Metal carbonyls

1. Polynuclear metal carbonyls:

Mn₂(CO)₁₀; it's preparations, structure and bonding

EAN Rule: according to which after 'CO' groups have donated a certain number of electron pairs to the zero valent metal atom through OC _____ M σ ____ bonding, the total number of electrons on the metal atom including those gained from CO molecules becomes equal to the number of the next inert gas.

Example; Mn₂(CO)₁₀

EAN Rule;

Electrons from two Mn atoms = $25 \times 2 = 50$

Electrons from 10 CO groups = 10 \times 2 = 20

Electrons from one Mn - Mn bond = $1 \times 2 = 2$

 \therefore EAN of two Mn – atoms of Mn₂(CO)₁₀ = 72

Therefore; EAN of one Mn – atom in $Mn_2(CO)_{10}$ = 72/2 = 36 (Kr₃₆)

<u>Alternative method</u>: In $Mn_2(CO)_{10}$, since each Mn – atom is attached with 5 CO groups & with another Mn – atom (one Mn – Mn bond), EAN of 'Mn' in $Mn_2(CO)_{10}$ is given by:

:: EAN of Mn - atom

= [Atomic number of Mn – atom] + [Electrons donated by five terminal carbonyl groups] + [Electrons donated by one Mn – Mn bond]

 \therefore EAN of Mn – atom = 25 + (5 × 2) + (1 × 1) = 36 (Kr₃₆)

<u>18 – Electron Rule</u>; According to this rule; in a stable metal carbonyl, total (ie; effective) number of electrons present in the valence shell (v. s.) of one metal atom is equal to 18. This number (ie; 18) is equal to *EN/n*; where 'n' is the number of metal (M) atoms in metal carbonyl, &

'EN' = *Number of Electrons present in the valence shell of metal in carbonyl*

= Number of Electrons in the valence shell in the free State + $(2 \times Number of CO ligands) + (2 \times Number of M - M bonds in the carbonyl)$

Example; Mn₂(CO)₁₀

<u> 18 – Electron Rule;</u>

$$Mn_2(CO)_{10}; Mn(25) = 3d^5 4s^2$$

2 $Mn = 2 \times 7e^- = 14e^-$
10 $CO = 10 \times 2e^- = 20e^-$

One Metal – Metal (Mn - Mn) bond = $1 \times 2e^{-} = 2e^{-}$

 \therefore Total electrons on two Mn – atoms = $14e^{-} + 20e^{-} + 2e^{-} = 36e^{-}$

Therefore; electrons on one $Mn - atom = 36e/2 = 18e^{-1}$

Structure & Bonding in Mn₂(CO)₁₀



The structure of dimanganese decacarbonyl consists of two manganese pentacarbonyl groups joined through a Mn - Mn bond distance of 2.79 A°. The formation of this metallic bond effectively adds one electron to each of the manganese atoms. Thus, manganese an element with odd atomic number from a binuclear carbonyl. Since the molecule does not have unpaired electrons, it is diamagnetic.

The infra-red absoption spectral and diffraction studies have shown that this molecule contains no bridging carbonyl groups and hence the molecule has non – bridged structure as shown. It is evident from the above figure that each Mn – atom is linked with five terminal carbonyl groups ($:O\vec{i}C \rightarrow Mn$) & with the other Mn – atom by Mn – Mn sigma – bond. Thus, each Mn atom has

five : $O \wr C \rightarrow Mn$ coordinate sigma bonds and one Mn – Mn sigma – bond. The presence of Mn – Mn bond has also been supported by the diamagnetic nature of Mn₂(CO)₁₀ molecule. It may be noted that each Mn – atom has an octahedral environment and two Mn(CO)5 units are joined solely by Mn – Mn bond.

