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Techniques of Characterizing Inorganic Complexes

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ABSTRACT

Structural characterization methods in Inorganic Chemistry are tools that lead every synthetic chemist to the final destination of synthesis. Therefore, in this article, the various methods of elucidating newly prepared ligands and the corresponding complexes are discussed. The methods, ranging from spectroscopic to non-spectroscopic have been discussed in principle, functions and uses.

Introduction

There is no doubt about the fact that the end of every organic synthesis is the beginning of co-ordination chemistry. This statement is born out of the fact that every inorganic synthetic chemist must prepare novel organic compounds (ligands) before onward co-ordination with metal ions to give the desired complexes. However, the organic compound (ligand) and the desired complex obtained must be structurally characterized before moving further to test the compounds for their possible applications. In structural characterization techniques, there are various methods that can be used to elucidate the bonding, structure and stereochemistry of the ligands and the complexes prepared. While the ligands are characterized by usual methods such as elemental analysis, infrared (IR), ultraviolet (UV) -visible and nuclear magnetic resonance (NMR) spectral techniques, it differs for complexes depending on the nature of the ligands and the metal ions involved. Ligands on complexation with some metal ions to form complexes having paired or unpaired electrons give diamagnetic or paramagnetic respectively [1]. There are many methods that are available for characterizing complexes starting from measurement of the physical characteristics such as melting point, boiling point, colour, conductivity, crystal shapes, elemental content, molar mass to spectroscopic or structural methods such as UV-vis absorption spectroscopy, IR absorption spectroscopy, Raman spectroscopy, Nuclear magnetic resonance, magnetic circular dichroism, cyclic voltammetry and x - ray methods. In all these methods, it has been established that molecular spectroscopy (mass spectroscopy) which provides more information is preferred for identification. Some of the common physicochemical methods adopted by inorganic chemists are discussed below [2].

Infrared (IR) Spectroscopy

The infrared spectra technique is used to identify the prepared coordination complexes, specifically on comparing with the free ligand spectra so as to locate the position of the donor atoms. Besides identifying the ligands the infrared spectra is also used to determine the position of absorption bands for the different active groups such as (C=N), (C=O), (C=S), (NH), (C=N–N=C), (M–S), (M–N), (M–O) and (M–X) where X is any halogen [3]. In the characterization of metal complexes, the basic theory involved is that the stretching modes of the ligands changes upon complexation due to weakening/strengthening of the bonds involved in the bond formation resulting in subsequent change in the position of the bands appearing in the IR spectrum. The changes in the structural features of the ligands are observed as changes in bands observed, mainly in the fingerprint region i.e., in the 1500 - 750 cm^{-1}. The bands due to the metal - ligand bonds are mainly observed in the far IR region i.e., 50 - 500 cm^{-1} [1]. In IR spectroscopy technique, the sample is placed in the path of an IR radiation source and its absorption of different IR frequencies is measured [4]. Solid, liquid, and gaseous samples can all be characterized by this technique. Each molecule has its own unique signatures. Therefore, IR spectroscopy may be employed to identify the type of bond between two or more atoms and consequently identify functional groups. IR spectroscopy is also widely used to characterize the attachment of organic ligands to organic/inorganic compounds and nanoparticles and surfaces. Because IR spectroscopy is quantitative, the number of a type of bond may be determined. The vibration frequencies depend on several factors including bond strength and the atomic mass. The bonds can be modified in different ways, in a similar manner to a spring. Chemical bonds may be contorted in six different ways: stretching (both symmetrical and asymmetrical), scissoring, rocking, wagging, and twisting. Absorption of IR radiation causes the bond to move from the lowest vibrational state to the next highest, and the energy associated with absorbed IR radiation is converted into these types of motions [5]. These combinations lead to absorption bands, not discrete lines, which are commonly observed in the mid IR region.

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Weaker bonds require less energy to be absorbed and behave as though the bonds are springs that have different strengths. More complex molecules contain dozens or even hundreds of different possible bond stretches and bending motions, which implies the spectrum may contain dozens or hundreds of absorption lines. This means that the IR absorption spectrum can be its unique *fingerprint* for identification of a molecule. A diatomic molecule, that has only one bond, can only vibrate in one direction. For a linear molecule (e.g. hydrocarbons) with n atoms, there are $3n$-5 vibrational modes. If the molecule is non-linear (such as methane, aromatics etc.), then there will be $3n$-6 modes. Samples can be prepared in several ways for an IR measurement. For powders, a small amount of the sample is added to potassium bromide (KBr), after which this mixture is ground into a fine powder and subsequently compressed into a small, thin, quasi-transparent disc (Figure 1). For liquids, a drop of sample may be sandwiched between two salt plates, such as NaCl, KBr and NaCl are chosen as neither of these compound shows an IR active stretch in the region typically observed for organic and some inorganic molecules [6].

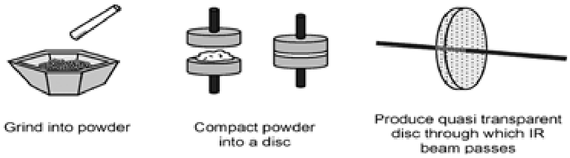
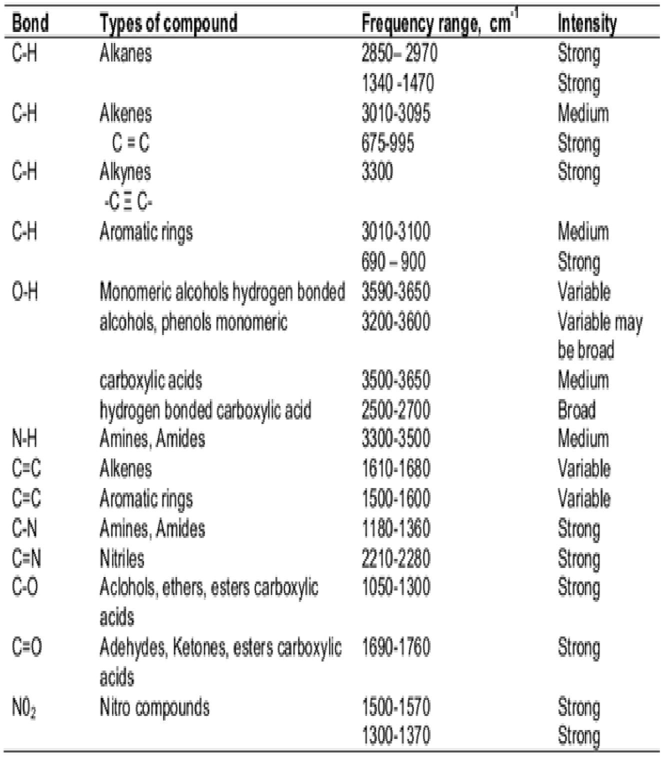


Figure 1. Varoius processes involved in IR spectra measurements.

