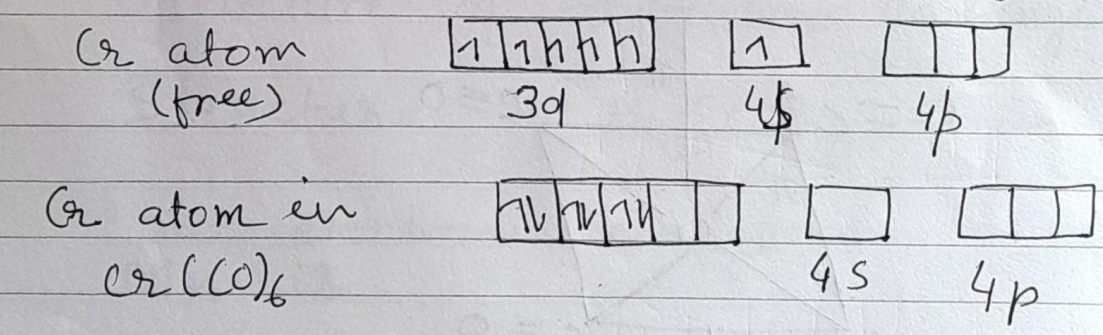
(3) Structure of $Cr(CO)_6$

The molecular formula suggest an octahedral configuration which is confirmed by the result of electron diffraction experiments. The electronic configuration of chromium is

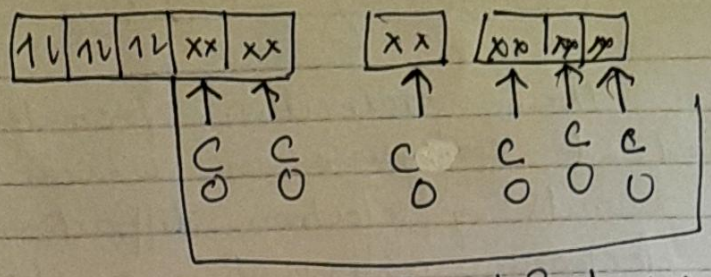
Cr_{24} — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

According to concept when chromium forms $Cr(CO)_6$ one electron of 4s orbital comes in 3d orbitals ~~paired up~~. ~~In this~~ and 3d orbitals have six electrons. Since CO is a strong ligand hence all the six electrons of 3d orbital paired up. In this way two 3d orbital, one 4s orbital and three 4p orbitals become empty and they are mixed and formed six d^2sp^3 hybrid orbitals. Now six molecule of CO donate a lone pair of electron to six vacant hybrid orbitals to form six $Cr \leftarrow CO$ σ bond. Therefore $Cr(CO)_6$ molecule is diamagnetic in nature and octahedral in geometry.



