CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-25, 21-03-2018

Summary of lecture 24

✓ Symmetrical and asymmetrical electron arrangement in t_{2g} and e_g orbital

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

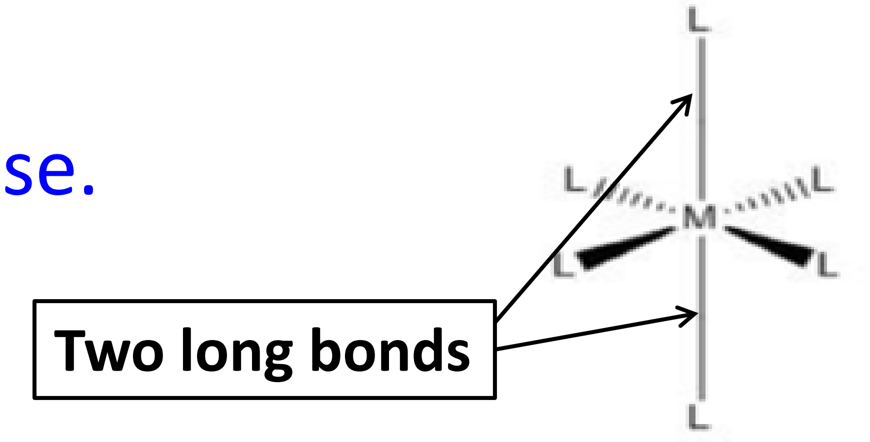
✓ Tetragonal elongation and compression

Summary of lecture 24

If d_{z^2} is filled and $d_{x^2-y^2}$ is unoccupied (i.e., dz^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 <u>tetragonal elongation</u>.

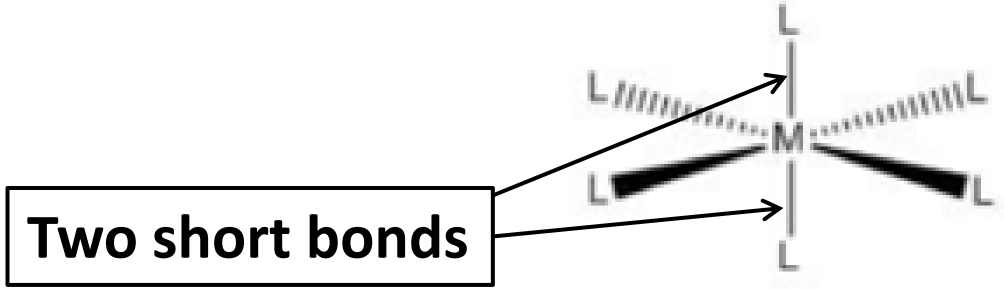


When we say d_{z^2} is filled similarly <u>to a smaller extent the d_{xz} and d_{yz} will be lowered compared to d_{xy}</u>.

Summary of lecture 24

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.

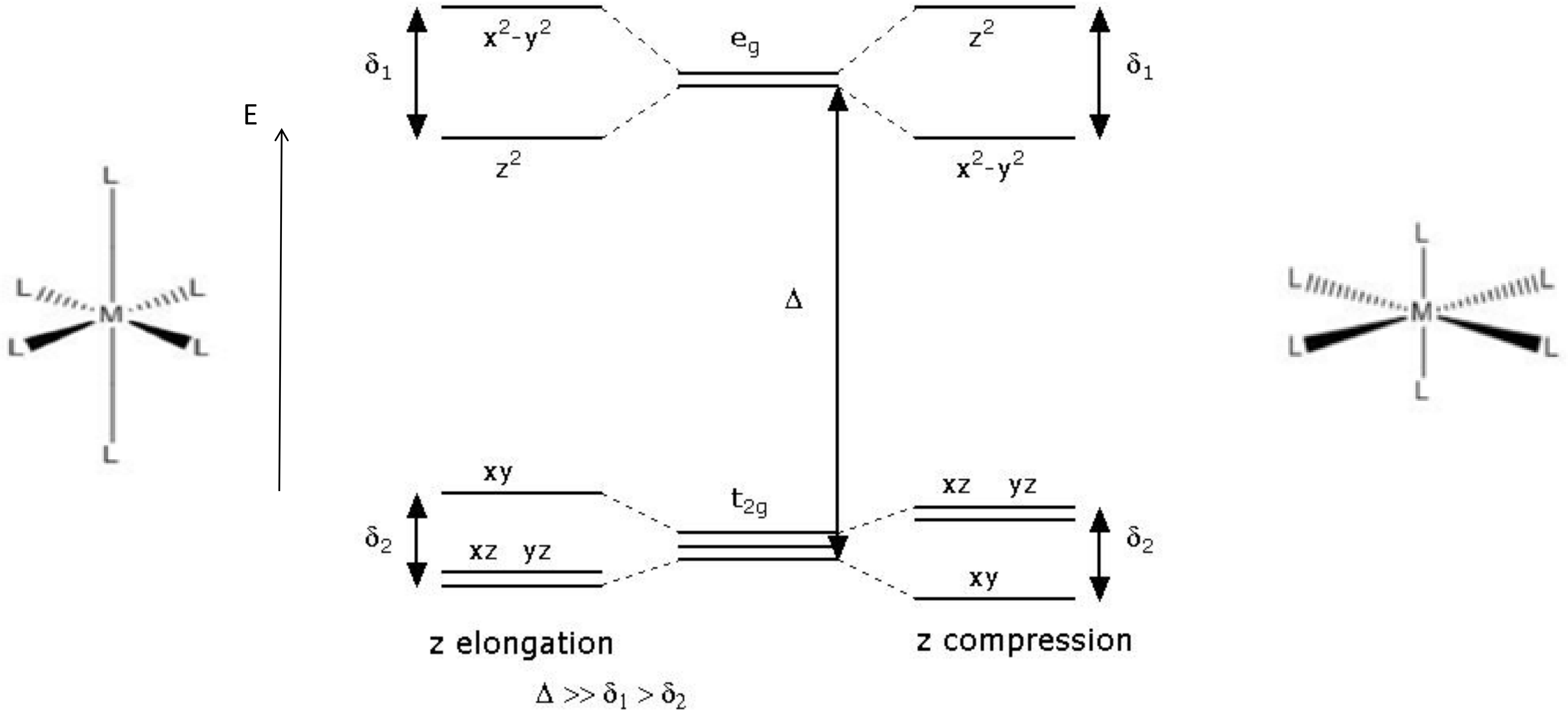
This leads to <u>tetragonal compression</u>.



When we say is $d_{x^2-y^2}$ 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 <u>d_{xy} will be lowered compared to d_{xz} and d_{yz}</u>.

