Coordination Chemistry

Transition Metals (incomplete d-orbitals)

Transition-metal compounds are often colored

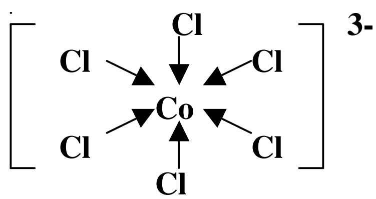
Transition metals form complex ions. Some complexes are neutral.
A **complex ion** is a metal ion with Lewis bases attached to it through coordinate covalent bonds. **Ligands** are the Lewis bases attached to the metal atom in a complex.

Examples of some ligands: $:NH_3$, $:CO$, $:CN^-$, $H_2O:$, $:Cl^-$, $:NO_2^-$

All ligands have a pair of electrons that may be shared with a metal. The formation of a coordinate covalent bond is the result of an acid-base reaction.

M^{n+} + **:**L → M **••**L
acid base

$[CoCl_6]^{3-}$



Exercise: What is the oxidation state of the metal in $[CoCl_6]^{3-}$?, $[Fe(CN)_6]^{4-}$, $[Ni(CO)_4]$, $[Cr(NH_3)_6]^{3+}$?

Ligands can be classified as:

Mondentate: Ligand that has one donor atom.
Bidentate Some ligands contain two donor atoms.

Oxalate, $C_2O_4^{2-}$

Ethylenediamine, en

•• ••
HN_2-CH_2-CH_2-NH_2

Polydentate: Ligands that contain 3,4,… donor atoms.

Coordination number: the total number of bonds the metal atom forms with ligands.

<u>**Exercise**</u>: what is the coordination number in each of the following?

a) $[Co(C_2O_4)_3]^{3-}$ b) $[Co(en)_3]^{3+}$

Bonding in Coordination Compounds

Theories of bonding should explain three important properties of transition metal complexes: structure, magnetic property, and color

Theories of bonding: 1) Valence bond theory and 2) Crystal Field Theory

Valence Bond theory

Ligands as a rule do not posses unpaired electrons, so the bonding in the complex must result from the overlap of ligands orbitals containing lone pairs of electrons with vacant orbitals on the metal ion, therefore, giving rise to a coordinate covalent bond.

Exercise 1 Predict the geometry and the magnetic property of $[Cr(H_2O)_6]^{3+}$.

Cr = $[Ar]4s^2 3d^4$ Cr(III) is a d^3 case

What is the geometry of the complex ion according to VSEPR theory? __________
What is the magnetic property? __________
How many unpaired electrons? ______________
Experimental measurements demonstrated the presence of three unpaired electrons.

Review hybrid orbitals of the central atom:

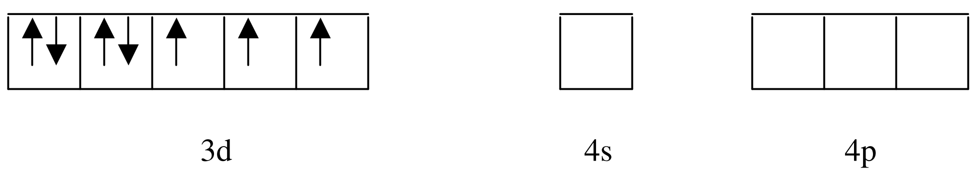
Hybrid orbitals	Atomic orbitals used	Number of hybrid orbitals	Electron-pair geometry
sp	**s + p**	**2**	**Linear**
sp^2	**s + p + p**	**3**	**Trigonal planar**
sp^3	**s + p + p + p**	**4**	**Tetrahedral**
$d\,sp^2$	**s + p + p + d**	**4**	**Square planar***
sp^3d or dsp^3	**s + p + p + p + d**	**5**	**Trigonal bipyramidal**
sp^3d^2 or d^2sp^3	**s + p + p + p + d + d**	**6**	**Octahedral**

Exercise 2:

$[Ni(CN)_4]^{2-}$ is diamagnetic while $[CoCl_4]^{2-}$ is paramagnetic with three unpaired electrons. Predict the geometry of each.

