Section 1

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The introduction of sulphur and nitrogen atoms in various organic compounds has resulted in important consequences towards the behaviour with the transition metals. Thiosemicarbazides and thiosemicarbazones are known to form a large number of complex compounds with transition and inner transition metal ion by bonding through sulphur and hydrazinic nitrogen. 2-Formyl Pyridine thiosemicarbazone and 1-Formyl isoquinoline thiosemicarbazone are known to possess antitumor activity\(^1\). Some complexes are also known to possess activity against tumor\(^2\), influenza\(^3\) and small pox\(^4\).

Coordination compounds play an important role in chemistry of other elements having electro positive values i.e. elements which form ions or compounds in which they are electrophilic and hence capable of binding donor molecules. First transition series elements show variable valency. The facts responsible for this behaviour of transition metals are presence of an incomplete 3d- shell of electrons, the comparative ease of loss of two or more electrons by the metal atom and availability of \(\delta\)- orbitals for bond formation.

Considerable complexes of sulphur containing ligands are known\(^5\)\(^-\)\(^7\). Sulphur possess a position in the
middle of electronegative series $F > O > N > Cl > Br > I > S > Se > C > Te > P > As > Sb$. This electronegativity is greatly influenced by the groups attached to donor atoms. It is therefore evident that for a unidentate ligand the coordinating ability depends not only on the electronegativity but on the total dipole moment ($\mu$) of the ligand 

$$\mu = P + P^I = P + \alpha E$$

where $P$ = the permanent dipole moment, $P^I$ = the induced dipole moment, $\alpha$ = the polarisability and the $E$ = the inducing electrostatic field.

Livingstone\(^{(8)}\) reviewed the complexes involving sulphur atom as donor viz. sulphides, thioethers, thiols and thiones. Sulphur atom has vacant $d$-orbitals which can be used for ($\delta\pi - \delta\pi^*$) bonding similar to those involved in transition metal having usual and unusually low oxidation states. Metal complexes of thiosemicarbazide and thiosemicarbazone were studied at length by Campbell\(^{(9)}\). Livingstone and Akbar Ali\(^{(10)}\) studied the carcinostatic and antiviral activity of sulphur nitrogen ligands and their complexes.

Some papers concerning the magnetic behaviour of transition metal complexes of mercaptocarboxylic\(^{(11-13)}\) acid, thiomalic\(^{(14-15)}\) acid and thiosalicylic\(^{(16,17)}\) acid are appeared in the literature. Sulphur give rise to both low and high spin complexes of transition metals. This is one of the explanation for anomalous magnetic properties of complexes formed from ligands involving sulphur as donor atom.
The magnetic behaviour of the lanthanides is fundamentally different from that of the d-block transition elements. The basic reason for the difference lies in the fact that the electrons responsible for the magnetic and spectral properties of lanthanide ions are 4f-electrons and the 4f-orbitals are very effectively shielded from interaction with external forces by the overlying 5S\(^2\) and 5p\(^6\) shells\(^{(19)}\). Therefore the state arising from various 4f\(^n\) configurations are only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in all its compounds. The magnetic properties of Lanthanides and their metal complexes have recently been reviewed by Sinha\(^{(19)}\), Forsberg and Taylor\(^{(20)}\).

The use of spectral and magnetic techniques have been widely made by Akbar Ali\(^{(21-28)}\), Campbell\(^{(29)}\) and Ablov\(^{(30-33)}\), cofreras et al.\(^{(34)}\) have recently prepared and studied the Pseudo-Octahedral complexes of the type \([\text{Cr (NCS)}\_n \text{L(6-n)}]\) where L is an organic ligand whose donor atom is (a) O (b) N (c) S (d) O and N (e) S and N, in most cases n = 4. Preti\(^{(35)}\) reported the electronic spectra of several manganese (II) complexes with cyclic thiones, and found them octahedral. Agarwal\(^{(36)}\) et al. reported the ultraviolet visible spectra of Rh (III), Ru (III), Pt (II), Pt(IV), Pd (II) and Pd (IV) complexes of 2, 4-di-thiouracil.

