Metal Complexes -- Chapter 25 (Sections 25.3 - 25.5)

1. Metal Complex -- consists of a set of ligands that are bonded to a central metal ion by coordinate covalent bonds.

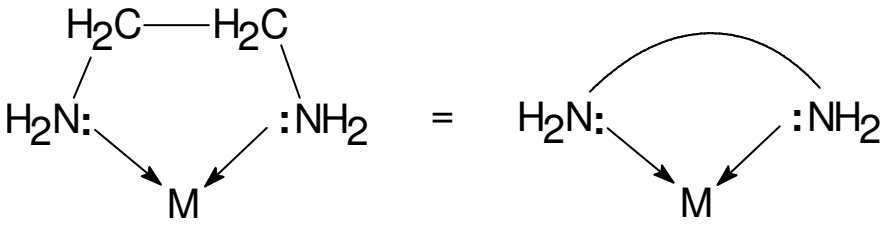
e.g., $Cu^{2+} + 4\,L \longrightarrow CuL_4^{2+}$ (L = NH_3, H_2O, etc.)

(a) Ligands are Lewis Bases and can be:

- *monodentate* -- one donor atom
  e.g., H_2O, NH_3, Cl^-, OH^-, etc.

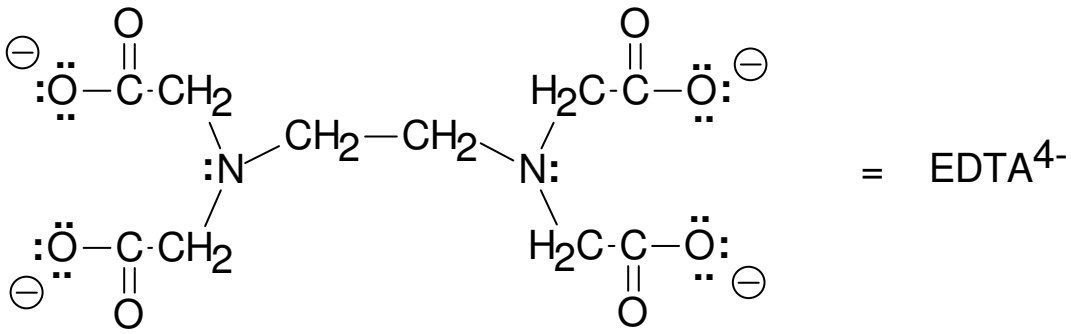
- *bidentate* -- two donor atoms

  e.g., ethylenediamine, $NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$ "en"



- *polydentate* -- more than two donor atoms

  e.g., EDTA -- ethylenediaminetetraacetic acid
  (6 donor atoms)



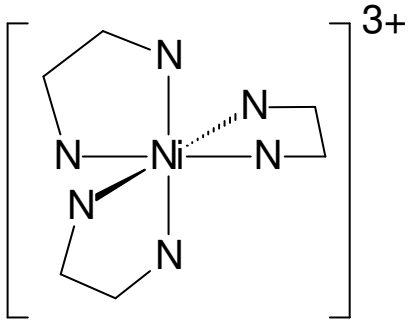
(b) **Writing Formulas of complex ions**

metal ion first, then ligands
total charge = sum of metal ion + ligands

e.g.,	metal ion	ligand	complex
	Cu^{2+}	H_2O	$Cu(H_2O)_4^{2+}$
	Co^{3+}	NH_3	$Co(NH_3)_6^{3+}$
	Fe^{3+}	CN^-	$Fe(CN)_6^{3-}$

(c) **Chelate Effect** - complexes with bi- or polydentate ligands are more stable than those with similar monodentate ligands

e.g., $Ni(en)_3^{3+}$ is more stable than $Ni(NH_3)_6^{3+}$



(d) **Nomenclature** -- study rules and examples in book!

Complex	Name
$Ni(CN)_4^{2-}$	tetracyanonickelate(II) ion
$CoCl_6^{3-}$	hexachlorocobaltate(III) ion
$Co(NH_3)_4Cl_2^+$	tetraamminedichlorocobalt(III) ion
$Na_3[Co(NO_2)_6]$	sodium hexanitrocobaltate(III)
$[Cr(en)_2Cl_2]_2SO_4$	dichlorobis(ethylenediamine)-chromium(III) sulfate

2. Coordination Number and Structure

Coord # = number of donor atoms attached to the metal center

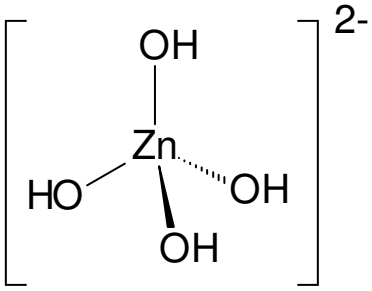
(a) Two-Coordinate Complexes -- linear structures

rare except for Ag^+

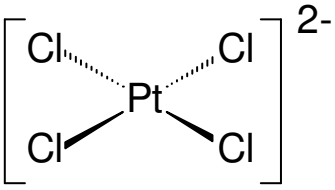
e.g., $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$

