

Chemistry of Transition Metals

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Chemistry of transition elements

اهداف دراسه المقرر:

دراسه المفاهيم والنظريات الاساسيه للعناصر الانتقاليه

مايدرس فى المقرر:

- Introduction of transition metals, types of ligands, isomers and nomination.
- Valence bond theory, hybridization, magnetic properties.
- Crystal field theory, ionic bonding, CFSE, thermodynamics measurement, color of complexes d-d transfer.
- Molecular orbitals theory, covalent bonding.
- Ligand field theory, nephelometry effect, interpretation of the spectrochemical series, bonding, selection rule.
- Energy level of free ion, Russell Saunders coupling scheme and J-J coupling in tetrahedral and octahedral complexes.
- Interpretation of the spectra using Orgal and Tanab-Sugano diagrams for allowed and not –allowed transformation.
- The Jahn Teller theorem.

تقويم المقرر:

المراجع الرئيسيه:

Advanced inorganic chemistry. F.Cotton & G. willkinson •

Inorganic chemistry. J.H.Huheey. •

مع تمنياتي للجميع بالاستفادة الكاملة من المقرر وان يكون النجاح حليفكم وان يجعل ما نقدمه خالصا لوجهه الكريم.

| | | | | | | | | | | | | | | | | | | | | | | | |
|---|-----------|--|-----------|---------------------------------------|-----------|-----------|-----------|--------------------|-----------|----------|------------|------------|--|--|--|--|------------|------------|------------|------------|------------|------------|--|
| | 1A (1) | | 2A (2) | | | | | | | | | | | | | | 3A (13) | 4A (14) | 5A (15) | 6A (16) | 7A (17) | 8A (18) | |
| 1 | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | | | | TRANSITION ELEMENTS <i>d</i> block | | | | | | | | | | | | | | | | | | | |
| 3 | | | 3B (3) | 4B (4) | 5B (5) | 6B (6) | 7B (7) | 8B (8) (9) (10) | | | 1B (11) | 2B (12) | | | | | | | | | | | |
| 4 | | | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | | | | | | | | | | | |
| 5 | | | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | | | | | | | | | | | |
| 6 | | | 57 La | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | | | | | | | | | | | |
| 7 | | | 89 Ac | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 | 111 | 112 | | | | | | | | | | | |

INNER TRANSITION ELEMENTS
f block

| | | | | | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|
| 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu |
| 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | 103 Lr |

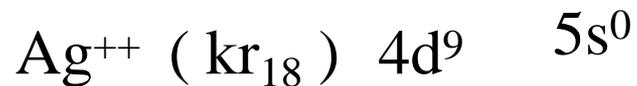
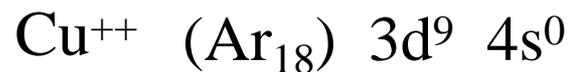
Principle of transition metal

General definition for transition element :

It is the element that in completely filled (d) or (f) sublevel in either the free or in one of its oxidation states .

The coinage metals which are (Cu₂₉ - Ag₄₇ - Au₇₉) are considered as transition elements ?

Although the orbitals of (d) sublevel are completely filled with electron because in their higher oxidation state Cu⁺⁺, Ag⁺⁺, Au⁺⁺⁺ contain (9) or (8) electrons in d sublevel



Zn_{30} , Cd_{48} , Hg_{80} , are non transition elements because the orbitals of (d) sublevel are completely filled with electrons in their free states or in their higher oxidation states .



Transition elements (Fe , Co , Ni) are used in the manufacture of alloys ?

Because these elements have nearly equal atomic radius.

Properties of transition metal

Electronic configuration.

variable oxidation state (oxidation number)

