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

I. Coordination Chemistry
2. Valence Bond Theory

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Coordination Chemistry: 20 Lectures

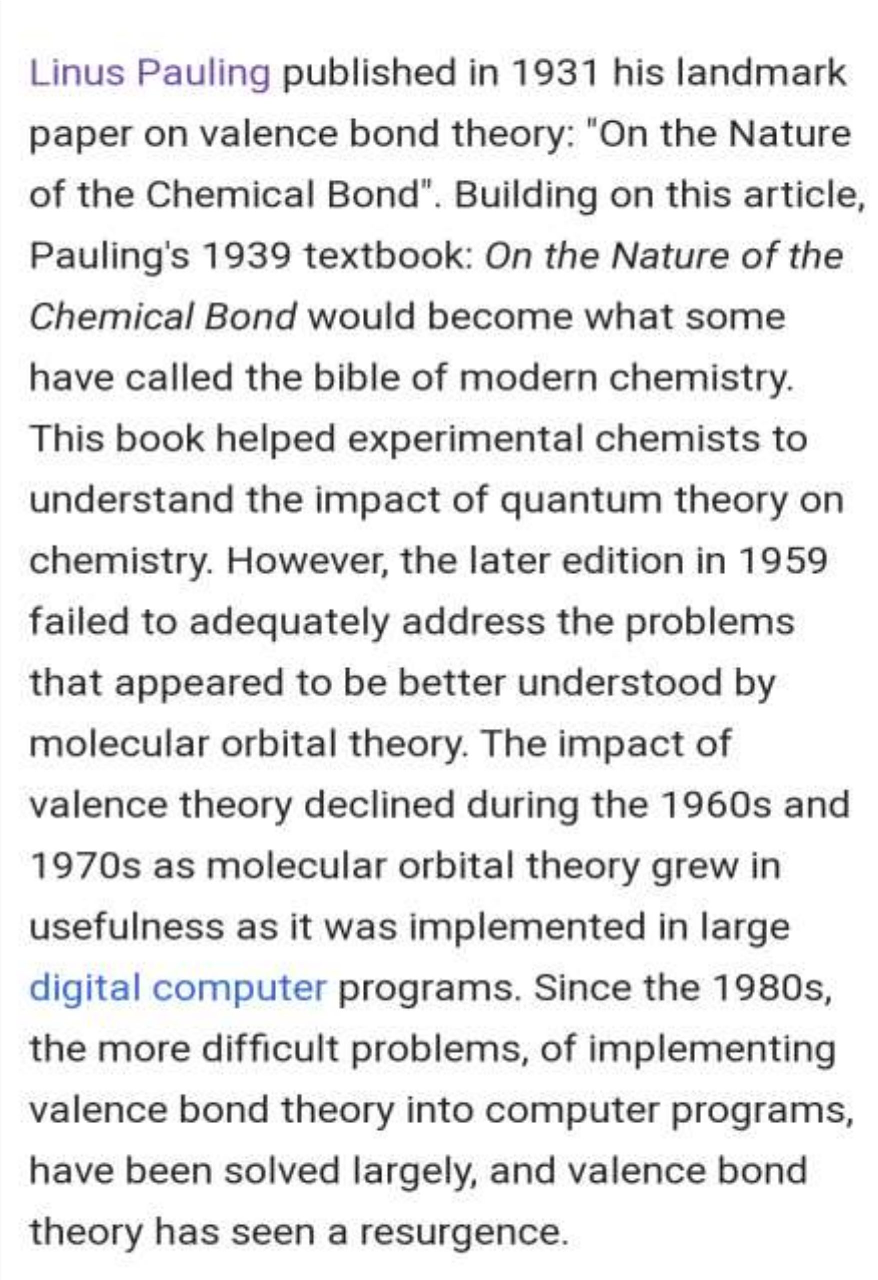
Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of 10 Dq (Δo), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of 10 Dq (Δo, Δt). Octahedral vs. tetrahedral coordination, 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.

