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Subject: Chemistry
Class for which the note is prepared: Semester-6
Paper: C13T (Inorganic Chemistry)
Topic: Organometallic Chemistry
Part 3

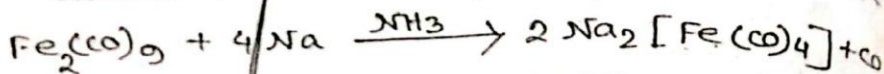
Comments- Study the whole topic thoroughly.

[N.B. - Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry]

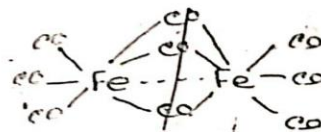
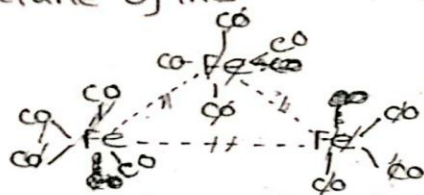
i) With NO it gives $\text{Fe}(\text{CO})_2(\text{NO})_2$ together with $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$



ii) Carbonylate anion is obtained in the reactⁿ with NO in NH_3 solⁿ



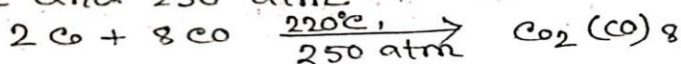
The structure of the molecule is shown



$\text{Co}_2(\text{CO})_8$ [Di-cobaltocta Carbonyl]

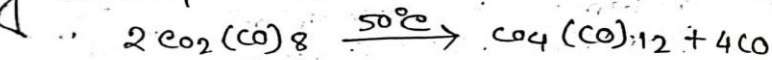
Preparation:

It can be prepared by the reactⁿ b/w CO and Co at 220°C and 250 atm.

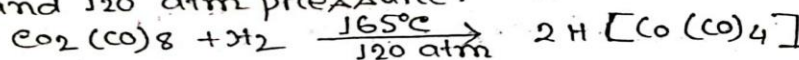


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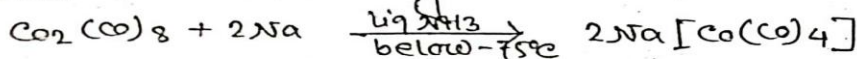
i) It is thermally decomposed at 50°C ⁱⁿ inert atmosphere to give $\text{Co}_4(\text{CO})_{12}$



ii) It is reduced to cobalt carbonyl hydride by the H_2 at 165°C and 120 atm pressure.



It is also reduced by Na in liq NH_3 below -75°C .



iii) It reacts with NO at 40°C and forms $\text{Co}(\text{CO})_3\text{NO}$.



Structure:

The struc^r of the molecule depends on whether this carbonyl is in solⁿ or in solid state. $\text{Co}_2(\text{CO})_8$ in these two states has different struc^r —

a) Structure of $\text{Co}_2(\text{CO})_8$ in solⁿ:

IR study of the solⁿ of the $\text{Co}_2(\text{CO})_8$ has shown that this molecule has no bridging carbonyl group i.e., $\text{Co}_2(\text{CO})_8$ in solⁿ has nonbridged structure.

In this structure each Co atom is linked with four terminal CO groups and with other Co atom by a Co---Co σ -bond. Thus each Co atom has four Co-CO coordinate σ -bond and one Co-Co σ -bond.

