CHAPTER II

EXPERIMENTAL METHOD
General: A wide variety of methods of variable precision and dependability are available for determining the structure of coordination compounds. These may be roughly divided into three groups:

a) Spectroscopic methods;
b) Macroscopic physical methods;
c) Chemical methods.

The Spectroscopic Method: It generally provides specific structural information of high precision. The important methods of this group are:

1) Infrared and Raman spectroscopy
2) Ultraviolet and visible (electronic) spectroscopy
3) Magnetic Resonance methods; viz.; Nuclear Magnetic Resonance and Electron spin Resonance
4) Diffraction method and,
5) Mass spectrometry.

Macroscopic Physical Methods: These methods indicate the general structure type rather than giving structural details. These involve measurement of gross physical properties such as melting point, boiling point, vapour pressure, electrical conductivity and magnetic susceptibility.
**Chemical Methods:** These methods are based on the chemical reaction of the compounds. The reliability of these methods is generally low and the information needs to be carefully examined. In the present work the following methods have been used to obtain structural informations.

1) Conductance measurements
2) Magnetic susceptibility measurements
3) Infrared spectral studies
4) Ultra-violet and visible spectral studies.

**Electrical conductivity** - The conductivity measurement is the simplest and most easily available technique for the characterization of compounds. It gives direct information regarding the ionic or covalent nature of a compound. The measurement of molar conductance ($\Lambda_m$) which is related to the conductance value is made in the following manner:

$$\Lambda_m = \frac{\text{Cell constant} \times \text{conductance}}{\text{Concentration of solute expressed in moles cm}^{-3}}$$

Generally solutions of approximately $10^{-3}M$ strength are used for the conductance measurement.

**Electrical conductivity in chlorosulphuric acid** - Walden$^1$ determined the specific conductivity of chlorosulphuric acid and found a value of $1.72 \times 10^{-4} \text{ esm}^{-1} \text{ cm}^{-1}$ at 25°C. Later Robinson and Ciruna$^2$ reported that the reagent grade chlorosulphuric acid (BDH, England) has a specific conductivity value of about
4.00 x 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ at } 25^\circ \text{C}. \text{ This acid was found suitable for conductance studies of most of the electrolytes.}

Theory of Electrical Conductivity in Chlorosulphuric Acid - The specific conductance \( (\kappa) \) of a solution is defined as follows:

\[
\kappa = \frac{1}{R_s}
\]

where \( R_s \) = specific resistance.

Since the resistance of any conductor

\[
R = R_s \frac{1}{a} \text{ Ohm}
\]

where \( l \) = distance between electrodes and

\( a \) = area of electrodes

On substituting \( R_s \) from equation (41) into the equation (42) it becomes

\[
R = \frac{1}{R} \frac{1}{a} \text{ Ohm}^{-1} \text{ cm}^{-1}
\]

where \( R \) is the resistance and \( \frac{1}{a} \) is the cell constant. For a solution containing ionic species \( 1, 2, 3, \ldots \) of concentration \( C_1, C_2, C_3, \ldots \). \( C_1 \) moving under potential gradient of one volt percentimeter, the velocities of ions \( U_1, U_2, U_3, \ldots \). \( U_1 \) are known as absolute ion mobilities. The relation between the absolute mobilities of the ions and the specific conductance under such condition is given by the relation

\[
\kappa = \frac{F}{1000} \sum C_1 Z_1 U_1
\]

where \( Z_1 \) is the charge carried by the \( i \)th ions and \( F \) is the
Faraday constant.

From the definition of ionic mobility ($t_i$) as

$$t_i = \frac{\mu_i}{m_i}$$

the equation (43) becomes

$$\mathcal{K} = \frac{1}{1000} \sum C_i z_i t_i$$

$$\mathcal{K} = \text{specific conductance in } \Omega^{-1} \text{cm}^{-1}$$

**The Cell Constant**

For a given cell the ratio $1/a$ is defined as the cell constant represented by $G$, then

$$G = R \mathcal{K}$$

where $R$ and $\mathcal{K}$ are resistance and specific conductance of the solutions respectively.

**Determination of Cell Constant** - The cell constant was first determined according to the method suggested by Jones and Bradshaw by using potassium chloride solution of known specific conductance. However, since the minimum conducting sulphuric acid is well established, we calibrate our cells using this secondary standard. The cell constant is given by the equation

$$G = 0.010433 \times \frac{1}{3}$$

where 3 is the minimum observed conductance for $H_2O-SO_3$ system.