Table1. Group frequencies of organic functional groups (Nworie et al, 2015; Morrrison and Boyd, 2002).



Bond	Types of compound	Frequency range, cm^{-1}	Intensity
C-H	Alkanes	2850– 2970	Strong
		1340 -1470	Strong
C-H	Alkenes	3010-3095	Medium
	C = C	675-995	Strong
C-H	Alkynes	3300	Strong
	-C Ξ C-		
C-H	Aromatic rings	3010-3100	Medium
		690 – 900	Strong
O-H	Monomeric alcohols hydrogen bonded	3590-3650	Variable
	alcohols, phenols monomeric	3200-3600	Variable may be broad
	carboxylic acids	3500-3650	Medium
	hydrogen bonded carboxylic acid	2500-2700	Broad
N-H	Amines, Amides	3300-3500	Medium
C=C	Alkenes	1610-1680	Variable
C=C	Aromatic rings	1500-1600	Variable
C-N	Amines, Amides	1180-1360	Strong
C=N	Nitriles	2210-2280	Strong
C-O	Aclohols, ethers, esters carboxylic acids	1050-1300	Strong
C=O	Adehydes, Ketones, esters carboxylic acids	1690-1760	Strong
$N0_2$	Nitro compounds	1500-1570	Strong
		1300-1370	Strong

Raman spectroscopy

It has been established that the combination of IR and Raman spectroscopy popularly known as vibrational spectroscopy gives complementary information for the exact functional groups present in a compound [7]. In the work of Skoog et al, 1998, Raman spectroscopy is applied for the qualitative and quantitative analysis of inorganic, organic and biological systems. In Raman spectroscopy, the spectra are always acquired by irradiating a sample with a powerful source of laser of visible or near infrared monochromatic radiation and the spectrum of the scattered radiation measured at an angle of 90° using a suitable spectrometer. Emitted radiation in Raman spectra can be of three types, stokes scattering, anti - stokes scattering and Rayleigh scattering. Rayleigh scattering has a wavelength that is exactly that of the excitation source and is more intense than stokes and anti-stokes scattering. In the same way, anti -stoke lines are less intense than stokes line. The polarizability of the molecule, intensity of the source and concentration of the active group in a molecule determines the power or intensity of a normal Raman peak. In the same way, Raman intensities is directly proportional to the concentration of the active species. For structural determination of molecules in Raman spectroscopy, the depolarization ratio is usually employed. Upon excitation of Raman spectra by plane polarized light radiation, the scattered radiation is found to be polarized to various degrees upon the type of vibration responsible for the scattering. The depolarization ratio is useful in correlating Raman line with modes of vibration and is dependent upon the symmetry of the vibrations responsible for scattering. Raman spectroscopy is a superior technique to infrared spectroscopy for the analysis of inorganic species since aqueous solutions can be used. In the same way, vibrational energies of metal -ligand bonds and estimation of ring size in paraffin are in the range of 100 to 700 cm^{-1} and 700 to 1200 cm^{-1} respectively which is a difficult region of the infrared to study. Consequently, Raman spectra are an invaluable tool for the elucidation of the composition, structure and stability of coordination compounds [8, 9]. In similarity, Raman spectra and infrared spectra are both useful in the identification of specific compounds since they have regions that are useful for functional group detection.

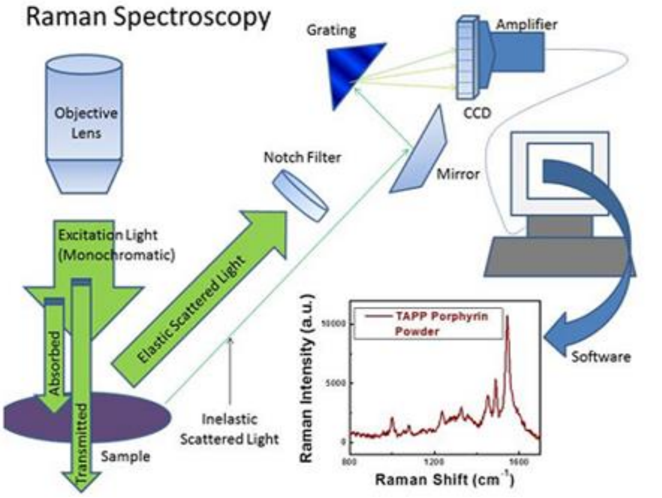


Figure 2. Diagram of Raman Spectroscopy adapted from Inworie et al 2015.

Electronic /UV-Visible Spectroscopy

Electronic spectroscopy is an important and valuable tool for most chemists to draw important information about the structural aspects of the complexes. It is widely utilized to quantitatively characterize organic, inorganic and nanosized molecules. The ligands, which are mainly organic compounds, have absorption in the ultraviolet region - hence do have bands in the region of the 200 to 350 nm of the electromagnetic spectrum- and in some cases these bands extends over to higher wavelength region due to conjugation. But upon complexation with transition metal ions, due to interaction with the metal ion there will be an interesting change in the electronic properties of the system. New features or bands in the visible region due to d-d absorption and charge transfer spectra from metal to ligand (M→L) or ligand to metal (L→M) can be observed and this data can be processed to obtain information regarding the structure and geometry of the compounds [10].

Electronic transitions can be transitions involving π, δ and n electrons. Transitions involving d and f electrons can also be involved in charge transfer. Transitions involving n- π* and π – π* transitions are the most common in the application of electronic spectroscopy to both organic compounds and inorganic anions as the absorption peaks are brought into an experimentally convenient spectral region of 200 to 700 nm. In these cases unsaturated functional groups to provide the π orbitals are required. n- π* transitions involve peaks of shorter wavelength (hypsochromic shift) whereas π - π* transitions involve peak of higher wavelength (bathochromic shift). Most transition metal ions absorb in the visible or ultraviolet region of the spectrum involving the d electrons whereas for the lanthanide and actinide series, absorption results from electronic transitions of 4f and 5f electrons. Many inorganic complexes exhibit charge transfer absorptions with very large molar absorptivities owing to the electron donor – electron acceptor properties exhibited by the species [11].

