The Chemistry of Coordination Compounds

Chapter 20

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Coordination Compounds and Complexes

$$Ag^+ + 2\,NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^- \rightarrow [Ag(NH_3)_2]Cl$$

Metal Ion — Base — coordination complex or complex ion — Counter Ion — Coordination compound

$$Cu^{2+} + 4\,CN^- \rightarrow [Cu(CN)_4]^{2-} + 2K^+ \rightarrow K_2[Cu(CN)_4]$$

Metal Ion — Base — complex ion — coordination compound

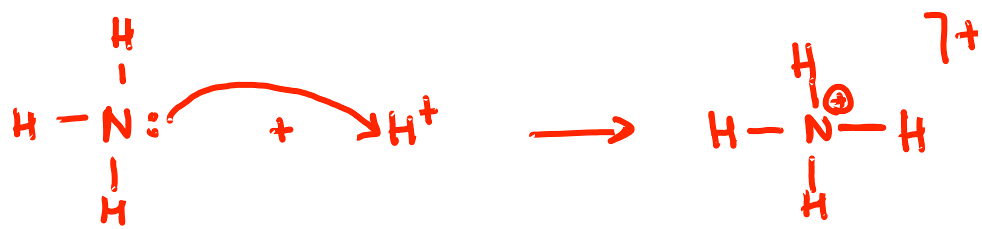
Coordination compounds are all soluble in H_2O (unless we tell you they are not soluble)

Acids and Bases

Consider the following acid-base reaction, which substance is the acid and which the base?

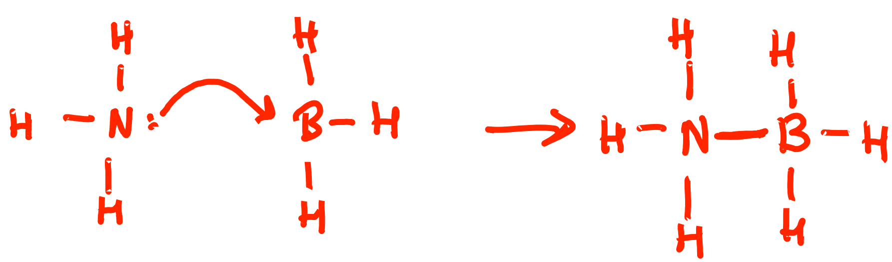
$$NH_3 \quad + \quad H^+ \quad \text{---->} \quad NH_4^+$$

Rewrite the reaction using lewis structures to depict the reactants and products:



Bases "donate" e^- Acids Accept e^-

What about the reaction between NH_3 and BH_3?



Metals and Ligands

How do these complexes form?

$M + nL \rightarrow ML_n$

# of ligands that react

metal ion or metal + base (ligands) → coordination complex

Ligand	Symbol	Name in Complexes
Azide	N_3^-	Azido
Bromide	Br^-	Bromo
Chloride	Cl^- 1-	Chloro
Cyanide	CN^-	Cyno
Fluoride	F^-	Fluoro
Iodide	I-	Iodo
Hydroxide	OH^-	Hydroxo
Carbonate	CO_3^{2-}	Carbonato
Oxalate	$C_2O_4^{2-}$	Oxalato
Oxide	O_2^-	Oxo
Nitrite	NO_2^- 1-	Nitro
Ammonia	NH_3	Ammine
Carbon Monoxide	CO	Carbonyl
Ethylenediamine	en	Ethylenediamine
Pyridine	C_5H_5N	Pyridine
Water	H_2O	Aqua

Coordination Number, Charge and Oxidation State

Number

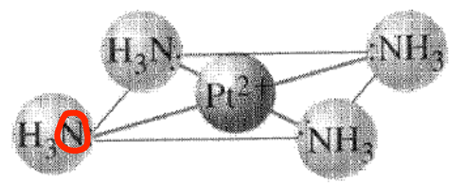
Coordination Number: # of Donor Atoms Bound to central metal