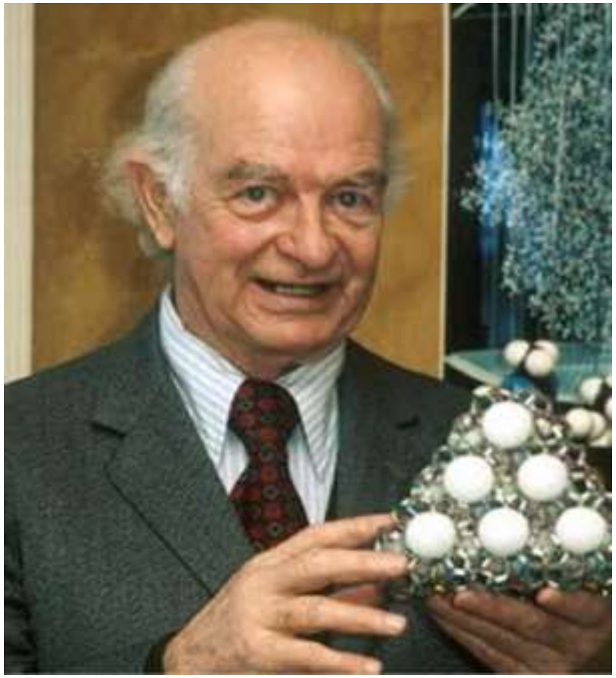
Coverage:

1. Valence Bond Theory

Linus Carl Pauling and The Valence Bond Theory



Linus Pauling published in 1931 his landmark paper on valence bond theory: "On the Nature of the Chemical Bond". Building on this article, Pauling's 1939 textbook: *On the Nature of the Chemical Bond* would become what some have called the bible of modern chemistry. This book helped experimental chemists to understand the impact of quantum theory on chemistry. However, the later edition in 1959 failed to adequately address the problems that appeared to be better understood by molecular orbital theory. The impact of valence theory declined during the 1960s and 1970s as molecular orbital theory grew in usefulness as it was implemented in large digital computer programs. Since the 1980s, the more difficult problems, of implementing valence bond theory into computer programs, have been solved largely, and valence bond theory has seen a resurgence.