A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through the resulting spectrum [12, 13]. Figure 2 below shows a typical UV-vis absorption experiment for a liquid sample. A beam of monochromatic light is split into two beams, one of them is passed through the sample, and the other passes a reference (the solvent in which the sample is dissolved). After transmission through the sample and reference, the two beams are directed back to the detectors where they are compared. The difference between the signals is the basis of the measurement. Liquid samples are usually contained in a cell (called a cuvette) that has flat, fused quartz faces. Quartz is commonly used as it is transparent to both UV and visible lights [14]. UV-vis spectroscopy offers a relatively straight forward and effective way for quantitatively characterizing both organic and inorganic atomic and nano-materials. Furthermore, as it operates on the principle of absorption of photons that promotes the molecule to an excited state; it is an ideal technique for determining the electronic properties of transition metal complexes. UV-vis spectroscopy is based on the measurement of the absorbance A or transmittance T of solutions in transparent cells with path length l (cm). The relationship between the concentration of the sample and the absorbance of the solution is linear as shown by Beer Lambert's law.

$A = \log T = Ecl$

A = Absorbance, T = transmittance, E = Molar absorptivity C= Concentration and l = path length

This technique along with other spectral techniques like EPR serves to find out the structural features and to calculate the bonding parameters and Racah Parameters (B and C) [15]. The electronic spectroscopy is also widely used to explore the change in the structural features with change in the pH of the medium. The electronic and structural features of the complexes are widely utilized to investigate the kinetics and mechanisms of the reactions involving transition metal complexes [4, 16].

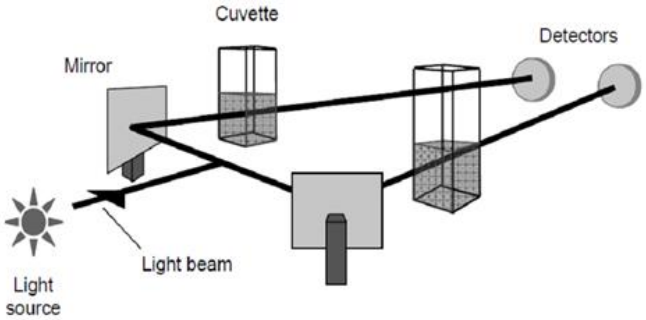


Figure 3. A schematic representation of UV-visible spectrophotometer

The electronic spectra of the ligands and metal complexes are usually recorded in DMSO as solvent [1]. In the spectra of the organic ligands, bands in the region 275–284 nm may be attributed to π - π* transitions which shows the aromatic nature of part of the ligands specifically. Also, bands which are found in the region 360–375 nm are due to the n - π* transition of the non-bonding electrons present on the ligands such as sulfur of the (CS), (CO) groups and nitrogen of the azomethine (CN) groups in the ligands [17]. Information obtained from the electronic spectra of the metal complexes can be used to assign tentatively the geometry of the metal complexes [18]. For example, the electronic spectra of Iron (III) complex that showed bands at 16,929 cm^{-1}, 23,587 cm^{-1}, 28,794 and 33,985 cm^{-1} are assignable to $^6A_{1g}$ to $^4T_{2g}$(G), $^6A_{1g}$ to ^4E_g, $^4A_{1g}$(G), $^6A_{1g}$ to $^4T_{2g}$(D), and $^6A_{1g}$ to $^4T_{1g}$(P), transitions, respectively. The electronic spectra of Cobalt (II) complexes that showed bands at 17,573 $cm^{-1}$and 21,890 cm^{-1} correspond to transitions, $^4A_2$(F) to $^4T_2$(F) and $^4A_2$(F) to $^4T_1$(F), respectively, supports the tetrahedral geometry around the d^7 Cobalt(II) ions. Rhodium (III) complexes exhibiting electronic spectra with transitions at 18,150 cm^{-1}, 20,498 cm^{-1} and 26,694 cm^{-1} resemble transitions for other hexacoordinated rhodium complexes [3] and therefore agree well with octahedral complexes. The ground state for Rhodium (III) ion is $^1A_{1g}$ in octahedral field, although in many instances only $^1A_{1g}$ to $^1T_{1g}$ spin allowed ligand field transitions to be observed. These transitions correspond to the $^1A_{1g}$ to $^3T_{1g}$, $^1A_{1g}$ to $^1T_{1g}$, and $^1A_{1g}$ to $^1T_{2g}$, respectively, which agree well with an octahedral geometry. The electronic spectra of Nickel (II) complexes and Palladium (II) complexes exhibiting bands around 18,288, 23,549 cm^{-1} and 21,890, 27,400 cm^{-1} are assignable to $^1A_{1g}$ to $^1A_{2g}$ and $^1A_{1g}$ to $^1B_{1g}$ transitions, respectively, supports the square planar geometry [19]. In the electronic spectra of Cr(III) complexes, bands at 17,648 cm^{-1}, 23,969 cm^{-1} and 27,605 cm^{-1} are assigned to $^4A_{2g}$(F) to $^4T_{2g}$(F), $^4A_{2g}$(F) to $^4T_{1g}$(F), and $^4A_{2g}$(F) to $^4T_{1g}$(P) transitions, respectively with octahedral geometry [20]. Again the electronic spectrum of Iron (III) complex and Manganese (II) complex may show very weak absorption bands, which may not help in assigning geometry, because the transitions are forbidden. The electronic spectra of the Copper (II) complex showing bands at 15,373 cm^{-1} and 19,580 cm^{-1} are assignable to $^2B_{1g}$ to $^2B_{2g}$ and $^2B_{1g}$ to ^2E_g transitions, respectively, corresponding to a distorted octahedral geometry around the copper ion [21].

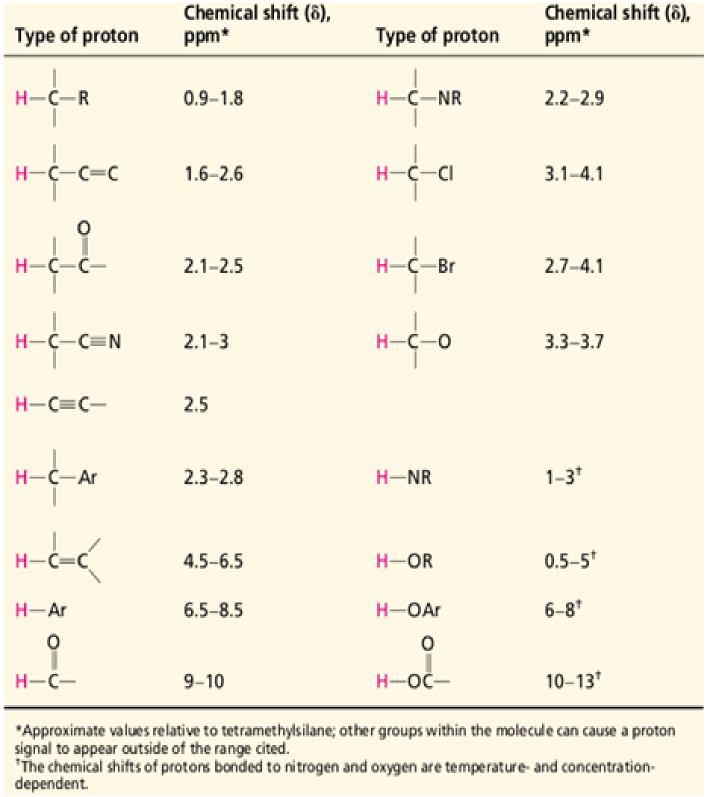
Nuclear Magnetic Resonance (NMR) Spectroscopy

