

Geometry of 4-Coordinated Complexes

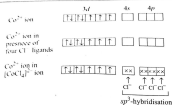
In these complex ions, the coordination number of the central metal cation/atom is four. Such complex ions or complexes may have either tetrahedral or square planar geometry.

Tetrahedral Complexes

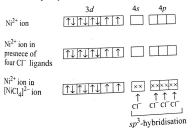
The tetrahedral complexes involve sp^3 or sd^3 -hybridisation. The orbitals involve in sp^3 -hybridisation are one s and three p (p_x , p_y and p_z). The orbitals involve in sd^3 -hybridisation are one s and three (d_{xy} , d_{yz} and d_{zx}) orbitals.

Examples of Tetrahedral Complexes

- (1) $[\text{CoCl}_4]^{2-}$ ion : In this complex ion Co(27) is present as Co^{2+} ion. Co atom has valence shell configuration $3d^7 4s^2$ and Co^{2+} has valence shell configuration, $3d^7$. Magnetic measurements indicate that this ion is paramagnetic and has three unpaired electrons. This is possible only if this complex ion is formed by sp^3 -hybridisation and has tetrahedral geometry.
-



- (2) [NiCl₄]²⁻ ion : In this complex ion Ni (28) is present as Ni²⁺ ion. Ni atom has valence shell configuration, 3d⁸4s² and Ni²⁺ has valence shell configuration, 3d⁸. Magnetic measurements indicate that this ion is paramagnetic and has two unpaired electrons. In this complex ion, all the eight 3d-electrons occupy all the five d-orbitals. Since Cl⁻ is a weak ligand so no pairing occurs in metal 3d-orbital. Thus no d-orbitals is available which can participate in hybridisation. The orbitals which participate in hybridisation are 4s and 4p (p_x, p_y and p_z). Thus this complex ion involves sp³-hybridisation.



... .. it has valence shell

plex

are

re

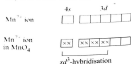
hell

ent

ent

3) Ni(CO)_4 : In this complex compound Ni is in zero oxidation state. It has valence shell configuration $3d^8 4s^2$. Magnetic measurements indicate that this complex is diamagnetic (no unpaired electron is present). In free Ni atom two electrons are unpaired and all the $3d$ -orbitals are occupied. In the presence of strong ligand (CO) the $3d$ -electrons become paired and one of the $3d$ -orbitals becomes vacant. Now the two electrons from $4s$ -orbital go to vacant $3d$ -orbital and all the $3d$ -orbitals become doubly filled. Thus the orbital available for hybridisation are $4s$ and $4p$ (p_x, p_y and p_z).

- (4) MnO_4^- ion : In this complex ion Mn is present as Mn^{7+} ion. Mn atom has valence shell configuration, $3d^5 4s^2$. In Mn^{7+} ion, all the $3d$ -orbitals are empty. There is sd^3 -hybridisation in MnO_4^- ion, which is shown as below:



Shape of this complex is tetrahedral and it is diamagnetic.



- (5) $\text{Cr}_2\text{O}_7^{2-}$ ion : In this ion oxidation state of Cr is +6. Valence shell configuration of Cr is $3d^5 4s^1$. Cr^{6+} has no electrons in $3d$ -orbitals. Each Cr^{6+} ion in this ion is sd^3 -hybridised and shape of $\text{Cr}_2\text{O}_7^{2-}$ is shown below:

