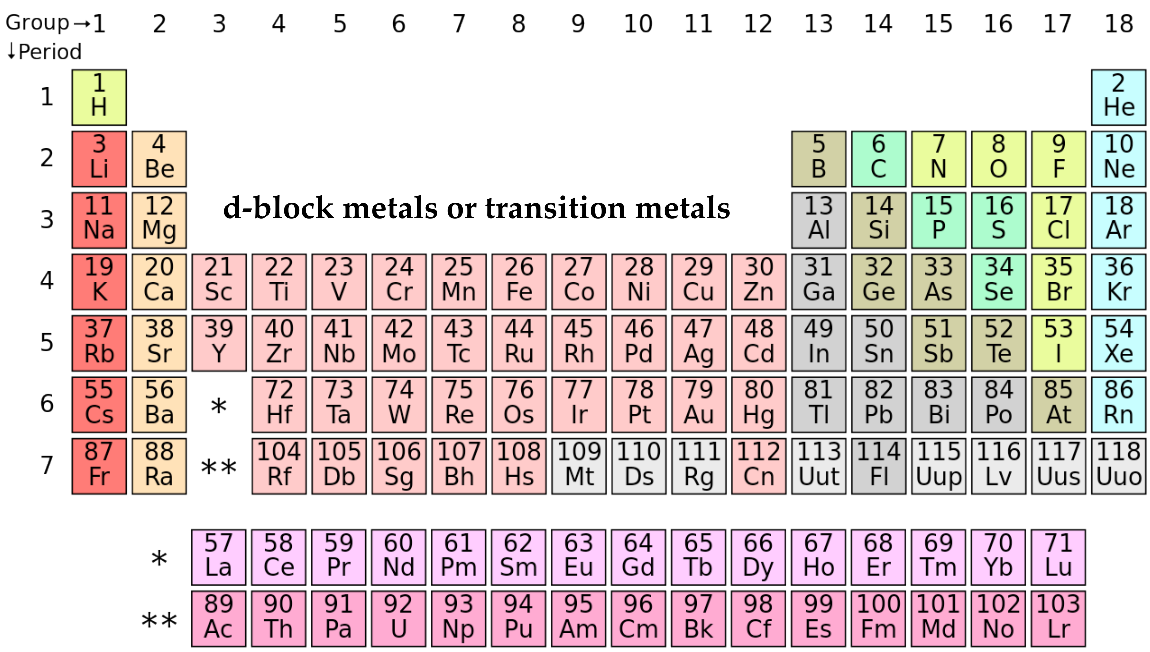
5.111 Lecture # 27 **Monday, November 17, 2014**

Reading For Today: 16.5-16.7 in 5th and 4th editions
Reading for lecture# 28: 16.8-16.11 in 4th and 5th editions

Topic: I. d-Block Metals or Transition Metals
II. Coordination Complexes (Chelate effect, Shapes, Isomers)
III. d-orbital Counting and d-orbitals

I. d-Block Metals or Transition Metals

Elements in groups 3-12 are d-block metals, often referred to as ____________ metals.



Periodic Table of the Elements, by DePiep 2013. Wikimedia Commons.

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 pharmaceuticals include: Cr, Co, Y, Tc, Ag, Cd, Pt, Au, Hg.

Roles of metals in biology include:
global cycling of nitrogen, carbon, hydrogen; biosynthesis of vitamins and deoxynucleotides; respiration; photosynthesis etc

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IN THEIR OWN WORDS

Dr. Sarah Bowman studies a protein from a pathogenic bacterium that is found in the stomach and is known to cause ulcers. She explains how the bacterium survives in the low pH environment of the stomach by using nickel-dependent proteins to buffer the acidity of its environment.

II. 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)

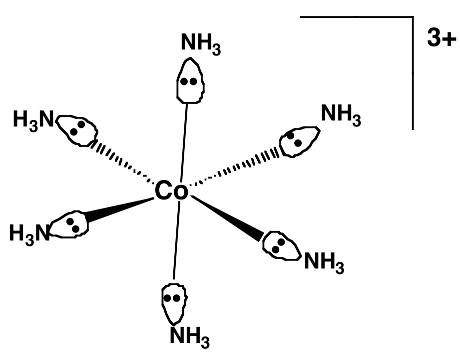
Examples of ligands:

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

Acceptor atoms are transition metals (Lewis __________– ___________________ one lone pair of electrons)

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

Coordination complexes are composed of metals that are surrounded by ligands.
Example:



Coordination number (CN) is the number of ligands bonded to the metal ion.

