Outline

- Properties of Transition Metals
- Coordination Chemistry
- Naming Coordination Compounds
- Structures of Complexes
- Theories in Coordination Chemistry

Properties of Transition Metals

1. Electron Configurations

Transition Metal Atoms

4s orbital filled before 3d orbital

Sc	$[Ar]4s^2 3d^1$	Ti	$[Ar]4s^2 3d^2$	V	$[Ar]4s^2 3d^3$
Cr	$[Ar]4s^1 3d^5$	Cu	$[Ar]4s^1 3d^{10}$	... are exceptions!	

Transition Metal Ions

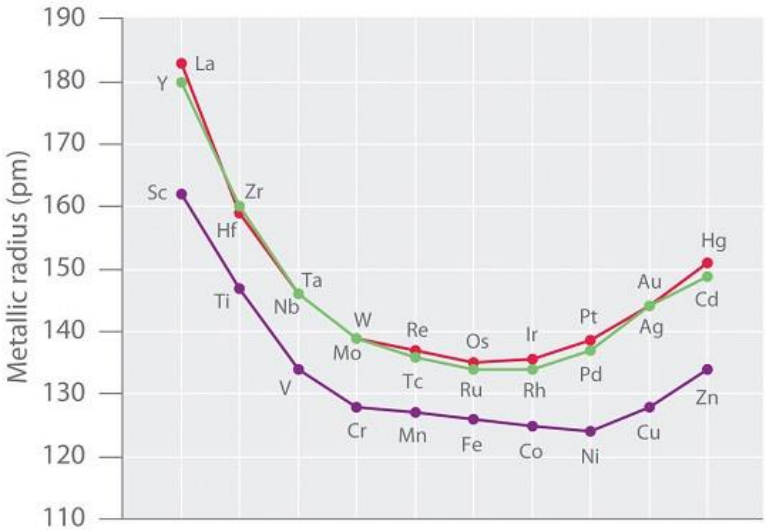
4s e^-'s removed before 3d e^-'s

Ti^{3+}	$[Ar]3d^1$	V^{3+}	$[Ar]3d^2$	Cr^{3+}	$[Ar]3d^3$

2. Atomic Radii

except Sc thru V, little variation of radii in first series (3d)…

d-electrons shield nuclear charge!



metals in the second series (4d) and third series (5d) have similar radii: <u>lanthanide contraction</u>

f-electrons don't shield the increasing nuclear charge…

electrons are drawn inward by increasing charge!

3. Catalytic Activity

transition metals are often key elements in catalysts

Ni	hydrogenation of oils
Pt, Pd, Rh	catalytic converter in automobiles
Fe_3O_4	synthesis of NH_3
V_2O_5	manufacture of H_2SO_4

4. Color and Magnetism

partially filled d-sublevels imparts color and magnetic properties to transition metal compounds

Coordination Chemistry

<u>Coordination Compounds</u> are compounds with a metal atom or ion surrounded by 2 or more atoms or ions

$$[Pt(NH_3)_6]Cl_4$$

Pt^{4+} ion surrounded by 6 NH_3 molecules

$$Pt(NH_3)_6{}^{4+}$$

<u>Complex Ions</u> (or Coordination Complexes) are ions with a metal atom or ion surrounded by 2 or more atoms or ions:

<u>Counterions</u> are anions or cations added to produce a neutral compound

$$Cl^-$$

Properties of coordination compounds and complex ions vary…

1. Color	$Co(NH_3)_6^{3+}$	yellow
	$Co(NH_3)_5NCS^{2+}$	orange
	$Co(NH_3)_5H_2O^{3+}$	red
	$Co(NH_3)_5Cl^{2+}$	purple

The color depends on the chemical groups attached to the transition metal

The attached chemical groups are called <u>ligands</u>

2. Coordination Number

The number of ligands surrounding a central atom or ion

Ox. No.	Typical Co. No.	Example
+1	2	$Ag(NH_3)_2^+$
+2	4, 6	$Pt(NH_3)_4^{2+}$
+3	6	$Co(NH_3)_6^{3+}$

3. Magnetism

Some are diamagnetic (no unpaired e^-'s), and some are paramagnetic (1 or more unpaired e^-'s)

Frog levitated in very strong magnetic field…

… as a result of the diamagnetic behavior of water!

4. Influence of d-electrons

d^0 very stable, difficult to produce moving to right

Sc^{3+}	(III)	
TiF_6^{2-}	(IV)	
CrO_4^{2-}	(VI)	Stable when
MnO_4^-	(VII)	bonded to oxygen!

