

Class - PG-II (Sem)

Subject - Inorganic chemistry.

Paper - Core course - V

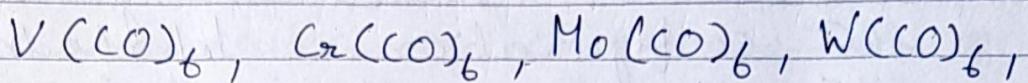
Unit - IX

Dr. Kumud Kumari

H. D. Jain college, Agra.

STRUCTURE OF METAL CARBONYLS —

① Structure of Mononuclear carbonyls —



$\text{Fe}(\text{CO})_5$, $\text{Ru}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$ are the

the example of mononuclear metal carbonyls. All these carbonyls ($-\text{C}\equiv\text{O}$, $-\text{CO}$) groups which are attached with the metal atom by linear $\text{M}-\text{C}\equiv\text{O}$ or $\text{M}-\text{CO}$ bonds. In $\text{M}-\text{C}\equiv\text{O}$ bond M atom is linked with C -atom of CO group, since O atom is more electronegative than C -atom. The number of CO groups attached with metal atom gives the coordination number of metal and hence determine the shape of the metal carbonyl. For example in $\text{Cr}(\text{CO})_6$, the C.N of Cr is 6, so the molecule has octahedral shape. Similarly $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ have trigonal bipyramidal and tetrahedral shape respectively.

Structure of $\text{Ni}(\text{CO})_4$ —

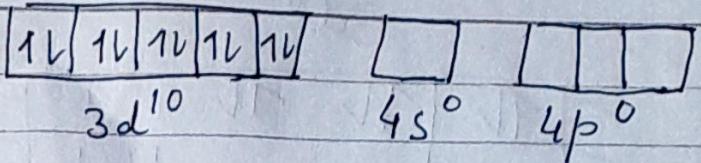
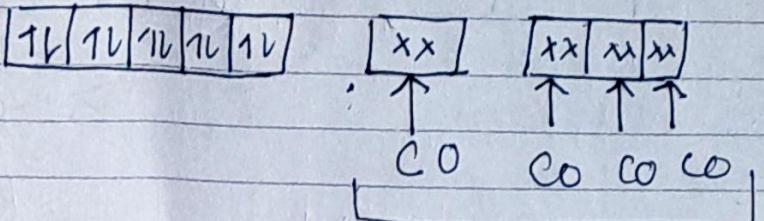
- (i) The vapour density of Nickel carbonyl and the freezing point of its solution in benzene indicate the molecular formula to be $\text{Ni}(\text{CO})_4$.
- (ii) Recent electron density diffraction studies on nickel carbonyl show that the configuration is tetrahedral and the $\text{Ni}-\text{C}\equiv\text{O}$ group is linear. The distance $\text{Ni}-\text{C}$ is found to be 1.82 \AA and that of $\text{C}-\text{O}$ is 1.15 \AA .
- (iii) Raman spectral studies have revealed that the oxygen atom is triply bonded to the carbon atom in the CO groups. Thus the nickel atom in the nickel carbonyl must be sp^3 hybridized. Since $\text{Ni}(\text{CO})_4$ molecule is diamagnetic, all the ten electrons present in the valence shell of Ni atom are paired.

Old orbital diagram

Free Nickel atom configuration is
 $\text{Ni}_{28} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

Free Ni atom $(3d^8 4s^2 4p^0)$	<table border="1"> <tr> <td>1V</td> <td>1H</td> <td>1I</td> <td>1J</td> </tr> </table>	1V	1H	1I	1J	<table border="1"> <tr> <td>1L</td> </tr> </table>	1L	<table border="1"> <tr> <td>1T</td> <td>1I</td> </tr> </table>	1T	1I
1V	1H	1I	1J							
1L										
1T	1I									
	3d ⁸	4s ²	4p ⁰							

(3)

