

## 8.4.3: Factors That Affect Ligand Field Splitting

### Magnitude of Ligand Field Splitting

The magnitude of the ligand field splitting ( $\Delta$ ) dictates whether a complex with four, five, six, or seven d electrons (in an octahedral complex) is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of  $\Delta$  (i.e.,  $\Delta > P$ ) yield a low-spin complex, whereas small values of  $\Delta$  (i.e.,  $\Delta < P$ ) produce a high-spin complex. The magnitude of  $\Delta$  depends on four factors: the valence of the metal, the principal quantum number of the metal (and thus its location in the periodic table), the geometry, and the nature of the ligand(s). Values of  $\Delta$  for some representative transition metal complexes are given in Table 8.4.3.1.

Table 8.4.3.1: Ligand Field Splitting Energies for Some Octahedral ( $\Delta_o$ )\* and Tetrahedral ( $\Delta_t$ ) Transition-Metal Complexes

Octahedral Complexes	$\Delta_o$ ( $\text{cm}^{-1}$ )	Octahedral Complexes	$\Delta_o$ ( $\text{cm}^{-1}$ )	Tetrahedral Complexes	$\Delta_t$ ( $\text{cm}^{-1}$ )
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	20,300	$[\text{Fe}(\text{CN})_6]^{4-}$	32,800	$\text{VCl}_4$	9010
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	12,600	$[\text{Fe}(\text{CN})_6]^{3-}$	35,000	$[\text{CoCl}_4]^{2-}$	3300
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	18,900	$[\text{CoF}_6]^{3-}$	13,000	$[\text{CoBr}_4]^{2-}$	2900
$[\text{CrCl}_6]^{3-}$	13,000	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	9300	$[\text{CoI}_4]^{2-}$	2700
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	13,900	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	27,000		
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17,400	$[\text{Co}(\text{NH}_3)_6]^{3+}$	22,900		
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21,500	$[\text{Co}(\text{CN})_6]^{3-}$	34,800		
$[\text{Cr}(\text{CN})_6]^{3-}$	26,600	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	8500		
$\text{Cr}(\text{CO})_6$	34,150	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	10,800		
$[\text{MnCl}_6]^{4-}$	7500	$[\text{RhCl}_6]^{3-}$	20,400		
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	8500	$[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$	27,000		
$[\text{MnCl}_6]^{3-}$	20,000	$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34,000		
$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$	21,000	$[\text{Rh}(\text{CN})_6]^{3-}$	45,500		
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	10,400	$[\text{IrCl}_6]^{3-}$	25,000		
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	14,300	$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41,000		

\*Energies obtained by spectroscopic measurements are often given in units of wave numbers ( $\text{cm}^{-1}$ ); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters:  $1 \text{ cm}^{-1} = 11.96 \text{ J/mol}$ .

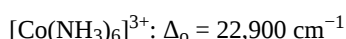
Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

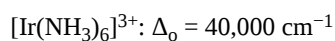
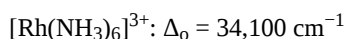
### Valence of the metal

Increasing the valence of a metal ion has two effects: the radius of the metal decreases and ligands are more strongly attracted to it due to Coulombic attraction. Both factors decrease the metal–ligand distance, which in turn causes the ligands to interact more strongly with the d-orbitals. Consequently, the magnitude of  $\Delta_o$  increases as the valence of the metal increases. Typically,  $\Delta_o$  for a M(III) is about 50% greater than for the M(II) of the same metal; for example, for  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $\Delta_o = 11,800 \text{ cm}^{-1}$ ; for  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ ,  $\Delta_o = 17,850 \text{ cm}^{-1}$ .

### Principal quantum number of the metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of  $\Delta_o$  increases with increasing principal quantum number:  $\Delta(3d) < \Delta(4d) < \Delta(5d)$ . The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:





The increase in  $\Delta$  with increasing principal quantum number is due to the larger [radial extension of the d orbitals as n increases](#). In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions. The increase in  $\Delta$  going from 3d to 4d and 5d is so large that all 4d and 5d metals will form low spin complexes.

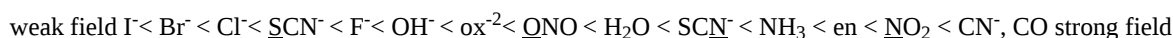
### Geometry of the complex

The number of ligands in a complex as well as how well the ligand geometry overlaps with the d orbitals is also a factor in the magnitude of the ligand field splitting. For example, comparing octahedral and tetrahedral geometries the octahedral geometry has 6 ligands, and those 6 ligands overlap directly with the two d orbitals that lie along the axes,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The tetrahedral geometry has fewer ligands than octahedral, and those ligands overlap less ideally with the ligands that lie between the axes,  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ . Because of this the ligand field splitting of a tetrahedral complex is generally less than half ( $\frac{4}{9}$  than an octahedral complex with the same metal and ligands. For example  $[\text{FeCl}_4]^-$  has a  $\Delta_t = 5,200 \text{ cm}^{-1}$  and  $[\text{FeCl}_6]^{3-}$  has a  $\Delta_o = 11,600 \text{ cm}^{-1}$ .

### Nature of the ligands

In crystal field theory ligands are all modeled as negative point charges, which means that all ligands should behave identically. Experimentally, it is found that the  $\Delta_o$  observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of  $\Delta_o$  decreases as the size of the donor atom increases. For example,  $\Delta_o$  values for halide complexes generally decrease in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$  because smaller, more localized charges, such as we see for F, interact more strongly with the d-orbitals of the metal. In addition, a small neutral ligand with a highly localized lone pair, such as  $\text{NH}_3$ , results in significantly larger  $\Delta_o$  values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series.

Ligands are classified as strong field or weak field based on the spectrochemical series:



Note that  $\text{SCN}$  and  $\text{NO}_2$  ligands are represented twice in the above spectrochemical series since there are two different Lewis base sites (e.g., free electron pairs to share) on each ligand (e.g., for the  $\text{SCN}$  ligand, the electron pair on the sulfur or the nitrogen can form the bond to a metal). The specific atom that binds in such ligands is underlined. Ligands on the weak field end of the series (halogens,  $\text{OH}$ ,  $\text{H}_2\text{O}$ ) will tend to form high spin complexes and ligands on the strong field end of the series ( $\text{CN}$ ,  $\text{CO}$ ,  $\text{NO}_2$ ) will tend to form low spin complexes. Intermediate ligands in the middle of the series could form high or low spin complexes depending on other factors.

#### How to determine if a complex is high or low spin

- How many d electrons does the complex have?
  - Only complexes with 4-7 d electrons have high spin and low spin configurations
- What period is the metal?
  - 3d metals could either be high or low spin
  - 4d and 5d metals will ALWAYS be low spin
- What is the geometry of the complex?
  - Tetrahedral complexes with 3d metals will almost always be high spin because  [\$\Delta\_t\$  is generally less than spin pairing energy](#)
  - Square planar complexes will almost always be low spin because they are favored over tetrahedral [when crystal field splitting is large](#)
  - Octahedral complexes could be either high or low spin
- What are the ligands?
  - Strong field ligands will form low spin complexes
  - Weak field ligands will form high spin complexes

- Intermediate field ligands could form high or low spin complexes. Additional information (like number of unpaired electrons) is needed

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