Summary of lecture 24



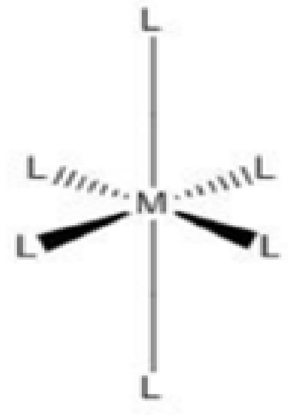
Symmetrically filled orbitals

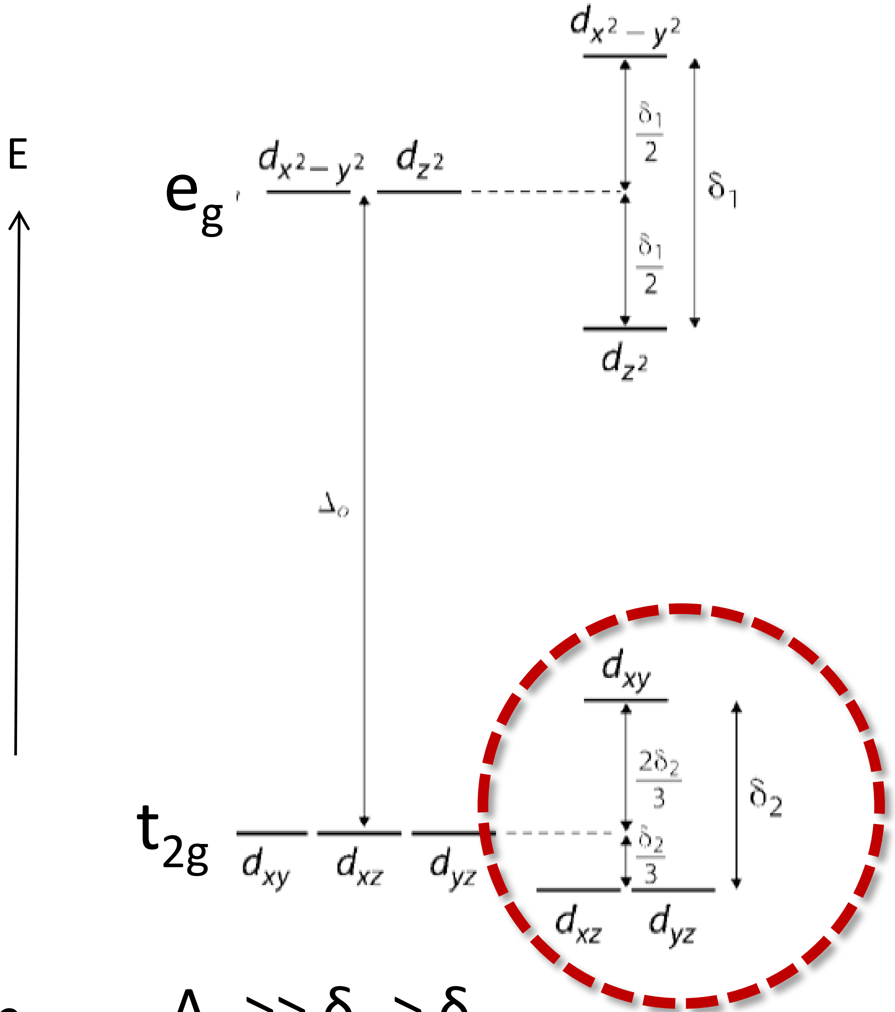
The e_g and t_{2g} splitting are similar to octahedral splitting

i.e., Consider the t_{2g} splitting in compression; The d_{xy} orbital is lowered by $2/3\delta_2$ w.r.t. original t_{2g} position and correspondingly the two orbitals d_{yz} and d_{xz} are raised by $1/3\ \delta_2$

Therefore for symmetric distribution no additional stability arises.

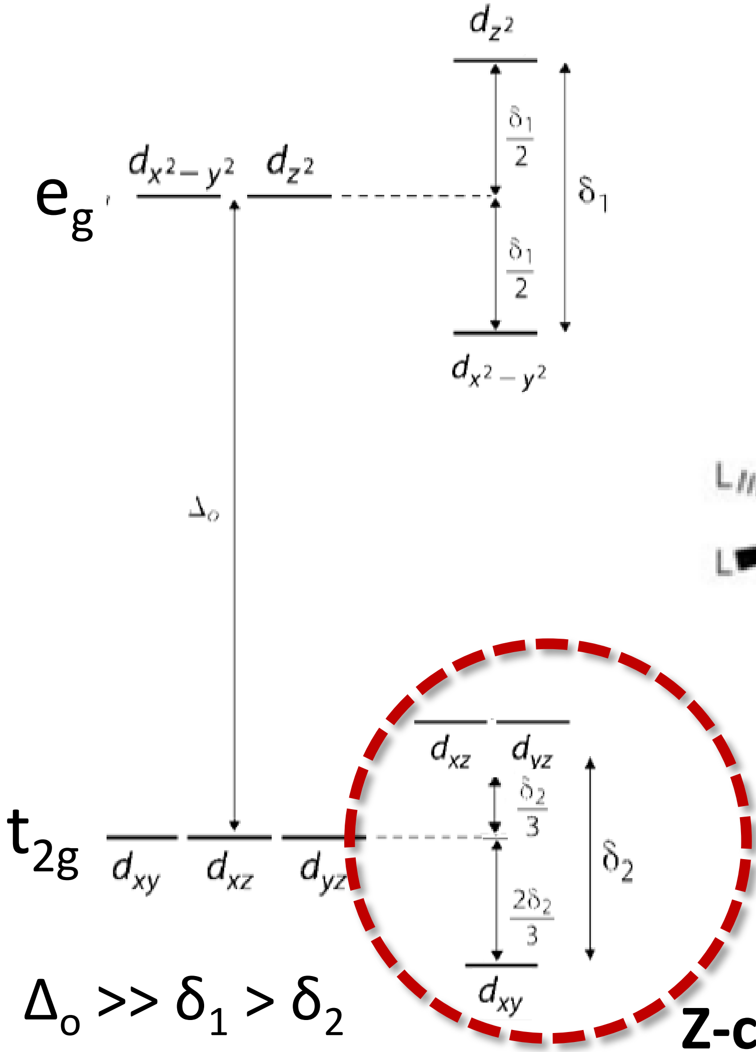
Symmetrically filled orbitals

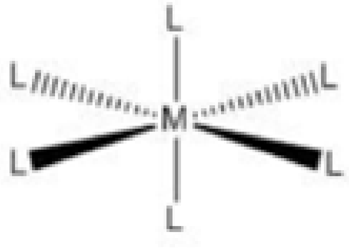




Z-elongation

$\Delta_o >> \delta_1 > \delta_2$





$\Delta_o >> \delta_1 > \delta_2$

Z-compression

Jahn-Teller theorem

In 1937, Jahn-Teller theorem explain why certain six-coordinated complexes undergo distortion to assume distorted octahedral (i.e., tetragonal) geometry.

This theorem states that “any non-linear molecular system possessing degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy and thus will remove degeneracy”.

NB: Jahn-Teller theorem only predicts the occurrence of a distortion; it <u>does not predict its nature or its magnitude</u>.

