



# **CHEM F111 : General Chemistry**

## **Semester II: AY 2017-18**

Lecture-24, 19-03-2018

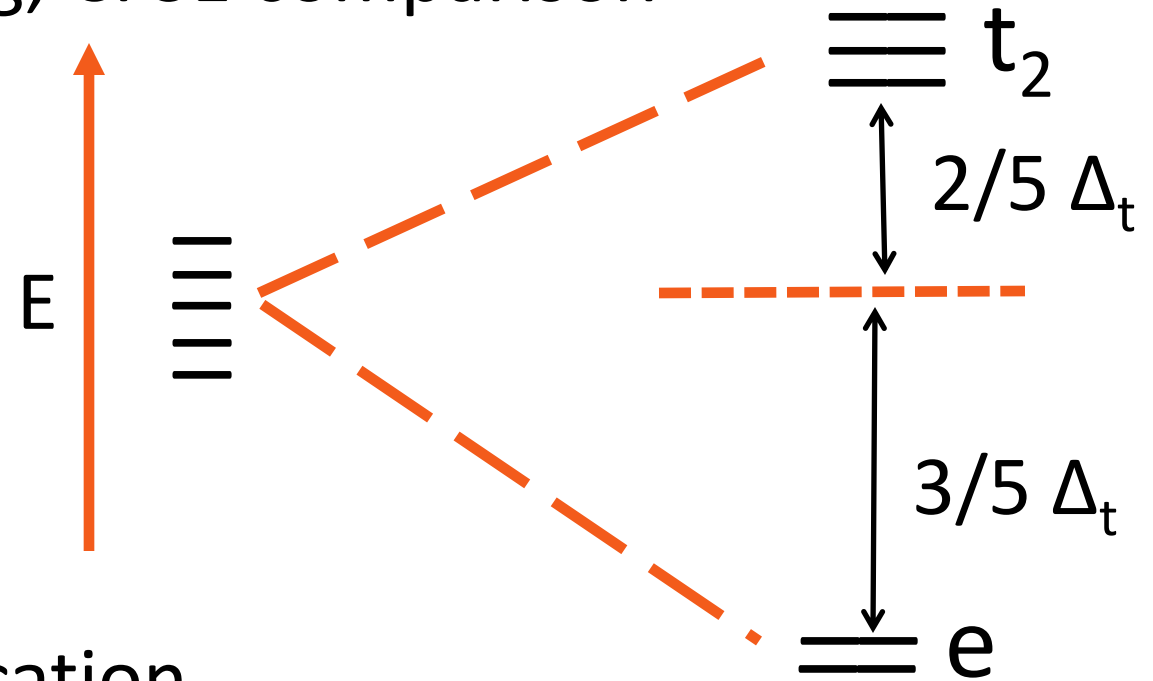
Mid semester copy distribution will be on 20/03/2018.

For room number and section wise details please check the notice in Nalanda.

# Summary of lecture 23



- ✓ Octahedral vs. tetrahedral splitting, CFSE comparison



- ✓ Crystal structure of spinel identification

In normal Spinel:  $(A^{2+}[B_2^{3+}]O_4^{2-})$ , In Inverse Spinel:  $(B^{3+}[A^{2+}B^{3+}]O_4^{2-})$

