



Chapter 22

COORDINATION CHEMISTRY

(Part II)

Dr. Al-Saadi

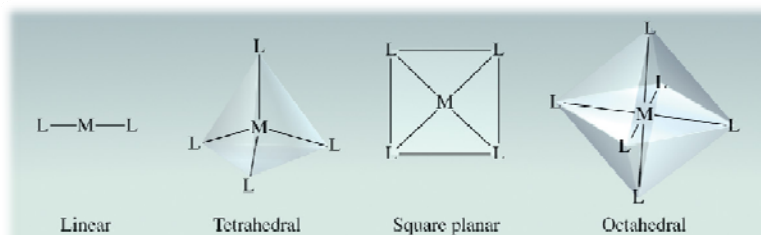
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Structure of Coordination Compounds

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- The geometry of coordination compounds plays a significant role in determining their properties.
- The structure is related to the coordination number.

Coordination Number	Structure
2	Linear
4	Tetrahedral or square planar
6	Octahedral



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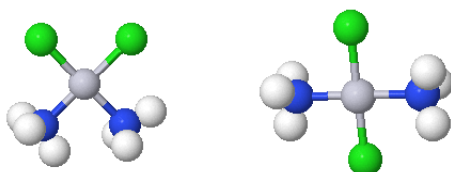
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Stereoisomerism

- In coordination chemistry, **stereoisomers** are coordination compounds whose ligands can have more than one way to be arranged around the metal ion.

- **Geometric**

- **Optical**



Two isomers of $[\text{PtCl}_2(\text{NH}_3)_2]$

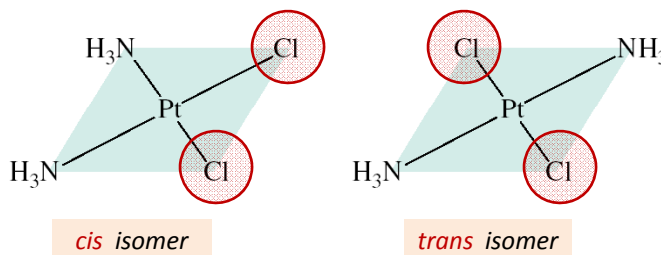
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Geometric Isomers

- Geometric isomers** can not be interconverted without breaking coordination covalent bonds. Distinctly different properties are found for geometrical stereoisomers.



cis isomer

trans isomer

Diamminedichloroplatinum(II)

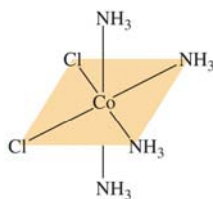
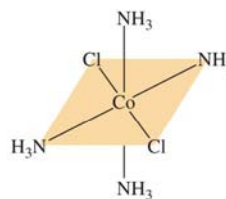
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Geometric Isomers

- **Geometric isomers** can not be interconverted without breaking coordination covalent bonds. Distinctly different properties are found for geometrical stereoisomers.

*cis isomer**trans isomer*

Tetraamminedichlorocobalt(III) ion

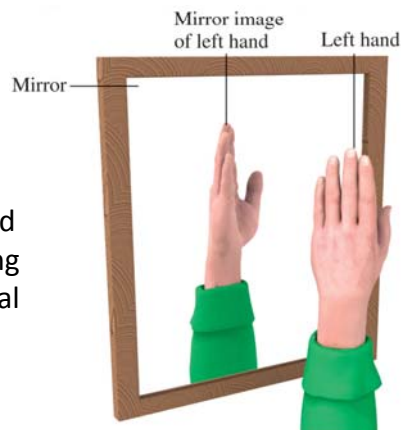
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Optical Isomers

- **Optical isomers** are :
 - mirror images, and
 - *nonsuperimposable*.
- Unlike geometric isomers, optical isomers have **identical** physical and chemical properties, such as boiling point, dipole moment and chemical reactivity. However, they have **different** optical properties.