Ni(II) = [Ar]d^8 Ni(II) is a d^8 case

Co(II) = [Ar]d^7 Co(II) is a d^7 case

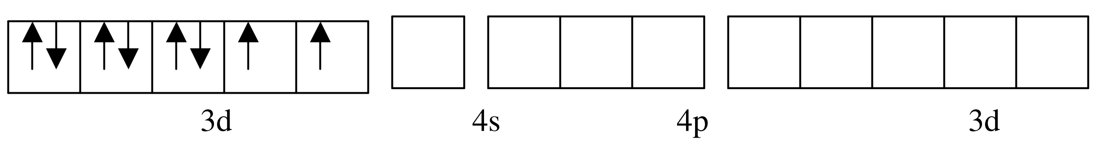


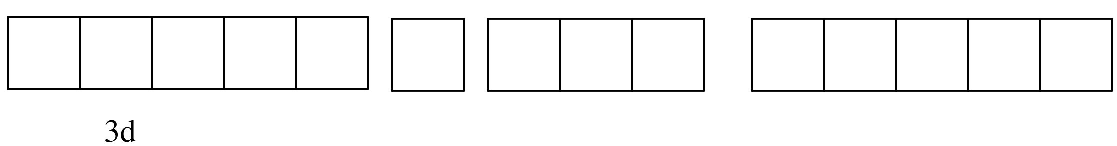
Summary: We can account for the structure and magnetic property of complex ions. Valence bond theory does not explain the color of the metal complexes

Exercise 3:

Predict the geometry and magnetic property of $[Ni(H_2O)_6^{2+}]$.

Since there are six coordinate covalent bonds, the geometry is ____________





In the last example there was no choice as to which type of bonding, inner-orbital or outer-orbital.

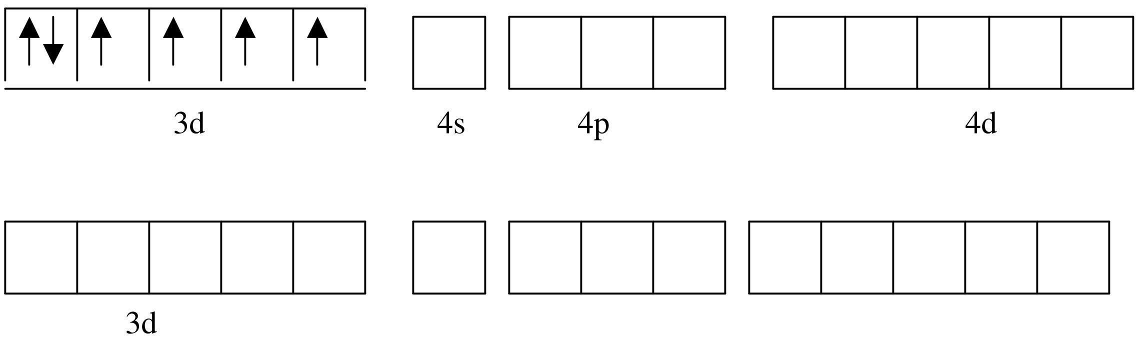
Next, let us look at a situation where we have a choice of outer-orbital and inner-orbital.

Exercise 4:

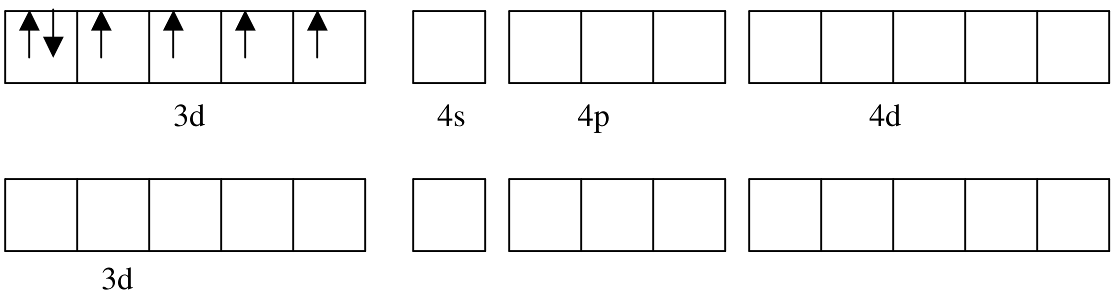
Consider the complex, ML_6, where the metal is a d^6 case and L is a monodentate ligand.

