Monodentate Ligands

- *possess only one accessible donor group*

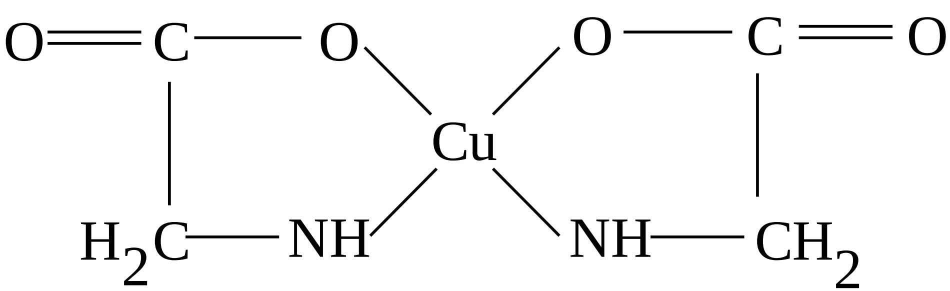
Example
*Water, H_2O - most **metal ions** exist as **aquo complexes** in water*

$Ag(H_2O)_2^+$ $Cu(H_2O)_4^{2+}$ $Fe(H_2O)_6^{3+}$

- *charge and coordination number are **NOT** related*

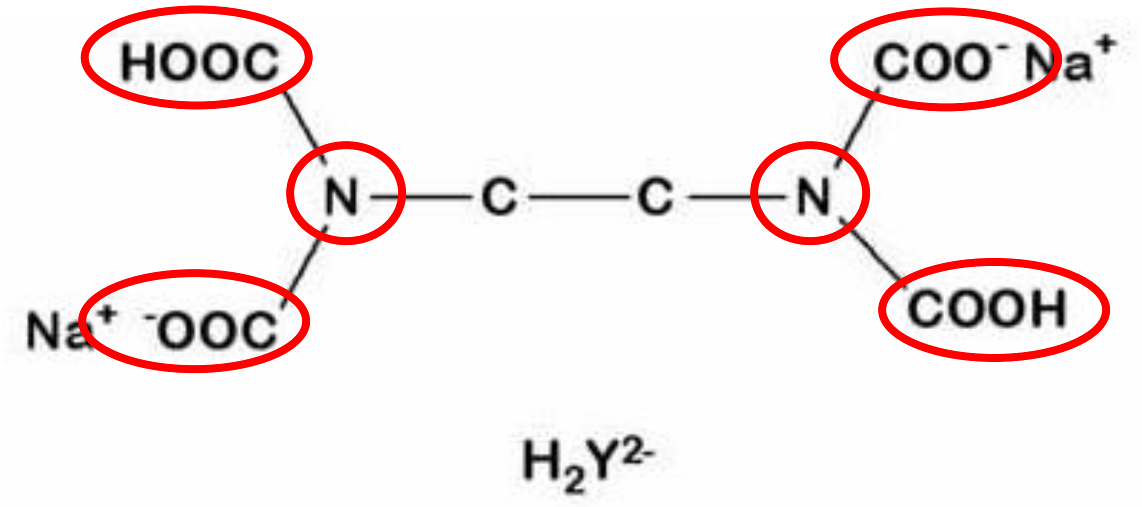
Chelate

- *complex formed when metal ion coordinates with two or more donor groups of a single ligand to form a 5- or 6-membered ring*



EDTA

- *the disodium salt is often used since it is more soluble*



- *has 6 donor groups*

Soluble Complexes

Complexation Reaction

$$M + L \leftrightarrows ML$$

$$K_f = \frac{[ML]}{[M][L]}$$

☛ K_f - *formation constant*

Distribution of Metal Among Several Complexes

Beta Expressions

- *the denominator for each beta expression is identical*

- *the denominator is an ascending power series in* **[L]**, *starting with* **$[L]^o$** *to* **$[L]^n$**

$$1 + K_{f1}[L] + K_{f1}K_{f2}[L]^2 + K_{f1}K_{f2}K_{f3}[L]^3 \ldots$$

Conditional or Effective Formation Constants

- **EDTA** *is a weak acid,* **H_6Y^{2+}**

$$c_{EDTA} = [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{c_{EDTA}}$$

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}}c_{EDTA}}$$

$$[Y^{4-}] = c_{EDTA}\alpha_{Y^{4-}}$$

$$K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]c_{EDTA}}$$

Conditional or Effective Formation Constants

Example

Calculate the conditional formation constant of **CdY^{2-}** *for both metal and ligand at the following pH values (a) pH = 5.0 (b) = 8.0. Assume that*

$\beta_{Cd^{2+}} = 4.5 \times 10^{-4}$.

