CHAPTER - 3

INFRARED SPECTROSCOPY

Section (i): General Introduction to Infrared Spectrometry

Infrared spectrophotometry is one of the most powerful tools available for solving problems of molecular structure and chemical identification. Although organic compounds are usually studied, inorganic compounds containing polyatomic cations or anions also give useful infrared spectra.

The infrared region lies between the visible and the microwave regions, extending from about 0.75 μm to about 1000 μm. Both wavelength (μm) and wave number (cm^{-1}) units are used to characterise infrared radiation. The relationship between the two is

$$\overline{\gamma}\,(cm^{-1}) = \frac{10^4}{\lambda(\mu m)} \quad \ldots\ldots\ldots (1)$$

TABLE – 3

Common sub-divisions of the Infrared spectrum

S.No.	Region	Type of energy level transition	Wavelength range (μm)	Wave number range (cm^{-1})
1.	Near infrared	Overtones	0.75 – 2.5	13300 - 4000
2.	Fundamental infrared	Vibrations, rotations	2.5 – 25	4000 - 400
3.	For infrared	Skeletal vibrations, Rotations	25 - 1000	400 - 10

The energy of radiation E is directly proportional to the wave number is given by Plank's equation.

$$E = h\overline{\gamma} = h\ \overline{\gamma}\ C \quad \ldots\ldots\ldots\ldots (2)$$

Where

h the Planck's constant = 6.62×10^{-27} erg - 3.

In marked contrast to the visible and near - ultraviolet regions, almost all substances show absorption in the infrared regions, the only exceptions being mono-atomic and homopolar molecules such as Ne, He, O_2, N_2 and H_2. Further more, no two compounds with different structures have the same infrared spectrum, except for optical isomers and certain high-molecular weight polymers differing only slightly in molecular weight. Hence infrared spectro photometry is an excelled as a general tool for molecular identification.

THEORY OF INFRARED ABSORPTION

Requirements for absorption :

There are two requirements for the absorption of electromagnetic radiation by matters (1) the radiations must have precisely the correct energy to satisfy the energy requirements of the material, and (2) there must be a coupling (or interaction) between the radiation and matter. Radiation in the infrared region has the proper magnitude of energy to cause vibrational transition. in molecules and the first requirement for absorption is satisfied if a given frequency of infrared radiation corresponds exactly to a fundamental vibrational frequency of a given molecule. To satisfy the second requirement for absorption, the molecule must undergo a change in dipola moment when the fundamental vibration occurs. If no change in dipole moment occurs when the molecule vibrates, there will be no interaction between the electro magnetic radiation and the non electromagnetic molecule and no absorption will take place regardless of the energy compatibility. Such a vibration is said to be infrared inactive.

The dipole moment of two equal and opposite charges is defined as the product of the charge and the distance separating them

$$\mu = \tau\, r \quad \ldots\ldots\ldots\ldots\ldots (3)$$

For a molecule, it is the effective centre of the positive and negative charges which is important, r being the distance between those centres. Fig.1 illustrates how the separation of charge in a polar molecule like water may be visualised. As will be shown momentarily, all the possible modes of vibration of a water molecule involve a change in dipole moment, and thus all its vibrational modes are infrared-active with a linear molecule like CO_2 however, its dipolement is zero. More important is that the change in dipolement is zero when the molecule is symmetrically stretched. Thus, the symmetrical stretch of CO_2 is infrared-inactive. On the other hand, an anti symmetrical (or asymmetrical) stretch involves a change in dipole moment, and thus this mode of vibration is infrared-active.

STRETCHING AND BENDING MODES OF VIBRATION

There are two kinds of fundamental vibrations for molecules stretching, in which the distance between two atoms increases or decreases, but the atoms remain in the same bond axis; and bending (or deformation), in which the position of the atoms changes relative to the original bond axis. The various stretching and bending vibrations of a bond occur at certain quantised frequencies. When infrared light of the same matching frequency is incident on the molecule, energy is absorbed and the amplitude of the vibration is increased. When the molecule revers from the excited state to the original ground state, the absorbed energy is released as heat.

