INORGANIC CHEMISTRY

Optical rotatory dispresion:-

* Optical rotatory dispresion is the variation in the optical rotation of a substance with a change in the wavelength of light. Optical rotatory dispresion can be used to find the absolute configuration of metal complexes. For example, when plane-polarized white light from an overhead projector is passed through a cylinder of sucrose solution, a spiral rainbow is observed perpendicular to the cylinder.

Principles of operation:-

* When white light passes through a polarizer, the extent of rotation of light depends on its wave length. Short wavelengths are rotated more than longer wavelengths, per unit of distance. Because the wavelength of light determines its color, the variation of color with distance through the tube is observed.

* This dependence of specific rotation on wavelength is called optical rotatory dispersion. In all materials the rotation varies with wavelength. The variation is caused by two quite different phenomena. The first accounts in most cases for the majority of the variation in rotation dispersion. It depends on the fact that optical activity is actually circular briefringence. In other words, a substance which is optically active transmits right circularly polarized light with a different velocity from left circularly polarized light.

Chirality:-

* In order for a molecule to exhibit circular birefringence and circular dichroism, it must be distinguishable from its mirror image. An object that cannot be superimposed on its mirror image is said to be chiral, and optical rotatory dispersion and circular dichroism are known as chiroptical properties.

* In the absence of magnetic fields, only chiral substances exhibit optical rotatory dispersion and circular dichroism. In a magnetic field, even substances that lack chirality rotate the plane of polarized light, as shown by Michael Faraday.

* Magnetic optical rotation is known as the Faraday effect, and its wavelength dependence is known as magnetic optical rotatory dispersion. In regions of absorption, magnetic circular dichroism is observable.

Circular dichroism:

* Circular dichroism (CD) is dichroism involving circularly polarized light. the differential absorption of left- and right handed light. Left-hand circular and right-hand circular polarized light represent two possible spin angular momentum states for a photon, and so circular dichroism is also referred to as dichroism for spin angular momentum

* Circular dichroism and circular birefringence are manifestations of optical activity. It is exhibited in the absorption bands of optically active chiral molecules. CD spectroscopy has a wide range of

applications in many different fields. Most notably UV CD is used to investigate the secondary structure of proteins. UV/Vis CD is used to investigate charge-transfer transitions. Near-infrared CD is used to investigate geometric and electronic structure by probing metal d → d transitions.

* Vibrational circular dichroism, which uses light from the infrared energy region, is used for structural studies of small organic molecules and most recently proteins and DNA.

Circular Polarization of light :-

* Electromagnetic radiation consists of an electric and magnetic field that oscillate perpendicular to one another and to the propagating direction, a transverse wave. While linearly polarized light occurs when the electric field vector oscillates only in one plane, circularly polarized light occurs when the direction of the electric field vector rotates about its propagation direction while the vector retains constant magnitude. At a single point in space, the circularly polarized vector will trace out a circle over one period of the wave frequency, hence the name.

Applications :-

* Thus CD can be used to survey a large number of solvent conditions, varying temperature, PH, salinity and the presence of various cofactors.

* CD spectroscopy is usually used to study proteins in solution, and thus it complements methods that study the solid state. This is also a limitation, in that many proteins are embedded in

membrane structures are often strongly scatterin
CD is sometimes measured in thin films.

* CD spectroscopy has also been done using semi conducting materials such as TiO_2 to obtain large signals in the UV range of wavelengths, where the electronic transitions for bimolecules often occur.

Magnetic circular dichroism:-

* Magnetic circular dichroism is the differential absorption of left and right circularly polarized light, induced in a sample by a strong magnetic field oriented parallel to the direction of light propagation. MCD measurements can detect transitio which are too weak to be seen in conventional optical absorption spectra, and it can be used to distinguish between overlapping transitions.

* Paramagnetic systems are common analytes, as their near-degenerate magnetic sublevels provide strong MCD intensity that varies with both field strength and sample temperature. The MCD signal also provides insight into the symmetry of the electronic levels of the studied systems, such as metal ion sites.