K_2CrO_4  $KMnO_4$ 

Color of CrO_4^{2-} and MnO_4^- due to <u>charge transfer</u>… electrons on O^{2-} are excited to empty d-orbitals by visible light

d^5 and d^{10} very stable

Mn^{2+} and Fe^{3+}	(d^5)
Ag^+ and Zn^{2+}	(d^{10})

d^3, d^6, d^8 form inert (stable) complexes

d^3	$Cr(H_2O)_6^{3+}$
d^6	$Co(NH_3)_6^{3+}$
d^8	$PtCl_4^{2-}$

d^4 very unstable

Cr^{2+} (d^4) $\rightarrow$ Cr^{3+} (d^3)

Naming Coordination Compounds

1. name cation first, anion second
2. ligands precede the central metal atom in the complex ion
3. negatively charged ligands end in –o
4. number of ligands indicated with a prefix (no mono-)
5. ligands are ordered alphabetically (ignore prefixes)
6. the name of the metal ion ends in –ate if the complex is negatively charge
7. a roman numeral (or 0) in parentheses indicates the ox. no. of the metal atom

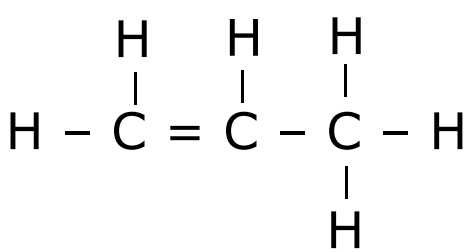
$[Pt(NH_3)_6]Cl_4$	hexaammineplatinum(IV) chloride
$[Pt(NH_3)_5Cl]Cl_3$	pentaamminechloroplatinum(IV) chloride
$Pt(NH_3)_2Cl_4$	diamminetetrachloroplatinum(IV)
$K[Pt(NH_3)Cl_5]$	potassium amminepentachloroplatinate(IV)
$Fe(CO)_5$	pentacarbonyliron(0)
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)
$K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III)

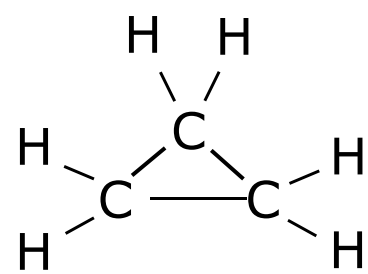
Structures of Complexes

The coordination number determines the structure…

If CN = 2, then linear
CN = 4, then tetrahedral (square planar if d^8)
CN = 6, then octahedral

<u>Structural Isomers</u> are compounds with the same chemical formula, but with the atoms bonded differently



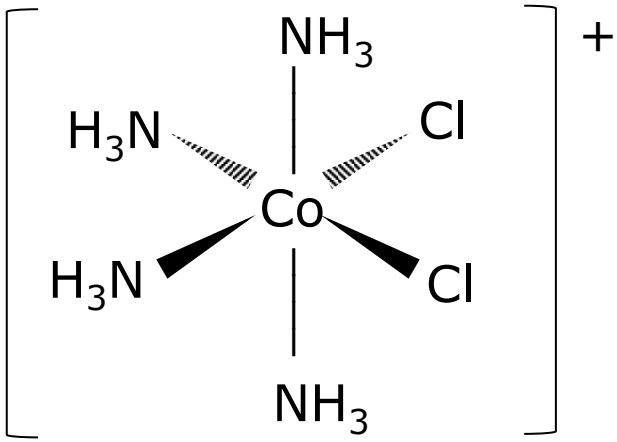


Both are C_3H_6…

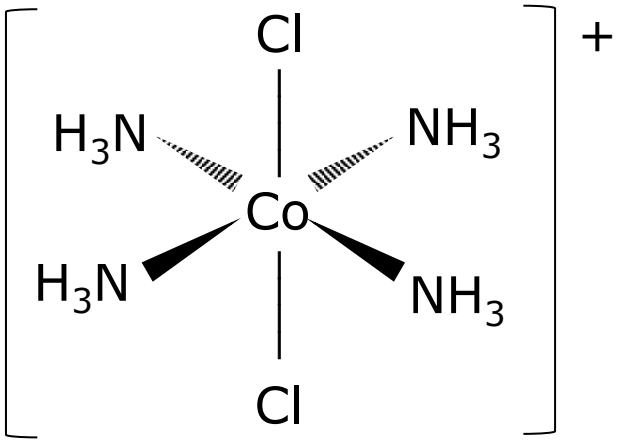
Structural isomers!

<u>Geometric Isomers</u> are compounds with the same chemical formula, but with different arrangements of the atoms

$Co(NH_3)_4Cl_2^+$ is octahedral shape and 2 geometric isomers…

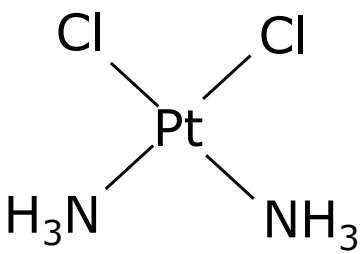


adjacent (cis)

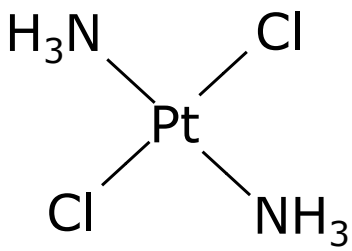


opposite (trans)

$Pt(NH_3)_2Cl_2$ is square planar (Pt^{2+} is d^8) and has 2 geometric isomers…

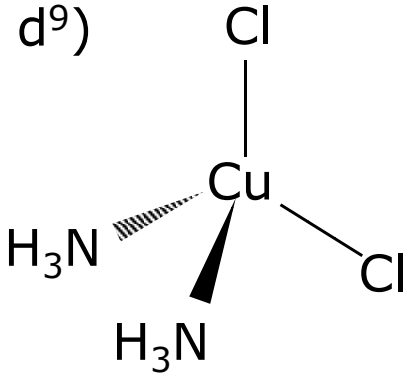


adjacent (cis)