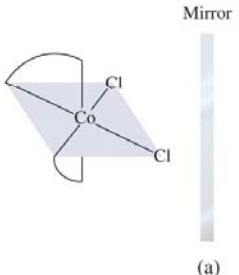


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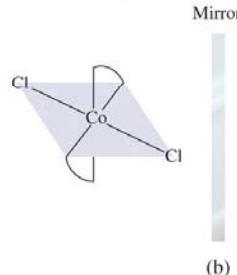
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Optical Isomers



(a)



(b)

Dichlorobis(ethylenediamine)cobalt(III) ion

cis

rotate in any manner

nonsuperimposable

"Enantiomers"

chiral

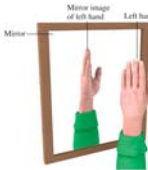
trans

rotate 90°

superimposable

"same compound"

achiral



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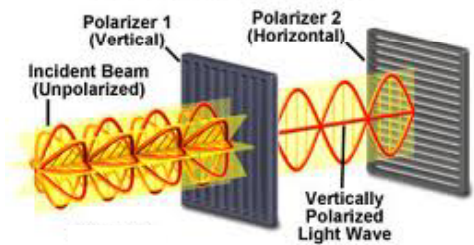
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Optical Activity of Enantiomers

- A pair of enantiomers rotate the plane of *plane-polarized light* in opposite directions.
- What is *plane-polarize light*?

Plane-polarized light oscillates only in a single plane, while ordinary light (that is not plane-polarized) oscillates in all directions.

Polarization of Light Waves

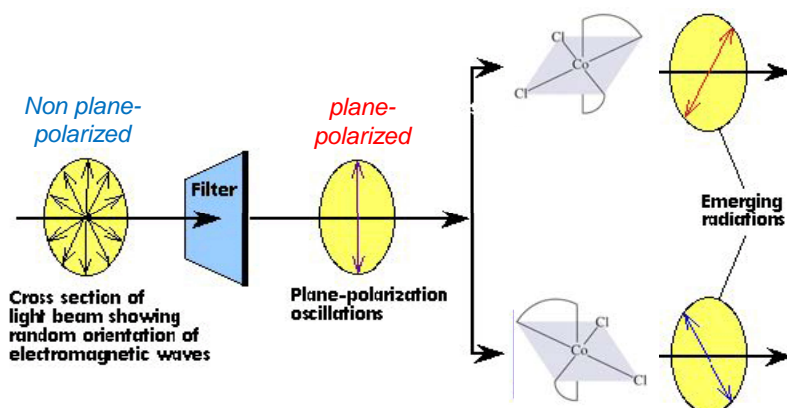


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Optical Activity of Enantiomers

- A pair of *enantiomers* rotate the plane of *plane-polarized light* in opposite directions.



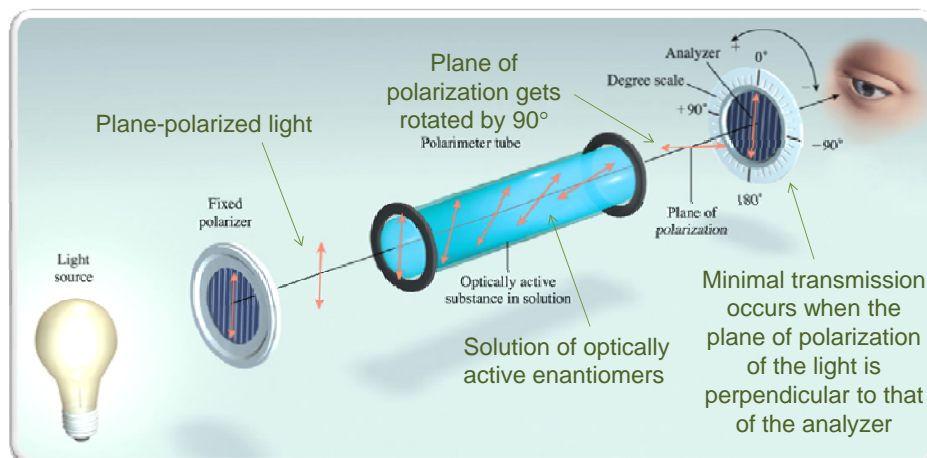
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Optical Activity of Enantiomers

- Measuring the rotation of polarized light by optical isomers.