Linus Carl Pauling
(1901-1994)
Nobel Prize -1954, 1962

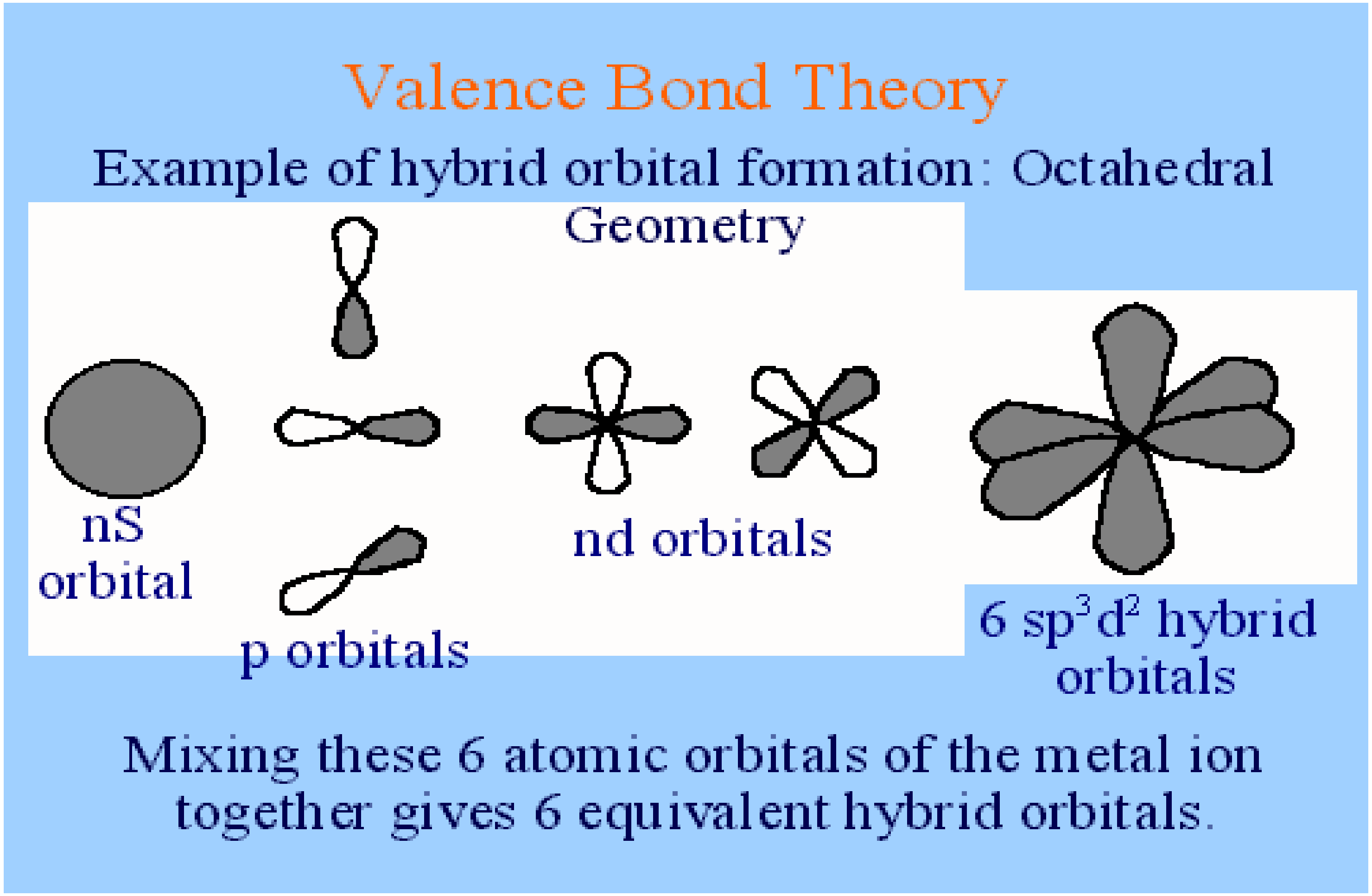
Valence Bond Theory

- **A covalent bond forms between two atoms when an orbital on one atom overlaps with the orbital on another atom**
  - ✓ **Total number of electrons on both orbitals is no more than two.**
- **In transition metal complexes, covalent bonds are formed via overlap of a completely filled ligand orbital and a vacant hybrid orbital on metal ion.**
- **Hybridization determines the geometry of the molecule**

If geometry is known, the hybrid orbitals of the metal ion used in the bonding is known.