The technique of high-resolution NMR is indispensable for structure elucidation of pure chemical compounds. It is a technique used to characterize ligands and diamagnetic complexes. Depending on the nucleus, the main types are ^1H (proton) and ^{13}C (carbon-13) and also ^{15}N, ^{17}O, ^{19}F, ^{29}Si, and

^{31}P NMR [22]. Proton NMR spectroscopy is important in identification and structural characterization of metal – ligands, organic and biochemical molecules such as protein, in the quantitative determination of absorbing species and in elemental analysis. NMR spectra are practically different from other spectra because there exist a direct proportionality between peak areas and the number of nuclei responsible for the peak. Carbon –13 NMR spectroscopy is advantageous compared to proton NMR spectroscopy in several ways; carbon -13 NMR provides information about the backbone of a given molecule rather than its periphery. It has higher chemical shift range of 200 ppm compared to 10 to 15ppm for the proton NMR. The limitation of carbon-13 NMR is its low signal strength and small magnetogyric ratio which makes the method less sensitive than proton. However, carbon-13 NMR is germane for structural elucidation which is dependent on chemical shifts with spin-spin data less important as compared to proton NMR [9]. There may be ^1D or ^2D versions of the spectra; the role of ^2D includes COSY (^1H - ^1H correlation) and HMQC (^1H - ^{13}C correlation). The use of ^1H - ^{13}C spectra used for identification has been growing [22]. In the classical approach to structure elucidation by spectral interpretation, reference tables of corresponding measure and values, chemical shifts and spin–spin coupling constants, accounting for signal multiplicity, are used. The two types of environmental shifts possible in NMR are chemical shift and spin splitting and are both crucial in structural analysis. Chemical shift is important in the identification of functional groups and determination of structural arrangements of groups as different functional groups has different characteristics. Spin-spin splitting occurs when the magnetic moment of the electrons of a nucleus interacts with the magnetic moments of immediately adjacent nucleus. Spin - spin splitting permits the determination of how different functional groups are connected in a molecule since atoms of only adjacent functional groups can split each other. The spectral values are very sensitive to changes in molecular configurations and conformations. So NMR techniques are of the first value in the solution of stereo-chemical problems. Now, there are two advanced approaches to identification/structure elucidation. First, a computer spectral simulation is applicable. NMR spectra are easily predictable for hypothetical structures, and can be used for comparison with spectra recorded for compounds. Second, such comparisons can be performed if reference databases comprising of experimental NMR spectra are available [2]. Samples for solution NMR spectroscopy are generally prepared using deuterated solvents. One reason for this is that, were non-deuterated solvents to be used (e.g. CH_3Cl in place of CD_3Cl) for a ^1H NMR spectroscopic experiment, the signals due to the solvent would ‘swamp’ those due to the sample. Deuterated solvents are commercially available, typically with > 99.5% ^2H label incorporated. The remaining unlabelled compound provides a useful internal reference signal in the ^1H NMR spectrum of the sample under study [23].

The more shielded a proton is, the greater must be the strength of the applied field in order to achieve resonance and produce a signal. A more shielded proton absorbs radio frequency radiation at higher field strength (upfield) compared with one at lower field strength (downfield). Different protons give signals at different field strengths. The dependence of the resonance position of a nucleus that results from its molecular environment is called its chemical shift. This is where the real power of NMR lies. The chemical shifts of various protons in a molecule can be different and are characteristic of particular structural features. Instead of measuring chemical shifts in absolute terms, we measure them with respect to a standard - tetramethylsilane $(CH_3)_4Si$, abbreviated TMS. The protons of TMS are more shielded than those of most organic compounds, so all of the signals in a sample ordinarily appear at lower field than those of the TMS reference [24].

Table 3a. Chemial shift representative type of proton (Carey, 2000).

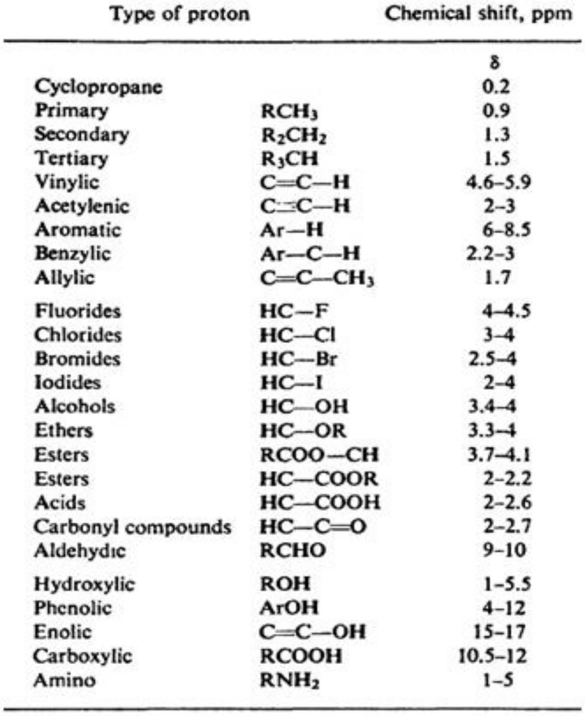


Type of proton	Chemical shift (δ), ppm*	Type of proton	Chemical shift (δ), ppm*
$H{-}\overset{\vert}{\underset{\vert}{C}}{-}R$	0.9–1.8	$H{-}\overset{\vert}{\underset{\vert}{C}}{-}NR$	2.2–2.9
$H{-}\overset{\vert}{\underset{\vert}{C}}{-}C{=}C$	1.6–2.6	$H{-}\overset{\vert}{\underset{\vert}{C}}{-}Cl$	3.1–4.1
$H{-}\overset{\vert}{\underset{\vert}{C}}{-}\overset{\overset{O}{\Vert}}{C}{-}$	2.1–2.5	$H{-}\overset{\vert}{\underset{\vert}{C}}{-}Br$	2.7–4.1
$H{-}\overset{\vert}{\underset{\vert}{C}}{-}C{\equiv}N$	2.1–3	$H{-}\overset{\vert}{\underset{\vert}{C}}{-}O$	3.3–3.7
$H{-}C{\equiv}C{-}$	2.5		
$H{-}\overset{\vert}{\underset{\vert}{C}}{-}Ar$	2.3–2.8	H—NR	1–3†
$H{-}\overset{\vert}{C}{=}C{<}$	4.5–6.5	H—OR	0.5–5†
H—Ar	6.5–8.5	H—OAr	6–8†
$H{-}\overset{\overset{O}{\Vert}}{C}{-}$	9–10	$H{-}O\overset{\overset{O}{\Vert}}{C}{-}$	10–13†

*Approximate values relative to tetramethylsilane; other groups within the molecule can cause a proton signal to appear outside of the range cited.

