5.111 Lecture 27
Transition Metals Topics: Formation of coordination complexes, coordination number, coordination complex notation, structures of coordination complexes, chelate effect, isomers, d-electron counting, and d-orbitals.
Chapter 16 p. 669-681 (p. 620-631 in 3rd ed).

From Wednesday's handout Now the answer to the biochemical question

How is vitamin B_{12} reduced in the body? Vitamin B_{12} is reduced by a protein called flavodoxin.

$E°$ for vitamin B_{12} is -0.526 V
$E°$ for flavodoxin is -0.230 V

Is the reduction of vitamin B_{12} by flavodoxin spontaneous?

$$\Delta E°(\text{cell}) = E°(\text{reduction}) - E°(\text{oxidation})$$
$$= E°(\text{vitamin } B_{12}) - E°(\text{flavodoxin})$$
$$= -0.526 \text{ V} - (-0.230 \text{ V}) = -0.296 \text{ V}$$

$$\Delta G° = -n\Im\Delta E° = -(1)(96485 \text{ Cmol}^{-1})(-0.296 \text{ V}) = +28.6 \text{ kJ/mol}$$

Vitamin B_{12} is a better reducing agent than flavodoxin. Vitamin B_{12} should reduce flavodoxin not the other way around. So why don't we all have heart disease and megaloblastic anemia?

Answer: S-adenosylmethionine provides the energy to drive the reaction. The ΔG° for the cleavage of S-adenosylmethionine is -37.6 kJ/mol

Today's material

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
			74 W				78 Pt	79 Au	80 Hg

Developed from Lippard & Berg 1994

d-block metals naturally occurring in biology – V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, W.

d-block metals used as probes of biological systems and/or drugs include Cr, Co, Y, Tc, Ag, Cd, Pt, Au, Hg.

Roles of metals in biology include

- global cycling of nitrogen, carbon, hydrogen
- radical reactions
- biosynthesis of vitamins
- biosynthesis of deoxynucleotides
- etc

Formation of coordination complexes

A key feature of transition metals is their ability to form complexes with small molecules and ions.

Positive metals ions can attract electron density, usually a lone pair of electrons from another atom or molecule to form a coordination complex.

Donor atoms are called ligands (Lewis _________ –typically _______ one lone pair of electrons)

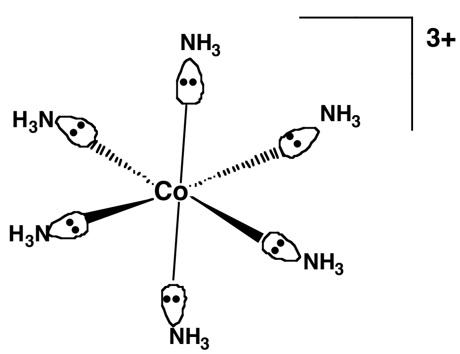
Examples of ligands:

:NO_2^-	:OCO_2^{-2}	:CN^-	:SCN^-	:NCS^-
$2e^-$	$2e^-$	$2e^-$	$2e^-$	$2e^-$
:OH^-	:OH_2	:NH_3	:CO	:NO^+
$2e^-$	$2e^-$	$2e^-$	$2e^-$	$2e^-$

Acceptor atoms are transition metals (Lewis acid –accept lone pair electrons)

Examples of transition metals: Ti, Cr, Mn, Fe, Co, Ni, Zn, Ir, Pt, etc

Coordination complexes ≡ metals surrounded by ligands. Example:



Coordination number (CN) is the number of ligands bonded to the metal ion.
Here CN = 6. Six ligands comprise the primary coordination sphere.

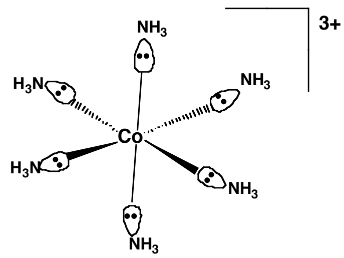
Typical CN's range from 2-12. Six is the most common.