Some of the various stretching and bending vibrations that can exist within a molecule are shown schematically in Fig.1. Bending vibrations generally require less

energy and occur at longer wavelengths (lower ν) then stretching vibrations. Stretching vibrations are found to occur in the order of bond strengths. For example,

$$\gamma C - C < \gamma C = C < \gamma C \equiv C$$

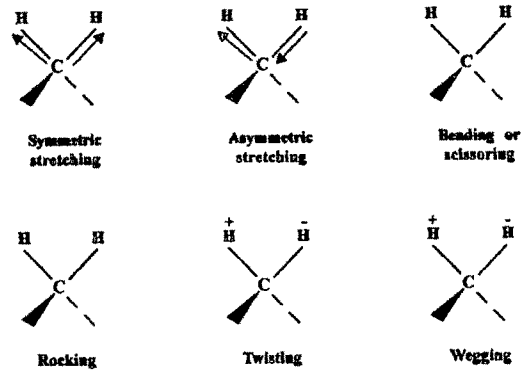

Fig. 1 : Different modes of vibrations of methylene group.

Number of fundamental vibrations :

A polyatomic non-linear molecule having a atoms has a total of 3n degrees of freedom and since 3 of these are overall translational degrees of freedom and 3(or 2 if the molecule is linear) are rotational degrees of freedom, there will be 3n-6 (3n-5 for a linear molecule) vibrational degrees of freedom. There are, therefore 3n-6 (or 3n-5) energy level patterns, each with its own spacing (i.e. v= 0 to v= 1 transition for each of the modes of vibration will normally have energies that are different from each other). If the vibrations corresponding to all these patterns are associated with oscillating dipole moments, there will be 3n-6 (or 3n-5) observed absorption bands. One finds for example, for H_2O vapour, absorptions centrad at 1595, 3652, 3756 cm^{-1}.

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The molecular motion that has the next higher energy level spacing after the rotation of molecules is the vibration of the atoms of the molecule with many atoms, 3n-6 becomes large and one expects very many vibrational transitions and a very complicated spectral pattern.

The molecular motion that has the next higher energy level spacing after the rotation of molecules is the vibrations of the atoms of the molecule with respect to one another. It will be shown that the study of the absorptions of radiation that result from translations among the vibrational energy levels lead to further detailed insight into the nature of the molecule.

It can be shown by wave-mechanical treatment that the energy of vibrational level is given by

$$\varepsilon Vib. = (v-1/2)h\gamma \text{ ergs} \quad \ldots\ldots (4)$$

Where γ is the vibrational quantum number having values 0, 1, 2.... and is the frequency is cycles / sec and is given by

$$\gamma = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$$

Where

f = force constant (dynes / cm) which gives the idea of toughness or strength of the bond.

μ = reduced mass = $m_1 m_2 / m_1 + m_2$ where m_1 & m_2 are the masses of the atoms of a bond.

It can easily seen from the ε Vib expression (4) that energy differences, $\Delta\varepsilon$ Vib, in successive vibrational levels will be given by

$$\Delta\varepsilon Vib = \frac{h}{2\Pi}\sqrt{\frac{f}{u}} \quad ergs$$

$$\frac{h}{2\Pi xhc}\sqrt{\frac{f}{u}} \quad cm^{-1}$$

$$\frac{1}{2\Pi c}\sqrt{\frac{f}{u}} \quad cm^{-1}$$

At room temperature, the value of KT is sufficiently small compared with typical values of $\Delta\varepsilon$ Vib so that most of the molecules are in the lowest allowed vibrational state. In a spectroscopic study, therefore, one investigates the absorption of radiation by these V = 0 state molecules.

Evaluation of various possible combination of atoms would that fundamental stretching vibrations fall in a frequency range of about 4000 to 800 cm^{-1} (2.5 to 12.5 μm) and fundamental bending modes extend from about 1700 to 400 cm^{-1} (6.0 to 25 μm). The region beyond 400 cm^{-1} (25 μm) is considered to be the far-infrared, and certain skeletal vibrations and lattice vibrations of crystals can occur in this region, in addition to pure rotational transitions of small molecules.