EDTA *(K_{a1} = 1.0 x 10^{-2}, K_{a2} = 2.1 x 10^{-3}, K_{a3} = 7.8 x 10^{-7}, K_{a4} = 6.8 x 10^{-11})*

Conditional or Effective Formation Constants

$$\alpha_{Y^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[H_3O^+]^4 + K_{a1}[H_3O^+]^3 + K_{a1}K_{a2}[H_3O^+]^2 + K_{a1}K_{a2}K_{a3}[H_3O^+] + K_{a1}K_{a2}K_{a3}K_{a4}}$$

☛ *at pH 5.0,* $\alpha_{Y^{4-}} = 4.90 \times 10^{-7}$

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \beta_0 = (2.9 \times 10^{16})(4.9 \times 10^{-7})(4.5 \times 10^{-4})$$

$$K_f'' = 6.4 \times 10^6$$

Conditional or Effective Formation Constants

- *at pH 8.0,* $\alpha_{Y^{4-}} = 6.70 \times 10^{-3}$

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \beta_0 = (2.9 \times 10^{16})(6.7 \times 10^{-3})(4.5 \times 10^{-4})$$

$$K_f'' = 8.74 \times 10^{10}$$

Conditional or Effective Formation Constants

Example

What is the equilibrium concentration of **Ni^{2+}** *in a solution with an analytical* **NiY^{2-}** *concentration of 0.0150 M at pH (a) 3.0 and (b) 8.0?*

$$Ni^{2+} + Y^{4-} \leftrightarrows NiY^{2-}$$

$$K_{NiY^{2-}} = \frac{[NiY^{2-}]}{[Ni^{2+}][Y^{4-}]} = 4.2 \times 10^{18}$$

$$[Ni^{2+}] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y] = C_T$$

$$[Y^{4-}] = \alpha_{Y^{4-}} C_T$$

Conditional or Effective Formation Constants

$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[NiY^{2-}]}{[Ni^{2+}]C_T}$$

$$[Ni^{2+}]^2 = \frac{[NiY^{2-}]}{K_f \times \alpha_{Y^{4-}}}$$

$$[Ni^{2+}] = \sqrt{\frac{[NiY^{2-}]}{K_f \times \alpha_{Y^{4-}}}}$$

- *at pH 3.0*

$$[Ni^{2+}] = \sqrt{\frac{0.0150}{(4.2\times 10^{18})(2.5\times 10^{-11})}} = 1.2\times 10^{-5}\,M$$

Titrations with EDTA

Calculating the Conditional Constant

$$K_{CaY^{2-}} = \frac{[CaY^{2-}]}{[Ca^{2+}]\alpha_{Y^{4-}}C_T}$$

$$K_f' = \alpha_{Y^{4-}} \times K_{CaY^{2-}} = \frac{[CaY^{2-}]}{[Ca^{2+}]C_T}$$

$$K_f' = (0.405)(5.0 \times 10^{10}) = 2.03 \times 10^{10}$$

EDTA Titration Techniques

Direct Titration

☛ *standard* **EDTA** *solution is added to the sample until an appropriate end point signal is observed*

Example

Mg^{2+}

$$Mg^{2+} + H_2Y^{2-} \leftrightarrows MgY^{2-} + 2H^+$$

$$MgIn^{-} + H_2Y^{2-} \leftrightarrows MgY^{2-} + HIn^{2-}$$

Solubility Equilibrium/Precipitation Reactions

Prediction of Precipitation

Example

Should precipitation occur when 50.00 mL of 5.0×10^{-4} M $\mathbf{Ca(NO_3)_2}$ is mixed with 50.00 mL of 2.0×10^{-4} M **NaF**?

