Chapter 2

Experimental methods
There are several physico-chemical methods available for the study of coordination compounds. A brief description of the techniques used in the investigation of the newly synthesized complexes described in the present work are given below:

1. Infrared Spectroscopy
2. Nuclear Magnetic Resonance Spectroscopy
3. Electron Paramagnetic Resonance Spectroscopy
4. Ultraviolet and Visible (Ligand Field) Spectroscopy
5. Cyclic Voltammetry
6. Magnetic Susceptibility Measurements
7. Molar Conductance Measurements
8. Elemental Analysis

INFRARED SPECTROSCOPY

Infrared absorption spectra are commonly obtained by placing the sample in one beam of a double beam infrared spectrophotometer and measuring the relative intensity of transmitted light. When the infrared light of the same frequency incident on the molecule the energy is absorbed and the amplitude of that vibration is measured. When the molecule reverse from the excited state to the original ground state, the absorbed energy is released as heat. The occurrence or non-occurrence of an infrared radiation is governed by the following selection rules:

1) In order for a molecule to absorb infrared radiation as vibrational excitation energy, there must be a change in the dipole moment of the molecule as
it vibrates.

ii) In absorption of the radiation, only transition for which change in the vibrational energy level is $\Delta V = 1$ can occur, since most of the transition will occur from state $V_o$ to $V_i$, the frequency corresponding to its energy is called the fundamental frequency.

The group frequency which are frequencies of certain groups are characteristic of the group irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the approximate region indicates the absence of that particular group in the molecule.

The infrared radiation is usually said to have wavelength lying between 0.8 m to 1000 m. The wave number, i.e. the number of waves per centimeter is used to characterize the radiation.

**Important group frequencies in the IR spectra pertinent to the discussion of the newly synthesized compounds.**

**N-H Stretching Frequency**

The N-H stretching vibration occur in the region 3300-3500 cm\(^{-1}\) in dilute solution\(^1\). The N-H stretching band shifts to lower value in the solid state due to extensive hydrogen bonding. Primary amines in dilute solutions, in non-polar solvents give two absorption bands in the above mentioned region, the first of which due to symmetric stretch is usually found near 3400 cm\(^{-1}\) and second which corresponds to asymmetrical modes is found near 3500 cm\(^{-1}\). These bands are usually 125-150 cm\(^{-1}\) apart. Secondary
amines show only a single N-H stretching in dilute solutions. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3310-3350 cm\(^{-1}\) (low intensity) in aliphatic, secondary amines and near 3490 cm\(^{-1}\) (much higher intensity) in heterocyclic secondary amines such as pyrazole and imidazole.

**Methyl Group Frequency**

Absorption arising from C-H stretching in the alkanes occurs in the general region of 2840-3000 cm\(^{-1}\). The position of C-H stretching vibration are among the most stable in the spectrum. An examination of a large number of saturated hydrocarbons containing methyl groups showed in all cases, two distinct bands occurring at 2960 cm\(^{-1}\) and 2870 cm\(^{-1}\). The first of these results from asymmetric stretching mode in which two C-H bonds of the methyl group are extending while the third one is contracting (\(\nu_{asy\cdot CH_3}\)). The second arises from symmetric stretching (\(\nu_{sy\cdot CH_3}\)) in which all three of the C-H bonds extend and contract in phase. The presence of several methyl groups in a molecule results in a strong absorption bands at these positions.

**C-N Stretching Frequency**

The C-N stretching absorption gives rise to strong bands in the region 1250-1350 cm\(^{-1}\) in all the amines. In primary aromatic amines there is one band in the region 1250-1340 cm\(^{-1}\) but in secondary amines two bands have been found in the region 1280-1350 cm\(^{-1}\) and 1230-1280 cm\(^{-1}\).
C=N Stretcing Frequency

Schiff's bases (RCH=NR, imines), oximes, thiazoles, iminocarbonates etc. show the C=N stretching frequency in the 1471-1689 cm\(^{-1}\) region\(^{1-2}\). Although the intensity of the C=N stretch is variable, it is usually more intense than the C=C stretch.

