



Octahedral vs. Tetrahedral Geometries

How do we tell whether a particular complex is octahedral, tetrahedral, or square planar? Obviously if we know the formula, we can make an educated guess: something of the type ML_6 will almost always be octahedral (there is an alternative geometry for 6-coordinate complexes, called trigonal prismatic, but it's pretty rare), whereas something of formula ML_4 will usually be *tetrahedral* unless the metal atom has the d^8 electron configuration, in which case it will probably be *square planar*. 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? To an extent, the answer is yes... we can certainly say what factors will encourage the formation of tetrahedral complexes instead of the more usual octahedral.

The Crystal Field Stabilization Energy (CFSE) is the additional stabilization gained by the splitting of the orbitals according to the [crystal field theory](#), against the energy of the original five degenerate d orbitals. So, for example, in a d^1 situation such as $[Ti(OH_2)_6]^{3+}$, putting the electron into one of the orbitals of the t_{2g} level gains $-0.4 \Delta_o$ of CFSE. Generally speaking, octahedral complexes will be favored over tetrahedral ones because:

- It is more (energetically) favorable to form six bonds rather than four
- The CFSE is usually greater for octahedral than tetrahedral complexes. Remember that Δ_o is bigger than Δ_{tet} (in fact, Δ_{tet} is approximately $4/9 \Delta_o$).

If we make the assumption that $\Delta_{tet} = 4/9 \Delta_o$, we can calculate the difference in stabilization energy between octahedral and tetrahedral geometries by referencing everything in terms of Δ_o .

Example 1: d^3 Stabilized Structures

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

SOLUTION

To answer this, the *Crystal Field Stabilization Energy* has to be calculated for a (d^3 metal in both configurations. The geometry with the greater stabilization will be the preferred geometry.

- For a d^3 *octahedral* configuration, the *Crystal Field Stabilization Energy* is

$$3 \times -0.4\Delta_o = -1.2\Delta_o \quad (1)$$

- For a d^3 *tetrahedral* configuration (assuming high spin), the *Crystal Field Stabilization Energy* is

$$-0.8\Delta_{tet} \quad (2)$$

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:

$$1.2 - 0.355 = 0.845 \Delta_o.$$

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

Table 1: Crystal Field Stabilization Energies (not splitting parameters). This table compares the values of the CFSE for octahedral and tetrahedral geometries, assuming high spin configurations. The units are Δ_o , and we're assuming that $\Delta_{tet} = 4/9 \Delta_o$.

	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



	Octahedral	Tetrahedral	Difference
d^3, d^8	1.2	0.36	0.84
d^4, d^9	0.6	0.18	0.42

These values can be plotted:



Figure 1: Crystal Field Stabilization Energy as a function of d-electrons for a hypothetical molecule in the octahedral (red dashed curve) and tetrahedral (black solid curve) geometries.

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 ordering of favorability of octahedral over tetrahedral is:

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

The units of the graph are Δ_o . So if we have strong field ligands present, Δ_o will be bigger anyway (according to the spectrochemical series), and any energy difference between the oct and tet lines will be all the greater for it. A bigger Δ_o might also push the complexes over to low spin. Similarly, as we saw previously, high oxidation states and metals from the 2nd and 3rd rows of the transition series will also push up Δ_o .

On the other hand, if large or highly charged ligands are present, they may suffer large interligand repulsions and thus prefer a lower coordination number (4 instead of 6). Consequently if you set out to make something that would have a tetrahedral geometry, you would use large, negatively charged, weak field ligands, and use a metal atom with a d^0 , d^5 or d^{10} configuration from the first row of the transition series (though of course having weak field ligands doesn't matter in these three configurations because the difference between oct and tet is 0 Δ_o). As Table 2 shows, you can find tetrahedral complexes for most configurations, but there are very few for d^3 and d^8 .

Table 2: Tetrahedral complexes of different d electron counts

d^0	MnO_4^-	d^5	MnCl_4^{2-}
d^1	TiCl_4^-	d^6	FeCl_4^{2-}
d^2	Cr(OR)_4	d^7	CoCl_4^{2-}

Contributors

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