Stability of Coordination Compounds

When the term stability is applied to coordination compounds (metal complexes) there can be two interpretations, thermodynamic or kinetic stability. Thermodynamic stability refers to the change in energy on going from reactants to products, i.e., \( \Delta G \) for the reaction. Recall that \( \Delta G = \Delta H - T \Delta S = -RT \ln K \), where \( \Delta H \) is the enthalpy, \( \Delta S \) the entropy and \( K \) is the equilibrium constant for the reaction. Kinetic stability refers to reactivity, generally ligand substitution. Substitution occurs extremely rapidly in some cases and extremely slowly in others. Complexes of the former type are referred to as labile and those of the latter type inert. Sometimes these two types of stability parallel one another, but often they do not, *vide infra*.

Thermodynamic stability often refers to the energetics and associated equilibrium constant for the reaction of an aquated metal ion with some other ligand (other than water).

\[
[Cu(OH_2)_4]^{2+} + 4 NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4 H_2O
\]

The overall equilibrium constant expression for this reaction, generally referred to as \( \beta_4 \), is defined in the usual fashion as \( \beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4} \). Note that overall equilibrium constants are designated as \( \beta \)'s and values for individual (step-wise) reactions as \( K \)'s. For simplicity the water molecules associated with the \( Cu^{2+} \) have been deleted. This reaction can be described as four individual reactions with individual step-wise equilibrium constants \( K_1, K_2, \ldots, K_4 \), i.e.,

\[
[Cu(OH_2)_4]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)_3(NH_3)]^{2+} + H_2O \quad \log K_1 = 4.22
\]
\[
[Cu(OH_2)_3(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)_2(NH_3)_2]^{2+} + H_2O \quad \log K_2 = 3.50
\]
\[
[Cu(OH_2)_2(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)(NH_3)_3]^{2+} + H_2O \quad \log K_3 = 2.92
\]
\[
[Cu(OH_2)(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + H_2O \quad \log K_4 = 2.18
\]

The decrease in successive step-wise constants is invariably observed and is due to several factors including statistics (number of replaceable positions), and increased steric interactions between the new ligands. Overall equilibrium \( \beta \) values from 1 to 4 can be defined as \( K_1, K_1K_2, K_1K_2K_3, \) and \( K_1K_2K_3K_4 \).

The speciation of copper(II) as a function of free ammonia concentration is shown in the Figure.
Equilibrium constants defined as shown above are termed formation constants or stability constants. Those for the reverse reaction are instability or dissociation constants. There can be some confusion here because in certain areas of chemistry and biology the term “stability constant” actually is defined as the dissociation constant.

The stability of the complex of a metal ion with a bidentate ligand such as ethylenediamine (en) is invariably significantly greater than the complex of the same ion with two monodentate ligands of comparable donor ability, i.e., for example two ammonia molecule. The is illustrated by the following data:

\[
\begin{align*}
[Cu(OH_2)_4]^{2+} + en &\rightleftharpoons [Cu(OH_2)_2(en)]^{2+} + 2 H_2O & \log K_1 &= 10.6 \\
\Delta H &= -54 \text{ kJ mol}^{-1}, \Delta S = 23 \text{ J K}^{-1} \text{ mol}^{-1}
\end{align*}
\]

\[
\begin{align*}
[Cu(OH_2)_4]^{2+} + 2 NH_3 &\rightleftharpoons [Cu(OH_2)_2(NH_3)_2]^{2+} + 2H_2O & \log \beta_2 &= 7.7 \\
\Delta H &= -46 \text{ kJ mol}^{-1}, \Delta S = -8.4 \text{ J K}^{-1} \text{ mol}^{-1}
\end{align*}
\]

This greater stability for complexes of chelate complexes is termed the **chelate effect**. Its origin is primarily in the differences in entropy between chelate and non-chelate complex reactions. The formation of chelate complexes results in greater disorder because of the formation of a larger number of free particles in the products whereas there is no change in the number of particles in the formation of comparable non-chelate complexes.

Ligand exchange is a good way to examine kinetic stability without complications from changes in $\Delta H$ for the reaction. Water exchange rates have been determined for a wide range of metal ions and oxidation states. A selection of these is given in the Table (next page). Although the absolute rate of exchange will differ for other ligands the values in the table can be used to gauge the relative reactivity of two metal ions or two different oxidation states of the same metal. There are several observations/conclusions that can be made from these data but before stating some of these some comments concerning the mechanism of these reactions are in order.

There are two limiting mechanisms for substitution reactions of coordination complexes, associative, which corresponds to the $S_N2$ reaction in organic chemistry, and dissociative, which corresponds to the $S_N1$ reaction in organic chemistry. Ligand exchange is a category of substitution reaction. In the limiting case of an associative reaction the entering ligand begins to interact with the metal as the bond to the departing ligand (leaving group) lengthens. In order for the entering ligand to bond to the metal there must be a vacant (preferably) or partially vacant orbital that is accessible to the entering ligand. In an octahedral complex only the $t_{2g}$ d orbitals are accessible as the $e_g$ orbitals and the $n+1$ s and p orbitals are blocked by the presence of the original six ligands. Associative processes are more likely for larger metal ions than for smaller so that they are more important early in a transition series and for heavier members of a family.
In the limiting case the dissociative process involves the formation of a five-coordinate intermediate as a result of complete bond dissociation to the departing ligand (leaving group). The five-coordinate intermediate then reacts with the new ligand (entering group) to reform a six-coordinate complex.