# Summary of lecture 23



## Explanation of Crystal Structure of Spinel using CFT:

Spinel,  $AB_2O_4$ : A(II); B(III);  $O^{2-}$

In normal Spinel:  $(A^{2+}[B_2^{3+}]O_4^{2-})$

A(II) occupy the tetrahedral sites

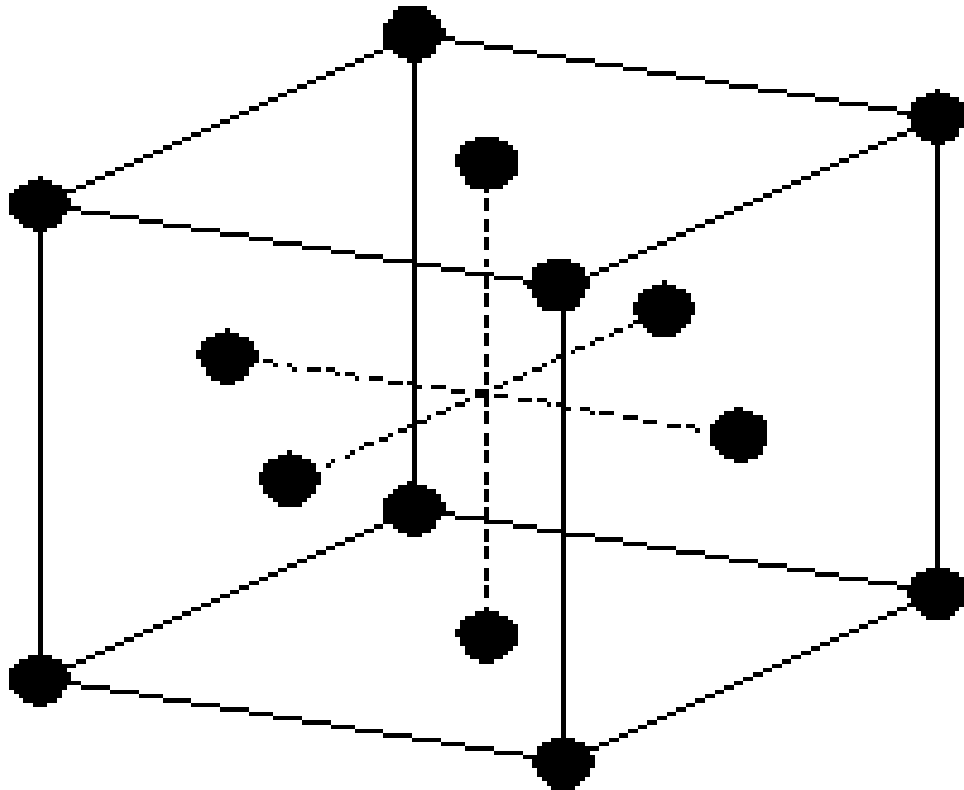
B(III) occupy the octahedral sites

In Inverse Spinel:  $(B^{3+}[A^{2+}B^{3+}]O_4^{2-})$

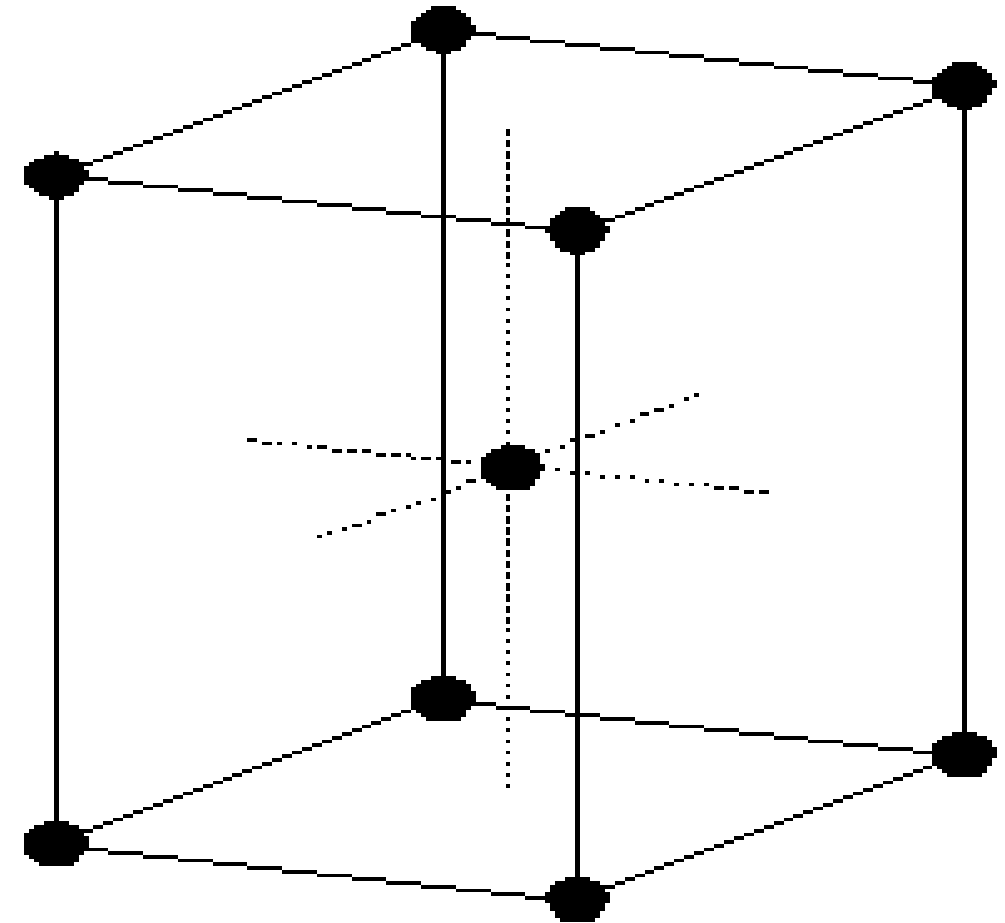
A(II) occupy the Octahedral sites

B(III) occupy the Octahedral and Tetrahedral sites

# Tetragonal distortion



z



Cube with an octahedron inside

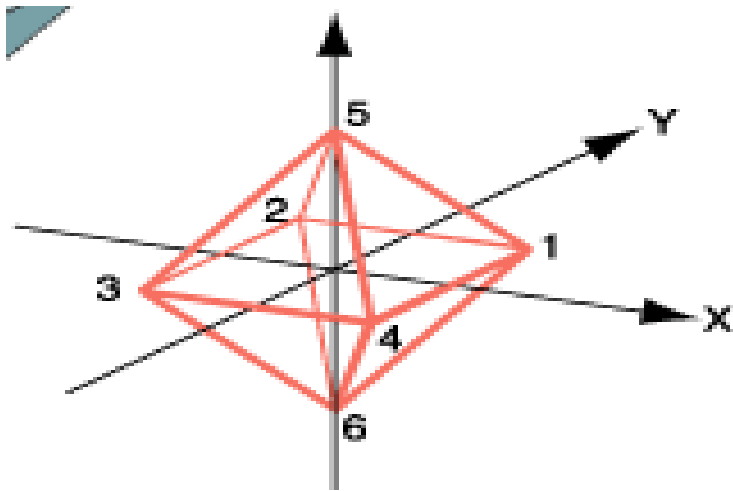
Tetragonal system

# Stability of a complex



Structure of coordination compounds are determined by **two factors**

- 1) Valence Shell Electron Pair Repulsions. These have to be minimized for a stable structure.
- 2) Repulsions between non-bonding d-electrons of the metal and the ligand electrons. These have also to be minimized.



1. All the six bond pairs are placed at similar positions then we get a regular octahedron (All bond lengths are same).

2. If the d-electrons in the metal are symmetrically placed w.r.t. an octahedral field.

# Distortion of Oh complexes



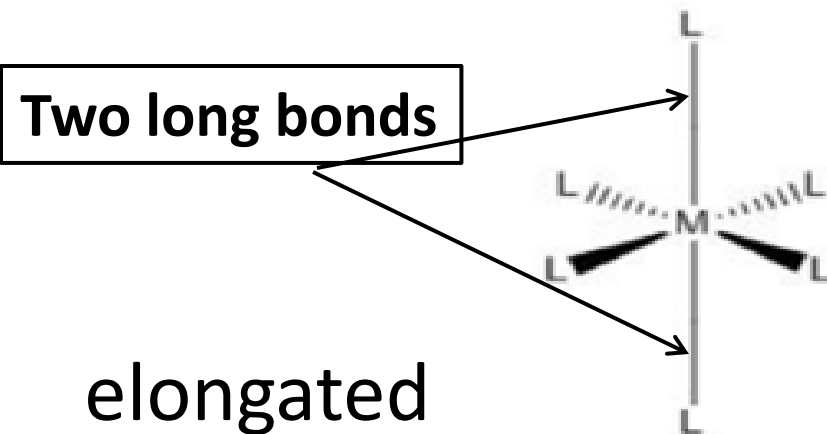
