

## Crystal Field Theory History

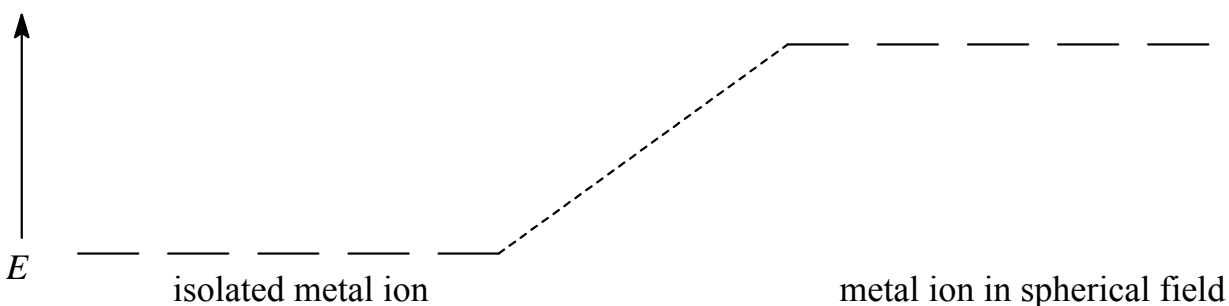
- 1929 Hans Bethe - Crystal Field Theory (CFT)
- Developed to interpret color, spectra, magnetism in crystals
- 1932 J. H. Van Vleck - CFT of Transition Metal Complexes
- Champions CFT to interpret properties of transition metal complexes
  - Show unity of CFT, VB, and MO approaches
- 1932 L. Pauling and J. C. Slater - VB theory
- Apply hybrid orbital concepts to interpret properties of transition metal complexes
  - Becomes dominant theory to explain bonding and magnetism until 1950s
  - Can't explain colors and visible spectra
- 1952 L. E. Orgel - Revival of CFT and development of Ligand Field Theory (LFT)
- Slowly replaces VB theory
  - Explains magnetism and spectra better
- 1954 Y. Tanabe and S. Sugano - Semi-quantitative term splitting diagrams
- Used to interpret visible spectra
- 1960s CFT, LFT, and MO Theories
- Used in conjunction with each other depending on the level of detail required
  - MO used for most sophisticated and quantitative interpretations
  - LFT used for semi-quantitative interpretations
  - CFT used for everyday qualitative interpretations

## CFT Principles

- CFT takes an electrostatic approach to the interaction of ligands and metal ions.
  - In purest form it makes no allowances for covalent M–L bonding.
- CFT attempts to describe the effects of the Lewis donor ligands and their electrons on the energies of  $d$  orbitals of the metal ion.
- ☞ We will consider the case of an octahedral  $ML_6$  ( $O_h$ ) complex first and then extend the approach to other complex geometries.

## Energies of $d$ orbitals in an Octahedral Complex

- ☛ Consider a spherical field ( $R_3$ ) equivalent to six electron pairs surrounding a central metal ion, M.
  - Ligand-metal electron repulsions will perturb the energies of the five degenerate  $d$  orbitals, making them rise in energy.