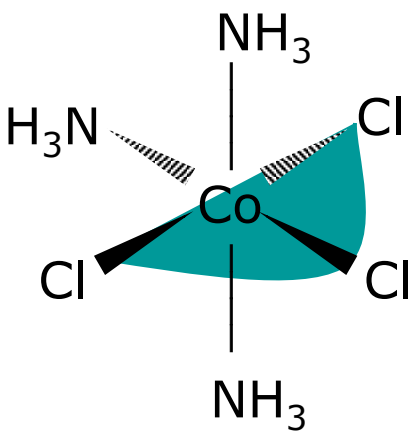


opposite (trans)

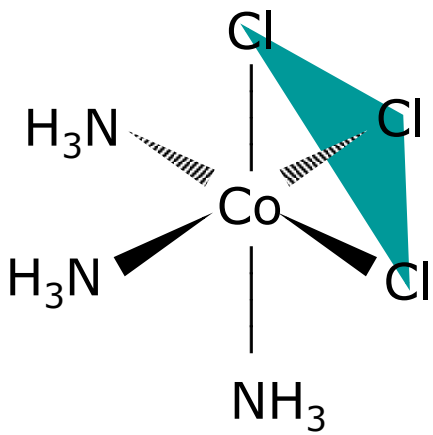
$Cu(NH_3)_2Cl_2$ is tetrahedral (Cu^{2+} is d^9) and has only 1 structure…



$Co(NH_3)_3Cl_3$ is octahedral and has 2 geometric isomers…



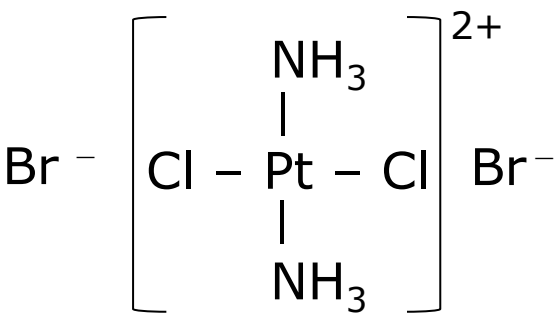
planar
(meridional)
or
(mer-)



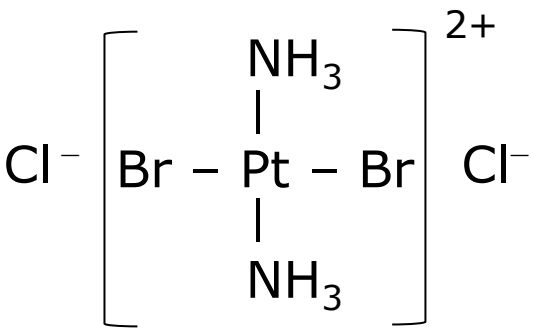
nonplanar
(facial)
or
(fac-)

Draw the trans-square planar coordination compounds...

$[Pt(NH_3)_2Cl_2]Br_2$



$[Pt(NH_3)_2Br_2]Cl_2$



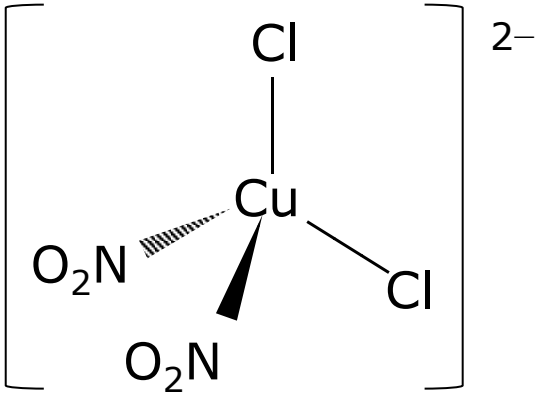
atoms are bonded differently, so structural (coordination) isomers

Coordination isomers have different names...

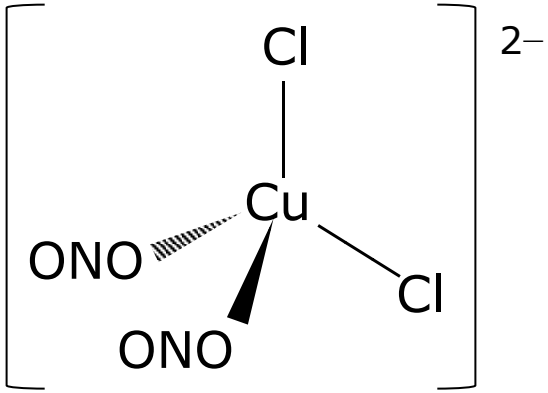
trans-diamminedichloroplatinum(IV) bromide
trans-diamminedibromoplatinum(IV) chloride

Draw the tetrahedral coordination complexes...