Coordination Complex Notation

$[Co(NH_3)_6]^{+3}\quad 3Cl^{-1}$

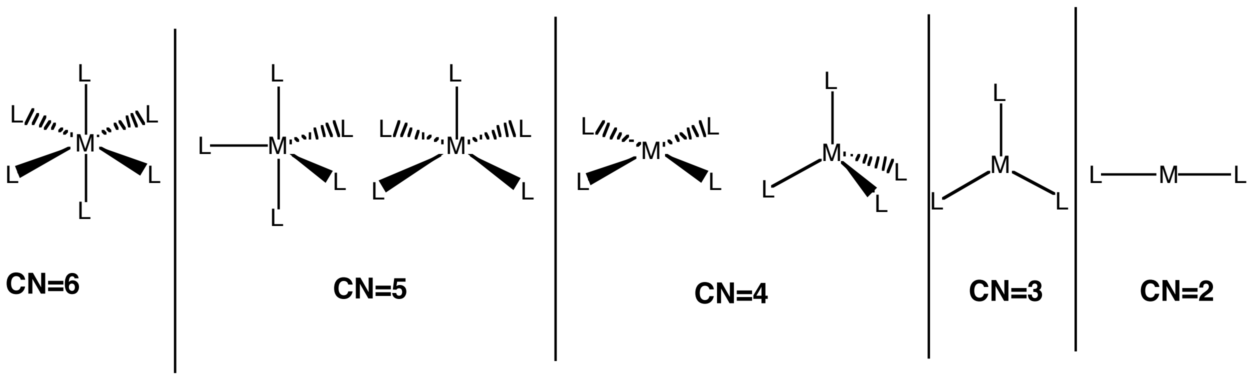
$\downarrow$

$[Co(NH_3)_6]Cl_3$



NH_3 within bracket is bound to Co, Cl outside bracket is a counter ion.

Structures of coordination complexes (M = Metal, L = Ligand)



__________	trigonal bipyramidal	square pyramidal	square planar	tetrahedral	trigonal planar	linear

Chelate Effect in Coordination Complexes

Ligands that bind a metal at one site are called unidentate or monodentate (one tooth).

Ligands that have two or more points of attachment to the metal are called chelating ligands and the coordination complexes are called chelates (greek for claws).

Bidentate – two points of attachment

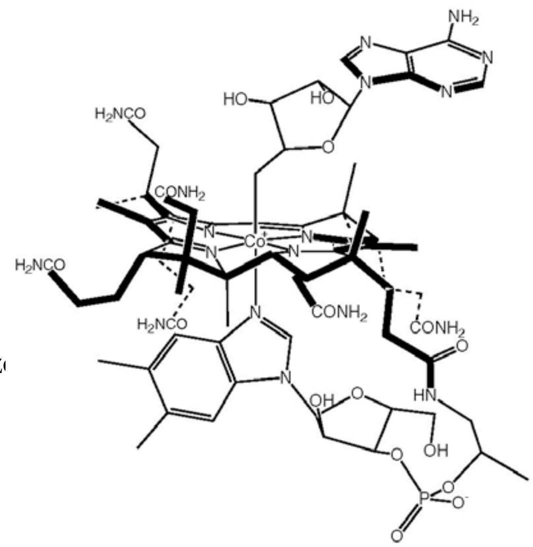
Tridentate –

Tetradentate - ex. corrin ring of B_{12}

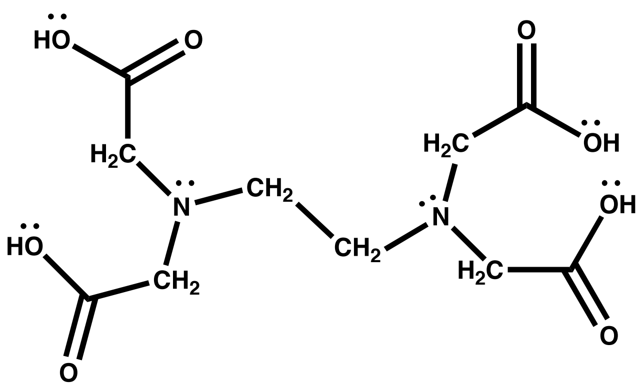
Hexadentate – ex. EDTA

Metal chelates are unusual stable. This is partly due to the favorable entropic factor accompanying release of non-chelating ligands (usually H_2O) from the coordination sphere.
Examples

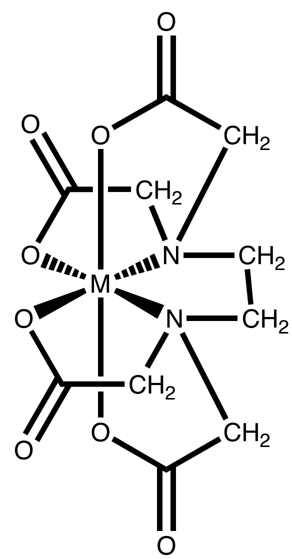
1. Vitamin B_{12}.
Cobalt is coordinated by a planar tetradentate ligand (corrin ring system). It is also coordinated by an upper axial ligand (5'deoxyadenosine) and a lower axial ligand (dimethylbenzimidaz



2. Ethylenediamine tetraacetic acid (EDTA).



Free EDTA



EDTA in complex with metal (M)

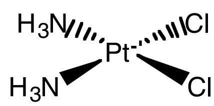
Binding of EDTA is entropically favorable. Six molecules of H_2O are released for every 1 molecule of EDTA bound.