Asymmetrically filled orbitals

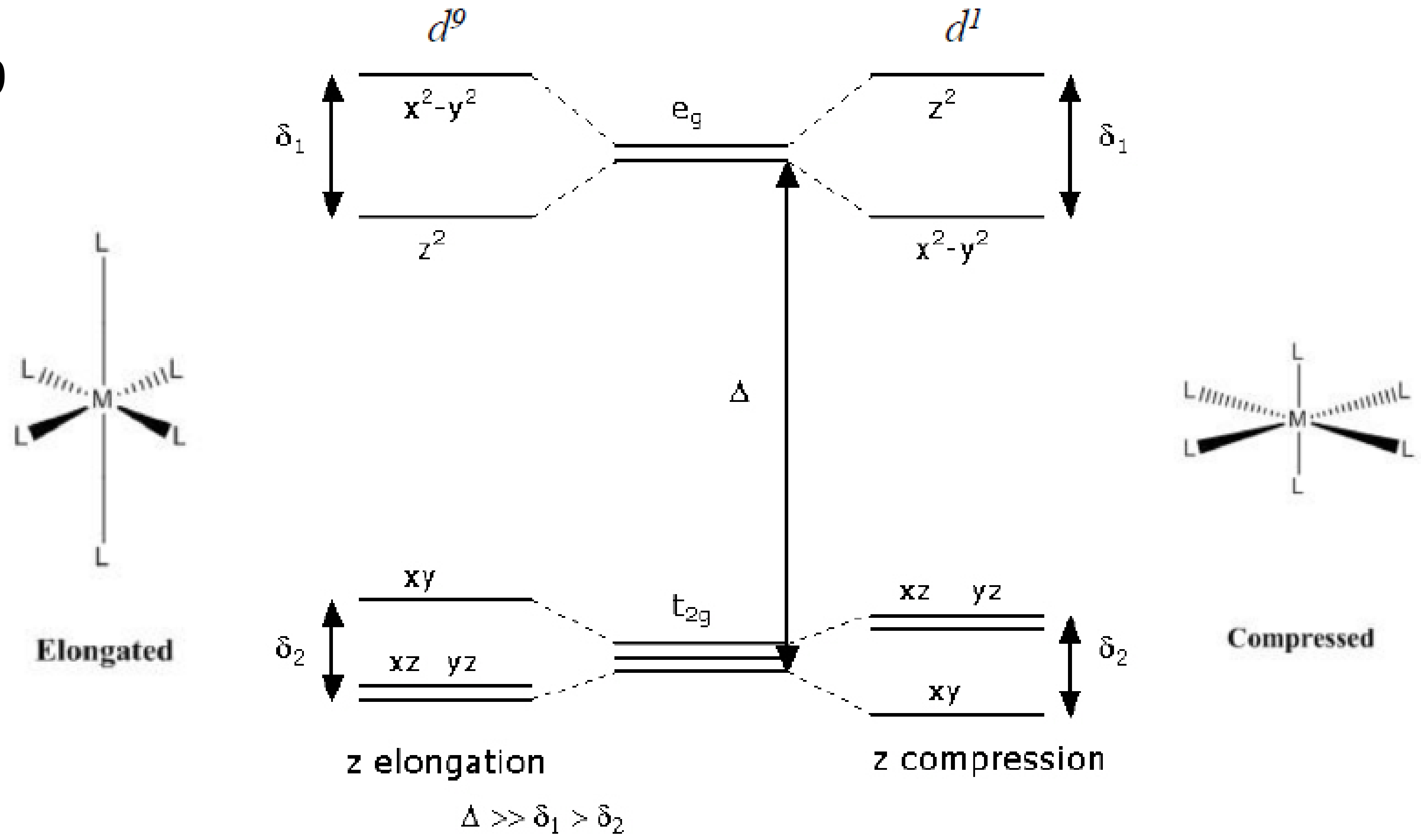
Unsymmetrical in e_g: Will it be Elongation or Compression

Which orbital will come down and how much will be the splitting is not given by the theorem.

In general electron in d_{z^2} has the repulsion only from two ligands whereas $d_{x^2-y^2}$ electrons have repulsion from 4 ligands. Hence in many cases d_{z^2} is filled and has lower energy than $d_{x^2-y^2}$ orbital.

Tetragonal elongation

d^1 vs. d^9



Distortions are more pronounced if the degeneracy occurs in an e_g orbital

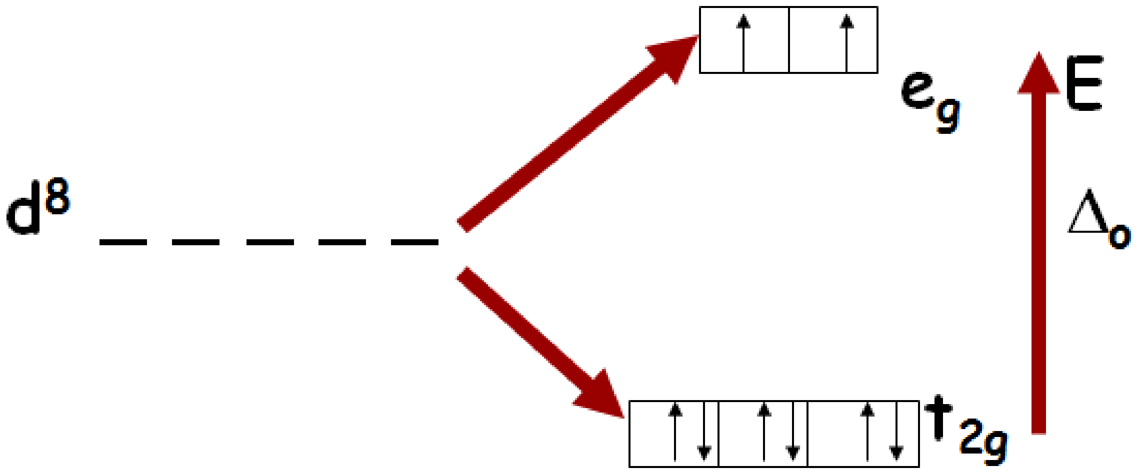
More example

Examples: $[Ni(H_2O)_6]^{2+}$; $[Ni(NH_3)_6]^{2+}$

Regular Octahedron ?

Yes ; d^8 No Jahn-Teller distortions

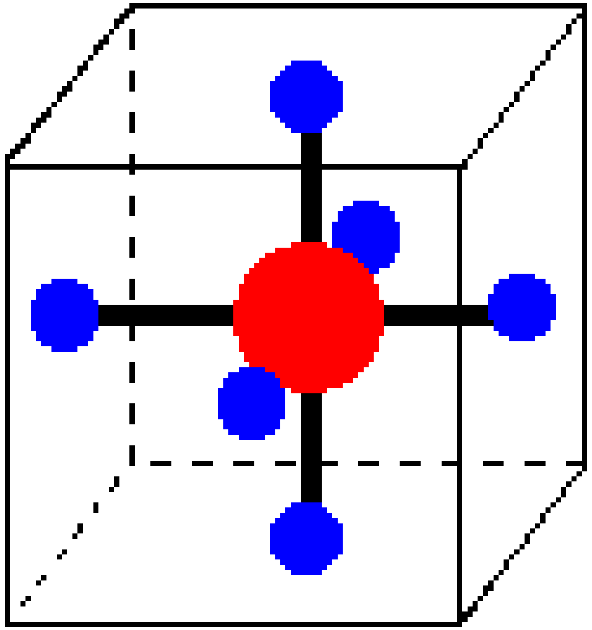
d^8 configuration in a strong/weak field is $t_{2g}^6 e_g^2$



Another example

Example: $[MnF_6]^{4-}$

Regular Octahedron



Jahn-Teller theorem is more important in $[Cu(H_2O)_6]^{2+}$ than in $[Cu(NH_3)_4(H_2O)_2]^{2+}$