We can predict whether the complex is inner-orbital (d^2sp^3) or outer-orbital (sp^3d^2) by measuring the magnetic property.

A)



B)

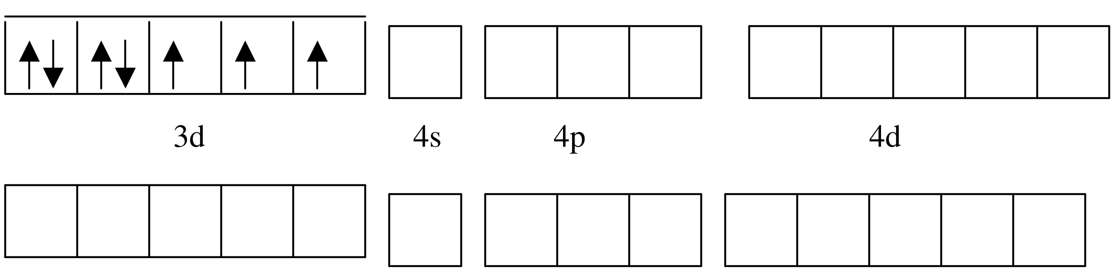


We can differentiate between the above electronic structures by examining the number of unpaired electrons.

Exercise 5

$[Co(NO_2)_6]^{4-}$ has one unpaired electron. Predict the geometry and the electronic structure (type of bonding) using VSEPR theory.

Co(II) is a d^7 case. Since there are six coordinate covalent bonds the geometry is_________

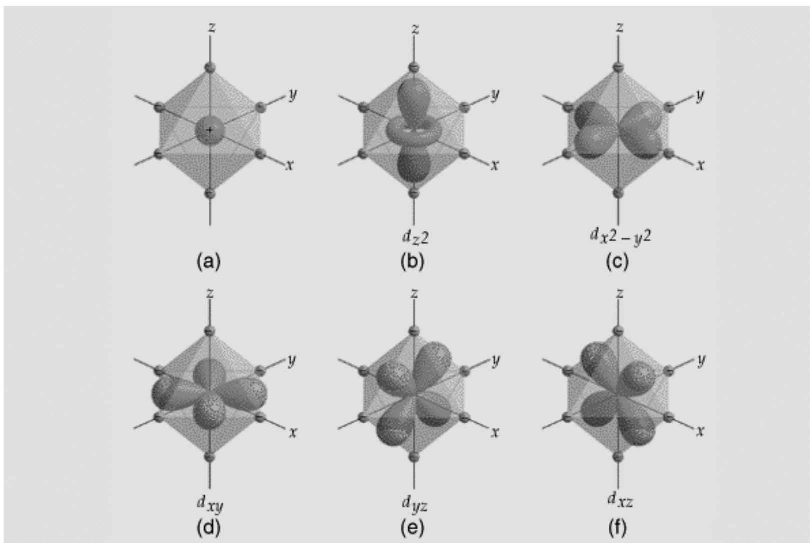


Here we couldn't have been able to predict the correct magnetic property.

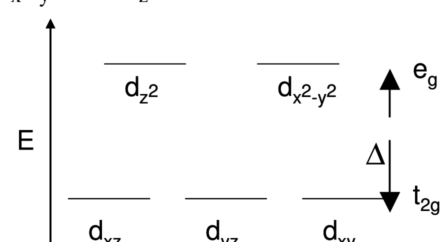
Summary: We can account for the structure and magnetic property of complex ions. Valence bond theory does not explain the color of the metal complexes.