Here CN = 6. _______ligands comprise the primary coordination sphere.

CN numbers typically range from 2-12. Six is the most common.

Coordination Complex Notation

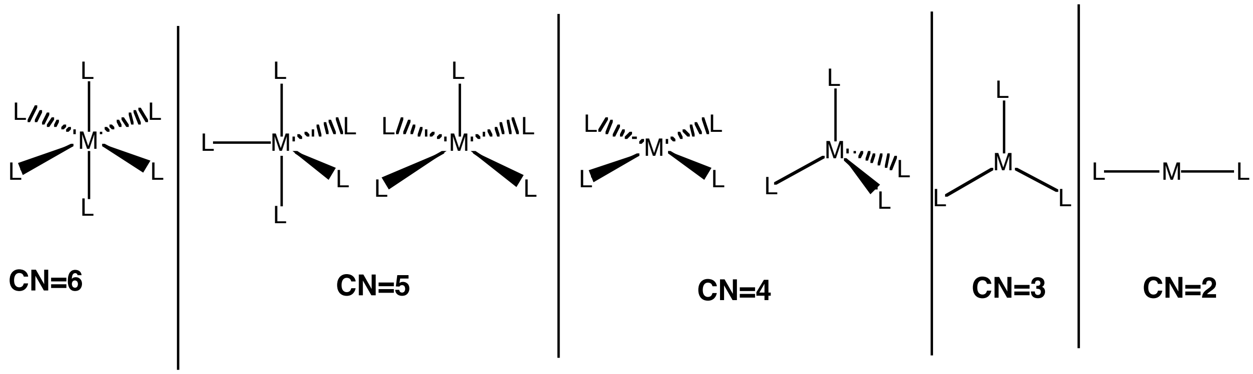
$[Co(NH_3)_6]^{+3}$ $3Cl^{-1}$

$\downarrow$

$[Co(NH_3)_6]Cl_3$

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

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



Chelates: another name for coordination complexes, from the Greek word for claws.
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Ligands ________________ a metal by binding with one or more sites of attachment

Monodentate (one tooth): one point of attachment

Bidentate: __________ points of attachment

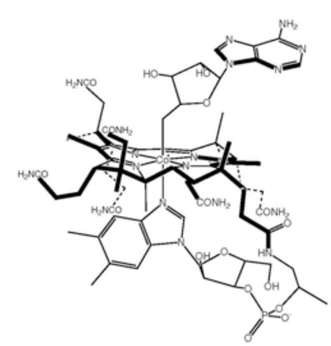
Tridentate: __________ points of attachment

Tetradentate : ________ points of attachment

Hexadentate: ________ points of attachment

Examples of multidentate chelates

1. Vitamin B_{12}.

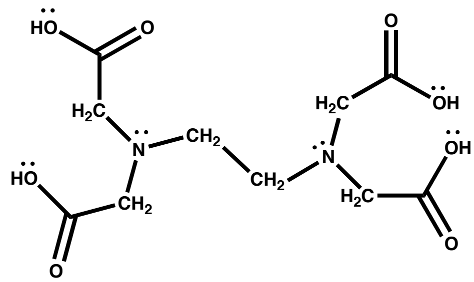


Cobalt is coordinated by a planar tetradentate ligand (corrin ring).

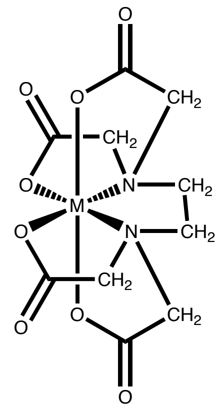
It is also coordinated by an upper axial ligand (5'-deoxyadenosine) and a lower axial ligand (dimethylbenzimidazole)

It’s structure was determined using X-ray crystallography by British Crystallographer Dorothy Crowfoot Hodgkin. She won the Nobel Prize in 1964 for this work and for determining the structure of pencillin.

