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BS Chemistry
VI Semester.
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Chapter - 1

INTRODUCTION

The charged or uncharged electron pair donor atoms or molecules which are bonded to the central metal atoms or ions are called ligands. Some of the commonly used simple ligands are neutral molecules containing N, O or P atoms. e.g: NH_3, CO, NO, H_2O. The charged ions such as Cl^-, OH^-, NO^+ etc can also act as ligands. One of the characteristics of transition metals is their ability to form complexes with such electron donor ligands. Some of the electron pair donor groups or ligands can react with metals in high positive oxidation state. e.g. H_2O, NH_3. In variety of neutral molecules such as CO and NO the stable complexes are obtained only with transition metals in low positive, zero or even negative formal oxidation states. In other words, these ligands can stabilize only the low oxidation states of metals. The property is due to presence of vacant orbitals in the ligands in addition to lone pairs. Lone pair of electrons on ligands are donated through σ-bonding to the vacant d-orbitals of transition metals which are incapable of retaining the charge density in low oxidation states. The charge density received by transitio metals through σ-bond is released back to the ligands on the vacant π-orbitals. Thus the high charge density on the metal created by the ligand is released back to the vacant π-orbitals of the ligand. The ability of accepting charge density back into the low-lying empty π-orbitals of ligands is called π-acceptor capacity or π-acidity. The term π-acidity is derived from Lewis acid concept where a species capable of accepting lone pair of electrons is called an acid. The typical examples of π-acceptor ligands which are capable of accepting the charge density from metals into vacant π-orbitals are CO, NO, isocyanides and certain unsaturated organic molecules. The organic compounds which can form will be beyond the scope of this book.

One of the most active areas of carbon monoxide commonly called "carbonyls". This is expected on the basis of utility of transition metal carbonyls for the synthesis of variety of organic and inorganic compounds some of which are of industrial importance". During the last three decades preparative and structural work involving metal carbonyls has provided a great stimulus. Firstly, Schutzenberger recognized carbon monoxides as a ligand when he could prepare $Pt(CO)_2Cl_2$. In 1890, Mond prepared tetracarbonylnickel, $Ni(CO)_4$ and the research interests increased tremendously, afterwards. So, much so that on 15th June, 1891 Mond in London and Berthelot in Paris were describing their independent discoveries of Pentacarbonyliron, $Fe(CO)_5$ to the Chemical Society, London and the French Academy of Sciences respectively. Later on synthesis of hundreds of metal carbonyls and their derivatives were carried out.

Various types of derivatives of metal carbonyls have been develop. In 1930, Hieber discovered the first two metal carbonyl hydride derivatives, $H_2Fe(CO)_4$ and $HCo(CO)_4$ which remained laboratory curiosity for a relatively long time. Transition metal carbonyl -hydrides have now been recognized as catalysts in industrial processes involving hydroformylation, olefin polymerization, and hydrogen exchange etc.

Transition metal complexes with NO are also known for many years. Although they have never attracted as much attention as as metal carbonyls, the studies of their preparation and properties continue to fluorish. It has now been recognized that transition metal nitrosyls are useful as selective homogeneous catalysts for certain reactions.

Chapter - II

TRANSITION METAL CARBONYLS

The most interesting π-acceptor ligand is carbon monoxide, Carbonyl derivatives of most of the transition metals are known. They are of considerable structural interest of there usefulness as catalysts in certain industrial processes is beyond any doubt.

Metal carbonyls can have simple or complicated molecular formulae. The carbonyl containing only one metal atom per molecule are called Mononuclear. They are the simplest metal carbonyls and are of type $M(CO)_X$ [$x = 4$ to 2].

"MONONUCLEAR CARBONYL"

Group V	Group VI	Group VIII	
$V(CO)_6$ Black crystals which sublime under vacuum Decomp. 70°	$^{24}Cr(CO)_6$ Colorless rhomble crystals. Sublimes m.p. 140°.	$^{26}Fe(CO)_5$ Toxic yellow liquid, m.p=20° b.p. 103°, Decomp 130°	$Ni(CO)_6$ Toxic colorless liquid m.p-25° b.p. 45° Decomp. 100°.
	$^{42}Mo(CO)_6$ colorless crystals sublime at 40°. Decomp. 150°	$^{44}Ru(CO)_5$ Colorless liquid m.p-22°, Sublimes; Decomp-50°	
	$^{74}W(CO)_6$ colorless crystals sublime	$Os(CO)_5$ colorless	

Binuclear contain two metal atoms in one have general formula $M(CO)_x$ = 8x10. Polynuclear metal also known contain more than two metal atom in a molecule.

BINUCLEAR CARBONYLS

Group VII	Group VIII	
$Mn_2(CO)_{10}$ Golden Yellow crystal. mp 1550° Decomp. 110°	$Fe_2(CO)_9$ Yellow Flakes Decomp 100°	$Co_2(CO)_8$ Orange red crystals m.p 51°.
$Te_2(CO)_{10}$ White m.p = 160°	$Os_2(CO)_9$ Orange crystal Decomp. 64 – 67°	$Ru_2(CO)_8$ Orange crystals m.p 76° Decomp. 76°
$Re_2(CO)_{10}$ Colorless monoclinic mp 177° Sublimes at 140° Decomp. 177°		$Ir_2(CO)_8$ Yellow green crystals Sublimes in CO at 160°.