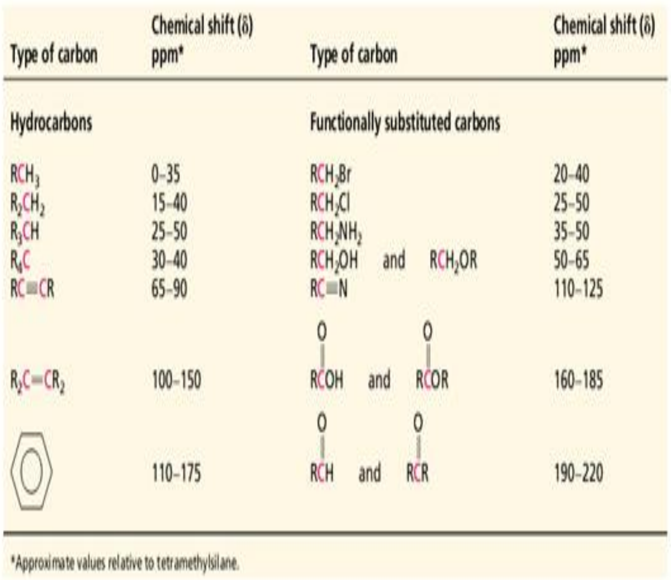
†The chemical shifts of protons bonded to nitrogen and oxygen are temperature- and concentration-dependent.

Table 3b. Characteristic chemical shift for proton (Morrison and Boyd, 2002).



Type of proton		Chemical shift, ppm
		δ
Cyclopropane		0.2
Primary	RCH_3	0.9
Secondary	R_2CH_2	1.3
Tertiary	R_3CH	1.5
Vinylic	C=C—H	4.6–5.9
Acetylenic	C≡C—H	2–3
Aromatic	Ar—H	6–8.5
Benzylic	Ar—C—H	2.2–3
Allylic	C=C—CH_3	1.7
Fluorides	HC—F	4–4.5
Chlorides	HC—Cl	3–4
Bromides	HC—Br	2.5–4
Iodides	HC—I	2–4
Alcohols	HC—OH	3.4–4
Ethers	HC—OR	3.3–4
Esters	RCOO—CH	3.7–4.1
Esters	HC—COOR	2–2.2
Acids	HC—COOH	2–2.6
Carbonyl compounds	HC—C=O	2–2.7
Aldehydic	RCHO	9–10
Hydroxylic	ROH	1–5.5
Phenolic	ArOH	4–12
Enolic	C=C—OH	15–17
Carboxylic	RCOOH	10.5–12
Amino	RNH_2	1–5

Table 3c. Chemial shift of representative type of carbon (Carey, 2000).



Type of carbon	Chemical shift (δ) ppm*	Type of carbon	Chemical shift (δ) ppm*
Hydrocarbons		Functionally substituted carbons	
RCH_3	0-35	RCH_2Br	20-40
R_2CH_2	15-40	RCH_2Cl	25-50
R_3CH	25-50	RCH_2NH_2	35-50
R_4C	30-40	RCH_2OH and RCH_2OR	50-65
$RC\equiv CR$	65-90	$RC\equiv N$	110-125
$R_2C=CR_2$	100-150	$R\overset{O}{\overset{\|}{C}}OH$ and $R\overset{O}{\overset{\|}{C}}OR$	160-185
	110-175	$R\overset{O}{\overset{\|}{C}}H$ and $R\overset{O}{\overset{\|}{C}}R$	190-220

*Approximate values relative to tetramethylsilane.

Mass spectroscopy

This is the most widely used of all the analytical tools since it provides scientists with valuable information about elemental components of samples of matter, gives the structures of inorganic, biological and organic molecules, gives qualitative and quantitative composition of complex mixtures, gives the structure and composition of solid surfaces and shows the isotopic ratios of atoms in the sample under investigation. The technique of molecular mass spectroscopy is superior to other spectral methods in the combination of features such as selectivity, generation of molecular mass/formula sensitivity, and combinability with chromatography [9]. Mass spectra can be used in two general ways: to prove the identity of two compounds and to help establish the structure of new compounds. The mass spectrum helps to establish the structure of new organic compounds (ligands) and the corresponding complexes in several ways: it can give an exact molecular weight; it can give a molecular formula or at least narrow the possibilities to a very few; and it can indicate the presence in a molecule of certain structural units [25]. Mass spectrometry differs from the other instrumental methods discussed in this article in a fundamental way. It does not depend on the absorption of electromagnetic radiation but rather examines what happens when a molecule is bombarded with high-energy electrons [24]. In molecular mass spectroscopy, the analyte/sample which may be a vapour is always bombarded with a stream of electrons that leads to loss of electron by the analyte and consequent formation of molecular ion with the same molecular weight as the molecule [9]. In the mass spectrometer, molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge, or m/z value. For most ions, the charge is 1, so that m/e is simply the mass of the ion. The set of ions is analyzed in such a way that a signal is obtained for each value of m/z that is represented; the intensity of each signal reflects the relative abundance of the ion producing the signal. The largest peak is called the base peak: its intensity is taken as 100, and the intensities of the other peaks are ex-pressed relative to it. A plot or even a list showing the relative intensities of signals at the various m/e values is called a mass spectrum, and is highly characteristic of a particular compound [25]. Figure 4 shows the diagram of a mass spectrometer. Ionization and fragmentation produce a mixture of particles, some neutral and some positively charged. To understand what follows, we need to examine the design of an electron-impact mass spectrometer, shown in a schematic diagram in Figure 4. The sample is bombarded with 70-eV electrons, and the resulting positively charged ions (the molecular ion as well as fragment ions) are directed into an analyzer tube surrounded by a magnet. This magnet deflects the ions from their original trajectory, causing them to adopt a circular path, the radius of which depends on their mass-to-charge ratio (m/z). Ions of small m/z are deflected more than those of larger m/z. By varying either the magnetic field strength or the degree to which the ions are accelerated on entering the analyzer, ions of a particular m/z can be selectively focused through a narrow slit onto a detector, where they are counted. Scanning all m/z values gives the distribution of positive ions, called a mass spectrum, characteristic of a particular compound [24].