- The six-coordinated complexes in which all the six distances between the ligand electron clouds and central metal ion are the same are said to be **regular** (i.e., symmetrical) octahedral complexes.
- On the other hand, the six-coordinated complexes in which the distances are not equal are said to be **distorted** octahedral complexes.
- Since their shape is changed (i.e., distorted) **this is called distortion**

# Distortion: tetragonal elongation



Tetragonal complexes may be obtained by any of the following two ways:

- (a) If the two trans ligands lying on the z-axis in an octahedron are moved away from the central metal cation so that their distance from the metal cation is slightly greater than it is for the other four ligands lying in the xy plane, we get a tetragonal structure.



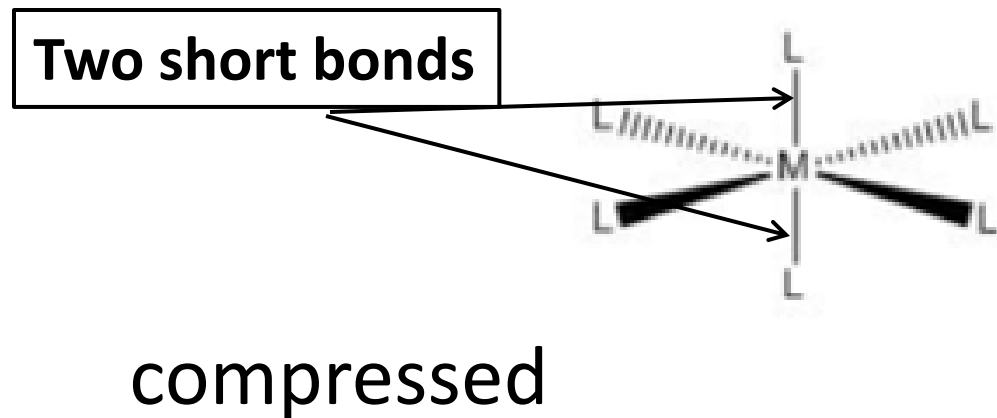
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  has a natural distortion due to different kinds of bonding (Cu-N and Cu-O)



# Distortion: tetragonal compression



(b) If the two trans ligands located at the z-axis are brought near the central metal cation so that their distance from the metal cation is **smaller** than it is for the other four ligands in the **xy plane**, we again get a **tetragonal structure**.