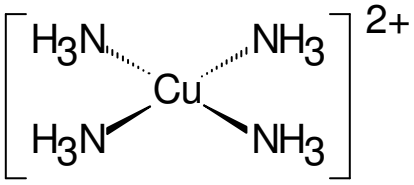
(b) Four-Coordinate Complexes -- two structural types

- **Tetrahedral** structures -- common for ions with filled d subshells, e.g., Zn^{2+} as in $Zn(OH)_4^{2-}$



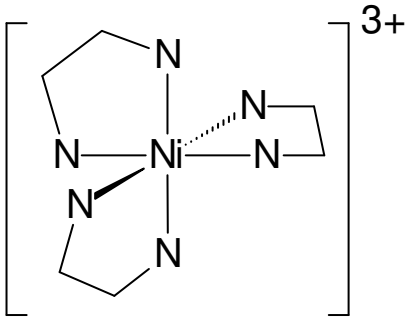
- **Square Planar** structures -- common for d^8 metal ions (Ni^{2+}, Pd^{2+}, Pt^{2+}) and for Cu^{2+} e.g.,

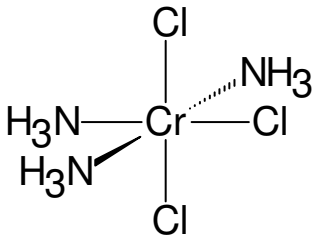




(c) Six-Coordinate Complexes -- the most common!

"always" octahedral structures, e.g.,





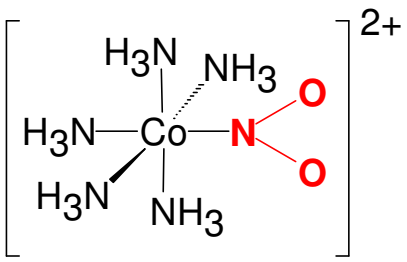
3. Isomers of Coordination Complexes

Isomers -- same chemical composition (formula) but different structures (due to either the arrangement of atoms or 3-D shape)

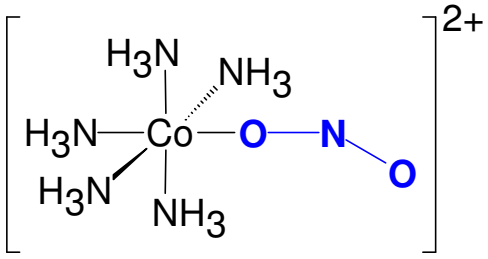
(a) Linkage isomers

same ligand, with different donor atoms

e.g., In $[Co(NH_3)_5NO_2]^{2+}$, the NO_2^- ligand can bind to Co through N ("nitro") or O ("nitrito").



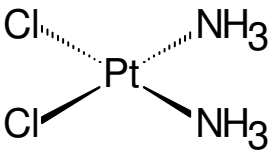
nitro complex



nitrito complex

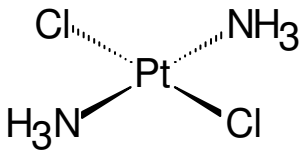
(b) Geometrical isomers

- **Square Planar complexes**



cis

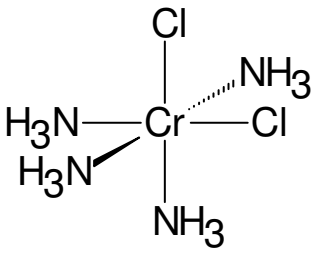
"cisplatin"
(anticancer drug)



trans

(no biological activity)

- **Octahedral complexes**



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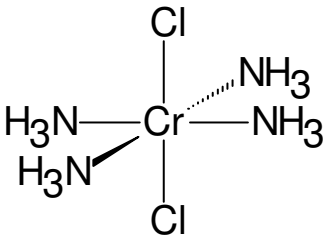
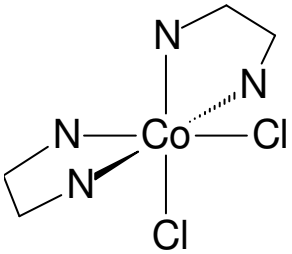
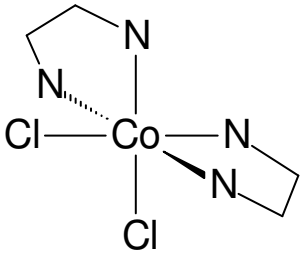


trans

(c) Enantiomers -- non-superimposable mirror images
also called "optical isomers"

