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

I. Coordination Chemistry

4. Crystal Field Theory

B. Energy of 3*d*-orbitals in Tetrahedral Field and Square-Planar Field

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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.

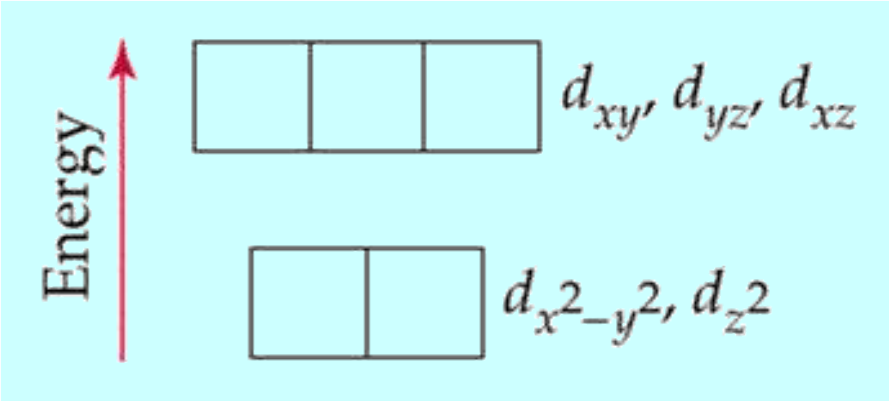
IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:

1. Energy of 3*d*-orbitals in Tetrahedral Field
2. Energy of 3*d*-orbitals in Square-Planar Field

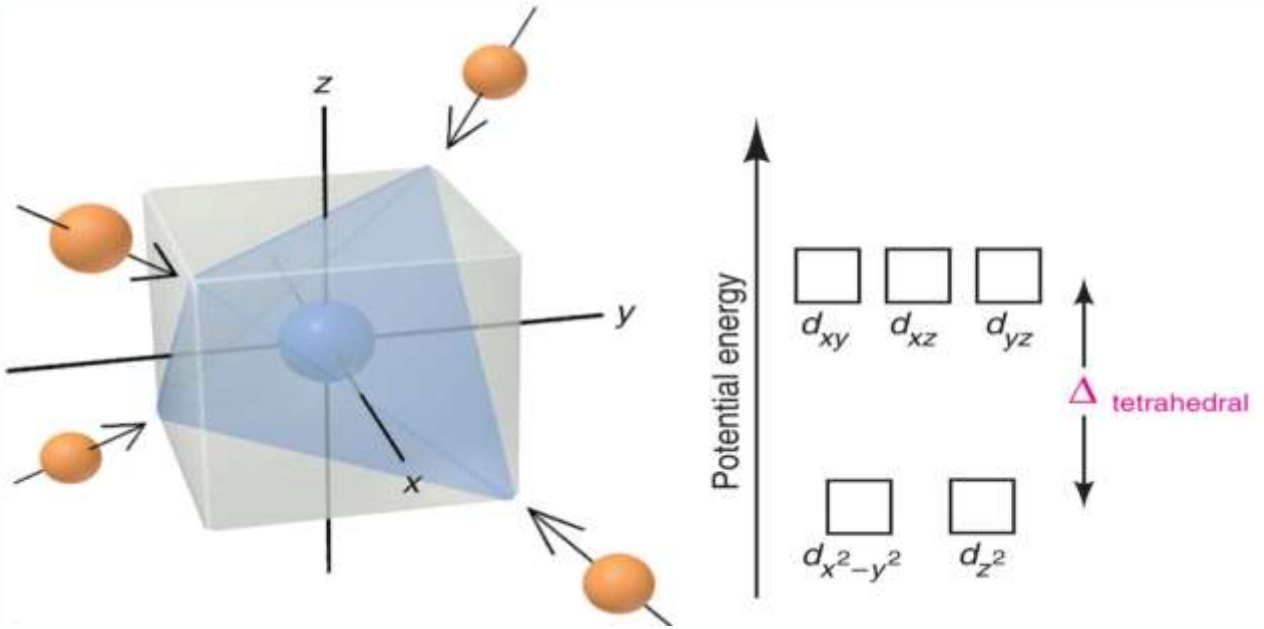
Tetrahedral Field

In a tetrahedral field the d_{xy}, d_{yz}, & d_{xz} orbitals are of higher Energy than the dx^2-y^2 and the dz^2 orbitals.



