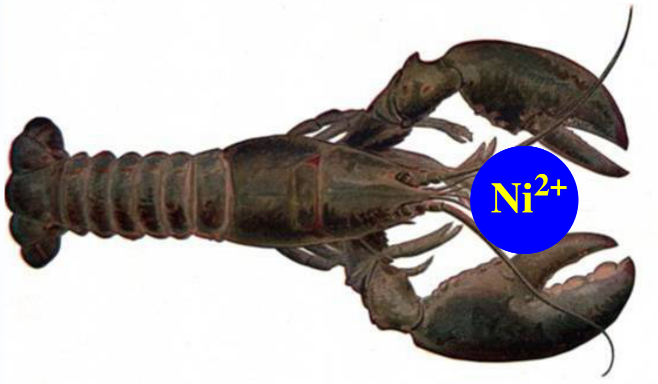
Inorganic Chemistry (CY11001)



Chelate Effect

Books to Refer:

Inorganic Chemistry by Shriver & Atkins

Inorganic Chemistry by James E. Huheey

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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					

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
  - Addition Compounds that loose identity in aq solutions
  - Example
    - $[Co(NH_3)_6]Cl_3$

Teeth of a ligand (teeth $\rightarrow$ dent)

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

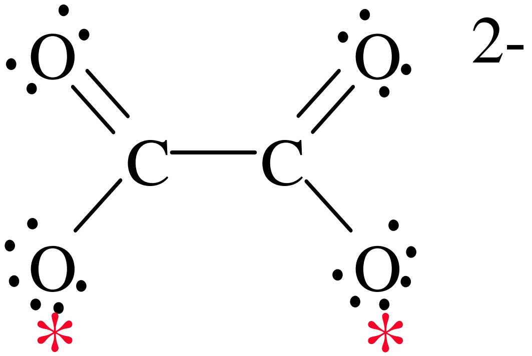
chelating agents

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

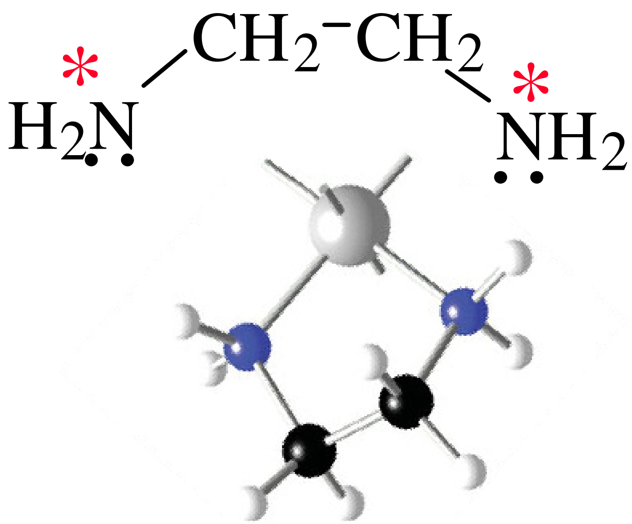
MONODENTATE					
Formula[a]	**Name as Ligand[b]**	**Formula[a]**	**Name as Ligand[b]**	**Formula[a]**	**Name as Ligand[b]**
Neutral Molecules					
NH_3	Ammine	NO	Nitrosyl	H_2O	Aqua
CH_3NH_2	Methylamine	CO	Carbonyl	C_5H_5N	Pyridine
Anions					
F^-	Fluoro	OH^-	Hydroxo	NCS^-	Thiocyanato-*N*
Cl^-	Chloro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