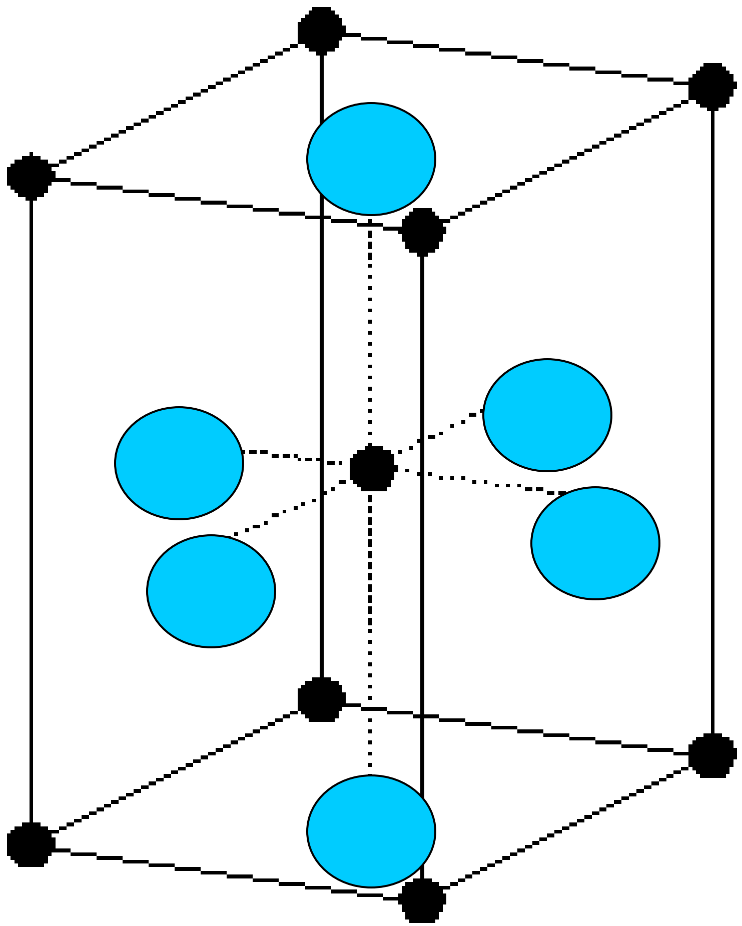
$[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a natural distortion due to different kinds of bondings. (Cu-N and Cu-O)

Another example

Example: $[Cu(H_2O)_6]^{2+}$

Regular Octahedron?

No ; d^9 Jahn-Teller distortion

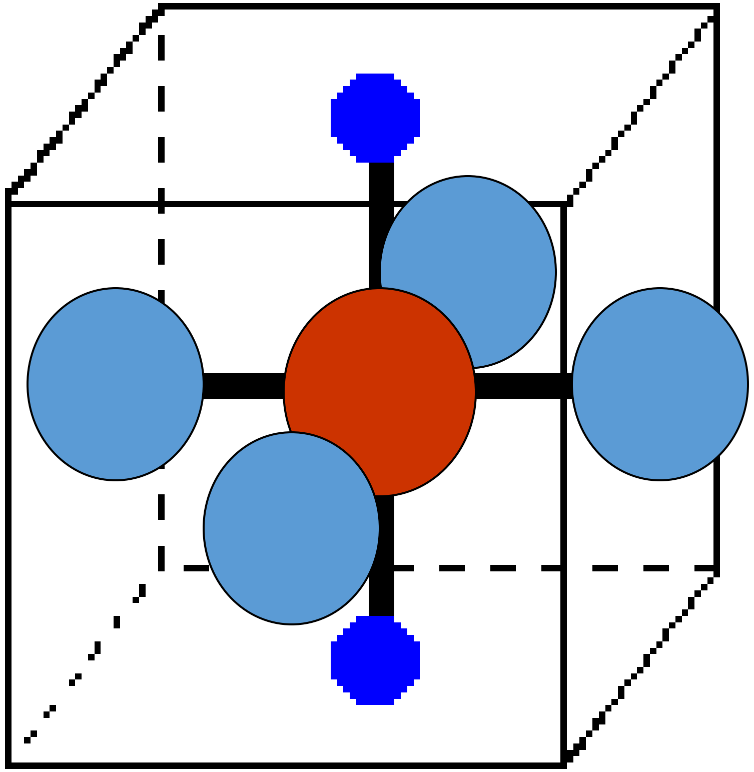


Tetragonal system

Another example

Natural distortion due to different kinds of bondings: No Jahn-Teller Distortion

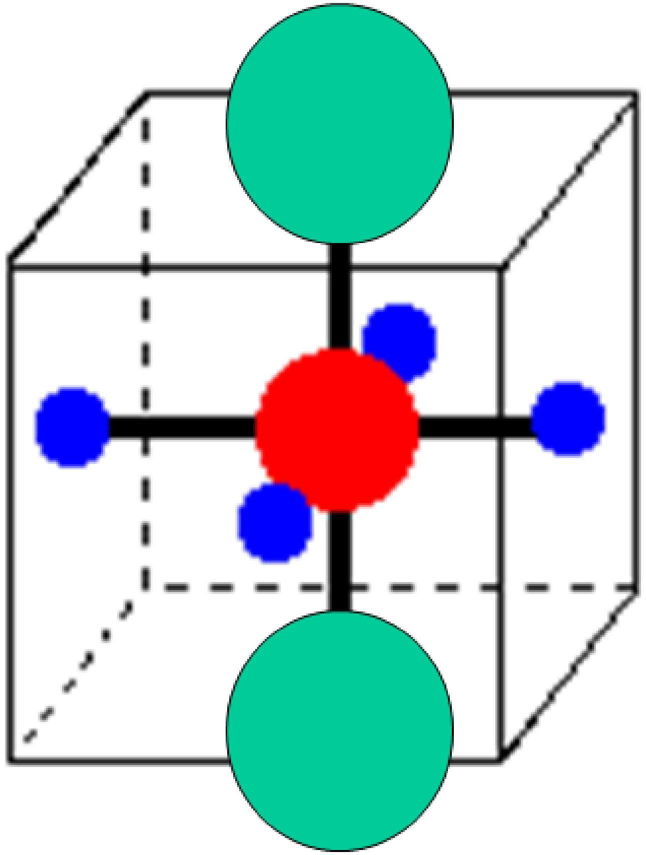
Example: $[MnF_2Cl_4]^{4-}$



Compression along z -axis

Example: $[MnF_4Cl_2]^{4-}$

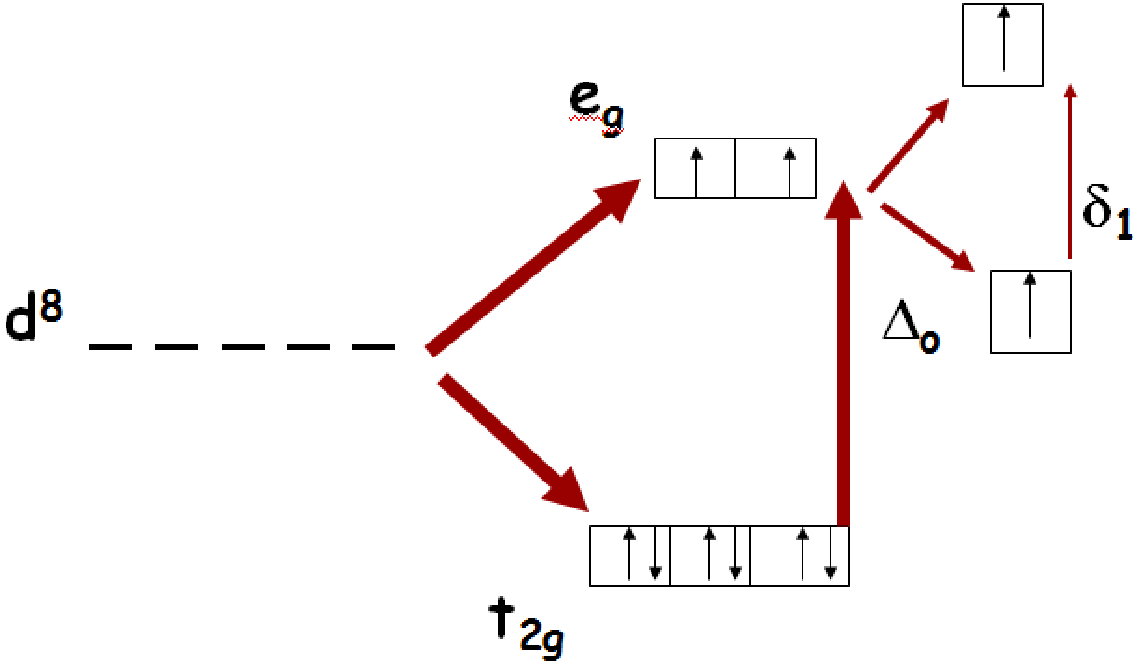
Elongation along z -axis



d^8 system

Consider back $[Ni(H_2O)_6]^{2+}$

d^8 system; even assuming the splitting of e_g level, there is no loss or gain of stability; as if e_g is intact or degenerate