Nitrogen is the donor atom

oxid number = +1

Linear

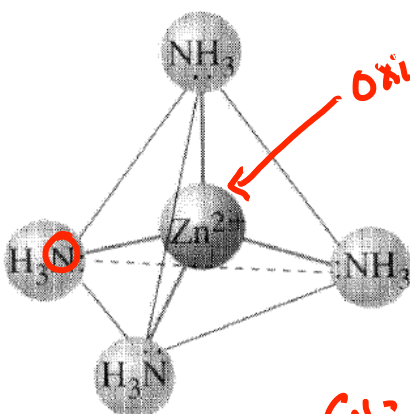
Coord Number = 2



Square planar

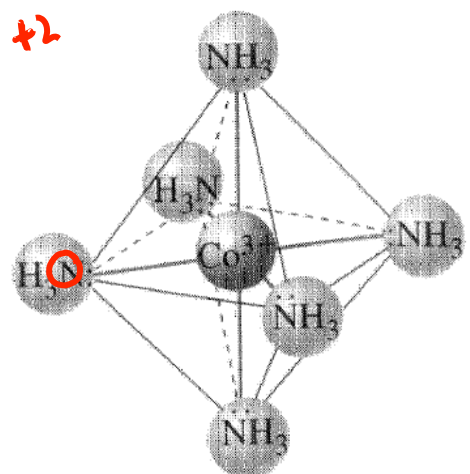
CN = 4

oxidation number = +2



Tetrahedral

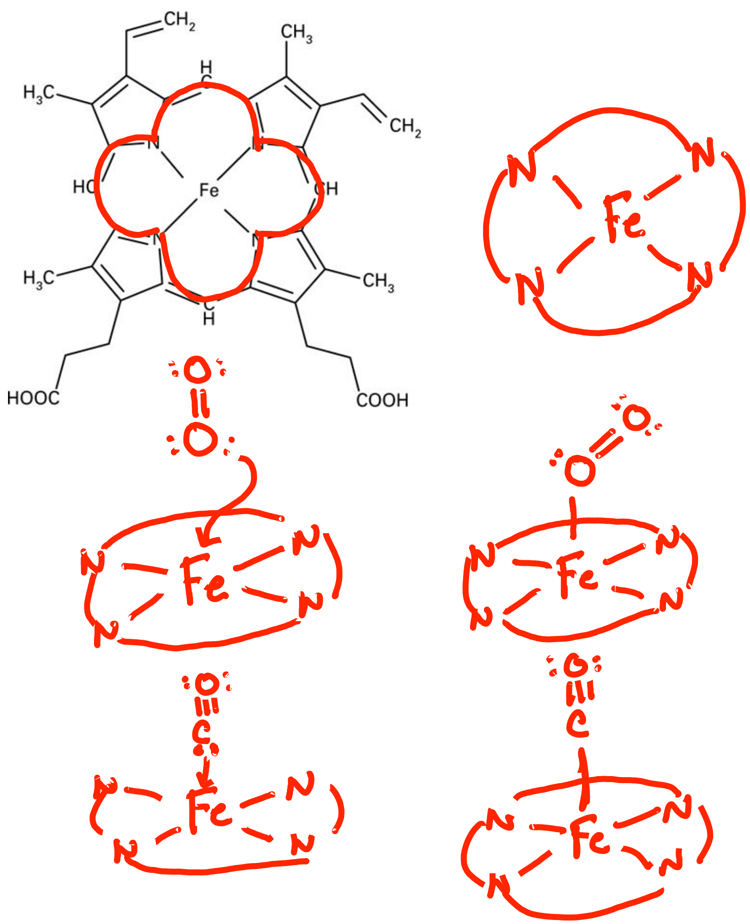
CN = 4



Octahedral

CN = 6

Coordination Compounds in Biological Systems



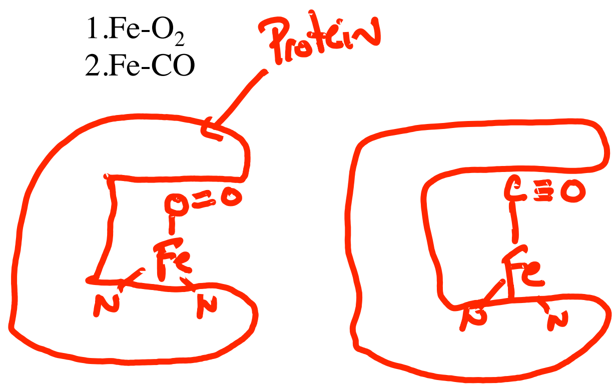
When O_2 binds to the iron in hemoglobin, what do you predict the O-O-Fe bond angle will be?

1.90
2.109.5
3.120
4.180

When CO binds to the iron in hemoglobin, what do you predict The O-C-Fe bond angle will be? (The carbon in CO binds the the Fe)
1.90
2.109.5
3.120
4.180

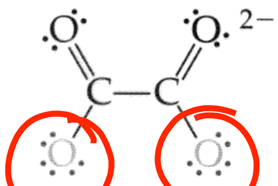
Will the Fe-O2 bond or the Fe-CO bond will be stronger in hemoglobin?

