{xy} - dz^2$ while the bad appearing at $Ca\ 25580\ cm^{-1}$ is assigned susceptibility of range 1.68 BM to 1.89 BM.

Lakshman Singh and coworker have synthesized a series of six complexes of general composition $(VOX_2.n(INH - NaPh)]$. (where $NaPh = N = Isonicotinamide-2-hydraxyl-1-Naphthali-dimine). The complexes were characterized through elemental analysis, conductance, molecular weight, magnetic moment, IR and electronic spectral data. The IR data of the complexes indicate the bidentate nature (N,O) of these complexes. T-G-A of the complexes were also studied.

In the IR spectra of the complexes a considerable negative shift in $\nu\ C = O$ in observed indicating a decrease in the stretching force constant of the $C = O$ band as a consequences of coordination through the carbonyl oxygen atom of the free base. The VO(II)
complexes show two bands in 13300 – 17500 cm\(^{-1}\) regions. These bands are not well developed. In some complexes a weak but well developed band in 22600 – 23000 cm\(^{-1}\) region has also been observed.

The highly selective catalytic spectrophotometric method for vanadium(V) have been reported by Pourreza et al\(^{90}\). The method is based on the catalytic effect of Vanadium(V) on calmagnetc bromate redox reaction, which is followed spectropotometrically by measuring the change in absorbance of calmagite at \(\lambda = 523\)nm using a fixed time method (5 min) under optimum condition. Vanadium can be determined in the range of 2-10 mg mol\(^{-1}\). The method was applied for the determination of vanadium in soil samples.

Recently Tapas Ghosh\(^{91}\) have been reported the mixed ligand oxovanadium (IV) complexes with N-Benzene sulphonyl L. Aspartic acid (H\(_3\)L) in the presence of 2,2' bipyridine or 1,10-phenanthroline (B) on reaction with VOSO\(_4\) in aqueous ethanolic medium at pH \(\sim 4.5\) afforded complexes of the type [V\(^{IV}\)O(HL)(B) (H\(_2\)O)]H\(_3\)L act as a bidentate dinegative ligand and coordinates the metal through the one deprotonated carboxylate-o- and deprotonated amide-N leaving the other carboxylic acid group free. The complexes have been characterized by elemental analysis magnetic susceptibility measurements and by IR & UV – spectroscopic techniques. The complexes are one electron paramagnetic (\(\mu_{\text{eff}} \approx 1.73\) BM) at room temperature v V = O
stretching frequencies indicated the hexa coordinated environment around the metal center. They exhibit two ligand field transition in the visible region.

P. Muralidhar Reddy et al. have been reported the synthesis characterization and electrochemical studied of some oxovanadium(IV) and vanadium(IV) complexes with carboxylamide ligand of (2z) – 4 – (2-acetyl hydrazine)-4-oxo.2- enoic acid (AOBEH), 4-(2-acetyl hydrazine-4-oxobutanoic acid (AOBAH), 2-(2-acetyl hydrazine carbonyl) benzoic acid (AHCBH), (2z)-4-(2-cyanophenyl amino)-4-oxobut-2-enoic acid (COBEH), 2-(2-Cyanophenyl) amino carbonyl benzoic acid (CACBH), (2z)-4-(1H.benzimidazol-2-glamino)-4-oxobut-2-enoic acid (BOBEH) and 4-(1H-benzimidazole-2-yl.amino)-4-oxo-butanoic acid (BOAH) and 2-(1-H benzimidazole-2-glamino) carbonyl benzoic acid (BY CBH) have been prepared and characterized by electronic NMR, ESR, spectra and thermal studies. The magnetic moment and electronic spectral studies suggests square pyramidal geometry to all the oxovanadium(IV) complexes and distorted geometry to the vanadium(IV) complexes with O₄ and Cl₂O₄ as donor sets from the ligands.