The fundamental-infrared region is conveniently divided into a group - frequency region from 2.5 - 8 μm and a finger print region from 8 to 25 μm. In the group frequency region, absorption bands tend to be characteristic of specific groups of atoms and relatively independent of the composition of the rest of the molecule. In

the finger print region, however, vibrational frequencies are prefoundly affected by the molecular structure as a whole, and therefore bends in this region are considered specific for a particular molecule ratherthan for a particular functional group. The uniqueness of a given molecule's spectrum in this region justifies calling this the finger print region.

In the finger print region, a given vibrational mode may be found anywhere ever a large range of requencies, depending on the structure of the moelcule as a whole. In the group-frequency region, however, the vibrational frequency, of a given functional group can be pin pointed to a much norrower range of frequencies, and thus the group-frequency region is extremely useful for diagnosing the presence or absence of certain functional groups.The region from 2.5 to 4 μm (4000to 25000 cm^{-1}) is restricted to hydrogen-stretching vibrations, the region from about 4 to 6.3 μm (2500 - 1600 cm^{-1}) emphasises double and triple-bond stretching and the region from about 6.3 to 8 μm contains mainly hydrogen bending vibrations.

Application of Infrared spectroscopy in Coordination Chemistry :

In the vibrational spectre of metal complexes three basic types of vibrations have to be considered.

1. Ligand vibrations, which are actually characteristic of the free ligand, although these vibrations change slightly on complex formation, if the spectrum of the pure ligand is known, they can be assigned to the corresponding bonds.
2. Skeletal vibrations, characteristics of the whole complex molecule.

3. Coupled vibrations, which may arise from the coupling of the vibrations of the ligands, or the coupling of a ligand vibration and skeletal vibration, or the coupling of various skeletal vibrations.

In a given complex the vibrating of the metal-donor atom bond give direct information on the strength and character of the coordinate bond. Therefore reliable identification of these vibrations is of particular interest to the coordination chemist. Owing to the heavy mass of the central atom and the relatively low order of the coordinate bond, the corresponding stretching frequency appears in the low frequency region.

Effect of complex formation on the symmetry of the ligand :

Coordination of the donor atom of the ligand to the central atom lowers the symmetry of the ligand. This decreases in symmetry gives rise to bands in the infrared spectrum which were not infrared-active in the free ligand, in accord with the selection rules. Bonds which are equivalent in the free ligand are not equivalent in the coordinated state; this may cause the splitting of certain bonds. This change can be readily seen in the spectre of simple ions, such as carbonate, sulphate or nitrate, and in the spectre of their complexes.

Infrared spectrometric investigation of problems in Coordination Chemistry :

Infrared spectrometry affords valuable information on the formation, structure, symmetry and stability of complexes. Vibrational bands due to the bond between the metal and the donor atom fo the ligand, and the changes in the vibrations of the ligand on complex formation, allow study of the stability and structural properties of complexes. Changes in the symmetry of the complexes, intermolecular and

intramolecular hydrogen bonding, back coordination, etc. can be recognised in the vibrational spectre fo the molecules.

Investigation of bond isomerism :

We speak of bond isomerism if a ligand containing two or more donor atoms can coordinate to a central atom in different ways, through one or another donor atom. For example, the rhodanide ion coordinates to some of the metals through the free electron pair of sulphur, and to other metals through the free electron pair of nitrogen. The first compounds are called thiocyanato, the latter isothiocyanato complexes.

Thiocyanate, isothiocyanate bond isomerism :

The infrared spectre of rhodanide ion and its metal complexes have to characteristic bands which are very easy to identify, the band of the S-C stretching vibration at 750 cm^{-1}, and the band of the > C = N stretching vibration appearing near 2050 cm^{-1}. The changes in vibrational frequency on complex formation depend upon whether the ion is bound to the metal through the sulphur or the nitrogen atom. In thiocyanate complexes the C-S bond becomes weaker then in rhodanide ion, while the strength of the N-C bond remains almost unchanged. Thus the mode of bonding of rhodanide to the central atom can be readily elucidated by an infrared spectrometric investigation of the complex in question.