Campbell\(^{(37-40)}\) et al. discussed the stereochemistry
of copper (II) and nickel (II) complexes of thiosemicarbazones on the basis of the metal ligand stretching vibrations (400 - 80 cm\(^{-1}\)). The X-sensitive bands are in the region of 250 cm\(^{-1}\) for chloride and 210 cm\(^{-1}\) for bromide. Gringras et al.\(^{(41)}\) studied the chelate forming capacity of the thiosemicarbazones of some diketones. Bahr\(^{(42)}\) suggested the structure of diacetyl-dithiosemicarbazone Cu (II). Several reviews\(^{(43-50)}\) have been appeared which exclusively dealt with the ligand field perturbations having octahedral, tetrahedral, square planar and tetragonal distribution of ligands around the central ion. Perumareddi\(^{(51-56)}\) has developed various energy equations for noncubic symmetry including quadrate, trigonal, and cylindrical ligand fields for \(d^2\), \(d^3\), \(d^7\) and \(d^8\) ions.

Infrared spectral measurements have been proved of immense utility in the determination of the structure of molecules and coordination compounds. Molecular vibrations show the presence or absence of certain functional groups, ligand chain length, multiple bonding, isomerism or bound state of ligand and the degree of molecular symmetry\(^{(57-69)}\). Schiff bases and thioureas are amongst the most important nitrogen and sulphur containing ligands which show remarkable pharmacological activity and have wide biological applications\(^{(70)}\). Perhaps the group N - C - S is of considerable chemotherapeutic interest and is responsible for the pharmacological activity\(^{(71)}\). It has been indicated
that the microbiol activity of these compounds is due to their ability to chelate traces of metal ions\(^{(72)}\). Several Schiff bases complexes have been well investigated\(^{(73-77)}\). However only recently the attention has been directed to the complexes of the transition metals with monofunctional tridentate Schiff bases containing O, N, O and -O, N-S sequences\(^{(78-80)}\), similarly 8-hydroxyquinoline and 4-hydroxy acridine\(^{(83)}\) are also fungitoxic as they are suitable ligands to chelate the essential metals involved in fungal metabolism, as did N-Aryl/Hetero aryl-2, 2-Disubstituted azomethines which are known potential fungicides\(^{(84)}\).

Multidentate ligands having the amine and the mercaptide groups have been reported to form quite stable chelate compounds with transition metals\(^{(85,86)}\). The amine and the mercapto group in 1,2 position behave as competitive nucleophiles, usually resulting in the formation of thiazolines. SUVOROVA et a.\(^{(87)}\) have reported that the reaction of salicylaldehyde or its halogen derivatives with B-mercapto ethylamine produces a large percentage of the Schiff base rather than a thiazoline. Tandon\(^{(88)}\) et al. reported the non transition metal complexes of salicyledene -2-mercaptopethylamine; and suggested that the central atom possess un-common penta coordinate state\(^{(89-91)}\).

Metals of first transition series particularly and various organic compounds containing N, S, or O and even elements of comparatively higher electronegativity such as As, P and Se have been used as ligands. In recent years
research on multidentate chelating agents (92-93) has been stimulated by a number of aspects such as their interesting and unique stereochemical properties, their wide spread occurrence in living matter and many practical applications. With the advent of multidentate ligands, coordination compounds bearing coordination number four, five, six, seven, eight and ten have been synthesized and studied. 2,4-Lutidine-1-oxide complexes of Lanthanide nitrates of the formula Ln(NO$_3$)$_3$ (2,4-Luto)$_4$ have been prepared and characterised (94,95) by chemical analysis, IR, NMR and conductance data. IR-data indicates both mono and bidentate nitrate groups in the complexes of La and Pr-nitrates and only bidentate nitrate groups in the other lanthanide complexes. The non electrolytic behaviour of the La- and Pr-nitrate complexes in acetonitrile in conjunction with the IR data for the nitrate groups suggest a coordination number of 8 or 9 for the lanthanide ions according to Whether, one or two nitrate groups are bidentate. Nair and Chacko (96) have reported the preparation and characterisation of complexes of 4-aminoantipyrine (aap) with lanthanide perchlorates (97) and nitrates (98) with the composition \[ \text{Ln (aap)$_6$ (ClO$_4$)$_3$}\] and \[ \text{Ln (aap)$_3$ (NO$_3$)$_3$}\] respectively. Unlike other lanthanide complexes the lanthanide thiocyanates complexes are quite novel in that the lanthanide ions themselves fall into two groups (the lighter ones and the heavier ones) as regards their coordinating ability. The
lighter lanthanides (La, Pr, Nd and Sm) show a ligancy of six and the heavier lanthanides (Gd and Dy) and Y show a ligancy of nine. In fact the possible geometries of five, seven and the complexes of higher coordination numbers are such that the structure of the ligand and nature of donor atoms play an important role in the stabilization of transition metal complexes in the usual states, square planar C₄ᵥ symmetry and Trigonal bipyramidal D₃h symmetry.