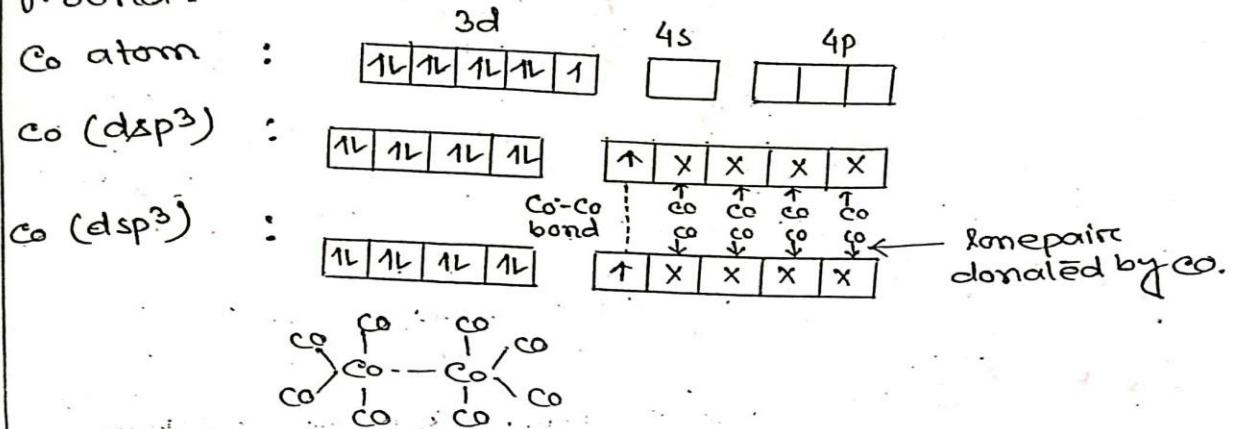


Fig: Non bridge structure of $Co_2(CO)_8$ in solid state.

b) In solid state:

IR study of this molecule in the solid state has indicated that this molecule has bridge structure. Valence shell electron configuration of Co atom in the free state is $3d^7 4s^2 4p^0$, when Co atom forms $Co_2(CO)_8$ molecule, one of the two electrons of 4s orbital is shifted to 3d orbitals and hence the valence shell configuration becomes $3d^8 4s^1 4p^0$. Now two 3d orbitals, one 4s orbital and all 4p orbitals combine together and produced six d^2sp^3 hybrid orbitals. Three hybrid orbitals are having one electron each while the remaining three hybrid orbitals, are vacant.

Now one singly filled d^2sp^3 hybrid orbital of both Co atoms overlap with both the singly filled sp^3 hybrid orbital of one bridging carbonyl gr. and formed two Co-Co bonding. In a similar way other two Co-Co bonds are also produced by one bridging carbonyl group. 3rd singly filled d^2sp^3 hybrid orbital of one Co atom overlap with the 3rd d^2sp^3 hybrid orbital of other Co atom and produces Co-Co bond. Each of the remaining three d^2sp^3 hybrid orbitals of each Co

atom accepts one lone pair of electrons donated by the terminal carbonyl groups of and forms Co-Co coordinate bond.

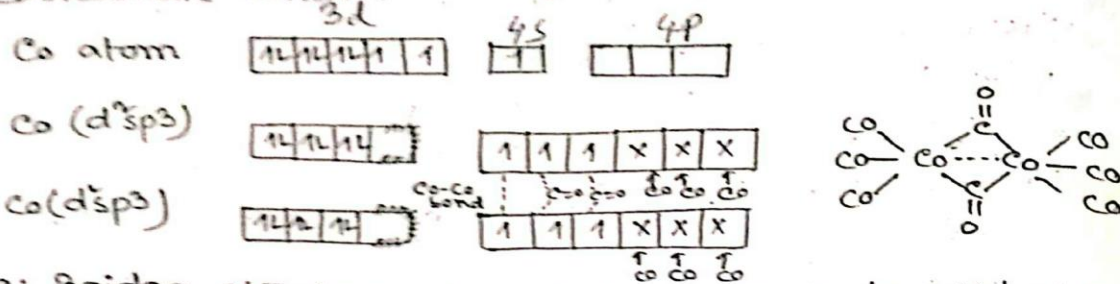


Fig: Bridge structure of $Co_2(CO)_8$ molecule in solid state.

$Ni(CO)_4$ [Nickel tetracarbonyl]

Preparation:

It is prepared by passing CO over finely divided metallic nickel at a temp^r below $100^\circ C$.

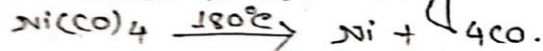


Properties:

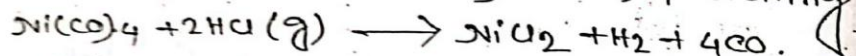
i) It reacts with H_2SO_4 as follows.