POLYNUCLEAR CARBONYLS

Group VIII

$Fe_3(CO)_{12}$ Green monoclinic crystals. Decomp. 140°	$Co_4(CO)_{12}$ Black solid Decomp. 60° to $Co_6(CO)_{16}$	$Ir(CO)_{12}$ Yellow solid sublimes in CO at 210°. Decomp 210° to $Ir_6(CO)_{16}$
$Ru_3(CO)_{12}$ Orange Yellow crystals	$Rh_4(CO)_{12}$ Red crystal Decomp 150°	
$Os_3(CO)_{12}$ Yellow crystals	$Rh_6(CO)$ Black solid	

EFFECTIVE ATOMIC NUMBER (EAN) RULE.

put forward by Sidgwick and Bailey is observed by transition metal carbonyls which show dimagnetic behaviour. The only exception to EAN rule is vanadium hexacarbonyl which has paramagnetic behaviour. A carbon monoxide group is required as asource of two valence electrons, so that in a simple mononuclear carbonyl, $M(CO)_X$ with one metallic atom in the molecule, the Effective Atomic Number of the metal, atomic number of the metal $+2X$ (where X is the number of CO groups) is always the atomic number of the next inert gas. e.g 36 in first row transition metal carbonyl, $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$; 54 in second row transition metal carbonyl, $Mo(CO)_6$, $Ru(CO)_5$ and 86, in third row transition metal carbonyls, $W(CO)_6$, $Os(CO)_5$ and $Pt(CO)_5$. For metals of odd atomic numbers the rules implies that there would be no stable simple mononuclear carbonyls but binuclear and certain polynuclear carbonyls are obtained. The EAN rule is very useful in preparative work in accounting for as well as predicting the stoicheiometries of complexes. Applying effective atomic number rule to $Fe(CO)_5$ (Atomic number of $Fe = 26 + 2X$, $X = 5$ or $26 + 2 \times 5 = 26 + 10 = 36$) the next inert gas configuration i-e 36 is reached. In case of binuclear and mononuclear carbonyls the metal-metal bonds are considered one electron donors. Thus $Mn_2(CO)_{10}$ has a Mn–Mn bond and each metal atom contains five CO groups. The atomic number of Mn being 25 and that five CO groups are attached to each Mn($25+10=35$). The next inert gas configuration 36 does not seem to have been reached. It should be born in mind that each metal contributes one electron to Mn–Mn bond which is to be added up making the figure of 35 by addition of one to 36. A simple way of recording the electron count is to assign some numbers to the metals. These numbers are called magic numbers and are the number of electrons required by a metal to reach the inert gas configuration in a complex. For the transition elements which form carbonyl complexes these numbers are

Oxidation State	G-IV	G-V	G-VI	G-VII	G-VIII		
	Ti	V	Cr	Mn	Fe	Co	Ni
1	15	14	13	12	11	10	9
0	14	13	12	11	10	9	8
−1	13	12	11	10	9	8	7

It must be remembered that transition metals in metal carbonyls are in Zero valent states because no net gain or loss of charge is expected on forming bonds with CO. In $Ni(CO)_4$ the nickel metal is in zero valent state and has magic number 8. This means that 8 electrons are needed by nickel to reach inert gas structure and to form a stable compound. Four ~~number of Ni° is 8)~~ carbon monoxide groups provide 8 electrons (each CO provides two electrons; the magic number of Ni° is 8) to reach inert gas configuration.

Similarly Cr has magic no. 12 which means that 12 electrons are by chromium in zero valent state To reach inert gas configuration which are provided by 6 CO group; hence the formula of chromium carbonyl is $Cr(CO)_6$.

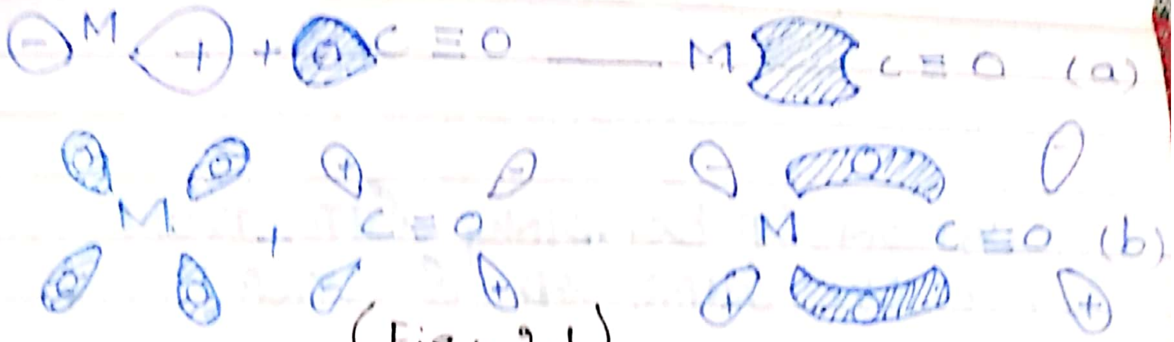
BONDING SITUATION IN METAL CARBONYL- NATURE OF THE METAL-CARBON BOND

Lewis basicity (electron pair donor ability) if CO is relatively low. and it is surprising to get stable metal carbonyls. especially when metals are in zero valent state and the monoxide remains as individual in the resulting molecules. A plausib explanation lies in the multiple natu of M-CO bond for which there is sufficient spectroscopic evidence.

The ability of CO group to stabilise metal atoms in low-positive zero, or low-negative oxidation states is believed to be due to the so calle "synergic bonding effect". A metal carbo σ-bond is formed by overlapp of a filled sp-hybrid orbital of carbon and a vacant hybrid orbital of the metal. e.g. sp^3 of nickel in $Ni(CO)_4$, dsp^3 of iron in $Fe(CO)_5$ and d^2sp^3 of molybdenum in $Mo(CO)_6$. At the same time π-bond are formed by overlapp of filled d-orbital of the metal with empty antibonding orbitals of CO groups. The drift of electron charge from metal dπ or hydrid dp π orbital into empty antibonding π^* CO orbitals will tend to make CO as a whole negative and consequently increases its basicity via the σ-orbital of carbon. At the same time drift of σ-bonding charge density to the metal would make CO more positive and would enhance the acceptor strength of its π-orbitals. Consequently charge density on metal dπ or dp π orbitals would be enhanced which would increase the ~~basis~~ ~~basicity~~ drift of metal electrons into

π^* orbitals of CO. This in term would increase the Lewis basicity of CO and a synergic bonding mechanism would mutually reinforce effect of metal and CO on one another. The dipole moment studies have indicated that moment of an M–C bond is only very low, about 0.5 D, thereby suggesting that no net charge density is shifted from CO to metal which also explains the zero valent state of metal.

The molecular orbital formulation is represented below.



(Fig: 2.1)

The formation of M–C σ-bond through unshared electron pair on carbon atom is represented in fig 2.1(a). At the same time, M–C bond formation takes place and is represented by Fig 2.1(b). The filled orbitals are represented by shaded lines.