<u>Uses</u>

Geometric Isomers

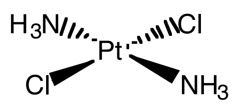
Geometric isomers can have vastly different properties.

$[Pt(NH_3)_2Cl_2]$ has two geometric isomers



potent anti-cancer drug

cisplatin

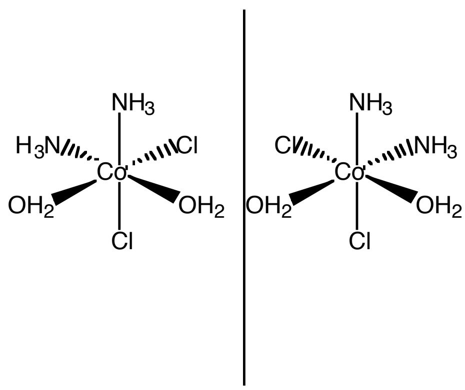


no known function

transplatin

Optical isomers (enantiomers) are non-superimposable mirror images of each other.

A complex that is not identical to its mirror image is also called a chiral complex.
Chiral molecules have different properties in chiral environments (such as a human body).



mirror plane

d-Electron Counting in Coordination Complexes

d-electron count of metal = group number (periodic table) -oxidation number of metal

1. find oxidation number:

For Co in $[Co(NH_3)_6]^{3+}$

NH_3 is neutral, so Co must be +3

2. d-count is 9-3 = 6 d^6

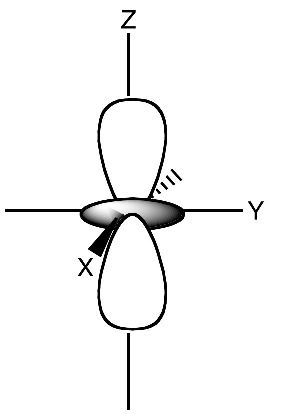
Practice with d-counts

Complexes	Oxidation number of metal	d-count
$[Ni(CO)_4]$		
$[Co(H_2O)_2(NH_3)Cl_3]^-$		

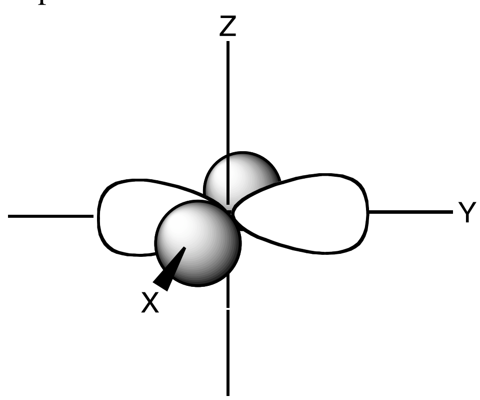
d Orbitals

There are five d orbitals: d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}.

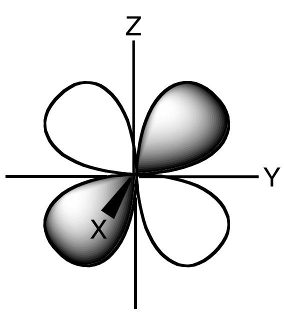
You need to be able to draw their shapes.



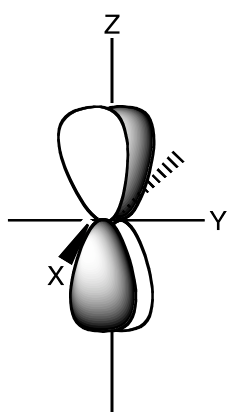
d_{z^2} has maximum amplitude along z and doughnut in xy plane



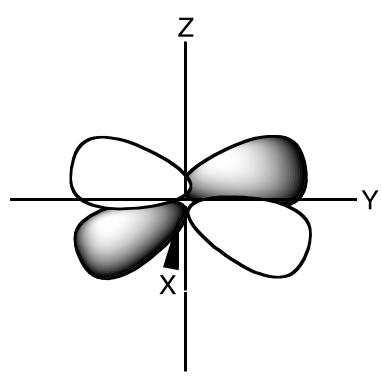
$d_{x^2-y^2}$ has maximum amplitude along x and y axes.



d_{yz} has maximum amplitude 45° to y and z axes



d_{xz} has maximum amplitude 45° to x and z axes



d_{xy} has maximum amplitude 45° to x and y axes