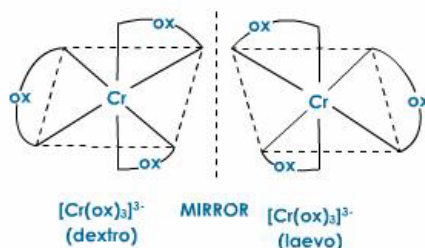
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Optical Activity of Enantiomers

- Optical isomers rotate polarized light in different directions:
 - Rotation to the right – **dextrorotatory** (*d* isomers).
 - Rotation to the left – **levorotatory** (*l* isomers).
- An equimolar mixture of two enantiomers (a pair of *d* and *l* isomers) forms **racemic mixture**.
 - Net rotation of polarized light is zero.



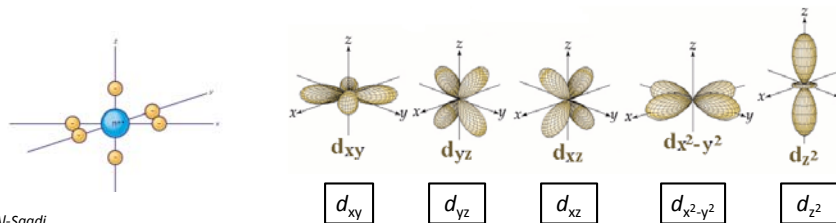
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Crystal Field Theory

- The **crystal field theory** (CFT) is a model that describes the bonding between complex ions and ligands in coordination compounds.
- According to CFT, bonding in coordination compounds arises due to electrostatic forces.
 - *Attraction* between the metal ion (atom) and the ligands.
 - *Repulsion* between the lone pairs on the ligands and the electrons in the *d* orbitals of the metal.



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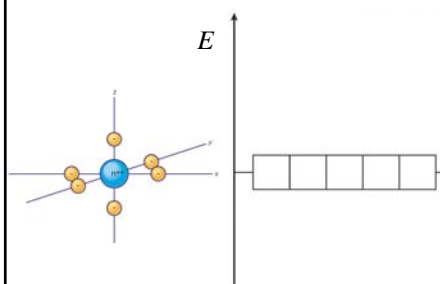
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Crystal Field Theory

- In the absence of ligands, the d orbitals are *degenerate*.

➔ *But what would be the case when the transition metal is bonded to six ligands and adopting an octahedral geometry?*



➤ In the presence of ligands, electrons in d orbitals experience different levels of repulsion for the ligand lone pairs.

➤ As a result (depending on the geometry) some d orbitals are shifted to a higher energy level and others to a lower energy level.

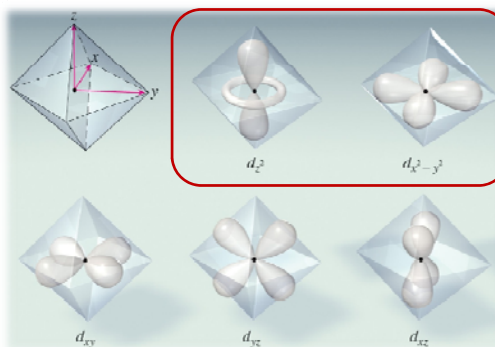
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Crystal Field Splitting

- In an *octahedral* complex:
 - the electrons in the d orbitals located along the coordinate axes experience stronger repulsions and, therefore, show an increase in energy.



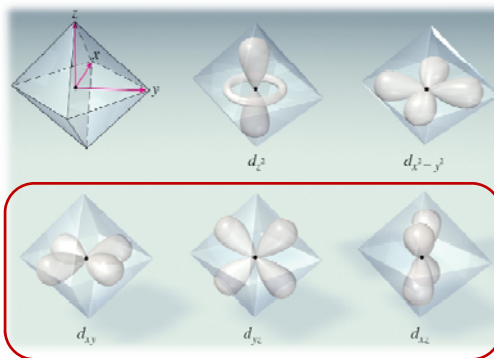
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Crystal Field Splitting

- In an *octahedral* complex:
 - the electrons in the *d* orbitals located 45° from the coordinate axes experience weaker repulsions and, therefore, show a decrease in energy.