1.Fe-O_2
2.Fe-CO

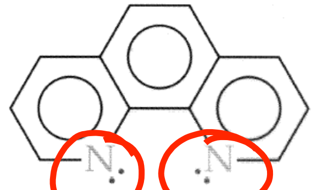


http://www.answers.com/topic/heme

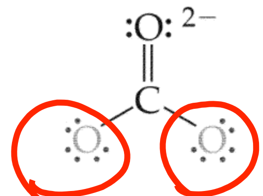
Polydentate Ligands



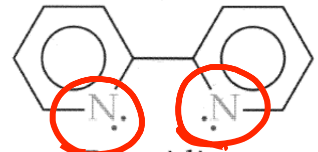
Oxalate ion



Ortho-phenanthroline
(*o*-phen)

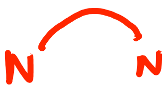


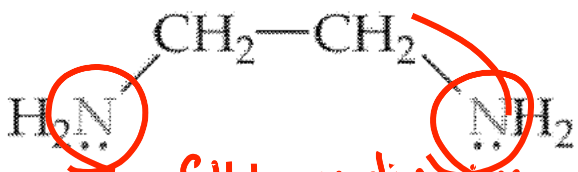
Carbonate ion



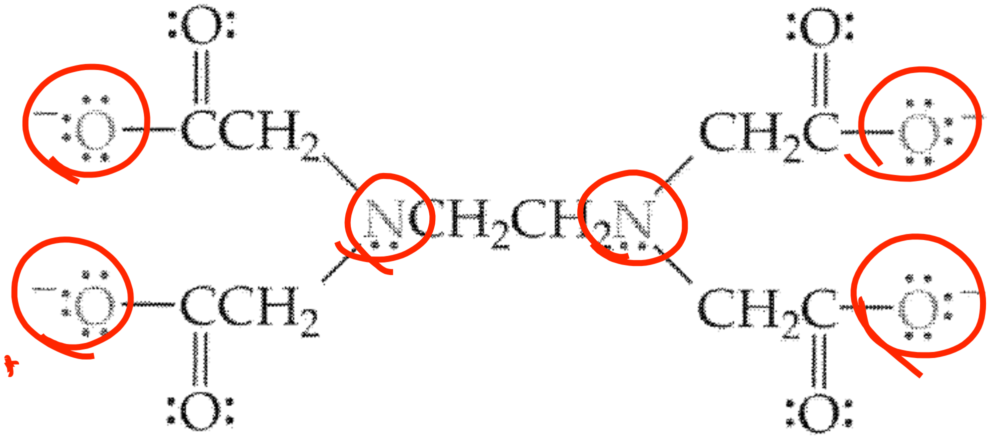
Bipyridine
(bipy)

en





Ethylenediamine
(en)