$Cu(NO_2)_2Cl_2^{2-}$



$Cu(ONO)_2Cl_2^{2-}$



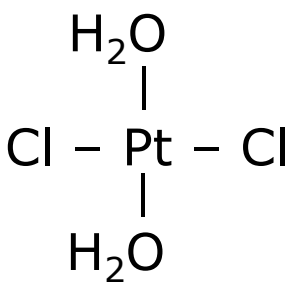
atoms are bonded differently, so structural (linkage) isomers

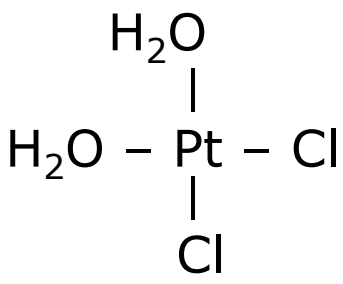
Linkage isomers have different names...

dichlorodinitrocuprate(II)
dichlorodinitritocuprate(II)

Draw the square planar isomers of...

$[Pt(H_2O)_2Cl_2]$





atoms are bonded the same but arranged differently, so geometric isomers

geometric isomers have similar names...

trans-diaquadichloroplatinum(II)

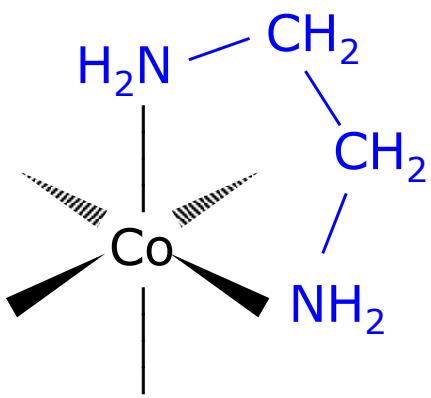
cis-diaquadichloroplatinum(II)

Ligands that bind to the metal at only 1 point are <u>monodentate ligands</u>

Ligands that bind to the metal at more than 1 point are <u>polydentate ligands</u>

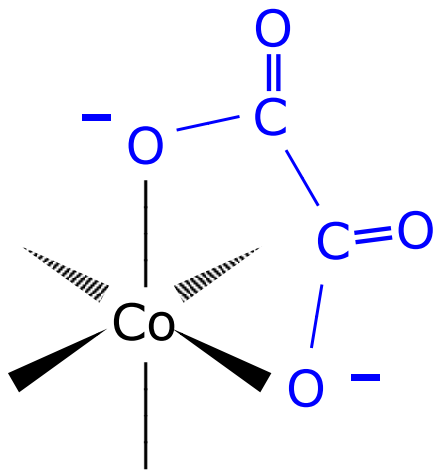
Bidentate:

ethylene**di**amine (en)



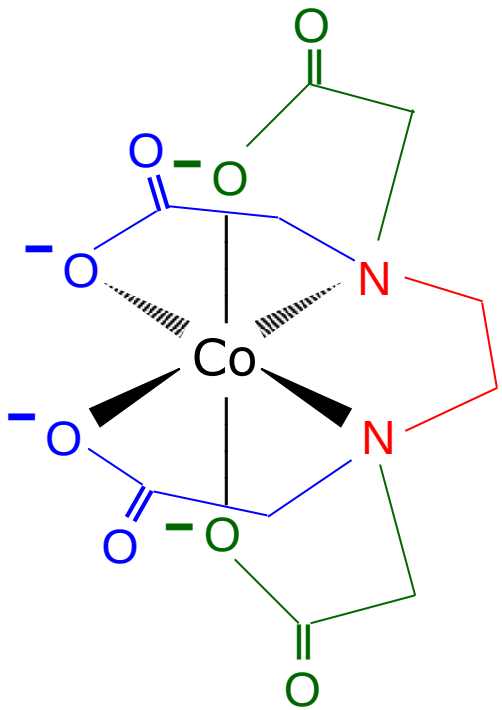
…bis(ethylenediamine)…

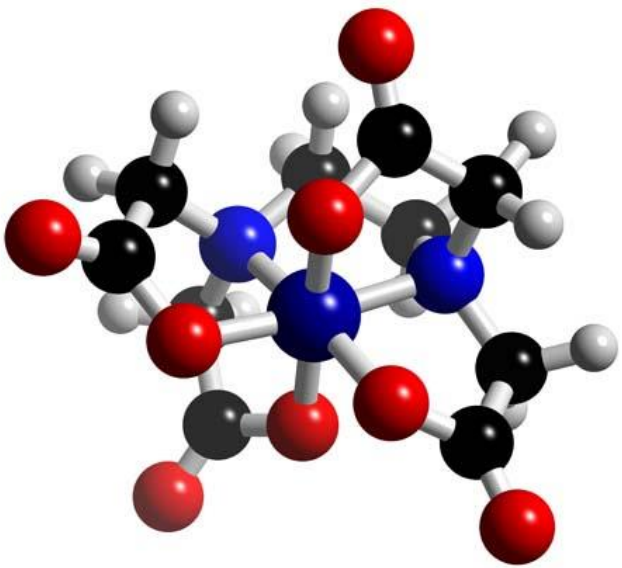
oxalate (ox) – "ethane**di**oate"