There are many subtleties to mechanisms of substitution of coordination complexes including simultaneous reaction by both pathways, but in the limit the associative mechanism is a second order reaction, first order in both complex and entering group (L), i.e., \( \text{rate} = k[\text{complex}][L] \). Dissociative processes are first order in complex only since the entering group is not involved in the rate limiting step, which is bond cleavage between the metal ion and the leaving group. The rate law is then rate = \( k[\text{complex}] \).

<table>
<thead>
<tr>
<th>([\text{ML}_n(\text{OH}_2)]^{n+})</th>
<th>(k/\text{s}^{-1})</th>
<th>([\text{ML}_n(\text{OH}_2)]^{n+})</th>
<th>(k/\text{s}^{-1})</th>
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<tr>
<td>([\text{Ti}(\text{OH}_2)_6]^{3+})</td>
<td>1.8 x 10^5</td>
<td>([\text{V}(\text{OH}_2)_6]^{3+})</td>
<td>5.0 x 10^2</td>
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<tr>
<td>([\text{Cr}(\text{OH}_2)_6]^{2+})</td>
<td>&gt;10^8</td>
<td>([\text{Cr}(\text{OH}_2)_6]^{3+})</td>
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<tr>
<td>([\text{Mn}(\text{OH}_2)_6]^{2+})</td>
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<td>([\text{Mn}(\text{OH}_2)_6]^{3+})</td>
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<td>([\text{Fe}(\text{OH}_2)_6]^{3+})</td>
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<td>([\text{Ru}(\text{OH}_2)_6]^{2+})</td>
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<td>([\text{Zn}(\text{OH}_2)_6]^{3+})</td>
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</tr>
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</table>

\(^a\)All rate constants are expressed as first order rate constants for comparative purposes even though some reactions are associative.
(1) An increase in oxidation state for the metal reduces the rate of exchange although there are obvious exceptions to this as indicated by the data for V(II) and V(III), and the exchange rate for Ti(III) appears very large compared to those of other trivalent ions (and even some divalent ions). The reason for this is that there is a large degree of associative character to reactions of the larger elements in a transition series and the activation energy for these reactions is directly related to the occupancy of the $t_{2g}$ orbitals. Ti(III) has only one $t_{2g}$ electron and V(III) only two, whereas V(II) has three $t_{2g}$ electrons.

(2) The fact that water exchange occurs more rapidly in $[\text{Rh(NH}_3)_5\text{OH}_2]^{3+}$ than in the corresponding Co(III) complex is attributed to a change in mechanism for the larger rhodium complex. There are two reasons for this. First, the much smaller Co$^{3+}$ ion (0.53 Å) can only react by a dissociative process, whereas the $t_{2g}$ orbitals of the larger rhodium ion (0.67 Å, Ir$^{3+}$ = 0.73 Å) are accessible to the entering group. Also bond strengths increase on going to heavier members of a family so that dissociative processes are necessarily slower.

(3) The much slower substitution of V(II) relative to the other first-row, divalent elements is also related to the absence of any $e_g$ electrons. In the crystal field model the presence of $e_g$ electrons means that there are increased electron-electron repulsions with ligand electron pairs and therefore longer and weaker bonds. In the molecular orbital model the $e_g$ orbitals are antibonding with respect to the metal-ligand interaction and the presence of electrons in these orbitals reduces the bond order for the metal-ligand interaction.

This point is also dramatically illustrated for the Fe(II)/Ru(II) and Ni(II)/Pd(II) complexes. The Fe(II), which is high spin, has two $e_g$ electrons, whereas the Ru(II) complex is low-spin and therefore has no $e_g$ electrons. Spin pairing in the Ru(II) complex is a result of the increased strength of its interaction with the six ligands, which also contributes to its decreased reactivity. The Ni(II) complex also has two $e_g$ electrons, whereas the four-coordinate, planar Pd(II) complex, like all planar d$^8$ complexes is diamagnetic. Clearly there are multiple effects here, but the absence of antibonding electrons and the greater metal-ligand bond strength are important contributors to the much lower reactivity of the Pd complex. Note that the reactivity of the Pt analog is still lower.

In the introduction it was indicated that thermodynamic stability and kinetic stability often parallel one another but that sometimes they do not. A vivid illustration of a case where they do not parallel one another is illustrated by the formation constant and ligand exchange rate constant for $[\text{Ni(CN)}_4]^{2-}$. The second order rate constant for CN$^-$ exchange is >5 x 10$^5$ M$^{-1}$ s$^{-1}$. However the complex is very stable since

\[
\beta_4 = \frac{[\text{Ni(CN)}_4]^{2-}}{[\text{Ni(OH}_2)_6]^{2+}][\text{CN}^-]^4} = 1.3 \times 10^{30}.
\]

The high rate of ligand exchange is not so surprising when one considers that both axial
positions in the square-planar complex are accessible and that salts of the square-pyramidal complex \([\text{Ni(CN)}_5]\) have been crystallized (and structurally characterized by x-ray diffraction).