

Lecture 9: Complexation Reactions and Metal Ion Speciation

Outline

1. Aqueous complexes and their components (ligands and metal ions)
2. Environmental importance of complexes in natural and engineered systems
3. Types of complexes
4. Factors that impact metal-ligand interactions
5. Complexation equilibrium constants

Aqueous complexes and their components (ligands and metal ions)

Complexes consist of a central metal ion and one or more ligands

Central metal ion

- has a positive charge
- acts as a Lewis acid (accepts electrons to form a chemical bond)
- defined by a *coordination number* (C_N) – number of ligands with which it is able to form bonds

Ligand – organic or inorganic compound that complexes a metal ion and acts as a Lewis base (donates electrons)

- have one or more pairs of electrons that are available to form bonds with metal ions (that is, not already in a bond)
- common examples include Cl^- , OH^- , CO_3^{2-} , NH_3 , organic molecules (CH_3COO^-)
- the most common ligand is H_2O ; metal ions are usually complexed by water molecules in solution, e.g., Zn^{2+} would actually be $\text{Zn}(\text{H}_2\text{O})_4^{2+}$

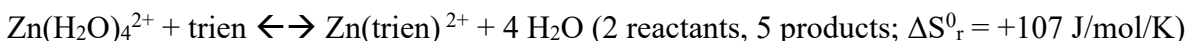
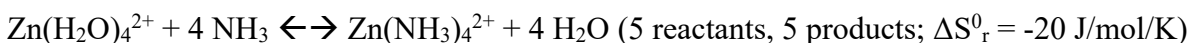
Monodentate ligand – one pair of electrons available to bond; e.g., Cl^-

Bidentate ligand – two pairs of electrons available to bond; e.g., oxalate, $\text{C}_2\text{O}_4^{2-}$

Multidentate ligand – more than one pair of electrons able to bond (unspecified number)

Chelates – ligands with two or more binding sites that form a ring structure around the central metal ion; “claws”

Binding strength between the ligand and ion tends to increase with increasing number of binding sites due to *entropy*. Compare the reactions between complexation of Zn^{II} by ammonia (monodentate) and by the organic chelator, trien (4 binding sites):



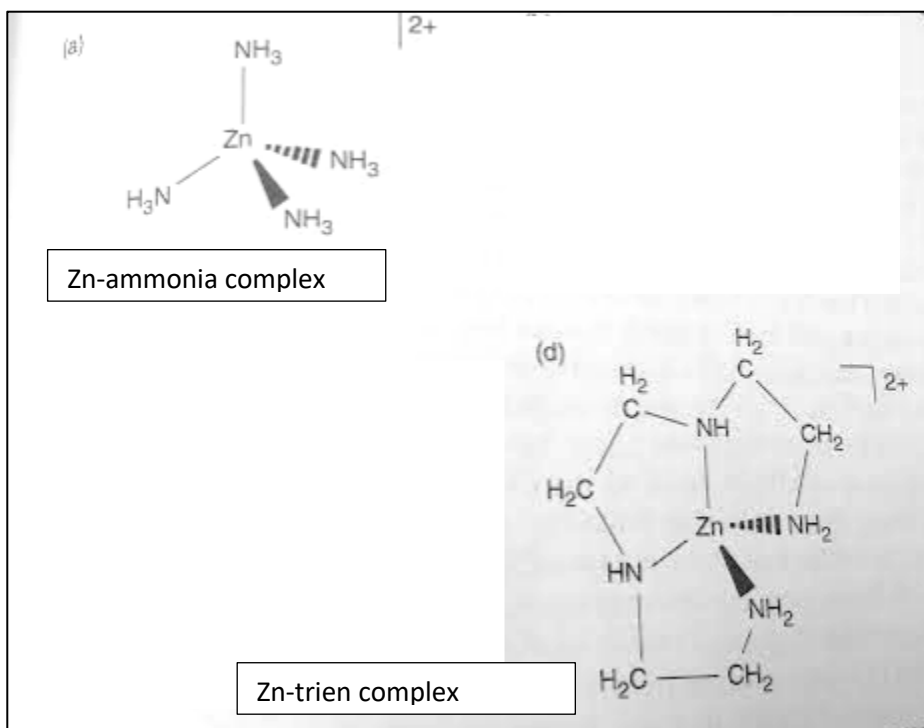
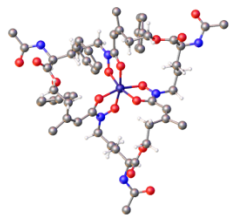


Figure 9.1

Environmental importance of complexes in natural and engineered systems

Why are complexes important in the environment?