Hybrid orbitals for common geometries in complexes

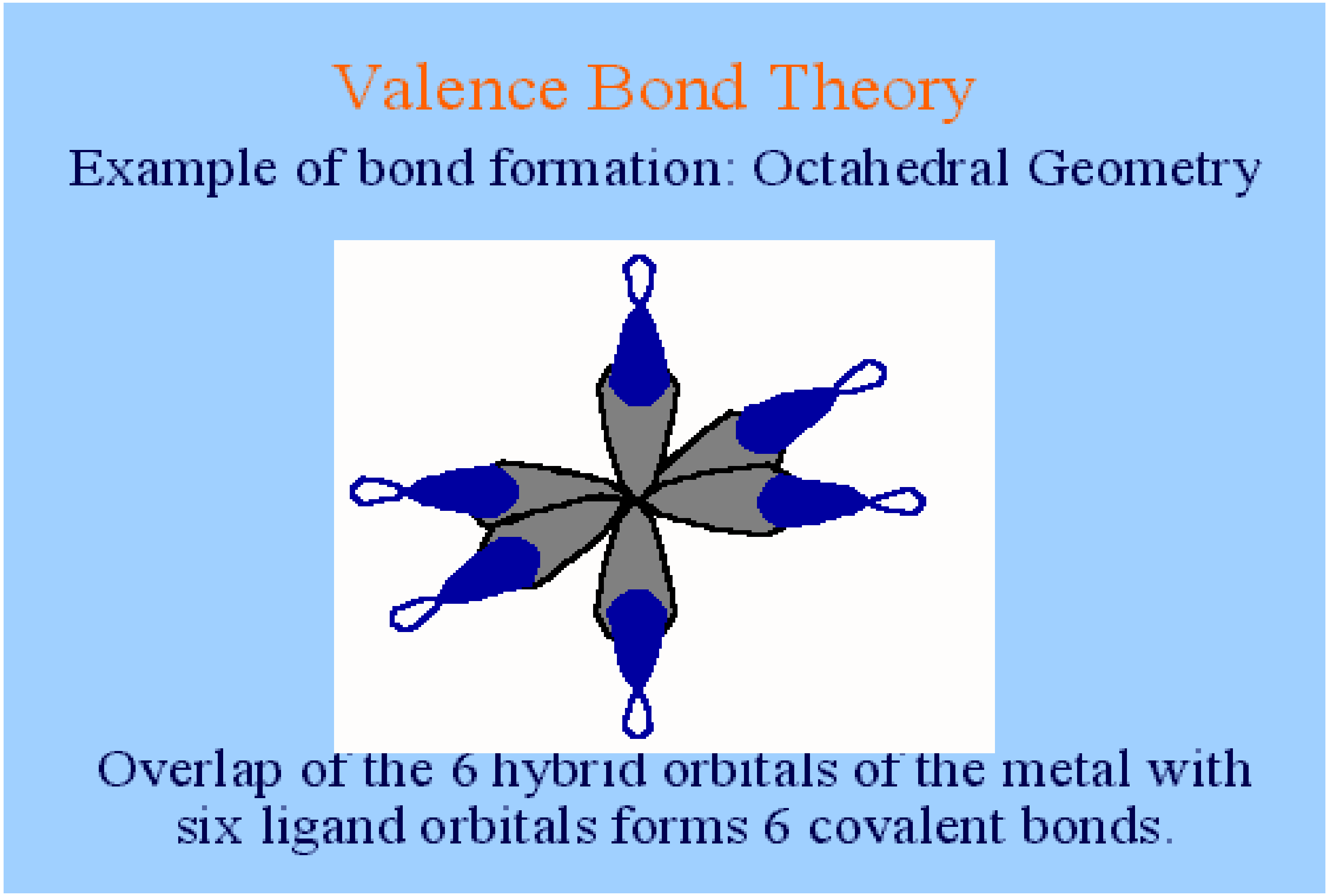
CN	Geometry	Hybrid orbitals
2	linear	sp
4	tetrahedral	sp^3
4	square planar	dsp^2
6	octahedral	d^2sp^3, sp^3d^2



Valence Bond Theory

Example of hybrid orbital formation: Octahedral Geometry

Mixing these 6 atomic orbitals of the metal ion together gives 6 equivalent hybrid orbitals.