O-H Stretching Frequency

The O-H stretching frequency is observed\(^{2-3}\) nearly in the same range as N-H frequencies (3400-3500 cm\(^{-1}\)). However, the observed absorption for N-H is normally narrower than for O-H. This is a useful means of distinguishing N-H and O-H stretching modes.

Amide Bands

All amides show a carbonyl absorption band known as the amide I band\(^{1-3}\). Its position depends on the degree of hydrogen bonding and thus on the physical state of the compound. The C=O absorption (amide I band) of amides occurs at longer wave length than normal carbonyl absorption due to the resonance effect. Primary amides have a strong amide I band in the region of 1650 cm\(^{-1}\) when examined in the solid phase. When the amide is examined in dilute solution the absorption is observed at a higher frequency, near 1690 cm\(^{-1}\). Simple open chain secondary amides absorb near at 1640 cm\(^{-1}\) when examined in solid state.

All primary amides show a sharp absorption band in dilute solution (amide II band) resulting from NH\(_2\) bending at a somewhat lower frequency than the C=O bond. Secondary acyclic amides in the solid state display
an amide II band in the region of 1500-1570 cm⁻¹. A weaker band near 1250 cm⁻¹ results from interaction between the N-H bending and C-N stretching (amide III band). A broad medium band in the 640-800 cm⁻¹ region in the spectra of primary and secondary amides results from out of plane N-H wagging.

**M-N Stretching Frequency**

The M-N stretching frequency is of particular interest since it provides direct information regarding the metal-nitrogen coordinate bond. Different amine complexes exhibited the metal-nitrogen frequencies in the region 300-450 cm⁻¹.

**M-O Stretching Frequency**

Metal-oxygen stretching frequency has been reported to appear in different region for different metal complexes. The \( \nu(M-O) \) band is usually broad and strong while the \( \nu(M-N) \) is usually sharp and strong as a larger dipole moment change is involved in the vibration of the M-O bond in comparison with that in the M-N bond and \( \nu(M-O) \) is expected to occur at higher energy than \( \nu(M-N) \).

**M-X Stretching Frequency**

Metal-halogen stretching vibrations are generally observed in the low frequency infrared region (200-400 cm⁻¹). In the complex \( \text{Cu}_2X_4 \) (pyridine - 1 - oxidase), a single band at 315 cm⁻¹ with shoulder at 325 cm⁻¹ must be due to the terminal Cu-Cl frequency.
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The nuclei of certain isotopes possess a mechanical spin or angular momentum. The NMR spectroscopy is concerned with nuclei having spin quantum number $I = 1/2$, examples of which include $^1$H, $^{31}$P, $^{19}$F etc.

For a nucleus with $I = 1/2$ there are two values for the nuclear spin angular momentum quantum number $m = \pm 1/2$ which are degenerate in the absence of a magnetic field, in presence of magnetic field, however, this degeneracy is destroyed such that the positive value of $m$ corresponds to the lower energy state and negative value to higher energy state separated by an energy gap $\Delta E$.

In an NMR experiment, one applies strong homogenous magnetic field causing the nuclei to precess. Radiation of energy comparable to $\Delta E$ is then imposed with radio frequency transmitter is equal to precision or Larmor frequency and the two are said to be in resonance. The energy can be transferred to and from the source and the sample and NMR signal is obtained when a nucleus is excited from low energy to high energy state.

ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

In 1936, Gorter demonstrated that a paramagnetic salt when placed in a high frequency alternating magnetic field, absorbs energy which is influenced by the application of a static magnetic field either parallel or perpendicular to the alternating magnetic field. Since then this
phenomenon has become a technique of immense importance in science.

It is well known that a paramagnetic ion has a magnetic moment and therefore its ground state is degenerate. If this ion is placed in a strong static magnetic field the degeneracy is lifted and the energy levels undergo a Zeeman splitting. Application of an oscillating magnetic field of appropriate frequency will induced transitions between the Zeeman levels and energy is absorbed from the electromagnetic field. If the static magnetic field is slowly varied, the absorption shows a series of maxima. The plot between the absorbed energy and the magnetic field is called the electron paramagnetic resonance spectrum.