<u>d²sp³ hybridization of each Mn – atom:</u>

Since it is evident from the non-bridged structure of dimanganese decacarbonyl that the number of sigma bonds by which each Mn – atom is linked with the terminal carbonyl groups and to the other Mn - atom is six, each Mn – atom has coordination number is equal to six and hence each Mn – atom is d^2sp^3 hybrised in Mn₂(CO)₁₀ molecule. Valence shell electronic configuration of Mn – atom in its free State is $3d^5 4s^2 4p^0$. When Mn – atom forms Mn₂(CO)₁₀ molecule both the electrons from **4s** orbital get shifted to **3d** orbitals and hence the configuration of Mn atom in Mn₂(CO)₁₀ becomes $3d^7 4s^0 4p^0$. In order to make d^2sp^3 hybridization possible, the distribution of seven electrons in 3d orbitals takes place in such a way that $3dz^2$ orbital becomes vacant and hence the configuration of Mn atom in Mn₂(CO)₁₀ molecule becomes $3d^2xy 3d^2yz 3d^2zx 3d^1_{x'y'}$ $3d^0z^2$. Now $3d_{x'y'}^2$, 3dz', 4s, 4px, 4py & 4pz orbitals (six orbitals) combine together to form six d^2sp^3 hybrid orbitals. 3dxy, 3dyz and 3dzx orbitals (each is completely filled) remain unhybridized. One of the six d^2sp^3 hybrid orbital is singly-filled while the remaining five are vacant.

*Mn (***Z**=25)



Electronic configuration: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s²



Thus, the valence shell configuration of Mn atom in d^2sp^3 hybridized state in $Mn_2(CO)_{10}$ molecule can be written as shown above. The singly filled d2sp3 hybrid orbitals of one Mn atom overlaps with the singly-filled d^2sp^3 hybrid orbitals of another Mn atom and gives Mn – Mn sigma bond. Thus Mn – Mn is formed by d^2sp^3 (*Mn*) – d^2sp^3 (*Mn*) overlap.

'sp' hybrid orbital of carbon atom of each CO group donates its lone pairs of electrons to vanact d^2sp^3 hybrid orbital on Mn atom and produces : $O\vec{i}C \rightarrow Mn$ coordinate sigma bond. Thus; this bond results by [sp (C) – d^2sp^3 – (Mn)] overlap.

Thus, we see that Mn – atom is linked with five CO groups by five : $O\vec{i}C \rightarrow Mn$ bonds and with one Mn – atom get paired and hence Mn₂(CO)₁₀ shows diamagnetic character the pairing of electrons occurs due to the formation of Mn – Mn bond.

Preparations of manganese decacarbonyl

i. It can be prepared by carbonylation of manganese iodide with carbon monoxide using mangnesium as a reducing agent.

$$2MnI_2 + 10CO + 2Mg \underbrace{25^{0}C, 210 \text{ atm}}_{25^{0}C, 210 \text{ atm}} Mn_2(CO)_{10} + 2MgI_2$$

OR

 $Mn_2(CO)_{10}$ is obtained when MnI_2 (prepared by special method) is reduced at high pressure of CO by Mg in diethyl ether. The yield of $Mn_2(CO)_{10}$ is only 1%.

$$\mathbf{Mn} + 2\mathbf{CuI} \qquad 500^{\circ}\mathbf{C} \qquad \mathbf{MnI}_2 + 2\mathbf{Cu}$$

 $(MnI_2 + 2Cu) + Mg$ CO, 25°C, 210 atm/16 hours $Mn_2(CO)_{10} + 2MgI_2 + CuI_2$

iii. $Mn_2(CO)_{10}$ has also been prepared in better yield by the reaction of $Mn(CH_3 - COO)_2$ with triethyl aluminium, $(C_2H_5)_3Al$ under CO at a pressure of 20 atmospheres at 100°C for 5 hours.

2Mn(CH₃COO)₂ + (C₂H₅)₃Al <u>CO, 100^oC, 20 atm/ 5 hours</u> Mn₂(CO)₁₀

The yield of carbonyl by this method is 53 – 60%

iv. Carbonylation of MnCl₂ in presence of benzophenone ketyl like (C₆H₅)₂CONa at 165°C gives 35% yield Mn₂(CO)_{10.}

$MnCl_2 + 2(C_6H_5)_2CONa$		$\mathbf{Mn}[\mathbf{CO}(\mathbf{C}_{6}\mathbf{H}_{5})_{2}]_{2}$
Mn[CO(C ₆ H ₅) ₂] ₂	CO, 165ºC, 140 atm	$Mn_2(CO)_{10} + (C_6H_5)_2CO$

v. More recently 48% yield of $Mn_2(CO)_{10}$ has been obtained by the carbonylation of methyl cyclopentadienyl manganese dicarbonyl, $(CH_3 - C_5H_4)Mn(CO)_3$ in presence of Na at 50 atmospheric pressure of CO and 125°C for 8 hours.