Chullikattil et al. have been reported that the chiral Schiff base ligand H₂L, prepared by the condensation of L. Phenylalaninol and 5-bromosalicyladehyde with Mn-II (CH₃COO)₂.4H₂O yielded dark brown complex (MnIVL₂)₀.5 DMF. It was characterized by elemental analysis, IR UV-visible, CD and
EPR spectroscopy, cyclic volumetry and room temperature magnetic moment determination. Single crystal x-ray analysis revealed that [MnIVL2]0.5 DMF crystallizes in the monoclinic P21 space group and six three solvent DMF molecules. In the crystal structure, each Mn(IV) complex, acting as the building unit undergoes supramolecular linking through C-H-....O bonds leading to an indicate hydrogen bonding network.

Higher valented manganese [Mn(IV)] is important in various biological system like the OECC oxygen evolving complex) of photosystem-II. In addition to their biological roles, Mn(IV) systems are also important with respect to asymmetrical catalysts. The role of Chiral Mn(IV) species in the catalytic asymmetric epoxidation of olefins has been the subject of some current publications. Tridentate ligands derived from substituted salicylaldehyde and chiral amino alcohols are among the “Priviledged” ligand templates, generally employed for various asymmetric transformation complexes of these ligand systems with metal ions such as Ti4+, V5+, Cu2+ etc have been successfully applied for various asymmetric transformations as chiral catalysis.

The IR spectrum of the Schiff base ligand, H2L exhibits a broad band at 3364 cm⁻¹ due to the intramolecularly hydrogen bonded ν OH. This band is absent in the complex revealing the deprotonation of the OH-group during complexation. Also the Schiff base exhibits ν C≡N band at 1633 cm⁻¹, which sifts to lower
energy ~20 cm\(^{-1}\) in the complex indicating nitrogen coordination of the ligand.

The synthesis and characterization of Cu(II), Co(II) and Mn(II) complexes of 2-(2'-hydroxy napthylazo)-5-benzoyl-benzimidazole have been reported by T. Chandrika Devi and coworkers\(^{101}\). Seven complexes of Cu(II) with the ligand-2-(2'-Hydroxynaphthylazo)-5-benzoyl benzimidazole (NABBI) with composition \([\text{Cu(NABBI)}_2X_2]\), where \(X = \text{Cl}^-, \text{Br}^-, \text{NO}_2^-, \text{ClO}_4^-, \text{CH}_3\text{COO}^-, \text{HCOO}^-\) or 1/2 \(\text{SO}_4^{2-}\) and nine complexes each of Co(II) and Mn(II) have been synthesized and characterized. The systematic analysis such as cation, anion estimation, elemental analysis, molar conductance, magnetic susceptibility and IR, UV-spectral studies have been confirmed the identity of the ligands and the distorted octahedral geometry of the complexes. Complexes for Mn(II) such as \([\text{Mn(NABBI)}_2\text{Cl}_2]\), \([\text{Mn(NABBI)}_2\text{Br}_2]\), \([\text{Mn(NABBI)}_2\text{I}_2]\), \([\text{Mn(NABBI)}_2\text{(NCS)}_2]\), \([\text{Mn(NABBI)}_2\text{(SO}_4^2\text{)}]\), \([\text{Mn(NABBI)}_2\text{(ClO}_4^-)_2]\), \([\text{Mn(NABBI)}_2\text{ac}_2]\), \([\text{Mn(NABBI)}_2\text{(NO}_3^-)_2]\) and \([\text{Mn(NABBI)}_2\text{(HCOO)}_2]\).

Hussan key pour and coworker\(^{102}\) have been prepared the two new Schiff bases macrocyclic complexes of \([\text{MnL(H}_2\text{O)}\text{Cl}_2\cdot\text{H}_2\text{O}\)] and \([\text{MnL}_2\text{(H}_2\text{O)}\text{Cl}_2]\) via cyclocondensation of 2,6-diacetyl pyridine and N,N' – bis - (2 - aminophenyl) 1, 3 - propandiamine respectively and have been characterized spectroscopically. The ligands are 16 and 17-membered pentaazamacrocycles. Macrocyclic complexes of Mn(II) are known
to exhibit as the active site of some manganese containing enzyme (e.g. SOD). The manganese ion in the biosite have the ability to catalyse the disproportionation of $\text{H}_2\text{O}_2$ to dioxygen and $\text{H}_2\text{O}$. Mn(II) also important for $\text{O}_2$ evolution mechanism in the photosynthesis process.

