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 ethylenediamine. It can bind to a metal via two donor atoms at once.

Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "chelate effect." 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 for a couple of reasons. 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.

Note

Multidentate ligands bind more tightly because of the chelate effect.

The chemical reasons for the chelate effect involve relative enthalpy and entropy changes upon binding a multidentate ligand. In terms of enthalpy, in order to completely remove a bidentate ligand, two coordinate bonds must be broken. That costs more energy than breaking one coordinate bond for a monodentate ligand.

In terms of entropy, which deals with the distribution of energy within a system, it is generally thought that bringing two molecules together (a bidentate ligand and a metal complex) costs less than bringing three molecules together (two monodentate ligands and a metal complex). That's because individual molecules are free to move around, tumble and vibrate independently. Once they come together, they have to do all these things together. Since these different types of motion represent different ways of distributing energy, if the system becomes more restricted, energy can't be distributed in as many states.

- Energy is lowered even more by two bonding interactions
- Compared to two separate donors, bidentate donation is entropically favoured

Example CC5.1.

Draw metal complexes using the ligands below and metal ions of your choice.
Example CC5.2.

One of the most common multidentate ligands is the cyclopentadienyl anion, often abbreviated Cp.

\[
\begin{array}{c}
\text{Cp} \\
\text{cyclopentadienyl anion (Cp)}
\end{array}
\]

1. CpH is easily deprotonated to form Cp\(^{-}\). Explain why.
2. How many electrons does Cp donate to a metal?
3. The archetypal Cp complex is ferrocene, Cp\(_2\)Fe, the structure of which was determined by Geoff Wilkinson, in work that led to him being awarded the Nobel Prize in 1973. Draw the structure of ferrocene.
4. Count the electrons on the iron in ferrocene.

Example CC5.3.

Explain the differences seen in the equilibrium constants for the formation of silver(I) complexes with the following alkenes:
1. \(\text{CH}_2\text{CHCHCH}_2\): \(K = 4.2\)
2. \(\text{CH}_2\text{CHCH}_2\text{CHCH}_2\): \(K = 10.2\)
3. \(\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CHCH}_2\): \(K = 28.8\)

There is some commonly used jargon used to describe how a potentially multidentate ligand is bound to a metal. One of these terms is "eta," Greek η, and the other is "kappa," Greek \(\kappa\). The first term, η, refers to the number of contiguous atoms in the ligand that are bound at the same time. That means the number of atoms in a row that are all directly bound to the metal. For example, an alkene which donates a pi bond is always bound η-2. Because the two carbons at either end of the double bond are already sharing the π electrons, then if the π electrons are donated to the metal, both of those carbons are bound directly to the metal.

The second term in common use, κ, simply describes how many atoms are bound to the metal. The atoms don't have to be next to each other. For example, in ethylenediamine or 1,2-diaminoethane, \(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\), the two nitrogen atoms can be bound to the metal at the same time, but none of the other atoms in between would be directly attached to the metal.

Problem CC5.4.

For each of the structures in Problems CC5.1 and CC5.2, describe the binding mode (for example, it is η² or it is κ³, etc).

Contributors

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