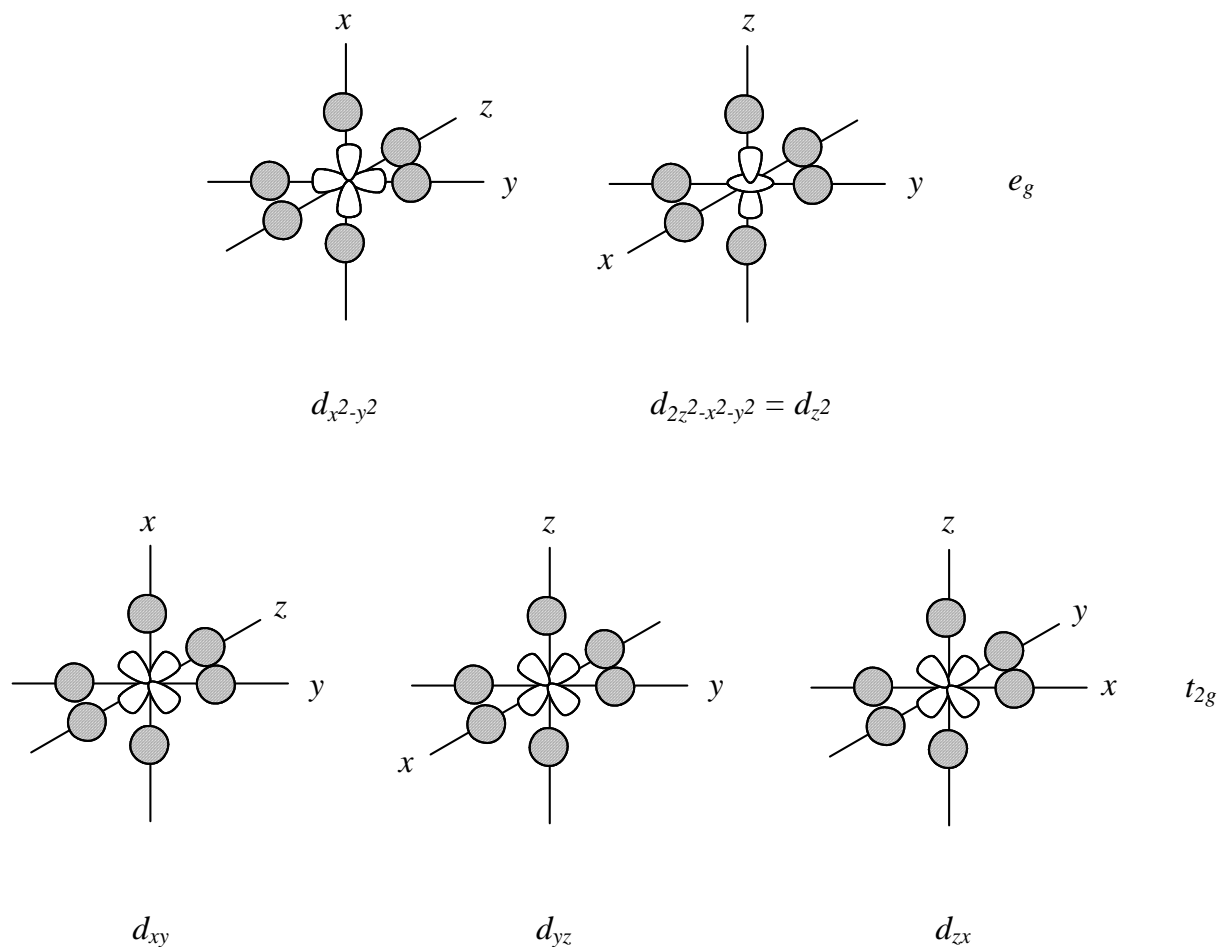


- ☛ Localize the six ligand pairs into the positions of an octahedron ( $R_3 \rightarrow O_h$ ).
  - Five-fold degeneracy among  $d$  orbitals will be lifted, in keeping with the direct product listings in the  $O_h$  character table.
  - The  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals constitute a triply degenerate set of  $t_{2g}$  symmetry.
  - The  $d_{x^2-y^2}$ ,  $d_{z^2}$  orbitals constitute a doubly degenerate set of  $e_g$  symmetry.<sup>1</sup>
- The energies of the  $t_{2g}$  orbitals and  $e_g$  orbitals relative to the perturbed energy of the hypothetical spherical field depend upon their orientation to the six ligand coordination positions.

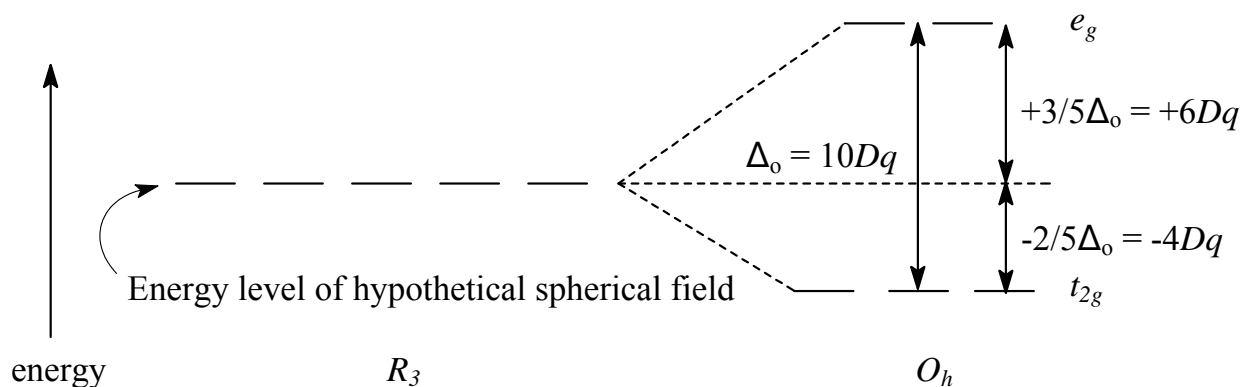
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<sup>1</sup>The vector product  $2z^2 - x^2 - y^2$  indicates the  $d$  orbital more commonly labeled  $z^2$ .

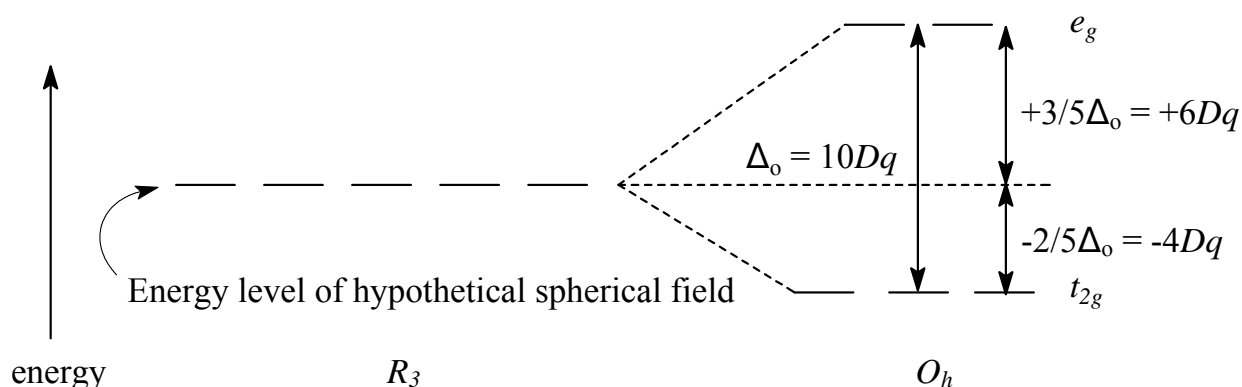
## ***d* Orbitals in an Octahedral Field**



- The  $e_g$  orbitals have lobes that point at the ligands and so will ascend in energy.
- The  $t_{2g}$  orbitals have lobes that lie between ligands and so will descend in energy.