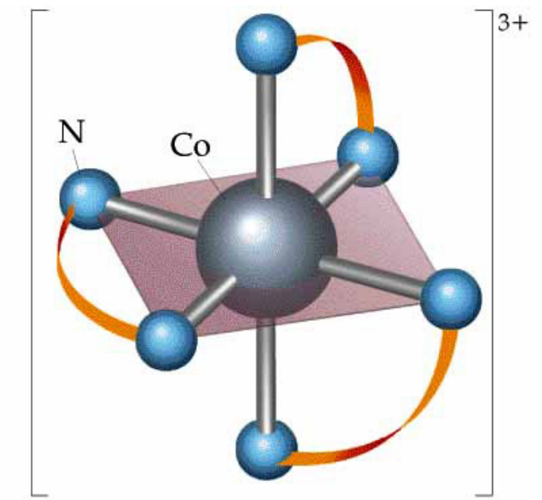
POLYDENTATE		
Name of Ligand[b]	**Abbreviation**	**Formula[a]**
Ethylenediamine	en	$H_2NCH_2CH_2NH_2$
Oxalato	ox	$[OOCCOO]^{2-}$
Ethylenediaminetetraacetato	EDTA	$[(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2]^{4-}$

oxalate ion

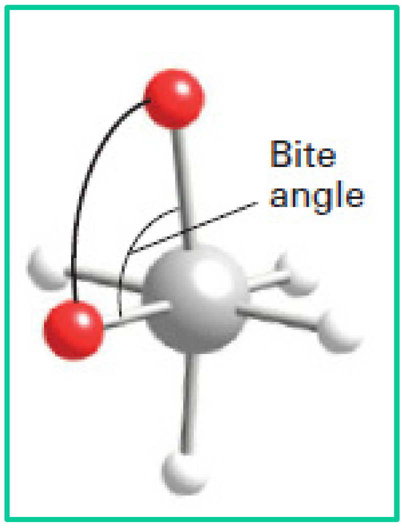


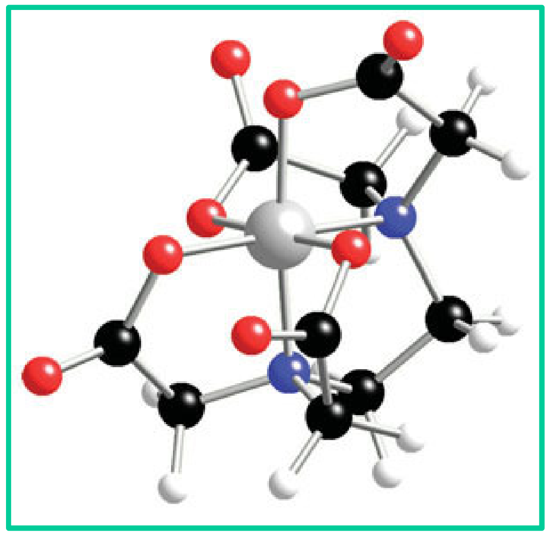
ethylenediamine





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





$[Ca(edta)]^{2-}$

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.

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 $\Rightarrow$ Stability constant

$M + L \rightarrow ML$	$K_{f1} = [ML]/[M][L]$
$ML + L \rightarrow ML_2$	$K_{f2} = [ML_2]/[ML][L]$
$ML_2 + L \rightarrow ML_3$	$K_{f3} = [ML_3]/[ML_2][L]$
$ML_{n-1} + L \rightarrow ML_n$	$K_{fn} = [ML_n]/[ML_{n-1}][L]$

solvent conc H_2O is of unit activity

K_f : strength of binding of ligand relative to water: strongly or weakly

stepwise formation conts to understand between structure & reactivity

$$M + nL \rightarrow ML_n$$

- K_{f1}, K_{f2}…. ⇒ Stepwise formation constant.
- To calculate concentration of the final product, use overall formation constant β_n:

- Relation among stepwise and overall formation const

$$\beta_n = [ML_n]/[M][L]^n$$

$$= K_{f1}\ K_{f2}\ K_{f3}\ \ldots.\ K_{fn}$$

$\Delta G^{\ominus} = -RT\ln(\beta)$

$\Delta G^{\ominus} = -2.303\ RT\log_{10}(\beta)$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

Coordination Equilibria & Chelate effect

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

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

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

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

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

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

$$\beta_4 = \mathbf{K_1\ K_2\ K_3\ K_4 = 10^{(2.65 + 2.10 + 1.44 + 0.93)} = 10^{7.12}}$$

What are the implications of the following results?