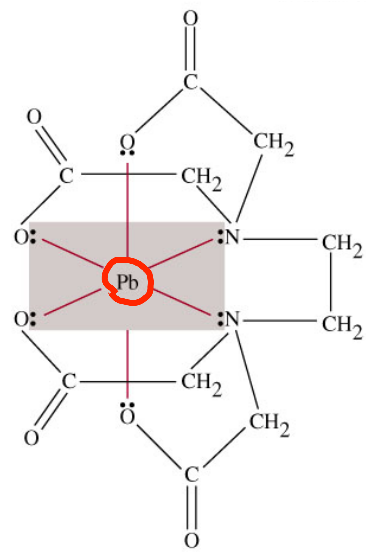


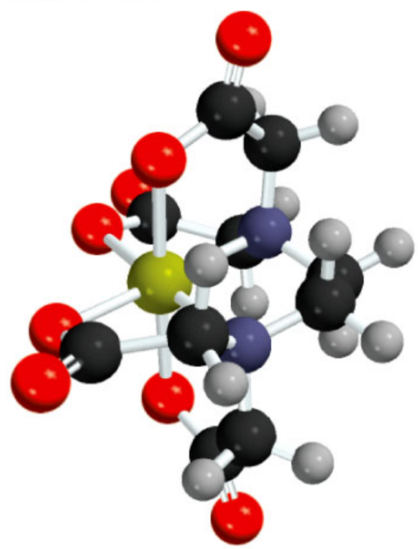
$[EDTA]^{4-}$

$Co^{3+} + 3\,en \longrightarrow$

$Co^{3+} + EDTA^{4-} \longrightarrow [Co(EDTA)]^{1-}$

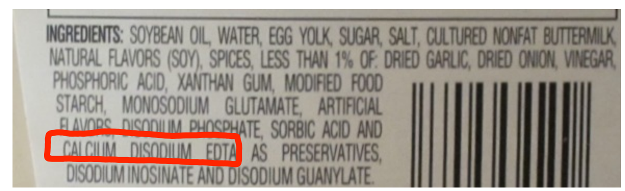
EDTA Complex of Lead





EDTA in FOOD

http://www.eatingrealfood.com/articles/edta-a-preservative-in-your-mayonnaise/



Sample Problems: Charge, Oxd Num, # d-electrons

For the following identify the charge on the complex, the oxidation state of metal, the coordination number of the metal, and number of d-electrons. When transition metals form compounds, the valence d-orbitals become lower in energy than the valence s-orbital causing all the valence electrons to fill the valence d-orbitals before filling the valence s-orbital!

+3
$[CoCl(NO_2)(NH_3)_4]Cl$

$[CoCl(NO_2)(NH_3)_4]^{+}$ → Cl^-

Coord No = 6

Neutral Co atom = $4s^2 3d^7$

In any complex = $3d^9$

$\boxed{\text{How many d electrons } Co^{3+} = 3d^6}$

Oxidation state Co + Charge from Ligands = Charge on complex

4 NH_3
1 Cl^-, 1 NO_2^-

Oxd St Co + −2 = +1

$\boxed{\text{Ox St Co} = +3}$

$K_3[Ni(CN)_4I]$

$3K^+$ ← → $[Ni(CN)_4I]^{3-}$

Coord No Ni = 5

Neutral Ni : $4s^2 3d^8$

In complex: $3d^{10}$

$\boxed{Ni^{2+} = 3d^8}$

Oxt state Ni + Charge from Ligand = Charge on complex

4 CN^-, I^-

Ox st Ni + −5 = 3−

Oxt St Ni = +2

Ni^{2+}

Naming Coordination Compounds

1. In names and formulas of coordination compounds, cations come first, followed by anions. If the complex is neutral start with step 2.

2. Name ligands, in alphabetical order, before metal.

3. Anionic ligands end in the letter 'o', neutral molecules as ligands are (mostly)unmodified

4. Use Greek prefixes di,tri, tetra etc to indicate the number of ligands, use bis, tris, tetrakis etc for chelating ligands that have di, tri already in their name. Do not consider the prefixes in the alphabetical ordering of the ligand names.

5. If the complex is an anion, its name ends in 'ate'.

6. The oxidation number of the metal is in parentheses in roman numerals following the name of the metal.

Name: $[CoCl_3(NH_3)_3]$ $\boxed{\text{triAmine trichloro cobalt (III)}}$

Possible Structures of for $\boxed{CrCl_3 \cdot 6\,H_2O}$

Cr^{3+}

Let us write some possible structures for this compound it has a coordination number =6

* $[Cr(H_2O)_6]Cl_3$
* $[Cr(H_2O)_4Cl_2] \cdot Cl \cdot 2H_2O$
* $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