## Crystal Field Splitting Energy, $\Delta_o$



- The energy gap between  $t_{2g}$  and  $e_g$  levels is designated  $\Delta_o$  or  $10Dq$ .
- The energy increase of the  $e_g$  orbitals and the energy decrease of the  $t_{2g}$  orbitals must be balanced relative to the energy of the hypothetical spherical field (sometimes called the *barycenter*).
  - The energy of the  $e_g$  set rises by  $+3/5\Delta_o = +6Dq$  while the energy of the  $t_{2g}$  set falls by  $-2/5\Delta_o = -4Dq$ , resulting in no net energy change for the system.

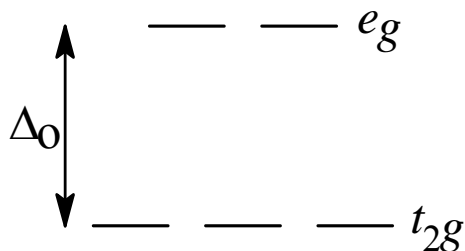
$$\begin{aligned}\Delta E &= E(e_g)\uparrow + E(t_{2g})\downarrow \\ &= (2)(+3/5\Delta_o) + (3)(-2/5\Delta_o) \\ &= (2)(+6Dq) + (3)(-4Dq) = 0\end{aligned}$$

- The magnitude of  $\Delta_o$  depends upon both the metal ion and the attaching ligands.
- Magnitudes of  $\Delta_o$  are typically  $\sim 100 - 400$  kJ/mol ( $\sim 8,375 - 33,500$   $\text{cm}^{-1}$ ).<sup>2</sup>

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<sup>2</sup>1 kJ/mol = 83.7  $\text{cm}^{-1}$

## Electron Filling of $t_{2g}$ and $e_g$ Orbitals



- Electrons fill  $t_{2g}$  and  $e_g$  orbitals in an aufbau manner, starting with the  $t_{2g}$  set, in accord with the Pauli exclusion principle and Hund's rule.
  - Spins of successively added electrons are parallel so long as the Pauli exclusion principle allows.
  - At the point when the set of  $t_{2g}$  orbitals is half filled, an additional electron must pair if it is to occupy one of the orbitals of the degenerate set.
  - But if the *mean pairing energy* ( $P$ ) is greater than  $\Delta_o$ , a lower energy state will result by putting the electron in the higher  $e_g$  level.
- For configurations  $d^1 - d^3$  and  $d^8 - d^{10}$  there is only one ground state configuration.
- For configurations  $d^4 - d^7$  there are two possible filling schemes depending on the magnitudes of  $P$  and  $\Delta_o$ .
  - A *high spin* configuration minimizes pairing by spreading the electrons across both the  $t_{2g}$  and  $e_g$  levels.
  - A *low spin* configuration minimizes occupying the higher energy  $e_g$  level by pairing electrons in the  $t_{2g}$  level.
- For a given metal ion, the pairing energy is relatively constant, so the spin state depends upon the magnitude of the field strength,  $\Delta_o$ .
  - *Low field* strength ( $\Delta_o < P$ ) results in a *high-spin* state.
  - *High field* strength ( $\Delta_o > P$ ) results in a *low-spin* state.

## High- and Low-Spin Configurations for $ML_6 O_h$

|          |                                   |                                     |                                    |                                     |                                     |                                     |                                     |
|----------|-----------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| $e_g$    | <u>—</u><br><u>—</u>              | <u>—</u><br><u>—</u>                | <u>—</u><br><u>—</u>               | <u>—</u><br><u>1</u>                | <u>—</u><br><u>—</u>                | <u>1</u><br><u>1</u>                | <u>—</u><br><u>—</u>                |
| $t_{2g}$ | <u>—</u><br><u>—</u><br><u>1</u>  | <u>—</u><br><u>1</u><br><u>1</u>    | <u>1</u><br><u>1</u><br><u>1</u>   | <u>1</u><br><u>1</u><br><u>1</u>    | <u>1</u><br><u>1</u><br><u>1↓</u>   | <u>1</u><br><u>1</u><br><u>1</u>    | <u>1</u><br><u>1↓</u><br><u>1↓</u>  |
|          | $d^1$                             | $d^2$                               | $d^3$                              | $d^4$<br>high<br>spin               | $d^4$<br>low<br>spin                | $d^5$<br>high<br>spin               | $d^5$<br>low<br>spin                |
| $e_g$    | <u>1</u><br><u>1</u>              | <u>—</u><br><u>—</u>                | <u>1</u><br><u>1</u>               | <u>—</u><br><u>1</u>                | <u>1</u><br><u>1</u>                | <u>1</u><br><u>1↓</u>               | <u>1↓</u><br><u>1↓</u>              |
| $t_{2g}$ | <u>1</u><br><u>1</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> | <u>1↓</u><br><u>1↓</u><br><u>1↓</u> |
|          | $d^6$<br>high<br>spin             | $d^6$<br>low<br>spin                | $d^7$<br>high<br>spin              | $d^7$<br>low<br>spin                | $d^8$                               | $d^9$                               | $d^{10}$                            |