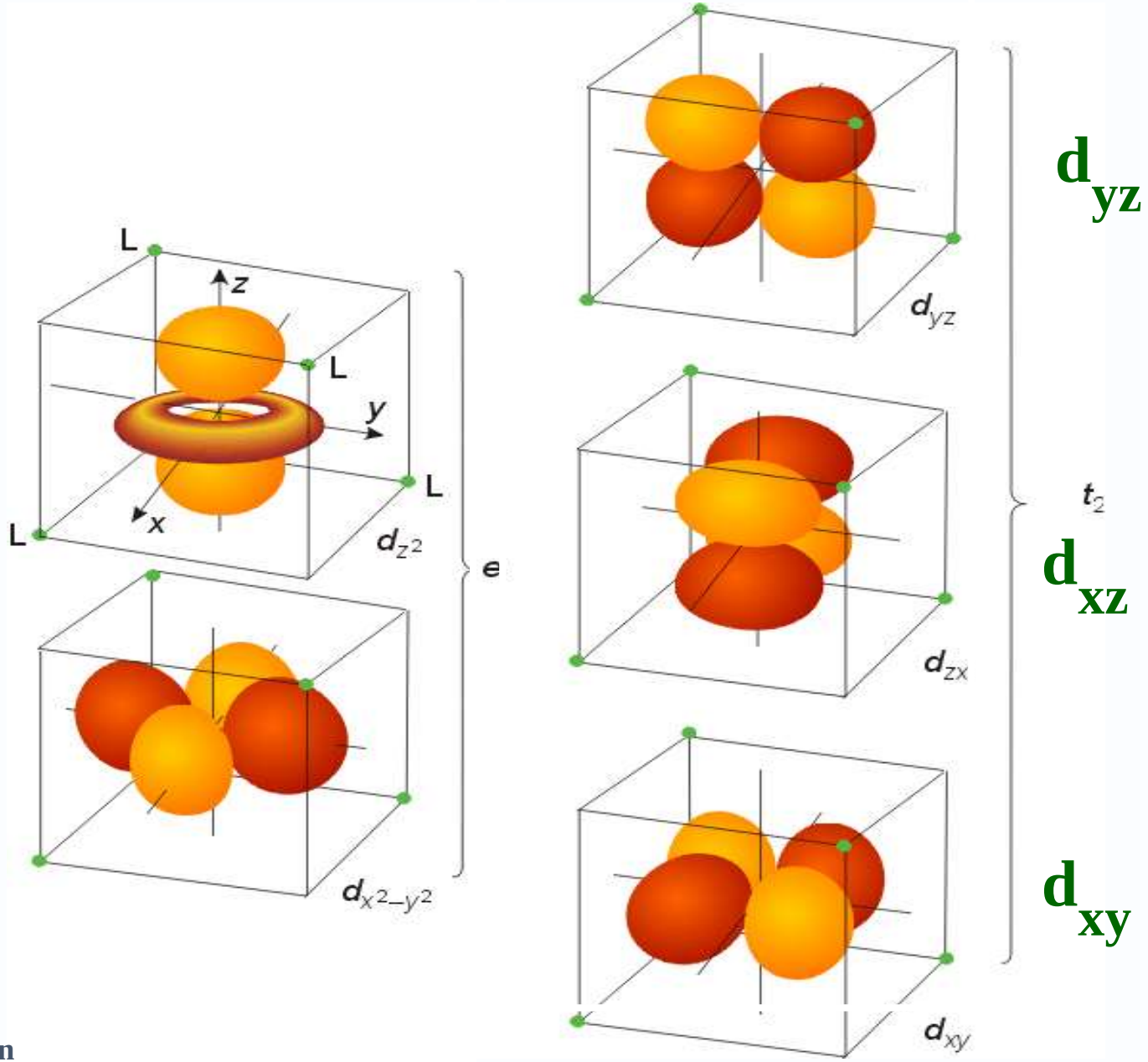
- **Because there are only 4 ligands, Δ for a tetrahedral field is smaller than Δ for an octahedral field.**
- **This causes all tetrahedral complexes to be high spin (unless told otherwise).**

Splitting of *d*-orbital energies by a tetrahedral field of ligands



The splitting of *d*-orbital energies is less in a tetrahedral than an octahedral complex, and the relative *d*-orbital energies are reversed. Only high-spin tetrahedral complexes are known because Δ is small.