1. Affects chemical behavior, for example, by changing net charge
 - a. E.g., the dominant form of Au^{3+} in the oceans is the complex $\text{Au}(\text{Cl})_4^-$
2. Can make a metal ion more or less sensitive to oxidation/reduction reactions
3. Complexation can keep metals soluble
 - a. E.g., Fe^{3+} is insoluble (forms $\text{Fe}(\text{OH})_3$) unless it's complexed by organic molecules such as siderophores (used by plants and microbes)



Siderophores: red = oxygen; gray = carbon; blue = nitrogen; dark blue=iron

4. Can increase or decrease bioavailability and toxicity
 - a. E.g., Al^{3+} is soluble at low pH and highly toxic, but toxicity is mitigated by complexation with F^- ions
5. Can increase mineral dissolution by removing dissolution products from the system

Types of complexes

1. Inner sphere complexes

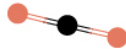

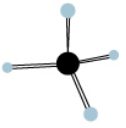

2. Outer sphere complexes

Inner sphere complexes

- “true” bonding; electron orbitals of the metal ion and ligand overlap
- NOT a covalent bond; electrons only come from one atom (the ligand)
- ligand atoms replace waters of hydration that surround a central metal ion

Coordination numbers – number of bonds a central metal ion can form

- typically range from 2 to 8, can be as high as 12, but are mostly 4 and 6
- $C_N = 2$; linear complex forms
- $C_N = 4$; tetrahedral complex forms ($[\text{CuCl}_4]^{2-}$; $[\text{CoCl}_4]^{2-}$); sometimes square planar ($[\text{PtCl}_4]^{2-}$; $[\text{XeF}_4]$)
- $C_N = 6$; octahedral complex forms ($[\text{Co}(\text{NH}_3)_6]^{3+}$); bonds can be symmetric or asymmetric

Coordinated No	Shape	Image	Example
2	Linear		$[\text{CuCl}_2]$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$
4	Square Planar		$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PdCl}_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral		$[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$ $[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
6	Octahedral		$[\text{Cu}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]^+$, $[\text{Co}(\text{en})_3]^{3+}$

Outer sphere complexes (ion pairs)

- Ligands form long range electrostatic bonds with hydrated metal ions (charges attract)
- The metal ion does not lose its waters of hydration
- Bonding orbitals between metal ion and ligand do not overlap
- Typically weaker than inner sphere complexes

Factors that impact metal-ligand interactions

1. Properties of the metal ion

Class A (hard acids)

- have highly stable electron configurations that are not easily distorted by ligands
- “hard spheres”
- Form relatively weak complexes, usually with small ligands (N, O, F)

- e.g., H^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Pb^{2+} , Al^{3+}

Class B (soft acid)

- have 10-12 electrons in their outer shell that can be easily distorted by ligands
- tend to form stronger complexes where they can covalently share electrons
- e.g., Cu^+ , Ag^+ , Au^+ , Hg^{2+} , Cd^{2+}

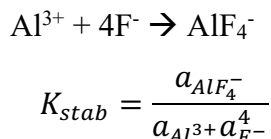
Borderline metal ions: Mn^{2+} , Fe^{2+} , Ni^{2+} , Cu^{2+}

2. Properties of the ligand

- 1) The number of binding sites – stability increases with increasing binding sites (entropy)
- 2) The size of the rings formed – steric effects limit stability (stability: five-membered ring > six-membered > seven-membered; optimal angles to provide optimal overlap of bonding orbitals); refers to the ligand's ability to adopt its preferred orientation
- 3) The nature of the ligand atom (e.g., N or O) – N tends to form stronger complexes than O

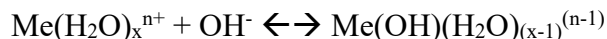
Complexation Equilibrium Constants

The stability of a given complex can be described by a stability constant, K_{stab} :

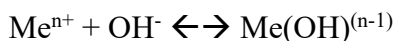


We can examine step-wise complex stability using hydroxide ions and a metal ion center (Me^{n+}):

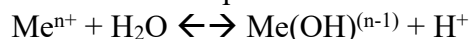
1. Hydroxide replaces a water of hydration:



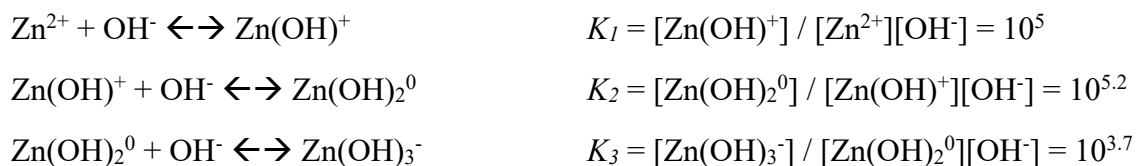
For simplicity:



This reaction can also be expressed in terms of protons:



This can happen as many times as it takes to satisfy a coordination number:



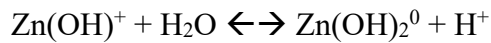
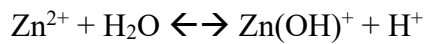


All of these species contribute to the concentration of total dissolved zinc:

$$[\text{Zn}^{\text{II}}]_{\text{T}} = [\text{Zn}^{2+}] + [\text{Zn(OH)}^+] + [\text{Zn(OH)}_2^0] + [\text{Zn(OH)}_3^-] + [\text{Zn(OH)}_4^{2-}]$$

These equations are difficult to use to predict the stability of any one given compound, so the reactions can be combined to yield a *cumulative stability constant*, β , that is expressed in terms of $[\text{H}^+]$ concentrations:

For example, combining the first two steps:



The cumulative equation becomes:

$$[\text{Zn(OH)}_2^0] = \beta_2 [\text{Zn}^{2+}] / [\text{H}^+]^2$$

So we can determine how much Zn^{2+} becomes complexed by OH^- groups *at a given pH*.