…tris(oxalato)…

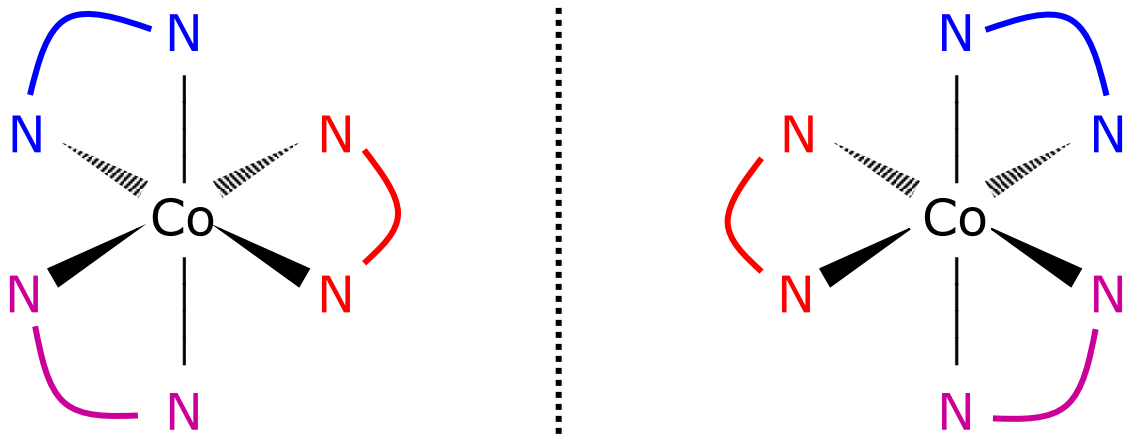
Hexadentate: ethylene**di**amine**tetra**acetate (EDTA), –4 charge





A polydentate ligand is called a chelating agent; complex that is formed is called chelate

Consider the tris(ethylenediamine)cobalt(III) ion: $Co(en)_3^{3+}$



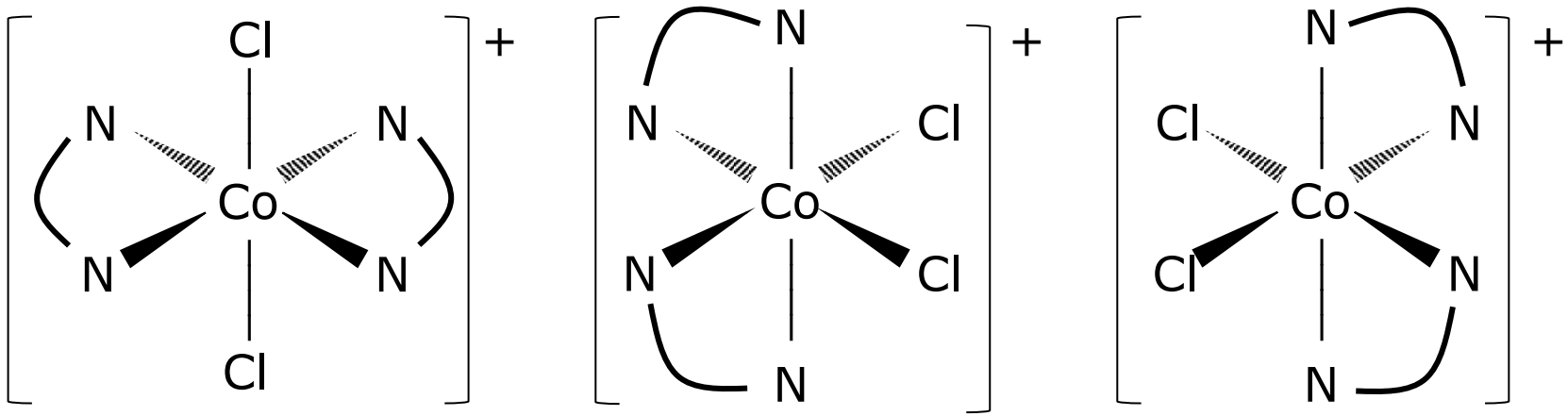
Not the same... They're mirror images of each other that are not superimposable

2 nonsuperimposable mirror images are called <u>enantiomers</u>, and are <u>optical isomers</u> (a type of stereoisomer)

Draw the isomers of dichlorobis(ethylenediamine)cobalt(III)...

$CoCl_2(en)_2^+$

Three isomers… 1 trans-chloro and 2 cis-chloro optical isomers



Theories in Coordination Chemistry

They attempt to explain:

geometries (shapes)
magnetism (paired or unpaired e^-'s)
color (electronic energy level differences)

1. Valence Bond Theory

assumes ligands are covalently bonded to the metal using hybrid metal orbitals

these orbitals overlap with a ligand orbital containing a lone pair of e^-'s, forming a <u>coordinate covalent bond</u>

