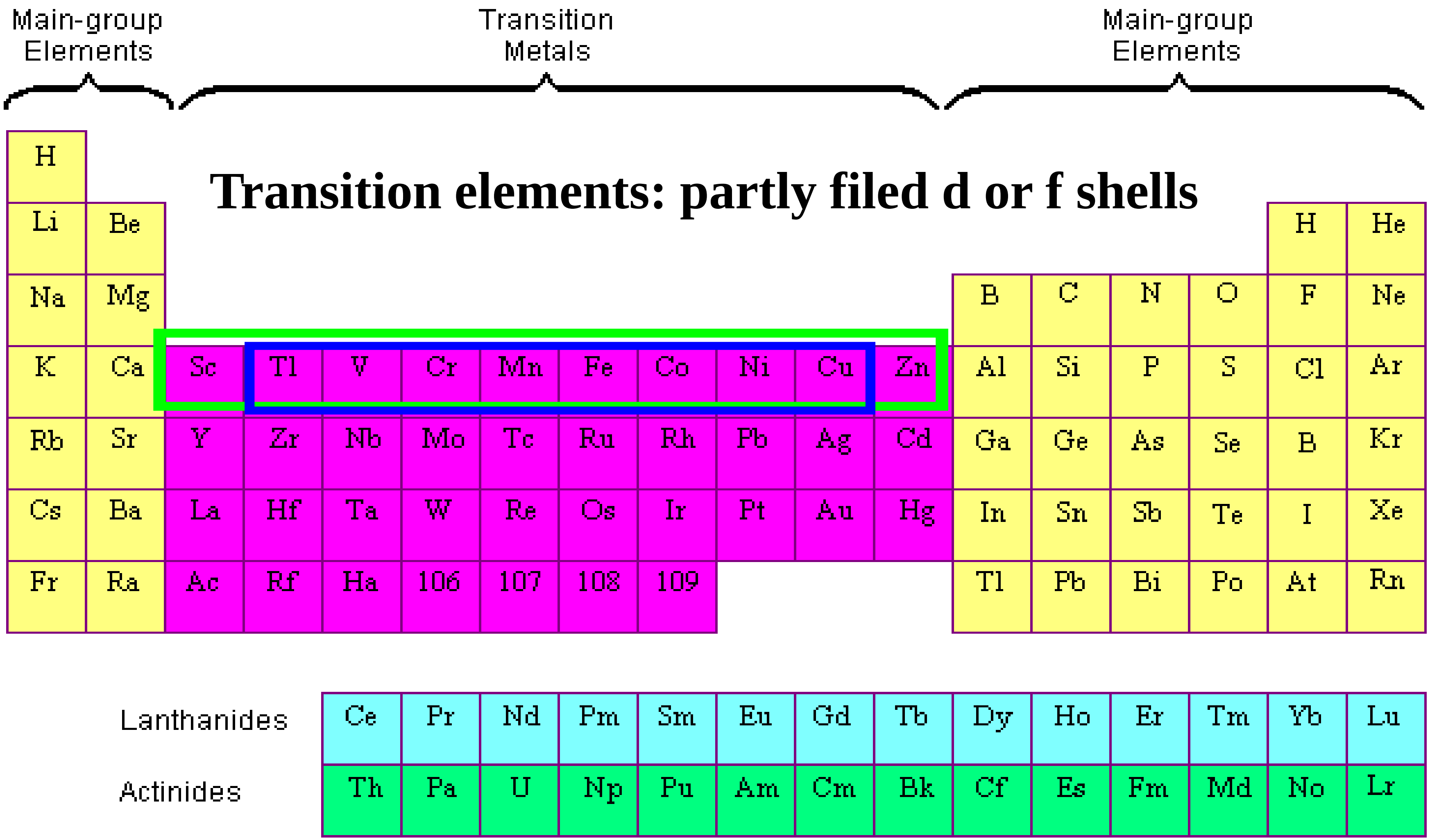
Coordination Chemistry

Transition elements: partly filed d or f shells



Tm complex: Variable valence

Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

Cu is the only element which affords Cu^{I} compounds without π-acceptor ligands

Complexes: **Have metal ion (can be zero oxidation state) bonded to number of ligands.**

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = metal = center of coordination

Transition metals can act as Lewis acid

Lewis base = ligand = molecules/ions covalently bonded to metal in complex

The term ligand (ligare [Latin], to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. The first use of the term in a British journal was by H. Irving and R.J.P. Williams in *Nature*, 1948, 162, 746.

For a fascinating review on 'ligand' in chemistry - *Polyhedron*, 2, 1983, 1-7.

Ligand: Lewis base – contain at least one nonbonding pair of electrons

$$Ni^{2+}(aq) + 6NH_3(aq) \rightarrow Ni(NH_3)_6{}^{2+}(aq)$$

Lewis acid **Lewis base** **Complex ion**

- Coordination compound
  - Compound that contains 1 or more complexes
  - Example
    - $[Co(NH_3)_6]Cl_3$
    - $[Cu(NH_3)_4][PtCl_4]$
    - $[Pt(NH_3)_2Cl_2]$

- **Ligands**
  - **classified according to the number of donor atoms**
  - **Examples**
    - **monodentate = 1**
    - **bidentate = 2**
    - **tetradentate = 4**
    - **hexadentate = 6**
    - **polydentate = 2 or more donor atoms**

chelating agents

monodentate, bidentate, tridentate etc. where the concept of teeth (dent) is introduced, hence the idea of bite angle etc.

Table 22.4 Some Common Ligands

MONODENTATE

Formula[a]	Name as Ligand[b]	Formula[a]	Name as Ligand[b]	Formula[a]	Name as Ligand[b]
Neutral Molecules					
NH_3	Ammine	NO	Nitrosyl	H_2O	Aqua
CH_3NH_2	Methylamine	CO	Carbonyl	C_5H_5N	Pyridine
Anions					
F^-	Fluoro	OH^-	Hydroxo	NCS^-	Thiocyanato-*N*
Cl^-	Chloro	NO_2^-	Nitrito-*N*	SCN^-	Thiocyanato-*S*
Br^-	Bromo	ONO^-	Nitrito-*O*	OSO_3^{2-}	Sulfato
I^-	Iodo	CN^-	Cyano	SSO_3^{2-}	Thiosulfato

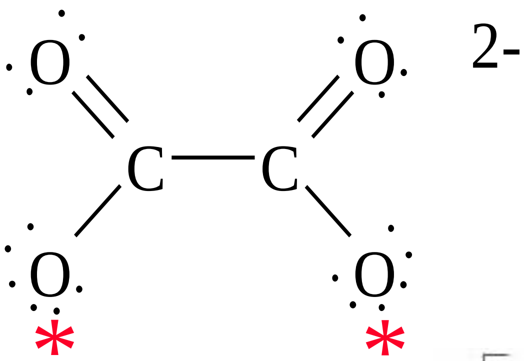
POLYDENTATE

Name of Ligand[b]	Abbreviation	Formula[a]
Ethylenediamine	en	$H_2NCH_2CH_2NH_2$
Oxalato	ox	$[OOCCOO]^{2-}$
Ethylenediaminetetraacetato	EDTA	$[(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2]^{4-}$

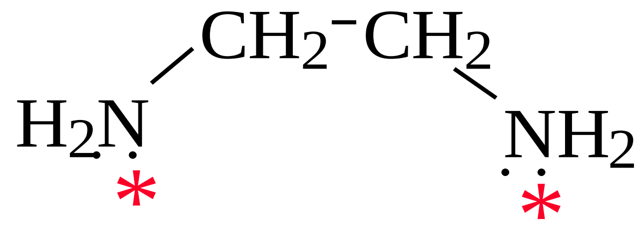
[a] Donor atoms are shown in red.

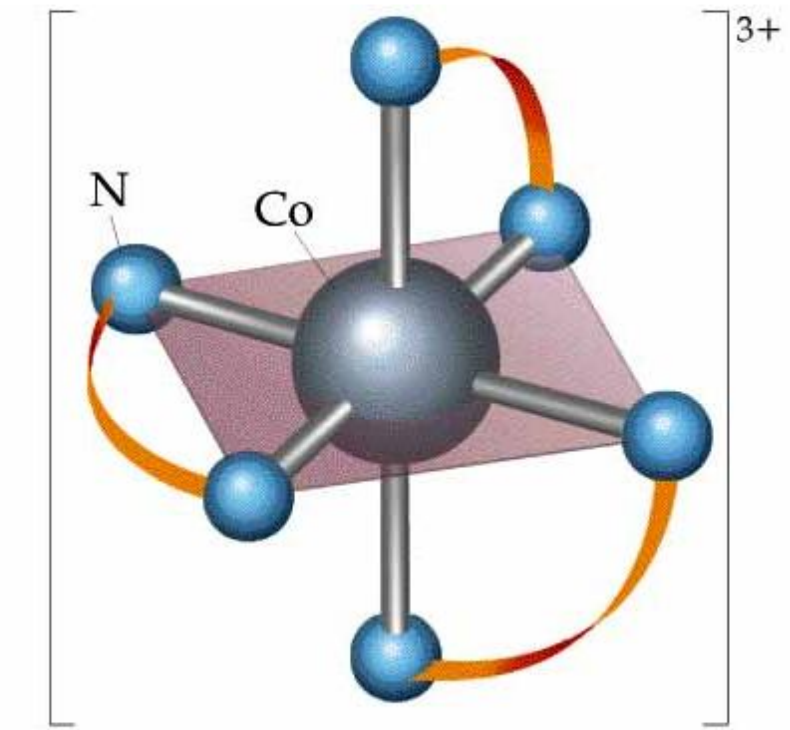
[b] Most neutral ligands carry the unmodified name, except for aqua, ammine, carbonyl, and nitrosyl. Anion ligand names end in "o," which requires changing the terminal *-e* to *-o* (for example, sulfate $\longrightarrow$ sulfato). With many common anions, an entire *-ide* ending is changed to *-o* (for example, cyanide $\longrightarrow$ cyano).

oxalate ion



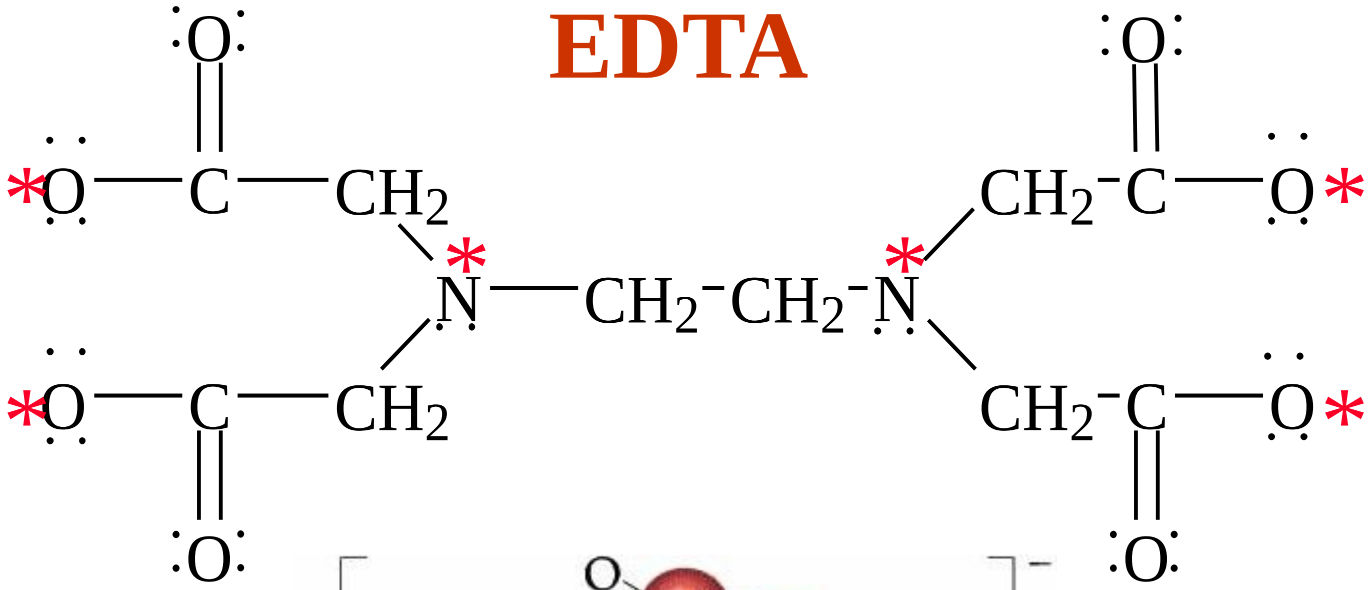
ethylenediamine

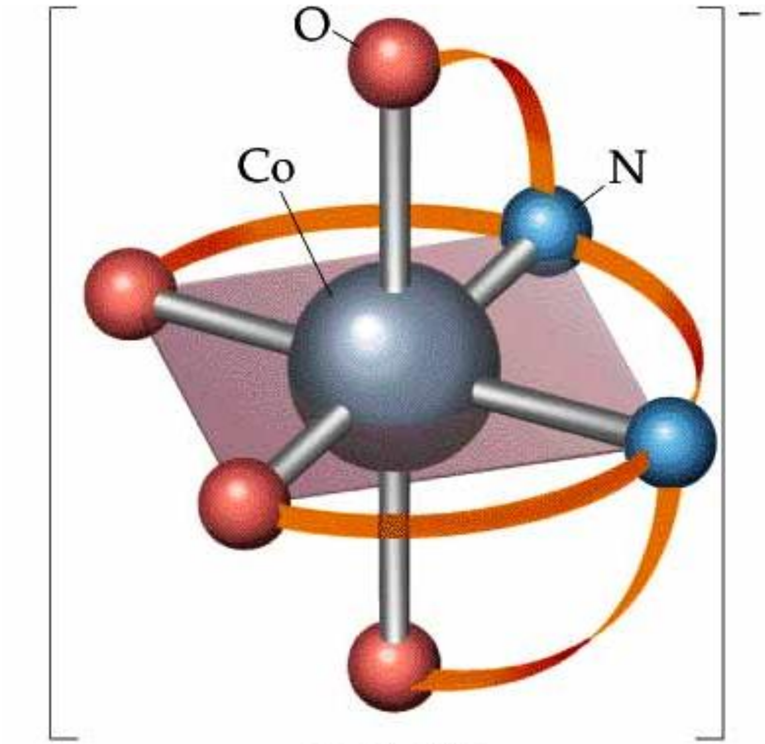




$Co(en)_3^{3+}$

EDTA



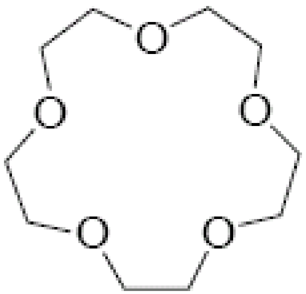


$CoEDTA^-$

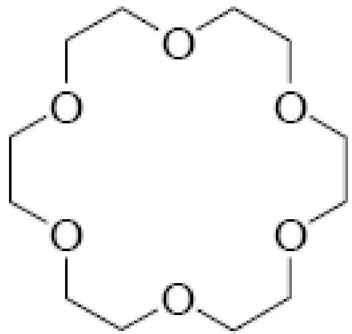
Macrocylic Ligands

Large ring compounds most commonly containing or O, N and/or S atoms

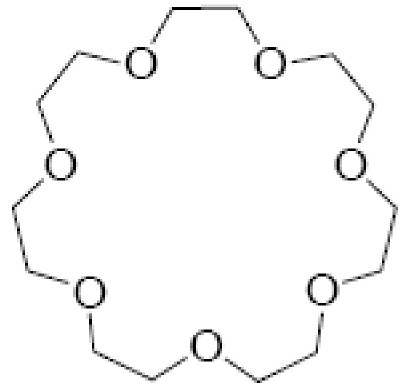
crown ether:



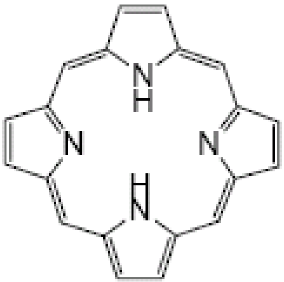
15-crown-5



18-crown-6

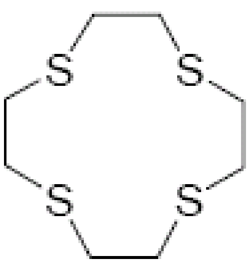


21-crown-7

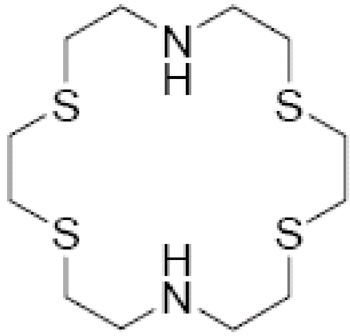


porphyrin

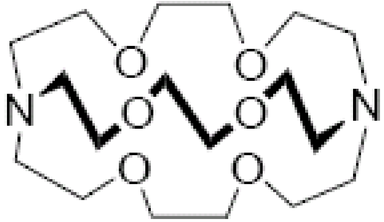
thia-crown ether:



aza-thia-crown:



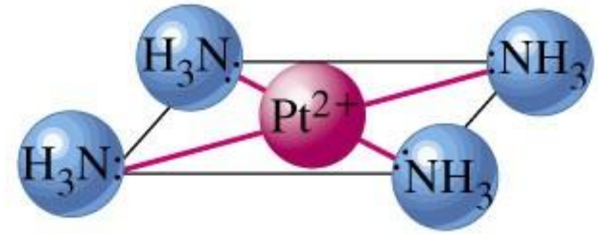
cryptand:



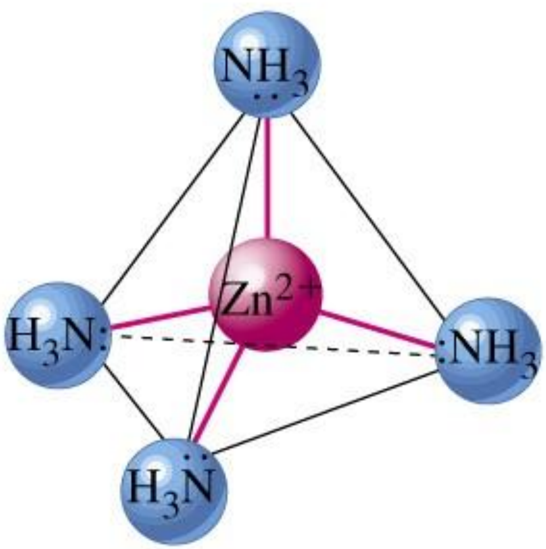
crypt-[222]

Coordination Numbers and Geometries:

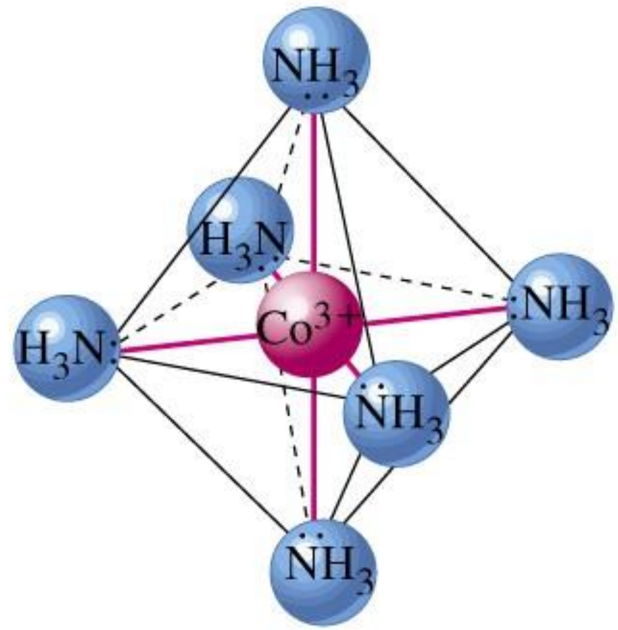
Linear



Square planar



Tetrahedral



Octahedral

Coordination Equilibria & Chelate effect

$$[Fe(H_2O)_6]^{3+} + NCS^- \rightarrow [Fe(H_2O)_5(NCS)]^{2+} + H_2O$$

$$K_f = [Fe(H_2O)_5(NCS)]^{2+} / [Fe(H_2O)_6]^{3+}[NCS^-]$$

Equilibrium constant K_f $\Rightarrow$ formation constant

$$M + L \rightarrow ML \quad K_1 = [ML]/[M][L]$$

$$ML + L \rightarrow ML_2 \quad K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \rightarrow ML_3 \quad K_3 = [ML_3]/[ML_2][L]$$

$$ML_{n-1} + L \rightarrow ML_n \quad K_n = [ML_n]/[ML_{n-1}][L]$$

Coordination Equilibria and Chelate effect

- K_1, K_2…. $\Rightarrow$ **Stepwise formation constant.**
- **To calculate concentration of the final product, use overall formation constant β_n:**
  - $\beta_n = [ML_n]/[M][L]^n$
  - $= K_1 \times K_2 \times K_3 \times \ldots. \times K_n$

Kinetic stability

Inert and labile complexes

The term inert and labile are relative

"A good rule of thumb is that those complexes that react completely within 1 min at 25^{o} should be considered labile and those that take longer should be considered inert."

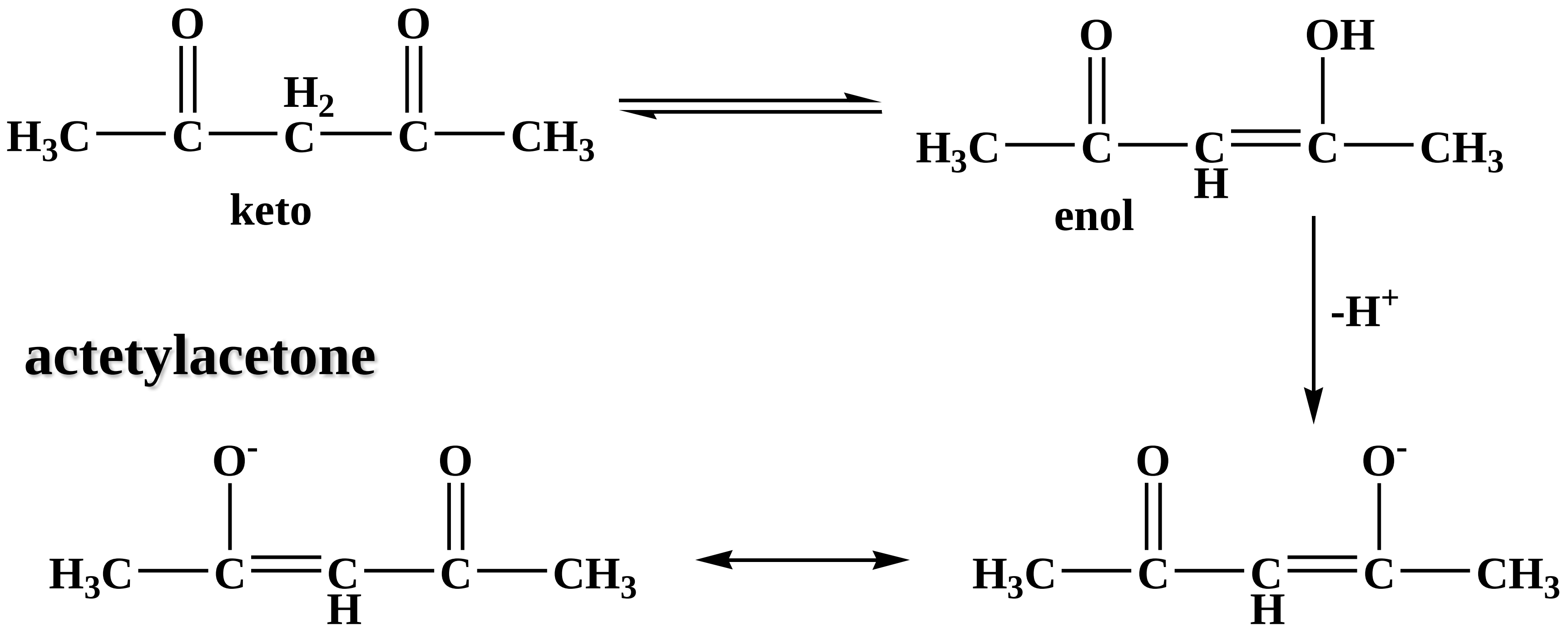
Thermodynamically stable complexes can be labile or inert

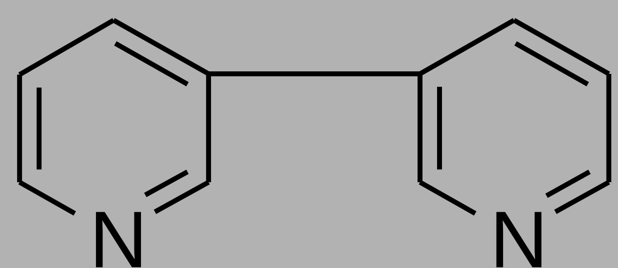
$[Hg(CN)_4]^{2-}$ $K_f = 10^{42}$ thermodynamically stable

$$[Hg(CN)_4]^{2-} + 4\ {}^{14}CN^- = [Hg({}^{14}CN)_4]^{2-} + CN^-$$

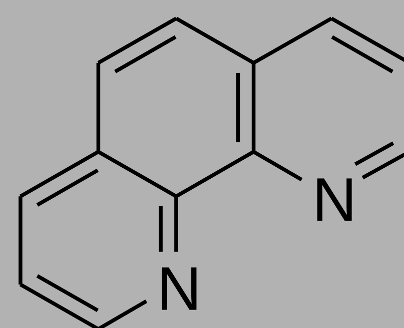
Very fast reaction **Labile**

actetylacetone





2,2'-bipyridine (bipy)



1.10 - penanthroline (phen)

Stepwise formation constant of complexes of M^{2+} generally increases steadily from Mn^{2+} to Cu^{2+} - Irving-William series

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$

Radius

Electrostatic effect

0.91>0.83>.82>0.78>0.69 Å

Example: $[Cd(NH_3)_4]^{2+}$

$Cd^{2+} + NH_3 \leftrightarrow [CdNH_3]^{2+}$ $K_1 = 10^{2.65}$

$CdNH_3]^{2+} + NH_3 \leftrightarrow [Cd(NH_3)_2]^{2+}$ $K_2 = 10^{2.10}$

$[Cd(NH_3)_2]^{2+} + NH_3 \leftrightarrow [Cd(NH_3)_3]^{2+}$ $K_3 = 10^{1.44}$

$[Cd(NH_3)_3]^{2+} + NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$ $K_4 = 10^{0.93}$

Overall: $Cd^{2+} + 4\ NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$

$\beta_4 = K1 \times K2 \times K3 \times K4 = 10^{(2.65 + 2.10 + 1.44 + 0.93)}$

$= 10^{7.12}$

What are the implications of the following results?

$$NiCl_2 + 6H_2O \rightarrow [Ni(H_2O)_6]^{+2}$$

$$[Ni(H_2O)_6]^{+2} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

$$[Ni(NH_3)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2\ (en) \rightarrow [Ni(en)_3]^{2+} + 6NH_3$$

Complex Formation: Major Factors

$$[Ni(H_2O)_6] + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

- NH_3 is a stronger (better) ligand than H_2O
- $\Delta_O\ NH_3 > \Delta_O\ H_2O$
- $[Ni(NH_3)_6]^{2+}$ is more stable
- $\Delta G = \Delta H - T\Delta S$ (ΔH -ve, $\Delta S \approx 0$)
- ΔG for the reaction is negative

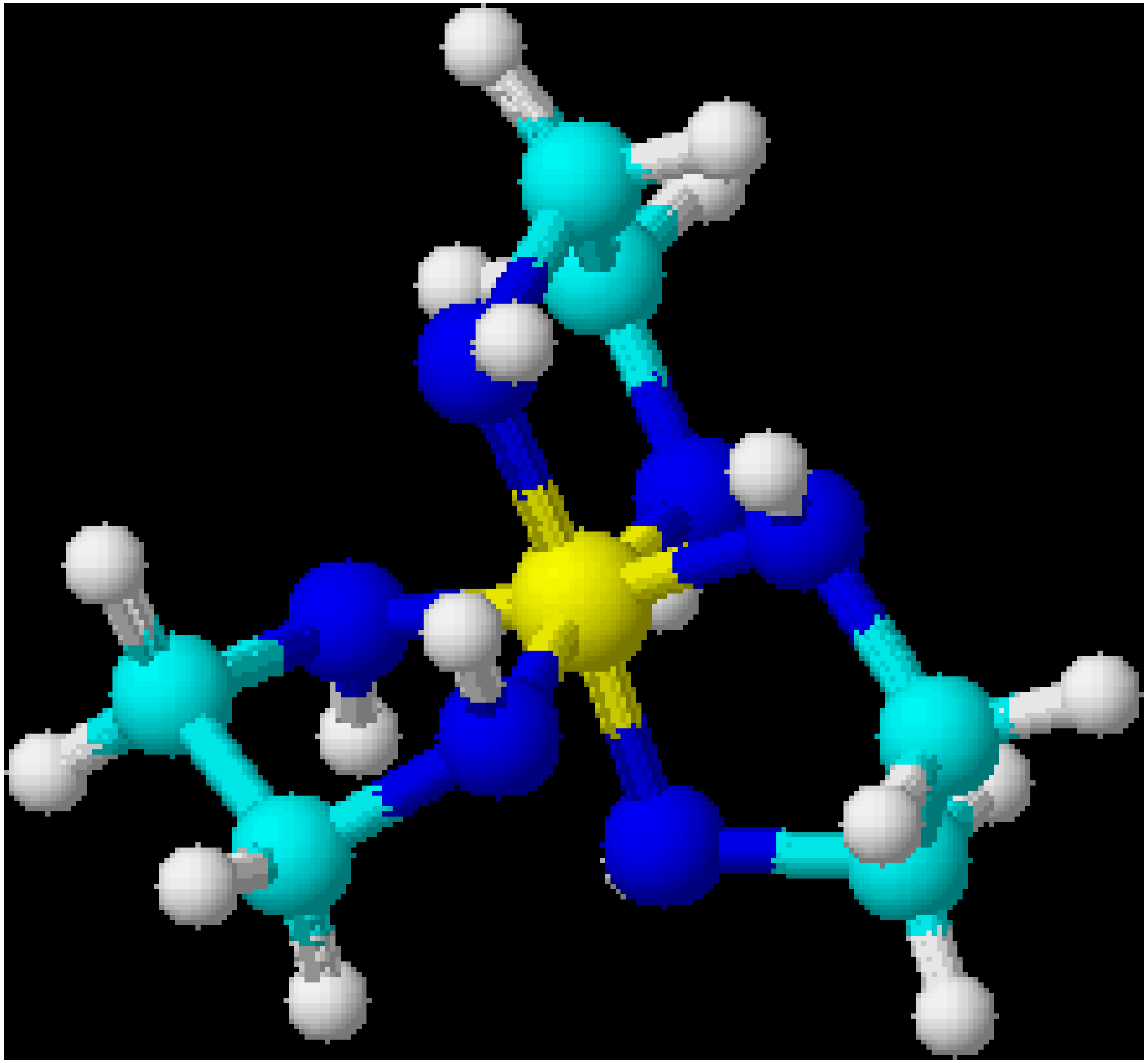
Complex Formation: Chelate Effect

- $[Ni(NH_3)_6]^{2+}$ + 3 $NH_2CH_2CH_2NH_2$ (en)

  $\rightarrow [Ni(en)_3]^{2+} + 6NH_3$

- en is bidentate ligand
- forms a 5 member ring known as *chelate ring*
- the complex is known as a *chelate*

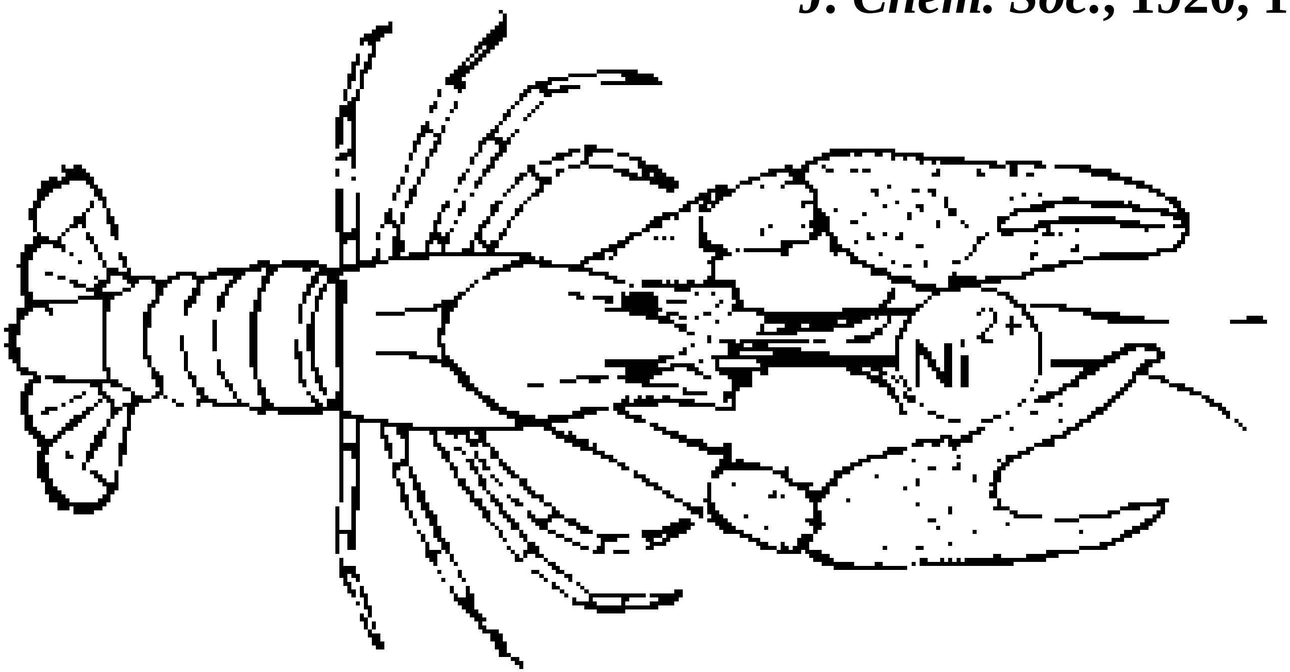
Complex Formation: Chelate Effect



Coordination Equilibria & Chelate effect

"The adjective chelate, derived from the great claw or chela (chely - Greek) of the lobster, is suggested for the groups which function as two units and fasten to the central atom so as to produce heterocyclic rings."

***J. Chem. Soc.*, 1920, 117, 1456**



The chelate effect or chelation is one of the most important ligand effects in transition metal coordination chemistry.

Complex Formation: Chelate Effect

$$[Ni(NH_3)_6]^{2+} + 3\ (en) \rightarrow [Ni(en)_3]^{2+} + 6NH_3$$

- **Formation of chelate ring $\Rightarrow$ reaction proceeds in forward direction & the product is stable. This stability is purely kinetic in nature. This is known as chelate effect.**
- $\Delta G = \Delta H - T\Delta S$ (ΔH -ve, ΔS ++ve)

Compare the β for $[Ni(NH_3)_6]^{2+}$ vs. $[Ni(en)_3]^{2+}$

hexa amine: $\beta_6 = 10^9$

Tris en: $\beta_3 = 10^{18}$ (Favored product)

Examine: $[Ni(NH_3)_6]^{2+} + 3\ en \leftrightarrow 6\ NH_3 + [Ni(en)_3]^{2+}$

$\beta_3 = 10^{9.7}$

Greater number of amine molecules enhances the disorder of the product, even though the metal complex is more ordered. (larger ΔS, more negative ΔG) For this process, ΔH is small, only -12 KJ; ΔG is -67 KJ, leaving -55 kJ for $-T\Delta S$.

$Cd^{2+} + 4\ NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$

Reaction of ammonia and en with Cd^{2+}

# of ligands	ΔG / $kJmol^{-1}$	ΔH / $kJmol^{-1}$	ΔS / $JK^{-1}mol^{-1}$	log β
2 NH_3 (1 en)	-28.24 (-33.30)	-29.79 (-29.41)	-5.19 (+13.05)	4.95 (5.84)
4 NH_3 (2 en)	-42.51 (-60.67)	-53.14 (-56.48)	-35.50 (+13.75)	7.44 (10.62)

Reaction of ammonia and en with Cu^{2+}

$[Cu(H_2O)_6]^{2+}$ + en = $[Cu(en)(H_2O)_4]^{2+}$ + 2 H_2O

Log K_1 = 10.6 ΔH = -54 kJ/mol ΔS = 23 J/K/mol

$[Cu(H_2O)_6]^{2+}$ + 2NH_3 = $[Cu(NH_3)_2(H_2O)_2]^{2+}$ + 2 H_2O

Log β_2 = 7.7 ΔH = -46 kJ/mol ΔS = -8.4 J/K/mol

Chelating agents:

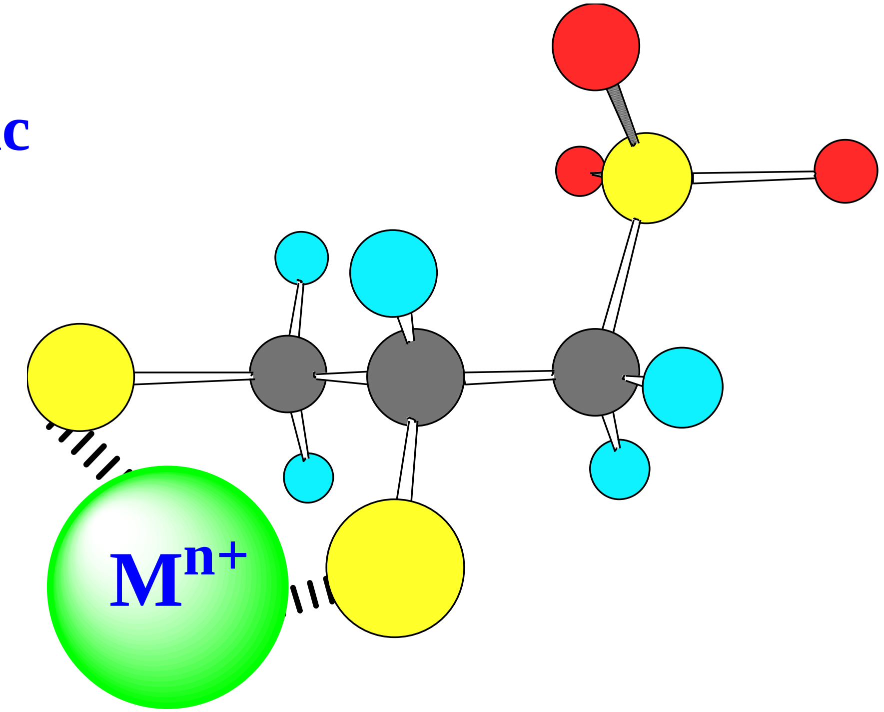
(1) Used to remove unwanted metal ions in water.

(2) Selective removal of Hg^{2+} and Pb^{2+} from body when poisoned.

(3) Prevent blood clots.

(4) Solubilize iron in plant fertilizer.

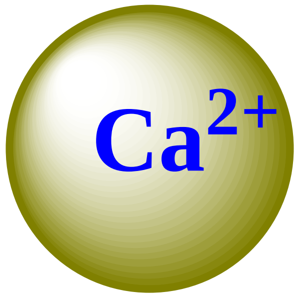
2,3-dimercapto-1-propanesulfonic acid sodium (DMPS)

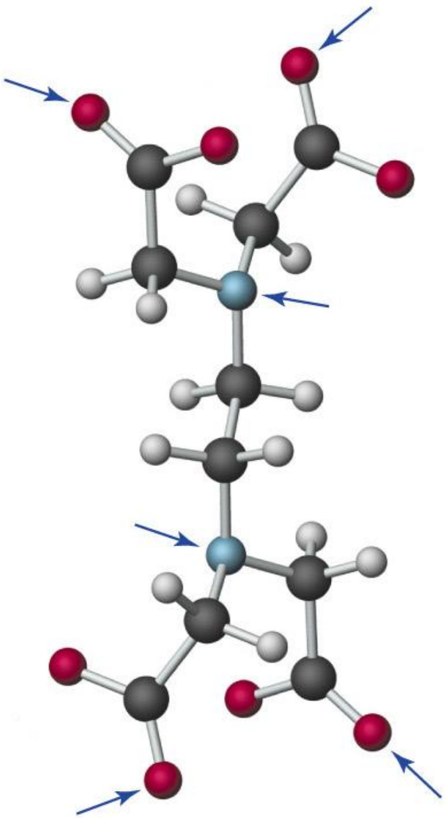


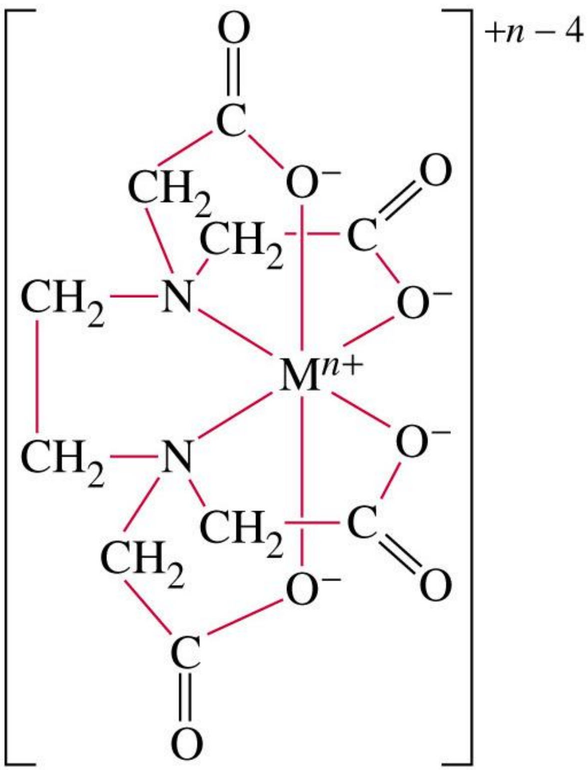
DMPS is a effective chelator with two groups thiols not only especially for mercury but also for lead, tin, arsenic, silver and cadmium.

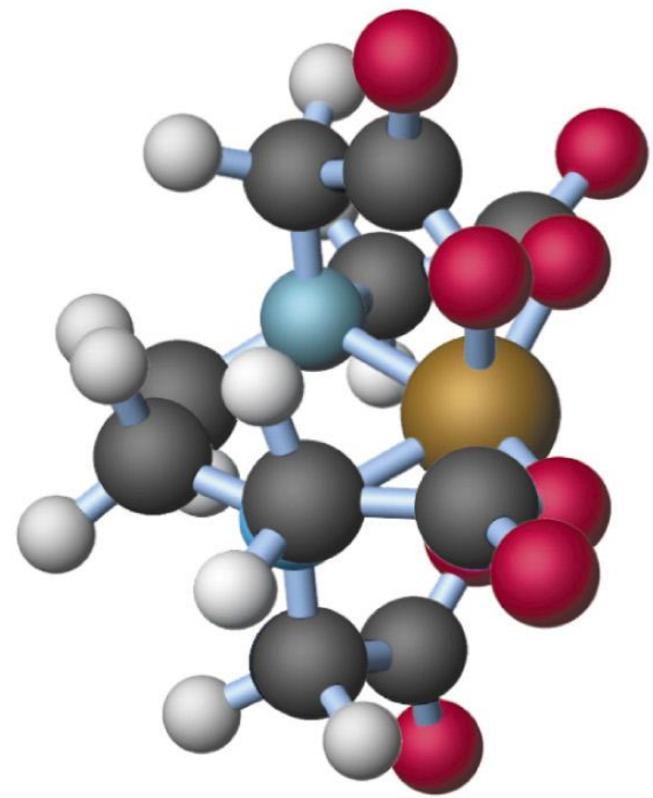
EDTA

Anticoagulant









Factors affecting the thermodynamic stability

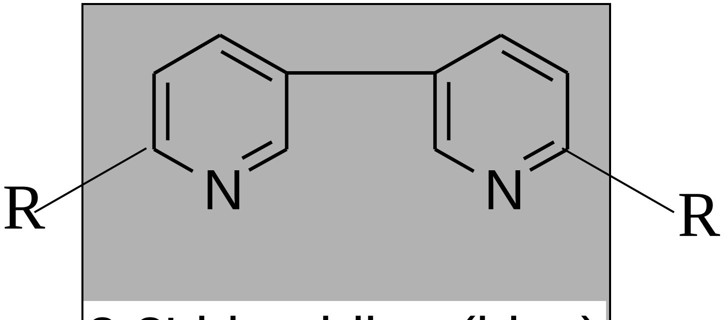
(a) Charge on the metal

For the formation of EDTA complex

Metal ion	logβ
V^{2+}	12.7
V^{3+}	25.9
Fe^{2+}	14.3
Fe^{3+}	25.1

(b) Steric effect

K (R=H) >> K (R=Me)



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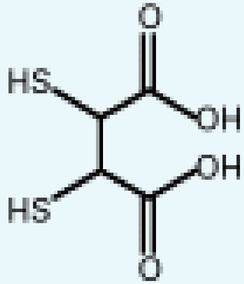
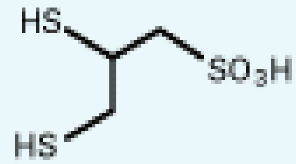
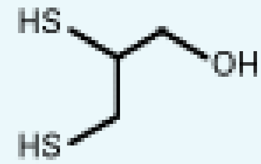


DMSA



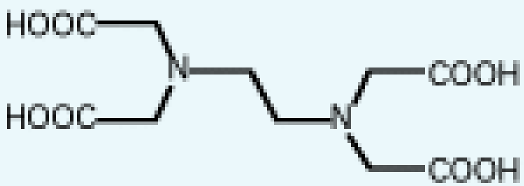
DMPS

2,3-dimercapto-1-propanesulfonic acid sodium

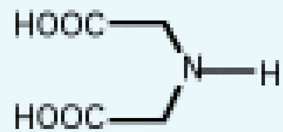


BAL

dimercaprol

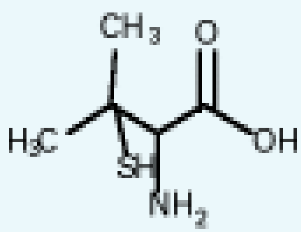


EDTA

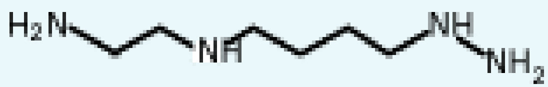


IDA

iminodiacetic acid



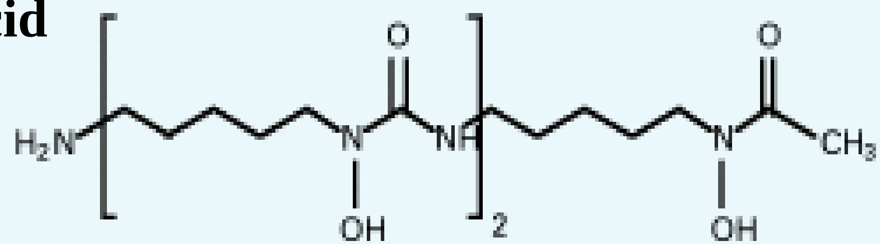
DPA



TETA

triethylenetetraatnine

dipicolinic acid



DFOA

desferrioxamine