$\text{K}_4\text{CuF}_6$ : the  $\text{Cu}^{2+}$  ion has two  $\text{F}^-$  at 1.95 Å and four at 2.08 Å

$\text{FeF}_6^{4-}$ : the  $\text{Fe}^{2+}$  ion has two  $\text{F}^-$  at 1.99 Å and four at 3.12 Å

# Symmetrical electronic arrangements



Electronic configuration	$t_{2g}$	$e_g$	Nature of ligand field	Examples
$d^0$	<div><div></div><div></div><div></div></div>	<div><div></div><div></div></div>	Strong or weak	$\text{TiO}_2$ , $[\text{TiF}_6]^{2-}$
$d^3$	<div><div>↑</div><div>↑</div><div>↑</div></div>	<div><div></div><div></div></div>	Strong or weak	$[\text{Cr}(\text{oxalate})_3]^{3-}$ , $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
$d^5$	<div><div>↑</div><div>↑</div><div>↑</div></div>	<div><div>↑</div><div>↑</div></div>	Weak	$[\text{MnF}_6]^{4-}$ , $[\text{FeF}_6]^{3-}$
$d^6$	<div><div>↑↓</div><div>↑↓</div><div>↑↓</div></div>	<div><div></div><div></div></div>	Strong	$[\text{Fe}(\text{CN})_6]^{4-}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$
$d^8$	<div><div>↑↓</div><div>↑↓</div><div>↑↓</div></div>	<div><div>↑</div><div>↑</div></div>	Weak	$[\text{NiF}_6]^{4-}$ , $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
$d^{10}$	<div><div>↑↓</div><div>↑↓</div><div>↑↓</div></div>	<div><div>↑↓</div><div>↑↓</div></div>	Strong or weak	$[\text{Zn}(\text{NH}_3)_6]^{2+}$ , $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

# Asymmetrical electronic arrangements



Electronic configuration	t <sub>2g</sub>	e <sub>g</sub>	Nature of ligand field	Examples					
d <sup>1</sup>	<table><tr><td>↑</td><td></td><td></td></tr></table>	↑			<table><tr><td></td><td></td></tr></table>			HS or LS	
↑									
d <sup>2</sup>	<table><tr><td>↑</td><td>↑</td><td></td></tr></table>	↑	↑		<table><tr><td></td><td></td></tr></table>			HS or LS	
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d <sup>4</sup>	<table><tr><td>↑↓</td><td>↑</td><td>↑</td></tr></table>	↑↓	↑	↑	<table><tr><td></td><td></td></tr></table>			Strong field (LS)	
↑↓	↑	↑							
d <sup>4</sup>	<table><tr><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑	↑	↑	<table><tr><td>↑</td><td></td></tr></table>	↑		Weak field (HS)	Cr(II) and Mn(III)
↑	↑	↑							
↑									
d <sup>7</sup>	<table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table>	↑↓	↑↓	↑↓	<table><tr><td>↑</td><td></td></tr></table>	↑		Strong field (LS)	Co(II) and Ni(III)
↑↓	↑↓	↑↓							
↑									
d <sup>9</sup>	<table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table>	↑↓	↑↓	↑↓	<table><tr><td>↑↓</td><td>↑</td></tr></table>	↑↓	↑	Either strong or weak	Cu(II)
↑↓	↑↓	↑↓							
↑↓	↑								

# $t_{2g}$ and $e_g$ orbital filling



Symmetrical and unsymmetrical  $t_{2g}$  and  $e_g$  orbital

The  $t_{2g}$  and  $e_g$  orbital which are empty ( $t_{2g}^0$  and  $e_g^0$ ), half-filled ( $t_{2g}^3$  and  $e_g^2$ ) or completely filled ( $t_{2g}^6$  and  $e_g^4$ ) are said to be **symmetrical orbitals**

$t_{2g}$  orbitals

- $t_{2g}^0, t_{2g}^3, t_{2g}^6$  symmetrical
- $t_{2g}^1, t_{2g}^2, t_{2g}^4$ , and  $t_{2g}^5$  unsymmetrical