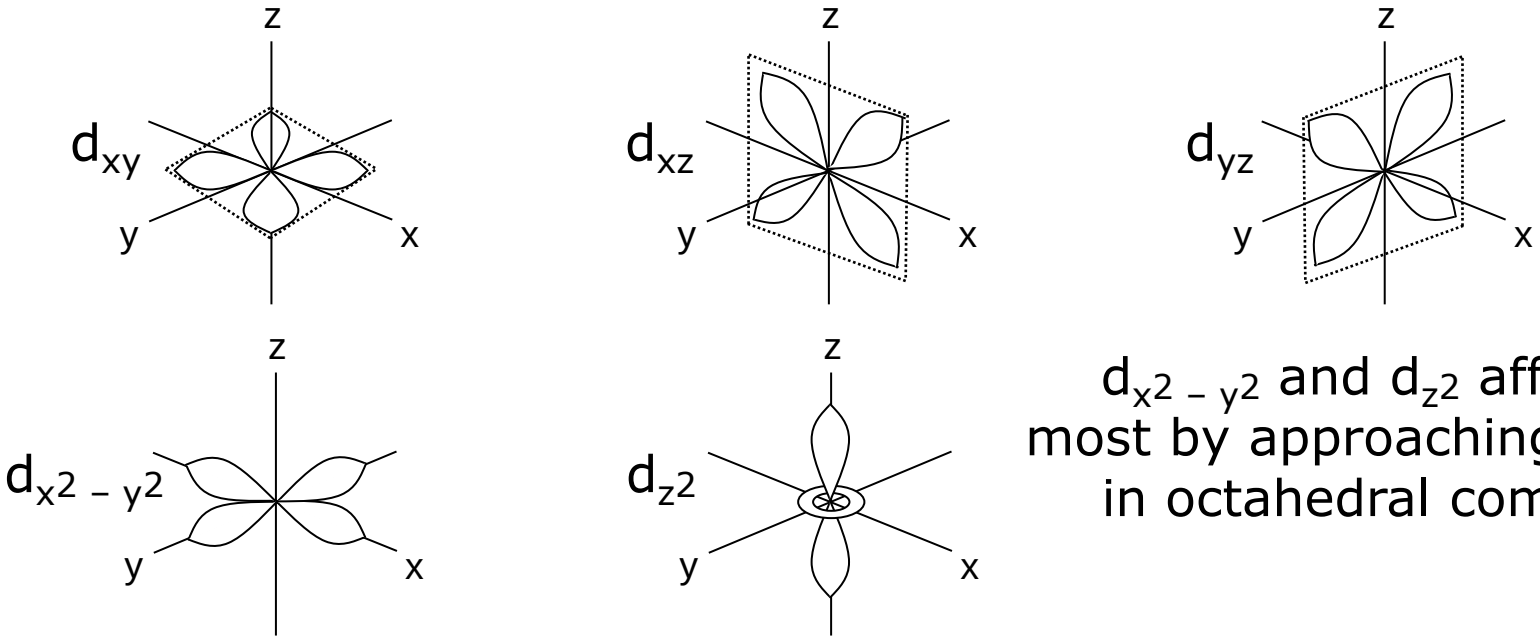
CN	Shape	Hybridization
2	linear	$s + p \rightarrow 2\ sp$
4	tetrahedral	$s + 3\ p \rightarrow 4\ sp^3$
	square planar	$s + 2\ p + d \rightarrow 4\ dsp^2$
6	octahedral	$s + 3\ p + 2\ d \rightarrow 6\ d^2sp^3$

$Cu(CN)_2^-$	CN = 2, linear	sp hybridization
$ZnCl_4^{2-}$	CN = 4, tetrahedral	sp^3 hybridization
$Pt(en)_2^{2+}$	CN = 4, square planar	dsp^2 hybridization
$Co(H_2O)_6^{3+}$	CN = 6, octahedral	d^2sp^3 hybridization

2. Crystal Field Theory

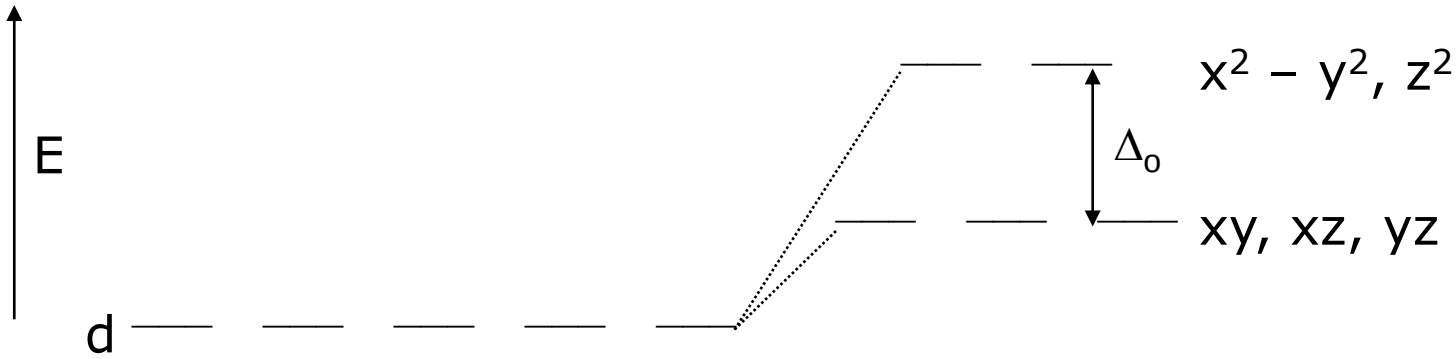
assumes ionic bonding between the ligands (negative) and the metal cation

lone pair e^-'s on ligands affect energies of the d orbitals



$d_{x^2-y^2}$ and d_{z^2} affected most by approaching ligands in octahedral complex!

