

Transition Elements and Complexes

Only responsible for material covered in class

Structure of complex compounds

Central **metal cation surrounded by ligands** (anions or molecules)

Ligand is bonded to metal through an electron pair

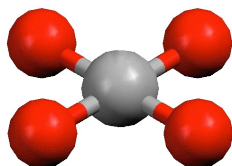
Ligands act like Lewis bases by donating an electron pair

Ligands bond in first coordination sphere [does not dissociate in water]

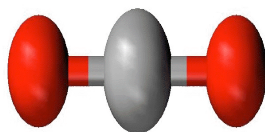
Coordination number- the number of atoms bonded directly to metal

Shapes and coordination numbers shown below

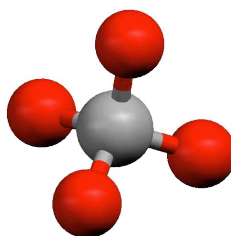
Octahedral most important



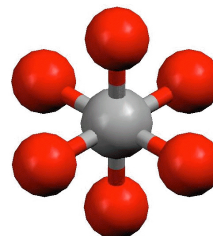
Square Planar (4)



Linear (2)



Tetrahedral (4)



Octahedral (6)

Examples of metals that could be in center of each of these (see below):

Pt - center

Ag - center

Cd - center

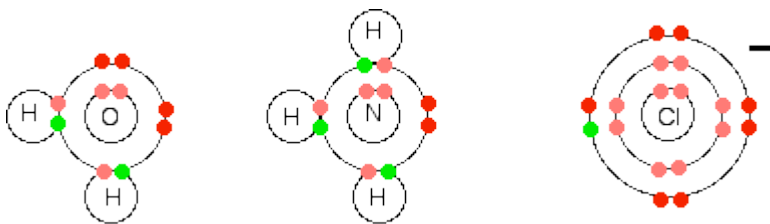
Co - center

<http://chemlab.truman.edu/CHEM121Labs/MolecularModeling1.htm>

Examples of ammonia molecules acting as ligands for each of above complexes



Pair of electrons on ligand donate to metal



<http://www.chemguide.co.uk/inorganic/complexions/whatis.html>

Can be bonded through ion or molecule

The active lone pair (in red) forms coordinate bonds with metal ions.

Charge of complex can be positive or negative and is the sum of parts

Most stable complexes metal ions that are transition elements or Group 3 (IIIA) or Group 4 (IVA) metals.

- 1) high positive charge
- 2) small ionic radius

<u>Complex</u>	<u>Charge of Complex</u>	<u># of species in H₂O</u>
[Pt (NH ₃) ₆] Cl ₄	+4	5
[Pt (NH ₃) ₅ Cl] Cl ₃	+3	4
[Pt (NH ₃) ₄ Cl ₂] Cl ₂	+2	3
[Pt (NH ₃) ₃ Cl ₃] Cl	+1	2
[Pt (NH ₃) ₂ Cl ₄]	0	1
K[Pt (NH ₃) Cl ₅]	-1	2
K ₂ [Pt Cl ₆]	-2	3

Examples [Pt (NH₃)₆] Cl₄ dissolves to [Pt(NH₃)₆]⁴⁺ and 4 Cl⁻
 K₂[Pt Cl₆] dissolves to 2 K⁺ and [Pt Cl₆]²⁻

The potassium and chlorine atoms not coordinated (outside of the []) will dissociate in water.

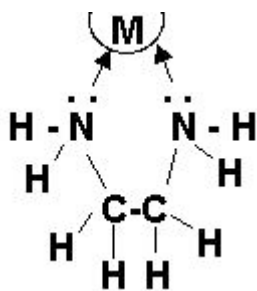
The ammonia molecules and chlorine ions coordinated (inside of the []) will NOT dissociate in water.

Ligand may form more than one bond with a metal

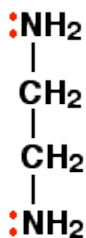
Types of Ligands

Unidentate – one bond

Bidentate – two bonds

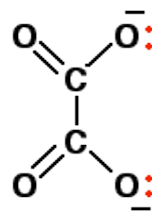


(1)



1,2-diaminoethane

(2)



ethanedioate ion

(2)

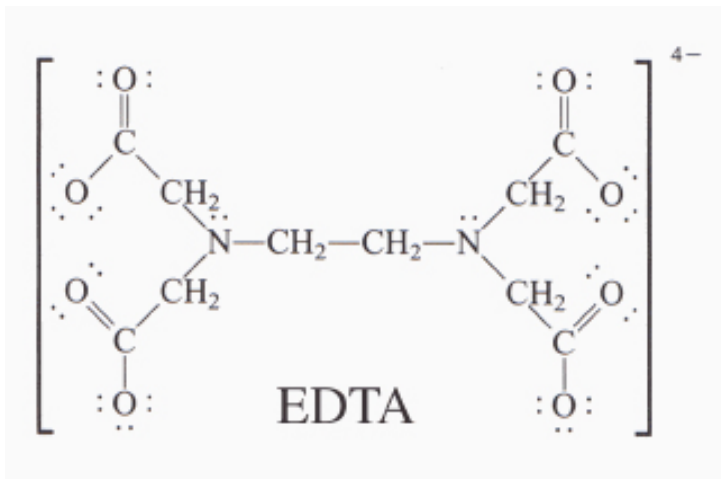
<http://www.bgsu.edu/departments/chem/faculty/endres/ch128/Calcium.htm> (1)