The synthesis and structural characterization of three dicyanamide complexes with Mn(II), Zn(II) and Cd(II) supramolecular architectures established of hydrogen bonding has been described by A. Majumdar$^{103}$. The three new cyanamido $[\text{N(CH}_2\text{)}_2]$ (dca) compounds of the formula $[\text{Mn(ac)(tptz)(dca)}(\text{H}_2\text{O})](\text{H}_2\text{O})_2$, $[\text{Zn(tptz)(dca)}_2].(\text{H}_2\text{O})_2$ and $[\text{Cd}_2(\text{tptz})_2(\text{dca})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (where as ac = acetate anion and tptz = 2.46 – tris-(2-pyridyl)1,3,5-triazine) have been synthesized. X-ray diffraction analysis revealed that the manganese atom is seven coordination with a pentagonal bipyramidal environment, Zn(II) square pyramidal and Cd(II) octahedral.

M. Shakir and coworkers$^{104}$ have reported the synthesis and physiochemical studies on the coordinating behaviour of chlorosulphate ion in metal tris (chlorosulphates) $[\text{M(SO}_3\text{Cl)}_3]$, (where M = Cr, Mn and Fe) and their complexes.

A number of reports on the industrial uses of chlorosulphuric acid where HSO$_3$Cl has been used as sulphating agent for various aliphatic as well as aromatic organic comounds$^{105}$ e.g. the preparation of (sulphatoalkyl)-sulphonium salts which are used as bactericides and as intermediates for textile auxiliaries, the
synthesis of cation exchange regions and anion-exchange membranes by sulphato cross linking of linear polystyrene, eliminating the use of divinyl benzene as cross-linking agent,\textsuperscript{106-107} the plating of plastic materials\textsuperscript{108} and as catalyst for esterification, acetylation of some carbohydrates\textsuperscript{109} and alkylation of aromatics\textsuperscript{110} the chloro-sulphonating ability of this system is used for the synthesis of a variety of chlorosulphates\textsuperscript{111-112}, oxychlorosulphate\textsuperscript{113} and mixed metal chlorosulphates\textsuperscript{114}. Therefore a few transition metal tris (chlorosulphates) M(SO$_3$Cl)$_3$ (M = Cr, Mn & Fe) and their complexes with well known strong donor bases such as methyl cyanide, pyridine acridine, 2,2’-bipyridine and triphenyl phosphine in order to examine the synthetic used of the SO$_3$Cl– moiety. Stereo chemistry and possible use as corrosion inhibitor.