complex ion formation

colored ions

catalytic activity

Magnetic properties

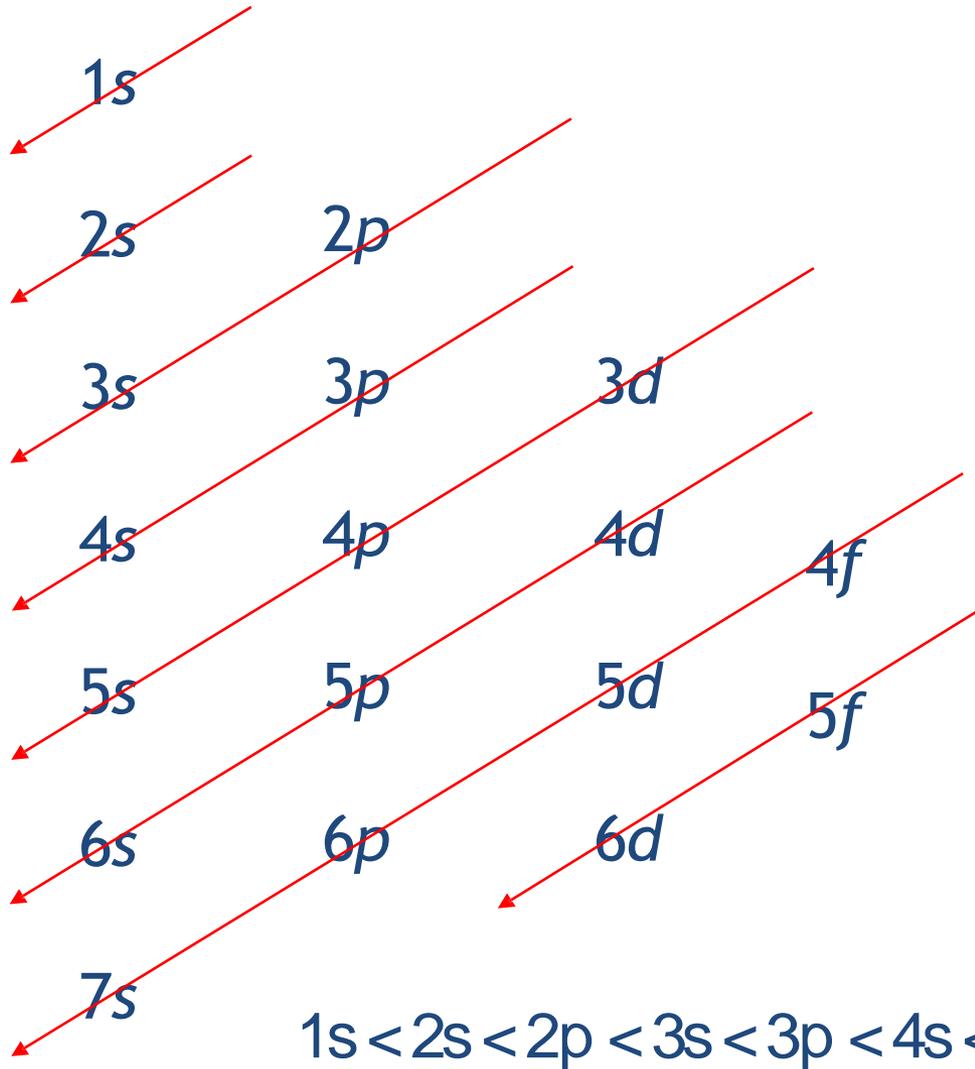
□ The general electronic configuration of these element is
 $(n-1)d^{1-10} ns^2$ ($n = 4$ to 7)

| | |
|------------------------|--|
| 1 st series | [Ar] 4s ^{1,2} 3d ¹⁻¹⁰ |
| 2 nd series | [Kr] 5s ^{0,1,2} 4d ¹⁻¹⁰ |
| 3 rd series | [Xe] 6s ^{1,2} 4f ¹⁴ 5d ¹⁻¹⁰ |
| 4 th series | [Rn] 7s ^{1,2} 5f ¹⁴ 6d ¹⁻¹⁰ |

- Transition metals **form ions** through the loss of the **ns** electrons before the (**n – 1**)**d** electrons.
- The definition of transition metal excludes **Zn, Cd and Hg**. The electronic configurations of Zn, Cd and Hg are represented by the general formula $(n-1)d^{10}ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

Electron Configuration

Filling Rules for Electron Orbitals



Aufbau Principle

Fill up” electrons in lowest energy orbitals

Pauli Exclusion Principle

no two electrons in an atom can have the same set of four quantum numbers (n , ℓ , m_ℓ and m_s)

Hund's rule

For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized’.



□ Generally, there are many factors affecting the filling up of (n-1)d and ns sublevels

1. Symmetrical distribution of electron:

It is well known that symmetry leads to stability. The completely filled or half-filled subshells have a symmetrical distribution of electrons in them and are therefore more stable. This effect is more dominant in d and f-orbitals.

□ Chromium (Z = 24)

Rules predict the configuration to be [Ar] 3d⁴ 4s². The correct configuration experimentally was found to be [Ar] 3d⁵4s¹.

[both 4s and 3d become half filled]. **Similar for (Mo) only**

□ Copper (Z = 29): E.C [Ar] 3d⁹4s² is not correct. The correct electronic configuration is [Ar] 3d¹⁰4s¹

[d- orbital is completely filled and 4s is half filled].

Similar for (Ag, Au, Rg)

Cr₂₄ and Cu₂₉ are abnormal from except electronic configuration ?

In case of chromium (Cr₂₄) Cr₂₄ : (Ar₁₈) 4S¹ 3d⁵ so these sublevels 4S and 3d becomes half filled this makes the atom has less energy and more stability .

24 Cr

42 Mo

74 W

106 Sg

In case of Copper (Cu₂₉) Cu₂₉ : (Ar₁₈) 4S¹ 3d¹⁰ so the sublevels 4S becomes half filled and sublevels 3d become completely filled this makes The atom has less energy and more stability.

29 Cu

47 Ag

79 Au

111 Rg

Ions

- Transition metals are defined as **metallic elements with an incomplete d sub-shell in at least one of their ions.**
- Form positive (+) ions by losing electrons.
- These electrons come from the 4s sub-shell first, then from the 3d sub-shell:

Fe atom: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

Fe²⁺ ion: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$

- Question : Explain why iron II is easily oxidized to iron III (where as) while Mn II in not easily oxidized to Mn III ?

