Chapter 11

EDTA Titrations

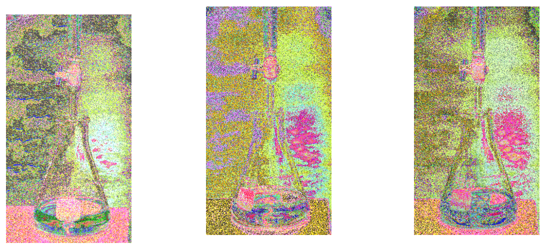
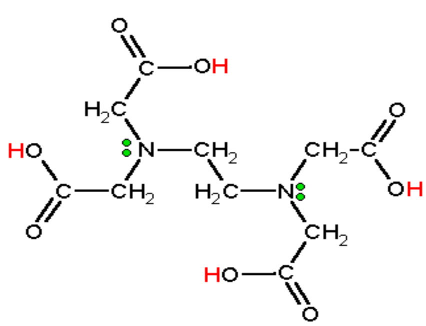
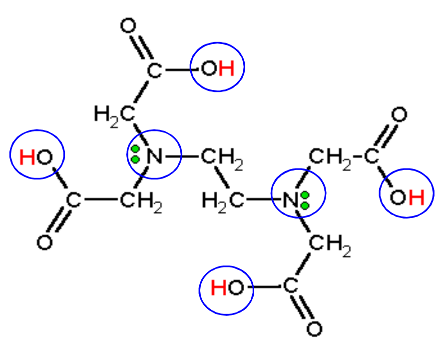


Image available at
http://homepages.ius.edu/DSPURLOC/c121/week13.htm

Structure of EDTA

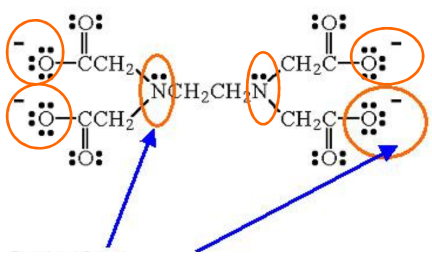
EDTA structure (H_4A) – a ***hexadentate*** *(6 binding sites* – circled) ligand





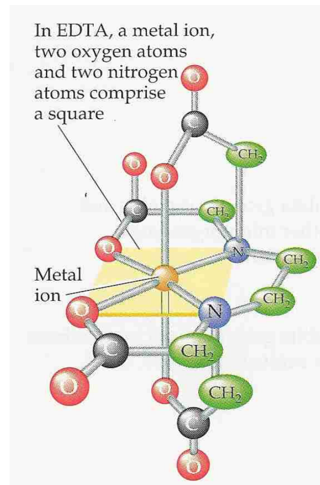
Structure of EDTA – Cont.

Fully deprotonated form, A^{4-}



Six metal binding sites: Amino-N (2) and carboxylate O (4)

Structure of metal ion-EDTA complex



http://www.benbest.com/nutrceut/EDTA.html

Background: *Lewis Acids and Bases*

A ***Lewis acid*** is a species that *accepts* lone pair electrons.

Q. What species would be a good Lewis acid?

Examples of Lewis acids:

- Metal cations (**M^{n+}**) – Ca^{2+}, Fe^{2+}, Al^{3+}
- Hydrogen ion **H^{+}**

A ***Lewis base*** is any species that *donates* lone pair electrons.

Q. What species would be a Lewis base?

Examples of a Lewis base:

Ions and molecules with lone pair electrons, such as:

- Cyanide, **:C ≡ N:⁻**
- Amino group, **$:NH_2R$**, and
- Carboxylate group, **$RCOO^-$** (draw lone pair e^-s)

NOTE: Both amino and carboxylate groups are present in EDTA

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A ***ligand*** is an atom or a group of atoms that form a complex with a metal ion

Examples of a ligand: Lewis bases (previous slide) like EDTA, CN^-, -NHR, $RCOO^-$

Complexometric titration = a titration based on complex formation

Examples:

- EDTA titration of metal ions like Ca^{2+} and Mg^{2+}
- Cyanide titration of silver ions: $Ag^+ + 2\ CN^- \rightarrow Ag(CN)_2^-$

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Classification of Ligands

1. **Monodentate** = binds to the metal ion through only one atom or binding site

<u>Example</u>: Cyanide, CN^-, binds through carbon only

$$Ag^+ \; + \; 2\, :\bar{C}{\equiv}N: \;\rightleftharpoons\; [:N{\equiv}C{-}Ag{-}C{\equiv}N:]^-$$

Lewis acid (electron pair acceptor) — Lewis base (electron pair donor) — Complex ion

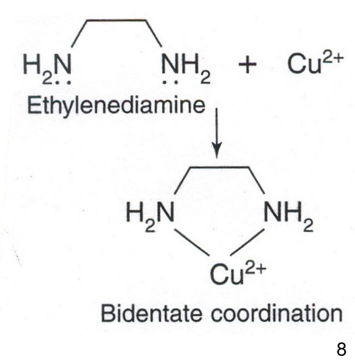
Ag to C bond;
No binding w/ N

Classification of Ligands (Cont.)

2. **Multidentate** = binds through more than one atom or binding site

(a) **Bidentate** = 2 binding sites

<u>Example</u>: Ethylenediamine, "en"

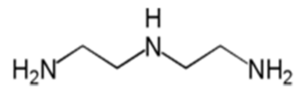


(b) **Tridentate** = 3 binding sites

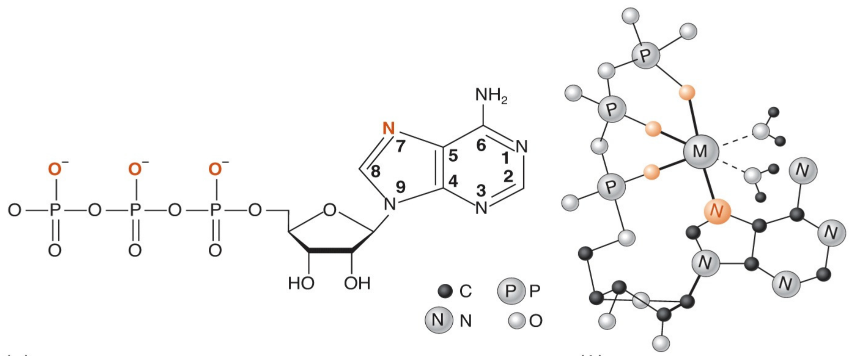
Multidentate ligands (Cont.)

(b) **Tridentate** = 3 binding sites

Example: Diethylenetriamine, "dien"



(c) **Tetradentate** = 4 binding sites; Example is ATP (Figure 11-2)



(*a*) (*b*)

- **3 O**'s and **1 N** (in orange) = 4 binding sites

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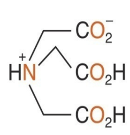
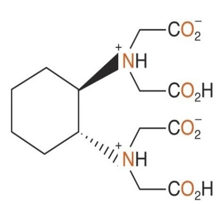
(d) **Pentadentate** = 5 binding sites

(e) **Hexadentate** = 6 binding sites; Example is EDTA

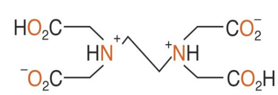
Some common **multidentate ligands** (from Figure 11-3)



NTA
Nitrilotriacetic acid



DCTA
trans-1,2-Diaminocyclohexanetetraacetic acid



EDTA
Ethylenediaminetetraacetic acid
(also called ethylenedinitrilotetraacetic acid)