Crystal Field Theory

Crystal field theory differs from valence bond theory in viewing the complex as held together by purely electrostatic attractions. That is, it ignores covalent bonding. The most significant aspects of the theory is its concern with the effect that the ligands have on the energies of the d-orbitals of the metal. The ligands are viewed as pointing their negative end in the direction of the metal cation. Consider an octahedral geometry: An octahedral complex is constructed by placing 6 ligands along the x, y, and z axes with the negative end of the dipole pointing at the metal ion.



When a complex is formed, electrons in the d-orbitals will feel an electrostatic repulsion and their energies will be raised. An electron in a $d_{x^2-y^2}$ or d_{z^2} orbital will be repelled more than an electron in one of the d_{xy}, d_{xz}, d_{yz} orbitals. Recall that the $d_{x^2-y^2}$ or d_{z^2} are pointing directly towards the ligands, while d_{xy}, d_{xz}, d_{yz} are pointing between the ligands at an angle of 45°. The energies of the the $d_{x^2-y^2}$ and d_{z^2} are raised more than the energies of the d_{xy}, d_{xz}, d_{yz} orbitals.



The effect of the ligand is to split the d-subshell into two sets of energy levels, t_{2g} and e_g. The diagram above shows the splitting of d-orbitals in an octahedral complex.

The magnitude of the crystal field splitting

For a given metal, different ligands have different effects on the magnitude of the splitting of the d-orbitals. The **spectrochemical series** below shows the ligands in the order of their ability to produce a large Δ. Sometimes, the relative positions of neighboring ligands in a series might be reversed **$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< NO_2^- < CN^-$**

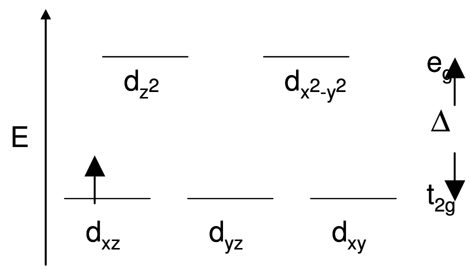
The magnitude of the crystal field splitting, Δ, depends on:

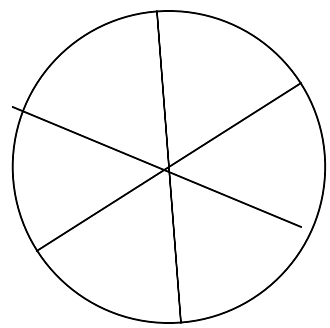
a) The ligand b) The metal c) The oxidation state of the metal

The origin of the color of complex ions

For most complexes, the crystal field splitting, Δ, is of the same magnitude as the energy of the visible light. When light strikes the complex, the electron in the t_{2g} level absorbs the component of light energy of proper frequency and gets raised to the e_g level. When a component of the visible light is absorbed by the electron, the complex displays the complement of the color of light that is absorbed.For example, $[Ti(H_2O)_6]^{3+}$ has a crystal field splitting, Δ, that corresponds to the energy of light in the yellow-green portion of the spectrum. When white light passes through a solution of $[Ti(H_2O)_6]^{3+}$ complex, yellow-green light is absorbed and the light emerges appears violet.

Light Absorption for $[Ti(H_2O)_6]^{3+}$





$[Ti(H_2O)_6]^{3+}$ is purple

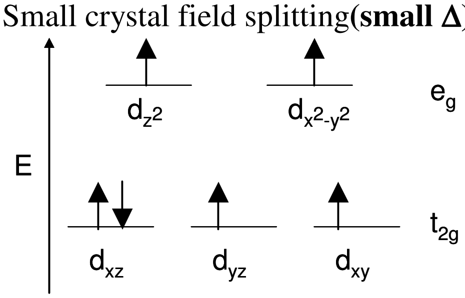
By examining the color of different complexes and their absorption spectra we can have an idea about the magnitude of Δ .The crystal field theory is useful in understanding the color and magnetic property of complexes.