A system of charges exhibits paramagnetism whenever it has a resultant angular momentum. Such paramagnetic system includes elements containing 3d, 4d, 4f, 5d, 5f, 6d, etc. electrons, atoms having an odd number of electrons like hydrogen, molecules containing odd number of electrons such as NO₂, NO etc. and free radicals which posses an unpaired electron like CH₃, DPPH etc. are among the suitable candidates for EPR investigation.

Splitting of energy levels in EPR occurs under the effect of two types of fields, namely the internal crystalline field and applied magnetic field. While studying a paramagnetic ion in a diamagnetic crystal lattice, two types of interactions are observed, i.e. interactions between the paramagnetic ions called dipolar interaction and interactions between the paramagnetic ion and the diamagnetic neighbours called crystal field interaction. For small doping amount of paramagnetic ion in the diamagnetic host, the dipolar interaction will be negligibly small. The latter interaction of paramagnetic ion with diamagnetic ligands modify the
magnetic properties of the paramagnetic ions. According to crystal field theory, the ligands influence the magnetic ion through the electric field with they produce at its site and their orbital motion get modified. The crystal field interaction is affected by the electrostatic screening by the outer electronic shells.

The dipole-dipole interaction arises from the influence of magnetic field of one paramagnetic ion on the dipole moments of the neighbouring, similar ions. The local field at any given site will depend on the arrangements of the neighbours and the direction of their dipole moments. Thus the resultant magnetic field on the paramagnetic ion will be the vector sum of the external field and the local field. This resultant field varies from site to site giving a random displacement of the resonance frequency of each ions and thus broadening the line widths.

Hyperfine interactions are mainly magnetic dipole interactions between the electronic magnetic moment and the nuclear magnetic moment of the paramagnetic ion. The quartet structure in the EPR of divalent copper ion and octect in the EPR of vanadyl ion are the results of the hyperfine interactions. The origin of this can be understood simply by assuming that the nuclear moment produces a magnetic field $B_N$ at the magnetic electrons and the modified resonance condition will be

$$E = \hbar \nu = g \beta \left| B + B_N \right|$$

where $B_N$ takes up $2I+1$, where $I$ is the nuclear spin.

There may be an additional hyperfine structure also due to the interaction between magnetic electrons and the surrounding nuclei called superhyperfine structure. The effect was first observed by Owens and Stevens in ammonium chloroiridate and subsequently for a number of
transition metal ions in various hosts²,³ in various hosts.

**ULTRA-VIOLET AND VISIBLE**

**LIGAND FIELDS** SPECTROSCOPY

Most of the compounds absorb light somewhere in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal all the five d orbitals viz. $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{x^2-y^2}$, and $d_{z^2}$ are degenerate. However, in coordination compounds due to the presence of ligands this degeneracy is lifted and d orbitals split into two groups called $t_{2g}$ ($d_{xy}$, $d_{yz}$, and $d_{xz}$) and $e_g$ ($d_{x^2-y^2}$ and $d_{z^2}$) in an octahedral complex and $t$ and $e$ in a tetrahedral complex. The set of $t_{2g}$ orbitals goes below and the set of $e_g$ orbitals goes above the original level of the degenerate orbitals in an octahedral complex. In case of the tetrahedral complexes the position of the two sets of orbitals is reversed, the $e$ going below and $t$ going above the original degenerate level. When a molecule absorbs radiation its energy equal in magnitude to $h\nu$ and expressed by the relation

$$E = h\nu$$

or

$$E = \frac{hc}{\lambda}$$

Where $h$ is Planck's constant, $\nu$ and $\lambda$ are the frequency and wavelength of the radiation, respectively and $c$ is the velocity of light.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon 'Russell Saunder Scheme' must be
introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as 'Term Symbols'.