$[Ni(H_2O)_6]^{+2} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$	$\log \beta = 8.6$
$[Ni(H_2O)_6]^{+2} + 3\ NH_2CH_2CH_2NH_2\ (en) \rightarrow [Ni(en)_3]^{2+} + 6H_2O$	$\log \beta = 18.3$
$[Ni(NH_3)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2\ (en) \rightarrow [Ni(en)_3]^{2+} + 6NH_3$	$\log \beta = 9.7$

now logK value: why? K =0.64 (logK = -0.2) to 1.25×10^5 (logK = 5.1)

Complex Formation: Major Factors

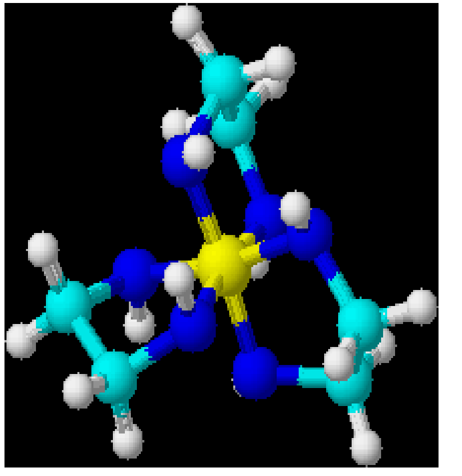
$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

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

When β increases ΔG becomes more –ve as $\Delta G^{\ominus} = -RT\ln(\beta)$
A more -ve ΔG can result from making ΔS +ve…..

Chelate Formation: Major Factors

$$[Ni(H_2O)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2\ (en) \longrightarrow [Ni(en)_3]^{2+} + 6NH_3$$



- en is bidentate and *chelating* ligand
- rxn proceeds towards right, ΔG negative
- $\Delta G = \Delta H - T\Delta S$ (ΔH small -ve, ΔS ++ve)
- rxn proceeds due to entropy gain
- log β = 18.3 (becomes higher)
- ΔS ++ve is the major factor behind chelate effect

Chelate Formation: Entropy Gain

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

$Cd^{2+} + 4\ MeNH_2 \leftrightarrow [Cd(MeNH_2)_4]^{2+}$

$Cd^{2+} + 2\ en \leftrightarrow [Cd(en)_2]^{2+}$

Ligands	log β	ΔG kJmol^{-1}	ΔH kJmol^{-1}	ΔS JK^{-1}mol^{-1}
4 NH_3	7.44	-42.5	- 53.2	- 35.5
4 $MeNH_2$	6.52	-37.2	-57.3	- 67.3
2 en	10.62	-60.7	-56.5	+13.8

$MeNH_2$ is satirically crowded

4 similar bonds are formed for all cases, yet formation of chelate containing complex is more favourable: greater stability: chelate effect

Substitution reactions

Rapid

slow

labile complexes

Inert complexes

These are kinetic terms.....

The term inert and labile are relative

"A good rule of thumb is that those complexes that react completely within 1 min at 25º 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**

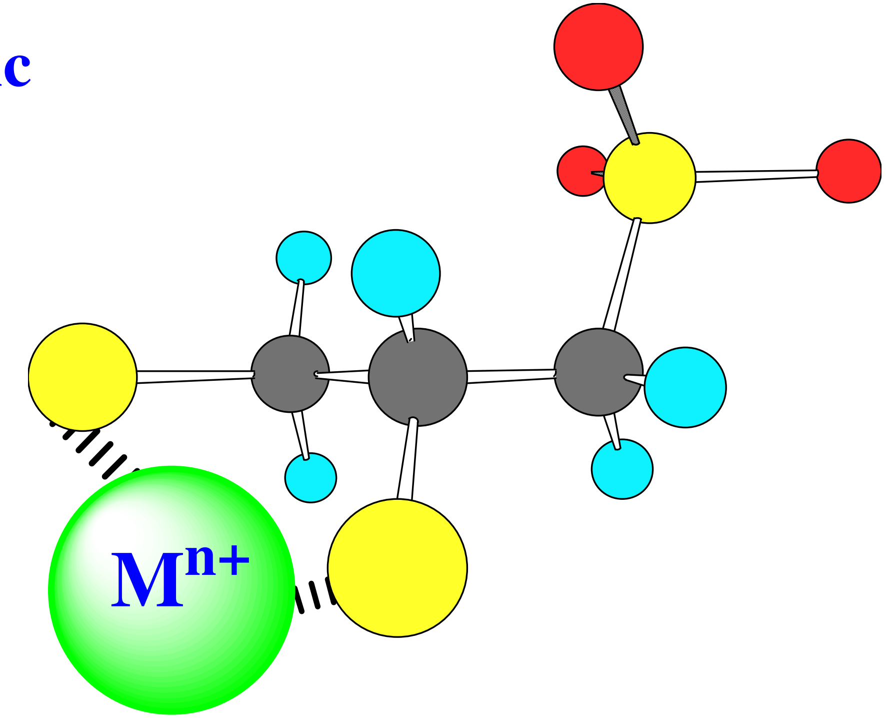
Chelating agents:

Used to remove unwanted metal ions in water.

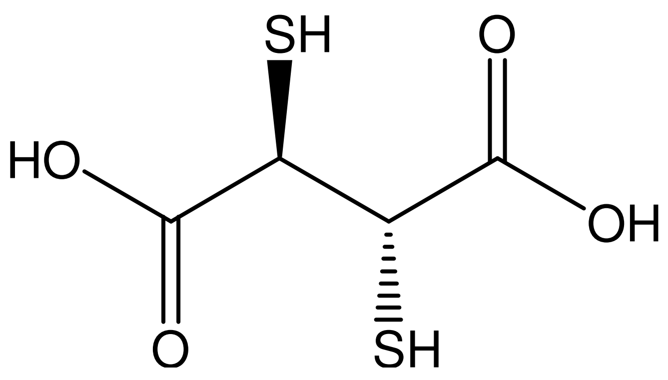
Selective removal of Hg^{2+} and Pb^{2+} from body when poisoned.

Important Chelating Ligands

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

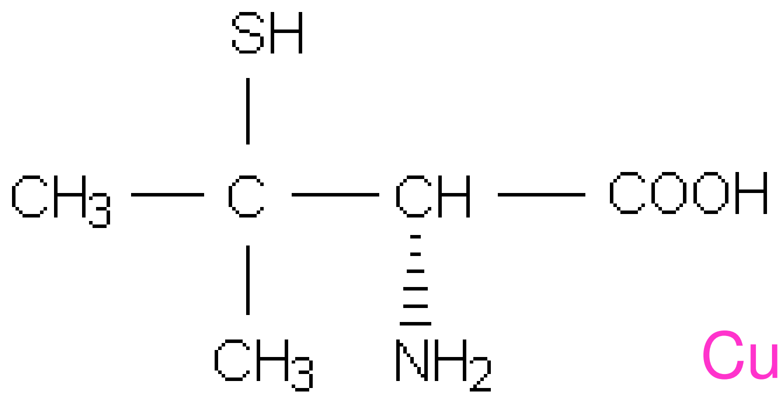


DMPS is a effective chelator with two groups thiols - for mercury, lead, tin, arsenic, silver and cadmium.



