

- of $[\text{FeBr}_2(\text{CO})(\text{NH}_3)_3]$ (A). Does (A) show optical isomerism?
3. Draw the **geometrical** and **optical** isomers of $[\text{NiBrCl}(\text{CO})(\text{NH}_3)_3]$.
4. $[\text{FeBr}_2(\text{acac})(\text{NH}_3)_2]$ shows **two** geometrical isomers (B) and (C). (C) shows optical isomerism. Draw and identify the structures of (B) and (C). Draw the optical isomer of (C). (acac⁻ = acetylacetonate ion)

Student Corner

Valence Bond Theory

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Metal centres of *d*-block form coordination compounds with ligands which can donate a pair of electrons. These ligands are known as *sigma* donors or Lewis bases. Some ligands that consist of suitable vacant orbitals accept electron density from the metal (back donation/bonding) to reduce the high charge density at the metal centre. These ligands (π -acceptors) make more stable complexes with the metal centre. Valence Bond Theory (VBT) is one of the theories put forward by Linus Pauling in 1940 to explain the nature of metal-ligand bonding in metal complexes. The assumptions of VBT are (i) central metal ion make use of vacant *s*, *p* and *d* orbitals and number of empty orbitals used is equal to its coordination number (C.N.), (ii) these orbitals hybridize together to form the same number of degenerate hybrid orbitals, (iii) each ligand has at least one orbital containing a pair of electrons which is donated to the metal centre.

In octahedral complexes, more stable inner-orbital complexes show d^2sp^3 hybridization whilst less stable outer-orbital complexes show sp^3d^2 hybridization. For example, $[\text{CoL}_6]^{3+}$ is an inner-orbital complex with a strong field ligand "L" and $[\text{CoL}'_6]^{3+}$ is an outer-orbital complex with a weak field ligand "L'" (see Figure 1). The energy of these outer-orbitals is quite high, as a result the outer-orbital complex is reactive (or labile).

Due to the influence of the strong field ligand L, $[\text{CoL}_6]^{3+}$ is a diamagnetic low-spin cation with no unpaired electrons, but $[\text{CoL}'_6]^{3+}$ is a paramagnetic high-spin cation with four unpaired electrons.

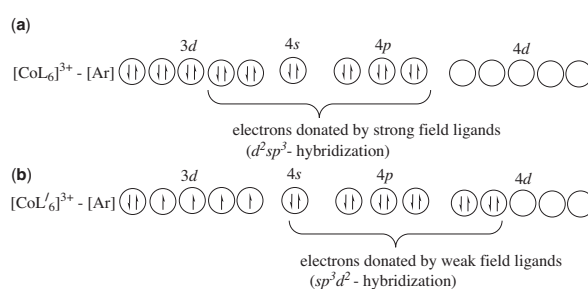


Figure 1: Hybridization of octahedral Co(III) complexes with (a) strong field ligands "L" (b) weak field ligand "L'".

When the C.N. of a complex is four it can have square-planar or tetrahedral geometry. Square-planar complexes have the d^8 electron configuration and are diamagnetic. On the other hand, most tetrahedral complexes are paramagnetic. Thus, square-planar complexes are low-spin complexes having dsp^2 hybridization. Most tetrahedral complexes are high-spin complexes with sp^3 hybridization.

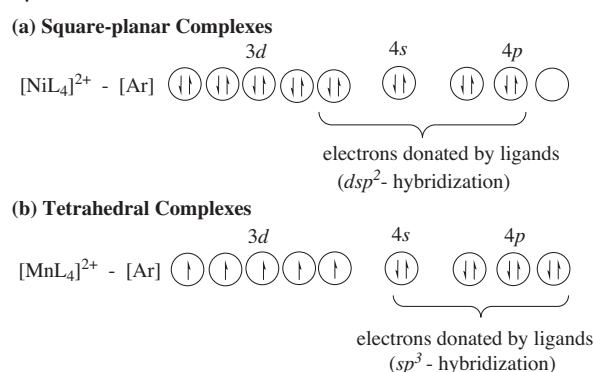


Figure 2: Hybridization of (a) square-planar complexes (b) tetrahedral complexes

Hybridization of *3d*-metal centres vary with the C.N. and the geometry of the coordination compounds as given in Table 1.

Table 1: Hybridizations occurring in the $3d$ - metal centres

C.N.	Hybridization (orbitals used)	Geometry
2	sp ($4s, 4p$)	Linear
3	sp^2 ($4s, 4p^2$)	Trigonal-planar
4	sp^3 ($4s, 4p^3$)	Tetrahedral
	dsp^2 ($3d_{x^2-y^2}, 4s, 4p_x, 4p_y$)	Square-planar
5	dsp^3 ($d_{z^2}, 4s, 4p^3$)	Trigonal-bipyramidal
	sp^3d ($4s, 4p^3, 4d_{x^2-y^2}$)	Square-pyramidal
6	d^2sp^3 ($3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p^3$)	Octahedral (inner-orbital)
	sp^3d^2 ($4s, 4p^3, 4d_{x^2-y^2}, 4d_{z^2}$)	Octahedral (outer-orbital)

Pauling made use of magnetic measurements to find out the number of unpaired electrons in a complex, which helped him to suggest the orbitals involved in the hybridization process.

The limitations of VBT are: it fails to explain the origin of color and magnetic properties of transition metal complexes. Thus, Crystal Field Theory (CFT) has become more powerful theory as it explains those two properties.

Problems

- Using VBT, predict the hybridization of iron in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ with $\mu_s = 4.9$ BM.
- Using VBT, predict the hybridization of Mn in $[\text{MnBr}_4]^{2-}$.
- Using VBT, predict the hybridization of cobalt in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ if the magnetic moment is zero BM.
- Show that all octahedral complexes of Ni^{2+} are outer-orbital complexes.
- Using VBT, predict the orbitals involved in the hybridization of the following.
(a) $[\text{FeF}_6]^{3-}$ (b) $[\text{Mn}(\text{CN})_6]^{3-}$ (c) $[\text{Fe}(\text{CO})_5]$

Student Corner

Opium Alkaloids

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Alkaloids constitute a class of nitrogen containing organic compounds that possess significant pharmacological properties. They occur mainly in plants and to a lesser extent in microorganisms and animals. The name alkaloid or 'alkali-like' was first introduced by the German chemist Wilhemm Meissner in the early nineteenth century.



Opium poppy seed pod

The study of alkaloids began in nineteenth century and the first alkaloid isolated in pure form was morphium by Friedrich Sertuner in 1805. This compound is commonly known as morphine and it is found in opium poppies. Opium is the dried milky exudate obtained from the unripe seed capsules of the opium poppy, *Papaver somniferum*. Opium has traditionally been smoked for pleasure, but it can also be used as an analgesic, sleep inducer and for treatment of coughs. However habitual users develop a craving for the drug as an addiction.