Applications:

* MCD can be used as an optical technique for the detection of electronic structure of both the ground states and excited states. It is also a strong addition to the more commonly used absorption to spectroscopy, and there are two reasons that explains this. First a transition buried under a

Stronger transition can appear in MCD if the first derivative of the absorption is much larger for the weaker transition or it is of the opposite sign.

Electronic Spectroscopy of Metal Complexes with dendritic ligands:-

* Combinations of suitably chosen metal ions and dendritic ligands may lead to giant metal complexes that display interesting spectroscopy properties, particularly as far as luminescence is concerned.

i) metal- centered

ii) Metal-to-ligand charge-transfer, or

iii) ligand- centered luminescence.

complexation of metal ions in borones:

application of electronic spectroscopy in the study of the Cu(II) – LiCl – H_2O system between 25 and 90C.

* The molar absorptivity coefficients and concentrations of each complex were then determined using a "model-free" analyses, which does not require any assumption about the chemistry of the system, other than the number of absorbing species present.

* Subsequently, the results from the "model-free" analysis were integrated with independent experimental evidence to develop a thermodynamic speciation model, where the logarithms of the equilibrium constants for Cu (II) – chloride formation reactions were fitted to the data using a non-linear least-squares approach.

IR AND RAMAN SPECTROSCOPY :-

Vibrational spectra of metal carbonyls :-

* Vibrational spectrum is more useful in the structural elucidation of simple molecules and complexes. Stretching frequencies are lower for heavier atoms and for weaker bonds and they vary only in a very narrow region of the spectrum.

* The existence and extent of M-C multiple bonding in metal carbonyls are well studied using IR spectrascopy. It is also possible to differentiate between bridging and terminal carbonyls groups using C-O absorption frequency. Since M-C stretching frequencies are in the same range with other types of vibrations, CO stretching frequencies are used. C-O gives strong sharp bands well separated from all other vibrational modes of the molecule.

* The CO molecules has a stretching frequency of 2143 cm^{-1}. The terminal CO groups in neutral metal carbonyls are found in the range 2125-1850 cm^{-1}. It shows that there is reduction in the bond order between C-O and extensive bonding between metal and carbon. For the isoelectronic series, the stretching frequencies are in the order $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$.

$[Ni(CO)_4]$ 2060 cm^{-1}; $[Co(CO)_4]^-$ 1890 cm^{-1}; $[Fe(CO)_4]^{2-}$ 1790

* In the carbonylate anions the metal has a greater tendency to be dispersed and hence M-C π-bonding will be very high. This decreases the bonding nature of C-O and hence the bond order. As the bond order b/w C-O is decreased, stretching frequency is decreased.

$$M^- - C \equiv O^+ \longleftrightarrow M=C=O$$

Since Iron carbonylate anion has more $\bar{e}^{n}$ density it has more back π-bonding character than cobalt carbonylate anion containing one electron than the nickel carbonyl. Hence the stretching frequency decreases in the order.

$[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$

Similar arguments are given for the hexacarbonyls of the transition metals.

$[Mn(CO)_6]^+ \sim 2090\, cm^{-1}$; $[Cr(CO)_6] \sim [2000\, cm^{-1}$; $[V(CO)_6]^- \sim 1680\, cm^{-1}$.

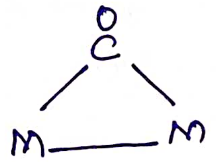
The greater the positive charge on the central metal atom, the less readily the metal can back bond electrons into the π* orbitals of the CO ligands. As a result, there is no π bonding between metal and carbon and the CO bond order is not decreased. It gives a values of 2090 cm^{-1}. In $[Cr(CO)_6]$, chromium back donates the dπ electrons to the π* orbital of carbon and there is decrease in the frequency to 2000 cm^{-1}. In the isoelectronic $[V(CO)_6]^-$, there is more negative charge on the metal. In order to prevent more charge accumulation on the metal atom, the excess electron is back donated to the π* orbital of CO. This increases the M-C bond order and decreases the C-O bond order. Hence $[V(CO)_6]^-$ has the stretching frequency of 1860 cm^{-1}.

$Cr(CO)_6$ has the stretching frequencies at 2100, 2000 and 1985 cm^{-1} whereas $[Cr(dien)(CO)_3]$ has two stretching modes at 1900 and 1760 cm^{-1}. In $Cr(CO)_6$, there is increase in the Cr-C bond order due to back donation of $\bar{e}^{ns}$ from chromium to carbon thereby reducing the CO bond order. When three CO ligands are replaced by the amine with low or nelegible back - accepting ability, the remaining three CO groups must accept all the d electrons from the metal to a greater extent than in $[Cr(CO)_6]$. This prevents the accumulation of the negative charge on the metal and increases the Cr-C bond order. As a result C-O bond order is decreased leading to the low frequency values at 1900 and 1760 cm^{-1}!

Competition for the π-electrons are observed for the complexes of the types Cis-Mo(dien)$(CO)_3$. Each CO group shares two metal dπ orbitals to receive electrons. In the hexacarbonyl each dπ-orbital of the metal is contributing equally to all the six ligands. If the electrons are fully used each M-C pair will have ½ of a π-bond since there are three pairs of electrons for three dπ-orbitals of the metal. If L is a poor π-bonding ligand, it will not be able to compete with the extremely good π-bonding CO ligand. Hence the electron density from the metal goes to the three CO ligands for back π-bonding and each M-C pair will have a full π-bond.

$$OC-M=L \longleftrightarrow OC=M-L$$

Thus the M-C bond order increases thereby weakening the C-O bond order. If L is CO, the two resonating forms will contribute equally to the back accepti electrons from the metal. If L is poorer π bonder, M=C will be more predominant. For such complexes the CO stretching frequencies are decreased. The stretching frequency values are affected by the electronegative groups present in the ligands



(a)

Doubly bridging

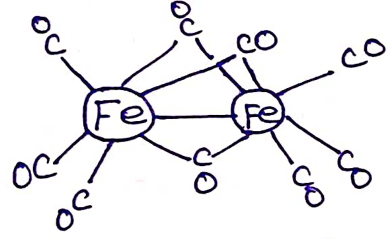
(b)

Triply bridging

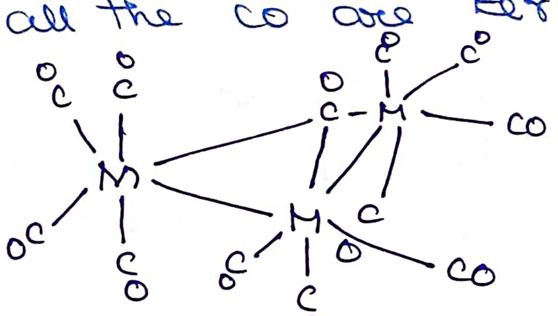
$OC-M-M-CO$

Terminal

$[Fe_2(CO)_9]$ has strong absorption bands in both the terminal and the bridging regions. This confirms the difference in the CO linkages in $Fe_2(CO)_9$. But for $[Os_3(CO)_{12}]$, the absorption frequencies are observed only above $2000 cm^{-1}$. This indicates that there is no bridging CO and all the CO are terminal.



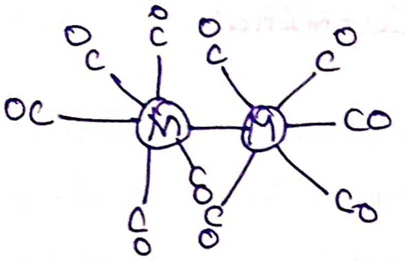
$Fe_2(CO)_9$ (D_{3h})



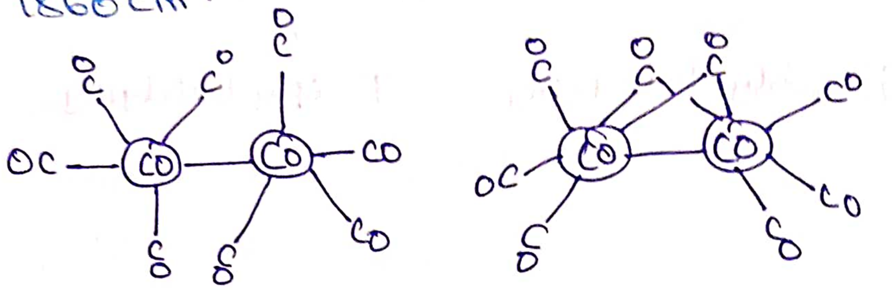
$M_3(CO)_{12}$ $M = Ru, Os$ (D_{3h})