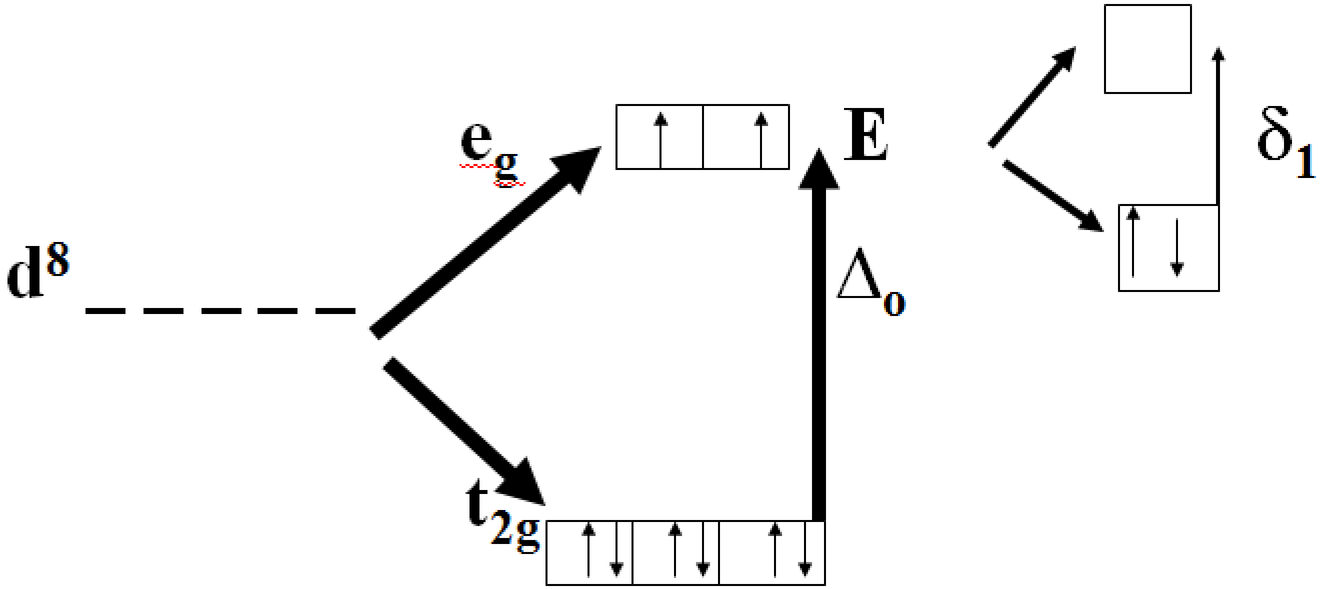
This is due to pairing energy > δ_1

d^8 system

Attempts to make $[Ni(CN)_6]^{4-}$ always yield $[Ni(CN)_4]^{2-}$

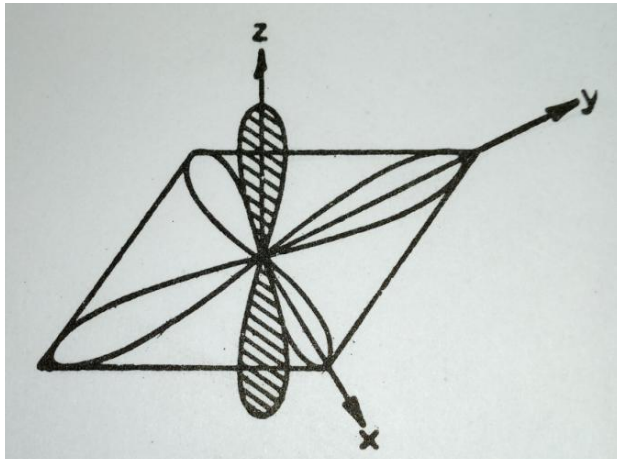
Here Δ_o is large and hence δ_1 is large and more than the pairing energy

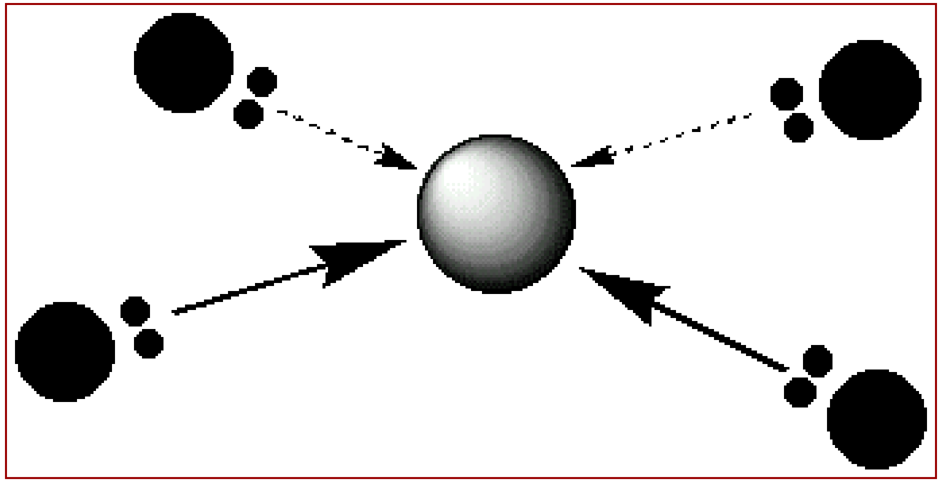
The e_g orbital which is occupied is d_{z^2}



d^8 square planar system

1) In this case there is no unpaired electron; diamagnetic.
2) d_{z^2} orbital is fully occupied whereas $d_{x^2-y^2}$ orbital is completely free.
3) Ligands approach only through the x,y directions and z direction is free of ligands due to high repulsion.
4) This gives rise to
   Square planar configurations.





