

## 5.10: Stability of Transition Metal Complexes

The crystal field stabilization energy (**CFSE**) is an important factor in the stability of transition metal complexes. Complexes with high CFSE tend to be **thermodynamically** stable (i.e., they have high values of  $K_a$ , the equilibrium constant for metal-ligand association) and are also **kinetically** inert. They are kinetically inert because ligand substitution requires that they *dissociate* (lose a ligand), *associate* (gain a ligand), or *interchange* (gain and lose ligands at the same time) in the transition state. These distortions in coordination geometry lead to a large **activation energy** if the CFSE is large, even if the product of the ligand exchange reaction is also a stable complex. For this reason, complexes of  $\text{Pt}^{4+}$ ,  $\text{Ir}^{3+}$  (both low spin  $5d^6$ ), and  $\text{Pt}^{2+}$  (square planar  $5d^8$ ) have very slow ligand exchange rates.

There are two other important factors that contribute to complex stability:

- **Hard-soft interactions** of metals and ligands (which relate to the **energy** of complex formation)
- The **chelate effect**, which is an **entropic** contributor to complex stability.

### Hard-soft interactions

Hard acids are typically small, high charge density cations that are weakly polarizable such as  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ , and  $\text{Cr}^{6+}$ . *Electropositive metals in high oxidation states* are typically hard acids. These elements are predominantly found in oxide minerals, because  $\text{O}^{2-}$  is a hard base.

Some hard bases include  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NH}_3$ .

The hard acid-base interaction is primarily **electrostatic**. Complexes of hard acids with hard bases are stable because of the electrostatic component of the CFSE.

Soft acids are large, polarizable, *electronegative metal* ions in *low oxidation states* such as  $\text{Ni}^0$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ , and  $\text{Au}^+$ .

Soft bases are anions/neutral bases such as  $\text{H}^-$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}$ ,  $\text{PR}_3$ ,  $\text{R}_2\text{S}$ , and  $\text{CN}^-$ . Soft acids typically occur in nature as sulfide or arsenide minerals.

The bonding between soft acids and soft bases is predominantly **covalent**. For example, metal carbonyls bind through a covalent interaction between a zero- or low-valent metal and neutral CO to form  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Co}(\text{CO})_4^-$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{W}(\text{CO})_6$ , and related compounds.

The preference for hard-hard and soft-soft interactions ("like binds like") is nicely illustrated in the properties of the copper halides:

- $\text{CuF}$ : unstable
- **$\text{CuI}$ : stable**
- **$\text{CuF}_2$ : stable**
- $\text{CuI}_2$ : unstable

The compounds  $\text{CuF}$  and  $\text{CuI}_2$  have never been isolated, and are thermodynamically unstable to disproportionation:



We will learn more about quantifying the energetics of these compounds in Chapter 9.

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