2. Ethylenediamine tetraacetic acid (EDTA).



Free EDTA



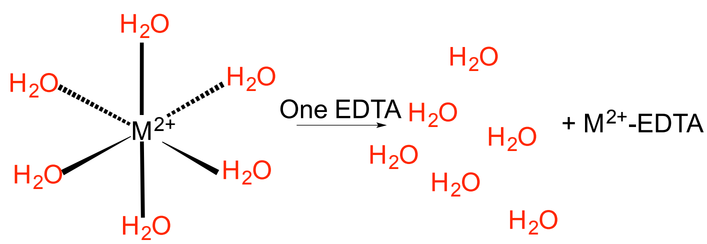
EDTA in complex with metal (M)

Geometry around M is

____

__________ dentate

Binding of EDTA is ______________________ favorable.



Six molecules of H_2O are released for every 1 molecule of EDTA bound.

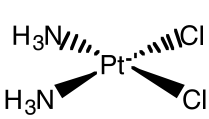
The Chelate Effect refers to the unusually ____________________ of metal chelates due to the favorable entropic factor accompanying release of non-chelating ligands (usually H_2O) from the coordination sphere.

Uses of EDTA

Isomers

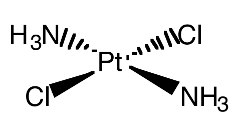
Geometric isomers can have vastly different properties.

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



potent anti-cancer drug

cisplatin



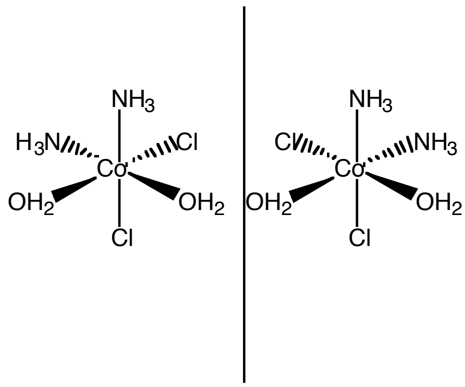
no known function

transplatin

Only when the Cl ligands on same side (cis to each other) can the molecule bind to DNA. Cisplatin cured Lance Armstrong of cancer.

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

Chiral molecules have different properties in chiral environments (such as a human body).



mirror plane

III. d-Electron Counting in Coordination Complexes and d-Orbitals

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

1. find oxidation number

for Co in $[Co(NH_3)_6]^{3+}$ = _________

Hint: NH_3 is a neutral ligand

2. d-count is 9 - _____ = _____ $d^{???}$

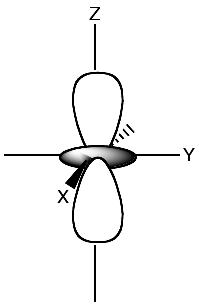
Practice with d-counts

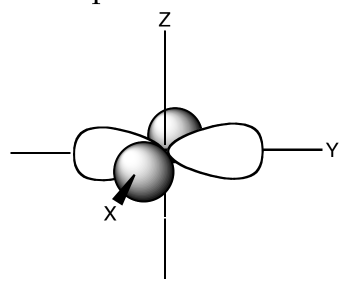
Complexes	Oxidation number of metal	d-count
$[Ni(CO)_4]$		
$[Co(H_2O)_2(NH_3)Cl_3]^-$		

d Orbitals

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

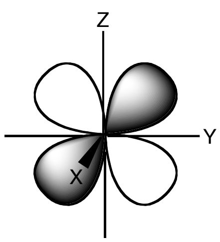
You need to be able to draw their shapes.

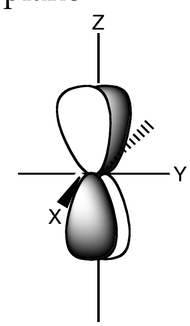


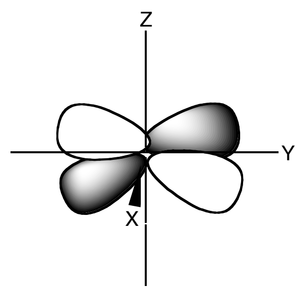


d_{z^2} has maximum amplitude along z and doughnut in xy plane

$d_{x^2-y^2}$ 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