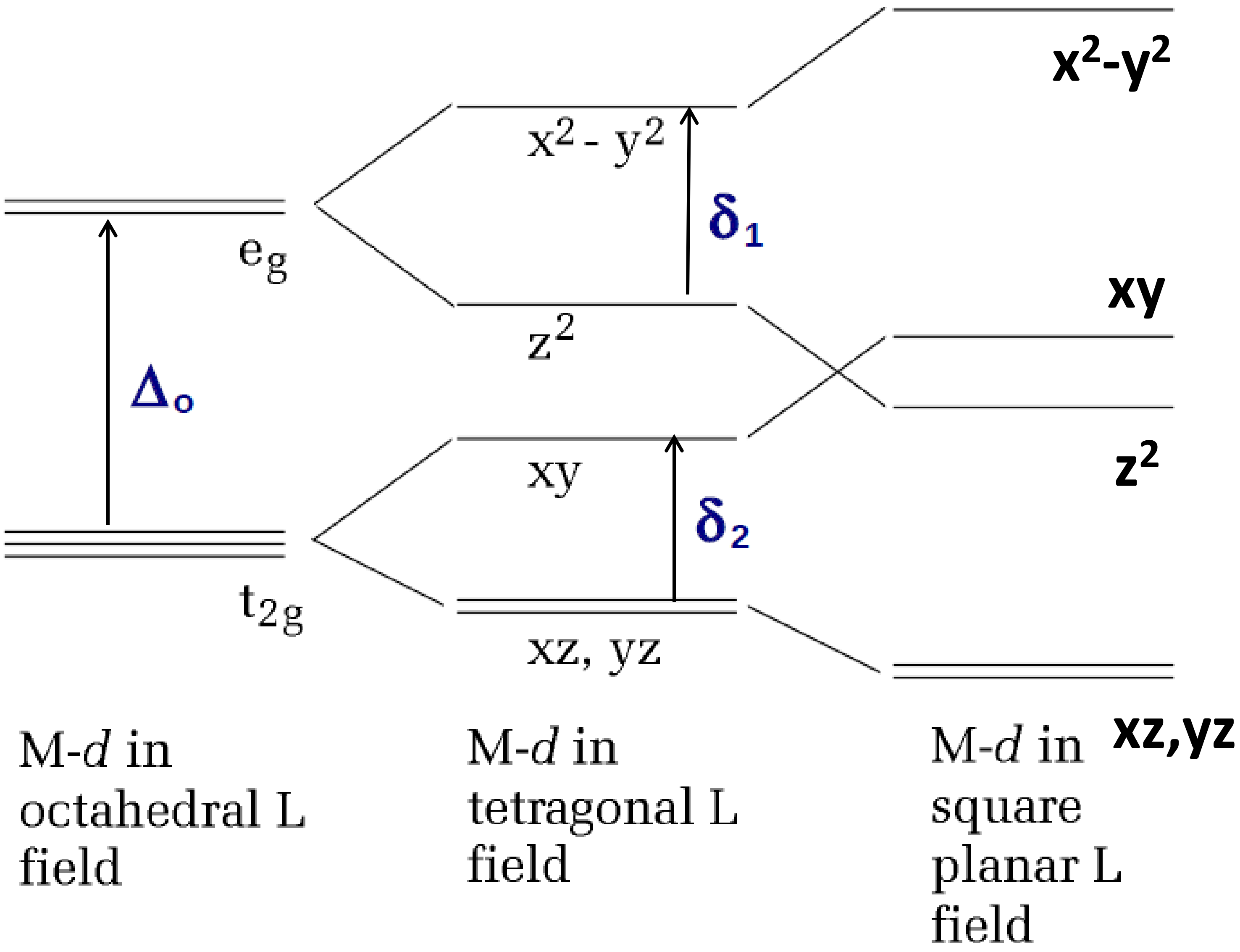
d^8 square planar system

5) δ_1 is large in $[Ni(CN)_4]^{2-}$ due to CN^-

6) δ_1 is large in Pt^{2+}, Pd^{2+} (d^8) systems due to size of metal ion. Most of the complexes of these metal ions are square planar in nature even with weak ligands.

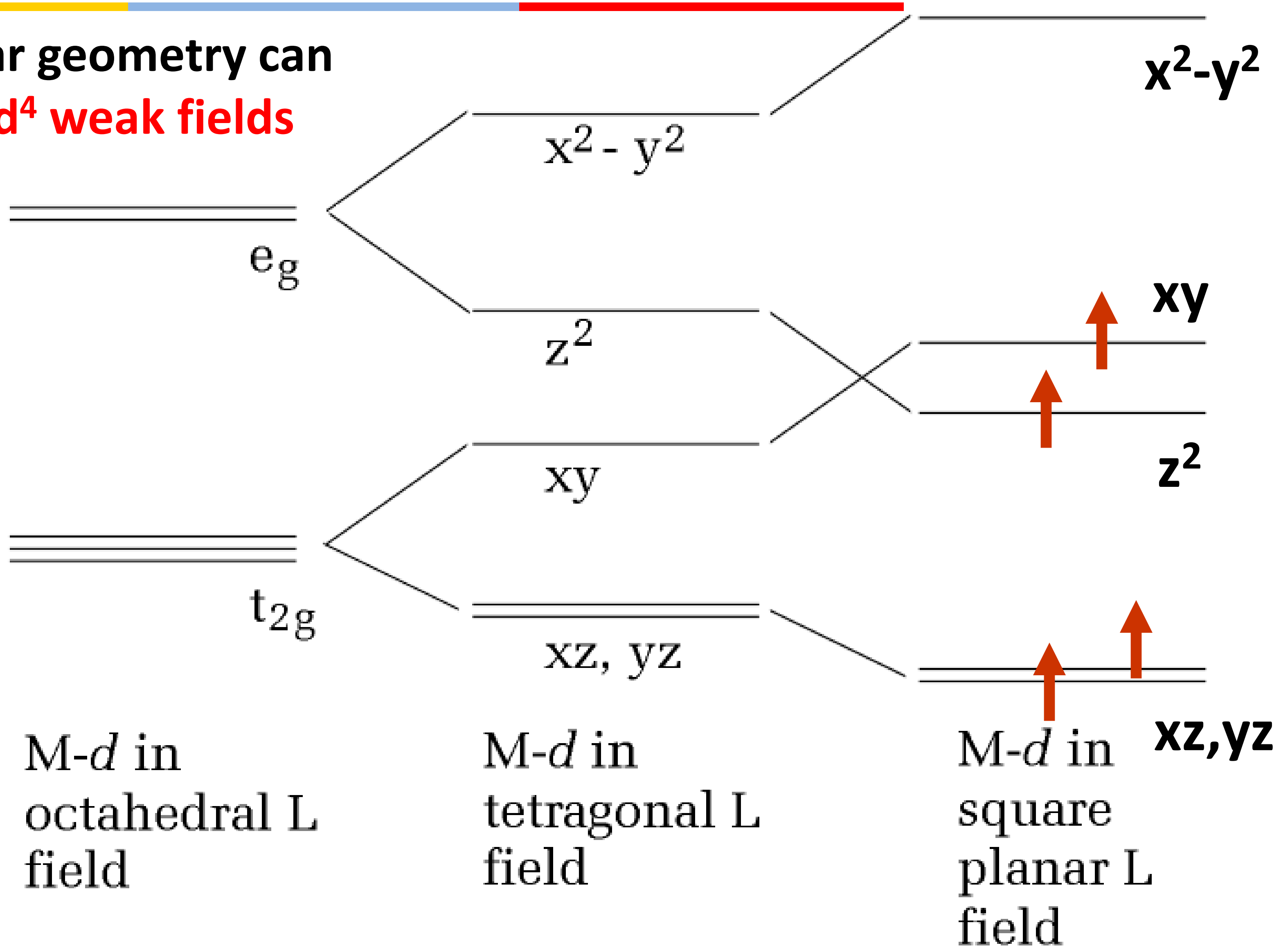
7) Square planar complexes can thus be assumed to be the extreme case of tetragonal elongation of octahedron. Two of the octahedral ligands are at infinite distance from the center of the octahedron.