- Answer :

- The electronic configuration of iron atom is : $Fe_{26} = (Ar_{18}) 4s^2 3d^6$

- Oxidation



- Iron III ions is more stable as the 3d sublevel is half filled it is more stable and the oxidation of iron (II) is facilitated but in the case of manganese atom the electronic configuration is :

- $Mn_{25} = (Ar_{18}) 4s^2 3d^5$

- $Mn^{++} 3d^5$

- Half- filled more stable

Oxidation →

$Mn^{+++} 3d^4$

less stable

Oxidation states of transition metals

Oxidation States

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure . As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions.

. Magnetic properties of d- & f- block elements

- ❑ Magnetic properties are determined by the number of unpaired electrons in the *d* orbitals of the metal ion.
- ❑ Most main-group ionic compounds are **colorless** and **diamagnetic** because the metal ion has **no unpaired electrons**.
- ❑ **Transition metal** ions with a d^0 or d^{10} configuration are also colorless and diamagnetic.
- ❑ Many **transition metal** ionic compounds are **highly colored** and **paramagnetic** because the neutral atom or one of their metal ion has one or more **unpaired electrons**. The spin only value of the magnetic moments μ_s or (μ_{eff}) can be calculated from the following relations.
$$\mu_{eff} = \sqrt{n(n+2)}B.M$$
$$\mu_{eff} = \sqrt{4s(s+1)}B.M$$
- ❑ where n is the number of unpaired electrons, s is the spin quantum number.

- magnetic properties:-

-Transition elements are paramagnetic due to the presence of unpaired electrons in the (d) or bitals .

| Paramagnetic substance | Diamagnetic substance |
|---|--|
| It is the substance which is attracted to the magnetic field due to the presence of unpaired electrons in (d) orbitals . | It is the substance which is repelled (not attracted) to the magnetic field due to the presence of electron which are paired in all (d) orbitals . |
| The magnetic moment is equal to the number of unpaired electrons in (d) sublevel such as Cu^{++} , Fe Ni , Mn , Co ,Sc | The magnetic moment is equal zero because electrons are paired in all orbitals such as zinc , sc^{+++} |

Which of the following elements paramagnetic and which is diamagnetic Zn , Cu^{++} , Fe^{++}

Write the order of momentum of these element .

Zn d^{10}

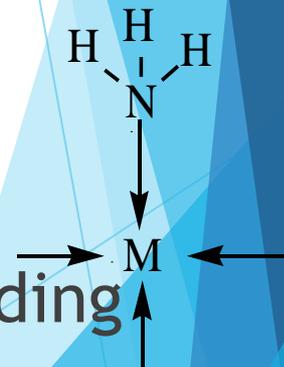
Number of unpaired electrons 0

Magnetic momentum 0

Diamagnetic

Coordination Compounds

- ▶ • Coordination compounds are species in which a:
 - ▶ central metal ion (or atom) is attached to a group of
 - ▶ surrounding molecules or ions by coordinate
 - ▶ covalent bonds.
- ▶ • Surrounding groups are called *Ligands*.
- ▶ • Central metal is a *Lewis acid*.
- ▶ • Ligand is a *Lewis base*.
- ▶ • The number of ligand donor atoms surrounding the
- ▶ central metal is called the *coordination number*.



Factors effecting complexation

1-size of the metal ion.

2-charge on the metal ion.

3-presence of vacant d orbitals on metal.

Werner coordination theory

Postulates:

1. In co-ordination compounds, central metal atoms exhibit primary valency and secondary valency.

The primary valency is ionizable. Secondary valency is not ionizable.

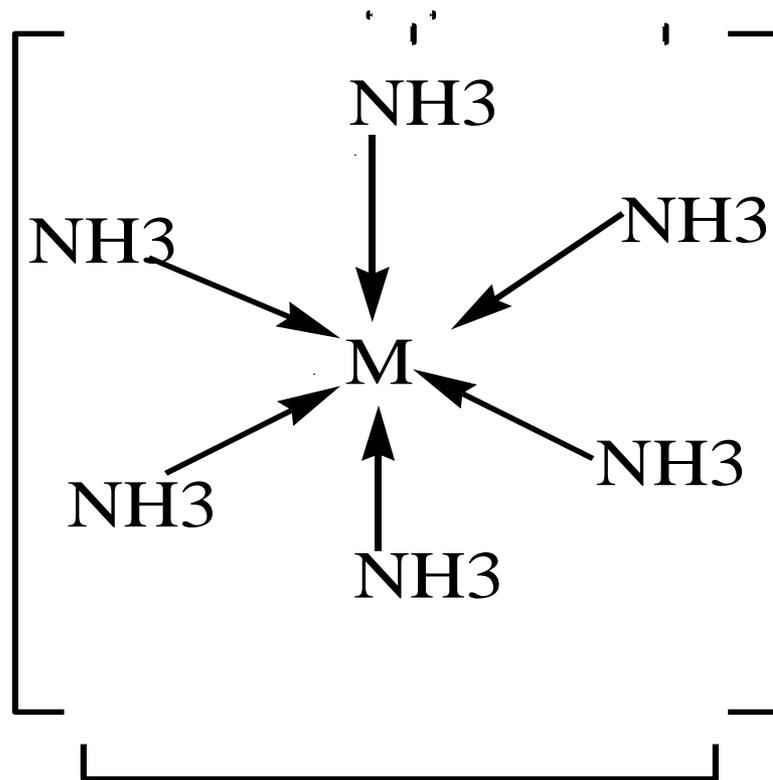
The primary valency corresponds to oxidation state.

