CHAPTER II

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The following techniques were employed to characterize the complexes

1. Infra-red spectroscopy
2. Ultra-voilet and visible (ligand-field) spectroscopy
3. Nuclear magnetic resonance spectroscopy
4. Electron paramagnetic resonance
5. Molar conductance measurements
6. Polarimetry
7. Cyclic voltammetry
8. Kinetic studies

Infra-red spectroscopy

The infrared spectroscopy is a useful technique to characterize a compound. It results from transition between vibrational and rotational energy levels. IR region of the electromagnetic spectrum covers a wide range of wavelength from 200 cm$^{-1}$ to 4000 cm$^{-1}$. It has been found that in IR absorption some of the vibrational frequencies are associated with specific groups of atoms and are the same irrespective of the molecules in which this group is present. These are called characteristic frequencies$^{189}$ and their constancy results from the constancy of bond force constants from molecule to molecule. The
important observation that the IR spectrum of a complex molecule consists of characteristic group frequencies which makes IR spectroscopy an unique and powerful tool in structural analysis.

**Ultraviolet and visible spectroscopy**

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

\[ E = hv \]

\[ = hc/\lambda \]

where \( h \) is Plank's constant, \( v \) and \( \lambda \) are the frequency and wavelength of the radiation respectively and \( c \) is the velocity of light. Most of the compounds absorb light 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. \( d_{xy}, d_{yz}, d_{xz}, d_{z^2} \) and \( d_{x^2-y^2} \) are degenerate. However, in coordination compounds due to the presence of ligands, this degeneracy is lifted and \( d \) orbitals split into two groups \( t_{2g} \) (\( d_{xy}, d_{yz} \) and \( d_{xz} \)) and \( e_g \) (\( d_{z^2} \) and \( d_{x^2-y^2} \)) in an octahedral complex and \( t \) and \( e \) in a tetrahedral complex. The set of \( t_{2g} \) orbitals goes below the original level of degenerate orbitals in octahedral complexes and the case is reversed in tetrahedral complexes.

Sometime 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.

**Nuclear Magnetic Resonance**

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 $^1H$, $^{31}P$ and $^{19}F$.

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. 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 $\Delta E$.

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 Spin Resonance**

EPR spectroscopy is the branch of absorption spectroscopy in which radiation having frequency in the microwave region is absorbed by paramagnetic energy levels of electrons with unpaired spins. The magnetic
energy splitting is done by applying a static magnetic field.

For an electron of spin $S = 1/2$, the spin angular momentum quantum number will have values of $m_s = +1/2$. In absence of magnetic field, the two values of $m_s$ i.e. $+1/2$ and $-1/2$ will give rise to a doubly degenerate spin energy state. If a magnetic field is applied, this degeneracy is lifted and leads to the non-degenerate energy levels. The low energy level will have the spin magnetic moment aligned with the field and correspond to the quantum number $m_s = -1/2$. On the other hand, the high energy state will have the spin magnetic moment opposed to the field and correspond to the quantum number $m_s = +1/2$.

**Conductance measurements**

The conductivity measurements 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,

$$\Lambda_m = \frac{\text{cell constant x conductance}}{\text{concentration of solute expressed in mol cm}^{-3}}$$
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 has a value of 75-95 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in nitromethane, 50-75 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in dimethylformamide 78-80 and 100-160 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in methylcyanide. Similarly, a solution of 2:1 electrolyte has a value of 150-180 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in nitromethane, 130-170 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in dimethylformamide and 140-220 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in methyl cyanide.

**Polarimetry**

Optical isomerism manifests itself by the rotation that certain molecules impart to the plane of polarized light when in gaseous, liquid or molten state or in solution. This rotation is observed and measured by a rather simple instrument, known as polarimeter. The specific rotation $[\alpha]$ of a dissolved substance is given by the expression

$$[\alpha] = \frac{\alpha}{l \times c}$$

where $\alpha$ is the observed rotation in degrees

- $l$ is the path length of the sample in decimeters
- $c$ is the concentration in grams per milliliter
The dependence on wavelength and temperature is indicated by subscripts and superscripts respectively. Thus $[\alpha]^{25}$ means the specific rotation at $25^\circ C$ measured at the wavelength of the sodium D line.

Optical rotation is generally measured using light from a sodium-vapour lamp, which gives essentially monochromatic radiation (the yellow sodium D line is a doublet at 5890 and 5896 A). A beam of light is polarized by passage through nicol prism (the polarizer), which consists of two calcite prisms cemented together so that only one of the two rays formed by double refraction is transmitted. The beam of polarized light passes through the solution and then through a second nicol prism. When no optically active material is placed between the prisms ($0^\circ$ rotation), the prisms are positioned at right angles so that no light is transmitted. When an optically active material is placed between the prisms, the analyzer must be turned in order to maintain the darkness in the field of view. The optical rotation is the angle by which the analyzer is turned in order to reach darkness. It is very difficult to determine by eye the setting for complete darkness, because positions near the completely dark position are very dark. Therefore, many instruments are constructed such that the field of view is divided into two equal parts, and the analyzer is adjusted so as to equalize the light intensity in each half of the field.
Cyclic voltammetry

Cyclic voltammetry involves the measurement of current-voltage curves under diffusion controlled, mass transfer conditions at a stationary electrode, utilizing symmetrical triangular scan rates ranging from a few millivolts per second to hundred of volts per second. The triangle returns at the same speed and permits the display of a complete polarogram with cathodic (reduction) and anodic (oxidation) waveforms one above the other. Two seconds or less is required to record a complete polarogram. (Fig. 17).