Square planar energy level

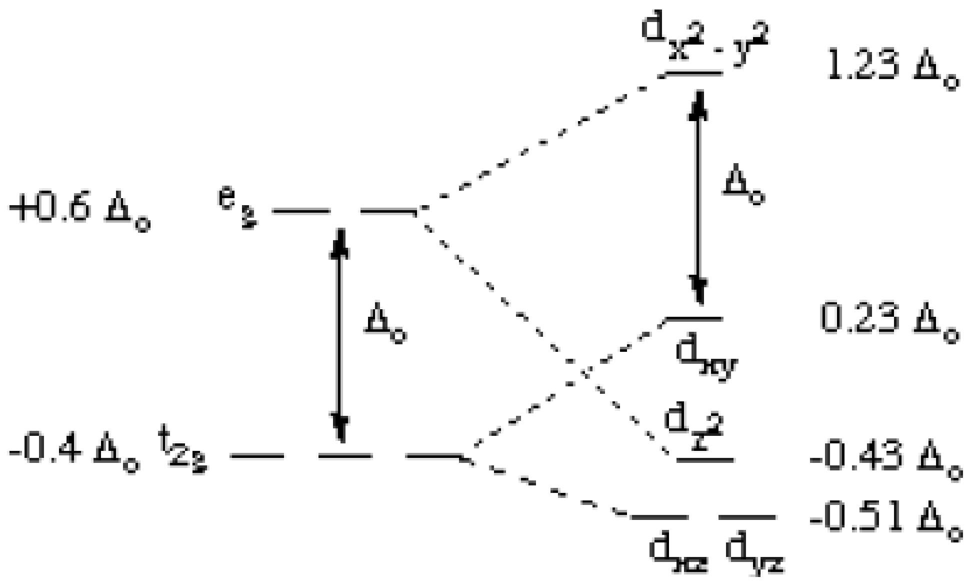


Square planar energy level

Square planar geometry can also arise in d^4 weak fields



Square planar energy level



Octahedral coordination

Square planar coordination (xy plane)

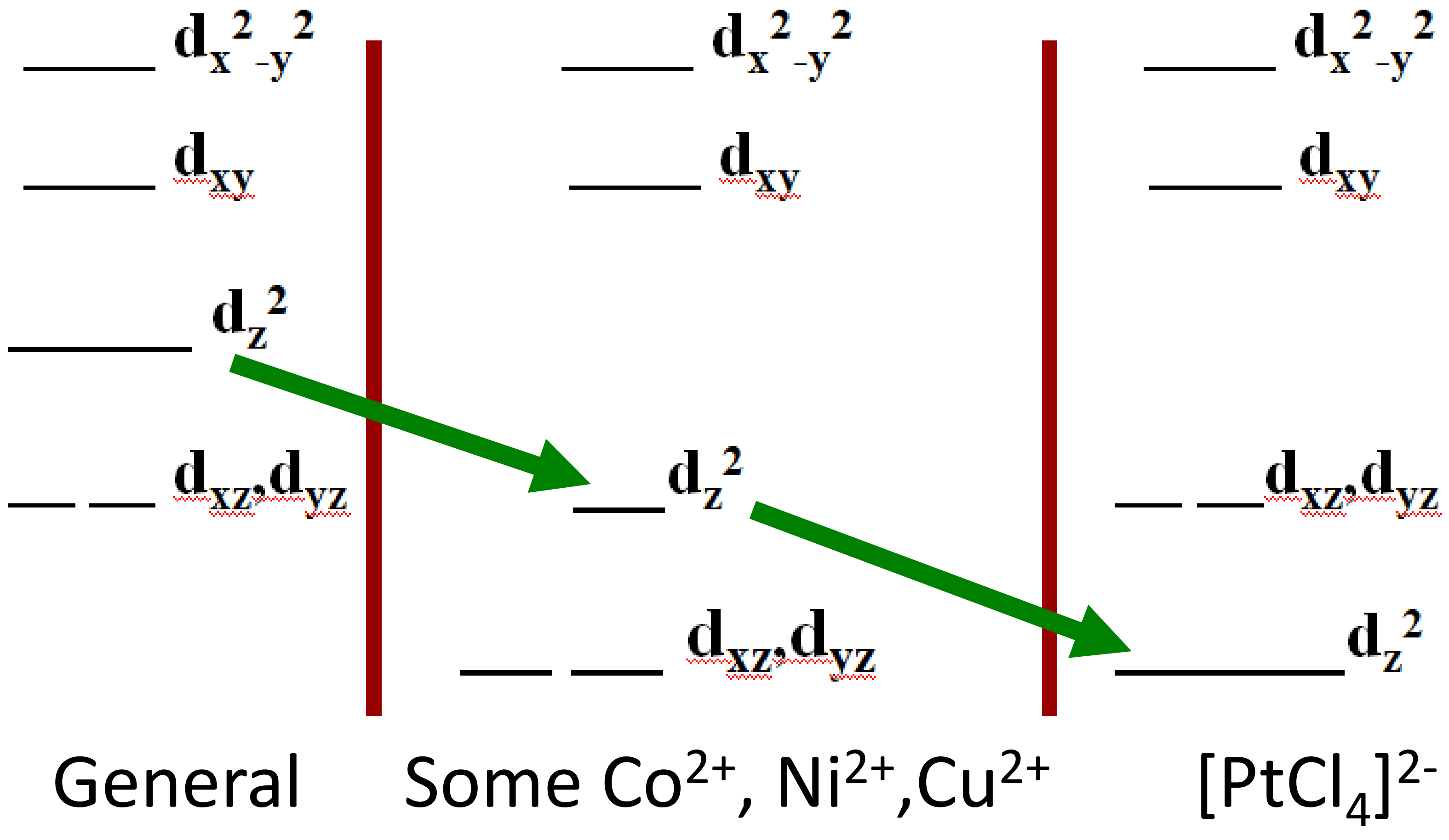
d^8 system

$$CFSE_{sq.\ pl.} = 4 \text{ electrons } (-0.51\ \Delta_o) + 2 \text{ electrons } (-0.43\ \Delta_o) + 2 \text{ electrons } (+0.23\ \Delta_o) + P$$
$$= -2.44\ \Delta_o + P$$

