

Electronic Configurations for Tetrahedral Complexes

- ❑ Tetrahedral splitting is seldom large enough to result in pairing of the electrons. As a result, low-spin tetrahedral complexes are not common.

d-electrons	configuration	CFSE
d^1	$e^1 t_2^0$	$-0.6 \Delta_t$
d^2	$e^2 t_2^0$	$-1.2 \Delta_t$
d^3	$e^2 t_2^1$	$-0.8 \Delta_t$
d^4	$e^2 t_2^2$	$-0.4 \Delta_t$
d^5	$e^2 t_2^3$	$0.0 \Delta_t$
d^6	$e^3 t_2^3$	$-0.6 \Delta_t$
d^7	$e^4 t_2^3$	$-1.2 \Delta_t$
d^8	$e^4 t_2^4$	$-0.8 \Delta_t$
d^9	$e^4 t_2^5$	$-0.4 \Delta_t$
d^{10}	$e^4 t_2^6$	$0.0 \Delta_t$

Tetrahedral Complexes

- ❑ If Δ_t is smaller than Δ_o ($\Delta_t = 4/9 \Delta_o$), why would tetrahedral complexes form?
- ❑ But what if we take a particular metal ion and a particular ligand? Can we predict whether it will form an octahedral or a tetrahedral complex, for example?
- ❑ If we make the assumption that $\Delta_t = 4/9 \Delta_o$, we can calculate the difference in stabilization energy between octahedral and tetrahedral geometries by referencing everything in terms of Δ_o .
- ❑ Example Problem:

Which is the preferred configuration for a d^3 metal: tetrahedral or octahedral?

Tetrahedral Complexes

- ❑ To answer this, the *Crystal Field Stabilization Energy* has to be calculated for a metal in both configurations. The geometry with the greater stabilization will be the preferred geometry.
- ❑ For a d^3 *octahedral* configuration, the *CFSE* is $3 \times -0.4 \Delta_o = -1.2 \Delta_o$
- ❑ For a d^3 *tetrahedral* configuration (assuming high spin), the *Crystal Field Stabilization Energy* is $-0.8 \Delta_t$
- ❑ Remember that because Δ_{tet} is less than half the size of Δ_o , tetrahedral complexes are often high spin. We can now put this in terms of Δ_o (we can make this comparison because we're considering the same metal ion and the same ligand: all that's changing is the geometry)
- ❑ So for tetrahedral d^3 , the Crystal Field Stabilization Energy is:
 $CFSE = -0.8 \times 4/9 \Delta_o = -0.355 \Delta_o$.
- ❑ And the difference in Crystal Field Stabilization Energy between the two geometries will be: $1.2 - 0.355 = 0.845 \Delta_o$.

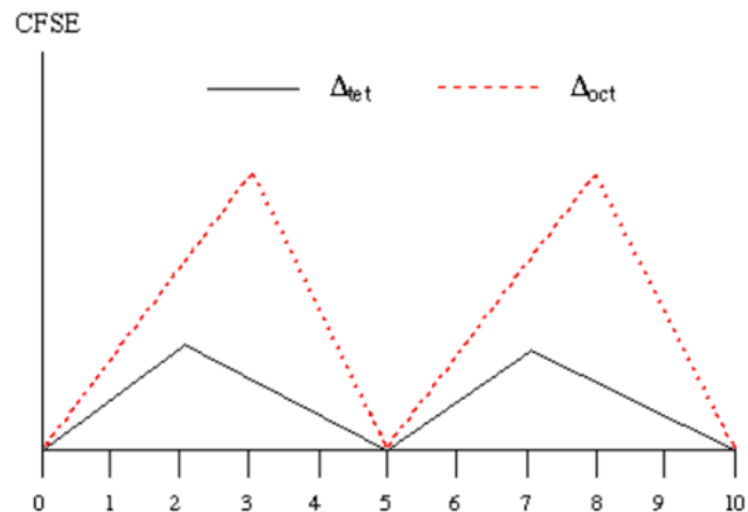
Tetrahedral Complexes

- If we do a similar calculation for the other configurations, we can construct a Table of Δ_o , Δ_t and the difference between them (we'll ignore their signs since we're looking for the difference between them).

	Octahedral	Tetrahedral	Difference
d^0, d^5, d^{10}	0	0	0
d^1, d^6	0.4	0.27	0.13
d^2, d^7	0.8	0.53	0.27
d^3, d^8	1.2	0.36	0.84
d^4, d^9	0.6	0.18	0.42

- Plot these numbers.

- Remember: These are CFSE numbers for hypothetical molecules in octahedral and tetrahedral geometry.



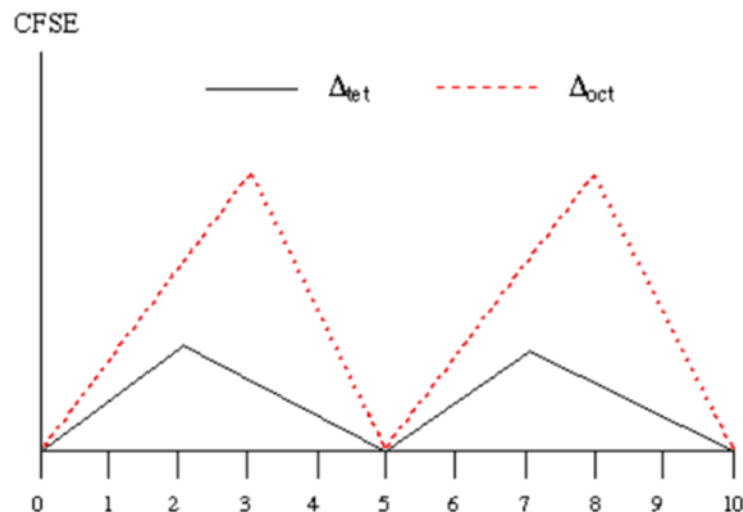
Tetrahedral Complexes

❑ Notice that the Crystal Field Stabilization Energy almost always favors octahedral over tetrahedral in most cases, but the degree of favorability varies with the *electronic configuration*.

❑ In other words, for d^1 there's only a small gap between the oct and tet lines, whereas at d^3 and d^8 there's a big gap. However, for d^0 , d^5 high spin and d^{10} , there is no CFSE difference between octahedral and tetrahedral.

❑ The order of favourability of octahedral vs tetrahedral is:

$$d^3, d^8 > d^4, d^9 > d^2, d^7 > d^1, d^6 > d^0, d^5, d^{10}$$

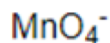


Tetrahedral Complexes: Summary

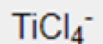
- ❑ The following factors favour tetrahedral complexes:
 - ❑ Use large ligands.
 - ❑ Use of metal ions with d^0 , d^5 , d^{10} configuration.
 - ❑ Use of weak field ligand with other d^x configurations

- ❑ Examples:

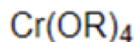
d^0



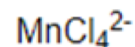
d^1



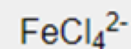
d^2



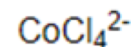
d^5



d^6



d^7



Did We Forget Square Planar Complexes?

- Imagine that we have an octahedral complex from which we are removing the axial ligands. As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy.
- The d_{z^2} 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 $d_{x^2-y^2}$ and the d_{xy} orbitals increase in energy. The splitting diagram for square planar complexes is more complex than for octahedral and tetrahedral complexes, and is shown below with the relative energies of each