Section (ii): INFRARED SPECTRA

Infrared spectra were recorded with a Perkin-Elmer IR 598 spectometer (4000 – 400 cm^{-1}) using KBR Pellets in IIT, Chennai. Infrared spectroscopy is one of the many valuable analytical techniques currently available to the chemist which is based on the interaction of electromagnetic radiation with the mater. By utilizing this spectroscopy, the presence of important functional groups in the compound, can be identified.

Peaks of IR spectra show the frequency of wave number of incident radiation on the x-axis and its transmittance on the y-axis. The wave number are used more often since it is directly proportional to the energy of vibration and as such modern IR instruments are linear in scale cm^{-1}. IR spectra of all the Cobalt (II), Nickel(II) Copper (II) and Zinc(II) complexes gave a considerable number of peaks observed and each corresponding to a particular vibrational transitional energy with ligand on complexation.

Interpretation of IR Spectra to Ligand and Its Metal Complexes:

The infrared spectrum of the ligand compared with the spectra of Cobalt(II), Nickel(II), Copper (II) and Zinc(II) complexes. The data is summarized in table 3.1 along with their assignment. The typical IR spectra are presented in figs 3.1, 3.2, 3.3 & 3.4

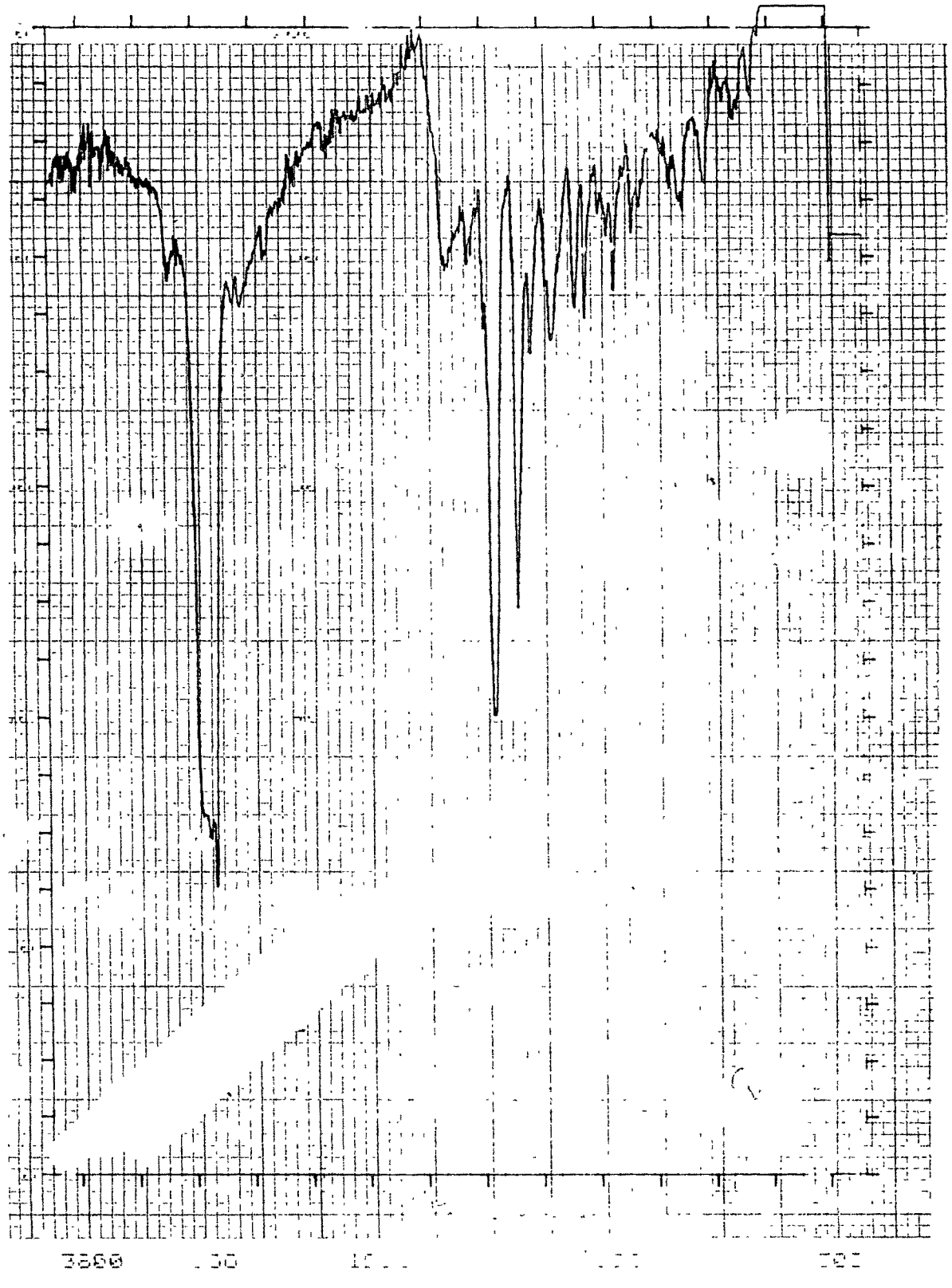
The infrared spectra of the ligand has shown a strong band at 1635 cm^{-1} due to the C=N stretching vibration of the azomethine group. On complexation this band is shifted to 1620 cm^{-1}, 1610 cm^{-1} and 1615 cm^{-1} for Cobalt(II), Nickel(II), Copper (II),

