

B.Sc.(H) Chemistry
Semester - IV
Core Course - VIII (CC-VIII)
Inorganic Chemistry - III



I. Coordination Chemistry

16. Coordination Numbers and Structures



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

Coordination Chemistry: 20 Lectures

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of $10 Dq$ (Δ_o), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of $10 Dq$ (Δ_o , Δ_t). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:

1. Coordination Numbers and Structures

Coordination Numbers and Structures

- **Factors considered when determining structures.**

The number of bonds. Bond formation is exothermic; the more the better.

VSEPR arguments

Occupancy of *d* orbitals.

Steric interference by large ligands.

Crystal packing effect.

It may be difficult to predict shapes.

Low Coordination Numbers (C.N.)

- C.N. 1 is rare except in ion pairs in the gas phase.
- C.N. 2 is also rare.

$[\text{Ag}(\text{NH}_3)_2]^+$, Ag is d^{10} (how?)

VSEPR predicts a linear structure.

Large ligands help force a linear or near-linear arrangement.

- $[\text{Mn}(\text{N}[\text{SiMePh}_2)_2)_2]$.
- C.N. 3 is more likely with d^{10} ions.

Trigonal-planar structure is the most common.

$[\text{Cu}(\text{SPPH}_3)_3]^+$, adopts a low C.N. due to ligand crowding.

Coordination Numbers 4

- **Tetrahedral and square planar complexes are the most common.**

Small ions and/or large ligands prevent high coordination numbers (Mn(VII) or Cr(VI)).

- **Many d^0 or d^{10} complexes have tetrahedral structures (only consider bonds).**

MnO_4^- and $[\text{Ni}(\text{CO})_4]$

Jahn-Teller distortion

Coordination Numbers 4

- **Square-planar geometry**

*d*⁸ ions (Ni(II), Pd(II), and Pt(II))



The energy difference between square-planar and tetrahedral structures can be quite small.

- **Can depend on both the ligand and counter-ion.**

Coordination Number 5

- **Common structures are trigonal bipyramid and square pyramid.**

The energy difference between the two is small. In many measurements, the five ligands appear identical due to fluxional behavior.

How would you modify the experiment to differentiate between the two structures?

- **Five-coordinate compounds are known for the full range of transition metals.**

Coordination Number 6

- This is the most common C.N. with the most common structure being octahedral.

If the *d* electrons are ignored, this is the predicted shape.

- $[\text{Co}(\text{en})_3]^{3+}$
- This C.N. exists for all transition metals (d^0 to d^{10}).

Distortions of Complexes Containing C.N. 6

- **Elongation and compression :**

Produces a trigonal antiprism structure when the angle between the top and bottom triangular faces is 60° .

Trigonal prism structures are produced when the faces are eclipsed.

- **Most trigonal prismatic complexes have three bidentate ligands (Figure 9-30).**
- **π interactions may stabilize some of these structures.**

The Jahn-Teller effect is useful in predicting observed distortions.

Higher Coordination Numbers

- **C.N. 7 is not common**
- **C.N. 8**

There are many 8-coordinate complexes for large transition elements.

- **Square antiprism and dodecahedron**
- **C.N.'s up to 16 have been observed.**

THANK YOU