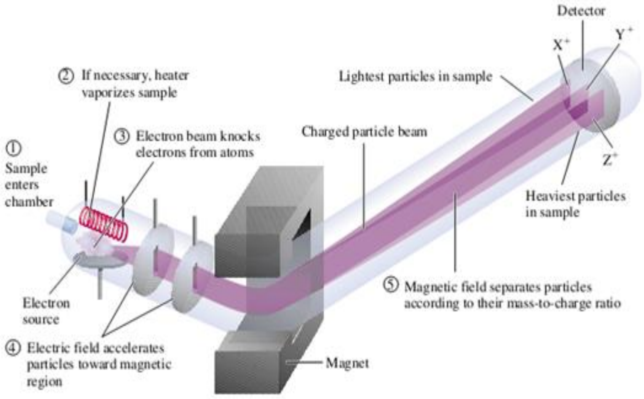


Figure 4. The mass spectrometer (Carey, 2000).

Mossbauer spectroscopy

Mossbauer spectroscopy is by no means as widely used as NMR spectroscopy. The Mossbauer effect is the emission and resonant absorption of nuclear γ-rays studied under conditions such that the nuclei have negligible recoil velocities when γ-rays are emitted or absorbed. This is only achieved by working with solid samples in which the nuclei are held rigidly in a crystal lattice. The energy, and thus the frequency of the γ-radiation involved, corresponds to the transition between the ground state and the short-lived excited state of the nuclide concerned. Table 4 lists properties of several nuclei which can be observed using Mossbauer spectroscopy [23]. The study of the Mossbauer effect can be illustrated by reference to ^{57}Fe spectroscopy. The basic apparatus includes a radioactive source, a solid absorber with the ^{57} Fe-containing-sample and a γ -ray detector. For ^{57}Fe samples, the radioactive source is ^{57}Co and is incorporated into stainless steel; the ^{57}Co source decays by capture of an extra-nuclear electron to give the excited state of ^{57}Fe which emits γ-radiation as it decays to its ground state. If ^{57}Fe is present in the same form in both source and absorber, resonant absorption occurs and no radiation is transmitted. However, if the ^{57}Fe in the source and absorber is present in two different forms, absorption does not occur and γ-radiation reaches the detector. Moving the source at different velocities towards or away from the ^{57}Fe absorber has the effect of varying the energy of the γ-radiation (i.e. by the Doppler effect). The velocity of movement required to bring about maximum absorption relative to stainless steel (defined as an arbitrary zero for iron) is called the isomer shift of ^{57}Fe in the sample, with units of mms^{-1}.

The isomer shift gives a measure of the electron density on the ^{57}Fe centre, and isomer shift values can be used to determine the oxidation state of the Fe atom. Similarly, in ^{197}Au Mossbauer spectroscopy, isomer shifts can be used to distinguish between Au(I) and Au(III). Three specific examples are chosen here from iron chemistry. The cation $[Fe(NH_3)_5(NO)]^{2+}$ has presented chemists with an ambiguity in terms of the description of the bonding which has, in some instances, been described in terms of an $[NO]^+$ unit bound to an Fe(I) centre.

Table 5. Properties of selected nuclei observed by Mossbauer spectroscopy. (Housecroft and Sharpe, 2005).

Nucleus observed	Natural abundance / %	Ground spin state	Excited spin state	Radioisotope source[†]
^{57}Fe	2.2	$\frac{1}{2}$	$\frac{3}{2}$	^{57}Co
^{119}Sn	8.6	$\frac{1}{2}$	$\frac{3}{2}$	^{119m}Sn
^{99}Ru	12.7	$\frac{3}{2}$	$\frac{5}{2}$	^{99}Rh
^{197}Au	100	$\frac{3}{2}$	$\frac{1}{2}$	^{197m}Pt

[†] m = metastable

Results of ^{57}Fe Mossbauer spectroscopy have revealed that the correct description is that of an $[NO]^-$ ligand bound to an Fe(III) centre. The formal oxidation states of the iron centres in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)6]^{3-}$ are +2 and +3; however, the closeness of the isomer shifts for these species suggests that the actual oxidation states are similar and this may be interpreted in terms of the extra electron in $[Fe(CN)_6]^{4-}$ being delocalized on the cyano ligands rather than the iron centre. Differences in isomer shifts can be used to distinguish between different iron environments in the same molecule. The existence of two signals in the Mossbauer spectrum of $Fe_3(CO)_{12}$ provided the first evidence for the presence of two types of iron atom in the solid state structure, a fact that has been confirmed by X-ray diffraction methods [23].

Magnetic measurements

In a magnetic field, the paramagnetic compounds will be attracted while the diamagnetic compounds repelled. In paramagnetic complexes, often the magnetic moment gives the spin only value corresponding to the number of unpaired electron. The variation from the spin only value is attributed to the orbital contribution and it varies with the nature of coordination and consequent delocalization. In some cases two magnetic centers may be coupled together and may result in extraordinary increase or decrease in the magnetic moment of the complex [23]. For example, a mononuclear complex of copper of the formula [CuLX] where Cu is in the +2 oxidation state, the complex is expected to have magnetic moment of 1.73 BM -corresponding to d^9 configuration, but in case of $[Cu(OAc)_2]$, the value is lower than 1.73 BM. This is explained on the basis of the assumption that the individual magnetic moments are aligned in opposite directions so that they cancel each other to some extent or can be ascribed as due to antiferromagnetic coupling. Thus the value of magnetic moment of a complex would give valuable insights into its constitution and structure. In some cases the variation in the magnetic moment can be explained on the assumption that the compound may be an equilibrium mixture of tetrahedral and square planar geometries- the number of unpaired electrons differ in either geometries and hence the magnetic moment [17]. The magnetic susceptibility measurements thus help to predict the oxidation state of the metal ion to a limited extent and to establish the possible geometry of the compound. The most widely adopted method for determining the magnetic moment of a complex is by Gouy's Method in which the weight difference experienced by a given amount of a substance in the presence and absence is measured. This is compared with that of a standard substance and magnetic moment is determined with the help of suitable equations. Faraday Balance and Vibration Susceptibility Magnetometer are the other instruments used for the magnetic susceptibility measurements [26].