The bonding Type represented in Fig 2.1 can be drawn in simplified manner as:

$$\underset{(a)}{M^{-}-C^{+}\equiv O^{+}:} \longleftrightarrow \underset{(b)}{M=C=\ddot{O}:}$$

There is sufficient experimental evidence to prove that the structures (a) and (b) actually exist in equilibrium and the metal carbonyl is a hydrid of these two structures. The main physical evidence in favour of multiple nature of M-CO bonds are bond lengths and infrared spectra. It is evident from the above discussion that with the increase of back donation from metal to CO, the M-C bond becomes stronger and the $C \equiv O$ bond correspondingly becomes weaker. This would result in shorter M-C and longer C-O bonds as compared to M-C single bonds and $C \equiv O$ triple bonds respectively.

EVALUATION OF BONDING SITUATION BASED ON INFRARED SPECTRA :-

The energy of most molecular vibrations correspond to the infrared region of the electromagnetic radiations. The molecules have vibration frequencies characteristics of the functional groups. The infrared spectra of metal carbonyl are found to be a useful source of information regarding structures are bonding situation. The comparison of CO stretching frequencies in carbonyl molecules with the stretching frequency of free CO provides sufficient information which can lead to certain qualitative conclusions.

Infrared spectrum of free carbon monoxide ν (CO) is observed at 2155 cm^{-1}. Terminal CO groups (CO groups at terminal positions to metals) in neutral metal carbonyls have stretching frequencies in the infrared (IR) range 2125 – 1850 cm^{-1}. Free carbon monoxide ; $C\equiv O$ has C to O triple bond. In other words bond order is about 3. When carbon monoxide reacts with metals to form metal carbonyls, the C to O bond order is decreased to back donation of charge density from metal d orbitals to antibonding orbitals on carbon of CO. With decrease in CO bond order the infrared stretching frequency also decrease to near about 2000 cm^{-1}. The stretching frequency values of CO in metal carbonyls thus depend upon the extent of back donation of charge density from M to CO. More than π-charge is drifted to CO from the metal, the structure (b) (fig 2.1) becomes more predominant. The infrared CO stretching frequency will decrease correspondingly. If charge density from metal is shifted completely to CO, the CO bond order will be about two and infrared frequency observed at about 1850 cm^{-1}. The structure (b) will be only contributing structure. (CO) stretching frequency in $Cr(CO)_6$ is at 2000 cm^{-1}. If the contributing structure is (a) IR frequency would have been at 2150 cm^{-1} and in case of structure (b) the ν CO would be at 1850 cm^{-1}. In case of $Cr(CO)_6$ the structure (a) and (b) seem to be contributing equally because the mean value of 2150 and 1850 Cm^{-1} (ca = 2000 cm^{-1}) is depicted in infrared spectrum. It can be safely said that the ν CO values in metal carbonyls is depend upon the predominant contributing structure (a) or (b). If the structure (a) is more predominant, the νCO frequen would be above 2000 cm^{-1} (towards higher wave numbers) and in case the structure (b) is more contributing, the νCO frequency will fall below 2000cm (towards lower wave numbers). This approximation can be applied to explain the behaviour and bonding situation in various metal carbonyls. A series of isoelectronic carbonyl species illustrating this trend are:

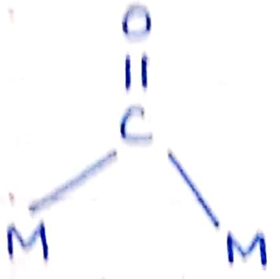
	$Mn(CO)_6^+$	$Cr(CO)_6$
$\nu(CO)$ cm^{-1}	2096	2000

$V(CO)_6^-$ $Ni(CO)_4$ $Co(CO)_4^-$
1859 2046 1883

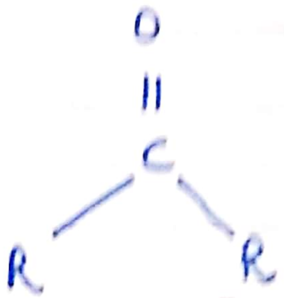
$Fe(CO)_4^{-2}$
1788

The neutral $Cr(CO)_6$ shows $\nu(CO)$ at 2000 cm^{-1} in which the structure (a) and (b) are equally contributing. In $Mn^+(CO)_6$ the positive charge on the metal means less charge density available to it. Therefore, the drift of π- charge from M to C will be to lesser extent. The contributing structure (a) becomes more predominant and $\nu(CO)$ stretching frequency shifted towards higher wave number i-e 2096 cm^{-1}. The carbonyl such as $V(CO)_6$ has accumulated negative charge density on metal. Hence more charge is released from metal to CO to observe the principle of electroneutrality. Shift of more charge density to antibonding orbital of C. result in the predominence of contributing structure (b). The $\nu(CO)$ stretching frequency in IR spectrum moves to lower wave number (1859 cm^{-1}). Similarly the ν_{CO} frequency further decreases on putting more negative charge density on the metal. Thus $Ni(CO)_4$ shows IR band at 2046 cm^{-1}. Increase of negative charge density on cobalt in $Co(CO)_4$ increases the tendency to release more charge density from metal to CO. The structure (b) becomes more predomint and $\nu(CO)$ stretching frequency will further shift to low wave number ($1883\ cm^{-1}$). Increase of -ve charge on metal will further increase the drift of charge density from metal to CO in order to release the excessive -ve charge. The carbonyl anion, $Fe(CO)_4^{2-}$ bears -2 charge on iron and the drift of charge density from M to CO become more intensive, thereby enhancing, the predominance of structure (b). This cause further lowering of $\nu(CO)$ stretching frequency to $1788\ cm^{-1}$. It is obvious that the infrared data are in complete agreement with the proposed resonating Structures (a) and (b) for metal carbonyls and that actual metal carbonyl structure is hybrid of these contributing structures. The infrared spectra of some commonly available carbonyls are shown in fig 2.2.