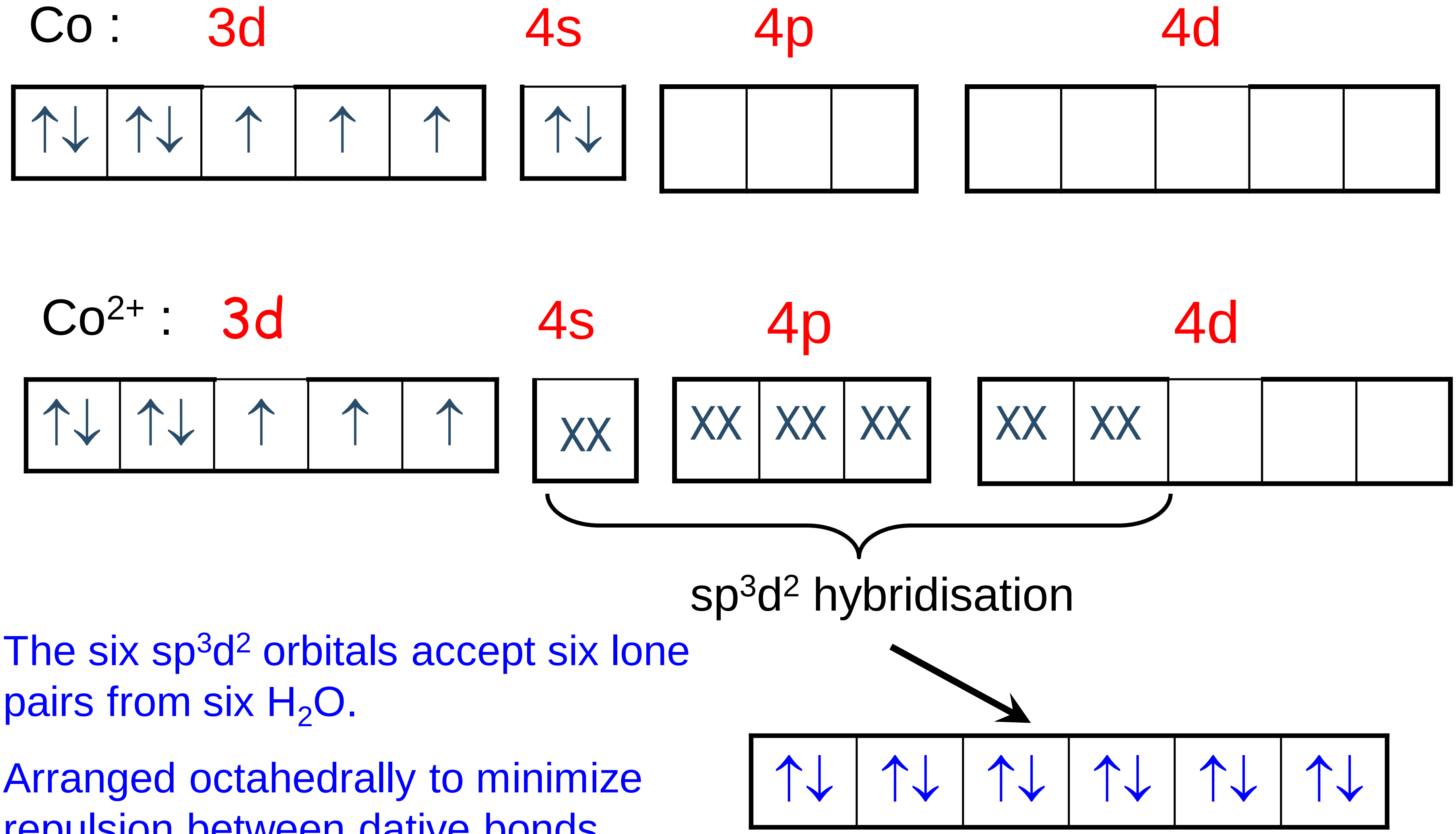


Valence Bond Theory

Example of bond formation: Octahedral Geometry

Overlap of the 6 hybrid orbitals of the metal with six ligand orbitals forms 6 covalent bonds.