Zinc (II) complexes respectively[1-13]. Suggesting the involvement of azomethine group (>C=N) in complexation conjugation of this group. With the wave number due to the reduction in electron density thereby indicating the coordination of the metal ion through the nitrogen atoms [14,27]. The intensity of –OH group is decreases due to the hydroxyl group indicates the participation of this group also in complexation[21]. The bands appearing in the region 440-380 cm^{-1} are assigned to the stretching frequencies of M-O[20,25] and M-N of the metal ligand bands respectively[19, 24, 31, 32]. The aromatic ring had showed the absorption peaks at 1480 cm^{-1}, 1450 cm^{-1}, 1410 cm^{-1} and 1500 cm^{-1}, 1490 cm^{-1}, 1450 cm^{-1}, 1410 cm^{-1} and 1500 cm^{-1}, 1450 cm^{-1},1430 cm^{-1},1390 cm^{-1} and 1420 cm^{-1},1400 cm^{-1} corresponding to the ligand and metal complexes respectively. The IR spectra of cobalt (II), Nickel(II), Copper(II) and Zinc(II) complexes exhibited a broad band around 3400 cm^{-1} which can be assigned to γ (OH) of water molecules associated in the complex formation [16,17]. The weaker bands at 810-770 cm^{-1}, 830-770 cm^{-1}, 820-790 cm^{-1}, and 810-760 cm^{-1} are assigned to –OH rocking and wagging vibrations respectively, of coordinated water in the complexes [22]. These results indicated that the ligand coordinated with the metal ion and the nitrogen and the deprotonated Oxygen, of the hydrogen group suggested structures of the ligand & complexes are likely to be that given below[15]. All these points clearly substantiate that the ligand behave like a bidentate ligand satisfying two coordinate sites of the metal atom[28-33]. It is also seen from IR studies that water is coordinated in majority of the metal complexes studies.

