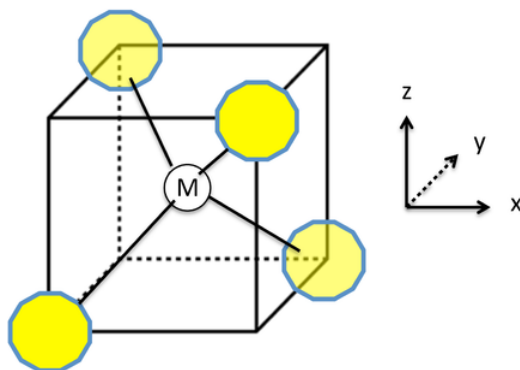


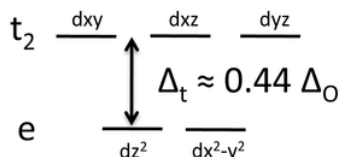
5.9: Tetrahedral Complexes

Tetrahedral complexes are formed with late transition metal ions (Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+}) and some early transition metals (Ti^{4+} , Mn^{2+}), especially in situations where the ligands are large. In these cases the small metal ion cannot easily accommodate a coordination number higher than four. Examples of tetrahedral ions and molecules are $[\text{CoCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$, and TiX_4 (X = halogen). Tetrahedral coordination is also observed in some oxo-anions such as $[\text{FeO}_4]^{4-}$, which exists as discrete anions in the salts Na_4FeO_4 and Sr_2FeO_4 , and in the neutral oxides RuO_4 and OsO_4 . The metal carbonyl complexes $\text{Ni}(\text{CO})_4$ and $\text{Co}(\text{CO})_4^-$ are also tetrahedral.

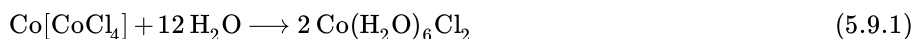


The splitting of the d-orbitals in a tetrahedral crystal field can be understood by connecting the vertices of a tetrahedron to form a cube, as shown in the picture at the left. The tetrahedral M-L bonds lie along the body diagonals of the cube. The d_{z^2} and $d_{x^2-y^2}$ orbitals point along the cartesian axes, i.e., towards the faces of the cube, and have the least contact with the ligand lone pairs. Therefore these two orbitals form a low energy, doubly degenerate e set. The d_{xy} , d_{yz} , and d_{xz} orbitals point at the edges of the cube and form a triply degenerate t_2 set. While the t_2 orbitals have more overlap with the ligand orbitals than the e set, they are still weakly interacting compared to the e_g orbitals of an octahedral complex.

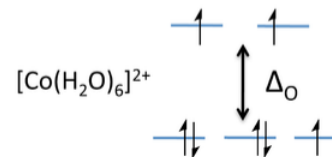
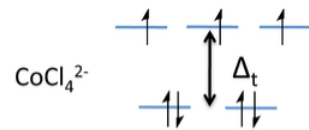
The resulting crystal field energy diagram is shown at the right. The splitting energy, Δ_t , is about 4/9 the splitting of an octahedral complex formed with the same ligands. For 3d elements, Δ_t is thus small compared to the pairing energy and their tetrahedral complexes are always high spin. Note that we have dropped the "g" subscript because the tetrahedron does not have a center of symmetry.



Tetrahedral complexes often have **vibrant colors** because they **lack the center of symmetry** that forbids a d-d* transition. Because the low energy transition is allowed, these complexes typically absorb in the visible range and have extinction coefficients that are 1-2 orders of magnitude higher than the those of the corresponding octahedral complexes. An illustration of this effect can be seen in Drierite, which contains particles of colorless, anhydrous calcium sulfate (gypsum) that absorbs moisture from gases. The indicator dye in Drierite is cobalt (II) chloride, which is a light pink when wet (octahedral) and deep blue when dry (tetrahedral). The reversible hydration reaction is:



(**deep blue**, tetrahedral CoCl_4^{2-}) (**light pink**, octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$)



This page titled [5.9: Tetrahedral Complexes](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Chemistry 310 \(Wikibook\)](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.