(a) Object and Scope:

In recent years the study of the chemistry of thiosemicarbazides and thiosemicarbazones has been given particular impetus because of their pharmacological and industrial uses e.g. derivatives of thiosemicarbazides have been used in the treatment of tuberculosis(69), influenza(100), small pox(101) and certain kinds of tumour(102). Their activity has frequently been thought to be due to their ability to chelate trace metal e.g. copper, the metal complexes themselves being the active ingredient(103). This is supported by the fact that Seleno semicarbazones in which S-atom is replaced by selenium are more active against fungi than the corresponding thiosemicarbazones. This difference in activity is attributed to the formation of metal complexes which would occur more readily in the case of seleno semicarbazones(104). p-acetamido benzaldehyde thiosemicarbazone found use in tuberculosis. According to
the Liebermeiter the tuberculostat activity of the above compounds can be enhanced with copper ions. The involvement of metal ions in cancer therapy has been discussed by a number of workers (105-107). Istatin thiosemicarbazone copper complex (108) has been used as an active antiviral drug. In thiosemicarbazide and thiosemicarbazone the toxicity may be due to \( N - C - S \) grouping which is of considerable chemotherapeutic interest and is perhaps responsible for their pharmacological propeties (109). Besides pharmacological activities, thiosemicarbazide also possess chelating ability due to dual potential sites at the thio- ketonic sulphur and hydrazinic or azomethine nitrogen which are ideally situated to be coordinated to the metal ions (110). The denticity of such ligands can be increased by extending the chain length of thiosemicarbazide by the introduction of such groups as amide and benzene rings with phenolic groups. By increasing the chain the idealized geometry get disturbed to form tetragonally distorted complexes.

Attempts have also been made to study whether the antifugal and antibacterial activities of such organic ligands are enhanced reduced or remain unaffected after complex formation. The effect of the metal ion and anion attached to metal complexes have also been observed.

The metal complexes of the ligands derived from \( \alpha \)-Benzamido ortho chloro cinnamic acid; 5-acetyl-2-hydroxy- Benzoic acid thiosemicarbazide and 1-hydroxy-2-naphthoic acid
thiosemicarbazide have not been studied so far though they present many interesting features worth investigating. To this end the present studies have been initiated. The ligands contain thioketosulphur, azomethine nitrogen and phenolic -OH as the potential donor sites to form five or six membered ring chelates with heavy metal ions. Besides throwing light on the coordinating ability of S,N,O the antifungal and antibacterial activity of the ligands and their metal complexes have been tested.

**Antifungal and antibacterial activities**:

Both ligands and the isolated complex were screened for their antifungal activity against the test fungus *Helminthosporium sativum* and *Alternaria alternata* by linear growth measurement method. The prepared complexes are also screened for antibacterial activity against the bacteria *Staphylococcus aureus* and *Escherichia coli* by employing the cut plate agar diffusion method. The antibacterial results of the compounds showed a variable activity against gram positive and gram negative bacteria.

Attempts have also been made to study whether the antifungal and antibacterial activities of the ligands are enhanced, reduced or remain unaffected after complex formation.

(b) **Antifungal and antibacterial activities**:

Numerous complexes of thiosemicarbazide and
thiosemicarbazones have been reported in the literature\(^{(111-119)}\) as pesticidal, fungicidal and against many diseases. The remarkable antituberculous activity of isoniazid\(^{(120-121)}\) has initiated a substantial amount of research on the transition metal complexes of pyridine carboxylic acid hydrazides and their derivatives. Some pyrazole based acid hydrazides have also been reported as pesticidal reagents\(^{(122)}\).

In view of antituberculosis\(^{(123-129)}\) and other pharmacological activities of metal thiosemicarbazides in biological systems, the physicochemical studies of the metal complexes are desired. A number of thiohydantoin derivatives are physiologically active and some of them have been reported to possess anticonvulsant\(^{(130)}\), antibacterial\(^{(131)}\), antifungal\(^{(132)}\), antihypertensive\(^{(133)}\) and such other properties. A variety of compounds both inorganic\(^{(134-136)}\) and organic have long been used to prevent the fungal and bacterial attack. Although organic compounds have proved superior over those derived from inorganic sources but in a number of cases it has been observed that some compounds have increased activity when administered as metal complexes\(^{(137)}\).