Ni atom in $\text{Ni}(\text{CO})_4$  $\text{Ni}(\text{CO})_4$ 

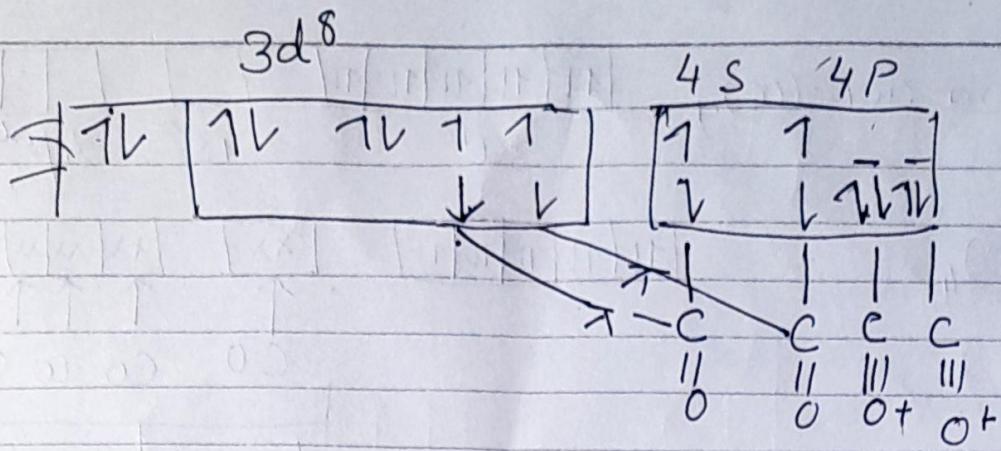
sp^3 hybridisation,
Tetrahedral shape
 $\text{Ni}(\text{CO})_4$.

Because of the formation of four $\text{OC} \rightarrow \text{Ni}$ bonds, a large negative charge accumulated on the central Ni atom.

This is not supported by experimental fact. In such a situation Pauling suggested that the double bonding occurs with the back donation of d-electron from Ni atom to CO ligands to such an extent that electro neutrality principle is obeyed. According to this principle the electron pair is not shared equally between Ni and C atom of CO ligands but gets attracted more strongly by C-atom which prevents the accumulation of negative charge on Ni-atom and is in keeping with the greater electronegativity of C-atom compared to Ni atom. ~~(Explain, NC)~~

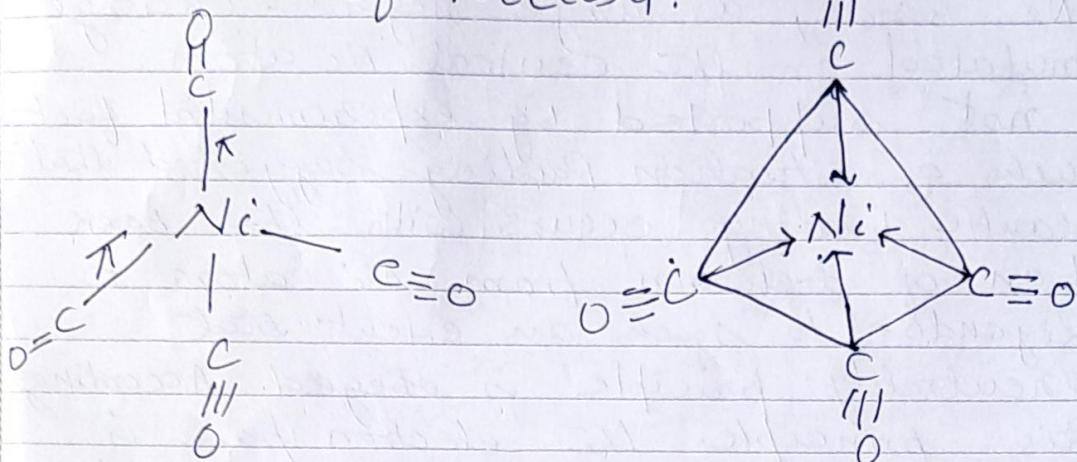
Recent orbital diagram —

(4)



sp^3 hybridisation

orbital diagram
of $\text{Ni}(\text{CO})_4$.



Bond structure,

Tetrahedral structure
of $\text{Ni}(\text{CO})_4$.

② $\text{Fe}(\text{CO})_5^-$ - Ironpentacarbonyl.

- The vapour density and the freezing point of Iron-pentacarbonyl in benzene solution indicate the molecular formula to be $\text{Fe}(\text{CO})_5^-$.
- Electron diffraction, Raman and infra-red sp studies of this compound

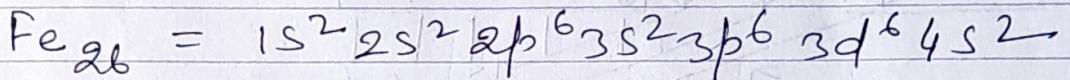
(5)

Show that $\text{Fe}(\text{CO})_5^-$ molecule has trigonal bipyramidal shape. Electron diffraction study of $\text{Fe}(\text{CO})_5^-$ in the vapour state has shown that Fe-C axial Fe-C basal bond lengths are 1.797\AA and 1.842\AA respectively. Therefore ironpentacarbonyl have regular trigonal bipyramidal shape.

(iii) The molecule is diamagnetic.