$e_g$  orbitals

- $e_g^0, e_g^4$  symmetrical
- $e_g^1, e_g^3$  unsymmetrical
- $e_g^2$ 
  - Symmetrical in HS complex
  - Unsymmetrical in LS complex

# Condition for distortion



No distortion condition:  $t_{2g}$  and  $e_g$  sets as **symmetrical orbitals**

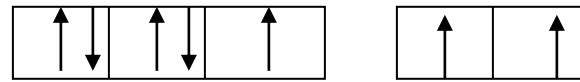
Condition for slight distortion: When d-orbitals of the central metal ion of an octahedral complex have  **$t_{2g}$  orbitals as unsymmetrical orbitals**, there occurs slight distortion in the complex

Condition for strong distortion: When the  **$e_g$  orbitals which point directly towards the ligands, are unsymmetrical** i.e., contain 1, 3, or 2 (only in LS complex) electrons, strong distortion

# Asymmetrical *d* electron distribution



$d^7$  weak field  $\longrightarrow$  unsymmetrical but the distortion is minimal

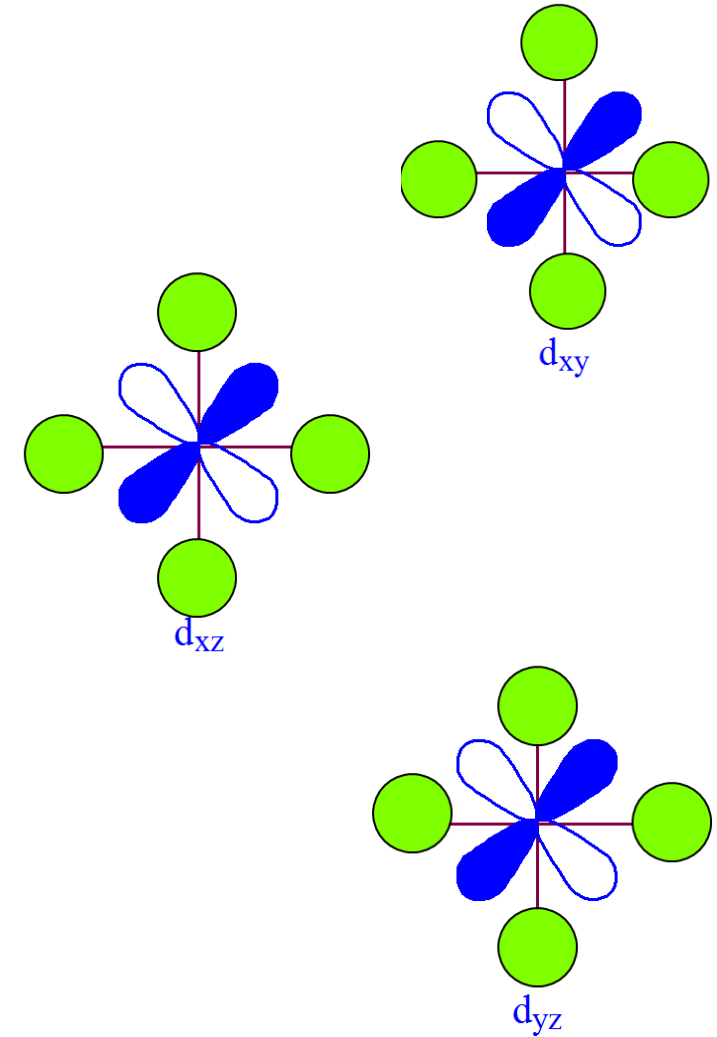
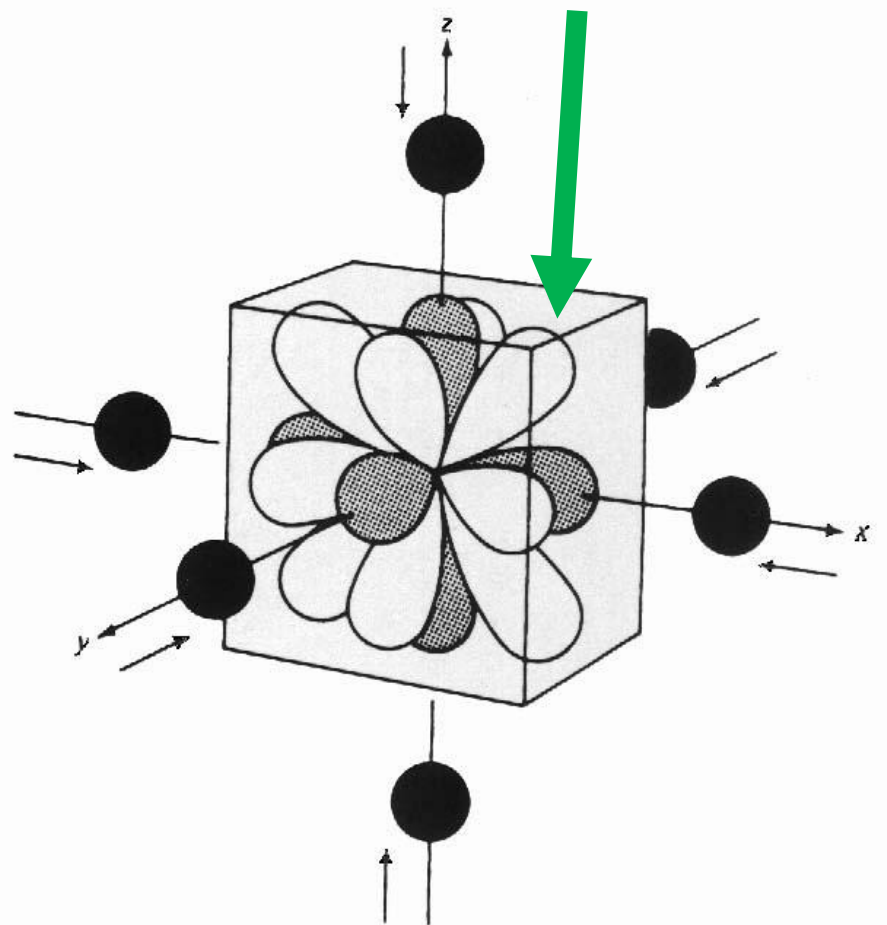
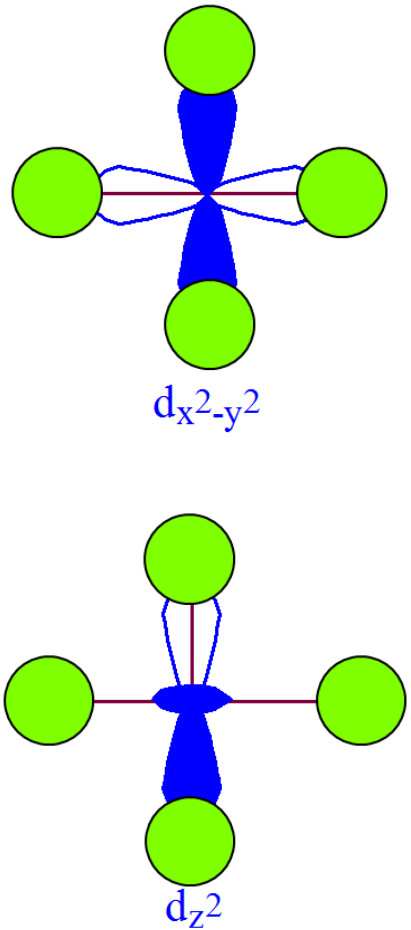