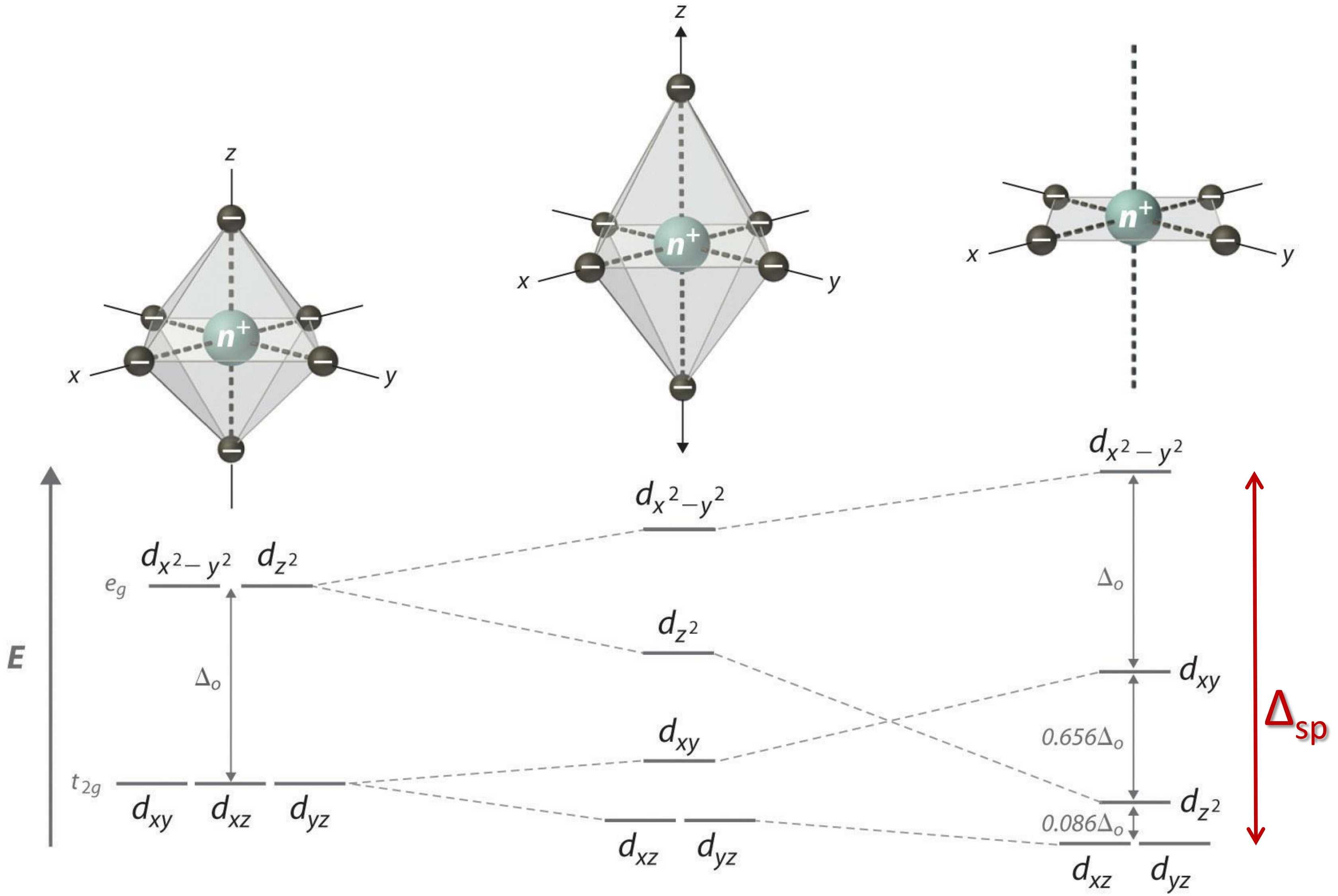
- The d_{z2} orbital falls the most, as its electrons are concentrated in lobes along the z-axis.
- The d_{xz} and d_{yz} orbitals also drop in energy, but not as much.
- Conversely, the d_{x2-y2} and the d_{xy} orbitals increase in energy.

Change in square planar energy level

If the tetragonal distortion (δ_1, δ_2) is large then d_{z^2} orbital can lie very low.

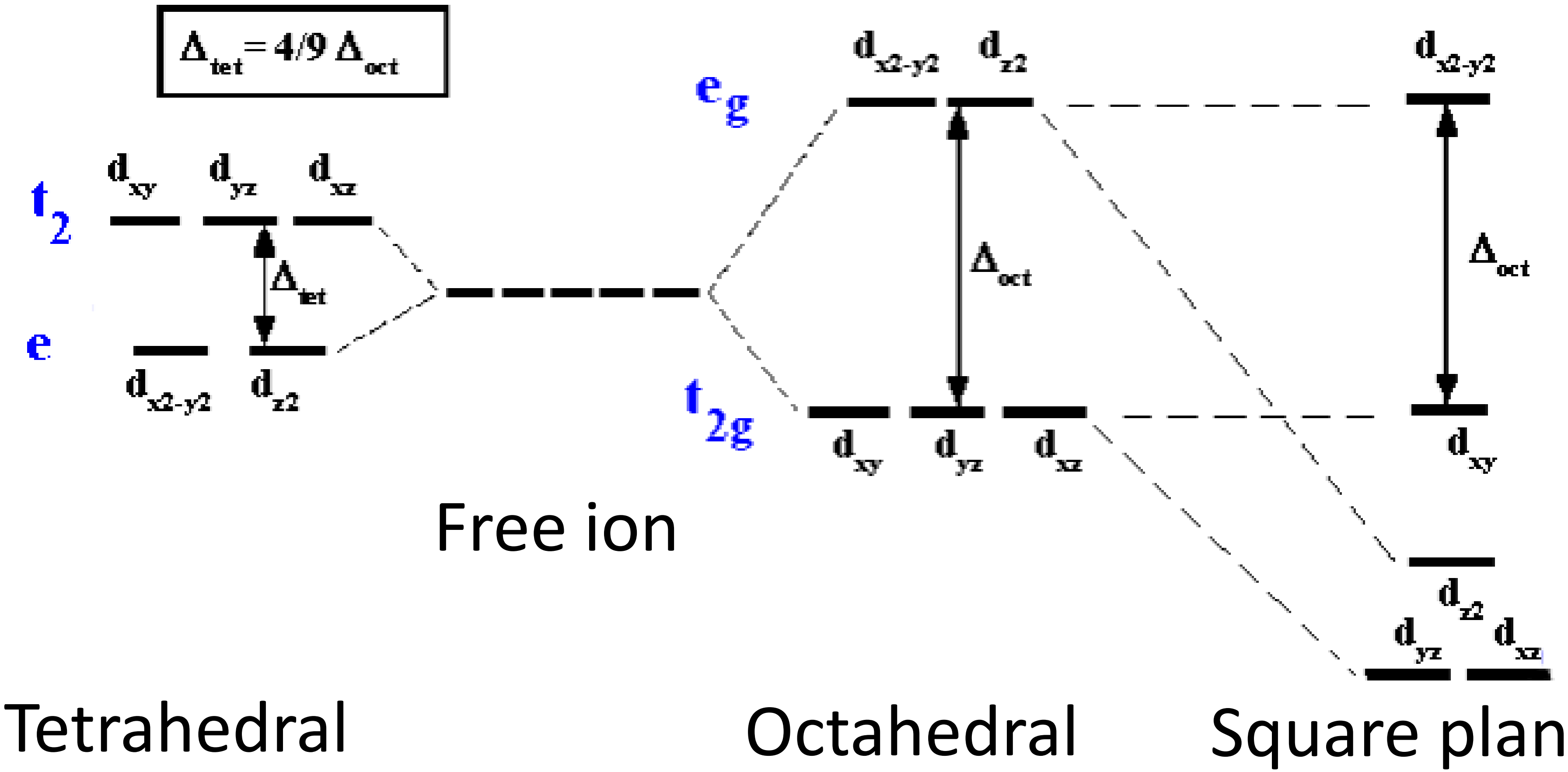


Oh vs. square planar geometry



Oh vs. square planar geometry

Energy levels of the d-orbitals in common stereochemistries



Stereochemistry of complexes

CFSE values also predict why Cu^{2+} ions forms square planar complexes rather than tetrahedral or octahedral complexes in both the fields

Cu^{2+} ion (d^9 system) has a much higher CFSE value in a square planar configuration (CFSE = 1.22 Δ_O) than in octahedral (0.6 Δ_O) or tetrahedral configuration (CFSE = 0.18 Δ_O)

Discussed topics……

- ✓ Jahn-Teller distortion
- ✓ Square planar system and energy levels
- ✓ Change in square planar energy level
- ✓ Octahedral vs. square planar geometry

Tetragonal elongation: an example (supporting slide)

Consider CrF_2 solid

Two different types of bond lengths

Cr-F 1.98 Å (4 bonds)

Cr-F 2.43 Å (2 bonds)

Why?

Consider $CrCl_2$ solid

Two different types of bond lengths

Cr-Cl 2.39 Å (4 bonds)

Cr-Cl 2.89 Å (2 bonds)