The electronic spectra of Cr(SO$_3$Cl)$_3$ exhibit two bands at 16,250 cm$^{-1}$ and 23,470 cm$^{-1}$ assignable to $^4T_{2g}(F) \leftarrow ^4A_{2g}(g)$ and $^4T_{1g}(F) \leftarrow ^4A_{2g}(F)$ transitions, respectively, in confirmation with an octahedral array around the Cr$^{+3}$ ions\textsuperscript{115-116}. The existence of a weak broad ligand field band at 20,720 cm$^{-1}$ which may assignable to the $^5T_{2g} \leftarrow ^5E_g$ transition, characteristic of an octahedral environment around the metal ion in Mn(SO$_3$Cl)$_3$\textsuperscript{117-118} However the electronic spectra of Fe(SO$_3$Cl)$_3$ exhibit two bands at 12,175 and 27,025 cm$^{-1}$ which may be assigned to $^4T_{1g}(G) \leftarrow ^6A_{1g}$ and $^4T_{2g}(D) \leftarrow ^6A_{1g}$ transitions, respectively. Suggesting an octahedral environment around the Iron(III) ion\textsuperscript{119-120}
Hong-Chang Yao et al\textsuperscript{121} have reported that the [Mn(O\textsubscript{2}Cr)\textsubscript{2}], (R = Me, Ph) with Na4.4MnO\textsubscript{4} in CH\textsubscript{3}CN or CH\textsubscript{3}CN/CH\textsubscript{2}Cl\textsubscript{2} in the presence of acetic acid. δ-cyclohexane phosphonic acid (C\textsubscript{6}H\textsubscript{9}PO\textsubscript{3}H\textsubscript{2}) and 2,2'-bipyridine or 1,10-phenanthroline result in three novel dodecamanganese (III) clusters [Mn\textsubscript{12}O\textsubscript{8}(O\textsubscript{2}CMe)\textsubscript{6} (O\textsubscript{3}P.C\textsubscript{6}H\textsubscript{5})\textsubscript{7} (bipy)\textsubscript{3}], [Mn\textsubscript{12}O\textsubscript{8}(O\textsubscript{2}CPh)\textsubscript{6} (O\textsubscript{3}PC\textsubscript{6}H\textsubscript{9})\textsubscript{7} (bipy)]\textsubscript{2} and [Mn\textsubscript{12}O\textsubscript{8}(O\textsubscript{2}CPh)\textsubscript{6}(O\textsubscript{3}PC\textsubscript{6}H\textsubscript{9})\textsubscript{7}(phen)\textsubscript{3}].

The protonation constant of an unsymmetrical Schiff base salicylidine (N-benzoyl) glycyl hydrazole (Sal. B\textsubscript{2}G\textsubscript{H}) and formation constant of its complexes have been described by R.K. Lonibala and coworkers\textsuperscript{122} through potentiometrically at different temperature in aqueous dioxan medium. Complexes of (Sal BzGH) with VO(IV), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been prepared.

Namboori et al\textsuperscript{123} have been reported about synthesis and characterization of Iron(III) Manganese(III) and chromium(III) complexes with N,N-ethylene-bis-(3-carboxy propenamide) and various anions such as Cl\textsuperscript{-}, Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SCN\textsuperscript{-}, HClO\textsubscript{4}\textsuperscript{-} (perchlorate) and CH\textsubscript{3}COO\textsuperscript{-}. The analysis data include elemental analysis, molecular weight determinations, molar conductance magnetic moment, infrared spectra and x-ray diffraction.

Electronic spectra of chromium(III) shows bands at around 33,170 and 26,660 cm\textsuperscript{-1}, which are due to charge transfer. The \textsuperscript{4}A\textsubscript{2g} \rightarrow \textsuperscript{4}T\textsubscript{1g} transition most probably observed by transition band at 26,660 cm\textsuperscript{-1}. The weak bands with maxima appearing at 21,670 cm\textsuperscript{-1}.
and at 15,500 cm\(^{-1}\) for the chloro complex are assigned to the \(^4A_{2g} \rightarrow ^4T_{1g}(F)\) transition. Electronic spectra of Fe(III) and Mn(III) complexes bands with maxima at 33,330 cm\(^{-1}\) and around 27,700 cm\(^{-1}\) which due to charge transfer transition.

A mixed ligand complexes of chromium(III) with salicylaldehyde thiosemicarbazone oxime and nitrogen, oxygen or sulphur donor ligands have been reported by Sarbeshwar Mishra and coworkers\(^{124}\). They reported the electronic spectra of the complexes exhibit two bands in the region 18500-19200 and 23200-23400 cm\(^{-1}\). These can be assigned to \(^4A_{2g} \rightarrow ^4T_{2g}\) and \(^4A_{1g} \rightarrow ^4T_{1g}\) transitions respectively. Which are typical of octahedral coordination. At room temperature (298 K) magnetic moment values around 379-385 BM for these complexes suggest their spin free nature.