Recently it has been found that pyrimidine-2-thione\(^{(138)}\) inhibits the synthesis of RNA leading to antitumour and \(^{(139,140)}\) antithyroid activity. Mercapto triazoles resemble pyrimidine thione in having the identical donors. Thiadiazole ring is reported to display fungicidal\(^{(141)}\) property by virtue
of $\text{N} - \overset{\text{C}}{\text{C}} - \text{S}$ linkage which is possible toxophore in many pesticides$^{142,143}$. Several metal chelates are known to possess bactericidal$^{144}$ fungicidal$^{145}$ and antiviral$^{146}$ activity. Likewise it has been found that metal chelates are more fungitoxic than the chelating agents themselves in several cases$^{147}$. Thiourea and thiocarbazone derivatives such as thiosemicarbazides and thiosemicarbazones have given particular impetus because of the discovery of their antifungal and antibacterial activities. It is known that the thiourea and its various derivatives have toxophoric $\text{N} - \overset{\text{C}}{\text{C}} - \text{S}$ grouping which of considerable chemotherapeutic interest and is perhaps responsible for their antifungal and antibacterial activity. Mason and Powell$^{148}$ point out that some chelates of oxine, notably those of copper are more fungitoxic than oxine alone. These observations led us to synthesis some new thiosemicarbazones and to investigate their antifungal activity if any.

**Literature review on**

'(i) **Electronic spectral studies**: 

Electronic structure of transition metal complexes have added much to our understanding during the past two decades$^{149-155}$ while a variety of experimental techniques have contributed to this progress, a central role has been played by electronic spectral spectroscopy in the visible
and ultraviolet spectral regions. Absorption experiments have probably played a greater role than emission studies, because the former yield information about the more excited states than the latter. The electronic transition responsible for the absorption bands frequently involve the rearrangement of electrons with in the partially filled d-shells of the central ion, although other types such as ligand to metal or metal to ligand charge transfer transitions may be observed. In recent years attention has been mainly concentrated on the d-d transitions as the simple ideas of ligand field theory suffice to interpret the broad features of the spectrum. Many reviews have been appeared in which the electronic spectral studies correlated with magnetic and spectral properties of transition metal complexes derived from nitrogen and oxygen donor ligands. The optical spectra may be favourably described in terms of a single ligand field parameter Dq and the Racah's interelectronic repulsion parameters A, B and C. These are generally viewed as empirical parameters to be determined from experimental data. In ligand field of symmetry lower than cubic such as tetragonal and trigonal which arise by the super imposition of an axial perturbation along the four fold or three fold axis of an octahedral potential, two additional parameters D \( \mu \) (\( \mu \) is \( S \) or \( \sigma \) thus giving rise to DS and D\( \sigma \)) D\( \nu \) (\( \nu \) is t and \( \kappa \) resulting in Dt and D\( \kappa \)) where \( S \) and \( \kappa \) refer to tetragonal and \( \sigma \) and \( \kappa \) are associated with the second order and the fourth
order spherical harmonics $v_2^0$ and $v_4^0$ respectively, and lead to an additional splitting of the otherwise degenerate electronic levels of the cubic symmetry. Thus in order to define the spectra of tetragonally distorted complexes three parameters $D_q$, $D_S$ and $D_t$ are needed. As a result in distorted octahedral systems or in mixed ligand complexes observations of the splittings of the cubic absorption bands can provide useful informations on the symmetry of the ligand fields.

Recently complete theory of paramagnetism in transition metal ions in the octahedral and tetrahedral $d^3$, $d^4$, $d^5$, $d^6$, $d^7$ electron configurations (156-159) and $d^2$ and $d^8$ electrons configurations in cubic (octahedral and tetrahedral), tetragonal ($D_{4h}$) and trigonal ($D_{3h}$) symmetry have been developed by König and Kremer. The magnetic moment is a function of octahedral and tetrahedral ligand field splitting parameter $D_q$ and the temperature for a fixed set of values of Racah parameters ($B$ and $C$) spin orbit coupling parameter ($\lambda$) and the orbital reduction ($K$), whereas in $D_{4h}$ and $D_{3h}$ symmetry this quantity has been found to be a function of the parameters $D_t$ or $D_T$, respectively. With these deductions the effect of variation in parameters values of $B$, $C$, $\lambda$ and $K$ can be investigated. These results can be used in an accurate comparison of the experimental data with the theoretical results.