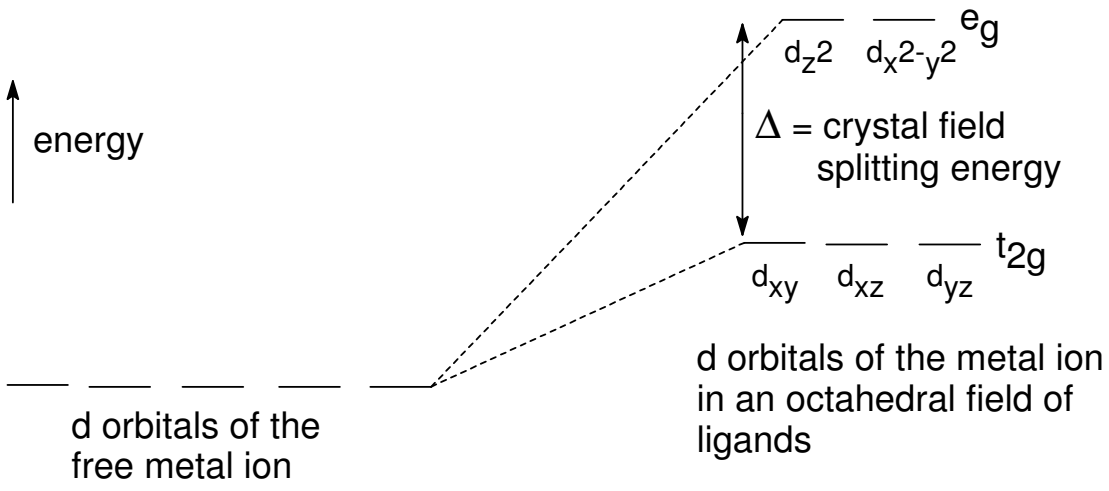




4. Crystal Field Theory
(Bonding in Transition Metal Complexes)

Metal complexes are usually highly colored and are often paramagnetic – such facts can be explained by a

"d-orbital splitting diagram"



The size of Δ depends on

- **the nature of the ligand**

  "spectrochemical series" -- Δ decreases:

CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^-
"strong field ligands" "weak field ligands"

- **the oxidation state of the metal**

  Δ is greater for M^{3+} than for M^{2+}

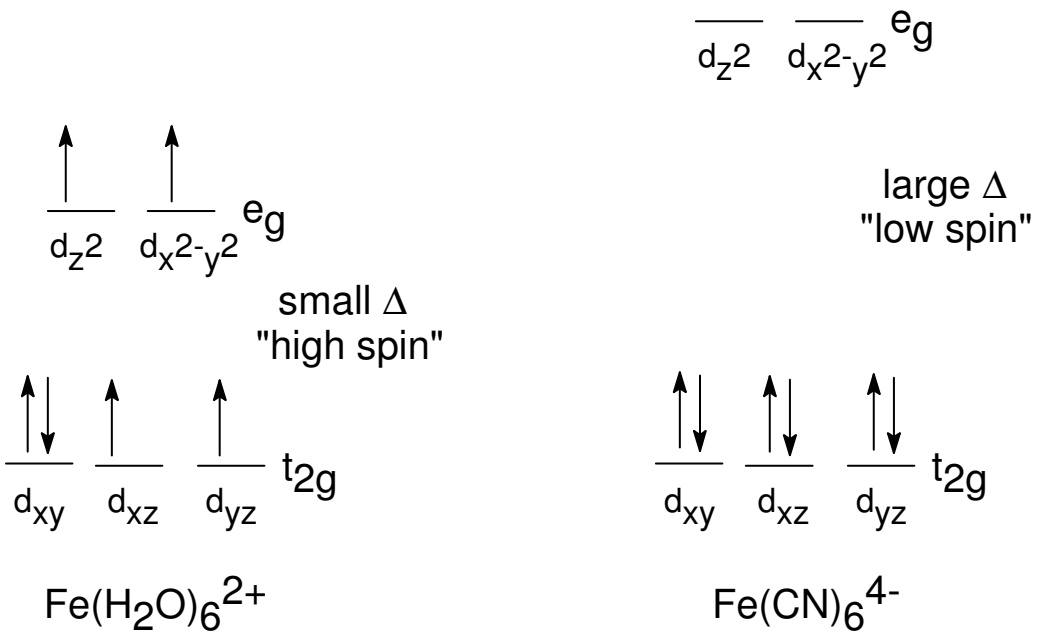
- **the row of the metal in the periodic table**

  for a given ligand and oxidation state of the metal, Δ increases going down in a group

  e.g., Δ is greater in $Ru(NH_3)_6^{3+}$ than in $Fe(NH_3)_6^{3+}$

Colors of metal complexes are due to electronic transitions between the t_{2g} and e_g energy levels

d orbital splitting diagrams for octahedral complexes



CN^- is a stronger field ligand than is H_2O which leads to a greater Δ value (i.e., a greater d orbital splitting)

as a result,

$Fe(H_2O)_6^{2+}$ is a "high spin" complex and is paramagnetic (4 unpaired electrons)

while,

$Fe(CN)_6^{4-}$ is a "low spin" complex and is diamagnetic (no unpaired electrons)

the CN^- complex with the larger Δ value absorbs light of higher energy (i.e., higher frequency but shorter wavelength)

OMIT: d orbital splitting diagrams for other geometries (i.e., tetrahedral and square planar)