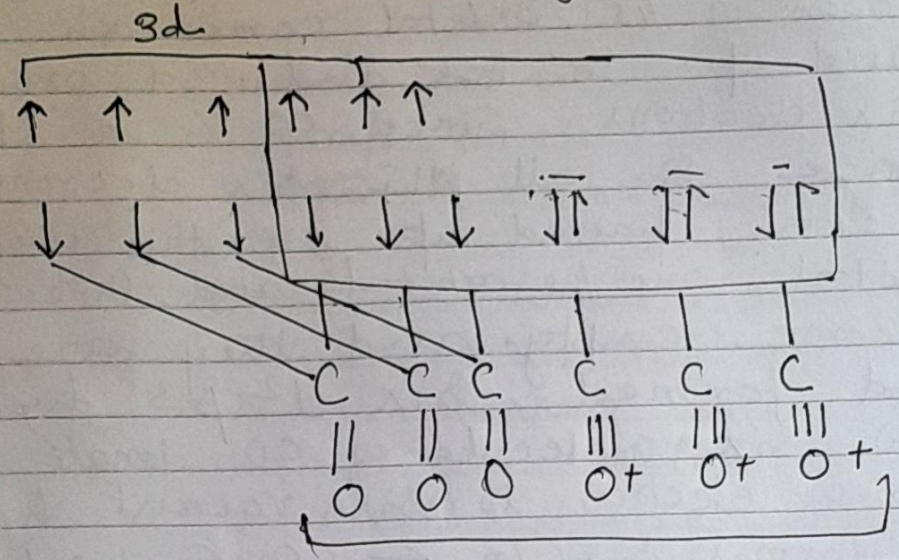
or

In $Cr(CO)_6$

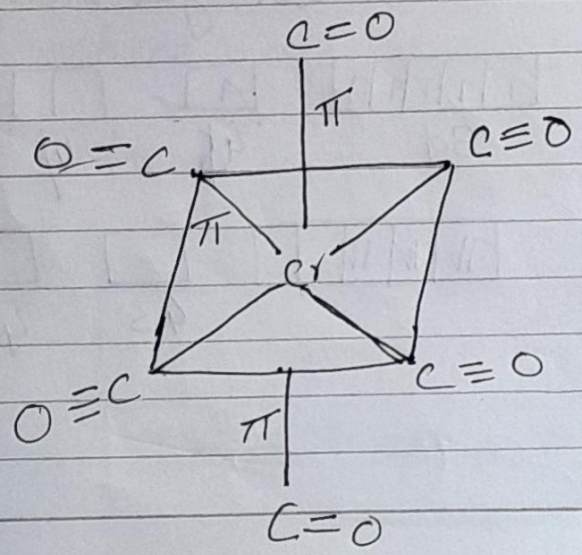


d^2sp^3 hybridisation

Recent orbital diagram



d^2sp^3 hybridisation



This bond structure of $Cr(CO)_6$ clearly reveals two kinds of bonds between chromium and carbonyl :

~~(a) Simple covalent Cr = CO and~~
~~(b) Double bond~~

(a) $Cr \equiv CO$ simple covalent bonds and
(b) $Cr \overset{\pi}{\rightarrow} Cr = CO$ Double bonds.

Each of the CO groups are linked to the metal atom by a σ bond out of six CO group three CO groups are linked by π bonds to the metal atom. The π bonds are made from the original d-orbitals of the metal atoms, So the CO group is not replaceble. Whereas the CO group linked with hybrid orbitals are bound to the metal atom by simple CO ionic bonds. Hence these ~~molecule~~ CO groups are replaceble by any other molecule.