## Crystal Field Stabilization Energy (CFSE)<sup>3</sup>

- Occupancy of electrons in  $t_{2g}$  and  $e_g$  orbitals results in an overall *crystal field stabilization energy* (CFSE), defined for octahedral complexes as<sup>4</sup>

$$\text{CFSE} = (-0.4n_{t_{2g}} + 0.6n_{e_g})\Delta_o + pP$$

where  $n_{t_{2g}}$  = number of electrons in  $t_{2g}$  orbitals

$n_{e_g}$  = number of electrons in  $e_g$  orbitals

$p$  = total number of electron pairs

$P$  = mean pairing energy

### Examples of CFSE Calculations

| Free Ion   | $O_h$            | CFSE Calculation                       | CFSE                |
|------------|------------------|--|---------------------|
| $d^3$      | $t_{2g}^3$       | $(3)(-0.4\Delta_o)$                    | $-1.2\Delta_o$      |
| $d^8$      | $t_{2g}^6 e_g^2$ | $[(6)(-0.4) + (2)(+0.6)]\Delta_o + 3P$ | $-1.2\Delta_o + 3P$ |
| $d^7$ low  | $t_{2g}^6 e_g^1$ | $[(6)(-0.4) + (1)(+0.6)]\Delta_o + 3P$ | $-1.8\Delta_o + 3P$ |
| $d^7$ high | $t_{2g}^5 e_g^2$ | $[(5)(-0.4) + (2)(+0.6)]\Delta_o + 2P$ | $-0.8\Delta_o + 2P$ |

- For  $d^n$  cases that could be high- or low-spin, the configuration that results in the lower CFSE for the  $\Delta_o$  of the complex is the spin state that is observed.
  - For the hypothetical case  $\Delta_o = P$ , neither state would be preferred, as the two CFSEs for  $d^7$  illustrate:
 
$$\text{CFSE}(d^7 \text{ low}) = -1.8\Delta_o + 3P = -1.8\Delta_o + 3\Delta_o = 1.2\Delta_o$$

$$\text{CFSE}(d^7 \text{ high}) = -0.8\Delta_o + 2P = -0.8\Delta_o + 2\Delta_o = 1.2\Delta_o$$
  - There are no cases for which  $\Delta_o = P$ .

<sup>3</sup>CFSE is also called Ligand Field Stabilization Energy (LFSE).

<sup>4</sup>Meissler & Tarr use  $\Pi_c$  for the  $\Delta_o$  term and  $\Pi_e$  for the  $P$  term in the defining equation. Some sources do not include pairing energy in calculating CFSE.



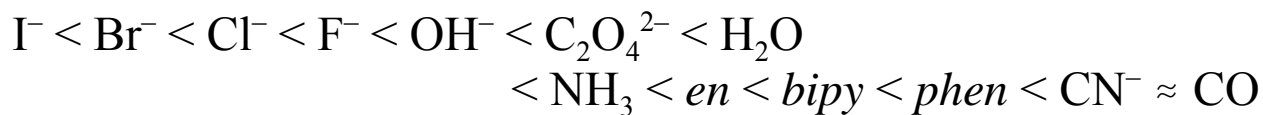
## Values of $\Delta_o$ , $P$ , CFSE and Resulting Spin State

| Complex                                  | $d^n$ | $P$ (cm <sup>-1</sup> ) | $\Delta_o$ (cm <sup>-1</sup> ) | State | CFSE                |
|--|-------|-------------------------|--------------------------------|-------|---------------------|
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | $d^4$ | 18,800                  | 13,900                         | high  | $-0.6\Delta_o$      |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ | $d^5$ | 24,000                  | 13,700                         | high  | 0                   |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | $d^6$ | 14,100                  | 10,400                         | high  | $-0.4\Delta_o + P$  |
| $[\text{Fe}(\text{CN})_6]^{4-}$          | $d^6$ | 14,100                  | 33,000                         | low   | $-2.4\Delta_o + 3P$ |
| $[\text{CoF}_6]^{3-}$                    | $d^6$ | 16,800                  | 13,000                         | high  | $-0.4\Delta_o + P$  |
| $[\text{Co}(\text{NH}_3)_6]^{3+}$        | $d^6$ | 16,800                  | 23,000                         | low   | $-2.4\Delta_o + 3P$ |
| $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | $d^7$ | 18,000                  | 9,300                          | high  | $-0.8\Delta_o + 2P$ |

- Values of  $\Delta_o$  depend on both the metal ion and the ligand.
- Most aquo complexes are high spin, because  $\text{H}_2\text{O}$  is a weak-field ligand.
- Almost all  $\text{Co}^{3+}$  ( $d^6$ ) complexes are low spin, including  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ , except  $[\text{CoF}_6]^{3-}$ , which is high spin.
- Second and third row transition metal ions tend to have low spin states.
  - These ions tend to have larger  $\Delta_o$  values.
  - Larger  $4d$  and  $5d$  orbitals result in smaller  $P$  values, owing to lesser electronic repulsions.
  - $4d$  and  $5d$  orbitals overlap with ligand orbitals, delocalizing electron density onto the ligands.