**Apparatus and experimental techniques** - The cell as designed by Solomons was used for the conductivity measurements (Fig.3).
CONDUCTIVITY CELL

Fig. 3
The typical cell consists of a tube approximately 10 cm long containing the electrodes and joining two 100 ml conical flasks. The electrodes were made from platinum foil (1 cm²) and were firmly fixed on the tube so that no displacement could occur. The conical flasks were fitted with socket (B - 14 standard joint) and were capped (B-14 standard joint) to exclude all moisture from the cell.

**Preparation of Electrode**

To eliminate electrode polarization resistance, it is necessary to cover the electrode with platinum black. The electrodes were platinized by electrolyzing the solution of chlor platiniac acid with a current of 20 milliamperes, reversing after every thirty seconds for about half an hour. After heavy coating the electrodes were annealed in a hot flame and then replatinized for another ten minutes. Thus stable deposits of platinum were obtained which did not flake over.

**Thermosat:**

The conductance measurements were carried out at 25 ± 1°C in a thermostat whose temperature was regulated by an automatic thermometer.

**General technique**

In order to carry out a series of conductivity measurements, a weighed amount of about 40 to 100 gms of the acid was taken in the previously cleaned and dried cell. Small known amounts of the solutes were added by means of a tube or a weighed
pipette depending on whether the solutes were solid or liquid. The solute was thoroughly mixed with the solvent in the cell by swirling the cell. Care was also taken to keep the caps of the conical flasks tightly closed so as not to allow escape of any gas from the cell. The conductivity of the solution was measured by the conductivity bridge (Systronic type 302).

**Determination of \( Y \) - values from conductometric measurements**

The number of moles of the anion \( \text{SO}_3\text{Cl}^- \) or the cation \( \text{H}_2\text{SO}_3\text{Cl}^+ \) of a solvent, self dissociation produced by each mole of the solute in chlorosulphuric acid\(^2\) is given by the symbol \( Y \). Its value can be determined from conductometric measurements in chlorosulphuric acid. It has been suggested that most of the current in the solution is carried by the \( \text{SO}_3\text{Cl}^- \) and/or \( \text{H}_2\text{SO}_3\text{Cl}^+ \) ions which conduct by an abnormal proton transfer mechanism similar to that found for \( \text{HSO}_4^- \) and \( \text{H}_3\text{SO}_4^+ \) in \( \text{H}_2\text{SO}_4 \) and \( \text{SO}_3\text{F}^- \) and \( \text{H}_2\text{SO}_3\text{F}^+ \) ion in \( \text{HSO}_3\text{F}^- \). Since it is known that potassium chloride behaves as a strong electrolyte in chlorosulphuric acid\(^2\) producing one mole of \( \text{SO}_3\text{Cl}^- \) per mole of the solute, the \( Y \) values of a base is determined by comparing its concentration with the concentration of potassium chloride that gives the same specific conductance i.e. (in Fig. 4).

\[
Y = \frac{0_y}{0_x} \quad (48)
\]

where \( 0_x \) is the concentration of the base and \( 0_y \) is the concentration of KCl which gives the same specific conductance as the base.
DETERMINATION OF $\gamma$ VALUE

$$\gamma = \frac{\text{# of moles of SO}_3\text{Cl} \text{ or H}_2\text{SO}_3\text{Cl}^+}{\text{moles of solute}}$$

![Diagram showing specific conductance vs concentration for KCl and Base. The ratio $\gamma = \frac{OY}{OX}$ is highlighted.](image)

Fig. 4
Infrared Spectroscopy

Infrared spectroscopy is a very useful technique to study molecular structure. A vast majority of the spectra of interest result from absorption experiments. Infrared absorption only occur for such movements (vibration or rotations) as are connected with an alteration of dipole moment of a certain molecule. The absorption of the infrared radiation sets the molecule into vibrational or rotational motion or a combination of both. Only certain discrete frequencies of vibration or rotation are permitted, the frequencies of the radiation which are absorbed or emitted must correspond to these frequencies.