The secondary valency corresponds to coordination number. (the central metal ion and ligands are not ionizable)

2. Every metal atom has a fixed number of secondary valencies (coordination number(s)).

3. The metal atom tends to satisfy both its primary valency as well as its secondary valency. Primary valency is satisfied by negative ions (metal ion has a positive charge) whereas secondary valency (coordination number) is satisfied either by negative ions or by neutral molecules. (In certain case a negative ion may satisfy both types of valences).

4. The coordination number or secondary valencies are always directed towards the fixed positions in space and this leads to definite geometry of the coordination compound.



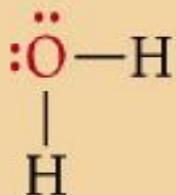
coordination sphere
secondary sphere

ionization sphere
primary sphere

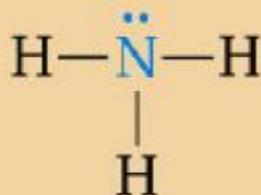
Types of ligands

- ▶ Ligands are classified into two broad categories:
- ▶ Monodentate and polydentate.
- ▶ Monodentate ligands are those which use only one donor atom for complexation.
- ▶ Polydentate ligands are those which use more than one atom for complexation.

Monodentate ligands



Water



Ammonia



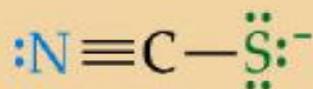
Chloride
ion



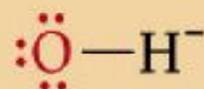
Cyanide
ion



Carbon
monoxide



Thiocyanate
ion

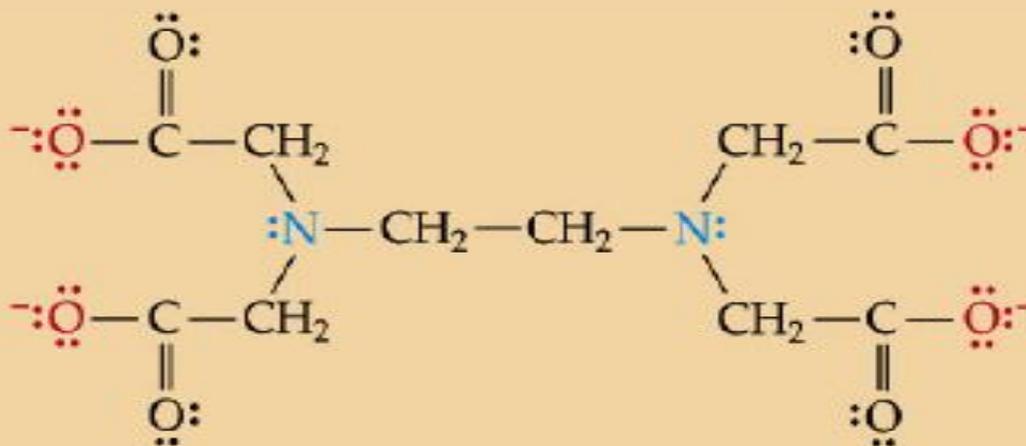
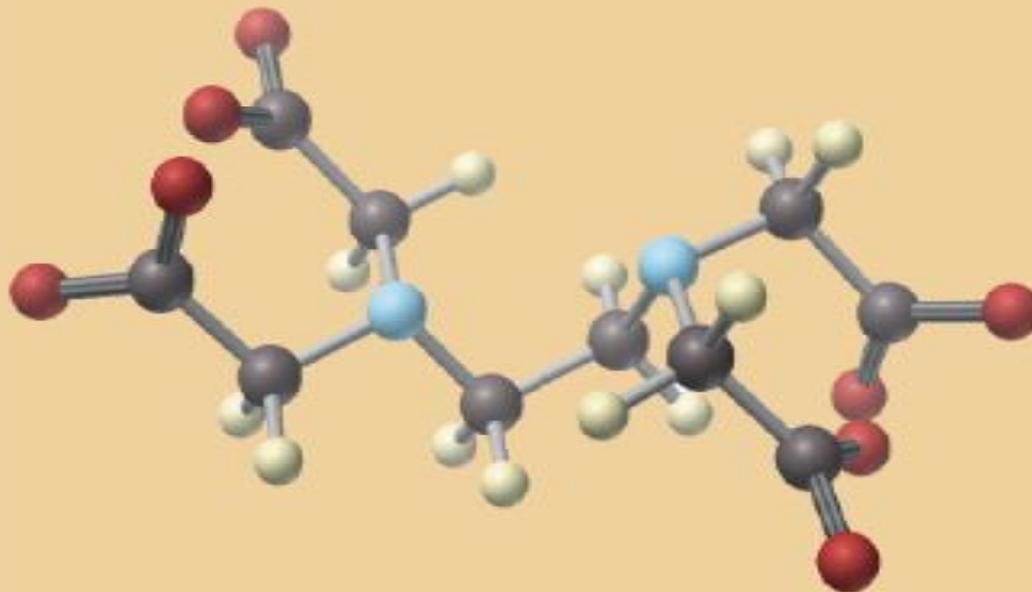