Anandan & coworkers\(^{124}\) have been reported the synthesis and characterization of same oxochromium(V) complexes using diethyl thiocarbamate (det) 4-motholiny dithio carbamate (morpdtc) and piperidinyl dithiocarbamate (pipdtc) as ligands. They have been reported the IR spectra of complexes exhibit a strong band in the range 990-1020 cm\(^{-1}\) indicting the presence of Cr = 0 stretching.

Catvel and coworkers\(^{126}\) have studie on segmental bidentate, tridentate- bidentate ligand both reacts with M" (M = Cr,Zn) and Ln" (Ln = La, Eu, Gd, Tb and Lu) to give the heterotricyclic triple standard helicates \([ML_n(M)(L_2)_3]^{7+}\) for \(M = Z^{n-}\). The isolated
complexes \([\text{ZnLnZn}L_3] \text{CF}_3\text{SO}_3_7 \) \((\text{Ln} = \text{Eu} \& \text{Tb})\) display only lanthanide centred luminescence arising from the pseudotricapped, trigonal prismatic \(\text{LnN}_9\) coordination site.

For \(M = \text{Cr}^{\text{II}}\) rapid air oxidation provides \(\text{Cr}^{\text{III}}\) and leads to the isolation of inert \([\text{Cr. Ln. Cr}L_3] \text{CF}_3\text{SO}_3_9 \) \((\text{Ln} = \text{Eu} \& \text{Tb})\) complexes in with divergent intramolecular \(\text{Ln} \rightarrow \text{Cr}\) energy transfer can be evidenced.

The elemental analysis, magnetic susceptibility measurement, IR electronic spectral data and thermal analysis of the products of the reaction of tetrasodium calix(4) arenesulphonate (TSCS) with \(\text{M(III)}\) nitrates \((\text{M} = \text{Cr, Co} \& \text{Fe})\) reveal that this reaction provides the metal aquo complexes \([\text{Cr(H}_2\text{O)}_6 \text{Na(TSCS)}_1 \text{10.5 H}_2\text{O}]\) \([\text{CO(H}_2\text{O)}_6 \text{Na} \text{[TSCS]}_7.5 \text{H}_2\text{O and [Fe(H}_2\text{O)}_6 \text{(Na) (TSCS)}_1 \text{10H}_2\text{O have been studied by H. Mohindra Chawala et al.}^{127}\)

R.C. Maurya and coworkers\(^{128}\) have studied on the synthesis and characterization of some mixed cyanonitrosyl \([\text{Cr NO}]^{3-}\) complexes of chromium (I) with 2-(2’-pyridyl) benzimidazole and related ligands. The electronic spectra of the complexes displays peaks at 705, 425, 345, 240 and 205 nm assigned to \(6e \rightarrow 2b_2 \ 6e \rightarrow 7e, \ 2b_2 \rightarrow 3b, \ 5e \rightarrow 2b_2\) and \(2b_2 \rightarrow 8e\) respectively. The strong bands at 1705, and 2140 \(\text{cm}^{-1}\) are assigned to \(\nu \text{ NO}^+\) and \(\nu \text{ CN}\) respectively. The \(\nu \text{ NH}\) band \((3300 \text{ cm}^{-1})\) of the free ligand remains unchanged in the spectrum of the complex. This suggests that the
NH-nitrogen of the imidazoline nuclear is not involved in bonding with chromium.

The $\nu \text{C}=\text{N}$ band of the imidazoline ring is observed at 1665 cm$^{-1}$ which is shifted to lower frequency at 1630 cm$^{-1}$ in the complex.