K_{sp} $\mathbf{CaF_2}$ $= 3.9 \times 10^{-11}$

Solubility Equilibrium/Precipitation Reactions

Factors Affecting Solubility

- *Common Ion Effect*
- *Complex Ion Formation*
- *pH*

Factors Affecting Solubility

Common Ion Effect

$$x = \sqrt{\frac{K_{sp}}{0.4}}$$

$$x = \sqrt{\frac{2.5 \times 10^{-13}}{0.4}} = 7.91 \times 10^{-7} M$$

$$[Pb^{2+}] = 0.10 + x \approx 0.10M$$

$$[IO_3^{-}] = 2x = 1.6 \times 10^{-6} M$$

Factors Affecting Solubility

Effect of pH

1. *Calculate the molar solubility of* **CuS** *in a solution in which the* [H_3O^+] *is held constant at (a) 1.0×10^{-1} M and (b) 1.0×10^{-4} M.* K_{sp} **CuS** = 8.0×10^{-37}.

2. *Calculate the molar solubility of* **$PbCO_3$** *in a solution buffered to a pH of 7.00.* K_{sp} **$PbCO_3$** = 7.4×10^{-14}.

Factors Affecting Solubility

Complex Ion Formation

☛ *solubility of ppt may increase*

Example

Calculate the molar solubility of **AgCl** *in 0.010 M* **NH_3** *(free uncomplexed* **NH_3***).*

Factors Affecting Solubility

Separating Ions by pH Control: Sulfide Separations

☛ $[H_2S]$ *in a saturated solution of the gas* $\approx 0.1\ M$

$$0.1 = [H_2S] + [HS^-] + [S^{2-}]$$

☛ $[H_2S] >> [HS^-] + [S^{2-}]$, $[H_2S] \approx 0.1\ M$

$H_2S + 2H_2O \leftrightarrows 2H_3O^+ + S^-$

$$K_{a1}K_{a2} = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]}$$

Precipitation Titration

Titration Curve

Example

Construct a titration curve for the titration of 50.00 mL of 0.0500 M **Cl^-** *with 0.100 M* **Ag^+**. *K_{sp}* **AgCl** = *1.8×10^{-10}. Plot p***Ag** *or p***Cl** *against the volume of titrant.*

$$Ag^+_{(aq)} \quad + \quad Cl^-_{(aq)} \quad \leftrightarrows \quad AgCl_{(s)}$$

$$K = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} = 5.6 \times 10^9$$

Precipitation Titration

Before Addition of Titrant

$$[Cl^-] = 0.0500\,M$$
$$pCl = -\log[Cl^-] = -\log 0.0500$$
$$pCl = 1.30$$

$$[Ag^+] = 0$$
$$pAg = indeterminate$$

Precipitation Titration

Addition of 10.00 mL Titrant

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.025} = 7.2 \times 10^{-9} M$$

$$pAg = -\log 7.2 \times 10^{-9} = 8.14$$

Problem Set in Complexometry

1. *Calculate the conditional formation constant for the nickel(II)-EDTA complex in a solution containing 0.500 M ammonium ion and 0.500 M free (uncomplexed) ammonia.*
   $\log K_f$ Ni(II)-EDTA = 18.6
   $Ni(NH_3)_6^{2+}$ $\log Kf_1 = 2.36$, $\log Kf_2 = 1.90$
   $\log Kf_3 = 1.55$, $\log Kf_4 = 1.23$
   $\log Kf_5 = 0.85$, $\log Kf_6 = 0.42$
   pK_a NH_4^+ = 9.26

2. *Calculate the conditional formation constant for the mercury(II)-EDTA complex in a solution of pH 11.0 containing 0.0100 M free (uncomplexed) cyanide ion.*
   $\log K_f$ Hg(II)-EDTA = 21.8
   $Hg(CN)_4^{2-}$ $\log Kf_1 = 18.0$, $\log Kf_2 = 16.7$
   $\log Kf_3 = 3.83$, $\log Kf_4 = 2.98$
   pK_a EDTA $pK_{a1} = 2.00$, $pK_{a2} = 2.67$, $pK_{a3} = 6.16$, $pK_{a4} = 10.26$