Hydroxide
ion

Structures of some common ligands

(a)

Hexadentate ligand



Ethylenediaminetetraacetate ion (EDTA⁴⁻)

Structures of some common ligands

(c)

Table 17.3 Different types of ligands

| | | |
|---|--------------|--|
| | Monodentate | |
| Fluoride | | $F^- \longrightarrow$ |
| Water | | $\begin{array}{c} H \\ \\ H-O \longrightarrow \\ \\ H \end{array}$ |
| Ammonia | | $\begin{array}{c} H \\ \\ H-N \longrightarrow \\ \\ H \end{array}$ |
| | Bidentate | |
| Ethylene diamine (en) | | $\begin{array}{c} CH_2-NH_2 \longrightarrow \\ \\ CH_2-NH_2 \longrightarrow \end{array}$ |
| Oxalate | | $\begin{array}{c} COO^- \\ \\ COO^- \end{array}$ |
| | Tridentate | |
| Diethylenetriamine (dien) | | $\begin{array}{c} H_2N \nearrow \\ \\ CH_2-CH_2-NH-CH_2-CH_2-NH_2 \\ \quad \quad \quad \nearrow \end{array}$ |
| | Tetradentate | |
| Nitrilotriacetic acid | | $\begin{array}{c} CH_2COO^- \\ \\ \leftarrow N-CH_2COO^- \longrightarrow \\ \\ CH_2COO^- \end{array}$ |
| | Pentadentate | |
| Ethylenediamine triacetic acid | | $\begin{array}{c} COO^- \quad OOC^- \\ \quad \quad \\ CH_2 \quad CH_2 \\ \quad \quad \\ H_2N \quad N \\ \quad \quad \\ CH_2-CH_2 \end{array}$ |
| | Hexadentate | |
| Ethylenediamine tetraacetic acid (EDTA) | | $\begin{array}{c} ^-OOC-CH_2 \quad \nearrow \\ \quad \quad \quad \\ ^-OOC-CH_2 \quad N-CH_2-CH_2-N \quad CH_2-COO^- \\ \quad \quad \quad \quad \quad \quad \\ ^-OOC-CH_2 \quad \quad \quad \quad \quad \quad \quad CH_2-COO^- \end{array}$ |

Comparison of 3d transition series with 4d/5d series

- ▶ Size.
- ▶ Oxidation states.
- ▶ Magnetic properties.
- ▶ Metal-metal bonding.
- ▶ Coordination number of complex.
- ▶ Abundance.

Nomenclature of complexes

- ▶ Positive ion is named first.
- ▶ **Rules for naming the Ligands**
- ▶ 1a. Ligands that act as anions which end in "-ide" are replaced with an ending "-o".
- ▶ Ex: Chloride-> Chloro.
- ▶ 1b. Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively.
- ▶ Ex: Nitrite->Nitrito Nitrate->Nitrato
- ▶ 2. Neutral molecules that are ligands carry their normal name with a few exceptions:
- ▶ H₂O-aqua
- ▶ NH₃-ammine
- ▶ CO-carbonyl
- ▶ NO-nitrosyl

Nomenclature of complexes

- ▶ **Rules for naming the metal center**
- ▶ When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman Numerals inside parenthesis. For example, in the examples above, Chromium and Cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as Cu(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Copper +2 will change into cuprate(II). Therefore, the last piece of information you need to memorize are some metals in complex anions. Here are the most common:
 - ▶ Iron -> Ferrate
 - ▶ Copper -> Cuprate
 - ▶ Tin -> Stannate
 - ▶ Silver -> Argentate
 - ▶ Lead -> Plumbate
 - ▶ Gold -> Aurate

Nomenclature of complexes

▶ Rules for naming the Ligands

▶ 1a. Ligands that act as anions which end in "-ide" are replaced with an ending "-o".

▶ Ex: Chloride-> Chloro.

▶ 1b. Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively.

▶ Ex: Nitrite->Nitrito Nitrate->Nitrato

▶ 2. Neutral molecules that are ligands carry their normal name with a few exceptions:

▶ H₂O-aqua

▶ NH₃-ammine

▶ CO-carbonyl

▶ NO-nitrosyl

▶ 3. The number of ligands present in the complex are noted with the prefixes which you memorized above. Prefixes always go before the ligand name. It is also important to know that prefixes are not included when ligands are named in alphabetical order. Also, ligands are always named first before the metal is named.