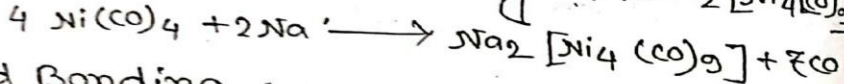
ii) When heated to $180^\circ C$ it gives Ni



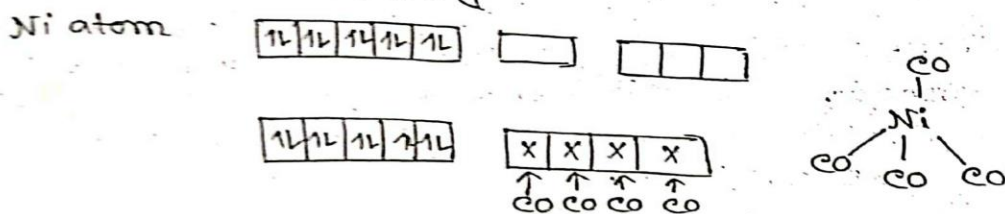
iii) Gaseous HCl decomposes the solⁿ of $Ni(CO)_4$ evolving H_2 and CO



iv) When $Ni(CO)_4$ solⁿ in THF is reduced by Na, $Na_2[Ni_4(CO)_9]$ is formed.



Structure and Bonding:



Use of IR absorption spectra of metallic carbonyls
 We know the stretching frequency ($\bar{\nu}$) is directly proportional to the bond strength. If bond length is longer i.e. bond strength is weaker then $\bar{\nu}$ will be

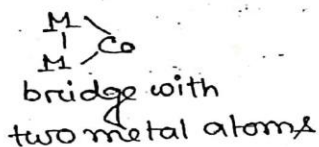
smaller. If the donation of electron density from metal to π^* orbital of CO increases, so increase the C-O bond length and decreases the bond strength and also decreases the value of $\bar{\nu}$. Thus a formal negative charge on a metal carbonyl anion results in slightly greater C-O bond lengths, and lowers C-O bond stretching frequency. The variation of the values of $\bar{\nu}$ are shown in table.

Species	$\bar{\nu}$ (cm ⁻¹)
free CO	2143
[Mn(CO) ₆] ⁺	2090
[Cr(CO) ₆] ⁰	2000
[V(CO) ₆] ⁻	1860
[Ti(CO) ₆] ²⁻	1750

Therefore as the extent of back bonding donation increases M-C bond order (increases) and C-O bond order decreases.

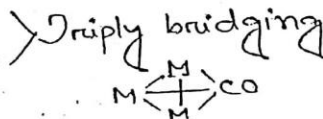
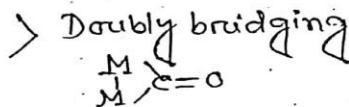
CO acts as a ligand. It can act as terminal bridge with two metal atom or bridges with three metal atoms.

M-CO
terminal



Thus as the no. of metal atom bonding with CO increases, the population of electron density to the carbonyl π^* orbital increases and decreases the C-O bond strength and also decreases the value of $\bar{\nu}$ as follows -

terminal
M-C≡O



$\bar{\nu} > 1900 \text{ cm}^{-1}$

$\bar{\nu} = 1850 - 1900 \text{ cm}^{-1}$

$\bar{\nu} = 1620 - 1730 \text{ cm}^{-1}$

Hence from the value of $\bar{\nu}$, we can easily differentiate

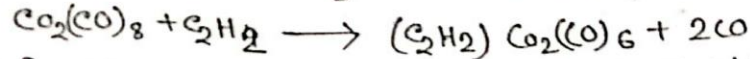
In the isoelectronic species $[\text{Mn}(\text{CO})_6]^+$, $[\text{Cr}(\text{CO})_6]^0$ and $[\text{V}(\text{CO})_6]^-$ the C-O stretching frequencies are 2090, 2000, and 1860 cm^{-1} respectively - Explain.

It has been established that in metal carbonyls the σ $\text{M} \leftarrow \text{CO}$ bond is formed as a result of donation of lone pair on carbon to an empty σ -orbital on metal. The $\text{M} \rightarrow \text{CO}$ back bonding also result from the overlap of filled $d\pi$ orbital of metal with empty antibonding low empty π^* MO of CO. Thus σ and π synergic mechanism of bonding makes the carbonyl very stable. As the extent of back bonding increases the C-O bond order decreases and M-C bond order increases. Consequently the C-O stretching frequency of the metal carbonyl will decrease with increase in the degree of back bonding. Any effect that increases the degree of back bonding will decrease the C-O stretching frequency.