A molecule having \( N \) atoms can undergo \( 3N - 6 \) fundamental modes of vibration (or \( 3N - 5 \) if it is a linear molecule). Each of these fundamental modes has associated with it a ground state energy, \( E = \hbar \nu \). In addition, vibration of higher frequencies can be excited with energy \( E = (n + \frac{1}{2}) \hbar \nu \) \( [n = 1, 2, 3, \ldots] \). The molecule is raised to the first excited level of the second normal mode of vibration by absorbing a photon having energy equal to the difference between subsequent levels. A photon of somewhat lower energy is required to excite the first mode, and the one of the higher energy excites the third mode. These three constitute the fundamental vibrational absorption spectrum of the molecules. Not all normal modes can be excited by the absorption of radiation. The vibrational selection rule dictated by the symmetry of a molecule determines
the spectroscopic activity, i.e., the occurrence of and non-occurrence of any vibration in the spectrum. These selection rules limit the changes in $3N-6$ modes of vibration in the following manner.

1. Only one of the quantum numbers can change a transition between vibrational levels arising from the emission or absorption of radiation.

2. The above change $\Delta v$ is +1 or -1.

3. For vibrations involving no change in dipole moment, $\Delta v$ must always be zero.

The above rules plainly indicate that each frequency observed in the spectrum is identical with the frequency of one of the molecular vibrations.

In addition to the characteristic frequencies, a spectrum also shows overtone and combination of absorption which arise from multiples of fundamental frequencies or sum and difference of such frequencies. Normally overtone and combination of absorptions are considerably weaker than the fundamental frequencies and are not of much significance.

The infrared radiation is usually said to have wave length lying between 0.8 $\mu$ to 1000 $\mu$. The wave number i.e., the number of wave per centimeter is used to characterize the radiation. It is from about 10,000 cm$^{-1}$ to 100 cm$^{-1}$ for the IR region.
The characteristic infrared frequencies found useful in the present discussion are as follows:

The infrared spectra of chlorosulphuric acid in solid, liquid and also in the vapour state at temperature up to 60°C were first obtained and examined by Savoie and Giguere. They suggested the dimerization of the acid even in vapour state. However, Chackalackal and coworkers have reported the infrared spectra of HSO₃Cl monomer as well as in associated form. The frequencies observed in the infrared spectra of the monomer have been assigned by these workers as characteristic of SO₂ rocking, S-Cl stretching, S-O-H stretching, SO₂ symmetric stretching, SO₂ asymmetric stretching and OH stretching vibrations. It was later indicated that the SO₃Cl⁻ ion which has C₃v symmetry is expected to exhibit six modes of vibrations, all of which should be infrared as well as Raman active. These have been conveniently described as a symmetric SO₃ stretching ν₁(A) and asymmetric SO₃ stretching ν₄(E), a symmetric SO₃ bending ν₃(A) and asymmetric SO₃ bending ν₅(E), S-Cl stretching ν₂(A) and S-Cl wagging ν₆(E). It has been shown from the study of a few alkali or alkaline earth metal chlorosulphates that the position of these characteristic bands are not much altered excepting for the symmetric SO₃ stretching ν₁(A) vibration which however, undergoes a shift to higher energy if there exists an increased interaction between the metal ion and the chlorosulphate group.
Ring vibration

Pyridine

The vibrational spectrum of pyridine shows three important ring vibrations, i.e., 16b (out of plane ring deformation) 6a and 8a (in plane ring deformation) observed at 403, 601 and 1578 cm\(^{-1}\) respectively\(^{11}\). All the three bands suffer considerable positive shifts on coordination of pyridine to metal ions and the magnitude of the shift depends on the stereochemistries of the complexes and one the metal atoms. The band at 601 cm\(^{-1}\) has been suggested to be more sensitive to the stereochemistry of the complexes. In tetrahedral, polymeric octahedral and octahedral complexes, it appears at 642, 631 and 625 cm\(^{-1}\) respectively\(^{12}\). In a few complexes, the doubling of above mentioned bands have also been reported which has been suggested to be due to intermolecular or intramolecular interaction of pyridine molecules of the unit cell.

2,2'-Bipyridine

The three important ring vibrations in the 2,2'-bipyridine, the out of plane ring deformation 16b and inplane ring deformation 6a and 8a, occur at 402, 619 and 1590 cm\(^{-1}\) respectively\(^{13}\). It has been reported that the two bands at lower wave length are very sensitive and after complexation undergo considerable positive shift.
Acridine:

The two strong bands observed at 1515 and 1555 cm\(^{-1}\) in the i.r. spectrum of the free acridine are attributable to \(\nu_C = C\) and \(\nu_{C=N}\) stretching vibration respectively\(^{14}\). It has been shown that a positive shift of about 75 cm\(^{-1}\) and 100 cm\(^{-1}\) is observed for the \(\nu_C = C\) and \(\nu_{C=N}\) vibrations respectively upon complexation of acridine to the metal ions, suggesting the coordination through the nitrogen atom of the pyridyl group\(^{14,15}\).