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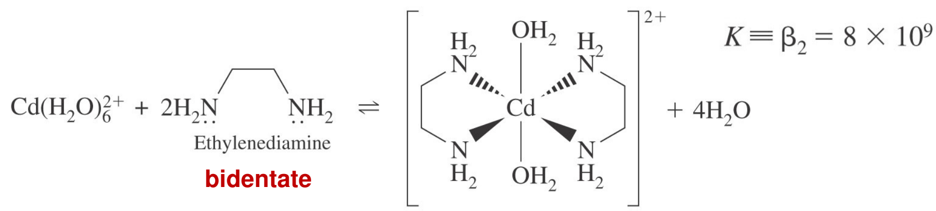
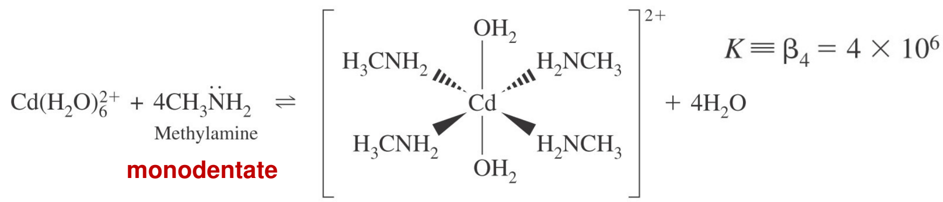
Chelate Effect

- The ability of *multidentate ligands* to form *more stable metal complexes* than those formed by similar monodentate ligands.





Harris, *Quantitative Chemical Analysis*, 8e

Q. Which complex is more stable?

- The first one (bidentate) --- has larger K or formation constant, β

NOTE: The term "**chelate**" comes from the Greek word *chela*, meaning claw.

EDTA

Short for ***ethylenediamine tetraacetic acid***

Why use EDTA?

- Readily available as a primary standard (usually the disodium salt)
- It forms 1:1 metal-ligand complex
- Large formation constants with many metal ions
- It forms stable, water-soluble metal complexes

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Properties of EDTA

(1) Acid-base

- The fully protonated form is ***hexaprotic***, H_6Y^{2+}
- The electrically neutral form is ***tetraprotic***, H_4Y
- The form commonly used in EDTA titrations is the disodium salt, Na_2H_2Y
- Because EDTA is polyprotic, the forms that exist in solution depend on pH

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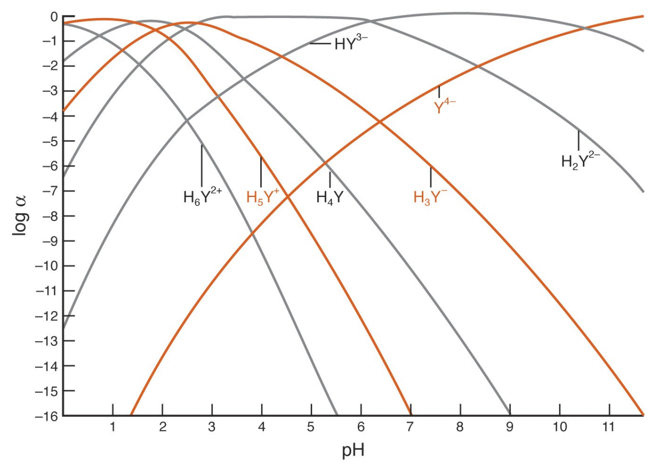
Forms of EDTA at various pH's



Q. What forms of EDTA exist at the following pH's: (a) 4.00 and (b) 10.00?

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Properties of EDTA – Cont.

(2) Ability to form metal-EDTA complexes

Formation constant (stability constant), K_f = the equilibrium constant for the reaction of a metal ion (M^{n+}) with a ligand.

- For EDTA, K_f is usually written in terms of Y^{4-}

Formation constant:

$$M^{n+} + Y^{4-} \leftrightarrow MY^{n-4} \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}]\ [Y^{4-}]} \qquad \text{(Eq-2)}$$

- By convention, K_f will be expressed in terms of Y^{4-}
- Note that Y^{4-} is *not the only form of EDTA* that complexes with M^{n+}

Q. How stable are these metal-EDTA complexes?

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Table 13-2 **Formation constants for metal-EDTA complexes**

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25°C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 (μ = 0.2)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C, μ = 0.2)	Ho^{3+}	18.62
Y^{3+}	18.09			Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 (μ = 0)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 (μ = 1.0)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°C, μ = 1.0)
Cr^{3+}	23.4				

NOTE: The formation constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 20°C, and ionic strength 0.1 M, unless otherwise noted.