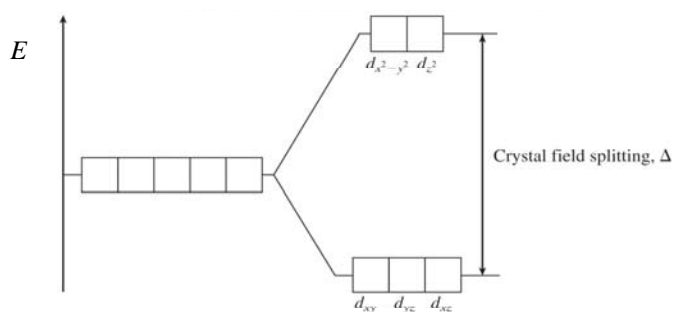


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Crystal Field Splitting




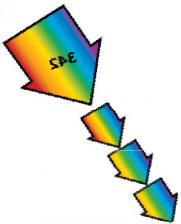


- The energy difference between the two sets of orbitals is called **crystal field splitting (Δ)**. The value of Δ :
 - depends on the nature of metal and ligands.
 - determines the color and magnetic properties.

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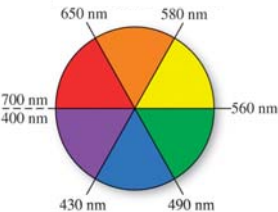
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Color

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- *Why do we see things colored?*
 - White light contains all wavelengths of visible region.
 - An object that is red absorbs all light but reflects the red component.
 - An object will also look red if it reflects all colors and absorbs only the green color, the **complementary color** of red.

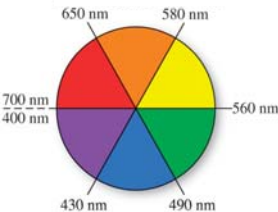
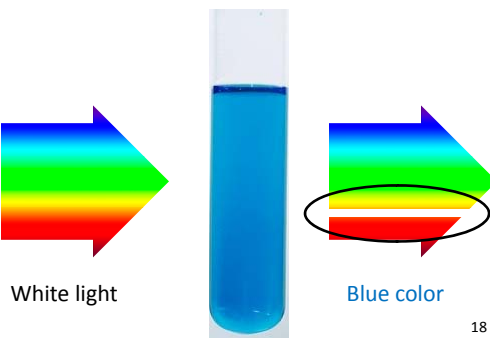


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Color

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- Consider hydrated cupric $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution. When the light passes through the solution,
 - only **orange** light is absorbed, and
 - the rest of the light passes through without being absorbed.
 Since **blue** is the *complementary color* of **orange**, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution appears to be blue.

White light Blue color

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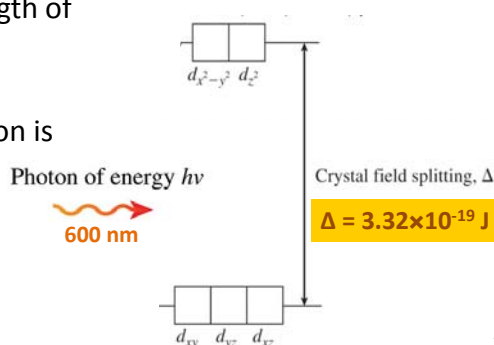
Color

- Because the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution absorbs in the orange region, the difference in energy between the two sets of d orbitals (which is the crystal field splitting) can be obtained from the wavelength of orange color.

The energy of one photon absorbed by one complex ion is given by:

$$\Delta E = h\nu$$

The energy absorbed by the complex ion is associated with the transition of one d electron from the low-energy to high-energy d orbitals.



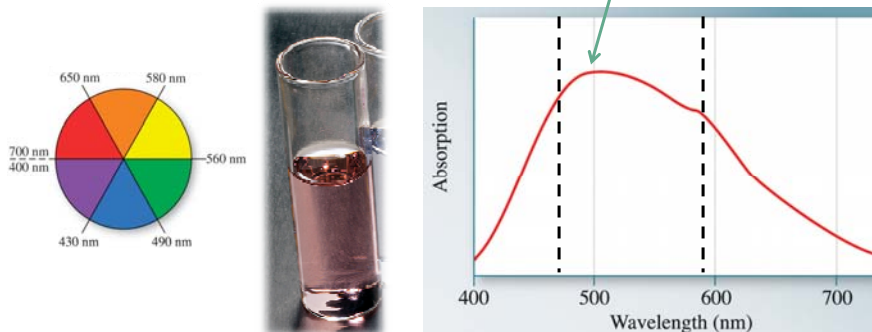
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Measurement of (Δ) for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

- Crystal field splitting can be measured using spectroscopy by locating the maximum absorption peak ($\lambda_{\text{max}} = 498 \text{ nm}$).
- Consider $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ion as an example.