The magnetic moment value (μ_{eff}) for some Fe(III) complexes have been reported to be 6.35 BM indicating a slight ferromagnetic behavior [27] and suggests the high spin state of Fe(III). For Ru(III) complexes, moments of 1.97 BM has been observed, indicating the presence of one unpaired electron and suggests low spin state of Ru(III). Co(II) complexes with μ_{eff} value of 3.92 BM corresponds to three unpaired electrons, and may suggests a spin free tetrahedral configuration. A d^6 Rh(III) complex will be diamagnetic as expected. The magnetic moment of 0 BM for the Ni(II) and Pd(II) complexes suggests a low spin square planar arrangement. The magnetic moment for Cr(III) complex with a value of 3.97 BM indicates the presence of three unpaired electrons. The μ_{eff} value for the Fe(III) and Mn(II) complexes with values of 2.63 BM and 2.60 BM, respectively, indicates the presence of one unpaired electrons and suggests the low spin state of Fe(III) and Mn(II). Higher values of magnetic moment may be due to a large orbital contribution. For Cu(II) complexes the μ_{eff} value of 1.96 BM corresponds to one unpaired electron [3].

X-ray Diffraction

The First Scientist who worked on X-ray diffraction (XRD) was a German Physicist, Von Laue in 1912 with the assumption that, “if crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and if X-rays were electromagnetic waves of wavelength about equal to the inter atomic distances in crystals, then it should be possible to diffract X-rays by means of crystals” [28]. Recently, X-ray diffraction is most extensively used technique for the characterization of materials. A lot of information can be extracted from the XRD data. This is an appropriate technique for all forms of samples, i.e. powder and bulk as well as thin film. Using this technique, one can get the information regarding the crystalline nature of a material, nature of the phase present, lattice parameter and grain size [29]. From the position and shape of the lines, one can obtain information regarding the unit cell parameters and microstructural parameters (grain size, microstrain, etc), respectively. In case of thin films, the change in lattice parameter with respect to the bulk gives the idea about the nature of strain present in the system. The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which depicts a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystal planes. According to Bragg’s law, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Fig. 2.3. The path differences introduced between a pair of waves travelled through the neighboring crystallographic planes are determined by the interplanar spacing. If the total path difference is equal to $n\lambda$ (n being an integer), the constructive interference will occur and a group of diffraction peaks can be observed, which give rise to X-ray patterns. The quantitative account of Bragg's law can be expressed as:

$$2d_{hkl} \sin \theta = n\lambda$$

where d is the interplanar spacing for a given set of *hkl* and θ the Bragg angle. The diffraction method is based on the effect of broadening of diffraction reflections associated with the size of the particles (crystallites). The major advantages of x -ray diffraction are: firstly, other modern spectroscopic method of analysis mainly focuses on characterization of the synthesized target at a molecular level within a short time whereas x -ray diffraction gives detailed information on the molecular assembly in the solid state, secondly, X-ray diffraction provides direct information on the arrangement of molecules in the organic solid state and lastly, the emergence of x-ray powder diffraction (XRPD) has provided an alternative to single crystal X- ray diffraction which focuses only on structural information. XRPD is now used for characterizing solid state supramolecular architectures (crystal structures) [30].

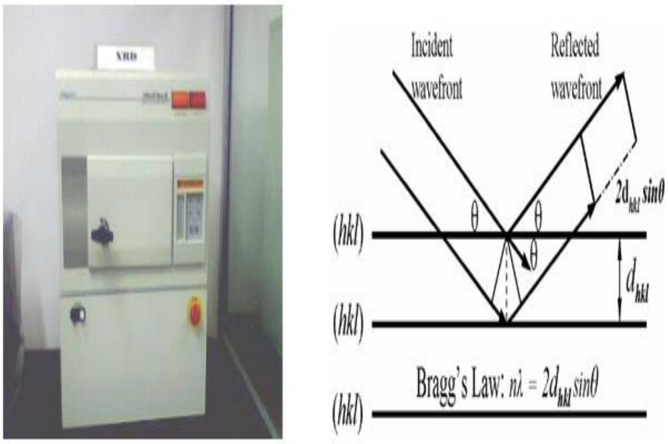


Figure 5. X-ray Diffractometer (XRD) Machine Geometrical illustrations of crystal planes and Bragg's Law.

X-Ray crystallography

The diffraction/scattering of X-ray radiations by array of atoms in a single crystal of a compound is exploited to establish the structure and geometry of the complexes. At present this versatile techniques is valued as the final word by many chemists for establishing the accurate structure of the complex compounds (Nworie et al, 2015). X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and causes the beam of light to spread into many specific directions. From the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. X-rays are useful to explore within crystals because they have wavelengths similar to the size of atoms [31].

X-ray crystallography is used to study many materials which form crystals like salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules. It is used to determine electron density, the mean positions of the atoms in the crystal, their chemical bonds, their disorderliness and various other information such as size of atoms, the lengths and types of chemical bonds. The method also revealed the structure and function of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as DNA. X-ray crystal structures can also account for unusual electronic or elastic properties of a material, shed light on chemical interactions and processes or serve as the basis for designing pharmaceuticals against diseases. X-Ray Crystallography uses the uniformity of light diffraction of crystals to determine the structure of a molecule or atom. In the measurement of crystal structure, X-ray beams are used to "hit" the crystallized molecule, while the electrons surrounding the molecule diffract as the X-rays hit them. This forms a pattern, this type of pattern is called the X-ray diffraction pattern.

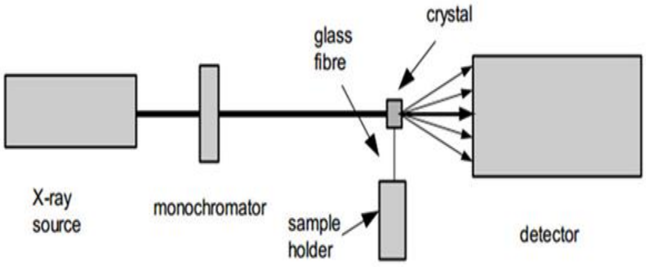


Figure 6. Set-up for X-ray crystallography measurements.

In other to carryout X-ray crystallography measurement, the first and often most difficult step is to obtain an adequate crystal of the material under study. The crystal should be sufficiently large (typically larger than 0.1 mm in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning. The second step is to place the crystal in an intense beam of X-rays, usually of a single wavelength (monochromatic X-rays), producing the regular pattern of reflections. As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflections. In the third step, these data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal. The final, refined model of the atomic arrangement-now called a crystal structure is usually stored in a public database. After the diffraction pattern is obtained, the data is then processed by a computer and the structure of the atom or molecule is deduced and visualized [31].

