A Study of the origin of the chelate effect

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Abstract : A chelate is a type of ligand. A multidentate (*dentate* is Latin for tooth) ligand that uses more than one atom to bind to a metal in a coordination complex, The metal is the electron-pair acceptor and the <u>chelating agent</u> the electron-pair donor. When binding to the <u>metal ion</u>, the chelate (ligand) forms a ring of atoms, of which the metal is one member. The chelate complex charge exactly neutralizes the charge on the metal ion. Most rings contain >4 and <8 atom members; the most stable typically is a 5-membered ring. Bidentate describes a chelate where two atoms from the chelate complex bond to the metal and tridentate would indicate three coordinating atoms. Many chelating extractants are weak acids, therefore, control of pH is important in many extracting schemes.

Key Words : chelate, Monodentate ligands, Bidentate ligands

Introduction

Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed". The halides, phosphines, ammonia and amines seen previously are monodentate ligands.

Bidentate ligands bind through two donor sites. Bidentate means "two-toothed". An example of a bidentate ligand is bis(dimethylphosphino) propane. It can bind to a metal via two donor atoms at once: it uses one lone pair on each phosphorus atom.
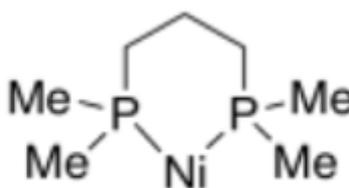
The Chelate Effect

Chelating ligands have higher affinity for a metal ion than analogous monodentate ligands. The **chelate effect** is the enhanced affinity of a chelating ligand for a metal ion compared to its monodentate ligand counterpart(s). This term comes from the Greek chelos, meaning "crab". A crab does not have any teeth at all, but it does have two claws for tightly holding onto something. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) is a bidentate ligand that binds metal ions more strongly than monodentate amine ligands like ammonia (NH_3) and methylamine (CH_3NH_2). Tridentate ligands, which bind through three donors, can bind even more tightly than bidentate, and so on.

Chemical reasoning for the Chelate Effect

The chelate effect can be explained using principles of thermodynamics. Recall that reactions are spontaneous when the Gibbs Free Energy change is negative $-\Delta G - \Delta G$; this is true when change in enthalpy is negative $(-\Delta H - \Delta H)$ and the change in entropy is positive (disorder increases, $+\Delta S + \Delta S$. (From the equation $\Delta G = \Delta H - T\Delta S \Delta G = \Delta H - T\Delta S$.)
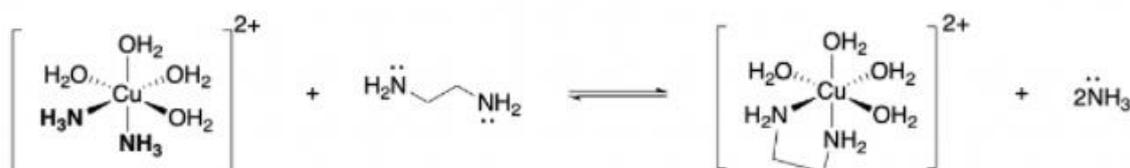
Consider the reaction shown below:

Figure 3.1.2.43.1.2.4: A reaction where one ethylenediamine (en) ligand replaces two ammonia ligands in a Cu(II) complex. The equilibrium constant for this reaction is approximately 1000 $(K \approx \approx 10^3)$, and so the equilibrium lies to the right.

Enthalpy

In each the reactant Cu complex and product Cu-complex in Figure 3.1.2.43.1.2.4, there are two N-Cu bonds. Electronically, the ammonia and en ligands are very similar, since both bind through N and since the Lewis base strengths of their nitrogen atoms are similar. The enthalpy change due to breaking two H_3N-Cu bonds and replacing them with two new N(en)-C bonds is almost zero. Thus, *enthalpy is <u>not</u> a major driving factor in the chelate effect.*
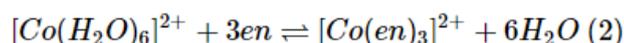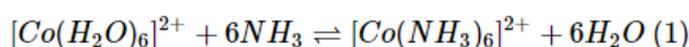
Entropy

In terms of entropy (disorder) there are two things to consider:

(1) The entropy from free rotation of the chelator. The chelator becomes somewhat constrained upon binding to the metal, and so this would result in small entropic penalty (loss in entropy). This is worth noting, but is a relatively small effect.

(2) The entropy from change in the number of molecules that can move freely. When a chelating ligand replaces several monodentate ligands, the result is an increase in the number of free molecules in the system, meaning a relatively large increase in entropy. This is the major energetic factor driving the chelate effect.

For example, when en replaces two ammonia ligands (Figure 3.1.2.43.1.2.4), the number of total molecules increases from two to three. Increasing the number of molecules by just one is enough to drive the reaction forward.

The example above gives a case when just one bidentate ligand is involved. When multiple bidentate ligands are involved, or when denticity increases, the chelate effect is enhanced further. Consider the two complexation equilibria in aqueous solution, between the cobalt (II) ion, Co^{2+}(aq) and ethylenediamine (en) on the one hand and ammonia, NH_3, on the other.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O \ (1)$$

$$[Co(H_2O)_6]^{2+} + 3en \rightleftharpoons [Co(en)_3]^{2+} + 6H_2O \ (2)$$

This means that ΔH must be very similar for the two reactions, since six Co-N bonds are formed in each case. Interestingly however, we observe that the equilibrium constant is *100,000 times larger* for the second reaction than it is for the first.

The big difference between these two reactions is that the second one involves "condensation" of *fewer particles* to make the complex. This means that the **entropy changes** for the two reactions are different. The first reaction has a ΔS value close to zero, because there is the same number of molecules on both sides of the equation. The second one has a positive ΔS° because four molecules come together but seven molecules are produced. The difference between them (ΔΔS) is about +100 J/mol-K. We can translate this into a ratio of equilibrium constants using:
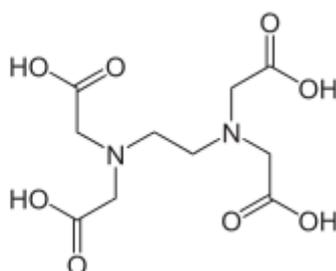
$$K_f(en)/K_f(NH_3) = e^{-\Delta\Delta G°/RT} \approx e^{+\Delta\Delta S°/R} \approx e^{12} \approx 10^5$$

Conclusion : The bottom line is that the chelate effect is **entropy-driven**. It follows that the more binding groups a ligand contains, the more positive the ΔS° and the higher the K_f will be for complex formation. In this regard, the hexadentate ligand ethylenediamine tetraacetic acid (EDTA) is an optimal ligand for making octahedral complexes because it has six binding groups. In basic solutions where all four of the COOH groups are deprotonated, the **chelate effect** of the $EDTA^{4-}$ ligand is approximately 10^{15}. This means, for a given metal ion, K_f is 10^{15} times larger for $EDTA^{4-}$ than it would be for the relevant monodentate ligands at the same concentration. $EDTA^{4-}$ tightly binds essentially any 2+, 3+, or 4+ ion in the periodic table and is a very useful ligand for both analytical applications and separations.

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