This configuration is **asymmetric** in  $t_{2g}$  but **symmetric** in  $e_g$  ; asymmetric filling in  $t_{2g}$  produces only **minimum distortion**.

This explanation is true for  $d^1$ ,  $d^2$ ,  $d^4$  (strong),  $d^5$  (strong),  $d^6$  (weak) also.

# Explanation for distortion

Consider the case  $\text{Ti}^{2+} \rightarrow d^2 \rightarrow t_{2g}^2$



# Explanation for distortion



If  $t_{2g}$  orbitals are **asymmetrically filled** then the distortion is **minimum** as these orbital point away from metal-ligand bonds.

If  $e_g$  orbitals are **asymmetrically filled** then the distortion is **large** as these orbital point directly along the metal-ligand bonds. The repulsions between different ligands will be different.



# Explanation for distortion



In a symmetrically filled case both the  $e_g$  orbitals,  $d_{x^2-y^2}$ ,  $d_{z^2}$  are both degenerate (of same energy).

However, if  $e_g$  orbitals are asymmetrically filled **the degeneracy is no longer maintained**. Then these d-electrons repel some ligands more than others and the octahedral environment **becomes distorted**. **Degeneracy of  $e_g$  orbitals is destroyed** (lifted).

# Tetragonal elongation

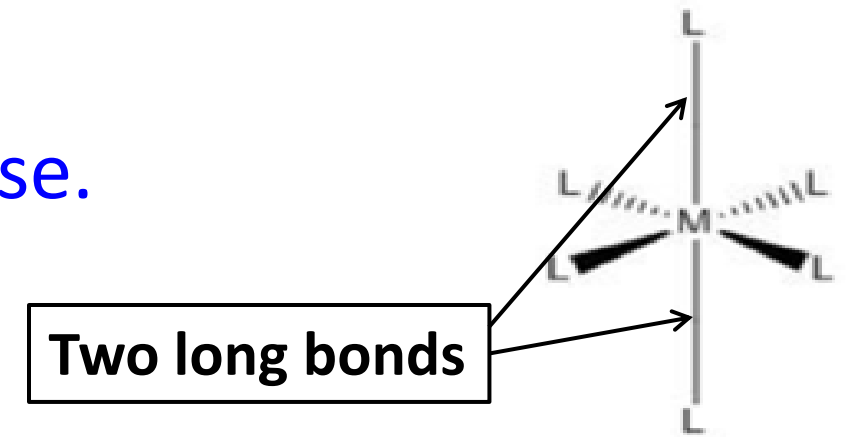


If  $d_z^2$  is filled and  $d_{x^2-y^2}$  is unoccupied (i.e.,  $d_z^2$  is in lower energy compared to  $d_{x^2-y^2}$ ), ligands which are approaching through z direction will be repelled more;

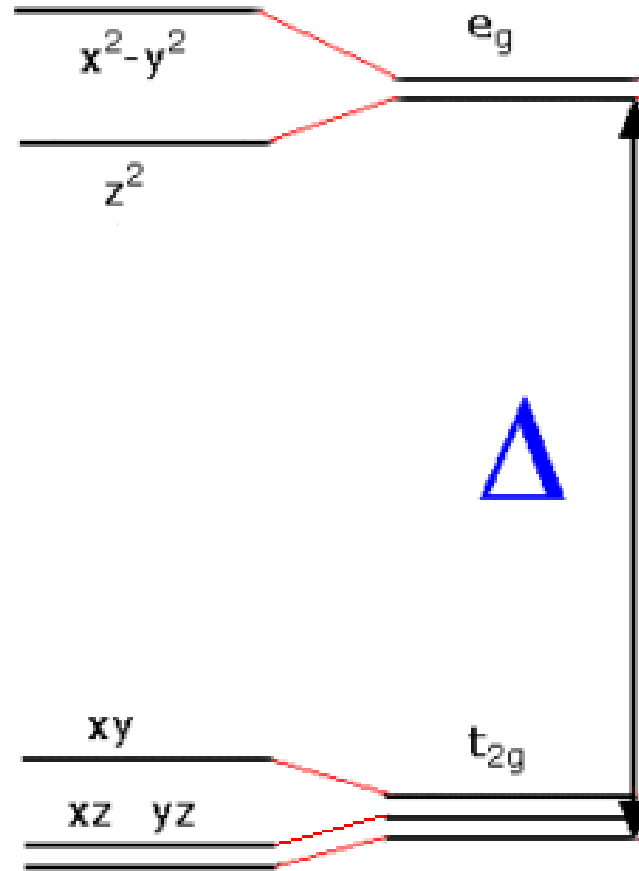
Bond lengths along +z and -z directions increase.

This leads to tetragonal elongation.

When we say  $d_z^2$  is filled similarly to a smaller extent the  $d_{xz}$  and  $d_{yz}$  will be lowered compared to  $d_{xy}$ .



# Jahn-Teller distortion



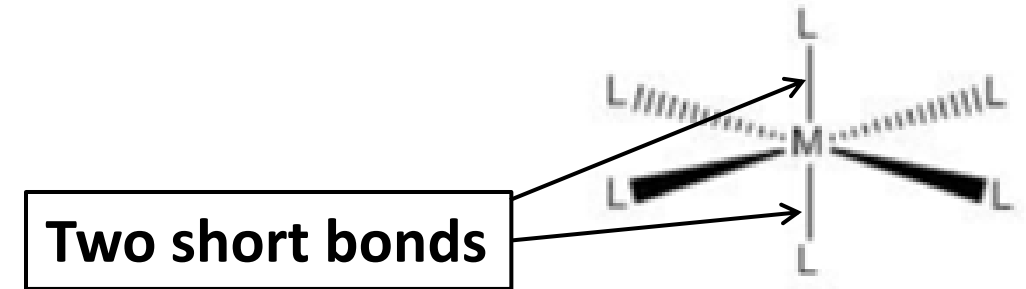
z elongation  
**2 long 4 short**

# Tetragonal compression



If  $d_{x^2-y^2}$  is filled ligands which are approaching through x, y direction will be repelled more; Bond lengths along +x, +y and -x, -y directions increase.