The synthesis and characterization of ten new mixed ligand complexes of titanium(III) and chromium(III) with phthalimide and amino acids (L-alanine, L-phenyl alanine, L = laucine tyrosine and L-proline), their spectra of present complexes shows $\nu \text{C}=\text{O}$ mode at $\sim$1700 cm$^{-1}$ compared to $\sim$1735 cm$^{-1}$ in free phthalimide. This have studied by Saidu et al.\textsuperscript{129} This decrease in frequency may be due to the mass effect. The observed $\nu \text{C}=\text{N}$ mode of free phthalimide at 1310 cm$^{-1}$ is shifted $\sim$1350 cm$^{-1}$ in the spectra of the complexes, suggesting there by N-formation and coordination the complexes sowe strong bands at 3120-3200 cm$^{-1}$ (NH$_2$) and 1560-1590 cm$^{-1}$ (C=O) indicating the coordination of amino acids through N- and O-donors. The complexes also show bands $\sim$1620 and $\sim$1390 cm$^{-1}$ due to $\delta \text{NH}_2$ and $\nu \text{C}=\text{O}$ mode. Chromium complexes have effective magnetic moment in the range of 3.69 – 3.95 B.M. corresponding to three unpaired electrons, constituent with octahedral stereochemistry.

A mechanistic studied on the bridge cleavage reaction of the dinuclear ethylene diguanide complexes of Ru(III), Co(III), Cr(III) and Rh(III) ions in acidic medium have been done by Chakarvorty et al.\textsuperscript{130}
Lec and coworkers\textsuperscript{131} have worked on the CrN layers of high crystal quality which are obtained at a low growth temperature of 500°C. X-ray diffraction studies indicate that the CrN layers grow along the $<111>$ direction with a cubic structure.

Cotton F. Albert\textsuperscript{132} has studied the preparation, structure bond length and properties of dichromium complexes containing metal multiple bonds between pairs of metals, such as dichromium tetraarboxylates and other paddle wheel complexes are present.

At “off-on” fluorescence chemosensor for the selective signaling of Cr(III) was designed exploiting the guest-induced inhibitors of photo-induced electron transfer signaling mechanism. It was reported by Sarkar et al.\textsuperscript{133}, the system shows 17-fold-selective chelation-enhanced fluorescence response in THF, the system is highly selective against the background of environmentally and boil eleveant metal ion.

Kar Tapas and coworkers\textsuperscript{134} have worked on a new octahedral chromium(III) complexes having-2,2'-bipyridine as a ligand system. Cis-$\text{[Cr(2,2'-bipy)_2(Cl)_{0.38}(PF_6)_{0.62}]$ was synthesized in methanol. Single crystal X-ray diffraction and shows that it possesses non-stoichiometry in its anionic primary covalency.\textsuperscript{134}

The reaction of sulphur(IV) with complex ions of chromium manganese, iron and cobalt(III) in aqueous medium have studied by A.C. Das et al.\textsuperscript{135}. Cr$^{\text{III}}$ from O-sulphito complexes while Mn$^{\text{III}}$ and Fe$^{\text{III}}$ forms S. bounded sulphito species. The oxygen bonded
sulphito species of Co$^{III}$ are transient intermediate which undergo sulphito ligand linkage isomerization and pacile redox reactionis. The ligand control on the kinetics of reversible substitution of S$^{IV}$ at Cr$^{III}$, Mn$^{III}$, Fe$^{III}$ and Co$^{III}$.

Mohanti and coworker$^{136}$ have worked on the synthetic and mechanistic aspects of the chemistry of complexes Cr(VI) compound. They reported that the oxidation of organic compounds is an important transformation in synthetic organic chemistry. The reaction of [Cr(H$_2$O)$_6$]$^{3+}$ with L-ornithine in acidic medium. The anionic reaction of L-ornithine (H$_3$L$^{2+}$) with Cr(III) has been studied by Mohanty et al.$^{137}$ over the range $3.0 \leq \text{pH} \leq 3.5; 40^\circ \leq 55^\circ$ and $0.025^\circ \leq \text{CH}_3L^{2+} \leq 0.2, I = 1.0 \text{ mol dm}^{-3}$ (KNO$_3$).

Biswas et al.$^{138}$ have studied on the new route to the synthesis of bis[N-(2-amino ethyl) salicylaldiminato] chromium (III) chloride monohydrate. The reaction of [Cr(Urea)$_6$]Cl$_3$.3H$_2$O with H$_2$ salen i.e. N-N'-ethyl bis (salicyladimine) in water-MeOH mixture (40:60 vol.) under reflux yielded-bis[$\mu$-(2-amino ethyl salicylaldiminato) chromium(III) chloride monohydrate [Cr(ae saldmn)].Cl.H$_2$O.