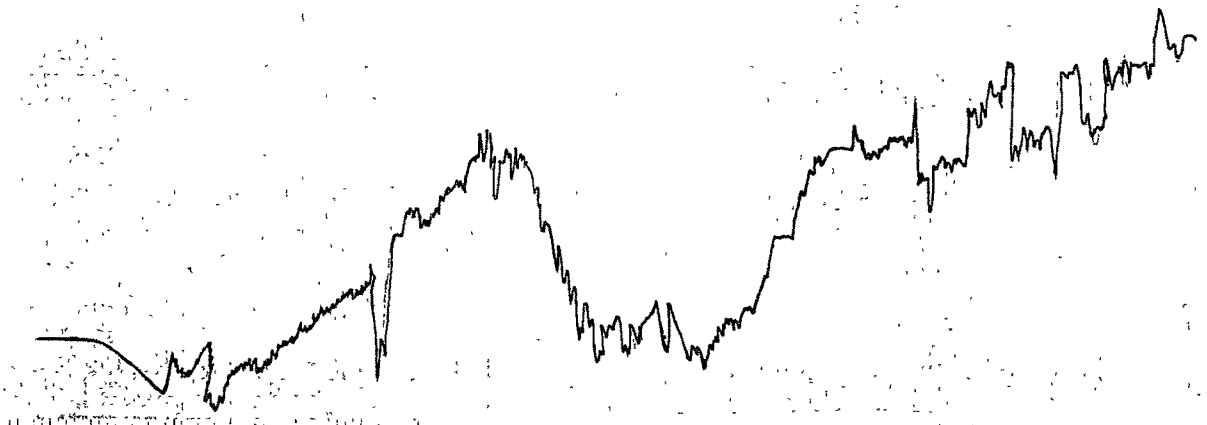
Table 3.1

Selected Ion Bonds (Cm^{-1}) Tentative Assignments

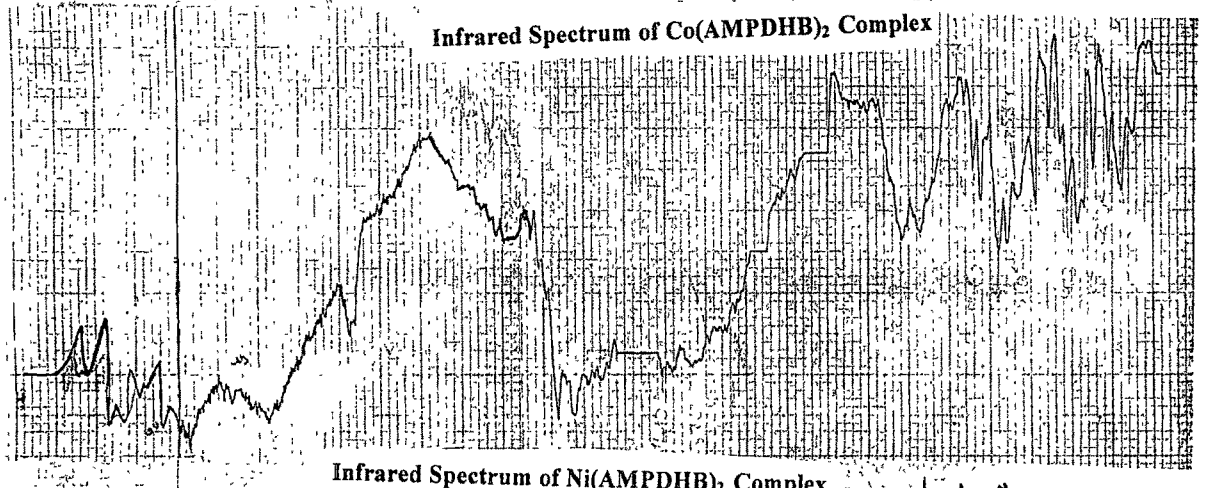
S.No.	Compound	γ C=N	γ C=O	γ Ar-C	γ M-O	γ M-N
1	AMPDHB	1635	1280	1535, 1500, 1410	490	430
2	Co $(AMPDHB)_2$	1620	1220	1480, 1450, 1410	440	406
3	Ni $(AMPDHB)_2$	1610	1210	1500, 1480, 1450, 1410	464	383
4	Cu $(AMPDHB)_2$	1610	1240	1500, 1450, 1430 1390	400	390
5	Zn $(AMPDHB)_2$	1615	1290	1420, 1400	400	388