$[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ → Neutral

How many of the above isomers conduct electricity? 3

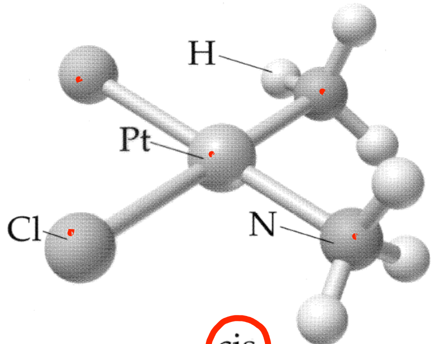
Same but different

Examples of isomers: structural isomers

Share the same ligands but different ligands are bound to metal

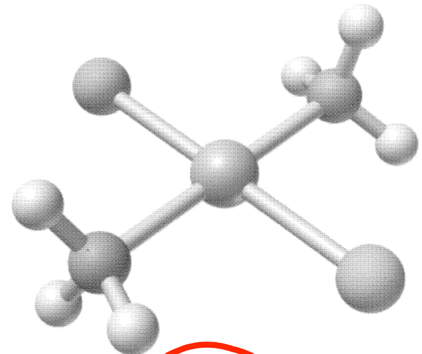
Isomers: Stereoisomers

The complex $[PtCl_2(NH_3)_2]$ has two isomers

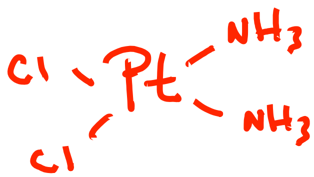


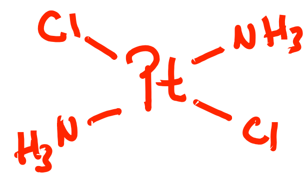
cis

same



trans

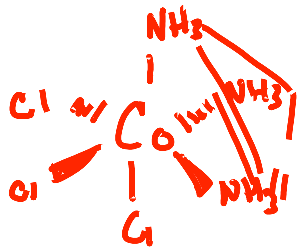




Stereoisomers: same but different arrangement in space

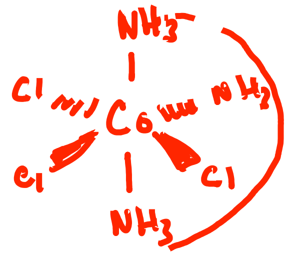
Isomers of Octahedral Complexes

Draw all of the isomers of $CoCl_3(NH_3)_3$



FAC

(FACIAL)



mer

(MERIDAL)

A cobalt compound has the composition of $Co(NO_2)_2Cl{\cdot}4NH_3$. When it is placed into water two ions are formed; when titrated with a silver nitrate solution, 1 mole of AgCl is formed for every 1 mole of compound that dissolves. The coordination number of the cobalt is six. Using all of this information determine the correct chemical formula for the cobalt complex?

$[Co(NO_2)_2(NH_3)_3Cl]NH_3$

$\swarrow$ $\searrow$

$Co(NO_2)_2(NH_3)_3Cl$ NH_3

Ag^+ No Cl^-

$[Co(NO)_2(NH_3)_4]Cl$

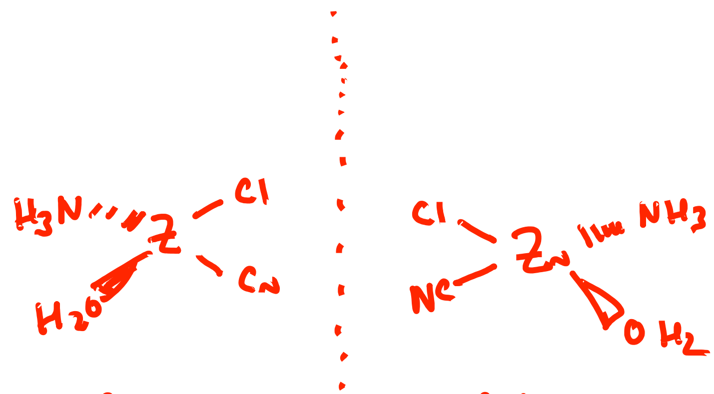
$\swarrow$ $\searrow$

$[Co(NO)_2(NH_3)_4]^+$ Cl^-

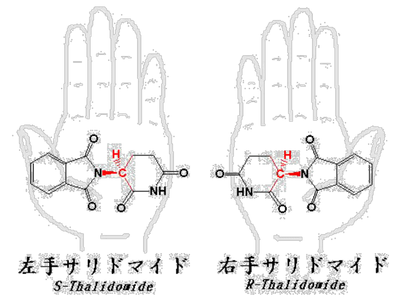
$Ag^+ + Cl^- \rightarrow AgCl$

Optical Isomers in Tetrahedral Complexes

Draw the isomers of $ZnCl(CN)H_2O(NH_3)$. The complex has a tetrahedral geometry.