(CH₃C₅H₄)Mn(CO)₃ + Na CO. 125^oC. 50 atm/ 5 hours Mn₂(CO)₁₀

Properties:

- *i)* It is a golden yellow crystalline substance. It has a melting point of 155oC and sublimes in vacuum.
- ii) It is slowly oxidized in air, especially in solution. In other words, it is oxidized by trace of amount of oxygen in solution; hence the solution must be stored in inert atmosphere.
- *iii)* It is soluble in organic solvents.
- iv) <u>Action of halogen:</u> Halogenation of dimanganese decacarbonyl proceeds with breaking of Mn – Mn bond and formation of carbonyl-halides (Mn(CO)₅X) as shown below:

 $Mn_2(CO)_{10} + Br_{2(1)}
40°C
2Mn(CO)_5Br
Mn_2(CO)_{10} + I_2
2Mn(CO)_5I$

The order of activity of halogen is as: I > Br > Cl

v) <u>Action of Li and Na</u>

Mn - Mn bond is broken by lithium in presence of tetra hydro furan (THF) and by Na in presence of liq. NH₃ and Li⁺ [Mn(CO)₅]⁻ is formed.

 $\mathbf{Mn}_{2}(\mathbf{CO})_{10} + 2\mathbf{Li} \qquad \mathbf{THF} \qquad \mathbf{2Li}^{+}[\mathbf{Mn}(\mathbf{CO})_{5}]^{-}$

 $\mathbf{Mn}_{2}(\mathbf{CO})_{10} + 2\mathbf{Na} \qquad \qquad \mathbf{liq. NH}_{3} \qquad \mathbf{2Na}^{+}[\mathbf{Mn}(\mathbf{CO})_{5}]^{-}$

vi) <u>Reduction</u>

When $Mn_2(CO)_{10}$ is reduced by hydrogen under 200 atmospheric pressure at a temperature of 200°C, carbonyl hydride is formed.

Mn₂(CO)₁₀ + H₂ 200 atm., 200°C 2HMn(CO)₅

- vii) Action of phosphines, arsines & stilbines With these materials Mn₂(CO)₁₀ gives monomeric paramagnetic compounds of the type, Mn(CO)₄(PR₃).
- viii) <u>Diamagnetic nature</u> $Mn_2(CO)_{10}$ is a diamagnetic substance. Diamagnetic character confirms the facts that all the electrons in $Mn_2(CO)_{10}$ are paired and Mn - Mn bond is also present in it.

Metal carbonyls

1. Polynuclear metal carbonyls:

<u>Co₂(CO)₈; it's preparations, structure and bonding in solution & Solid state</u>

EAN Rule: according to which after 'CO' groups have donated a certain number of electron pairs to the zero valent metal atom through OC _____ M σ ____ bonding, the total number of electrons on the metal atom including those gained from CO molecules becomes equal to the number of the next inert gas.

Example; Co₂(CO)₈

EAN Rule;

Electrons from two Co atoms = $27 \times 2 = 54$

Electrons from 8 CO groups = 8 \times 2 = 16

Electrons from one Co - Co *bond* = $1 \times 2 = 2$

 \therefore EAN of two Co – atoms of Co₂(CO)₈ = 72

Therefore; EAN of one Mn – atom in $Mn_2(CO)_{10}$ = 72/2 = 36 (Kr₃₆)

<u>Alternative method:</u>

a) <u>Co₂(CO)₈ in solution</u> – In solution Co₂(CO)₈ has non – bridged structure in which each Co – atom is linked with four terminal CO groups & with another Co – atom (one Co – Co bond). Thus, EAN of Co – atom is given by:

: EAN of Co – atom

= [Atomic number of Co – atom] + [Electrons donated by four terminal carbonyl groups] + [Electrons donated by one Co – Co bond]

