

BONDING IN COORDINATION COMPOUNDS

Apart from playing an important role in various life processes like photosynthesis, oxygen transportation and storage, coordination compounds have shown their usefulness in medicinal and analytical chemistry also such as treatment of metal toxicity, hardness of water



Werner's theory

It gives an idea about the structures of complex compounds.

Postulates of Werner's theory

- Metals possess two types of valencies; primary valency (oxidation number) and the secondary valency (coordination number).
- A metal atom tends to satisfy both primary as well as secondary valencies.
- Secondary valencies satisfied by ligands are directional while primary valencies satisfied by negative ions are non-directional in nature.

Limitations of Werner's theory

- Werner's theory could not explain
 - the complex forming property of only certain elements.
 - directional characteristics of bonds.
 - characteristic magnetic and optical properties of complexes.

Valence bond theory

It describes the bonding in terms of hybridised orbitals of the central metal atom or ion, it explains the shapes of complexes and relation between the observed magnetic behaviour and bond type.

Postulates of VBT

- The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number which hybridise together.
- The vacant hybrid orbitals form coordinate bond with ligands. These bonds are of equal strength and directional in nature.

Hybridisation and geometry of complexes

oordination	Type of	Geometry
no.	hybridisation	of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral
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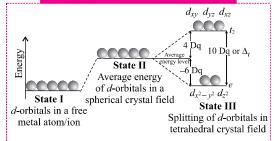
Limitations of VBT

- It could not explain the colour and electronic spectra of complexes.
- It could not explain the structure of $[Cu(NH_3)_4]^{2+}$ ion.
- It could not explain why the pairing of electrons occurs in the presence of strong ligands.

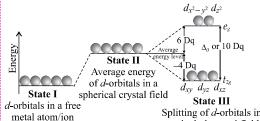
Crystal field theory (CFT)

According to CFT, under the influence of ligand field, degeneracy of d-orbitals is destroyed and they split into two or more energy levels. The extent of splitting depends upon the strength of ligand.

Tetrahedral complexes



Octahedral complexes



Splitting of d-orbitals in octahedral crystal field

Spectrochemical series

Arrangement of ligands in the order of increasing field strength.

 $I^- < Br^- < S^{2-} < SCN^- < Cl^ < F^{-} < OH^{-} < C_{2}O_{4}^{2-}$ $< H_2O < NCS^- < NH_3 <$ $en < NO_2^- < CN^- < CO$.

Increasing order of CFSE (Δ_o)

- If $\Delta_o < p$, then complex is high spin.
- If $\Delta_o > p$, then complex is low spin.

Jahn-Teller distortion

- If the *d*-orbitals are asymmetrically filled, they will repel some ligands in the complex more than the others. This results in distortion of octahedral complexes.
- Distortion caused by asymmetric filling of t_{2g} is too small to measure.
- Asymmetric filling of e_q orbitals causes a significant distortion.

 $e_g: d_{x^2-y^2} d_{z^2}$ Four long bonds and two short bonds.

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 d^4 (high spin), d^7 (low spin) and d^9 configurations show Jahn Teller distortion.