$Mn_2(CO)_{10}$ has two conformational isomers, eclipsed and staggered with respect to rotation around the metal-metal bond axis. the eclipsed from has D_{4h} symmetry and has three absorptions in IR and four in Raman spectra. The staggered from has D_{4d} symmetry and has the same no. of IR (3) and Raman (4) spectral vibrations. Thus it is not possible to distinguish D_{4h} and D_{4d} from Ir and Raman spectra alone. $[Mn_2(CO)_{10}]$ has stretching bands only in the range 2044 - $1980 cm^{-1}$ while $[Co_2(CO)_8]$ has bands in the range 2071 - $2022 cm^{-1}$ and at 1860 and $1858 cm^{-1}$. It suggests that in $[Mn_2(CO)_{10}]$ all the CO ligands are terminal in nature whereas in $[Co_2(CO)_8]$, both terminal and bridging CO groups are present.

* For terminal groups the frequency range is around 2000 cm^{-1} and for the bridging co the frequency range is 1860 cm^{-1}.



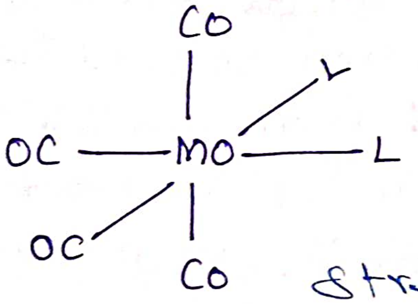
$M_2(CO)_{10}$, M = Mn, Tc, Re
(D_{4d})



$Co_2(CO)_8$ two isomers
(D_{3d}, C_{2v})

* In the trans - [$PtCl_2L(CO)$] complex, the stretching frequency for L = NH_3, Pyridene and NMe_3 decreases in the order pyridine > NH_3 > NMe_3. The electron density on N is higher for NMe_3 due to inductive effect of methyl group than ammonia than pyridine.

Geometry and number of stretching vibrations:-



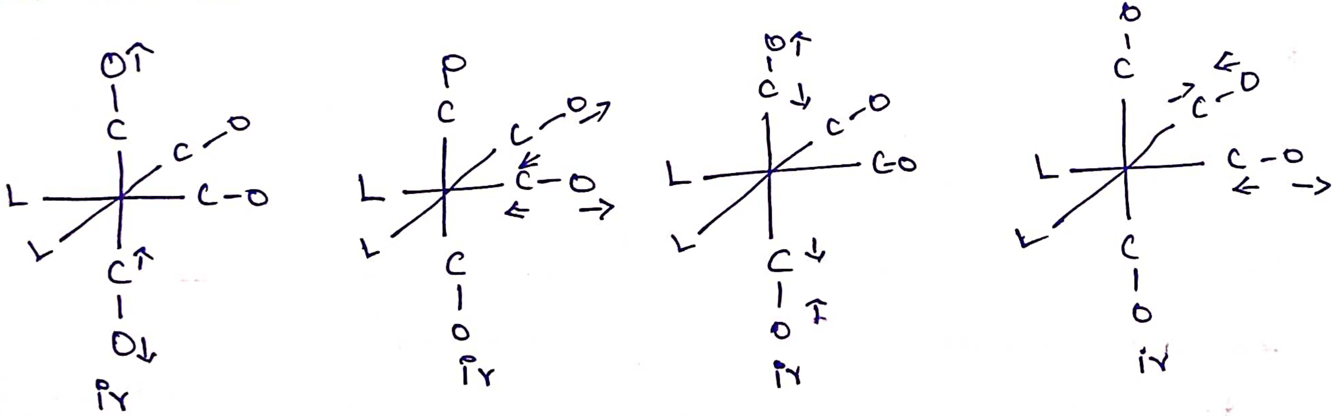
* There is one stretching mode for each bond in molecule. The no. of CO ligands in a complex may be be counted by simply counting the CO stretching bands in the IR spectrum. But the symmetry selection rules govern the activity of the various stretching motions. The no. of bands also depend on the rotation axis.

* Let there are cis- and trans- isomers of [$ML_2(CO)_4$]. In the cis- compound, the two CO groups trans to each other must be treated together. The other two are mutually cis. These two pairs of CO ligands are not equivalent but two sets of two. Each pair is related by a C_2 axis, say a

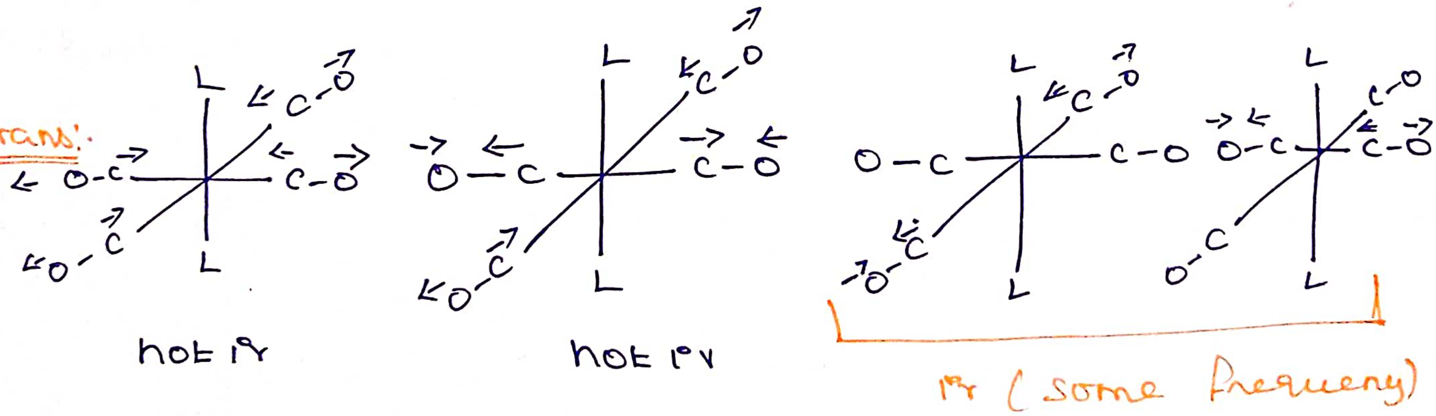
b components. The two pairs of bonds define two planes at right angles to each other. Therefore one of the two b components is b_1 and the other b_2. The two a_1 modes, one b_1 and one b_2 are in the CO stretching region. Thus four infrared bands are observed for the cis isomer and it is found at 2016, 1915, 1900 and 1890 cm^{-1} when $L = (C_2H_5)_3P$. All the four are IR and Raman active.

* The four CO groups of trans isomer are all symmetry-related giving a_1', b_2' and e' stretching modes, only one e' is IR active and all three are Raman active.

Cis:-



trans:-



Raman Spectroscopy application in Inorganic Systems:-

X-ray diffraction has been developed into a standard method of determining structures of solids in inorganic systems.

* Compared to XRD, it is usually necessary to obtain other information besides vibrational information from IR / Raman in order to elucidate the structure.

* IR and Raman are fast and simple analytical method, and are commonly used for the first approximation analysis of an unknown compound.

* Raman spectroscopy and IR have different selection rules. Rs detects the polarizability change of a molecule, while IR detects the dipole momentum change of a molecule.

* Homonuclear diatomic molecules are all IR inactive, fortunately, the vibration modes for all the homonuclear diatomic molecules are always Raman spectroscopy active.

Resonance Raman Spectroscopy :-

* RR is a Raman spectroscopy technique in which the incident photon energy is close in energy to an electronic transition of a compound or material under examination. The frequency coincidence can lead to greatly enhanced intensity of the Raman scattering, which facilities the study of chemical compounds present at low concentrations.

Applications :-

* The main advantage of RR spectroscopy over non-resonant Raman spectroscopy is the large increase in intensity of the bands in question (by as much as a factor of 10^6).