:: EAN of Co – atom = $27 + (4 \times 2) + (1 \times 1) = 36$ (Kr₃₆)

b) <u>Co₂(CO)₈ in solid state</u> – In solid state Co₂(CO)₈ has bridged structure in which each Co – atom is linked with three terminal CO groups, two bridging CO groups & one Co – atom (one Co – Co bond). Thus, EAN of Co – atom is given by:

: EAN of Co – atom

= [Atomic number of Co – atom] + [Electrons donated by three terminal carbonyl groups] + [Electrons donated by two bridging carbonyl groups] + [Electrons donated by one Co – Co bond]

 \therefore EAN of Co – atom = 27 + (3 × 2) +(2 × 1) + (1 × 1) = 36 (Kr₃₆)

- <u>18 Electron Rule</u>; According to this rule; in a stable metal carbonyl, total (ie; effective) number of electrons present in the valence shell (v. s.) of one metal atom is equal to 18. This number (ie; 18) is equal to *EN/n*; where 'n' is the number of metal (M) atoms in metal carbonyl, &
- 'EN' = Number of Electrons present in the valence shell of metal in carbonyl

= Number of Electrons in the valence shell in the free State + $(2 \times Number of CO ligands) + (2 \times Number of M - M bonds in the carbonyl)$

Example; Co₂(CO)₈

18 – Electron Rule;

 $Co_2(CO)_{8}$; $Co(27) = 3d^7 4s^2$ 2 $Co = 2 \times 9e^- = 18e^-$ 8 $CO = 2 \times 8e^- = 20e^-$

One Metal – Metal (Co – Co) bond = $1 \times 2e$ - = 2e-

 \therefore Total electrons on two Co – atoms = $18e^{-} + 16e^{-} + 2e^{-} = 36e^{-}$

Therefore; electrons on one CO – atom = $36e/2 = 18e^{-1}$

Structure & Bonding in Co₂(CO)₈

a) <u>Non – bridged structure of Dicobalt Octacarbonyl molecule, CO₂(CO)₈ molecule in <u>solution</u></u>

The infra-red study of the solution of CO2(CO)8 has no bridging carbonyl groups ie; $CO_2(CO)_8$ in solution has non – brigded structure.



In this structure each CO – atom is linked with four terminal CO group (OC \longrightarrow Co) & with other Co – atom by a Co – Co σ – *bond*. Thus, each CO – atom has four OC \longrightarrow Co coordinate σ – *bonds* and one Co – Co σ – *bond*. The presence of Co – Co bond has also been supported by the diamagnetic nature of CO₂(CO)₈ molecule. Co – Co bond length is 2.52 A° has been determined by electron diffraction study.

<u>dsp³ hybridization of each CO – atom</u>

Since it is evident from the non-bridged structure $CO_2(CO)_8$ molecule, the number of σ – *bonds* by which each CO – atom is linked with terminal carbonyl groups and to the other Co – atom is five, each CO – atom is dsp³ hybridized in $CO_2(CO)_8$ molecule.

Valence shell electronic configuration of Co – atom in its free state is $3d^7 4s^2 4p^0$. When Co – atom forms CO₂(CO)₈ molecule, both electrons from 4s orbital get shifted to 3d orbitals and hence the valence shell configuration of Co – atom in CO₂(CO)₈ becomes $3d^9 4s^0 4p^0$. These two configurations have been shown at (a) and (b) respectively.

Now one 3d – orbital ie., $3dz^2$ (which is singly – filled with electron) one 4s orbital (vacant) and all the three 4p – orbitals (vacant) combine together and give five dsp^3 hybrid orbitals.

Thus, we can see that four 3d orbitals (each of which is completely filled) remain unhybridized. One of the five dsp³ hybrid orbitals has one electron (singly-filled) while the remaining four are vacant. dsp³ hybridized state of Co – atom has shown at (c).

Co (Z=27)



Electronic configuration: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁷ 4s²

<u>Note:</u> dsp³ hybridisation of Co – atom in Co₂(CO)₈ molecule in solution. Each pair of coloured arrows indicates electron pair donated by C – atom of CO molecule (ligand).