Nomenclature of complexes

- ▶ Representative examples:
- ▶ Complexes with neutral coordination sphere:
 - ▶ $[\text{Co}(\text{NH}_3)_3\text{ClCNNO}_2]$
 - ▶ $[\text{Ni}(\text{PF}_3)_4]$
 - ▶ $[\text{PdI}_2(\text{ONO})_2(\text{H}_2\text{O})_2]$
- ▶ Complexes with cationic coordination sphere:
 - ▶ $[\text{Fe}(\text{CH}_3\text{NC})_6]\text{Br}_2$
 - ▶ $[\text{Ni}(\text{NH}_3)_2(\text{en})](\text{CH}_3\text{COO})_2$

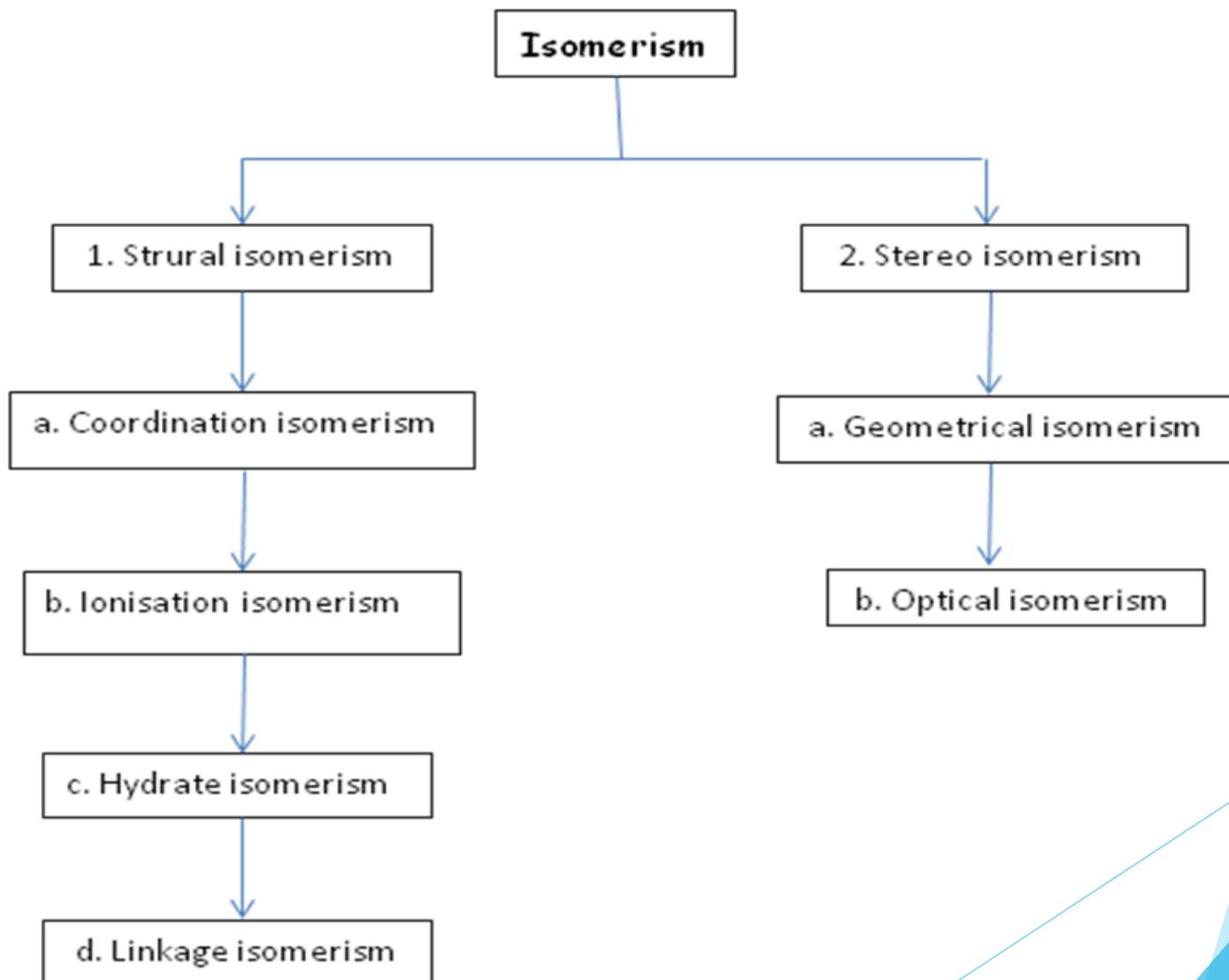
Nomenclature of complexes

- ▶ Complexes with anionic coordination sphere:
 - ▶ $\text{K}_3[\text{Fe}(\text{CN})_6]$
 - ▶ $\text{Na}[\text{OsCl}_5\text{N}]$
 - ▶ $\text{Na}[\text{Au}(\text{CN})_6]$
- ▶ Complexes with cationic and anionic coordination spheres:
 - ▶ $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$
 - ▶ $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$

Nomenclature of complexes

- ▶ Complexes with bridging ligands:
- ▶ $(\text{CO})_3\text{Fe}-\mu-(\text{CO})_3\text{Fe}(\text{CO})_3$
- ▶ $[\text{Br}_2\text{Pd}-\mu-\text{Br}_2\text{PdBr}_2]^{-2}$
- ▶ $\text{PF}_3\text{ClPd}-\mu-\text{PdPF}_3\text{Cl}$