## Spectrochemical Series

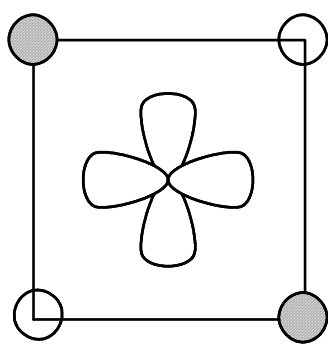
- For a given metal ion, the magnitude of  $\Delta_o$  depends on the ligand and tends to increase according to the following *spectrochemical series*:



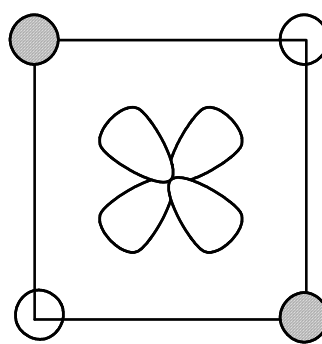
- *en* = ethylenediamine, *bipy* = 2,2'-bipyridine, *phen* = *o*-phenanthroline
- Ligands up through  $\text{H}_2\text{O}$  are *weak-field ligands* and tend to result in high-spin complexes.
- Ligands beyond  $\text{H}_2\text{O}$  are *strong-field ligands* and tend to result in low-spin complexes.

## Tetrahedral Crystal Field Splitting

- The same considerations of crystal field theory can be applied to  $ML_4$  complexes with  $T_d$  symmetry.
  - In  $T_d$ ,  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals have  $t_2$  symmetry and  $d_{x^2-y^2}$ ,  $d_{z^2}$  orbitals have  $e$  symmetry.
- Relative energies of the two levels are reversed, compared to the octahedral case.
  - No  $d$  orbitals point directly at ligands.
  - The  $t_2$  orbitals are closer to ligands than are the  $e$  orbitals. This can be seen by comparing the orientations of the  $d_{x^2-y^2}$  orbital ( $e$  set) and  $d_{xy}$  orbital ( $t_2$  set) relative to the four ligands.



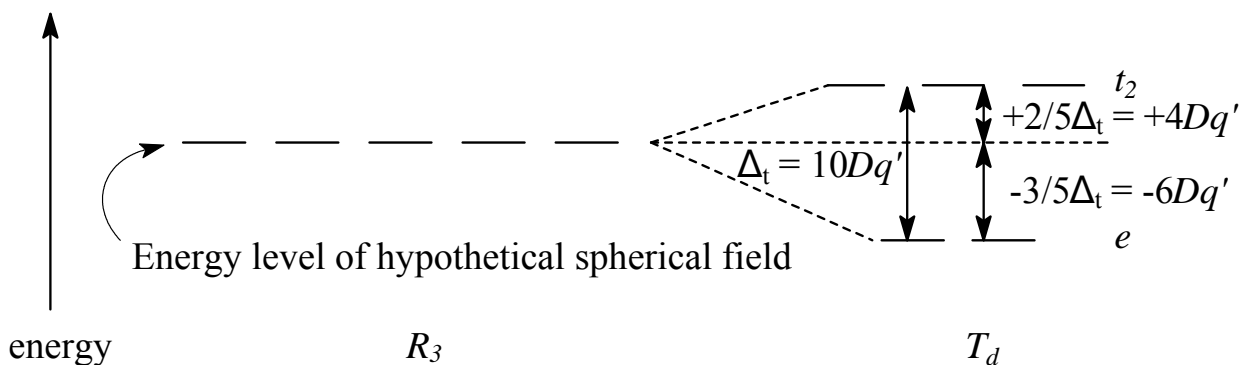
$d_{x^2-y^2}$



$d_{xy}$

- The difference results in an energy split between the two levels by  $\Delta_t$  or  $10Dq'$ . Relative to the barycenter defined by the hypothetical spherical field
  - the  $e$  level is lower by  $-3\Delta_t/5 = -6Dq'$
  - the  $t_2$  level is higher by  $+2\Delta_t/5 = +4Dq'$

## Tetrahedral Crystal Field Splitting - cont.



- In principle, both high and low spin configurations are conceivable for  $d^3-d^6$   $ML_4 T_d$  complexes.
- With extremely rare exceptions, only high spin configurations are observed.
  - $\Delta_t$  is much smaller than  $\Delta_o$ .
  - For a given ligand at the same M-L distances, it can be shown that  $\Delta_t = (4/9)\Delta_o$ .
  - $\Delta_t \ll P$  in ordinary complexes, so high spin is favored.
- The crystal field stabilization energy for tetrahedral complexes is calculated from the following equation:

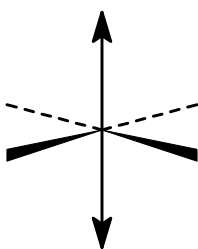
$$CFSE(T_d) = (-0.6n_e + 0.4n_{t_2})\Delta_t + pP$$

## Crystal Field Splitting for Other Geometries

- We can deduce the CFT splitting of  $d$  orbitals in virtually any ligand field by
  - Noting the direct product listings in the appropriate character table to determine the ways in which the  $d$  orbital degeneracies are lifted
  - Carrying out an analysis of the metal-ligand interelectronic repulsions produced by the complex's geometry.
- Sometimes it is useful to begin with either the octahedral or tetrahedral splitting scheme, and then consider the effects that would result by distorting to the new geometry.
  - The results for the perfect and distorted geometries can be correlated through descent in symmetry, using the appropriate correlation tables.
  - Can take this approach with distortions produced by ligand substitution or by intermolecular associations, if descent in symmetry involves a group-subgroup relationship.