The deductions arrived at by correlating the electronic and magnetic characteristics of transition metal complexes have been amply supported by the vibrational
spectra studies. The vibrational spectra especially the far IR region has been of specific importance in the assignment of the (M – L) vibrations. Very recently such studies led to differentiate between the stereochemistry, configuration and nature of the (M – L) bond in transition metal complexes (160-162).

From the above discussion it is quite clear that definite conclusion can be deduced regarding the stereochemistry, configuration, oxidation state of the central metal ion and the nature of metal donor link by correlating vibrational, electronic spectral and magnetic characteristics of transition metal ions both in cubic and noncubic fields.

In the present thesis an attempt has been made to apply the various theories at least in semiquantitative manner supplemented by experimental observations to determine the structure and configuration of various metal chelate compounds with bulky ligands having N, O and S as the potential sites.

(ii) Magnetic studies:

The measurement of the magnetic moment has been one of the most important tools for predicting bond type oxidation state and stereochemistry in complex compounds. Since long this technique is in used for determining the structure of inorganic compounds (163-165). Magnetic susceptibility measurements of paramagnetic and diamagnetic compounds have been very useful in revealing an accurate
description of many physicochemical properties of solids. A single crystal in general shows directional properties depending upon the inherent symmetry in its physical and chemical nature and the magnetic susceptibility in different directions of the crystal is different.

The anomalous magnetic behaviour observed in the heavy transition metal complexes has been explained in terms of
(i) the increase in the spin-orbit coupling constant $\Lambda$ of the metal involved.
(ii) The greater crystal field effects due to large energy separation ($\Delta_{oh}$) between $t_2g$ and eg orbitals.
(iii) the preponderance of intermediate form of coupling over Russel-Saunder's coupling and
(iv) the influence of antiferro magnetic information.
Although magnetic studies (166-171) of complexes are being carried out from a very long time, but the main attention has been confined to the complexes of first row transition metal ions. The inclusion of spin orbit coupling effects into strong field configurations throughout the transition block by Kotani (172) made a considerable advance towards explaining the observed large difference between magnetic moment of first, second and third row transition elements for a given configuration and their dependence on temperature.

In recent years coordination compounds in their solid state have been reported to show deviations may be categorised in such a way that one type occurs when the electron pairing energy of a complex lies between the ligand
field strengths of possible high spin and low spin forms and results in a high spin - low spin equilibrium which has been observed in number of systems. A second type arises from the antiferromagnetic- interactions between the unpaired electrons of two or more metal atoms in a complex. Anomalous magnetic behaviour has also been observed in case of various transition metal complexes.

In several series of complexes deviations \(176,177\) from normal diamagnetic and paramagnetic behaviours have been found to be the result of the coordination of the metal atom of one molecule of a complex with the donor atoms of other molecules in such a way that the metal atom achieves pseudo octahedral configuration. Sangal et al. \(178\) have studied the Dipicolinic acid hydrazide complexes of oxovanadium at room temperature, the value of which lie in the range 1.65 - 1.73 B.M. These values are well within the range reported for oxovanadium (IV) complexes when the orbital contribution is completely quenched \(179,180\).

Cobalt (II) complexes of iminophosphoranes \(181\) show deviation of magnetic moment value from the spin only value of 3.88 B.M. but lie well within the limits (4.1 - 4.8 B.M.) expected for tetrahedral or approximately tetrahedral. The relatively high value of \(\gamma\) the spin orbit coupling constants of the complexes indicate only a small amount of (CO - N) orbital overlap, confirming thus the weakness of the ligands.
2-Benzylpyridine N-oxide complexes with transition metal perchlorates have been studied by Speca and coworkers\(^{182}\). The magnetic moments of the new paramagnetic metal ion complexes are normal for high spin \(d^5-d^8\) compounds or the \(d^9\) configuration\(^{183}\). The moments of the Co\(^{2+}\) and Ni\(^{2+}\) complexes are within the range of values reported for other penta coordinated complexes of these metal ions with aromatic amine\(^{184-186}\) N-oxide. Naidu and Naidu\(^{187}\) while studying the thermal, spectral, ESR and magnetic studies of complexes of copper (II) with O-hydroxychalcones come a cross abnormal value of magnetic moments, which they explained because of electron spin and orbital motion the magnetic moment of Cu (II) may range from a value of 1.73 B.M. (no orbital contribution) to 2.2 B.M. Different degrees of orbital contribution are predicted in square planar and tetrahedral environments. In the former geometry, no orbital moment is expected by virtue of a non-degenerate ground state. In the latter however an orbital contribution is expected because the Jahn-Teller effect prevents a rigorously degenerate ground state. Moments that contain large orbital contributions have been used as evidence for pseudo tetrahedral fields in bis (Cu (II) compounds\(^{188-190}\).