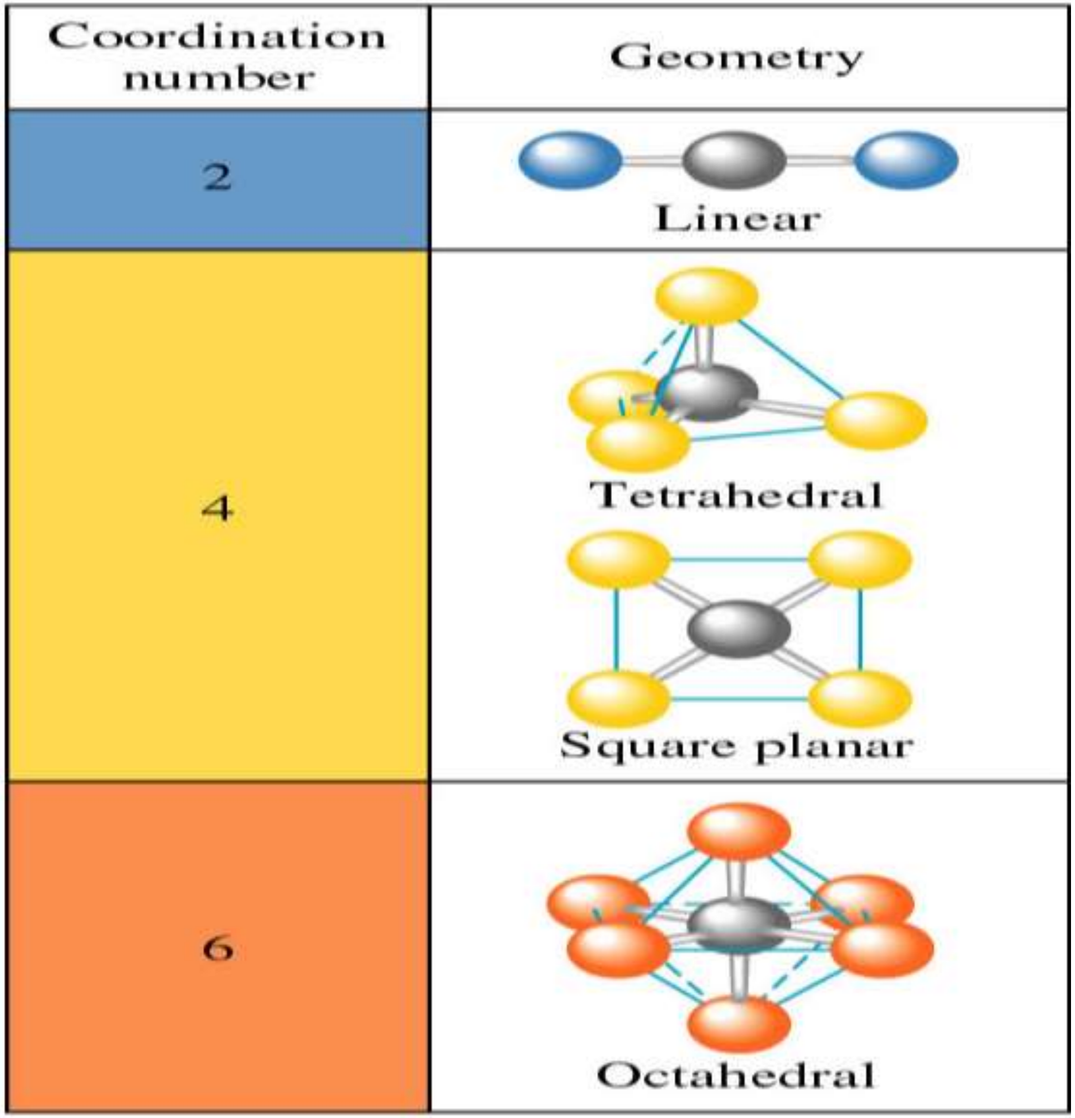
$[Co(H_2O)_6]^{2+}$



The six sp^3d^2 orbitals accept six lone pairs from six H_2O.