Arrangements of *d*-Orbitals in Tetrahedral Field



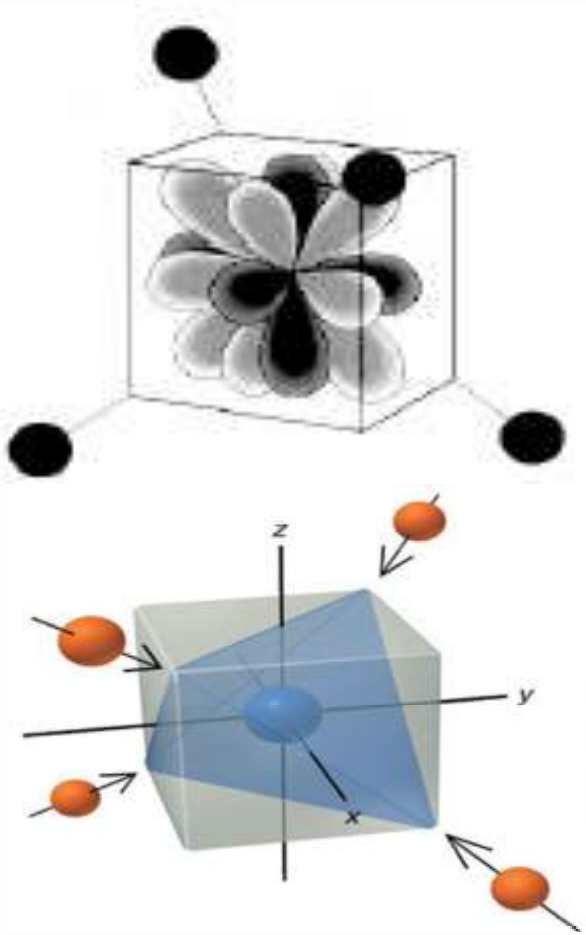
d_{z^2}

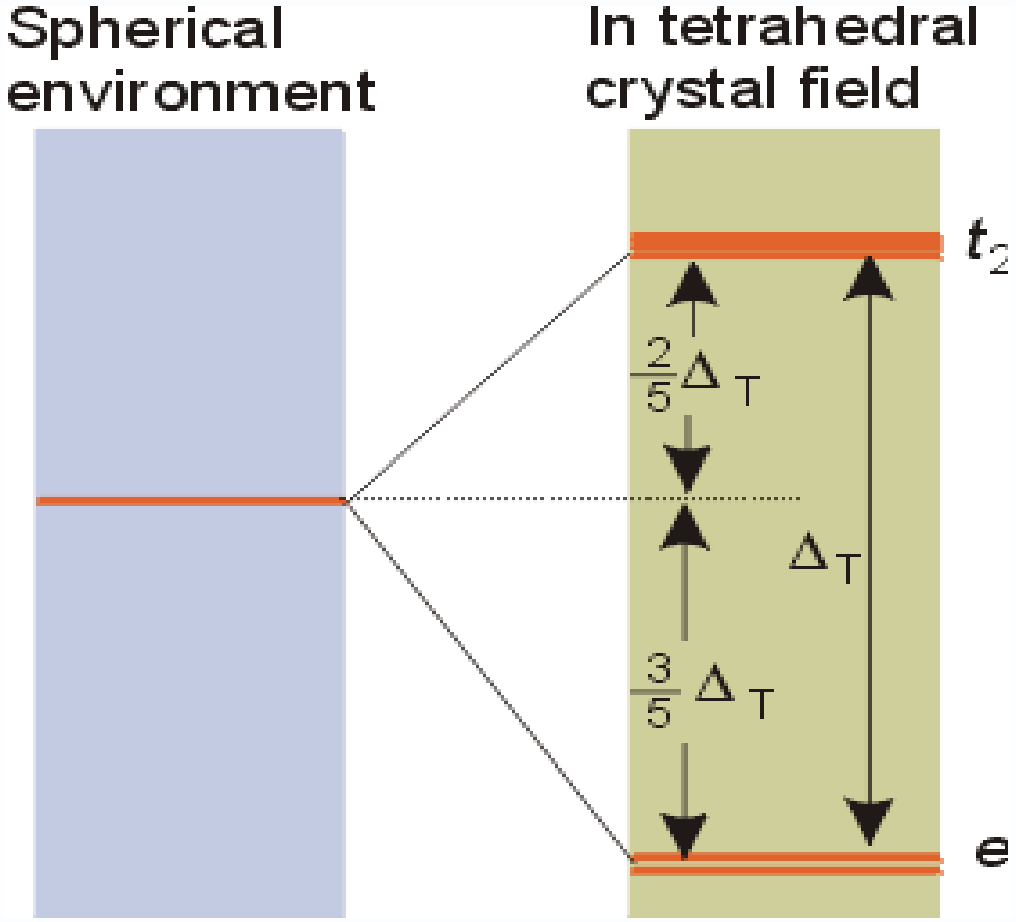
$d_{x^2-y^2}$

d_{yz}

d_{xz}

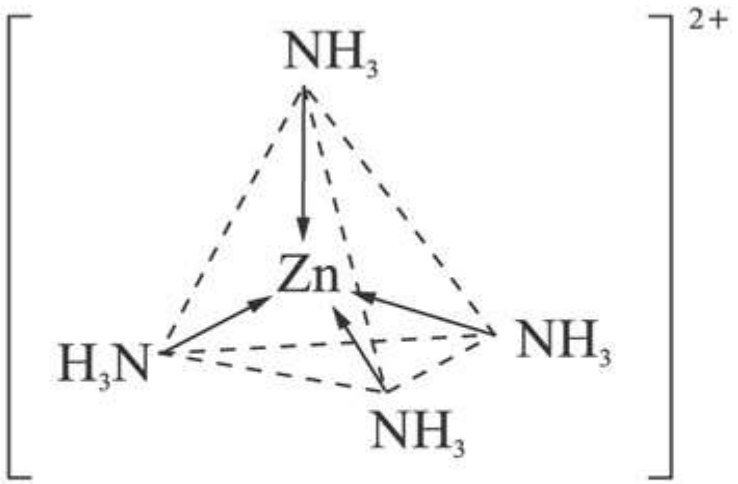
d_{xy}


z
y
x

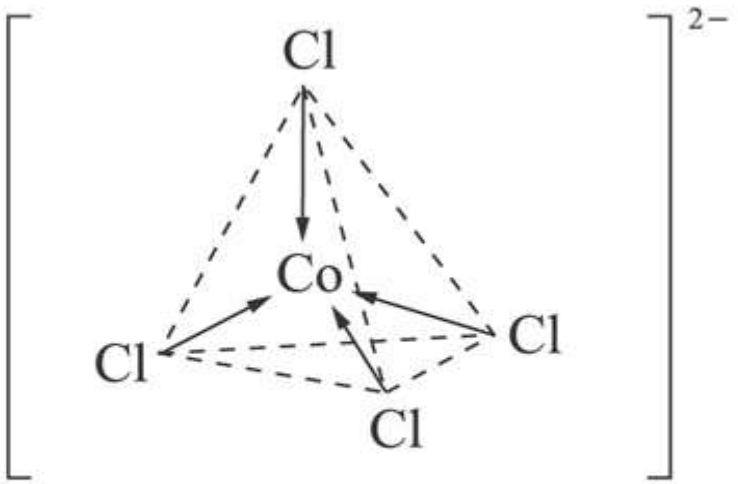