C-N Stretching

The C-N stretching absorption gives rise to strong bands in the region 1350-1350 cm\(^{-1}\) in all the amines.

N-H Stretching

The N-H stretching vibrations occur in the region 3500-3300 cm\(^{-1}\) in dilute solutions\(^{16}\). The N-H stretching bands shift to lower values in the solid state due to extensive hydrogen bonding. Primary amines in the dilute solution in non-polar solvents give two absorption bands in the above mentioned region. The first band arising from the symmetric stretching is usually found nearly at 3500 cm\(^{-1}\) and the second which arises from the corresponding asymmetrical mode is found at nearly 3400 cm\(^{-1}\). These bands are usually 125-150 cm\(^{-1}\) apart.

N-H deformation

For the deformation frequencies of the NH\(_2\) group in primary amines four characteristic peaks should appear. But the
only definite assignment has been done in the case of scissoring vibration, generally observed in the region 1650-1590 cm\(^{-1}\)\(^{17}\). The lower frequency deformation vibrations of the NH\(_2\) group have not been investigated in detail. The NH\(_2\) twisting, wagging and torsional vibrations in methyl amine have, however, been assigned to 1455, 780 and 264 cm\(^{-1}\) respectively.

**M-N Stretching Vibrations**

The metal nitrogen stretching frequencies is of particular interest since it provides direct information regarding the coordination. It appears in low frequency region. The M-N stretching frequency depends on the following factors:

1. Mass of the metal and ligand,
2. Oxidation number of the metal ions
3. Coordination of metal ions
4. Geometry of the complex
5. Basicity of the ligand molecule
6. Bridging or non bridging anion
7. Ligand field stabilizing energy.

Recently i.r. spectroscopic studies have been used for characterizing the various solid metal and non-metal fluorooand chlorosulphates by studying the characteristic fluorosulphate and chlorosulphate group frequencies\(^{10,13,21}\).

**Experimental technique**

It has been shown that AgCl prism can be used as a window material for studying strong acid solution\(^{22}\). Thin layer polyethylene and teflon sheets have also been successfully used by some workers\(^{20-23}\). In the present studies i.r. spectra of the solid compounds milled in Fujol have been recorded on a Perkin-
Elmer Model 621 and 735 spectrophotometer at room temperature. The mulls were pressed into a homogeneous thin film in an envelope cell made up of polyethylene sealed from all sides. All manipulations were carried out in a dry box filled with dry nitrogen. Although there is a high background absorption of the polyethylene, it is transparent enough in the 1500-2000 cm⁻¹ range to enable the study of the characteristic chlorosulphate vibration which occur in this region.

**Magnetic susceptibility measurements**

Magnetoochemistry finds its most rewarding application to the problems dealing with the coordination compounds. It is possible to calculate the magnetic moment of unknown compounds from the measured values of magnetic susceptibility. Useful information regarding the assignment of suitable structure in the molecule is obtained by the proper interpretation of the magnetic moments.

Generally the following types of magnetic behaviour are found in chemical substances (i) paramagnetism, (ii) diamagnetism, (iii) ferromagnetism and (iv) anti ferromagnetism. The magnetic effect that arises from the motions of the electrons is known as diamagnetism and the spin and orbital angular moments of electrons give rise to the phenomenon of paramagnetism. Ferromagnetism or antiferromagnetism arises as a result of interaction between dipole of neighbouring atoms.
The possession of the spin and orbital angular momentum forms an atomic system into micromagnetic dipole with a moment:

$$\mu = (L + 2S) \beta b$$  \hspace{1cm} (49)

where \(L\) and \(S\) stand for total angular and total spin angular moment (in units of \(h/2\pi\)) respectively and \(\beta b\) is Bohr magneton.