In the isoelectronic species $[\text{Mn}(\text{CO})_6]^+$, $[\text{Cr}(\text{CO})_6]^0$ and $[\text{V}(\text{CO})_6]^-$, the first contains metal in +1 state the second contained metal in 0 state and third contained metal in -1 state i.e., the (+)ve charge density on metal is gradually increases. Such increase in electron density on metal will facilitate back bonding and the extent of back bonding increases in the order $[\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6]^0 < [\text{V}(\text{CO})_6]^-$. The M-C bond order increases and CO bond order decreases and consequently the C-O stretching frequencies will be in the same order. That is why in the isoelectronic species $[\text{Mn}(\text{CO})_6]^+$, $[\text{Cr}(\text{CO})_6]^0$ and $[\text{V}(\text{CO})_6]^-$ the stretching frequencies of CO are 2090, 2000, 1860 cm^{-1} respectively.

What happens when dicobalt octacarbonyl is allowed to react with C_2H_2 .

C_2H_2 co-ordinates to Co atoms in dicobalt octacarbonyl to form the alkyne complex dicobalt ^{hexa}acetylene and two moles of Co are eliminated in this reaction.



Elimination of two moles of CO indicates that acetylene acts as four electron donor and both pair of its π electrons are involved in bonding to two Co atoms.

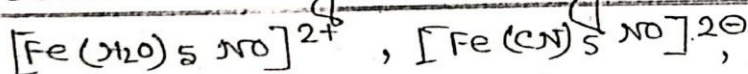
Metallic Nitrosyl Complex :

We know that NO molecule can be represented by the structure $N \equiv \ddot{O}$. When this molecule loses its unpaired electron on 'N' atom, it is converted into NO^+ ion ($N \equiv \ddot{O}^+$). Similarly when NO molecule accepts an electron from metal ion (M^{n+}) it is converted into NO^- ion [$N \equiv \ddot{O}^-$]. Since NO^+ and NO^- both have electron pair on N atom they can be attached with a transition metal atom and form the complex compounds. These complex compounds are called metallic nitrosyls.

Classification of metallic Nitrosyl :

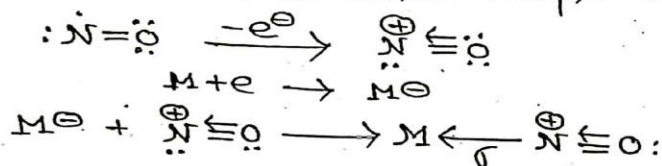
Depending on whether NO molecule is present NO^+ or NO^- in the metallic nitrosyl these complex compounds have been classified into the following categories.

Metallic nitrosyl containing NO^+ ion :



$[Fe(NO)_2(CO)_2]^0$ are the example of metallic nitrosyl which contain NO^+ ion. The presence of NO^+ gr. in this is confirmed by the fact that IR absorption frequency of NO^+ group in these complexes falls in the region 1600-1900 cm^{-1} .

In metallic nitrosyl having NO^{\oplus} ion, at first NO molecule loses the unpaired electron present in π^*_{2p} orbital of 'N' atom and this electron is transferred to the metal atom so that NO molecule is converted into NO^{\oplus} ion and the valency of the metal atom is reduced by one unit i.e., M is converted into M^{\ominus} ion. Now NO^{\oplus} ion which is isoelectronic with CO molecule donates the lone pair of electrons residing on N-atom to M^{\ominus} ion. Both these steps can be shown as follows:



There is another type of bond is also formed b/w the metal and NO^{\oplus} ion. This bond is formed by the overlap of suitably filled metal orbital with the vacant π^*_{2p} MO of NO^{\oplus} ion. $M \xrightleftharpoons{\pi} \overset{\oplus}{\text{N}}\equiv\ddot{\text{O}}$:

Fig: formation of synergic bond b/w M and NO^{\oplus} ion.

In these nitrosyls $M-N-O$ bond angle is closed to 180° and hence these nitrosyls are called linear nitrosyls.