The singly-filled dsp³ hybrid orbitals of one Co – atom overlaps with the singly-filled dsp³ hybrid orbital of the other Co – atom and produces Co – Co σ – *bond*. This Co – Co σ – *bond* is produced by [dsp³ (Co) – dsp³ (Co)] overlap. sp – hybrid orbital on C – atom of each terminal Co group donates its lone pair of electrons to the vacant dsp³ hybrid orbital on Co – atom and gives OC — Co coordinate σ – *bond*, i.e., this bond results by [sp(C) – dsp³(Co)] overlap. Thus, we can see that each CO – atom is linked with four Co groups by OC — Co bonds and with one Co – atom by Co – Co bond. It may be seen here that all the electrons of both Co – atoms become paired and hence CO₂(CO)₈ shows diamagnetic character. The pairing of electrons takes place due to the formation of Co – Co bond.

b) Bridged structure of Dicobalt Octacarbonyl Molecule, CO2(CO)8 in solid state

Infra – red study of $CO_2(CO)_8$ molecule in the solid state has indicated that this molecule has bridged structure as shown below:



 d^2sp^3 hybridization of each Co – atom. Since it is evident from the above figure that the number of σ – *bonds* by which each Co – atom is linked with three terminal carbonyl groups, two bridging carbonyl groups and to the other Co – atom is six, each Co – atom has a coordination number equal to six and hence each Co – atom is d^2sp^3 hybrized in CO₂(CO)₈ molecule. Valence shell electronic configuration of Co – atom in the free state is $3d^7 4s^2 4p^0$. When Co – atom forms CO₂(CO)₈ molecule, one of the two electrons of 4s orbital is shifted to 3d orbitals and hence the valence shell configuration of Co – atom becomes $3d^8 4s^1 4p^0$. These two configurations have been shown at (a) and (b).

Now the two 3d orbitals ie., $3d_{x^2-y^2}^2$ and $3dz^2$ (both are singly-filled), one 4s orbital (singly filled) and all three 4p orbitals (all are empty) combine togather and produce six d^2sp^3 hybrid orbitals. Thus, we can see that three 3d orbitals (each of which is completely filled) remain unhybridized. Three hybrid orbitals are having one electron each while the remaining three hybrid orbital are vacant. Thus, the valence shell configuration of Co – atom in d^2sp^3 hybrized state can be depicted as shown at (c).



Electronic configuration: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁷ 4s²





<u>Note:</u> dsp³ hybridisation of Co – atom in Co₂(CO)₈ molecule in solid state. Each pair of coloured arrows indicates electron pair donated by C – atom of terminal carbonyl group; CO while the dot (●) represents an electron donated by C – atom of bridging carbonyl group.

Now one singly filled d^2sp^3 hybrid orbital of both Co – atom overlaps with both the singly-filled sp^2 hybrid orbitals of C – atom of one bridging carbonyl group and form two Co – C bond in **(Co)**₂ – *C*= \ddot{O} :



Unusual overlap of two singly – filled d^2sp^3 hybrid orbitals on two Co – atoms to form $Co_2(CO)_8$ molecule in solid state.

In a similar way other two Co - C bonds are also produced by one bridging carbonyl group. Thus, we see that four Co - C bonds are obtained. Here C – atom belongs to bridging carbonyl group. It is easy to understand that each of these four bonds results by $[d^2sp^3(Co) - sp^2(C)]$ overlap, third singly filled d^2sp^3 hybrid orbital of the other Co – atom and produces Co – Co bond. Thus, we can say that Co – Co bonds results by $[d^2sp^3(Co) - d^2sp^3(Co)]$ overlap. each of the remaining three d^2sp^3 hybrid orbital (each is vacant) of each Co – atom accepts one lone pair of electrons donated by the sp hybrid orbital on C – atom of terminal carbonyl group and forms $:O\vec{i}C \rightarrow Co$ coordinate bond. Thus, six $:O\vec{i}C \rightarrow Co$ coordinate bonds are obtained. Obviously, this bond is obtained by $[sp(C) - d^2sp^3(Co)]$ overlap. the above discussion shows that each Co – atom is linked with three terminal carbonyl groups by $:O\vec{i}C \rightarrow Co$ bonds. It may be noted that all the electrons in both Co – atoms become paired and hence $Co_2(CO)_8$ molecule shows diamagnetic character. The pairing of electrons occurs due to the formation of Co – Co bond. The formation of various bonds in $Co_2(CO)_8$ has shown in the figure.