For the case when spin-orbit coupling can be essentially neglected, that is, the multiplet splitting of the ground term is compared with \(K\) (\(\lambda \ll K\) where \(\lambda\) is spin orbit coupling constant), the effective magnetic moment is given by

$$\mu_{\text{eff}} = \left[ L(L+1) + 4S(S+1) \right]^{\frac{1}{2}} \text{B.M.}$$  \hspace{1cm} (50)

In another extreme where \(\lambda \gg K\) and the multiplicity splitting is so great that virtually all ions are in the ground component of multiplet for the usual temperature of measurements,

$$\mu_{\text{eff}} = g [J(J+1)]^{\frac{1}{2}} \text{B.M.}$$  \hspace{1cm} (51)

where \(g\) is the Lande factor and is given by the expression:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$  \hspace{1cm} (52)

where \(J, S\) and \(L\) are total angular momentum, total spin angular momentum and total orbital angular momentum. While this expression describes the value of \(\mu_{\text{eff}}\) for the rare earth complexes, the equation often applied for the complexes of transition metals is:
\[ \mu_{\text{eff}} = \left[ L (L + 1) + 4S (S + 1) \right]^{1/2} \text{B.M.} \quad (53) \]

It is, however, only valid for complexes of \( \text{Co}^{2+} \) and \( \text{Ni}^{2+} \) and generally pure spin formula given below is used.

\[ \mu_{\text{eff}} = [4 S (S + 1)]^{1/2} \text{B.M.} \quad (54) \]

i.e., the orbital angular momentum contribution is neglected. While spin magnetic moment is insensitive to environment of metal ions, 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 fully equivalent orbital by rotation about that axis.

Practically the magnetic moment value of an unknown complex is obtained from the measured magnetic susceptibility which is defined as follows:

If a magnetic field is applied to a substance, then the flux \( B \) within the substance is given by a formula:

\[ B = H + 4 \pi I \quad (55) \]

where \( H \) is the magnitude of the applied field and \( I \) is known as the intensity of magnetization. The magnetic permeability is \( B/H \) and is given by

\[ \frac{B}{H} = 1 + 4 \pi \left( \frac{I}{H} \right) = 1 + 4 \pi K \quad (56) \]
K is called volume susceptibility. Conventionally, instead of volume susceptibility, gram susceptibility ($\chi_g$) is used, where magnetic susceptibility is considered on the weight basis. $\chi_g$ when multiplied by the molecular weight of the complex and corrected for diamagnetic value gives rise to $\chi_M^{\text{corr}}$. The $\mu_{\text{eff}}$ value is calculated from $\chi_M^{\text{corr}}$ by expression

$$\mu_{\text{eff}} = 2.84 \left( \chi_M^{\text{corr}} \times T \right)^{\frac{1}{2}} \text{B.M.} \quad (57)$$

T is absolute temperature at which the experiment is performed.

Magnetic susceptibility may or may not be dependent on temperature. A relationship for paramagnetic susceptibility and temperature is given by Curie’s law $\chi_M = C/T$ where C and T are Curie constant and absolute temperature. Magnetic moment should not depend on temperature for complexes where this law is valid. In general, however, deviations are found and $\mu_{\text{eff}}$ values depend on temperature. Within a certain temperature range ($30 - 40^0 K$) the dependence of $\chi_M$ upon T is represented by

$$\chi_M = \frac{C}{T - \theta} \quad (C = \text{Curie Weiss Constant}) \quad (58)$$

**Experimental technique**

The present compounds were analysed on a Vibrating Sample Magnetometer Model 155 which directly gives the values without diamagnetic correction with the help of the following equations:

$$\mu_{\text{eff}} = \sqrt{2.84 \frac{R}{W \cdot M} \times T \times M} \quad (59)$$
\[ R = \text{Reading on magnetometer} \]
\[ T = \text{Temperature (A)} \]
\[ M = \text{Molecular weight of the substance} \]
\[ W = \text{Weight of the sample} \]
\[ H = \text{Applied magnetic field in gauss.} \]

Magnetic measurement of a few compounds was also carried out by using the Gouy method at 383°C as given below:

The solid compounds were finally powdered and filled in the Gouy tube very carefully in a dry box filled with dry nitrogen. The tube containing the material was a suspended vertically between the poles of an electromagnet. The length of the tube was so adjusted that its lower end remained under the influence of magnetic field. The weight of the tube containing the sample was known with the magnet on and off. The Gouy tube was calibrated with standard \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \).

