General Chemistry I
Tutorial 10

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Outline

1. Quiz
2. Crystal Field Theory
3. Ligand Field Theory

Quiz 12.1

For the following octahedral complexes, draw a diagram of the d electron configuration and determine the number of unpaired d electrons.

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

b) $[Fe(CN)_6]^{3-}$

Quiz 12.2

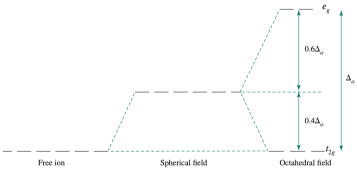
a) Why is CO a strong-field ligand?
b) Why is I^- a weak-field ligand?

Crystal Field Theory

In this theory, only **electrostatic interaction** are considered.

When L approaches M, d orbitals of M are perturbed by the electrons in L, leading to the splitting of degenerated d orbitals. When the d orbitals of a metal ion are placed in an octahedral field of ligand electron pairs, any electrons in these orbitals are repelled by the field.

As a result, the $d_{x^2-y^2}$ and d_{z^2} orbitals, which have e_g symmetry, are directed at the surrounding ligands and are raised in energy. The d_{xy}, d_{xz}, and d_{yz} orbitals (t_{2g} symmetry), directed between the ligands, are relatively unaffected by the field.



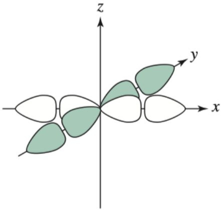
Some of phenomenons cannot be explained by CFT: Why CO and CN^- always lead to large orbital splitting? Why NH_3 leads to larger orbital splitting compared to halogen?

Ligand Field Theory(in octahedral symmetry)

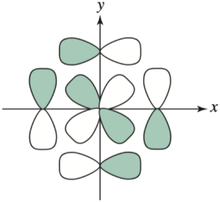
Ligand Field Theory(LFT) is based on **molecular orbital theory**.

According to their symmetry, d orbitals can be divided into 2 groups.

Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital

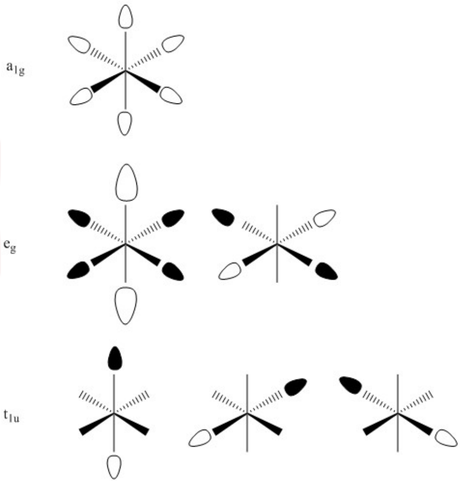


Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

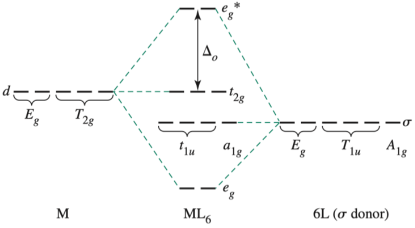


Pi bonding interaction between four ligand orbitals and metal d_{xy} orbital

Ligand Group Orbitals



Only d Orbitals 😋



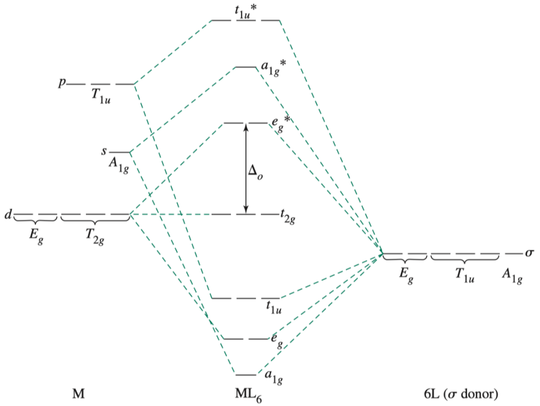
Remark 3.1

As σ orbitals are of lower energy, electrons of central metals are located in t_{2g} and $e_g{}^*$ orbitals. (T stands for triply degenerate and E stands for doubly degenerate)

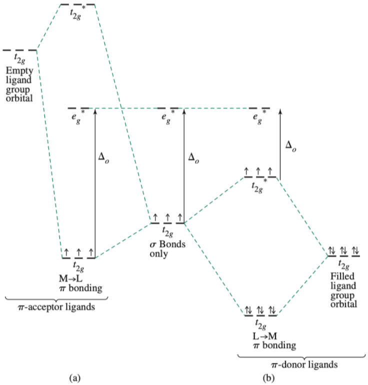
Remark 3.2

Stronger σ donors lead to larger orbital splitting.

s and p Orbitals Included 🤔



π Donor and Acceptor 😅



Remark 3.3

π ***donor*** *leads to* ***smaller*** Δ_o *and* π ***acceptor*** *leads to* ***larger*** Δ_o.

Trends in Orbital Splitting 🥲

Remark 3.4

In 6 coordinated complexes (octahedral), trends in orbital splitting are here as follows:

$$\pi \text{ acceptor} > \sigma \text{ donor} > \pi \text{ donor}$$

$$CO, CN^- > NO_2{}^- > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$$

You guys don't need to memorize but just comprehend.