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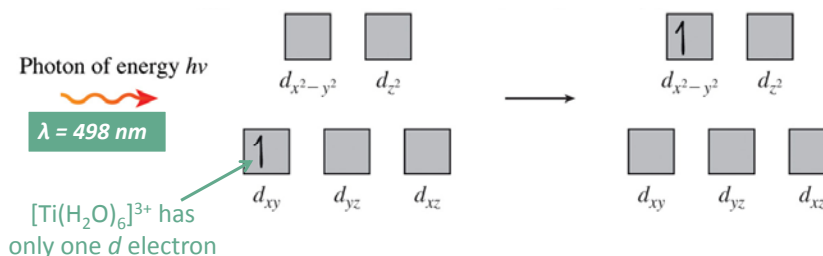
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Measurement of (Δ) for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

- The value of crystal field splitting (Δ) can be calculated for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

$$\Delta = 3.99 \times 10^{-19} \text{ J}$$

$$= 240 \text{ kJ/mol}$$



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Color

- Aqueous solutions of various first-row transition metals exhibit different colors.

Why??

Due to the different crystal field splitting in different metals.



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Spectroscopic Series

- Aqueous solutions of the same transition metal but with different ligands also exhibit different colors.

Why??

Different ligands have different effects on the value of Δ . This can be predicted by the *spectroscopic series*:



→
Increase of ligand strength

weak-field ligand

smaller Δ

strong-field ligand

larger Δ



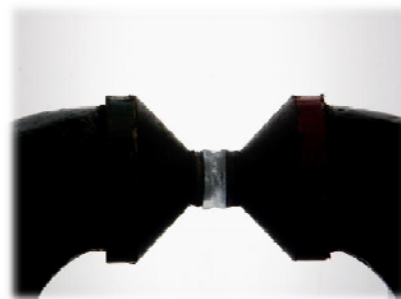
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Magnetic Properties

- The magnitude of the crystal field splitting also determines the magnetic properties of a complex ion.
- Complex ions can be:
 - Paramagnetic. (at least one unpaired d electron exist)
 - Diamagnetic. (no unpaired d electrons exist)



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Magnetic Properties

- Small values of Δ favor a *maximum* number of unpaired spin.
 - **High-spin** complexes.
 - F^- is a *weak-field* ligand on the spectrochemical series.

Hund's rule

Fe³⁺ ion has five *d* electrons

[FeF₆]³⁻

Sc Ti V Cr Mn Fe Co Ni Cu

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Magnetic Properties

- Large values of Δ are unfavorable for electron promotion, resulting with *minimum* number of unpaired spin.
 - **Low-spin** complexes.
 - CN^- is a *strong-field* ligand on the spectrochemical series.

Fe³⁺ ion

[FeF₆]³⁻ [Fe(CN)₆]³⁻

High-spin complex *Low-spin complex*

Sc Ti V Cr Mn Fe Co Ni Cu

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Magnetic Properties

How many unpaired spins would you expect the $[\text{Cr}(\text{CO})_6]^{2+}$ ion to have?