It may be pointed out that relatively low $\nu(CO)$ values in neutral carbonyls can be attributed to the presence of brigding carbonyl have bonds similar to ketones. The ketonic CO has

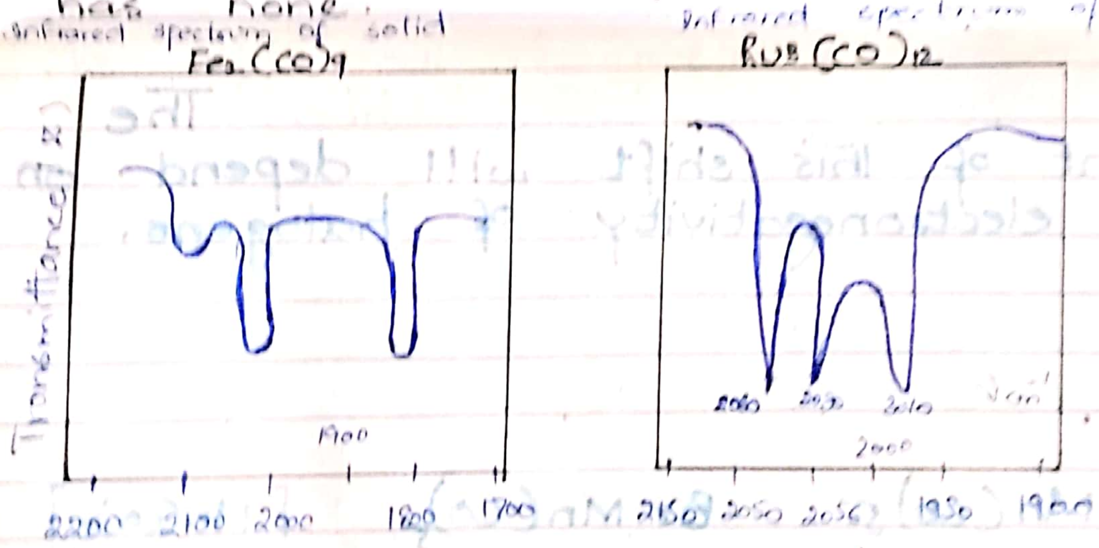


Bridging Carbonyl



Ketone

IR band near 1800 cm⁻¹ and similar values would be expected for bridging carbonyls. The infra red spectra in the CO stretching region of solid $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ in solution are given in fig 2.2 (a) and (b) respectively, $Fe_2(CO)_9$ has bridging CO but $Ru_3(CO)_{12}$ has none.



(a) (b)

As CO groups in a metal carbonyl are replaced by other ligand which are stronger σ- donors but weaker π acceptor. ν(CO) (max) will decrease. The π charge density from metal to stronger σ- donor ligand other than CO will be drifted more towards CO and wave number.

The infrared spectra of $Ni(CO)_4$ derivatives with then phenomenon.

	$Ni(CO)_4$	$Me_3PNi(CO)_3$	$(Me_3P)_2Ni(CO)_2$
$\nu(CO)\ cm^{-1}$	2046	1943	1934

Conversely, ligands which have tendency to inhibit transfer of e^- density from metal to the π - CO orbital by creating +ve charge on the metal cause $\nu(CO)(max)$ to rise. e.g. halogens being e^- withdrawing atom would creat electropositive centre on the metal resulting in the shift of $\nu(CO)$ to higher wave number. The extent of this shift will depend on the electronegativity of halogens. More electronegative chlorine atom will result in the greater increase of $\nu(CO)$ to higher wave number.

$ClMn(CO)_5$	$BrMn(CO)_5$	$[IMn(CO)_5]$
2138, 2054	2133, 2050	2125, 2044

Subtle changes in CO stretching frequency also observed as groups bonded to ligand atoms are changed. e.g:- in complexes of the type $(R_3P_3).Mo(CO)_3$, $\nu(CO)$ decreases with decreasing electronegativity of group R, viz

	$\nu(CO)\ cm^{-1}$
$(F_3P)_3Mo(CO)_3$	2074 , 2026
$(Cl_3P)_3Mo(CO)_3$	2041 , 1989
$(C_6H_5PCl_2)_3Mo(CO)_3$	2016 , 1943
$[(C_6H_5)_2PCl]_3Mo(CO)_3$	1977, 1885
$[(C_6H_5)_3P]_3Mo(CO)_3$	1989 , 1835

Phosphines are similar to carbonyl groups as regards their π-acceptor capacity. In phosphines 3d orbitals of the phosphorous atoms are vacant, but extent of their overlapp with filled metal d-orbital depends on nature of the group attached to the ligand atom. More electronegative fluorine effectively contracts the phosphorous 3d orbitals making π-bonding b/w phosphorous and metal more effective. More charge density shifts towards phosphine groups and less toward CO group. The structure (a) become more predominant and $\nu(CO)$ shifts to slightly higher wave number ($\nu(CO)$ in $Mo(CO)_6$ in 2000 cm^{-1}) Chlorine and phenyl groups are less electronegative and less effective in this respect. Consequently, there is increase in flow of charge to the metal during σ-bond formation. The increase in e^- charge density on metal would be released through π-bonding to CO to a longer extent resulting in more contribution of structure (b) and consequent decrease in ν(CO), as is observed.

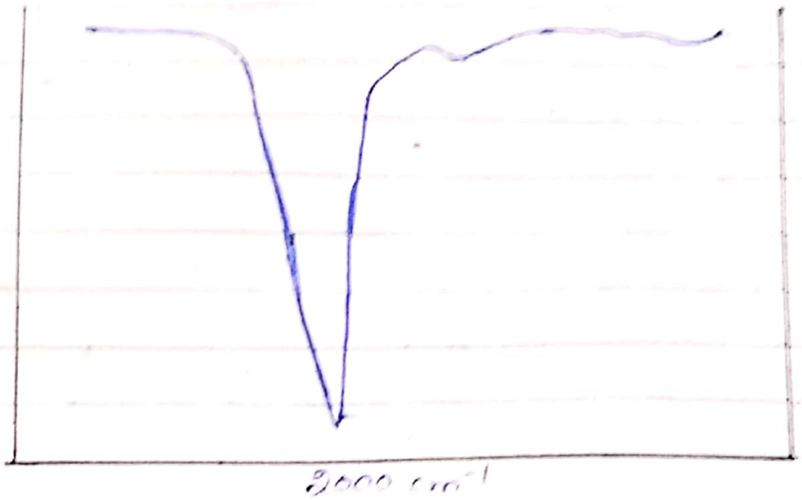
As the extent of back donation of the CO group increase for structurally released compounds, the Metal-carbon bond might be expected to become shorter and the carbon-oxygen bond longer. Thus in complexes $Mo(CO)_6$ and dien $Mo(CO)_3$ (dien-diethylenetraimine) a change in Mo-C bond order from 1.5 & 2.0 is obtained as expected. Consequently, the ν(CO) decreases to lower wave number in the later complex, due to conseqent decrease in ν(CO), as is observed, decreases to lower wave number in the later complex, due to consequent decrease in C-O bond order.