Spherical environment
In tetrahedral crystal field
t_2
$\frac{2}{5}\Delta_T$
Δ_T
$\frac{3}{5}\Delta_T$
e

Tetra-coordinated Tetrahedral Complexes

Examples:



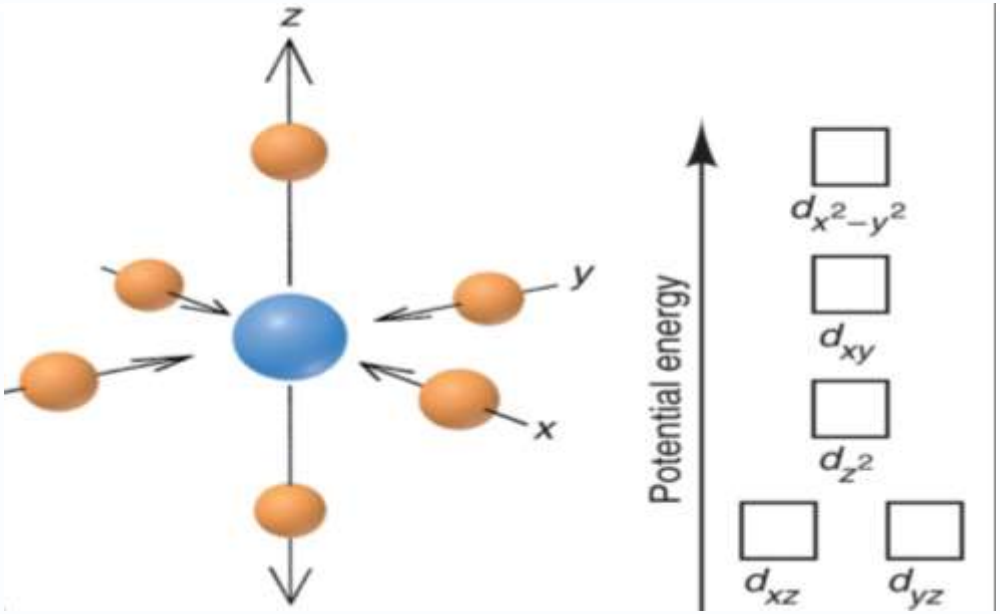
Tetraamminezinc(II) ion,
$[Zn(NH_3)_4]^{2+}$