## Crystal Field for Tetragonally Distorted $ML_6$

- A tetragonal distortion to an octahedron results from any change in geometry that preserves a  $C_4$  axis.
  - Tetragonal distortion occurs whenever two *trans* related ligands are differentiated from the remaining four.
- A useful tetragonal distortion to consider involves equally stretching two *trans* related ligands, thereby causing a descent in symmetry  $O_h \rightarrow D_{4h}$ .



- The stretching occurs along the  $z$  axis, leaving the four positions in the  $xy$  plane equivalent to each other.
- Ultimately, such a stretching leads to removal of the two ligands, leaving a square planar  $ML_4$  complex.

## Splitting of $d$ Orbital Degeneracies – $O_h \rightarrow D_{4h}$

- From a correlation table that links the groups  $O_h$  and  $D_{4h}$  it can be determined that the two  $e_g$  orbitals of the octahedral field become nondegenerate as  $a_{1g}$  and  $b_{1g}$  in the  $D_{4h}$  tetragonal field.
  - From the direct product listings in the  $D_{4h}$  character table

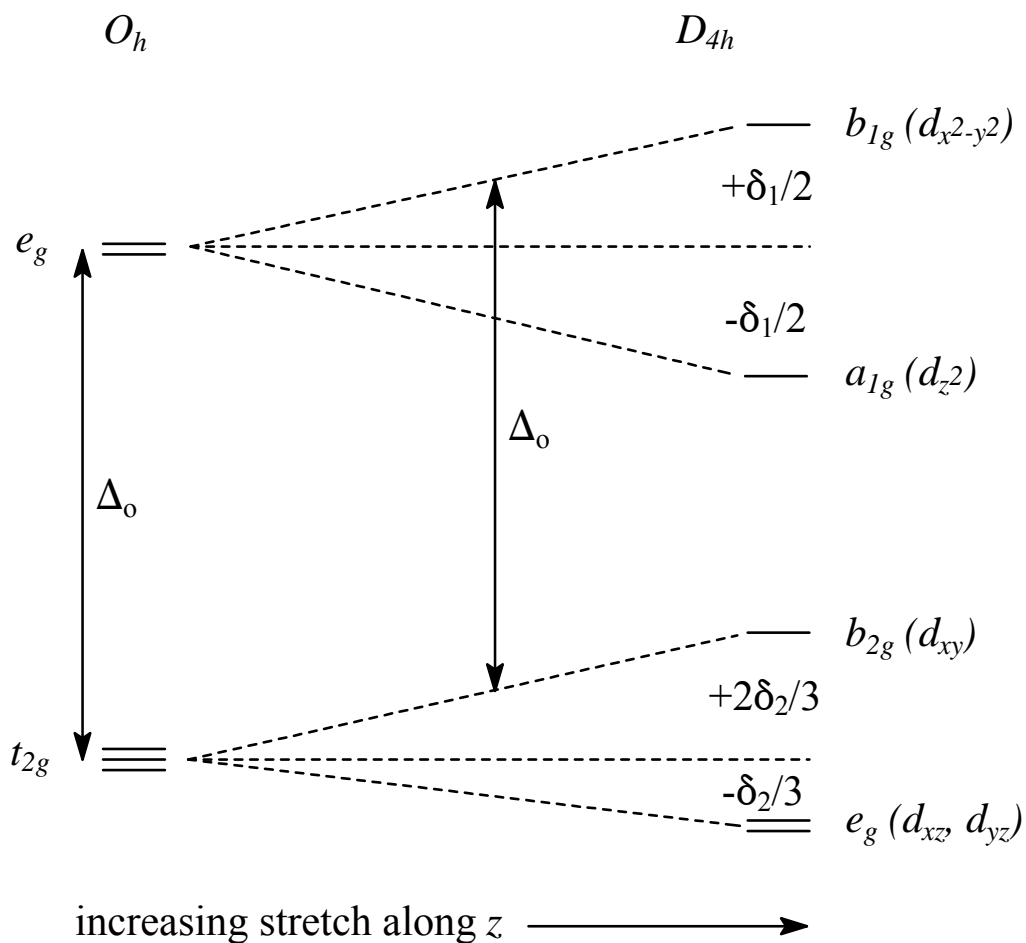
$$a_{1g} = d_{2z^2-x^2-y^2} (= d_{z^2})$$
$$b_{1g} = d_{x^2-y^2}$$

- From the correlation table it can also be shown that the degeneracy among the  $t_{2g}$  orbitals in  $O_h$  is partially lifted to become  $b_{2g}$  and  $e_g$  in the  $D_{4h}$  tetragonal field.
  - From the direct product listings in the  $D_{4h}$  character table

$$b_{2g} = d_{xy}$$
$$e_g = (d_{xz}, d_{yz})$$

- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in those  $d$  orbitals that have substantial electron distribution along  $z$ .
  - Thus the energies of the  $d_{xz}$ ,  $d_{yz}$ , and  $d_{z^2}$  orbitals are lowered.
- If we assume that the stretch along  $z$  is accompanied by a counterbalancing contraction in the  $xy$  plane, so as to maintain the overall energy of the system, then the orbitals with substantial electron distribution in the  $xy$  plane will experience increased repulsions.
  - Thus, the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals rise in energy.