The terminal M-C-O bonds are often bent. Molecular orbital calculations have shown that the π^*-orbitals of tricarbonyl groups can be divided into the symmetry sets which are orthogonal. This leads to a difference in the degree of occupation of the orbitals and hence to bending of the M-C-O bonds.

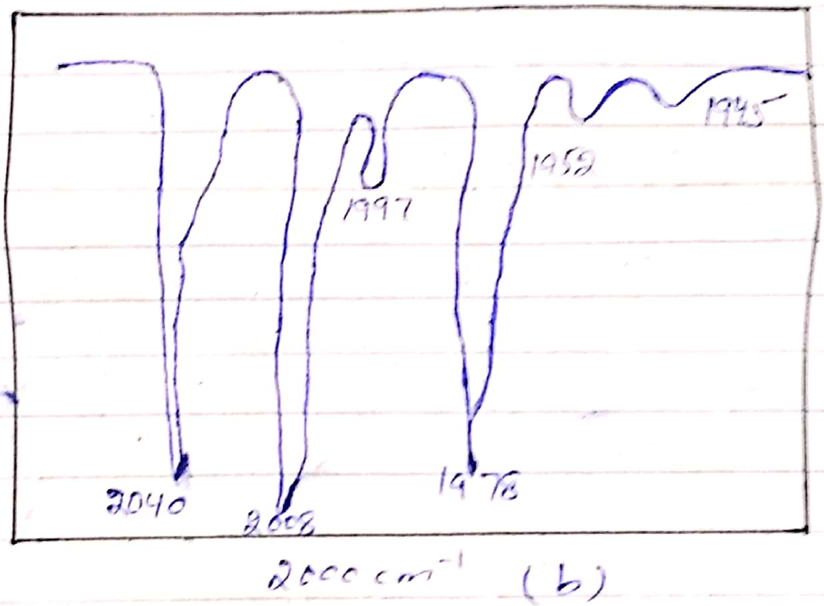
In addition to the terminal carbonyls, many metal carbonyl compound contain carbon monoxide groups bonded simultaneously to two or three metal atoms. The bonding CO groups contribute one e^- to each of the metal atoms to from localized σ- pairing with metal e^-. The π- bonding with bridging carbonyl group is more complicated than with terminal CO ligand but undoubtelly occurs and may be character. The IR of a bonding carbonyl group shows a stretching frequency around 1550 cm^{-1} but this is variable and the lowest reported so far is 1616 cm^{-1} in $[C_5H_5Ru(CO)]_4$. The presence of a carbonyl stretching frequency in the region of 1850 cm^{-1} does not necessary indicate the presence of a bridging carbonyl group unless CO ligands are present in a neutral carbonyl species.

Substitution of a strong σ-donor ligand with no π- acceptor capacity bonded to the metal atoms results in the transfer of electron density from the metal to the antibonding orbitals of the CO group to a large extent with tremendous contributing of structure (b) and of C-O bond order.

Thus the IR spectrum of the (diene) $Mo(CO)_6$ gives $\nu(CO)$ at 1883 and 1723 cm^{-1}. Infrared spectra of $Mo(CO)_6$



(a)



(b)

(a). Infrared spectrum of $Mo(CO)_5$
(b) Infrared spectrum of $Mn_2(CO)_{10}$

MOLECULAR STRUCTURE OF METAL CARBONYL:-

Infrared, dipole moment studies, nuclear magnetic resonance spectroscopy (NMR). Mossbauer spectroscopy, magnetic susceptibility measurements, electron diffraction amd mass spectroscopy have all given useful information about the structure of metal carbonyls and their derivatives. However

X-ray diffraction studies have been the most important in elucidating their structures.

It has already been discussed that metal carbonyls obey effective atomic number (EAN) rule and resort to next inert gas configuration. The structures of the mononuclear carbonyls $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ are well established and are given in Table 2.4

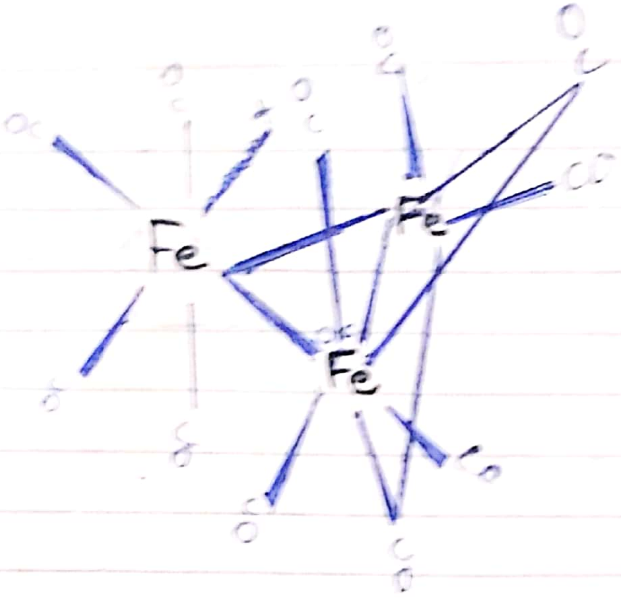
Compound	Metal bonds	St. & Symmetry	
$Ni(CO)_4$	sp^3	Tetrahedral	T_d
$Fe(CO)_5$	dsp^3	Trigonal bipyramid	D_3h
$Cr(CO)_6$	d^2sp^3	Octahedral	Oh
$V(CO)_6$	d^2sp^3	Octahedral	Oh

The three structural types, i.e tetrahedral, trigonal, - bipyramidal and octahedral are often encountered among simple carbonyls and their derivatives. The carbonyls of ruthenium and osmium $Ru(CO)_5$ and $Os(CO)_5$ have trigonal bipyramidal structures like $Fe(CO)_5$.