(iii) Infrared spectral studies:

Infrared studies of organic compounds used as ligands in preparing complexes have been made to identify various modes of vibrations and hence their structures. This
technique has provided a powerful and useful unambiguous method of structural determination for complexes of transition metals. Based on these studies many conclusions of the general nature and feasible with respect to ligand chain strength, presence or absence of certain, functional groups, multiple bonding, hydrogen bonding, isomerism, bound state of ligands, degree of symmetry, but lately it has been also possible to decide alternative stereochemistries (191-193).

In general the vibrations originating in the ligand appear in the high frequency region, and those originating in the coordinate bonds appear in the far i.r. region. The analysis of low frequency spectra provide direct information about the coordination bounds, whereas high frequency spectra reveal the secondary effect of coordination on the ligands. These secondary effects on coordination on ligand vibrations is the key to elicit whether coordination has taken place or not and if so then at what points. The most conclusive proof of coordination taking place is the appearance of several new modes of vibration e.g. $\nu(M-N)$, $\nu(M-S)$, $\nu(M-O)$ or metal-halogen in the far I-R region. The frequencies observed in infrared spectra are the functions of the mass as well as the force constant and on this account the band shifts are the function of metals. As a rule the direction of the shift depends upon relative electronegativities of L and X atoms in the ligand $LX_n$. 
The data on metal-halogen stretching frequencies can be used to ascertain the dependance of \( v(M-X) \) vibrations on the oxidation number, mass and coordination number and on the stereochemistries, of complexes. Making use of symmetry arguments, relationship between \( v(M-X) \) vibrations and stereochemistry has been established. Such studies are of particular importance where the metal atom has a closed shell of valence electrons and hence the electronic absorption spectra and magnetism yield no conclusive information regarding the stereochemistry.

However, it may be mentioned that the \( (M-L) \) stretching vibrations are rarely pure, coupling with other normal modes of vibrations of the same symmetry in the molecule is generally expected. The title metal-halogen, metal- sulphur, or metal- nitrogen used should be taken to infer that a particular absorption band arises primarily but not necessarily totally, from such as a normal coordinate.

Several papers (194-196) have been reported concerning the assignments possibility of coordination, metal- ligand bond nature, stability of nitrogen and or oxygen donor complexes of metal ions belonging to all the three transition series. Because of relative heaviness of metal atom and low bond order of the coordinate links both \( r(M-N) \) and \( r(M-O) \) frequencies have been reported to appear in the lower frequency region \( \approx 500\text{cm}^{-1} \) and \( \approx 300\text{cm}^{-1} \) respectively in a large number of complexes.
Narang et al. have isolated the complexes of amino pyrine with metal (II) perchlorates and found that it acts a bidentate ligand and belongs to the pyrazole group. The negative shift (197-198) in V (C = O) by ~ 50cm⁻¹ and V(C - N) by ~ 30cm⁻¹ in copper (II) complex suggest that aminopyrine has two sites of coordination with metal. In other complexes however, a strong bond at 1090cm⁻¹ due to ionic perchlorate (199) overlaps the V(C - N) vibration. The perchlorate vibrations between 1085 - 1090cm⁻¹ and 620 - 625cm⁻¹ are due to V₃ and V₄ modes respectively. A weak band V₁ is observed at 940cm⁻¹ in the complexes and it is due to crystal field effect. The absence of splitting of these bands indicates tetrahedral symmetry of the perchlorate and hence its ionic nature. The coordinated water absorbs between 3400 - 3500cm⁻¹ r(O - H) in Fe (II), Ni (II) and Cu (II) complexes. Bending vibration of H₂O overlaps with the carbonyl frequency. The H₂O rocking frequencies occur between 835 - 845cm⁻¹ indicating that water is coordinated to the metal ion (200). The non ligand M - O and M - N vibrations are observed at 450 - 400cm⁻¹ and 330 - 300cm⁻¹ respectively (201, 202).