## Orbital Splitting from a Stretching Tetragonal Distortion

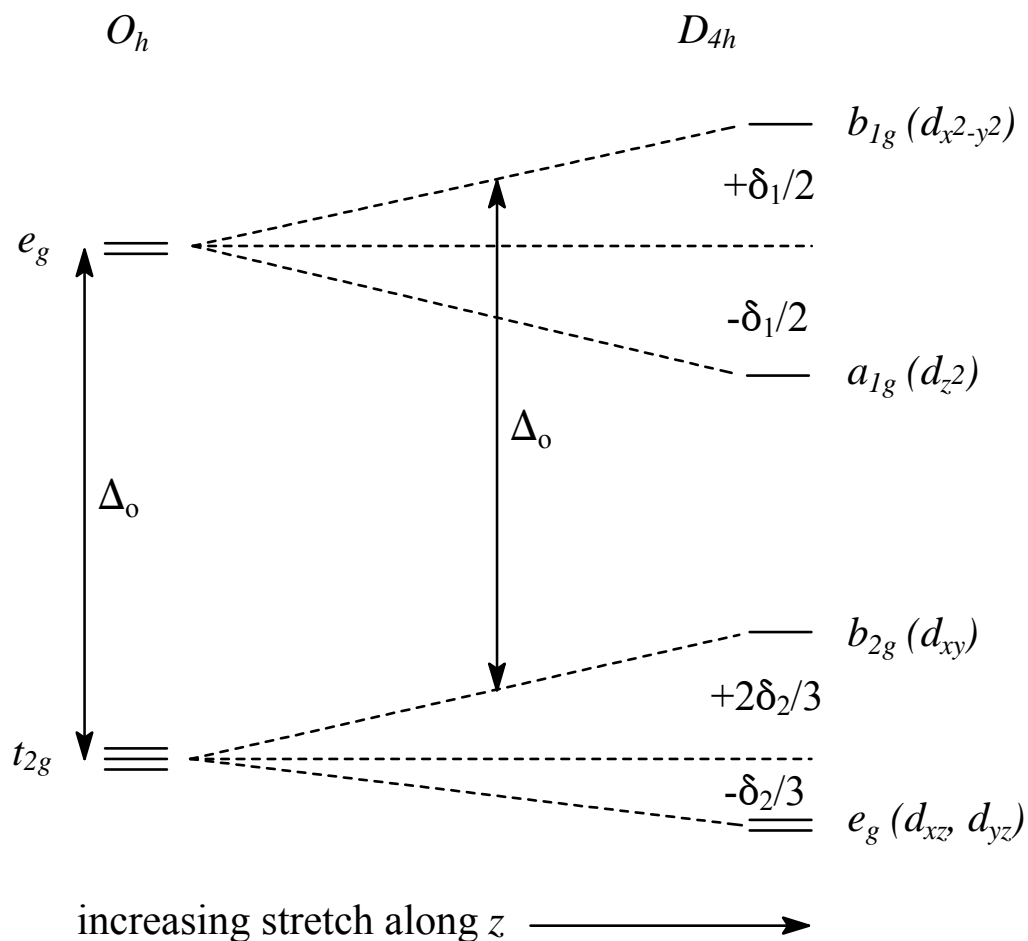


- The upper  $e_g$  orbitals of the perfect octahedron split equally by an amount  $\delta_1$ , with the  $d_{x^2-y^2}$  orbital ( $b_{1g}$  in  $D_{4h}$ ) rising by  $+\delta_1/2$  and the  $d_{z^2}$  orbital ( $a_{1g}$  in  $D_{4h}$ ) falling by  $-\delta_1/2$ .
- The lower  $t_{2g}$  orbitals of the perfect octahedron split by an amount  $\delta_2$ , with the  $d_{xy}$  orbital ( $b_{2g}$  in  $D_{4h}$ ) rising by  $+2\delta_2/3$ , and the degenerate  $d_{xz}$  and  $d_{yz}$  orbitals ( $e_g$  in  $D_{4h}$ ) falling by  $-\delta_2/3$ .