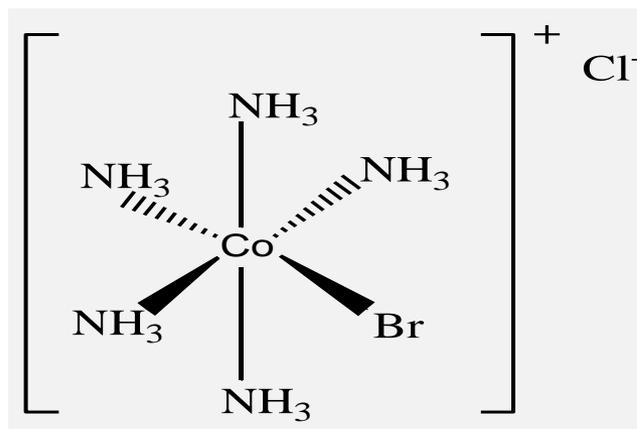
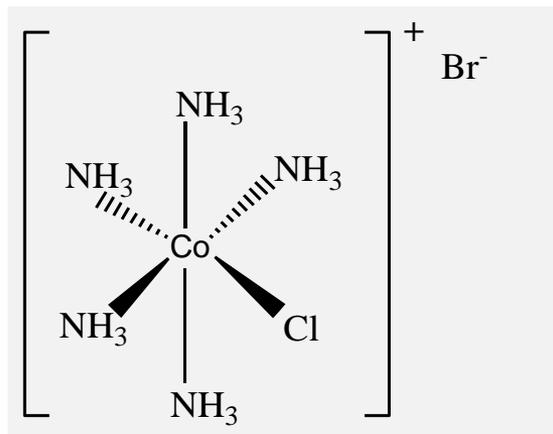
Types of Isomerism



1. Structural Isomerism

The interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Example : $[\text{Co}(\text{NH}_3)\text{Cl}]\text{Br}$ $[\text{Co}(\text{NH}_3)\text{Br}]\text{Cl}$
and $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$



Ionization isomerism

- ❖ The exchange of groups between the complex ion and the ions outside the complex
- ❖ Example: $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$ produce different ions in solution

C) Hydrate isomerism :

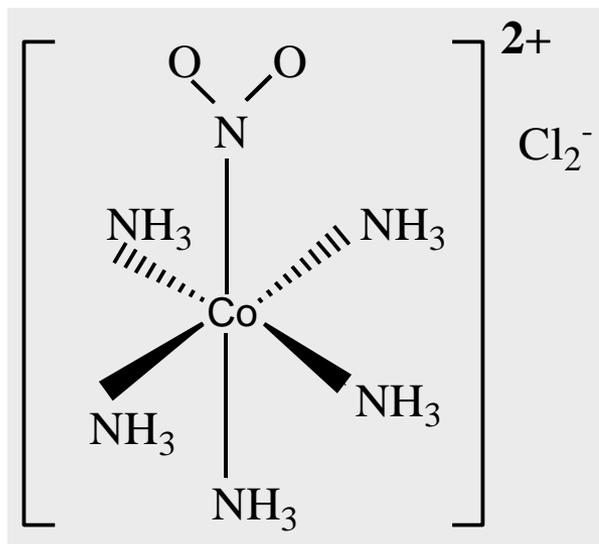
- ❖ It occurs when water forms a part of the coordination entity or is outside it

| | | |
|--|------------|----------------------|
| ❖ $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ chlorines) | violet | (three ionic |
| ❖ $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ chlorines) | green | (two ionic |
| ❖ $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ | dark green | (one ionic chlorine) |

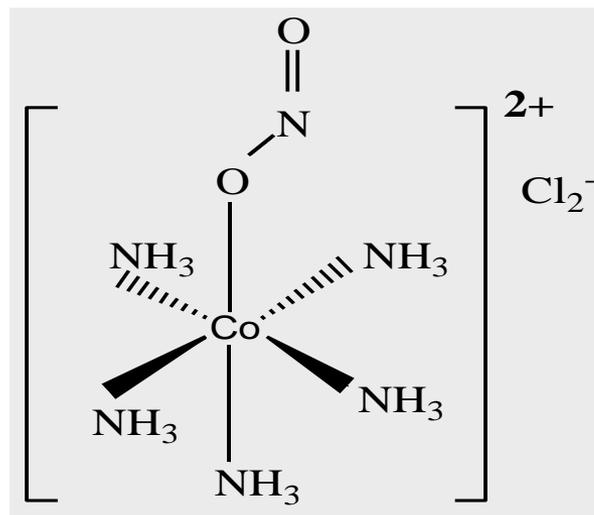
Linkage isomerism

❖ arises in a coordination compound containing ambidentate ligand.

