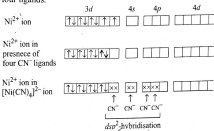


## Square Planar Complexes

The square planar complexes involve  $dsp^2$  or  $sp^2d$  hybridisation.  $X^{-L}$

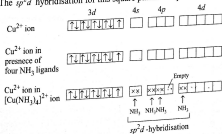
### Example of Square Planar Complexes

- (1)  $[\text{Ni}(\text{CN})_4]^{2-}$  ion : In this complex ion Ni (28) is present as  $\text{Ni}^{2+}$  ion. Ni atom has valence shell configuration  $3d^8 4s^2$  and  $\text{Ni}^{2+}$  ion has valence shell configuration,  $3d^8$ . A free  $\text{Ni}^{2+}$  ion has eight  $3d$ -electrons, two of which are unpaired in accord with the Hund's rule. Magnetic measurements indicate that this complex ion is diamagnetic (no unpaired electron is present). In the presence of strong ligand ( $\text{CN}^-$ ) all the electrons are paired up leaving one  $3d$ -orbital vacant. This vacant  $3d$ -orbital is hybridised with the  $4s$  and two of the  $4p$  ( $p_x$  and  $p_y$ ) orbitals to give the square planar  $dsp^2$  hybrids. These four hybrids form bonds to the ligands by accepting lone pair of electrons from each of the four ligands.



- (2)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion : In this complex ion Cu (29) is present as  $\text{Cu}^{2+}$  ion. Cu atom has valence shell configuration,  $3d^{10} 4s^1$  and  $\text{Cu}^{2+}$  ion has valence shell configuration,  $3d^9$ . This complex ion may have either tetrahedral or square planar geometry. Magnetic measurements do not indicate whether the complex is tetrahedral or square planar as both the complexes have one unpaired electron. Physical measurements like X-rays diffraction and esr spectroscopy indicate that this complex have square planar geometry. Huggin suggested (modern view)  $sp^2d$  hybridisation rather than  $dsp^2$  hybridisation.

The  $sp^2d$  hybridisation for this square planar complex is shown below:



Table

Complex	Oxidation State	Configuration	Valence Bond Description	No. of unpaired electrons
1. $[\text{V}(\text{H}_2\text{O})_6]^{3+}$	+3	$3d^2$		2
2. $[\text{Cr}(\text{CN})_6]^{4-}$	+2	$3d^4$		2
3. $[\text{Cr}(\text{NH}_3)_6]^{3+}$	+2	$3d^4$		4
4. $[\text{Co}(\text{NO}_2)_6]^{4-}$	+2	$3d^7$		1
5. $[\text{Fe}(\text{CN})_5\text{NO}]^{-}$	+2	$3d^0$		0
6. $[\text{PtF}_6]^{-}$	+4	$5d^0$		0
7. $[\text{Ni}(\text{NH}_3)_6]^{2+}$	+2	$3d^8$		2
8. $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$	+1	$3d^6 4s^1$		0
9. $[\text{FeCl}_4]^{-}$	+2	$3d^6$		4
10. $(\text{CuX}_4)^{-}$ [X=Cl <sup>-</sup> , Br <sup>-</sup> , CNS <sup>-</sup> ]	+2	$3d^9$		1
11. $[\text{Cu}(\text{CN})_4]^{-}$	+2	$3d^9$		1
12. $[\text{PtCl}_4]^{-}$	+2	$5d^8$		0

### Shapes of $d$ -Orbitals

Since  $d$  orbitals are often used in coordination complexes it is important to study their shapes and distribution in space. The five  $d$  orbitals are not identical and the orbitals may be divided into two groups. The three  $t_{2g}$  orbitals have identical shape and point between the axes,  $x$ ,  $y$  and  $z$ . These  $d$ -orbitals are  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ . The two  $e_g$  orbitals have different shapes and point along the axes. These orbitals are  $d_{x^2-y^2}$  and  $d_{z^2}$ .