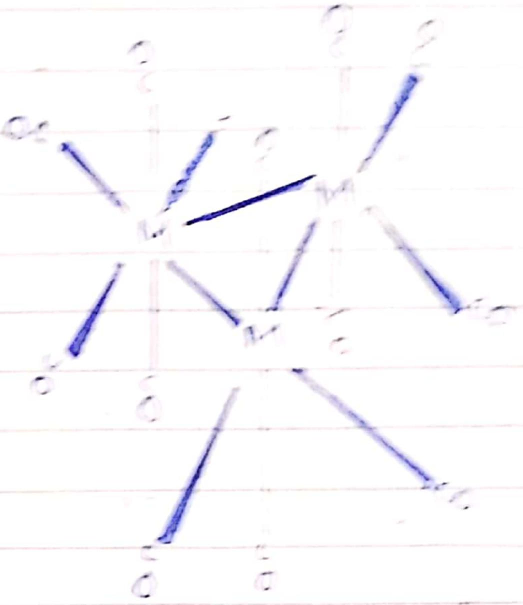
The molecular structures of some typical binuclear and polynuclear carbonyls as confirmed by X-ray diffraction and representative principal structural type are shown in 2.4. Broad ends indicate groups nearer to the eye or above the plane and vice versa. These molecular structures have all been studied in detail. The carbonyls of Group VII ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$) have no bridging carbonyls. Five CO groups on each Mn contribute 10 electrons (two electrons by each CO) to Mn and 1 e^- required by Mn is provided by metal-metal (Mn–Mn) bond making total of 11 e^- provided to Mn which is the magic number of this metal. On the basis of EAN rule these 11 e^- when added to the atomic number of Mn (25) would give the atomic number of next inert gas, krypton (atomic no. 36) [(*) structures]

The structure of linearcarbonyl di-iron $Fe(CO)_9$ can be described in terms of two octahedral sharing a common face formed by the carbon atom of the bridging carbonyl group. The molecular structure in the crystal has been firmly established. Each terminal CO group contribute 1 e^- to the bonded metal. The three terminal CO group provided 6 e^- and 3 bridging CO group 3 e^- to each metal making a total of 9 e^-. One e^- is provided to each Fe by metal-metal (Fe–Fe) bond making a total of 10 e^- provided to Fe which is its magic number. Addition of these 10 e^- to the atomic no.

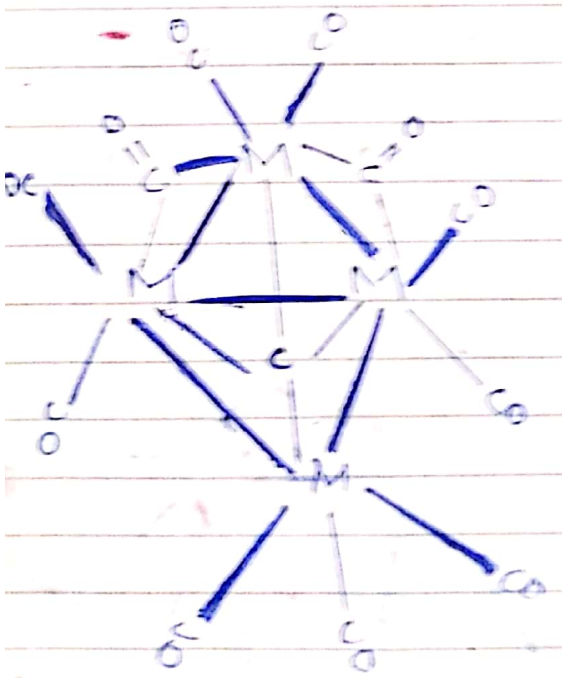
24 (b)



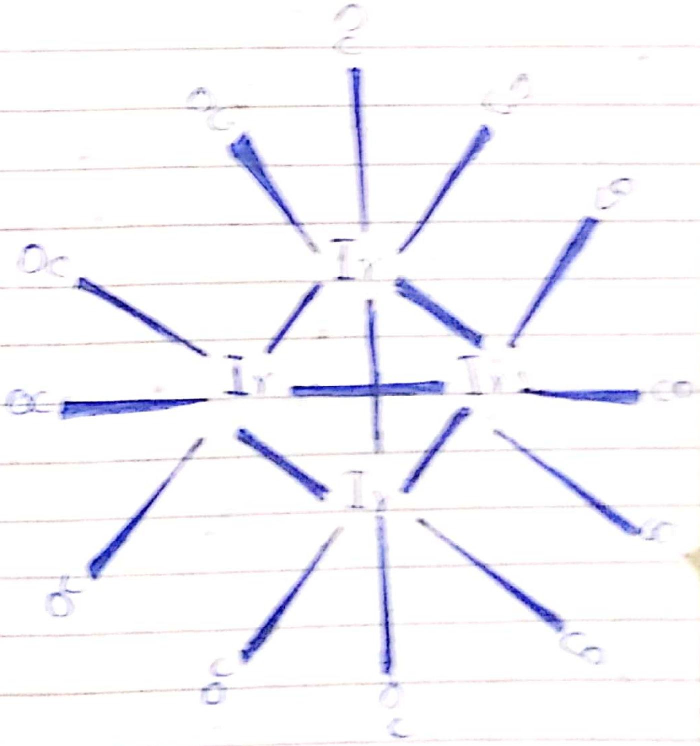
$Fe_3(CO)_{12}(2_v)$



$M_3(CO)_{12}$ {M = Ru, Os (D_3h)

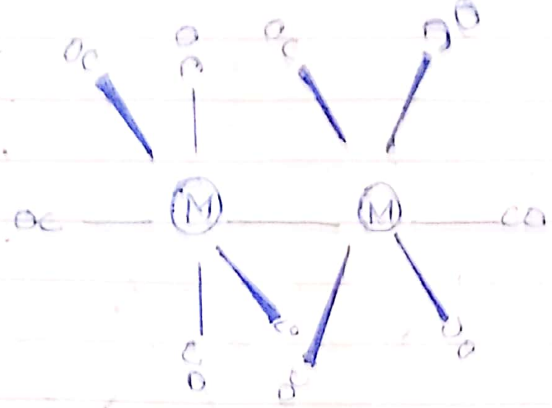


$M_4(CO)_{12}$, M = Co, Rh (C_{3v})



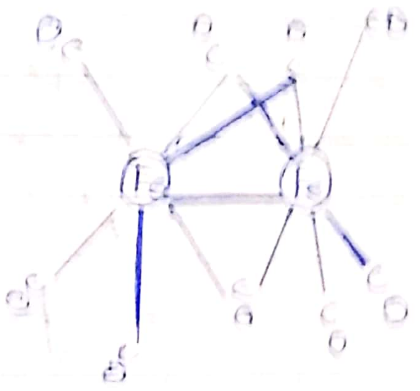
$Ir_4(CO)_{12}$

[(*) Structures]

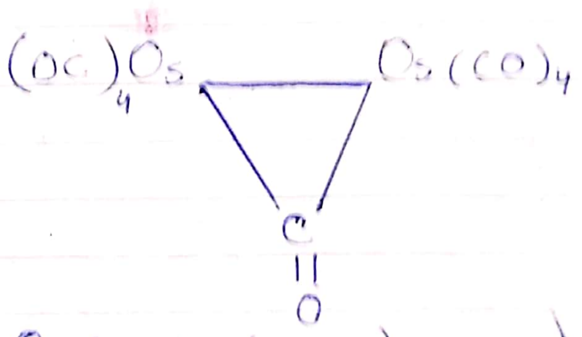


$M_2(CO)_{10}$

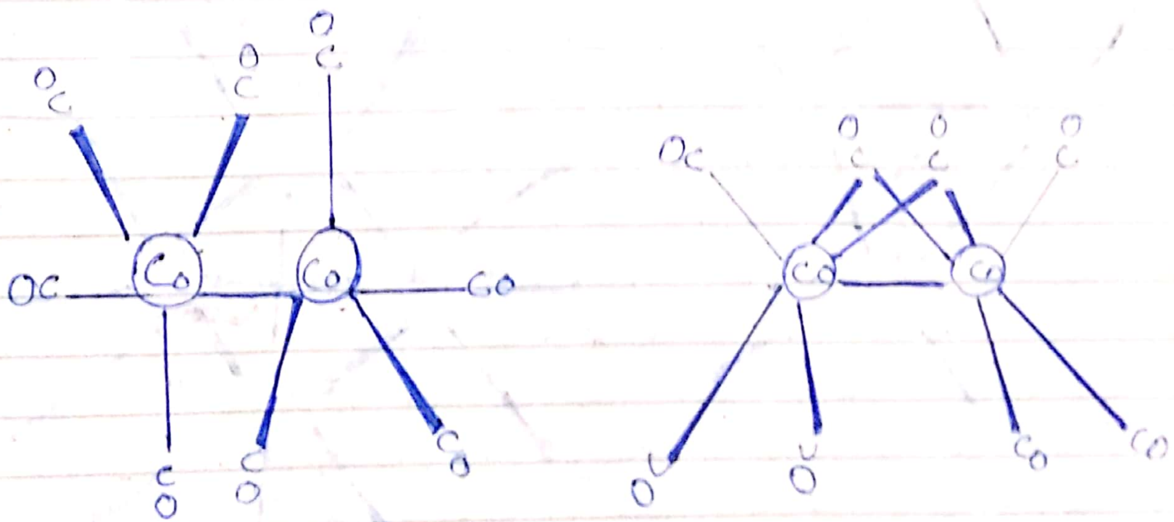
M = Mn, Tc, Re (D_4d)



$Fe_2(CO)_9$ (D_3h)



$Os_2(CO)_9$ (C_{2V})



$Co_2(CO)_8$ two isomers (D_3d', C_{2V})

of iron (26) mates again a total of 36, atomic no. of next inert gas, krypton. The st. of $Fe_2(CO)_9$ can also be discussed in terms of orbitals. Iron atoms use eg d orbitals and 4s as well as 4p orbitals, in forming six bonds to the carbonyl ligands. A dz^2 orbital arising from a linear combination of the t_{2g} set, can strongly overlap with corresponding orbital of the other iron atom. The bonding combination of dz^2 type orbitals can be assumed to contain an $\bar{e}$ pair which accounts for diamagnetism.

Increasing degree of polymerization is observed in moving from left to right in the Periodic Table. i-e $W(CO)_6$, $[Re(CO)_5]_2$ $[Os(CO)_4]_3$ and $[Ir(CO)_3]_4$ reflecting on increasing tendency to form metal-metal bonds. The molecular st. of $Fe_3(CO)_{12}$ can be considered to arise from $Fe_2(CO)_9$ in which one brigding CO group is replaced by an $Fe(CO)_4$ group. The latter is bonded to two iron-iron bonds, 2.76 Å in length. The other metal-metal bond is 2.56 Å A long, and the two bridging carbonyl groups are some what unsymmetrically located. The 12 carbonyl groups are approximately located at vertices of an icosahedron.

The infrared spectrum

of $Fe_3(CO)_{12}$ is interesting because although the W(CO) bonds attributable to bridging carbonyl groups are observed, their intensity is much lower than expected on the basis of structure. Shown in Fig 2.4. In addition to that the two observed terminal carbonyl group bonds are far fewer than the nine expected. It appears than in solution dodecacarbonyl-tri-iron rearrange to some extent to another structure. When IR spectrum of a soln. of $Fe_3(CO)_{12}$ in dichloromethane is taken at -78° the intensity of peaks due to the bridging carbonyl groups increases relative to those of terminal carbonyls. This indicates that there is an equilibrium in solution between the structure given in Fig 2.4 and the one consisting of three identical $Fe(CO)_3$ groups positioned at the vertices of an equilateral triangle and linked in pairs to one another by a bridging CO group and an iron-iron bond.