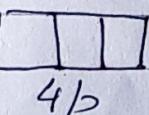
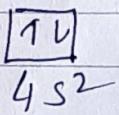
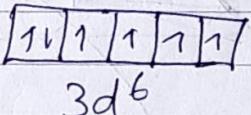
Old orbital diagram.

Electronic configuration of

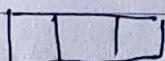
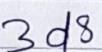
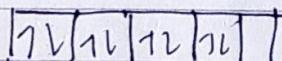


In this molecule Fe is in zero oxidation state and since it is diamagnetic, all the eight electron in the valence shell get paired. So the valence shell configuration of Fe atom in $\text{Fe}(\text{CO})_5^-$ become $3d^8 4s^0$. $\text{Co} \rightarrow \text{Fe}$ σ -bond results by the overlap between empty $d\text{sp}^3$ hybrid orbital of Fe atom and doubly-filled sp hybrid orbital on carbon in CO molecule.

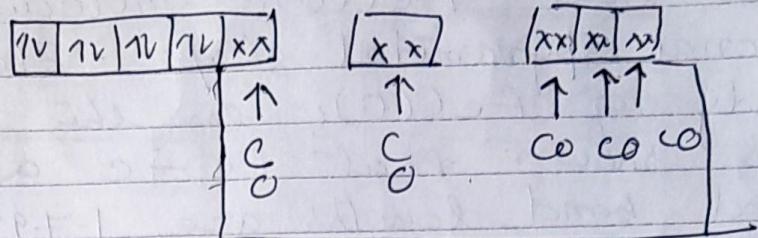
Fe free atom



Fe atom in $\text{Fe}(\text{CO})_5^-$

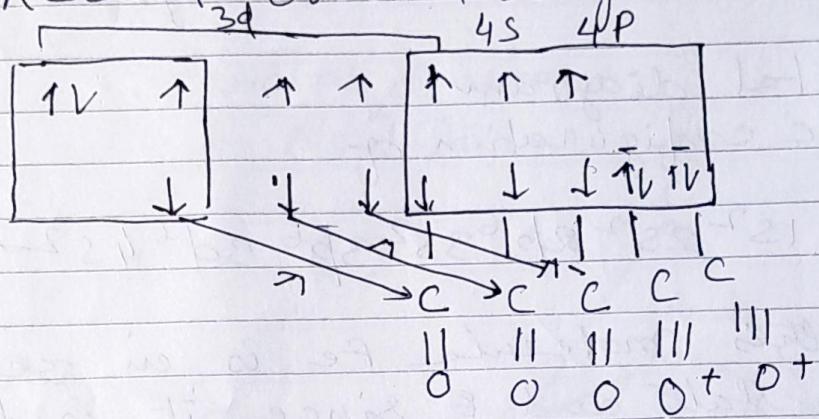


Fe(CO)₅
molecule

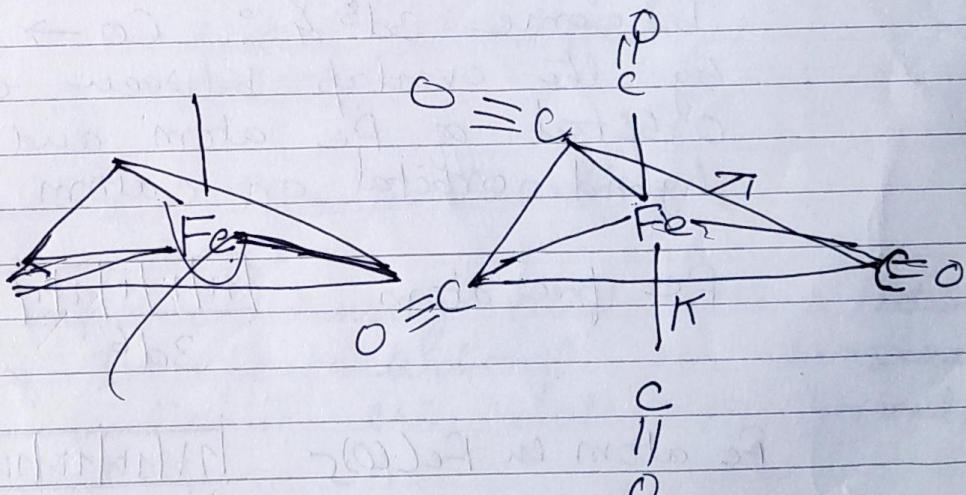


dsp³ hybridisation
ignored

Recent orbital diagram —



dsp³ hybridisation



Fe(CO)₅ molecule.