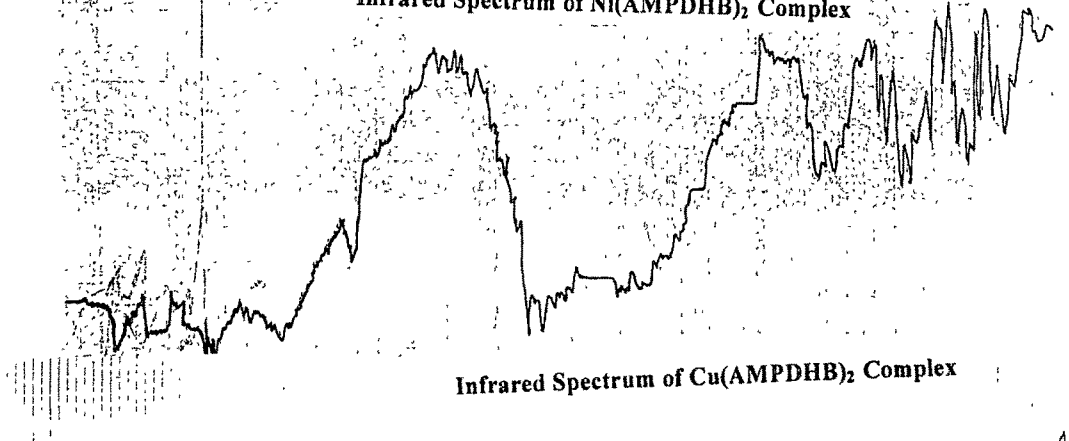
Infrared Spectrum of AMPDHB (Ligand)



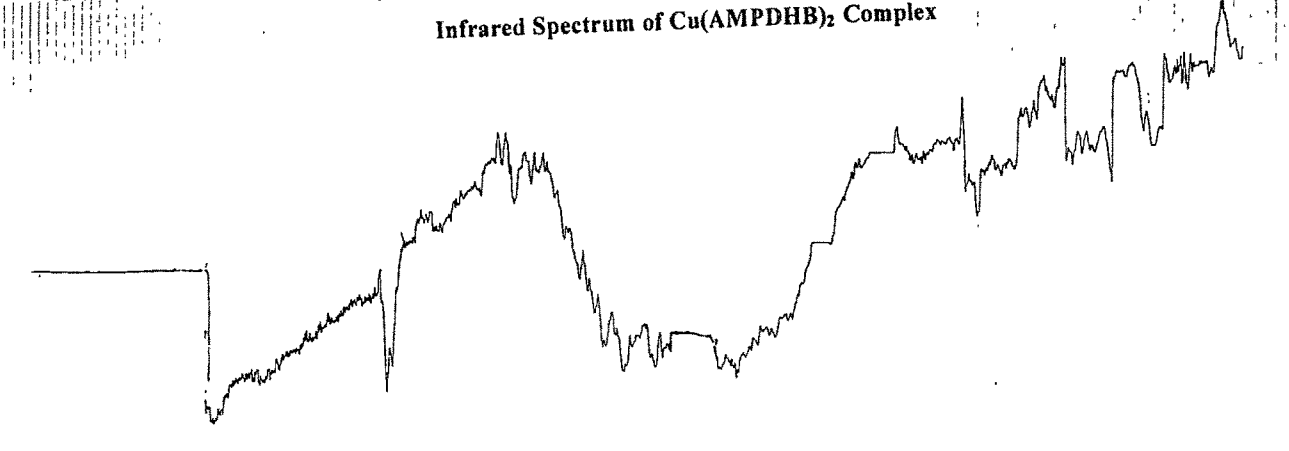
Infrared Spectrum of $Co(AMPDHB)_2$ Complex



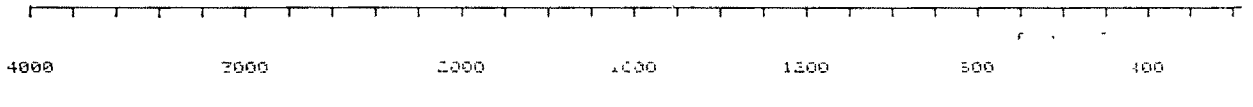
Infrared Spectrum of $Ni(AMPDHB)_2$ Complex



Infrared Spectrum of $Cu(AMPDHB)_2$ Complex



Infrared Spectrum of $Zn(AMPDHB)_2$ Complex



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