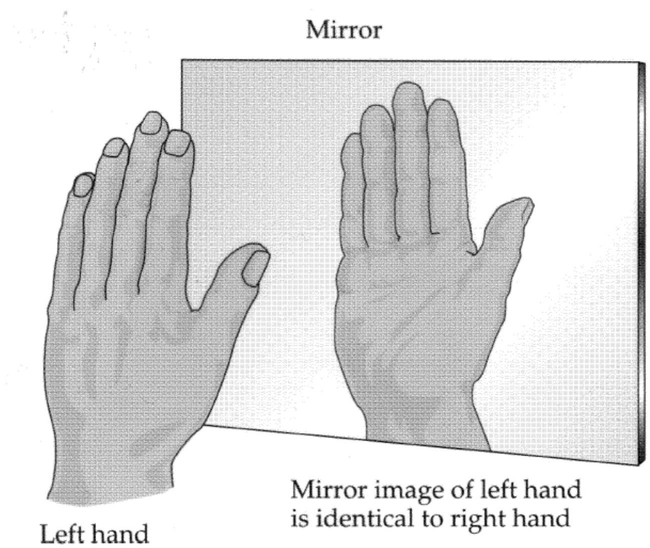
CHIRAL CHIRAL



Structures with a nonsuperimposible mirror image are said to be CHIRAL

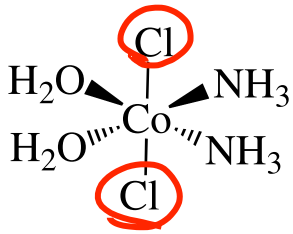
Chiral mirror are called enantiomers

Structures with superimposible mirror images are ACHIRAL

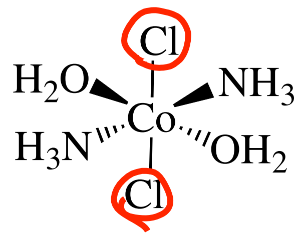


Optical Isomers in Octahedral Complexes

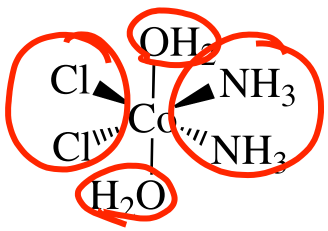
Which of the following octahedral complexes of Co are **chiral** and **achiral**?



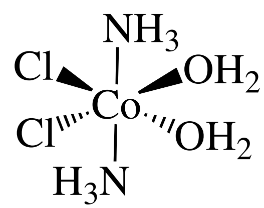
ACHIRAL



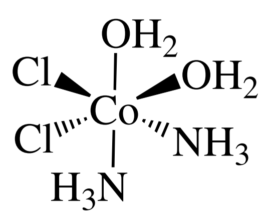
ACHIRAL



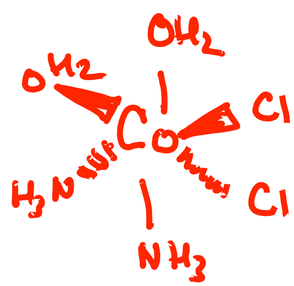
ACHIRAL



ACHIRAL



CHIRAL



CHIRAL

IF molecule has A plane of symmetry it is ACHIRAL

SHORT HAND APPROACH

- Two identical trans Ligands ACHIRAL !

OR

- Two pairs of identical Ligands that are opposite of each other ACHIRAL

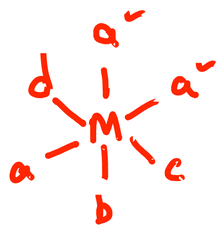
Isomers of Octahedral Complexes

Draw all of the unique isomers of an octahedral coordination complex with a central metal atom, M, and the ligands a,a,a,b,c,d .

To generate these unique isomers we are going to use something known as a *trans table*. This table is generated by listing the pairs of ligands that are trans to each other in a given compound or complex. For every octahedral coordination complex there are always three sets of trans ligands, each unique isomer will have a different set of trans ligands.

We will approach the problem in two steps: (1) use the trans table to systematically determine all of the unique isomers for the complex with metal atom M, and the ligands a,a,a,b,c,d and (2) determine if each of these isomers is chiral or achiral.

#1



a	b
a	a
c	d

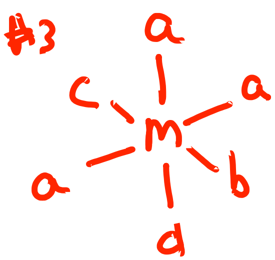
ACHIRAL

#2

a	c
a	a
b	d

ACHIRAL

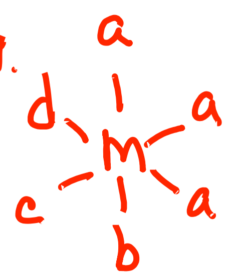
#3



a	d
a	a
c	b

ACHIRAL

#4.



a	b
a	c
a	d

CHIRAL + mirror image #5

Five Isomers

Reactions of Coordination Compounds

$$[CuCl_4]^{2-} + 4\,H_2O \longrightarrow [Cu(H_2O)_4]^{2+} + 4\,Cl^-$$

green

pale-blue

Crystal-Field Theory

Crystal Field Theory: A way of describing the bonding in coordination complexes that accounts for properties of the complex lie color, magnetism etc.