SOURCE: A. E. Martell and R. M. Smith, *Critical Stability Constants,* Vol. 1 (New York: Plenum Press, 1974), pp. 204–211.

❖ **Most metal ions (except for Group IA) form stable complexes (large K_f) with EDTA**

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Metal Ion Indicators

Metal ion indicators = compounds that change color when they bind to a metal ion (Table 3-3)

Desirable properties

- Must bind to the metal ion, but
- Must release the metal ion to EDTA at the equiv. point

  i.e. Metal-Indicator complex must be weaker (smaller K) than metal-EDTA complex

Equilibrium reaction: (Charges are omitted for simplicity)

$$\text{M-In} + \text{EDTA} \rightleftharpoons \text{M-EDTA} + \text{In}$$

Metal-indicator complex **(Color 1)** — **(Colorless)** — **Free indicator** **(Color 2)**

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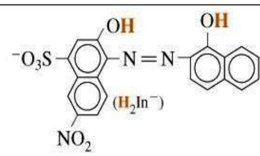
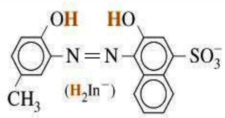
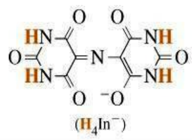
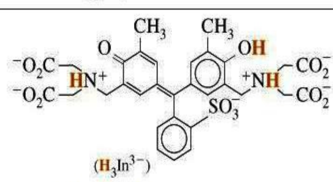
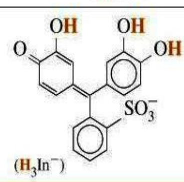
Indicators for EDTA Titration

Table 13-3 Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}

- Note that like acid-base indicators, these metal ion indicators' ***colors vary with pH***

Indicators for EDTA Titration – Cont.

Xylenol orange		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 =$ 10.47	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyrocatechol violet		$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Indicators for EDTA Titration – Cont.

Specific example: *Calmagite*

Calmagite

This indicator has acid-base properties:

$$H_2Indic \underset{}{\overset{pH\ 8.1}{\rightleftharpoons}} HIndic^{2-} \overset{pH\ 12.4}{\rightleftharpoons} Indic^{3-}$$

(red) (blue) (orange)

Since the metal complexes are red, the indicator is only useful in the range of pH 8.1 - 12.4.

Presence of Cu(II), Ni(II), Fe(III) or Al(III) can block the indicator.

NOTE: A metal is said to **block** an indicator if it does not freely dissociate from that indicator.

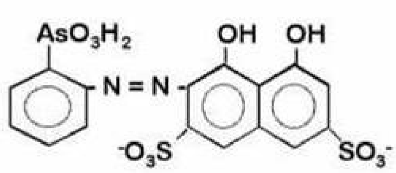
Indicators for EDTA Titration – Cont.

Another specific example: *Arsenazo I*

Arsenazo I

A useful indicator for Ca(II), Mg(II) and rare earths.

Not blocked by Cu(II) or Fe(III).



http://ull.chemistry.uakron.edu/analytical/Complex/

Metal Ion Indicators – Cont.

$$M\text{-}In + EDTA \rightleftharpoons M\text{-}EDTA + In$$

Metal-indicator complex **(Color 1)** — **(Colorless)** — **Free indicator** **(Color 2)**

- **Beginning of titration:** Small amount of **In** added forms colored M-In complex
- **During titration:** EDTA (titrant) added ***binds first to*** M^{n+} that is not complexed with In
- **At the end point:** A small excess of EDTA ***displaces In*** from M-In complex; Color changes as In is released

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EDTA Titration Techniques

Direct titration = metal analyte is titrated with *standard EDTA* to the end point