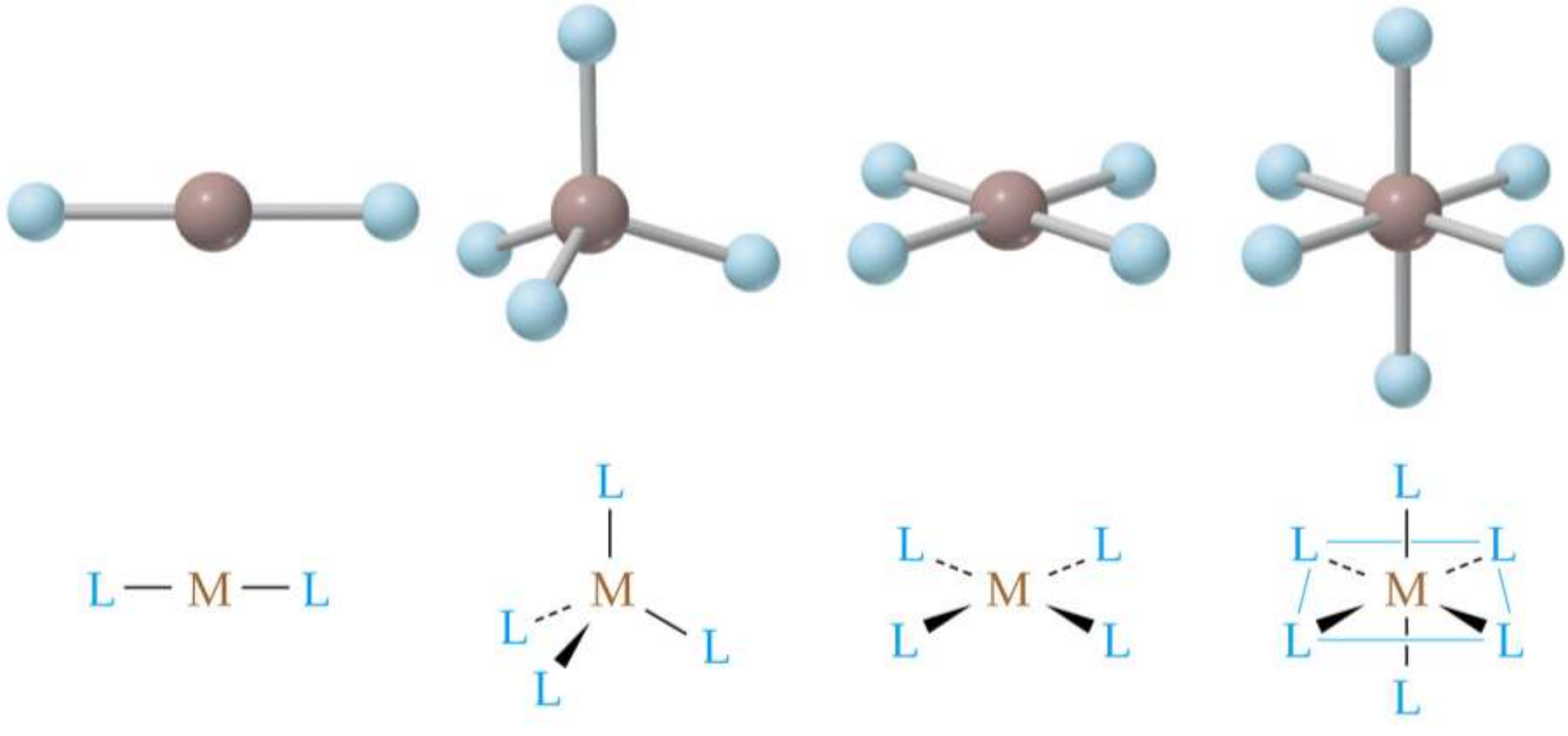
Arranged octahedrally to minimize repulsion between dative bonds.