Free metal ion... In octahedral complex...

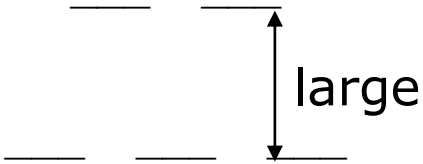


The difference in energy between the d orbitals in a metal ion complex is called the <u>splitting energy</u> (Δ_o)

If Δ_o is large, the complex is called a <u>low-spin complex</u>

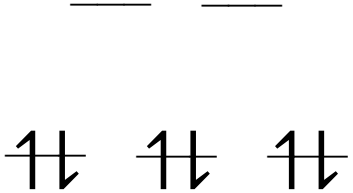
If Δ_o is small, the complex is called a <u>high-spin complex</u>

$Co(NH_3)_6^{3+}$ is a low-spin complex



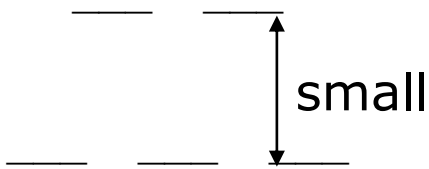
Co^{3+} has 6 d e^-'s

With large Δ_o, the 6 e^-'s cannot spread through the 5 orbitals



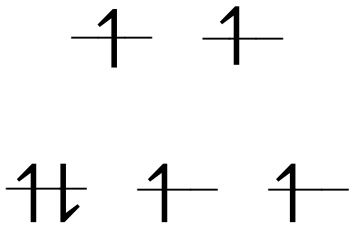
$Co(NH_3)_6^{3+}$ is diamagnetic

CoF_6^{3-} is a high-spin complex



Co^{3+} has 6 d e^-'s

With small Δ_o, the 6 e^-'s can spread through the 5 orbitals



CoF_6^{3-} is paramagnetic

The stronger the electrostatic field the metal is in, the greater Δ_o

$Co(NH_3)_6^{3+}$	large Δ_o	strong-field
CoF_6^{3-}	small Δ_o	weak-field

Spectrochemical series gives relative field strengths for ligands:

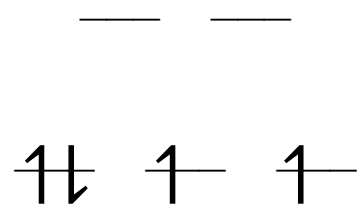
$$\underbrace{CO > CN^- > en > NH_3}_{\text{strong-field ligands}} > H_2O > OH^- > \underbrace{F^- > Cl^- > Br^- > I^-}_{\text{weak-field ligands}}$$

Predict the number of unpaired electrons and magnetism in $Cr(CN)_6^{4-}$.

Cr^{2+} has 4 d e^-'s (ignore ligand e^-'s)

CN^- is a strong-field ligand... so large Δ_o

<u>2 unpaired e^-'s</u> (paramagnetic)

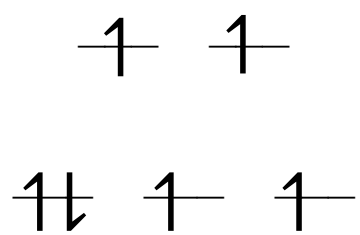


Predict the number of unpaired electrons and magnetism in $FeCl_6^{4-}$.

Fe^{2+} has 6 d e^-'s

Cl^- is a weak-field ligand... so small Δ_o

<u>4 unpaired e^-'s</u> (paramagnetic)