- a) 0
- b) 1
- c) 2
- d) 3
- e) 5

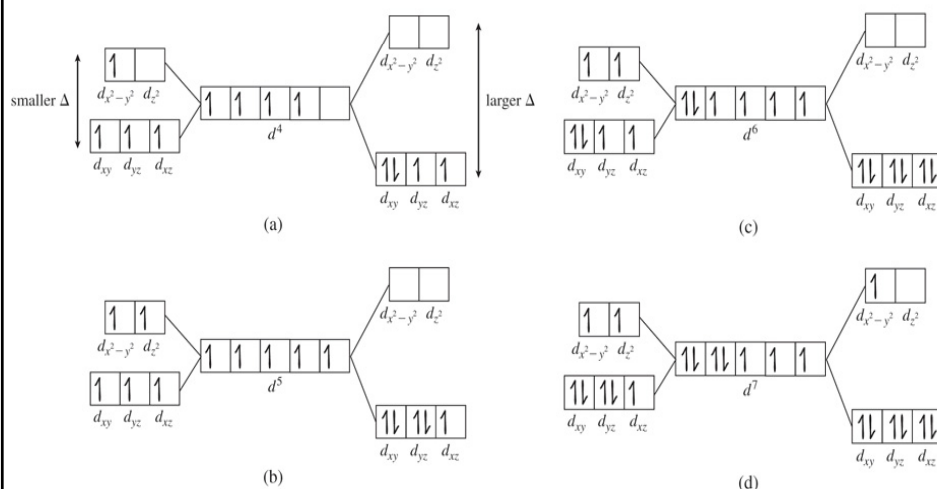


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Orbital Diagrams for Specific d Orbital Configurations



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Magnetic Properties

Which of the following metal ions can potentially form both low-spin and high-spin complexes? (Select all that apply.)

- a) Ti^{2+}
- b) Cu^+
- c) Fe^{2+}
- d) Ni^{2+}
- e) Cr^{3+}

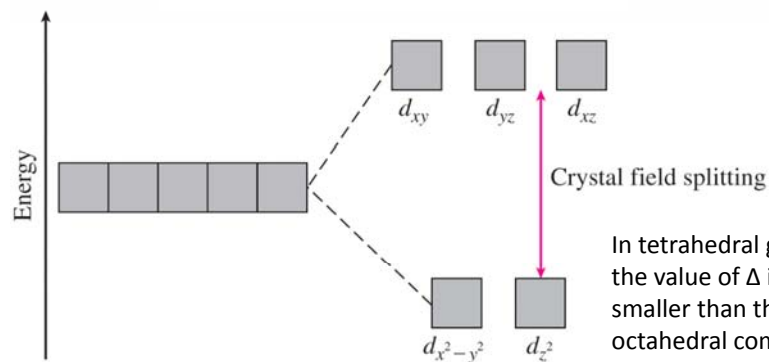
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
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Crystal Field Splitting with a Tetrahedral Geometry



In tetrahedral geometry, the value of Δ is usually smaller than the case of octahedral complex ions because of the smaller effect of the ligands.

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Crystal Field Splitting with a Square-Planar Geometry

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The splitting in the square planar geometry is the most complicated. The crystal field splitting can not be defined here because more than one energy level are involved.

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Reactions of Coordination Compounds

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- Complex ions undergo **ligand exchange** (or *substitution*) reactions in solution.

A ligand exchange reaction is a reaction in which one ligand (or more) in a complex ion is replaced by a different one (or more).

- Example: Exchange of NH_3 with H_2O

$$[\text{Co}(\text{NH}_3)_6]^{3+} + 6\text{H}^+ + 6\text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{3+} + 6\text{NH}_4^+$$

K_f of $[\text{Co}(\text{H}_2\text{O})_6]^{3+} = 1 \times 10^{20}$

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Reactions of Coordination Compounds

- Rates of exchange reactions vary widely.
- Exchange reactions are characterized by:
 - **Thermodynamic stability** – measured by K_f
 - Large K_f values indicate stability.
 - Small K_f values indicate instability.
 - Thermodynamically stable complexes can be labile or inert. Same is said for thermodynamically unstable complexes.
 - **Kinetic lability** – tendency to react.
 - *Labile* complexes undergo *rapid* exchange.
 - *Inert* complexes undergo *slow* exchange.

Review Questions

The formula of the complex compound potassium diamminetetrabromocobaltate(III) is :

- A) $K [Co (NH_3)_2 Br]_4$
- B) $K_2 [Co (NH_3)_2 Br_4]$
- C) $K_4 [Co (NH_3)_2 Br]$
- D) $K [Co (NH_3)_2 Br_4]$

Review Questions

According to the crystal field theory, how many unpaired electrons are present in the complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$? Water molecules are weak field ligands.

- A) 1
- B) 4
- C) 2
- D) 5

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Review Questions

Which of the following compounds can show **BOTH** geometric and optical isomerisms?

- A) $[\text{Pd}(\text{NH}_3)_2 \text{Cl}_2]$
- B) $[\text{Ni}(\text{en})_3] \text{Cl}_2$
- C) $[\text{Co}(\text{en})_2 \text{Cl}_2] \text{Cl}$
- D) $[\text{Cu}(\text{NH}_3)_4] \text{Cl}_2$

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