## Magnitudes of the $\delta_1$ and $\delta_2$ Splittings

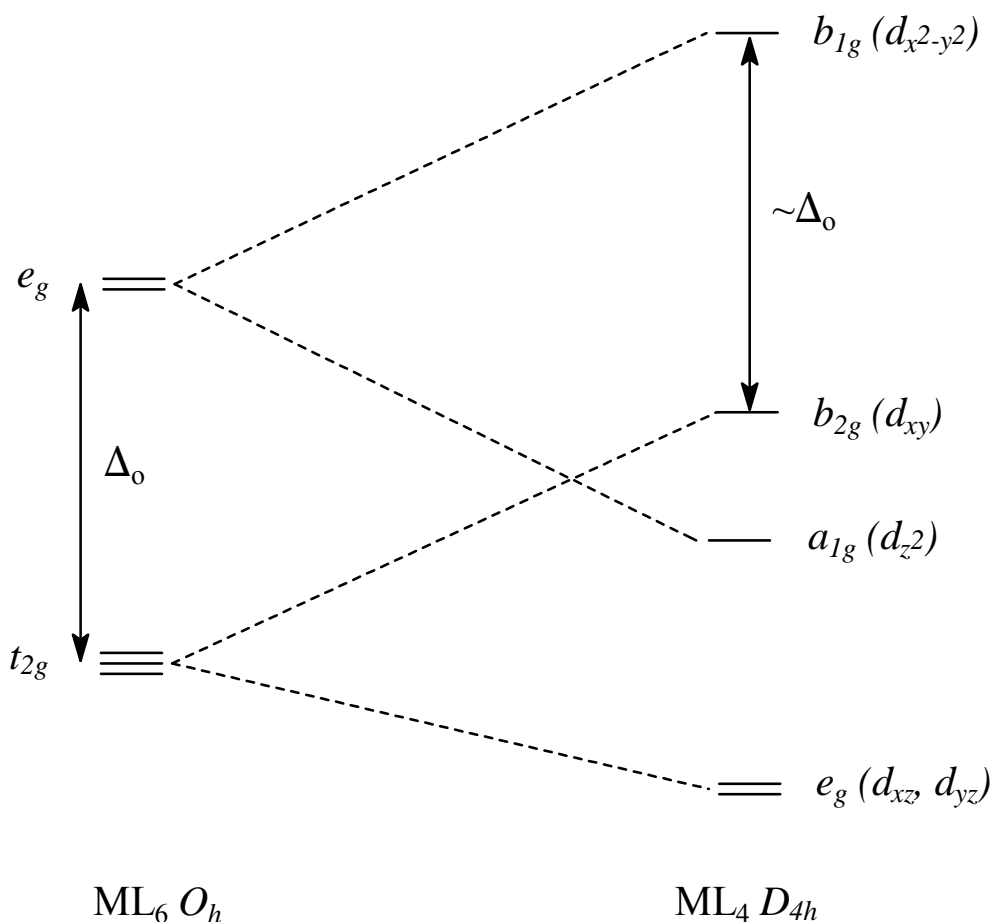
- Both the  $\delta_1$  and  $\delta_2$  splittings, which are very small compared to  $\Delta_o$ , maintain the barycenters defined by the  $e_g$  and  $t_{2g}$  levels of the undistorted octahedron.
  - The energy gap  $\delta_1$  is larger than that of  $\delta_2$ , because the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are directed at ligands.
  - The distortion has the same effect on the energies of both the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals; i.e.  $\delta_1/2 = 2\delta_2/3$ .
- As a result, the energies of both the  $d_{x^2-y^2}$  and  $d_{xy}$  rise in parallel, maintaining a separation equal to  $\Delta_o$  of the undistorted octahedral field.



- Note that  $\delta_1/2 = 2\delta_2/3$  implies that  $\delta_1 = (4/3)\delta_2$ .

## Square Planar $ML_4$ Complexes

- If we imagine continuing the stretching of M-L bonds along  $z$ , the orbital splittings will become progressively greater, producing successively larger values of  $\delta_1$  and  $\delta_2$ .
- Eventually the two ligands will be removed, resulting in a square planar  $ML_4$  complex.
- At some point before this extreme the  $a_{1g}$  ( $d_{z^2}$ ) level may cross and fall below the  $b_{2g}$  ( $d_{xy}$ ) level, resulting in the following splitting scheme.<sup>5</sup>



<sup>5</sup>The ordering of the lower four  $d$  orbitals probably varies among square planar complexes and has been the subject of much debate. See A. B. P. Lever, *Inorganic Electron Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984, p. 537ff. and references therein.

## ML<sub>4</sub> (D<sub>4h</sub>) vs. ML<sub>4</sub> (T<sub>d</sub>)

- Most square planar complexes are  $d^8$  and less often  $d^9$ .
- In virtually all  $d^8$  cases a low spin configuration is observed, leaving the upper  $b_{1g}$  ( $d_{x^2-y^2}$ ) level vacant in the ground state.
  - This is expected, because square planar geometry in first-row transition metal ions is usually forced by strong field ligands.
  - Strong field ligands produce a large  $\Delta_o$  value.
  - The energy gap between the  $b_{2g}$  ( $d_{xy}$ ) and  $b_{1g}$  ( $d_{x^2-y^2}$ ) levels is equivalent to  $\Delta_o$ .
    - ☞ A large  $\Delta_o$  value favors pairing in the  $b_{2g}$  ( $d_{xy}$ ) level, a low-spin diamagnetic configuration for  $d^8$ .
- Tetrahedral  $d^8$  is a high-spin paramagnetic configuration  $e^4t_2^4$ .
  - ☞ ML<sub>4</sub> (D<sub>4h</sub>) and ML<sub>4</sub> (T<sub>d</sub>) can be distinguished by magnetic susceptibility measurements.
- Ni<sup>2+</sup> ion tends to form square planar, diamagnetic complexes with strong-field ligands (e.g., [Ni(CN)<sub>4</sub>]<sup>2-</sup>), but tends to form tetrahedral, paramagnetic complexes with the weaker-field ligands (e.g., [NiCl<sub>4</sub>]<sup>2-</sup>).
- With second and third row transition metal ions the  $\Delta_o$  energies are inherently larger, and square planar geometry can occur even with relatively weak field ligands; e.g., square planar [PtCl<sub>4</sub>]<sup>2-</sup>.