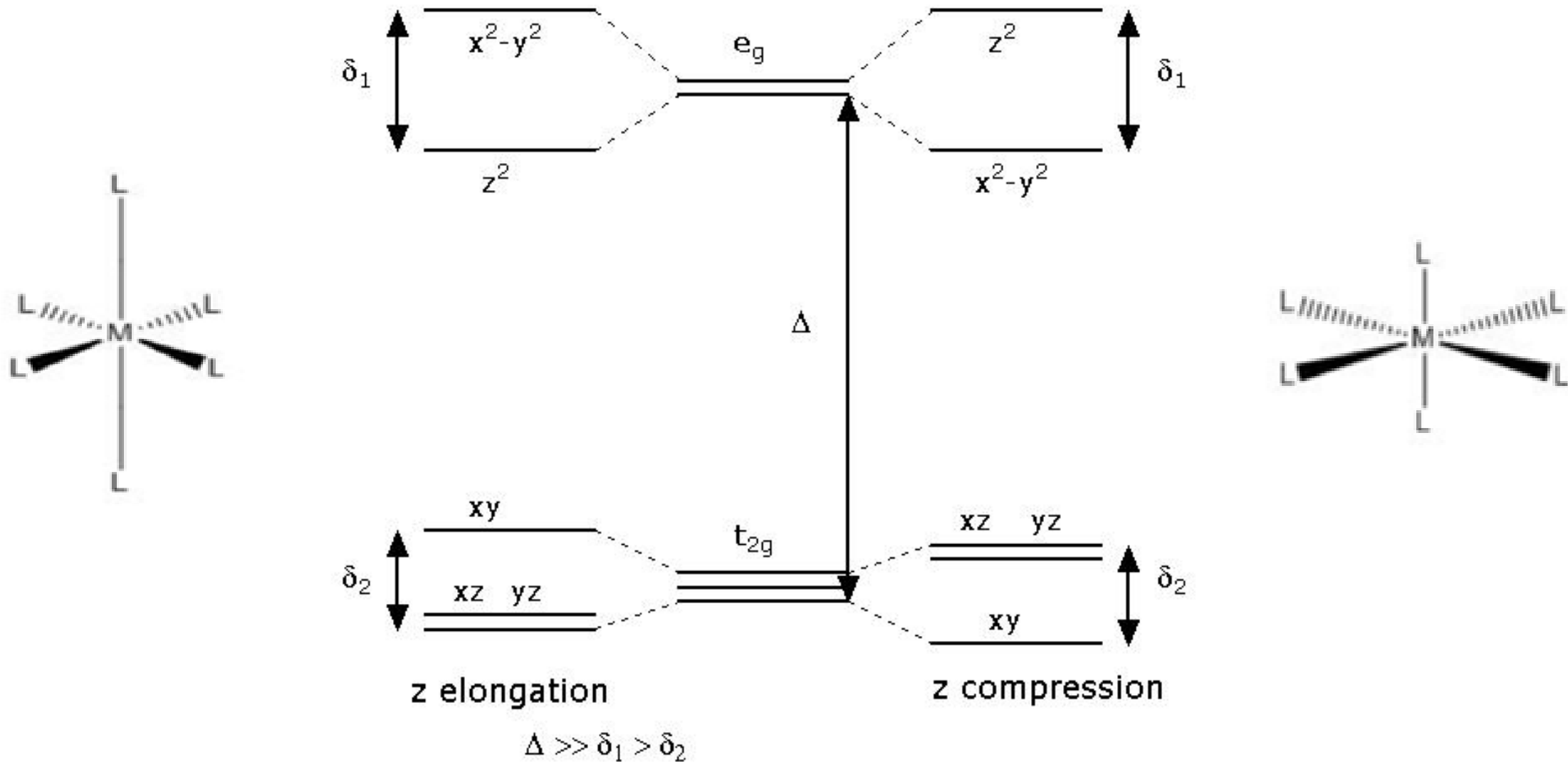
This leads to tetragonal compression.



When we say  $d_{x^2-y^2}$  is filled and  $d_z^2$  is unoccupied then it means that  $d_{x^2-y^2}$  is in lower energy compared to  $d_z^2$

Similarly to a smaller extent the  $d_{xy}$  will be lowered compared to  $d_{xz}$  and  $d_{yz}$ .

# Jahn-Teller distortion



# Discussed topics.....

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- ✓ Symmetric and asymmetric filling of  $t_{2g}$  and  $e_g$  orbitals
- ✓ Explanation for distortion
- ✓ Tetragonal elongation and compression

# Distortion of Oh complexes (supporting slide)



Distorted octahedral complexes may be of the following three types:

- (a) **Diagonally distorted octahedral complexes**, which are obtained when the distortion of a regular octahedron takes place along a two-fold axis
- (b) **Trigonally distorted octahedral complexes** in which the distortion takes place along a three-fold axis
- (c) **Tetragonally distorted octahedral complexes**, which are also known as **tetragonal complexes**. These are obtained when the distortion of a regular octahedron takes place along a four fold axis