High-spin versus low-spin:

Examine the magnetic property of Co(III) in an octahedral environment

a)**Weak crystal field**

Small crystal field splitting**(small Δ)**

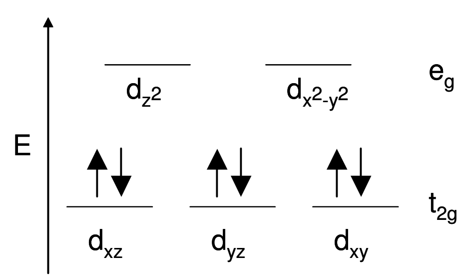


$E_{pairing} > \Delta_{promotion}$

High-spin

b) **Strong crystal field**

Large crystal field splitting**(large Δ)**



$E_{pairing} < \Delta_{promotion}$

Low-spin

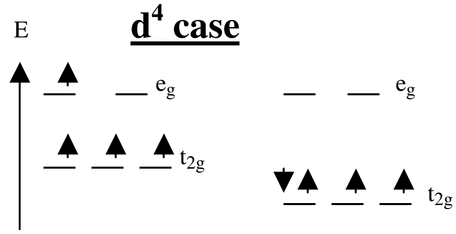
High spin complex: a complex in which there is minimum pairing of electrons in the d orbitals of the metal atom. That is, maximum number of unpaired electrons.

Low spin complex: a complex in which there is mmaximum pairing of electrons in the d orbitals of the metal atom. That is, minimum number of unpaired electrons.

Crystal field theory versus Valence Bond theory: In terms of the Valence Bond theory, the high-spin complex is equivalent to outer-orbital complex (sp^3d^2) and the low-spin complex is equivalent to inner-orbital complex (d^2sp^3).

High Spin vs Low Spin Examples High Spin vs Low Spin Examples

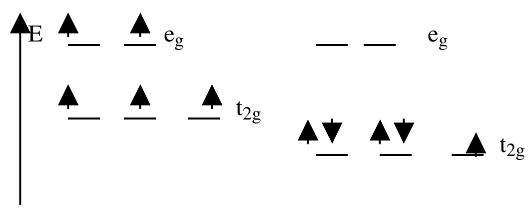
d^4 case



Δ is small
high-spin complex

Δ is large
low-spin complex

d^5 case



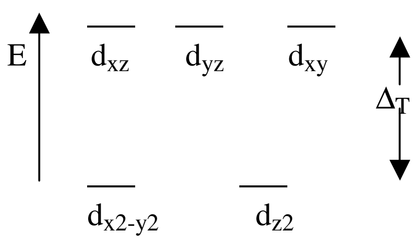
Δ is small
high-spin complex

Δ is large
low-spin comple

Tetrahedral complexes:

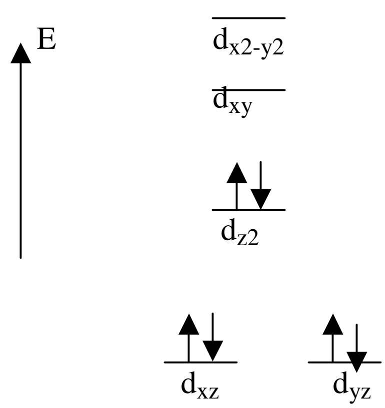
- Tetrahedral complexes are ALWAYS high-spin (small Δ_T).
- Tetrahedral splitting produces opposite order of octahedral splitting.

d_z2 and $d_x2\text{-}_y2$ are lower in energy than d_{xz},d_{yz}, and d_{xy}



Square planar complexes

You do not need to memorize the splitting in a square planar environment.



Isomerism in Coordination Compounds

Isomers are compounds with the same molecular formula but with different arrangement of atoms. Isomers have different properties.

A) Structural isomers. The atoms are connected to each other in a different sequence.

1) **Linkage isomers (manner of attachment)**

← **S-C-N⁻** and **SCN⁻ →**

thiocyanato **isothiocyanato**

← **O-N-O⁻** and **O-N-O⁻** ↓

Nitrito **nitro**

2) **Coordination isomers** exist in compounds that have two of coordination. Isomers arise through the exchange of ligands between those coordination spheres.