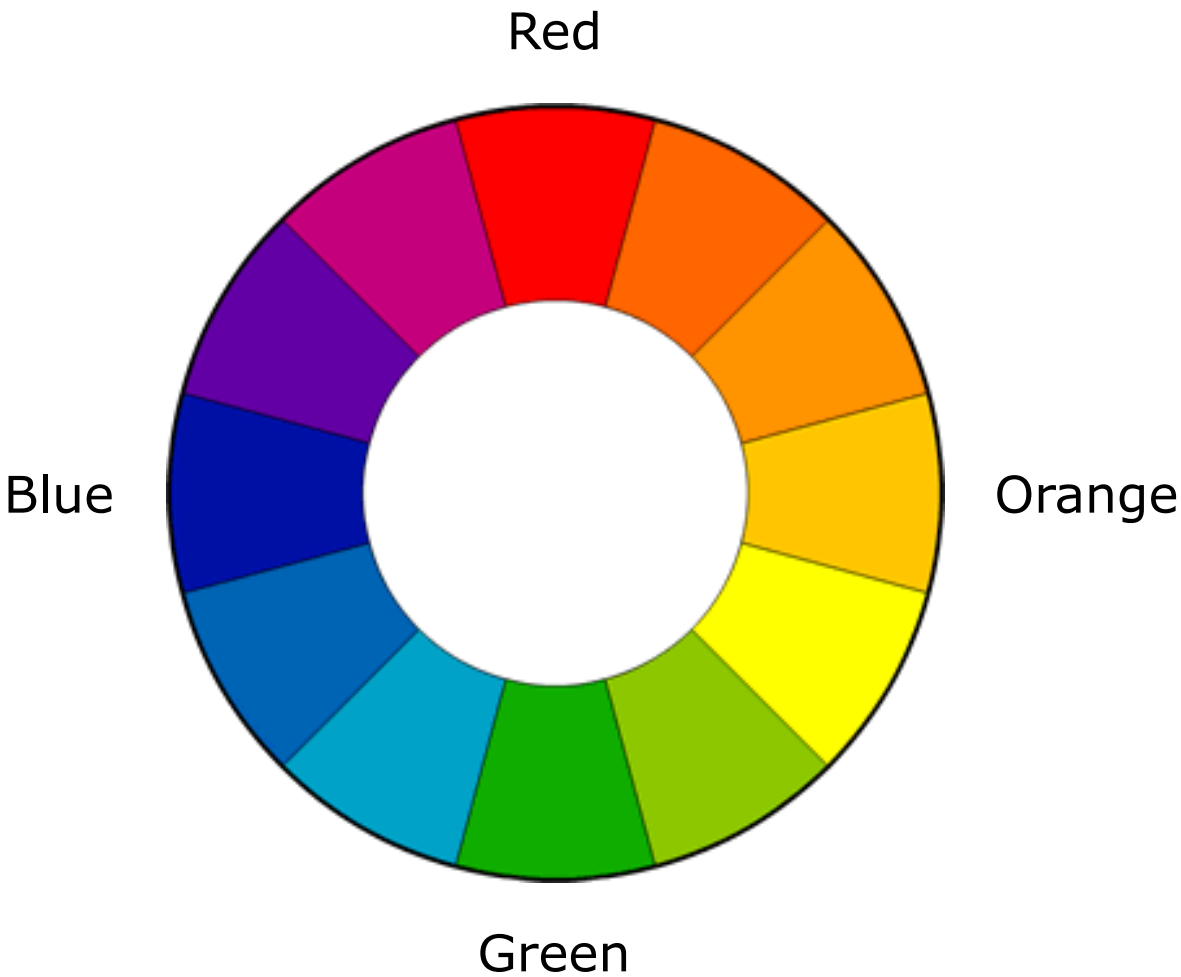


Crystal field theory can be used to explain colors of coordination compounds (complexes)

e^-'s are promoted from low d-orbitals to high d-orbitals with absorption of photons of visible light

color we observe is the <u>complement</u> (or leftovers) of absorbed light

A solution of...	absorbs...	and appears...
$Co(NH_3)_6^{3+}$	blue (450 nm)	orange
$Co(NH_3)_5H_2O^{3+}$	green (500 nm)	red
trans-$Co(NH_3)_4Cl_2^+$	red (680 nm)	green


Red
Orange
Green
Blue

Wavelength of light absorbed determined by Δ_o

$$\Delta_o = \frac{h\,c}{\lambda}$$

$h = 6.626 \times 10^{-34}$ J s

$c = 2.998 \times 10^{8}$ m s^{-1}

λ = wavelength absorbed (m)

What is the splitting energy of $Co(CN)_6^{3-}$ which absorbs 290 nm light?

$$\Delta_o = \frac{h\,c}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{290 \times 10^{-9}\ \text{m}} = \underline{6.8 \times 10^{-19}\ \text{J}}$$

What's Δ_o (in kJ/mol) of $Co(NH_3)_6^{3+}$ which absorbs 440 nm light?

$$\Delta_o = \frac{h\,c}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{440 \times 10^{-9}\ \text{m}} = 4.5 \times 10^{-19}\ \text{J}$$

$$4.5 \times 10^{-19}\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{6.022 \times 10^{23}}{1\ \text{mol}} = \underline{270\ \text{kJ/mol}}$$

What wavelength of light does CoF_6^{3-} absorb if Δ_o = 155 kJ/mol?

$$\frac{155\ \text{kJ}}{\text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}} = 2.57 \times 10^{-19}\ \text{J}$$

$$\lambda = \frac{h\,c}{\Delta_o} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{2.57 \times 10^{-19}\ \text{J}} = \underline{773 \times 10^{-9}\ \text{m}}$$

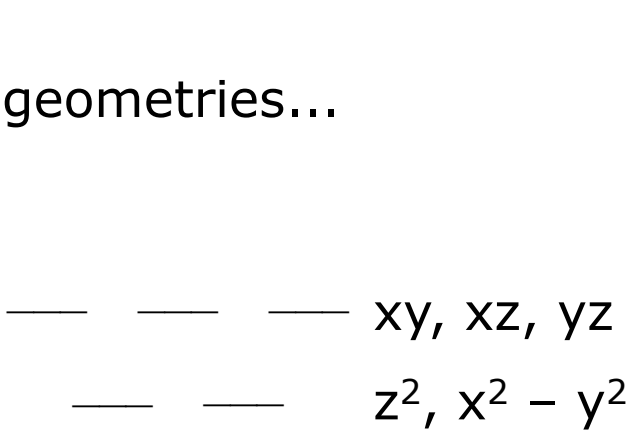
(or 773 nm)

d-Orbital energies are split for other geometries...

tetrahedral

ligands point at d_{xy}, d_{xz}, and d_{yz}

so they have higher energies



square planar

ligands point right at $d_{x^2 - y^2}$,

near d_{xy}, and donut of d_{z^2}