METAL HETERO NUCLEAR, CARBONYLS:-

Many mixed metal carbonyls are known in which their molecular st. consist of two or more different metal atoms Such mixed metal carbonyls are called heteronuclear ~~consist~~ carbonyl.

and some of them are presented in Table 2.5. These polynuclear carbonyl have either a sequence or cluster of metal atoms. These carbonyls are obtained by condensation

$$Mn_2(CO)_{10} + Re_3(CO)_{10} \xrightarrow[hexane]{\Delta} ReMn(CO)_{10}$$

$$Fe(CO)_5 + Ru_3(CO)_{12} \longrightarrow FeRu_2(CO)_{12} + Fe_2Ru(CO)_{12} + 3CO$$

Metathetical reactions involving carbonylamines and carbonyl halides also give heteronuclear carbonyls.

$$NaMn(CO)_5 + Re(CO)Cl \longrightarrow (CO)_5MnRe(CO)_5 + NaCl.$$

-: Table 2.5 :-

Heteronuclear Metal carbonyls.

$(CO)_5MnCo(CO)_4$

$(CO)_5ReCo(CO)_4$

$(CO)_5MnRe(CO)_5$

$[(CO)_5Mn]_2Fe(CO)_4$

$[(CO)_5Re]_5Fe(CO)_4$

$Fe_2Ru(CO)_{12}$

$FuOs_2(CO)_{12}$

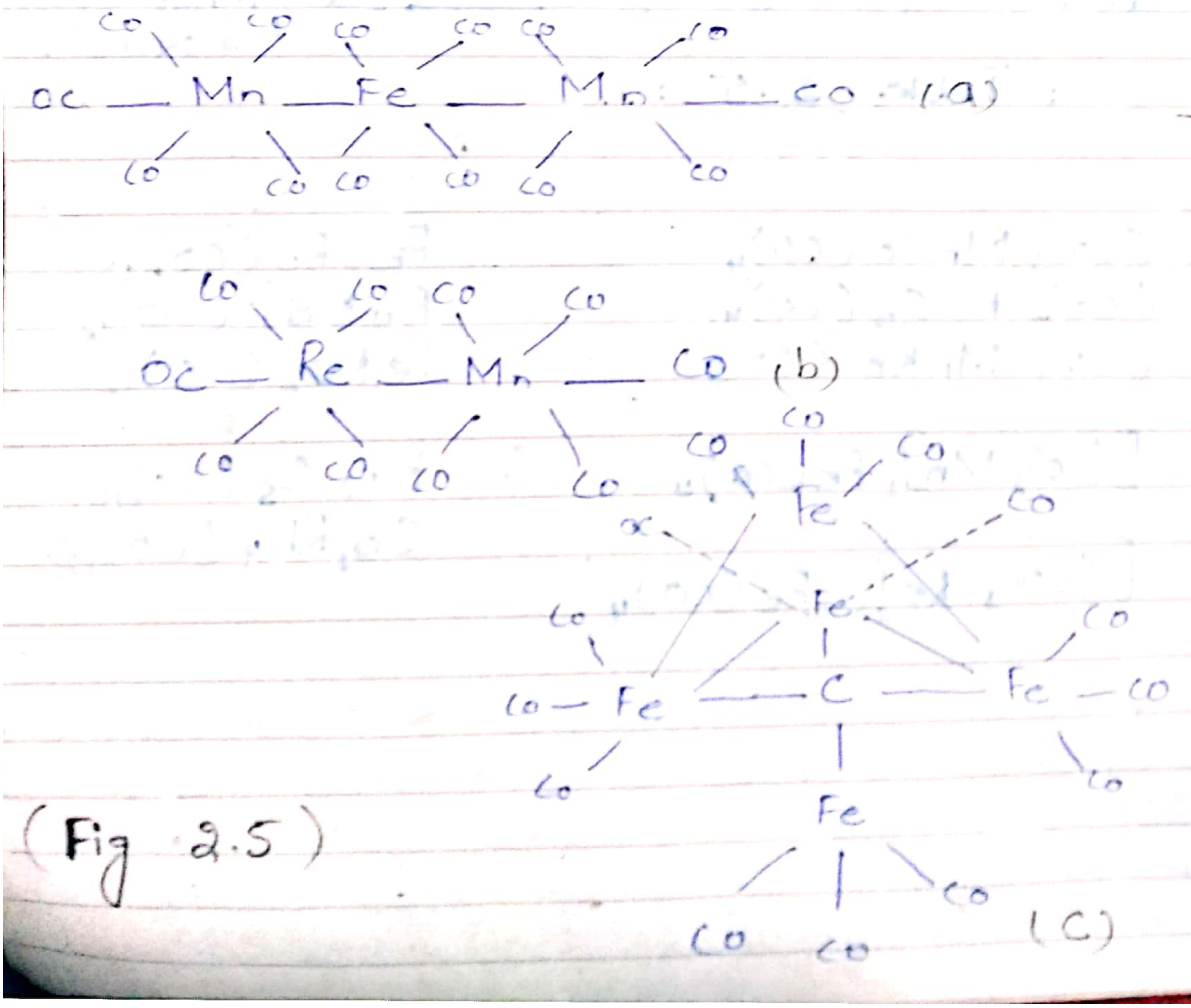
$FeRu_2(CO)_{12}$

$Ru_2Os(CO)_{12}$

$Co_2Rh_4(CO)_{12}$

The examination of $Mn_2Fe(CO)_{14}$ by X-ray reveals Mn–Fe–Mn structure (Fig 2.5). Several binuclear with hetero-metal atoms are known in which they have molecular structure closely related to those of homonuclear species from which they are derived i-e $Re(CO)_{10}$ · (fig 2.5) (b)

Many polynuclear metal carbonyls have been characterized in which non metal atoms to an intrinsic part of the carbonyl structure The typical examples are $C[Fe(CO)_3]_5$ (fig 2.5) (c). $S[Co(CO)_3]_3$ and $HRe_2Mn(CO)_{12}$ and there structures have been published by Xray methods. Several "carbide" cluster - compound have recently been discovered. i-e $CRu_5(CO)_{17}$



(Fig 2.5)