Tetrachlorocobaltate(II) ion,
$[CoCl_4]^{2-}$

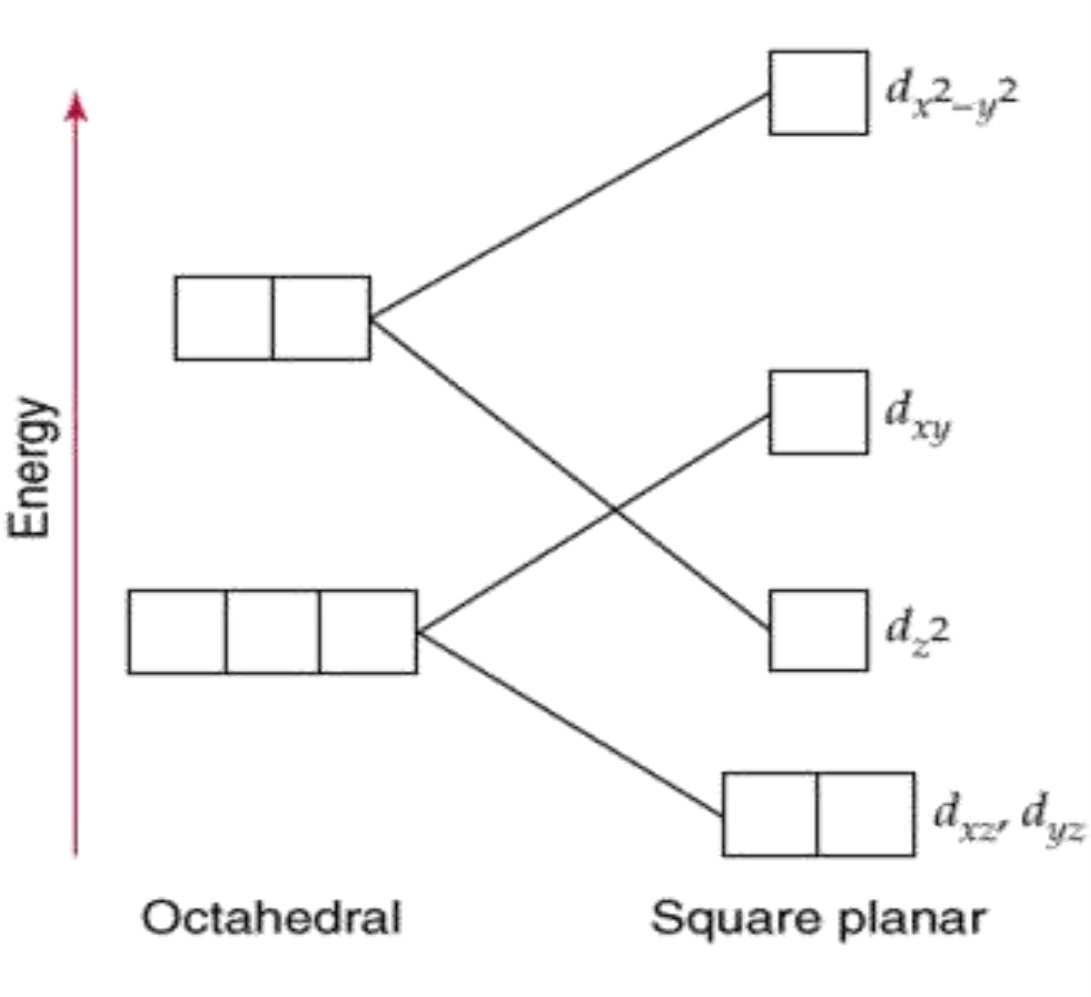
Square-Planar Field

Square planar complexes can be thought of as octahedral complexes with the two ligands along the *z*-axis removed.