$M^+ + nL \longrightarrow MLn$ where M = metal, L = Ligand, n = 1,2,3,4,5,6 (# of liangds..)

Electrostatic interactions : like charges repel, opposite charges attract.

The 5 d-orbitals:

d_{xy} d_{xz} d_{yz} d_{z2} d_{x2-y2} $\xrightarrow[\text{A metal by six ligands}]{\text{Surround}}$

d_{z^2} $d_{x^2-y^2}$ High energy $\boxed{e_g}$

d_{xy} d_{yz} d_{xz} Low energy $\boxed{t_{2g}}$

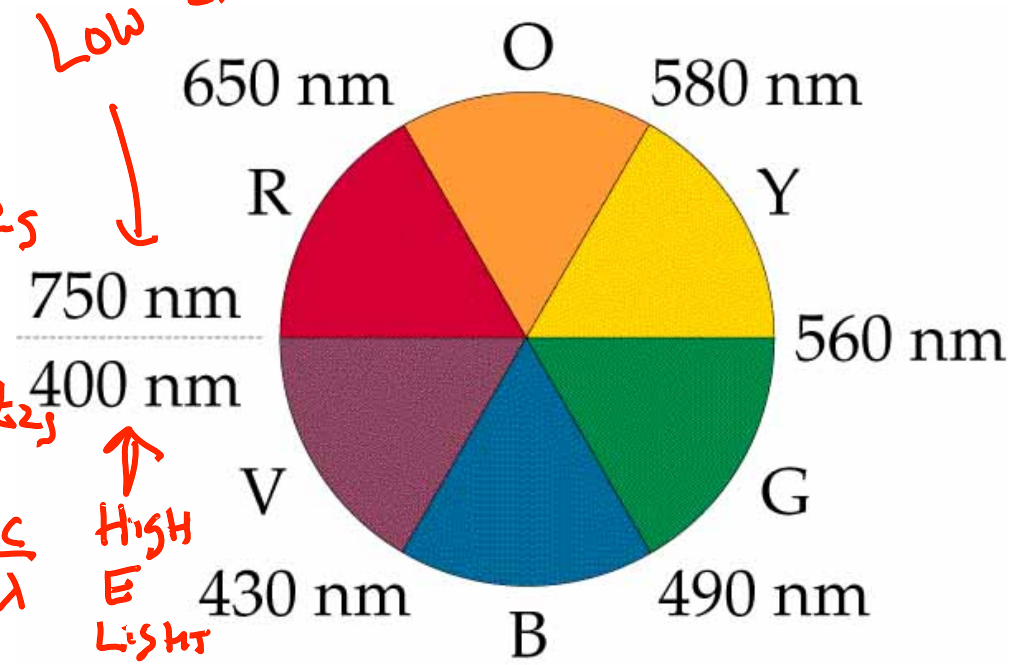
Color and Coordination Compounds

The color of a substance tell us about size of the orbital energy level gap

Why do molecules have a color? Because molecules absorb a certain frequency of light while transmitting all the non-absorbed frequencies. The color we see results from the transmitted not the absorbed light.

Why do molecules absorb certain frequencies of light? Because the frequency of light absorbed is of the exact energy needed to promote an electron from a lower energy level orbital to a higher level one.