The orbital angular momentum of electrons in a filled shell vectorically add up to zero. The total orbital angular momentum of an incomplete d shell electron is obtained by adding L value of the individual electrons, which are treated as a vector with the component ml in the direction of the applied field. Thus

\[ L = \sum ml = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \]

S P D F G H I

The total spin angular momentum \( S = \sum S_i \) where \( S_i \) is the value of spin angular momentum of the individual electrons. S has a degeneracy equal to \( 2S+1 \), which is also known as 'Spin Multiplicity'. Thus a term is finally denoted as '8L'. For example, if \( S = 1 \) and \( L = 1 \), the term will be \( 3P \) and similarly if \( S = 1 \frac{1}{2} \) and \( L = 3 \), the term will be \( 4F \).

In general the terms arising from a d\( ^n \) configuration are as follows.

\[
\begin{align*}
d^1 d^9 & : \quad ^2D \\
d^2 d^8 & : \quad ^3F, ^3P, ^1G, ^1D, ^1S \\
d^3 d^7 & : \quad ^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P \\
d^4 d^6 & : \quad ^5D, ^3H, ^3G, ^3F(2), ^3D, ^2P(2), ^1I, ^1G(2), ^1F, ^1D(2), ^1S(2) \\
d^5 & : \quad ^4S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S.
\end{align*}
\]

Coupling of L and S also occurs, because both L and S if non-zero, generate magnetic fields and thus tend to orient their moments with respect to each other in the direction where their interaction energy is least. This coupling is known as 'LS Coupling' and gives rise to the
resultant angular momentum denoted by the quantum number $J$ which may have quantized positive values from $|L+S|$ upto $|L - S|$ e.g. in the case of $^3P$ ($L = 1, S = 1$), $^4F$ ($L = 3, S = 1{\frac{1}{2}}$) possible values of $J$ representing state, arising from term splitting are 2, 1 and 0 and $4{\frac{1}{2}}, 3{\frac{1}{2}}, 2{\frac{1}{2}}$ and $1{\frac{1}{2}}$. Each state specified by $J$ is $2J+1$ fold degenerate. The total number of states obtained from a term is called the multiplet and each value of $J$ associated with a given value of $L$ is called component. Spectral transitions due to Spin-orbit coupling in an atom or ion occurs between the components of two different multiplets while LS coupling scheme is used for the elements having atomic number less than 30, in that case spin-orbital interactions are large and electrons repulsion parameters decrease. The spin-angular momentum of an individual electron couples with its orbital momentum to give an individual $J$ for that electron. The individual $J$'s couple to produce a resultant $J$ for the atom. The electronic transitions taking place in an atom or ion are governed by certain 'Selection Rules' which are as follows

1. Transitions between states of different multiplicity are forbidden.
2. Transitions involving the excitation of more than one electron are forbidden.
3. In a molecule, which has a centre of symmetry, transitions between two gerade or two ungerade states are forbidden.

It is possible to examine the effects of crystal field on a polyelectron configuration. The ligand field splitting due to cubic field can be obtained by considerations of group theory. It has been shown that an S state remains unchanged. P states does not split, a D state splits into
two and F states into three and a G state into four states are tabulated below. This holds for an octahedral ‘Oh’ as well as tetrahedral ‘Td’ symmetry.

\[ S \to A_1 \]
\[ P \to T_1 \]
\[ D \to E + T_2 \]
\[ F \to A_2 + T_1 + T_2 \]
\[ G \to A_2 + E + T_1 + T_2 \]

Transition from the ground state to the excited state occurs according to selection rules described earlier. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse of that for this ion in a tetrahedral field.

Sometimes due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultraviolet region of the spectrum. Such spectra are known as ‘Charge Transfer Spectra’ or redox spectra. For metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transition. However, these should be clearly discerned from the ligand bands which might also occur in the same region.

**Cyclic Voltammetry**

Cyclic voltammetry is used principally to characterize the properties of compounds and to study the mechanisms of redox reactions. In this technique a triangular waveform is applied to the working electrode. Unlike ordinary polarography, in which the ramp is applied over a period of a few
minutes, in cyclic voltammetry the time is on the order of seconds. Furthermore, in cyclic voltammetry the ramp is then reversed to bring the potential back to its initial value at time \( t_2 \) the cycle may be repeated many more times.