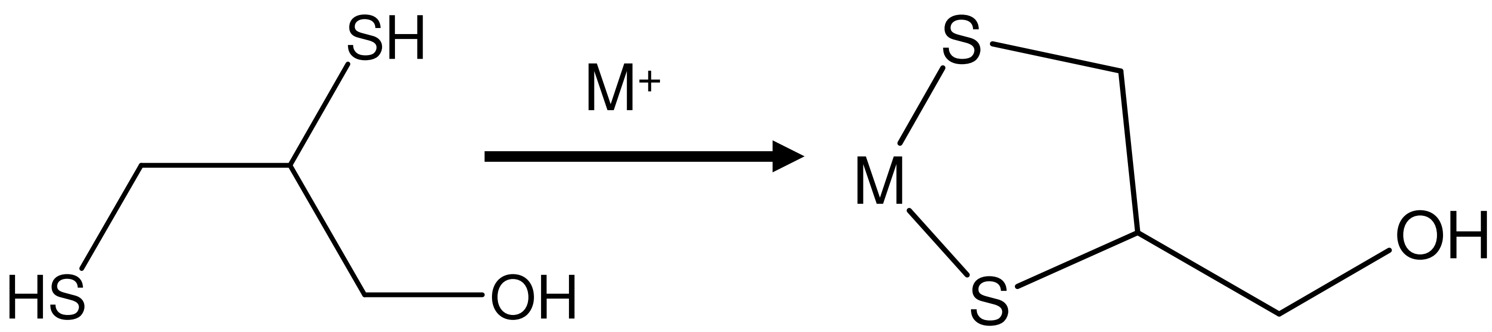
(R,S)-2,3-dimercaptosuccinic acid

As, Cu, Pb, Hg



D-Penicillamine

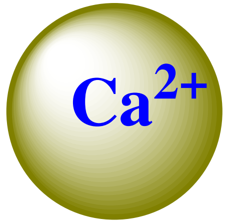
Cu
As
Hg
Au
Pb



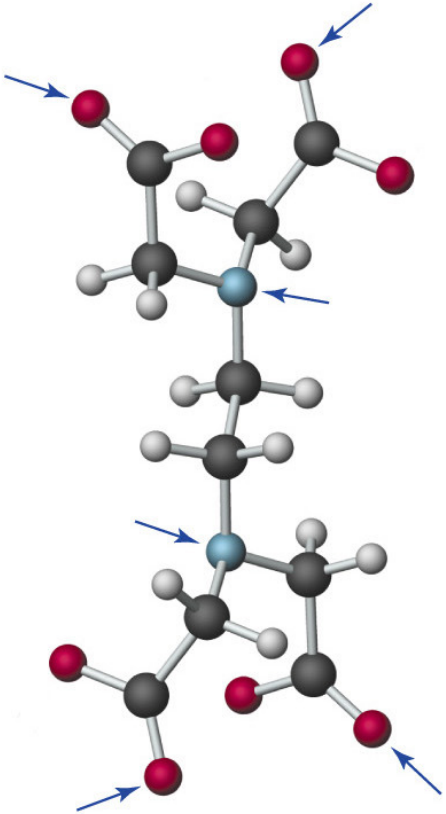
Dimercaprol

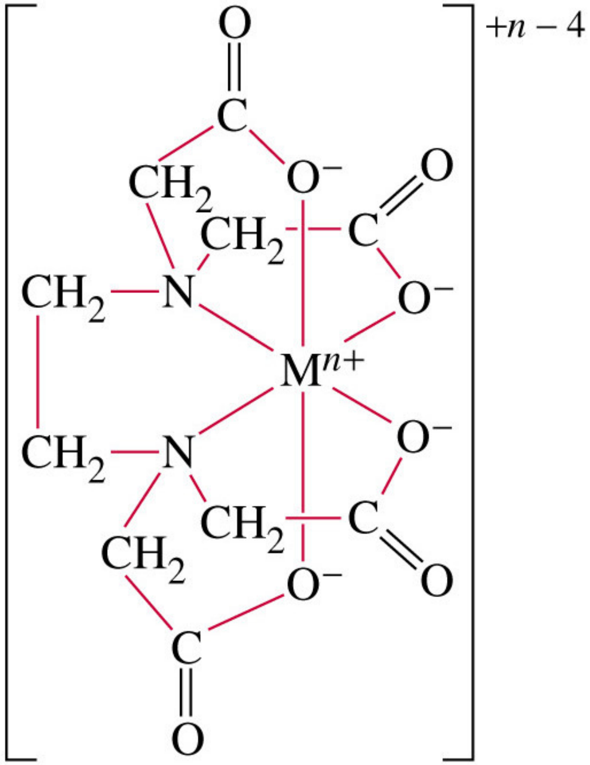
As
Hg
Au
Pb

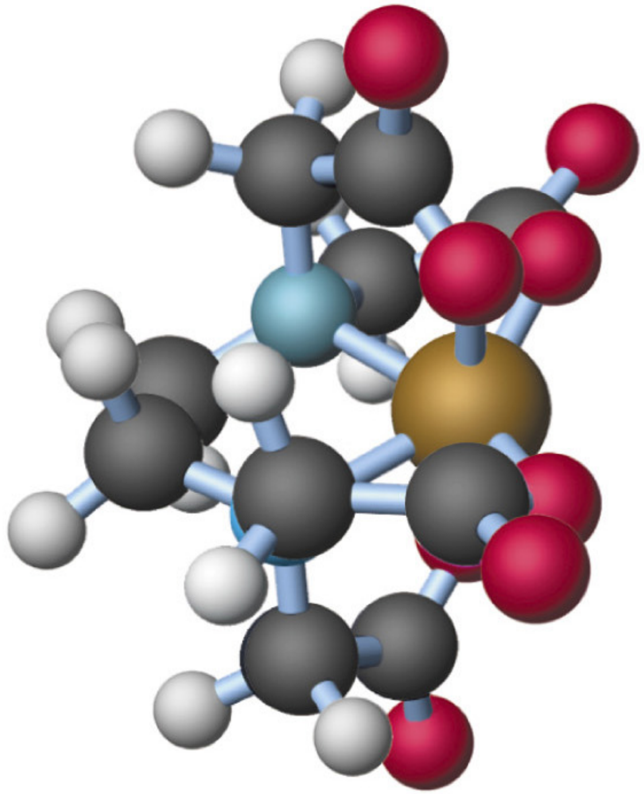
Important Chelating Ligands
EDTA



Anticoagulant

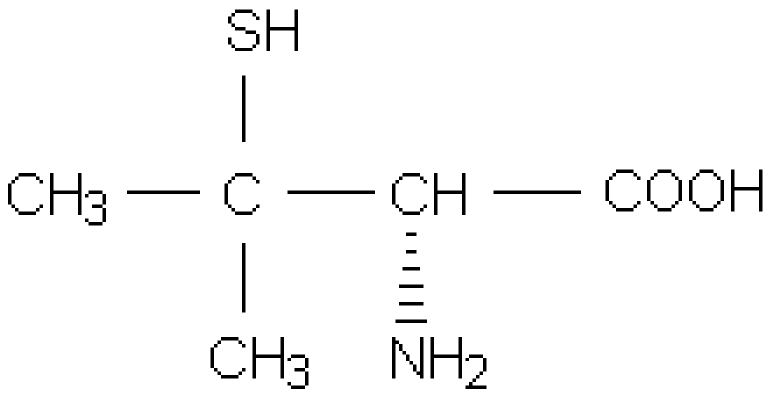






chelation therapy

chelation therapy

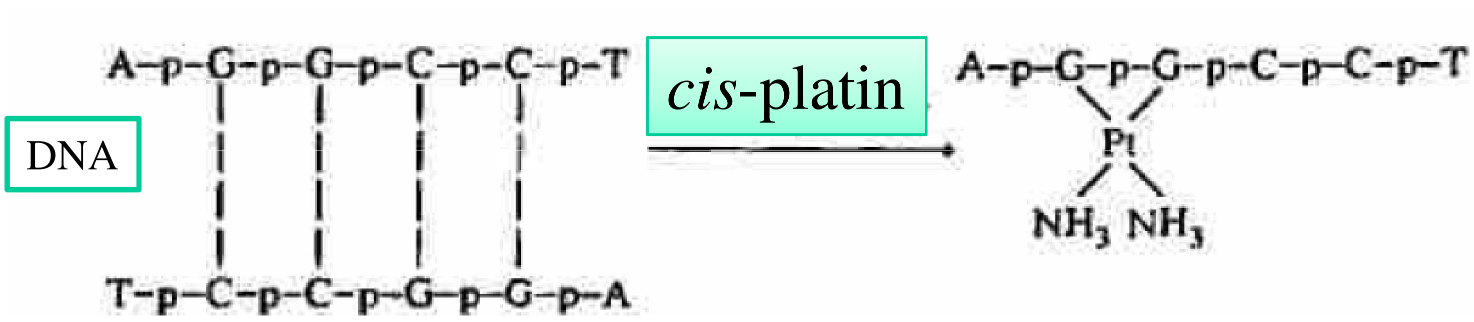


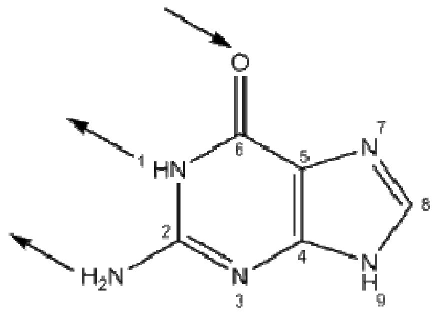
D-Penicillamine