<http://www.chemguide.co.uk/inorganic/complexions/whatis.html> (2)

Multidentate ligands

Multidentate ligands can coordinate 2, 3, 4, 5, or 6 positions

Ethylenediaminetetraacetate (EDTA)



http://www.progressivegardens.com/growers_guide/plantnut.html

Can wrap around metal and bond at six positions in octahedral complex

EDTA used to bind to Hg to treat heavy metal poisoning, prevent atoms from binding in body

Porphyrin and Hemoglobin – example of multidentate ligand

Porphyrin- molecule can bind four nitrogens with metal – quadridentate

Hemoglobin contains Fe^{2+} that binds to oxygen

Hemoglobin picks up O_2 in lungs and releases in body tissue

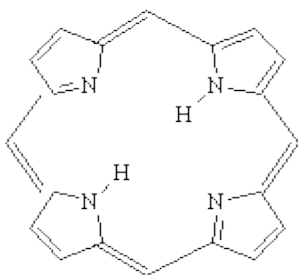
$\text{Hemoglobin} + \text{O}_2 \rightleftharpoons \text{oxyhemoglobin} + \text{H}_2\text{O}$

Fe octahedral ligand: 4 to ring, 1 to protein, and 1 to O_2 or water

Chlorophyll contains Mg^{2+} held by porphirin ring and is the green pigment of plants that acts as catalyst for conversion of

$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 (\text{glucose}) + \text{O}_2$

Chlorophyll absorbs sunlight



http://www.mercola.com/2002/mar/23/chlorophyll_hemoglobin.htm

Basic structure of porphirin ring

Porphyrin- porphirin with substituted groups on it

Thermodynamic or Kinetic Limits

Labile complexes rapidly undergo reactions in which ligands are replaced

Nonlabile or inert complexes will not exchange ligands or will do so only very slowly

Distinction between rate (how fast, kinetics) and extent of reaction (how far, thermodyn.)



$K = 10^{-34}$ reactants favored

products not form (say it is thermodynamically limited)



$K = 10^{22}$ products favored

This second reaction is a very slow process - can take weeks in dilute acid to convert so it is practically inert (say it is rate limited)

Other cases may be very rapid exchange of ligands

Extra Material below (will not cover)

Naming Transition Compounds - Simple Nomenclature

1. If naming a salt, name the cation first
2. Name the parts of a complex in alphabetical order including anions, neutral molecules, and metal ions
3. Anionic ligands given -o ending

OH^-	hydroxo	CN^-	cyano
O^{2-}	oxo	CNO^-	cyanato
S^{2-}	thio	$\text{C}_2\text{O}_4^{2-}$	oxalate
Cl^-	chloro	NO_3^-	nitrate
F^-	fluoro	NO_2^-	nitro
CO_3^{2-}	carbonato	SO_4^{2-}	sulfate
4. Neutral ligands names not changed except:

H_2O	aqua
NH_3	ammine
CO	carbonyl
NO	nitrosyl
5. Number of ligands indicated by a prefix (di-, tri-, tetra-, penta-, hexa-) and for multidentate (bis-, tris-, tetrakis-)
6. Oxidation number of metal is given as a Roman numeral in parentheses
7. If complex is an anion then ending -ate is used but not changed for neutral or cation

The following examples illustrate further applications of the IUPAC guidelines:

$\text{Na}_2[\text{FeEDTA}]$	Sodium ethylenediaminetetraacetateferrate (II)
$[\text{Co}(\text{en})_3]\text{Cl}_3$	Tris(ethylenediamine) cobalt (III) chloride
$[\text{Zn}(\text{NH}_3)_4](\text{NO}_3)_2$	Tetraamminezinc nitrate
$\text{K}[\text{Ag}(\text{CN})_2]$	Potassium Dicyanosilver (I)
$[\text{Rh}(\text{NH}_3)_5\text{Br}]\text{Br}_2$	Pentaamminebromorhodium (III) bromide

Bonding in complexes

Ligands donate a pair of electrons to form coordinate covalent bonds with the central metal ion

More involved theories deal with details of

- Electronic configuration
- Electronic energy levels
- Spatial location of orbitals
- Valence Bond theory
- Crystal Field theory
- Molecular Orbital theory

Be aware that d^2sp^3 (or sp^3d^2) hybrid orbitals on metal form octahedral spatial orientation



sp^3d^2 orbitals

http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/10.html