$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

3) **Ionization isomers**

$[Cr(NH_3)_5SO_4]Br$ and $[Cr(NH_3)_5Br]SO_4$ $[Pt(NH_3)_4(OH)_2]SO_4$ and $[Pt(NH_3)_4SO_4](OH)_2$

$[Co(NH_3)_5NO_3]Br_2$ and $[Co(NH_3)_5Br]NO_3$

B) **Stereoisomers** The atoms are bonded to each other in the same order, but differ only in how the atoms are oriented in three dimensions.

1) **Geometric isomers** may exist in complexes of general formula :

a) $\mathbf{Ma_4b_2}$ (a and b are monodentate ligands)

b) $\mathbf{Ma_2b_2}$ (a is bidentate and b is monodentate ligands)

c) $\mathbf{Ma_3b_3}$ (a and b are monodentate)

2) **Optical isomers** have identical chemical and physical properties but only differ in the way they interact with a plane of polarized light. The plane of polarization is rotated through some angle, ϑ . They bear the same structural relationship to each other as the right and left hands.. They are nonsuperimposable mirror images of one another. Molecules that are asymmetric may exhibit optical isomerism.

Dextrorotatory

Levorotatory

Racemic mixture

a) Any octahedral complex containing three bidentate ligands can exist as two optical isomers. General formula **Ma_3** (a is a bidentate ligand)

b) The cis-form of complex ions containing two bidentate ligands and two monodentate ligands. General formula cis -**Ma_2b_2**(a is a bidentate ligand and b is monodentate ligand).

Rules for Naming Coordination Compounds

1. The cation is named first, then the anion if the substance is an electrolyte
2. The coordinated ligands are named before the metal ion.
3. The names of all negative ligands end in "o"
   chloro (Cl^-), carbonato (CO_3^{2-}), cyano (CN^-), nitro (NO^{2-}), hydroxo (OH^-)
   bromo (Br^-), fluoro (F^-), oxalato ($C_2O_4^{2-}$), Oxo (O^{2-})
4. Coordinated water is called "aqua"; ammonia is called "ammine"; carbon monoxide is called "carbonyl".
5. For a comlex **cation or a complex compound**, the ligands are listed first, in alphabetical order, and the metal next, followed by a roman numeral that indicates the oxidation number of the metal. (The Greek prefixes as per #6 below are ignored in determining the alphabetical order.) A complex **anion** is named the same way except the metal is given the suffix "ate" regardless of its oxidation state. When there is a Latin name for the metal, it is usually used to name the anion.

Copper = Cuprate		Gold = Aurate	
Iron = Ferrate		Lead = Plumbate	
Silver = Argentate		Tin = Stannate	

6. The number of ligands of each kind is indicated by the Greek prefixes: mono (usually omitted), di, tri, tetra, penta, hexa, hepta, octa. When the name of the ligand has a number prefix, the number of ligands is denoted with bis (2), tris (3), tetrakis (4).
7. The oxidation state of the central metal of a complex is shown by a Roman numeral in parenthesis.

Examples:

Exercise

A. Name the following complex compounds or ions:

1. $[Cu(H_2O)_6]Br_2$ 1. ____________________
2. $[Cr(NH_3)_4Cl_2]Cl$ 2. ____________________
3. $K_3[FeF_6]$ 3. ____________________
4. $[Zn(OH)_4]^{2-}$ 4. ____________________
5. $[Co(H_2O)_4Cl_2]Cl$ 5. ____________________
6. $[Fe(NH_3)_4]^{2+}$ 6. ____________________
7. $K_2[SnCl_6]$ 7. ____________________

B. Write the formula for each of the following complex compounds or ions.

1. Tris(ethylenediamine)cobalt (III) chloride 1. ____________________
2. Diamminetetrabromoplatinum (VI) bromide 2. ____________________
3. Tetracyanonickelate (II)ion 3. ____________________
4. Diamminesilver (I) ion 4. ____________________
5. Sodium tetracyanocuprate (I) 5. ____________________
6. Silver hexacyanoferrate (II) 6. ____________________