8.6.4: Tetrahedral Complexes

Transitions in tetrahedral complexes are Laporte-allowed

Tetrahedral metal complexes often have more intense electronic transitions than their octahedral counterparts. This is due to the fact that the $d-d$ transitions in a tetrahedron are allowed by the Laporte selection rule, while $d-d$ transitions in an octahedral complex are Laporte-forbidden. Recall that the Laporte selection rule applies to centrosymmetric complexes only. The Laporte rule applies to octahedral complexes but not to tetrahedral complexes because a tetrahedron does not have a center of inversion. Notice that the terms (and orbital labels) in a tetrahedron do not include the g subscripts that are present under octahedral symmetry (Figure 8.6.4.1). The splitting pattern of a tetrahedral complex is exactly opposite to the octahedral case. In the case of a tetrahedron, however, the "g" subscripts are inappropriate because of the tetrahedron's lack of a center of inversion, and transitions between the terms in a tetrahedron do not violate the Laporte Rule.

Another way to explain this in terms of electron transitions between orbitals is through the orbital mixing required to form a tetrahedral complex. Orbital types (i.e., s, p, d) must mix to form the moleculare orbitals of a tetrahedral transition metal complex. The mixing of s and p orbitals with the d orbitals allows transitions that are forbidden in the case of pure d-orbitals.

It is also worth noting that $\Delta_t = \frac{4}{9}\Delta_o$. The smaller Δ for transition metals means that the tetrahedral complexes can absorb at a lower energy and longer wavelength relative to an analogous octahedron.

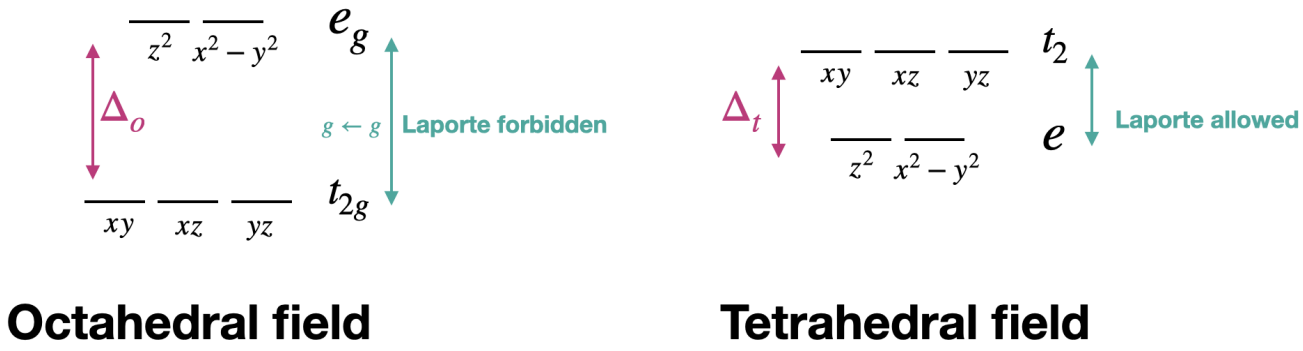

Figure 8.6.4.1: $d-d$ transitions in octahedral complexes are Laporte-forbidden, while those in tetrahedral complexes are Laporte-allowed. (CC_BY_SA; Kathryn Haas)

Tanabe-Sugano diagrams for tetrahedral complexes

Due to the opposite splitting pattern, the transitions for a d^n tetrahedral complex are sufficiently represented by the d^{10-n} Tanabe-Sugano diagram (just drop the g subscripts from the diagrams). For example, the electronic spectrum of a d^8 tetrahedral complex (e.g., $[\mathrm{Ni(H_2O)_6}]^{2+}$) can be interpreted using the d^2 Tanabe-Sugano diagram.