- chelating agents can be used therapeutically to treat problems caused by toxic elements
- essential elements can be toxic if present in too great quantity
- this the case of WILSON’s disease, a genetic disease involving build up of excessive quantity of Cu in body
- D-penicillamine is used as a cheating agent for this chelation therapy (purple complex)

cis-platin

- A slightly different mode of therapy involves use of cis-diaminedichloroplatinum (II) or cis-platin in cancer treatment.
- Exact action of drug is unknown
- Binding of cis-platin with DNA seriously interfere with the ability of GUANINE bases to undergo Watson-Crick base pairing





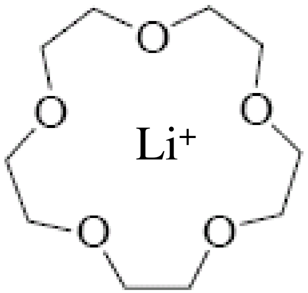
Guanine

Important Chelating Ligands

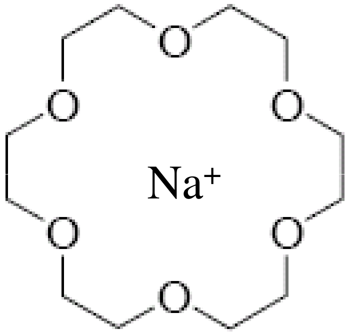
Macrocylic Ligands

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

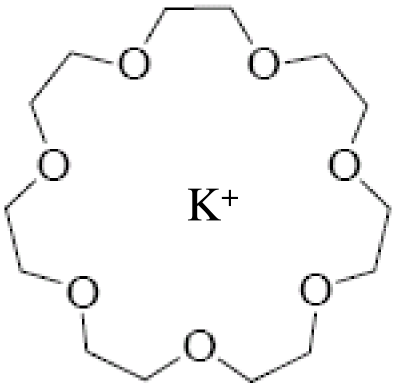
crown ether:



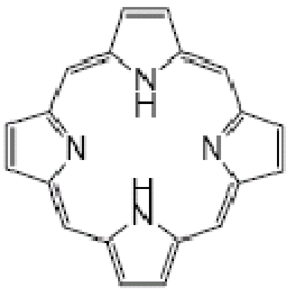
15-crown-5



18-crown-6

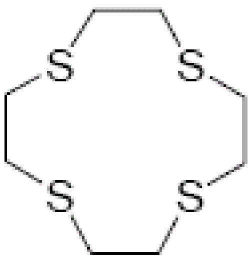


21-crown-7

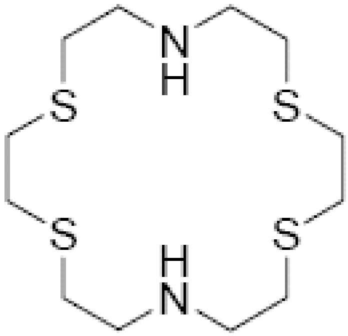


porphyrin

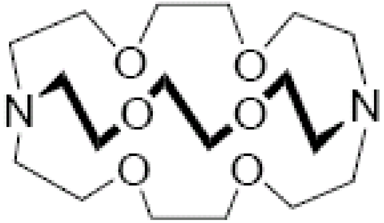
thia-crown ether:



aza-thia-crown:



cryptand:



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