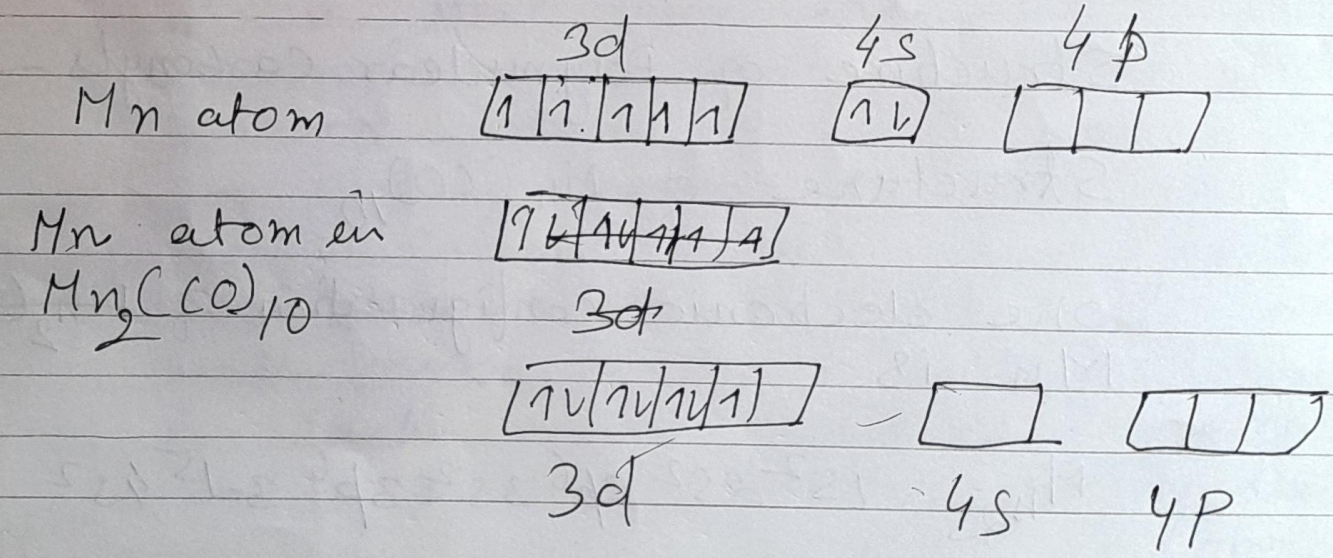
Structure of Polynuclear Carbonyls —

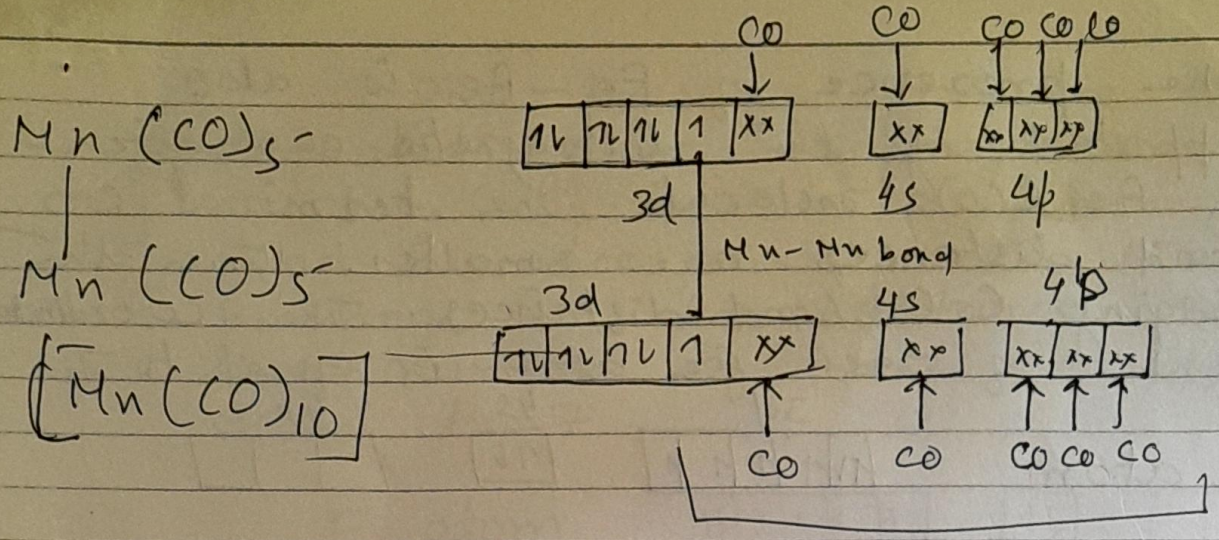
Structure of $Mn_2(CO)_{10}$

The electronic configuration of ~~$Mn_2(CO)_{10}$~~ Mn is

Mn_{25} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Thus there are five unpaired 3d-electrons and one paired 4s electrons. When CO molecules come to Mn atoms there atom gets paired and only one unpaired electrons remains in 3d orbitals. Each Mn atom gets hybridised and forms six d^2sp^3 hybrid orbitals. Out of six hybrid orbitals only one hybrid orbital have one electron. Each Mn atom has octahedral geometry and is attached with five carbonyl groups and is directly bonded to the other metal atom. The five CO molecule donate lone pair of electrons to five vacant hybrid orbitals to form five Mn ← CO σ bonds. Now both $Mn(CO)_5$ groups are having one unpaired electron each of which overlaps to form Mn–Mn bond. In this way the molecule become diamagnetic with octahedral geometry. The two octahedrals get rotated through 45°C from the eclipsed position.





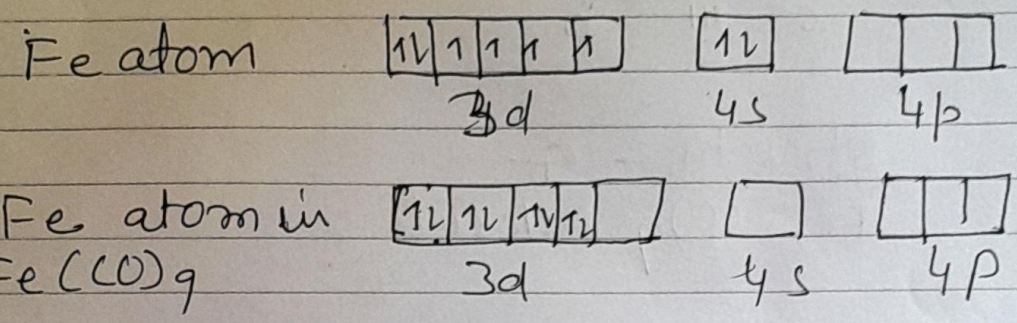
d^2sp^3 hybridisation.