H.L. Nigam$^{139}$ has worked of the literature on $^6A_{1g} \leftrightarrow ^2T_{2g}$ spin cross over in Fe(III) dithiocarbamate for the last three decades has been reviewed and kinetics and mechanism of spin-cross over in these system have been discussed.

The complexes of divalented Mn, Co, Ni, Cu, Zn, Cd and have been prepared with azodye ligands bis $[3,3'$-di (p-
nitrophenylazo)] 2,2'-dihydroxydinaphthalene (LH$_2$) and bis [3,3'-di (m-hydroxyphenylazo)] 2-2'-dihydroxy naphthalene (L'H$_4$) were studied by B.B. Mahapatra et al.\textsuperscript{140} the spectra of the Mn$^{II}$ complexes exhibit three bands at around 16725, 17130 and 19310 cm$^{-1}$ which are ascribed to $^6$Ag $\rightarrow$ $^4$T$_{1g}$ ($\sigma_1$), $\rightarrow$ $^4$T$_{2g}$ ($\sigma_1$) and $\rightarrow$ $^4$T$_{1g}$ $^4$Eg ($\sigma_1$) transitions respectively in support of an octahedral stoichiometry around Mn$^{II}$ ion.\textsuperscript{141}

Very recently Rashmi Tripathi and coworkers\textsuperscript{142} have reported complexes of Zn(II) Fe(II) and Fe(III) of 3,4-subsituted trizole have been isolated in solid state and characterized on the basis of elemental analysis, magnetic, UV-visible and IR spectral data. Physico-chemical data provide evidences for the existence of tetrahedral configuration for Zn(II) and octahedral for Fe(II) and Fe(III) complexes. A large number of transition metal complexes of variety of substituted triazoles have been synthesized.\textsuperscript{143-146} The isolation and characterization of Zn(II) and Fe(III) complexes with 4-amino-3-ethyl-5-mercapto, 1,2,4-trizole (LH) and 4-amino-3-methyl-5-mercaptor-1,2,4-triazole (LH) having thioamide moiety.\textsuperscript{147-148} UV and visible spectra of complexes in DMF display very strong broad bands around 250 and 255 nm for LH and LH respectively which may be assigned to charge transfer bands.\textsuperscript{149} These bands are shifted (~10~15 nm) after complexation indicating the thickness of ligand with metal ions. A new strong absorption band is observed in the region of 468 ± 1 nm in all Fe(II) and Fe(III) complexes assigned to $^6$A$_{1g}$ $\rightarrow$ $^4$T$_{2g}$ transitions.\textsuperscript{150} The disappearance of νSH band at 2450 and 2445 cm$^{-1}$ in LH and L,H
respectively after complexation indicate the absence of thiol tautomeric form of ligand in all complexes.\textsuperscript{151}

The compounds of Cerium-Iron transition metal mixed oxides of the type CeFeTO\textsubscript{4} (where T = Fe, Cr, Mn & Co) have been prepared by solid state reaction technique and characterized by XRD pattern have reported by U.P. Singh and coworkers\textsuperscript{152}. The compounds are essentially electronic conductors with $\sigma$ values lying in the range $10^{-7}$ to $10^{-3}$ $\Omega^{-1}$ m$^{-1}$ around 400 K. The maximum value of $\sigma$ has been observed for Ce Fe MnO\textsubscript{4} and lowest for CeFe\textsubscript{2}O\textsubscript{4}. CeFe\textsubscript{2}O\textsubscript{4} is essentially on ionic compound as has been confirmed by magnetic susceptibility measurement.\textsuperscript{153} Hence the material will contain Ce$^{3+}$, Fe$^{2+}$ and Fe$^{3+}$ ions. Iron is multivalent and it is natural to think that conduction in this compound occurs via hopping of electrons localized on Fe$^{2+}$ to Fe$^{3+}$ sites. The happing of electrons in LuFe\textsubscript{2}O\textsubscript{4} has already been observed through Mossbaur studies.\textsuperscript{154-155}