- As a consequence the four planar ligands are drawn in closer towards the metal.
- Relative to the octahedral field, the dz^2 orbital is greatly lowered in energy, the d_{yz}, and d_{xz} orbitals lowered in energy, the d_{xy}, and dx^2-y^2 orbitals are raised in energy.
- Most d^8 metal ions form square planar complexes.
- The majority of complexes are low spin (i.e. diamagnetic).
- Examples: Pd^{2+}, Pt^{2+}, Ir^{+}, and Au^{3+}.

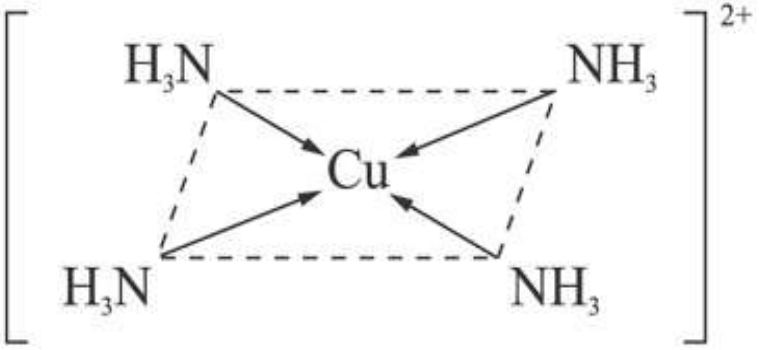
Splitting of *d*-orbital energies by a square planar field of ligands.



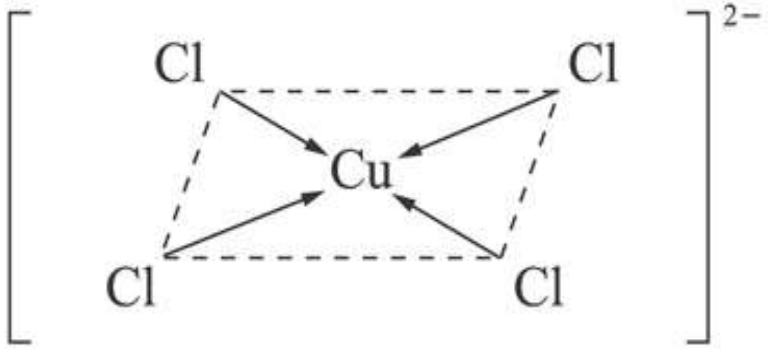
Square planar complexes are low-spin and usually diamagnetic because the four pairs of *d* electrons fill the four lowest-energy orbitals.

Tetra-coordinated Square Planar Complexes

Examples:

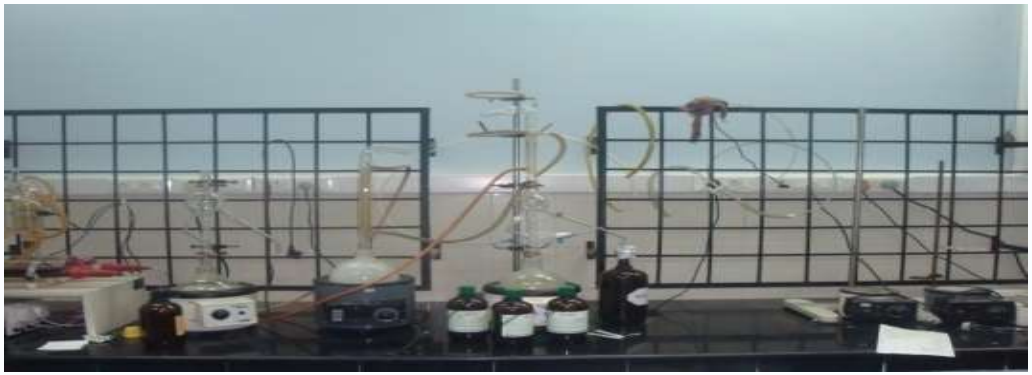


Tetraamminecopper(II) ion,
$[Cu(NH_3)_4]^{2+}$



Tetrachlorocuprate(II) ion,
$[CuCl_4]^{2-}$

Thank You



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