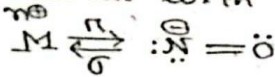
2) Metallic nitrosyls containing NO^{\ominus} ion:

$[\text{Co}(\text{CN})_5(\text{NO})]^{3-}$ and $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$ are the examples of metallic nitrosyls which contain NO^{\ominus} ion. These complexes contain spin paired Co^{+3} ion with $t_{2g}^6 e_g^0$ configuration. The presence of NO^{\ominus} group in these complexes is confirmed by the fact that the IR absorption frequency of the NO^{\ominus} gr. in these complexes falls in the region $1120 - 1200 \text{ cm}^{-1}$.

In the metallic nitrosyls having NO^{\ominus} ion NO molecule accepts one electron from metal ion and it itself converted into NO^{\ominus} ion. In NO^{\ominus} ion N is sp^2 hybridised. The two lone pairs of electrons on N^{\ominus} are present in two sp^2 hybrid orbitals.

When NO^\ominus ion gets attached with the central metal atom in nitrosyls, one of the lone pair placed in an sp^2 hybrid orbital is donated to the vacant orbital of the metal and $\text{M} \leftarrow \overset{\ominus}{\text{N}}=\ddot{\text{O}}$ σ -bond is formed. The other lone pair of electrons located in other sp^2 hybrid orbital. The metallic nitrosyl containing NO^\ominus are bent nitrosyl since the $\text{M}-\text{N}-\text{O}$ bond angle in those nitrosyls is in the range of $120^\circ - 140^\circ$.

After formation of $\text{NO}^\ominus \rightarrow \text{M}$ σ -bond there arises a π -bond b/w the metal and NO^\ominus ion. This π bond is formed by the overlap of suitably filled metal ion orbital with the vacant π^* MO.



① Metallic Nitrosyl Containing $\overset{\oplus}{\text{NO}}$ as well as NO^\ominus ions

There are some metallic nitrosyl in which 'NO' exist as NO^\oplus as well as NO^\ominus . $\text{Fe}(\text{NO})_4$ is an example of this type of nitrosyls. This complex is represented as $[\overset{+1}{(\text{NO})}_3 \text{Fe} \overset{-1}{(\text{NO})}]^0$. Since NO group absorbs in both the regions $1600 - 1900 \text{ cm}^{-1}$ (for NO^\oplus ion) and $1100 - 1200 \text{ cm}^{-1}$ (for NO^\ominus ion).

② Calculation of EAN of the central metal atom in metallic nitrosyl compound :

Metallic nitrosyl compound	electrons donated by metal atom	electrons donated by NO^\oplus or NO^\ominus	Electrons donated by other atom	EAN of metal atom
1. Metallic nitrosyl containing NO^\oplus ion				
i) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$	$(26-1) = 25 (\text{Fe}^+)$	$1 \times 2 (\text{NO}^+) = 2$	$5 \times 2 (5\text{H}_2\text{O}) = 10$	37
ii) $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$	$26-2 = 24 (\text{Fe}^{+2})$	$1 \times 2 (\text{NO}^+) = 2$	$5 \times 2 (5\text{CN}^-) = 10$	36 (K π)
iii) $[\text{Fe}(\text{NO})_2(\text{CO})_2]^0$	$26+2 (\text{Fe}^{-2}) = 28$	$2 \times 2 (\text{NO}^+) = 4$	$2 \times 2 (\text{CO}) = 4$	36 (K π)
2. Nitrosyl containing NO^\ominus ion				
i) $[\text{Co}(\text{CN})_5(\text{NO})]^{3-}$	$27-3 (\text{Co}^{+3})$	$1 \times 2 (\text{NO}^\ominus) = 2$	$5 \times 2 = 10$	36 (K π)
ii) $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{1+}$	$24 (\text{Co}^{+3})$	$2 (\text{NO}^\ominus)$	$5 \times 2 = 10$	36 K π .

Solve the following problems

1. Explain the structure of $\text{Co}_2(\text{CO})_8$ in solution and solid state.

2. In the isoelectronic species $[\text{Mn}(\text{CO})_6]^+$, $[\text{Cr}(\text{CO})_6]$ and $[\text{V}(\text{CO})_6]^-$, the C-O stretching frequency are 2090, 2000 and 1860 cm^{-1} respectively — Explain.

3. What happens when dicobalt octa carbonyl is allowed to react with C_2H_2 ?