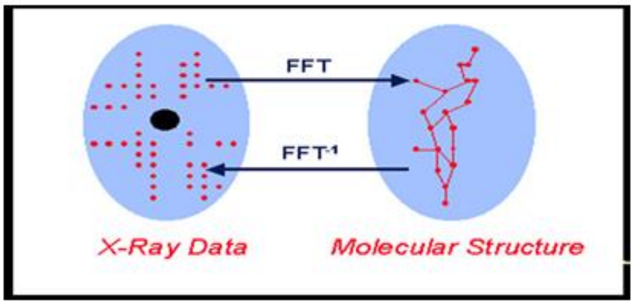


Figure 7. Processing of X-ray diffractions into molecular structure.

Electron paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR)

The Electron paramagnetic resonance (EPR) or Electron spin resonance (ESR) is used for the determination of the number of unpaired electrons, geometry about the metal centre and the ligands surrounding the metal for a paramagnetic compound. The NMR though related to EPR and sometimes the same is usually used for diamagnetic compounds.

A new technique that combines the two methods is Electron Nuclear Double Resonance spectroscopy (ENDOR) [2, 11]. Electron spin resonance spectroscopy is an analytical technique used for studying metal complexes, inorganic radicals or organic radicals and biomolecules. Electron spin resonance also regarded as electron paramagnetic resonances is based on the fact that an electron is a charged particle which spins around its axis which invariably causes it to behave like a magnet. Electron spin resonance spectroscopy is a very powerful and sensitive method of characterizing electronic structures of materials with unpaired electrons [10]. Electron spin resonance is a technique based on the interaction of unpaired electron spins with an external magnetic field. In ESR, the electrons in the lower energy level of the spectrometer magnet are excited to the upper energy level while the sample is exposed to fixed microwave irradiation. A modern form of ESR/EPR is ENDOR (electron nuclear double resonance) which has high resolution and capable of measuring nuclear magnetic transition frequencies in paramagnetic systems. The important application of ENDOR is that the NMR spectrum of nuclei which interacts with a paramagnetic center is measured. Although ENDOR is a very powerful tool the limitations include the need for advanced equipment which is costly and generation of sufficiently high radio frequency power as well as the coil to generate the appropriate magnetic field which is often a hindrance [10]. Also important to note is that ENDOR technique needs low temperature for measurement and as well a sensitive ESR spectrometer [32].

Circular Dichroism (CD)

Circular Dichroism (CD) spectroscopy has been empirically used in inorganic chemistry and in particular co-ordination chemistry for analytical information and structural elucidation of transition metal complexes with enantiometric ligands. Studies have revealed that not only is CD used to measure the degree to which transition metal complexes are structurally analyzed; it offers a versatile tool for abstracting important information on the interaction of metal ions with large biologically active molecules such as proteins and DNA. Circular dichroism spectroscopy is importantly used in speciation studies. It has been established that when a metal ion and a chiral compound are dissolved in an aqueous solution and a circular dichroism spectrum is in the visible range as a result of d-d transitions, there is evidence of complexation and if there is absence of chiral ligand, bound to the metal ion, CD is zero [33]. The importance of circular dichroism spectroscopy is the application of its spectra in speciation studies. This is applied for identifying complex species, establishing equilibrium models, in detecting interactions of metal ions with biological molecules, to follow reactions of co-ordinated ligands and for the calculation of stability constants of complexes [9].

Magnetic Circular Dichroism (MCD)

Magnetic circular dichroism (MCD) a hybrid technique which is based on the ability of all matter to rotate the plane of polarized light in the presence of a magnetic field combines both spectroscopic and magnetic properties to measure the magnetic and electronic properties of a compound. The method is importantly most useful for paramagnetic compounds and can be used in a mixture if transition arising from the various species can be identified. The major limitation to this however, is that the process is usually performed at low temperature (<77K) and the process uses strain free glasses therefore limiting its use [11].

Thermogravimetric Analysis

Thermogravimetry is a kind of analysis that is used for the determination of a material's thermal stability. This is normally achieved by heating a fraction of the sample while monitoring the weight change. In other words, it involves a group of technique in which the physical and or chemical properties of a material is recorded against time or temperature variation when the sample temperature follows a program that is pre-established. There are two thermogravimetric methods: the derivative thermogravimetry (DTG) which determines mass change due to dehydration, decomposition or oxidation and differential scanning calorimetry (DSC) or differential thermal analysis (DTA) which deals with thermal effects such as phase transitions, decompositions and oxidations. In determining the changes in mass of a complex due to water loss/decomposition either of the two thermogravimetric methods is used. Thermogravimetric analysis of complexes are used to abstract information about the thermal stability of complexes, decide whether water molecule if present in a complex is in the inner or outer co-ordination sphere and suggest a general scheme for the thermal degradation of a complex [28, 34] Thermal analysis methods have been used for the evaluation of materials and product such as determination of thermal stability, degradation degree, quality control thermal life time prediction, thermo oxidative stability and assessment of environmental impact on the materials as products [35, 36].

Cyclic Voltammetry

Cyclic voltammetry is an important analytical technique in redox chemistry. It is widely used to study the redox behavior of the coordinated complexes. It gives an insight into the stability of the compound under investigation against electrolytic oxidation and reduction in the solution. In this technique, the potential of a small stationary working electrode is changed linearly with the time starting from a potential where no electrode reaction occurs and moving to potentials where reduction or oxidation of a solute (material being studied) occurs. After traversing the potential region in which one or more electrode reaction takes place, the direction of the linear sweep is reversed and the electrode reactions of the intermediates and products formed during the forward scan, often can be detected. The technique can be carried out using a suitable reference, working and counter electrodes, the selection of which can be made depending on the nature of the compound and the solvent used, in the presence of a supporting electrolyte [37]. The supporting electrolyte is usually added to repress the migration of charged reactants and products. Depending on the type of systems, measurements can be made using degassed (N_2 bubbling for 10 minutes) solution in DMF (10^{-3}M) containing 0.1 M tetrabutyl ammonium tetrafluoroborates as supporting electrolyte. The three electrode system consists of a glassy carbon (working) platinum wire (counter or auxiliary) and Ag/AgCI (reference) electrodes. Having knowledge of the species involved and an idea about the redox properties, one can select the range of voltages, and the variation in voltammogram can be recorded at different sweep rates [1]. The peaks in the forward and reverse sweeps can be interpreted to assess the stability of the species. Depending on the nature of the voltammogram obtained they may be termed as reversible ($i_{pa} = i_{pc}$), quasi-reversible ($i_{pa} > i_{pc}$)

and irreversible process. If some chemical reaction occurs the return peak of the cyclic voltammogram will be reduced in magnitude, and it will be completely absent if the reaction half-life is much less than the scan duration. The cyclic voltammetric techniques can also be utilized, coupled with electronic spectroscopy, to obtain information about the presence of a new species formed during the oxidation-reduction process and the related stereo chemical and structural change [38, 39].

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