The gram susceptibility was calculated by the following formula.

\[
\chi_g = \frac{\Delta W_{\text{unk.}} W_{\text{std}}}{W_{\text{unk.}} \Delta W_{\text{std}}} \times \chi_{\text{std}} \quad (60)
\]

\( W_{\text{corrected}} = \Delta W (\text{sample + tube}) - \Delta W (\text{empty tube}) \)

\( \chi_g \) = gram susceptibility of unknown

\( \Delta W_{\text{unk.}} \) = change in the weight of the unknown with magnet on and off.

\( W_{\text{unk.}} \) = weight of unknown
\( \Delta W_{\text{std.}} = \) change in the weight of standard with magnet on and off

\( W_{\text{std.}} = \) weight of the standard

\( \chi_{\text{std.}} = \) gram susceptibility for the standard

(5.92 x 10^{-6}) for CuSO_4·5H_2O)

The molar susceptibility (\( \chi_m \)) of the compound was calculated from gram susceptibility multiplying it with molecular weight of the compound. The diamagnetic correction of 40.1 x 10^{-6} C.G.S. unit was used for SO_3Cl^- ion. The value has been obtained by assuming that the correction for SO_3Cl^- ion would be the same as that for the isostructural SO_3F^- and SO_4^2- ions. The corrected value of \( \chi_m \) was substituted in the following formula and the effective magnetic moment (\( \mu_{\text{eff}} \)) was calculated.

\[ \mu_{\text{eff}} = 2.84 (\chi_m \text{ corr. } T)^{1/2} \]  

(61)

4. Ultra-violet and visible (electronic) spectroscopy:

When a molecule absorbs radiation its energy is increased. This increased energy is equal to the energy of photon expressed by the relation

\[ E = h\nu \]

or \[ E = hC/\lambda \]

(62)

where \( h \) is Planck's constant \( \nu \) and \( \lambda \) are the frequency and wave length of the radiation respectively and \( C \) is the velocity of light.
Most of the compounds absorb light somewhere in the spectral region between 200 to 1000 nm. These transitions correspond to the excitation of electrons of molecule from ground state to higher state.

When a molecule absorbs radiation, the absorption spectra of rare earth metal compounds arise from electronic transition within 4f levels. These transitions occur after removal of degeneracy in the 4f orbitals in the presence of external crystal field. The rare earth metal ion differs from each other by number of electrons in the 4f orbitals which are effectively shielded from interaction with ligand and metal by electron in the 5s and 5p orbital. However, in case of transition elements where d electrons take an active part in bonding and a change in the environment of central metal ions frequently causes a substantial variation in the absorption spectra, whereas such effects are less drastic in the lanthanide series.

The absence of significant interaction between ligand and 4f orbital is supported by observation that complexing groups have only small effects upon the magnitude of the permanent magnetic moment of the tripositive ion$^{24-28}$ or upon the positions of their sharply defined characteristic absorption bands in the u.v.-visible region$^{27-32}$. A comparison of the absorption spectra of variety of rare earth metal complexes with that of the lanthanide ions provides three important
distinguishable features which are thought to be the result
of superimposing fields of different strength around the
lanthanide ions. These are

(1) in the complexes the observed bands are generally shifted
to higher wave number although cases of "blue shift" has also
been reported.

(2) there is splitting of certain of the bands into several
small maxima, and

(3) there is variation in the specific absorptivity of an
individual peak.

However, when the lanthanide ions are in the presence of the
species that can not be expected to associate strongly the
spectra remain unchanged.

The usefulness of absorption spectrum analysis to
ascertain the nature of bonds between the central lanthanide
ion and the ligand donor group is limited. As the 4f levels
are little effected by change in the environment, the absorp­
tion spectra are substantially identical whether the ion is
solvated or not associated with chelating agents. The small
splitting of characteristic absorption are in no doubt due to
the effect of crystal fields upon the J levels of the central
ions. It has been suggested by Jorgenson that the occurrence
of slight shift in the absorption bands are due to the effect
of crystal fields upon certain parameters related to the inter-
electronic repulsion among the 4f electrons.

**Experimental Techniques**

Diffused reflectance spectra of the present compounds were recorded on a Carl-Zeiss VSU-2P spectrophotometer using MgO as reflectance standard at 25°C. The u.v.-visible spectra for the sodium selenite and sodium tellurite in chlorosulphuric acid recorded on a Pye Unicam Model PU - 8800 Spectrophotometer.
REFERENCES


31. O. Bometsa Suomen Kemistilehti, 317, 30 (1944).