Non – bridged structure of $Co_2(CO)_8$ found in its solution is reported to exist in equilibrium with the bridged structure in solid state.

Co - Co bond which is obtained by the overlap of two singly – filled d^2sp^3 hybrid orbitals on two Co - atoms is bent because of unusual overlap of two d^2sp^3 hybrid orbitals.

Preparations of Dicobalt Octacarbonyl

i. It can be prepared by the reaction between CO and reduced metallic cobalt at 200°C and 250 atm.

$$\frac{2C_0 + 8CO}{220^{\circ}C, 250 \text{ atm}} C_{0_2}(CO)_8$$

ii. It can be also synthesized by the reaction of dry CO at 200°C and 200 atm in presence of metallic copper on certain binary compounds of cobalt such as CoS and CoX₂. Here Cu forms Cu₂S or CuX.

iii. It can be prepared by the action of CO and H_2 on CoCO₃ under high pressure and high temperatures.

$$2C_0CO_3 + 2H_2 + 8CO \qquad \underbrace{120-220^0C, 250-300 \text{ atm}}_{C_02(CO)_8} + 2CO_2 + 2H_2O$$

iv. It can be prepared by the action of an acid on a solution of $Co(CO)_4$. Hydrogen is evolved and $Co_2(CO)_8$ is left behind.

 $2H^{+}[Co(CO)_{4}]^{-}$ $Co_{2}(CO)_{8} + H_{2}$

v. It can be prepared by thermal decomposition of Co(CO)₄H.

Properties:

- i) $Co_2(CO)_8$ is an orange brown crystalline substance having melting point of 51oC. It is soluble in alcohol, ether and carbon tetrachloride. The carbonyl is air sensitive both in the solid and solution state.
- ii) <u>Action of heat:</u>

It is thermally decomposed at 50oC in an inert atmosphere to give tetra cobalt decacarbonyl, $Co_4(CO)_{12}$

2Co₂(CO)₈ 50°C Co₄(CO)₁₂ + 4CO

iii) Action of air:

On exposure to air, dicobalt octahedral is converted into deep violet basic carbonate of cobalt.

iv) <u>Reduction</u>

a) It is reduced to cobalt hydride, $H^+[Co(CO)_4]^-$ by H_2 at 165°C and at 120 atmospheric pressure.

 $Co_2(CO)_8 + H_2$ 120 atm., 165°C $2H^+[Co(CO)_4]^-$

 $Co_2(CO)_8$ is also reduced by Na metal in liq. NH₃ below -75°C or tetrahydrofuran (THF).

v) <u>Disproportionation reactions:</u>

There are two types of reactions in case of Co₂(CO)₈.

a) Strong bases having nitrogen or oxygen donor atoms cause proportionation into Co(+2) and CO(-1). For example;

$$2Co_{2}(CO)_{8} + 12NH_{3} \qquad 2[Co(NH_{3})_{6}][Co(CO)_{4}]_{2} + 8CO$$

b) With isocynides, phosphines, arsines and stilbines; however the disproportionation reaction gives penta-coordinate Cobalt(I) cation.

 $Co_2(CO)_8 + 5CNR$ [Co(CNR)₅][Co(CO)₄] + 4CO

vi) <u>Reaction with NO:</u> Co2(CO)8 also reacts with NO at 40oC and forms Co(CO)₃NO.

 $Co_2(CO)_8 + 2NO$ <u>Co</u>(CO)₃(NO) + 2CO

In Co(CO)3(NO), NO group appears to be more firmly held with Co – metal atom than CO groups. This is confirmed by the fact that CO groups can be replaced by the amines very easily. Eg; the action of phen on Co(CO)₃(NO) gives [Co(CO)(phen)(NO)].

Co(CO)₃(NO) + phen [Co(CO)(phen)(NO)] + 2CO

vii) <u>Reaction with halogens:</u> The halogens decompose Co₂(CO)₈ according to the following reaction:

 $Co_2(CO)_8 + 2X_2$ 2CoX₂ + 8CO