Consider the reaction

\[ \text{O} + \text{ne} \rightarrow \text{R} \quad \text{(i)} \]

Assuming semi-infinite linear diffusion and a solution containing initially only species O. With the electrode held at a potential \( \text{E}_i \), where no electrode reaction occur.

The potential is swept linearly at \( v \) v/sec so that the potential at any time is

\[ \text{E}(t) = \text{E}_i - vt \]

or \[ \text{E}_{\text{peak}} = \text{E}_{1/2} - 0.0285 \]
The rate of electron transfer is so rapid at the electrode surface that species O and R immediately adjust to the ratio according to the Nernst equation which is as follows

\[ C_0(0,t) = C^*_0 - \left[ nF\pi D_\sigma \right]^{1/2} \int_0^t \frac{1}{t^1/2} \mathrm{d}t \]

\[ i = nFAC^*_0 (\pi D_\sigma^{1/2} \sigma \sigma) \]  

The measured parameters of interest on these i-E curves (cyclic voltammograms) are \( i_{\text{pa}} / i_{\text{pc}} \), the ratio of peak currents, and \( E_{\text{pa}} - E_{\text{pc}} \), the separation of peak potentials. For a Nernstian wave with stable product, the ratio \( i_{\text{pa}} / i_{\text{pc}} = 1 \) regardless of scan rate, \( E_{\text{h}} \) and diffusion coefficients, when \( i_{\text{pa}} \) is measured from the decaying current as a base line.
The difference between $E_{pa}$ and $E_{pe}$ ($\Delta E_p$) is a useful diagnostic test of a Nernstian reaction. Although $\Delta E_p$ is slightly a function of $E_\lambda$, it is always close to $2.3RT/nF$.

The technique yields information about reaction reversibilities and also offers a very rapid means of analysis for suitable systems. The method is particularly valuable for the investigation of stepwise reactions and in many cases, direct investigation of reactive intermediates.

**Kinetic studies**

In a closed constant volume system, the rate of a chemical reaction is defined as the rate of change with time of the concentration of any of the reactants and products. The concentration can be expressed in any units of quantity per unit volume e.g. moles per liter, moles per cubic centimeter. The rate will be defined as positive quantity regardless of the component whose concentration change is measured.

Consider the general chemical reaction

$$aA + bB \rightarrow cC + dD$$

The rate can be expressed as

$$\frac{-dA}{dt}, \frac{-dB}{dt}, \frac{dC}{dt}, \text{ or } \frac{dD}{dt}$$

where A, B, C and D designate the concentration in arbitrary units.
The rate of a chemical reaction is not measured directly instead the concentration of one of the reactants or products is determined as a function of time. A common procedure for determining the reaction order is to compare the experimental results with integrated rate equations for reactions of different orders. For a first order rate equation, integrating by separate variables using integration limits such that at $t = 0, c = c_o$ and at $t = t, c = c$.

$$-\frac{dc}{dt} = kc$$

or

$$\ln \left( \frac{c_o}{c} \right) = kt$$

If the reaction is first order, a plot of $\ln c$ or $\log c$ versus time should give a straight line with a slope of $-k$ or $-k/2.303$ respectively (Fig. 18). The dependent variable chosen is the decrease in concentration of reactant. If this variable is designated as $x$ and $c_o$ is the initial concentration,

$$\frac{dx}{dt} = k(c_o-x)$$

$$\ln \frac{c_o}{(c_o-x)} = kt$$

Fig. 18
If, however, the conditions for a given reaction are such that one or more of concentration factors are constant or nearly constant during a reaction, these factors are included in the constant $k$. In this case, the reaction is said to be of pseudo-nth order or kinetically of nth order where $n$ is the sum of the exponents of those concentration factors which alter the reaction. This situation is true for catalytic reactions where the concentration of catalysts remains constant throughout the reaction, if one reactant is in large excess over another so that during the reaction there is only a small percentage change in the concentration of the former reactant.

All kinetic experiments were performed at room temperature under pseudo-first order conditions using a systronic 119 spectrophotometer. For the interaction of the complexes with DNA, the buffer containing tris(hydroxymethyl)aminomethane hydrochloride (5 mmol dm$^{-3}$), NaCl, pH-7.0 (50 mmol dm$^{-3}$) with varying DNA concentrations was used. A solution of Calf Thymus DNA in the buffer gave ca. 1.91:1 ratio of UV absorbances at 260 and 280 nm.

In another set of kinetic experiments, the absorbance changes of Co$^{II}$ complexes at 428 nm and 620 nm ($\lambda_{\text{max}}$ of Co$^{II}$) respectively, under varying concentrations of oxygen (1 x $10^{-3}$ to 5 x $10^{-3}$) mol$^{-1}$ dm$^{-3}$ was monitored spectrophotometrically. Pseudo-first order rate constants ($k_{\text{obs}}$) were obtained by linear least square regression method.