Common Coordination Numbers of Transition Metal Complexes



Coordination number	Geometry
2	Linear
4	Tetrahedral Square planar
6	Octahedral

Common Coordination Geometries



Linear

Tetrahedral

Square planar

Octahedral

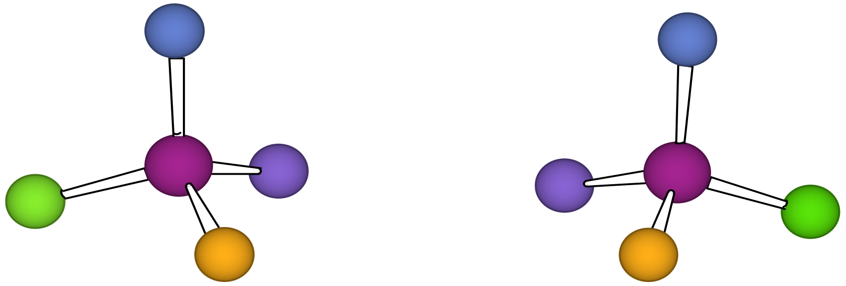
Tetrahedral Complexes

optical isomerism

$[CoCl_4]^{2-}$

$[MnO_4]^-$

$[NiCl_4]^{2-}$



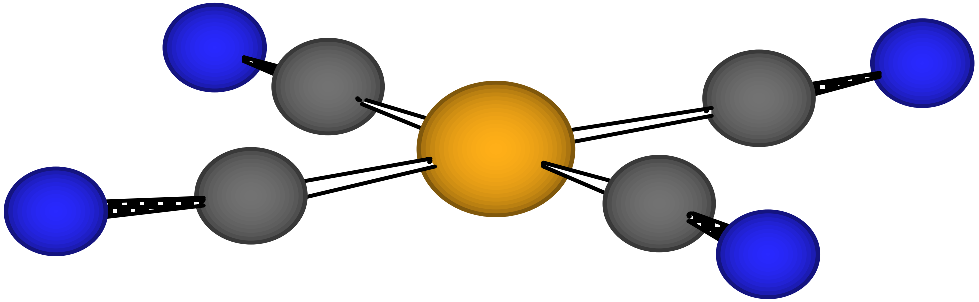
non-superimposable mirror images

Favoured by steric requirements

large ligands e.g. Cl^-, Br^-, I^-

small metal ions …with pseudo-noble gas configuration e.g. Zn^{2+}

Square Planar Geometry



e.g. $[PtCl_4]^{2-}$

$[AuBr_4]^{-}$

$[Pd(CN)_4]^{2-}$

Square planar complexes are formed by d^8 metal centres

***i.e*. group 10** **Ni^{2+}, Pd^{2+}, Pt^{2+}, Au^{3+}**

Color of a complex depends on; (i) the metal, (ii) its oxidation state & (iii) ligands (i.e., everything)

For example, pale blue $[Cu(H_2O)_6]^{2+}$ versus dark blue $[Cu(NH_3)_6]^{2+}$.

Partially filled *d* orbitals usually give rise to colored complexes because they can absorb light from the visible region of the spectrum.

- **The color of the complex is the sum of the light not absorbed (reflected) by the complex.**

Transition metal complexes that are paramagnetic have unpaired e$^-$'s & those that are diamagnetic have no unpaired e$^-$'s.

- ➢ **Consider the *d*^{6} Co metal ion:**

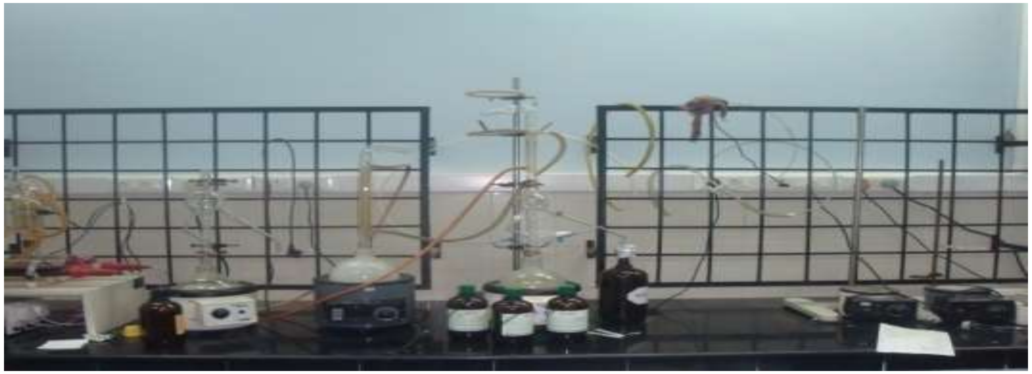
  $[Co(NH_3)_6]^{3+}$ has no unpaired electrons, but $[CoF_6]^{3-}$ has four unpaired electrons per ion.

  (note, s e$^-$'s are lost first before d e$^-$'s in a metal cation)

- ❖ **We need to develop a bonding theory to account for both color and magnetism in transition metal complexes.**

Since the spectrum for $[Ti(H_2O)_6]^{3+}$ has a maximum absorption at 510 nm (green & yellow), & transmits all other wavelengths, the complex is purple.

Thank You



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