X-ray diffraction has also shown that $Mn_2(CO)_{10}$ has directly linked Mn atoms. The infrared absorption spectrum has indicated that the molecule has no bridging carbonyl group between the two Mn atoms.

Structure of $Fe_2(CO)_9$.

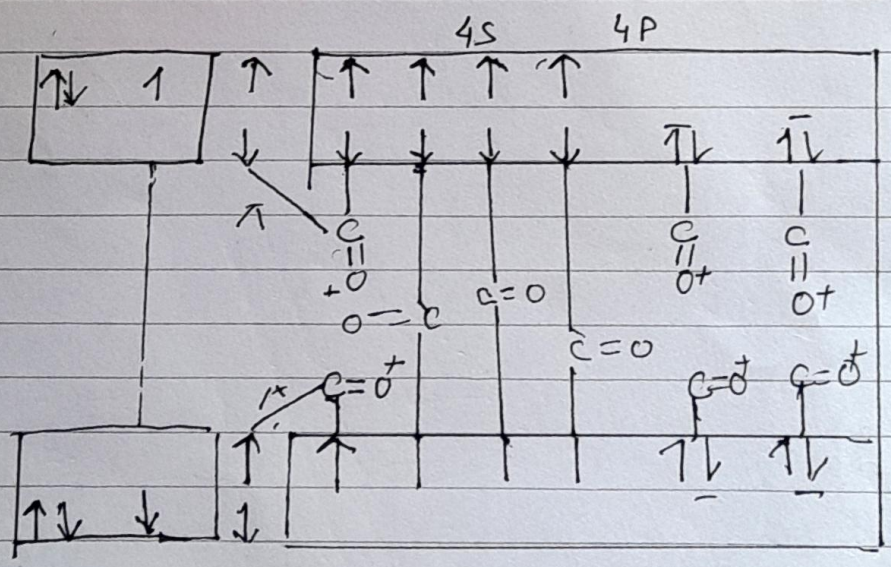
X-ray crystallography study has shown that there are three ketonic carbonyl groups which bridge the two ~~carbonyl groups~~ Fe atoms. The remaining six carbonyl groups are terminal. The ketonic carbonyl groups are linked ~~to~~ each ~~other~~ metal atom by single covalent bonds. These terminal CO groups are linked to each metal atoms by coordinate bonds. Each Fe atom is directly linked with the other Fe atom by σ bond

The presence of Fe–Fe is also supported by the diamagnetic character of $Fe_2(CO)_9$ molecule. The terminal C=O bond distance are smaller than the bridging C–O bond distance. The coordination number of each Fe atom is equal to 7.

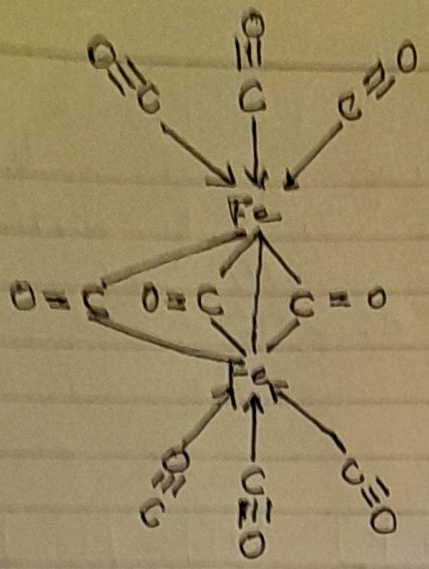


d^2sp^3 hybridisation.

Recent orbital diagram



Bond structure of $Fe_2(CO)_9$.



structure of
$Fe_2(CO)_9$ molecule.