- Metal solution is buffered to a pH at which K_f' for metal-EDTA complex is large
- Indicator is selected so that the color of ***free In*** is distinctly different from the color of metal-In complex

Back titration = a known excess of standard EDTA is added to the analyte (M^{n+}); Unreacted EDTA is then titrated with a standard solution of a second metal ion

Used when:

- The analyte precipitates in the absence of EDTA, or
- The analyte reacts too slowly with EDTA during titration, or
- The analyte blocks (i.e. does not freely dissociate from) the indicator

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Water Hardness

Exercise: To determine water hardness you used EDTA titration using 0.0800 M EDTA. You titrated 50.00 mL of water sample, which required 10.68 mL of EDTA to reach the end point. Assume that water hardness is only due to Ca^{2+}, (a) determine the molar concentration of Ca^{2+} ion and (b) water hardness as ppm $CaCO_3$ in the water sample. [MM_{CaCO3} = 100.1 g/mol]

$$\frac{\text{moles } Ca^{2+}\text{ion}}{1\text{ L}} = \frac{(\text{molarity EDTA})\ (\text{mL EDTA added})}{50.00 \text{ mL of water sample titrated}}$$

$$\frac{\text{moles } Ca^{2+}\text{ion}}{1\text{ L}} = \frac{(.0080\text{ M})\ (10.68\text{ mL})}{50.00\text{ mL water}} = .0017\text{ M}$$

$$\text{ppm } CaCO_3 = \frac{(\text{mol } Ca^{2+})}{(1\text{ L})}\frac{(1\text{ mol } CaCO_3)}{(1\text{ mol } Ca^{2+})}\frac{(100.1\text{ g } CaCO_3)}{(1\text{ mol } CaCO_3)}\frac{(10^3\text{ mg})}{(1\text{ g})}$$

$$\text{ppm CaCO} = \frac{(.0017\text{ moles})(1\text{ mol } CaCO_3)(100.1\text{ g } CaCO_3)(10^3\text{ mg})}{(1\text{ L})\ (1\text{ mol } Ca^{2+})(1\text{ mol } CaCO_3)(1\text{ g})} = 170\text{ ppm}$$

http://homepages.ius.edu/DSPURLOC/c121/week13.htm

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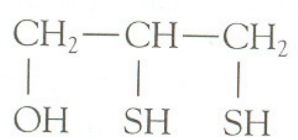
Chelation therapy

- Administers a chelate that binds to the metal more strongly than does the enzyme. Ex. BAL



British Anti-Lewisite

Chelating agents were introduced into medicine as a result of the use of poison gas in World War I. The first widely used chelating agent, dimercaprol, also named **British Anti-Lewisite,** or **BAL**, was used as an antidote to the arsenic based poison gas, Lewisite. BAL bound the arsenic in Lewisite, forming a water soluble compound that entered the blood-stream, allowing it to be removed from the body by the kidneys and liver.

http://en.wikipedia.org/wiki/Chelation_therapy

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EDTA – History, Uses, etc

EDTA: History
Introduced in the United States in 1948
1950-1990 Benefits of **chelation therapy** were recognized by the medical community as a treatment for:

- heavy metal and radiation toxicity
- snake venom poisoning
- digitalis intoxication
- cardiac arrhythmia

Sources of EDTA
Found in many foods as an additive

- Unwanted metals get into foods from the soil and machinery during harvesting and processing
- Unwanted metals *degrade foods* by catalyzing the oxidation of fats in foods

EDTA reacts with these metals by forming tightly bound complexes, preventing metal-catalyzed degradation of food

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EDTA – History, Uses, etc

Principal Uses

- Heavy metal toxicity
- Reversal of artherosclerosis
- Restoration of memory
- Degenerative diseases
- Arthritis, scleroderma, and lupus

EDTA: Chelation Therapy
Andrea Jones and Arlen Rash, http://www.geocities.com/chadrx/edta.html

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