Cyclic voltammograms are recorded either with an oscilloscope or with a fast X-Y recorder. The initial portions of the current-potential curves looks like ordinary polarograms, with a residual current followed by a cathodic wave-instead of leveling off at the top of the wave, the current decreases as the potential is increased further. This happens because the electroactive species becomes depleted in the region around the electrode surface. In the copper curve, at the time of the maximum voltage \( t_1 \), the cathodic current has decayed to a fairly small value. After \( t_1 \), the potential change is reversed, but a cathodic current continues to flow because the potential is still negative enough to reduce the analyte. When the potential become sufficiently less negative, the reduced analyte in the layer around the electrode surface begins to be oxidized. This gives rise to an anodic wave. Finally, as the reduced species is depleted, the anodic current decays back toward the initial value of the residual current.

In a reversible electrode reaction, the redox reaction is fast enough to maintain equilibrium concentrations of reactant and product at the electrode surface as the electrode potential is varied. The peak anodic and peak cathodic currents have equal magnitudes in a reversible process, and the difference in potential between the peaks is

\[
E_{pa} - E_p = \frac{2.22 \ RT}{nF} = \frac{57.0}{n} \text{ mV}
\]
where $E_{pa}$ and $E_{pc}$ are potential at which the peak anodic and peak cathodic currents are observed and $n$ is the number of electrons in the half reaction. The halfwave potential, $E_{1/2}$ lies midway between the two peak potentials. With an irreversible reaction, the cathodic and anodic peaks become more drawn out and more separated. At the limit of irreversibility, where the oxidation is very slow, no anodic peak would be seen.

Cyclic voltammetry is widely used to characterize the redox behaviour of compounds and to elucidate the kinetics of electrode reactions and competing chemical reactions. Common electrodes of Pt, C, Au, or Hg permit the study of either oxidations or reductions. Nonaquous solvents such as alcohols, dioxane, acetonitrite, dimethyl sulfoxide, and dimethylformamide are routinely employed with supporting electrolytes such as LiCl, LiClO$_4$ or tetraalkylammonium salts.

**MAGNETIC SUSCEPTIBILITY MEASUREMENTS**

The determination of magnetic moments of transition metal complexes have been found to provide ample information in assigning their structure. The main contribution to bulk magnetic properties arises from magnetic moment resulting from the motion of electrons. It is possible to calculate the magnetic moments of known compounds from the measured values of magnetic susceptibility.

There are several kinds of magnetism in substances viz. diamagnetism, paramagnetism and ferromagnetism, or antiferromagnetism.
Most compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the closed shell electrons with an applied magnetic field. In the closed shell the electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighbouring atoms.

If a substance is placed in a magnetic field \( H \), the magnetic induction \( B \) with the substance is given by

\[
B = H + 4\pi I
\]

Where \( I \) is the intensity of magnetization. The ratio \( B/H \) is called the magnetic permeability of the material and is given by

\[
B/H = 1 + 4\pi(I/H) = 1 + 4\pi K
\]

Where \( K \) is called the magnetic susceptibility per unit volume or volume susceptibility. \( B/H \) is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of the sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum \( B/H = 1 \).

When magnetic susceptibility is considered on the weight basis, the gram susceptibility \( (\chi_g) \) is used instead of volume susceptibility. The \( \mu_{\text{eff}} \) value can then be calculated from the gram susceptibility multiplied by the molecular weight and corrected for diamagnetic value as

\[
\mu_{\text{eff}} = 2.84 \sqrt{\chi \text{ gram}} \cdot \text{T.BM}
\]

Where \( T \) is the absolute temperature at which the experiment is performed.
The magnetic properties of any individual atom or ion will result from some combination of these two properties that is the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus. The magnetic moments are usually expressed in Bohr magnetons (BM). The magnetic moment of a single electron is given by

\[ \mu_s = (\text{in BM}) = g \sqrt{S(S+1)} \]

Where \( S \) is the spin quantum number and \( g \) is the gyromagnetic ratio.