Low Energy Light



— — e_g $\xrightarrow[\text{energy}]{\text{ADD}}$ ↿ — e_g

↿ — — t_{2g} — — — t_{2g}

$E = h\nu = E = h\frac{c}{\lambda}$

HIGH E LIGHT

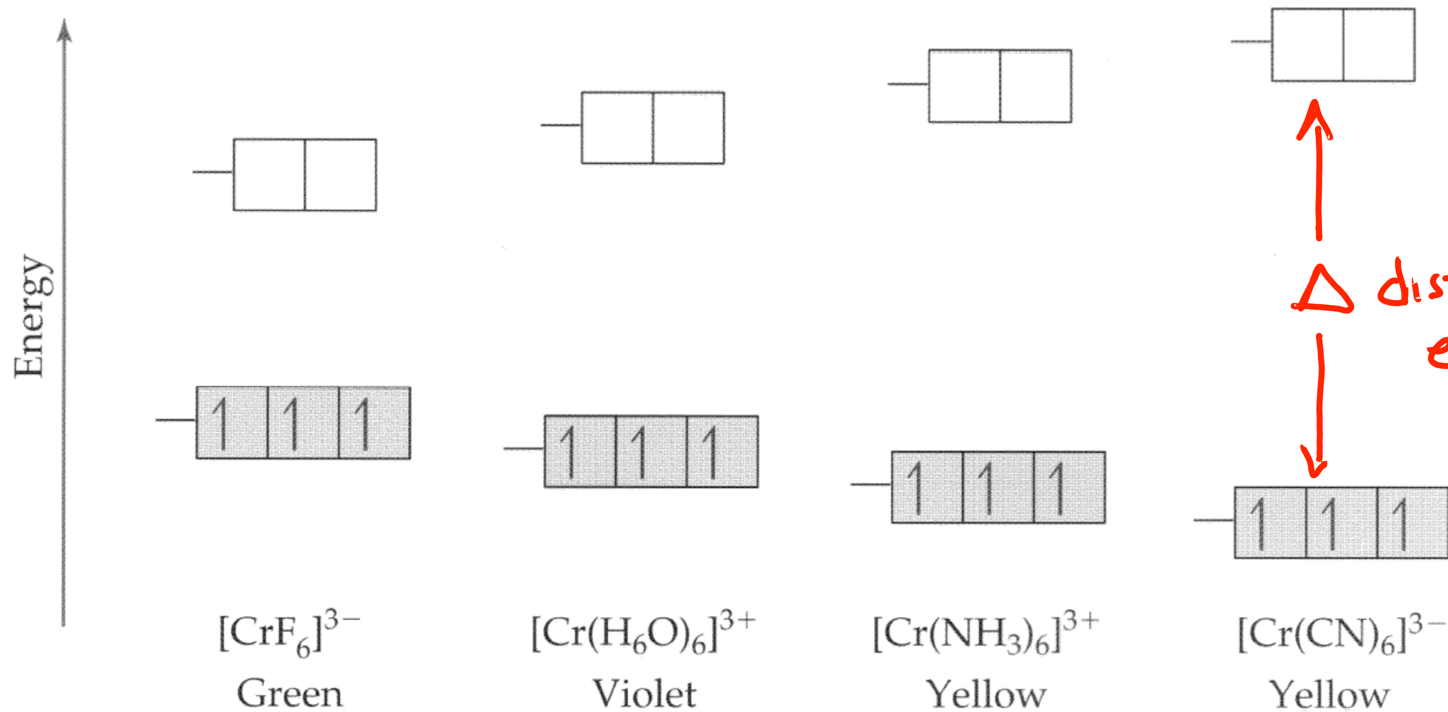
Spectrochemical Series

Ligands determine the size of the orbital energy level gap, Δ

$$\boxed{Cl^- < F^- < H_2O < NH_3 < en < NO_2^- \text{ (N-bonded)} < CN^-}$$

know this!

Weak Field Ligands: make smaller gap, Δ → Strong-Field Ligands: make larger gap, Δ



Δ distance between e_g and t_{2g} orbitals

Electron Configurations

How do electrons fill the d-orbitals in an octahedral complex

d^1: e_g

t_{2g}

t_{2g}^1

d^2:

t_{2g}^2

d^3:

t_{2g}^3

d^4:

Weak Field

$t_{2g}^3 e_g^1$

High Spin

d^4:

Strong Field

t_{2g}^4

Low spin
most paired electrons

Coordination Chemistry: Putting It All Together

Consider a metal, M, that has a neutral electron configuration of $[Ar]4s^2 3d^6$. The metal can become oxidized and react with either six cyanide or fluoride ligands produce four coordination complexes: MF_6^{3-}, $M(CN)_6^{3-}$, $\boxed{MF_6^{4-}}$, $\boxed{M(CN)_6^{4-}}$. Which complex has the d electron configuration below?

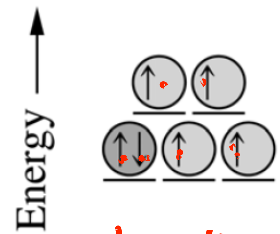
Neutral Atom $4s^2 3d^6$

Complex $3d^8$

M^{2+} $3d^6$

Oxid St + Lig Charge = Complex Charge

$+2 + 6^-$ $4-$



$t_{2g}^4 e_g^2$

$\boxed{MF_6^{4-}}$

Weak Field F^-

(High Spin)

$M(CN)_6^{4-}$

Strong Field

(Low Spin)