Neelam Richharia et al\textsuperscript{156} have reported on the synthesis and characterization of Fe(III) peroxchromate, FeCrO\textsubscript{4}(OH).H\textsubscript{2}O. In this complex Fe(III) and Cr(VI) were tested positive by usual quantitative taste. The compound was found insoluble in common organic solvent such as ethyl acetate but resolved to some extent in water pH = 5.95 at 25°C into soluble chromic acid and ferric oxide. For a mixture of Fe(III) chromate (0.5g) and water (50 ml) the pH was noted to be 5.95 at 25°C FTIR (kBr): 3300 brs, $\nu$H\textsubscript{2}O/H, 1620s,
ν (H₂O); 9565 and 800 bars cm⁻¹ ν CrO₄, mossbawer (298 k δ = 0.69 and ∆E = Negligible (mm/sec)) (HS Fe³⁺) µₑₑ (25°C) = 5.74 B.M.

A series of molecular assemblies constructed from a π. Conjugated redox active bipyridinium cation-1,4-bis(4’-pyridyl-1-pyridino) phthalazine (BPyph) and magnetic dimetallic oxalate bridged trimeric clusters has been reported by Yan-Qiong Sur et al¹⁵⁷, synthesized and characterized by elemental analysis, IR, TGA, X-ray single, crystal diffraction and magnetic susceptibility studies.

The molecular assemblies formulated as (BPyPh)₂ [M”(H₂O)₂ [M”(C₂O₄)₃]₂] 12.5 H₂O (where M” = Fe and Cr, M”” = Mn or Co( is isostructural.

Hong-Xing Ward et al¹⁵⁸ have worked on the condensation of ferrocenylcarboxaldehyde and P-methyl or p-chlorobenzylamine in methanol resulted in ferrocenylaldines which were reduced by lithium Aluminium hydride.

The synthesis, reactivity and magnetostructural properties of Fe””, Fe”’-O-Fe”” and Zn””, Fe”’ – O – Fe”” complexes of a tetraaminodiphenolate macrocycle were studied by Pupa Biswas and coworkers.¹⁵⁹ The mononuclear Iron (III) complexes [Fe(LH₂)(H₂)Cl] (ClO₄)₂. 2H₂O and [Fe(LH₂)(H₂O)₂] (ClO₄)₃.H₂O have been prepared by reacting [Pb(LH₂)] (ClO₄)₂ with FeCl₃.6H₂O and Fe(ClO₄)₃.6H₂O respectively.
Optimal condition for the complexation of Fe(II) and (III) with 1-nitro-2-naphthal-3,6-disulphonic acid in two buffer solutions and the reduction of Fe(III) with ascorbic acid or hydroxyl amine were founded by spectrophotometry and chromaticity measurements. Chemical analysis and chromaticity characterization of complexes in solution were dated two complexes formed depending on the oxidation state of Iron molar coefficient of the chromaticity functions were 20 to 30 times higher than molar absorptivities. The complexes exhibited abnormal light absorption maxima (710-720 nm) among the known 1-nitro-2-naphthal-3,6-disulphonate.

Very recently Prasad & coworkers have reported the electrochemical behaviour of oxovanadium(IV) complexes \([\text{VO}(\text{bipy})_2\text{]}\) and \([\text{VO}(\text{phen})_2]^{2+}\) (where, \text{bipy} = 2,2'-bipyridine and \text{phen} = 1,10-phenanthroline have been examined in DMSO and DMF with 0.1M TBAP using cyclic voltammetry at a Pt working electrode.

Thus, the synthesis characterization and biological activity studies on \(\text{VO}_2\) (I), Mn(II), Fe(II), Cr(III) and VO(IV) with Isonicotanic acid hydrazide are a need of current demands and I have choosen this work for research purposes.
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