For \( Mn^{2+}, Fe^{3+} \) and other ions whose ground states are \( S \) states there is no orbital angular momentum. In general however, the transition metal ions in their ground state \( D \) or \( F \) being most common, do possess orbital angular momentum. For such ions, as \( Co^{2+} \) and \( Ni^{2+} \), the magnetic moment is given by

\[ \mu_{S+L} = g \sqrt{4S(S+1) + L(L+1)} \]

in which \( L \) represents the orbital angular momentum quantum number for the ion.

The spin magnetic moment is insensitive to environment of metal ion, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and thereby an orbital magnetic moment with reference to a given axis it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis.

For octahedral complexes the orbital angular momentum is absent for \( A_{1g}, A_{2g} \) and \( E_g \) term, but can be present for \( T_{1g} \) and \( T_{2g} \) terms. Magnetic moments of the complex ions with \( A_{2g} \) and \( E_g \) ground terms may depart from the spin only value by a small amount. The magnetic moments of
the complexes possessing T ground terms usually differ from the high spin value and vary with temperature. The magnetic moments of the complexes having a $^6A_{ig}$ ground term are very close to the spin only value and are independent of temperature.

For octahedral and tetrahedral complexes in which spin-orbit coupling causes a split in the ground state an orbital moment contribution is expected. Even no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with higher states can appear due to spin-orbit coupling giving an orbital moment contribution.

Practically the magnetic moment value of the unknown complex is obtained on Gouy magnetic balance. Faraday method can also be applied for the magnetic susceptibility measurement of small quantity of solid samples.

The gram susceptibility is measured by the following formula,

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{\text{std.}}}{\Delta W_{\text{std.}}} \cdot \chi_{\text{std.}}$$

Where  
\[X_g\] = Grams susceptibility  
\[\Delta W\] = Change in weight of the unknown sample with magnet on and off.  
\[W\] = Weight of the known sample.  
\[\Delta W_{\text{std.}}\] = Change in weight of standard sample with magnets on and off  
\[W_{\text{std.}}\] = Weight of standard sample.  
\[\chi_{\text{std.}}\] = Gram susceptibility of the standard sample.
CONDUCTANCE MEASUREMENTS

The conductivity measurement is one of the simplest and easily available techniques used to study the nature of complexes. It gives direct information regarding whether a given compound is ionic or covalent. For this purpose the measurement of molar conductance \( \Lambda_m \) which is related to the conductance value in the following manner is made,

\[
\Lambda_m = \frac{\text{Cell constant} \times \text{Conductance}}{\text{Concentration of solute expressed in mol cm}^3}
\]

Conventionally solutions of \( 10^{-3} \) M strength are used for the conductance measurement. Molar conductance values of different types of electrolytes in a few solvents are given below; A 1:1 electrolyte may have a value of 75-95 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in nitromethane, 50-75 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in dimethyl formamide\(^{14-16}\) and 100-160 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in methyl cyanide. Similarly a solution of 2:1 electrolyte may have a value of 150-180 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in nitromethane, 130-170 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in dimethyl formamide and 140-220 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in methyl cyanide.

ELEMENTAL ANALYSIS

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. Carbon, hydrogen and nitrogen analyses were carried out with a Thomas and Coleman analyser, Carlo Erba 1108. Sulphur and chlorine were analysed by conventional
methods. For the metal estimation, a known amount of complex was decomposed with a mixture of nitric, perchloric and sulphuric acids in a beaker. It was then dissolved in water and made up to a known volume so as to titrate it with standard EDTA. For sulphur and chlorine estimation, a known amount of the sample was decomposed in a platinum crucible and dissolved in water with a little concentrated nitric acid. The solution was then treated with either silver nitrate or barium chloride solution. The precipitate was dried and weighed.
REFERENCES


7. C.J. Gorter, Physica, 1936, 3, 1006