❖ Example: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$



$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2^-$ (Red)

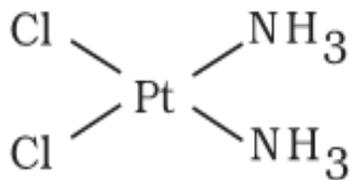


$\text{Co}(\text{NH}_3)_5(\text{ONO})\text{Cl}_2^-$ (Yellow)

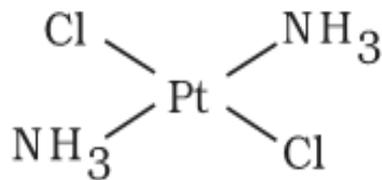
2. Stereoisomerism

a) Geometrical isomerism: cis and trans square planar

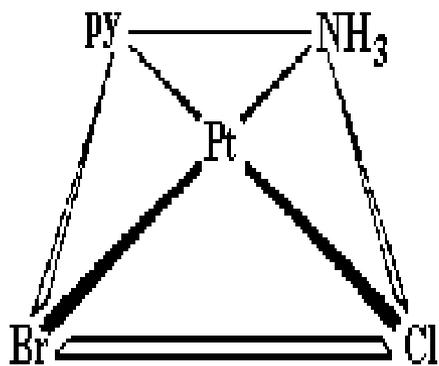
Example :



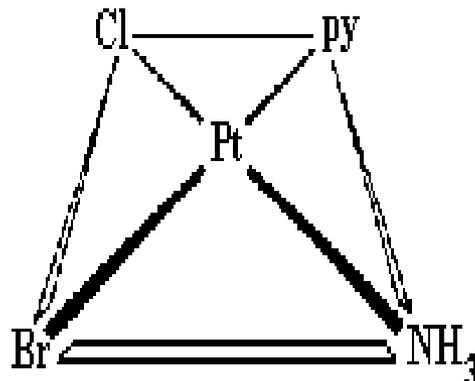
cis



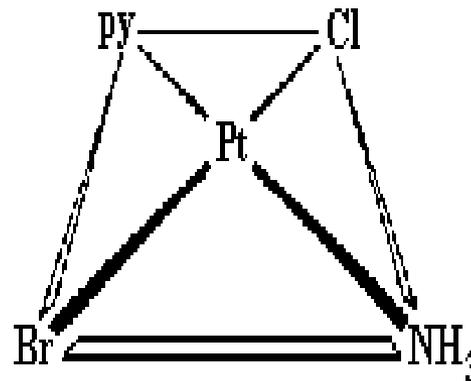
trans



(i)



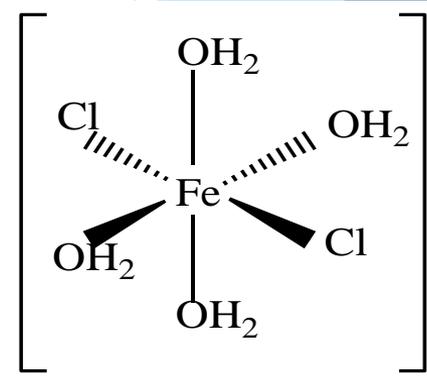
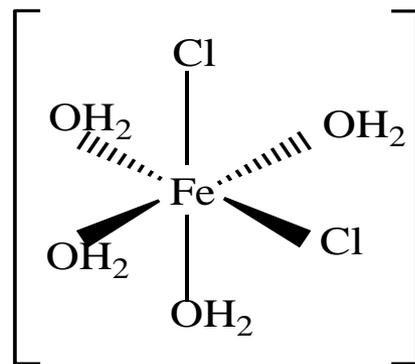
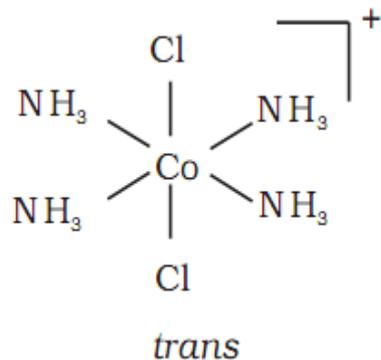
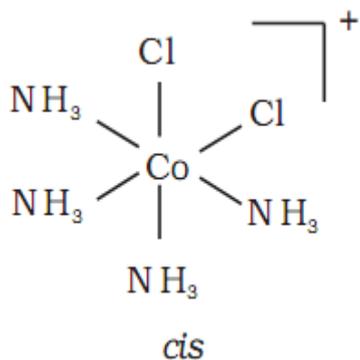
(ii)



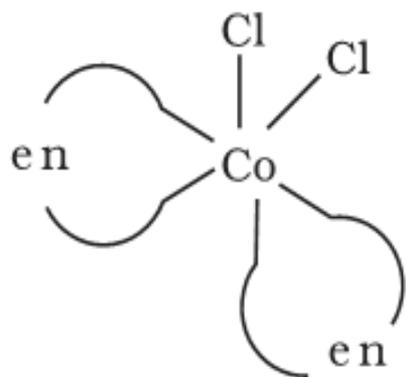
(iii)

Geometrical isomerism in Octahedral complex

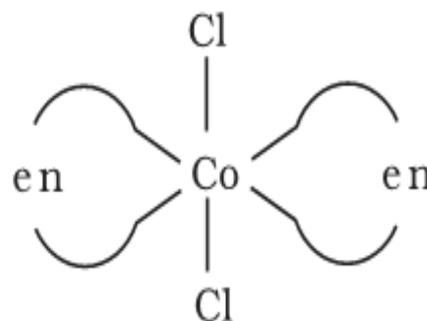
Ma_4b_2 type (cis and trans isomers)



MAA_2b_2 type - Three isomers (two cis and one trans)



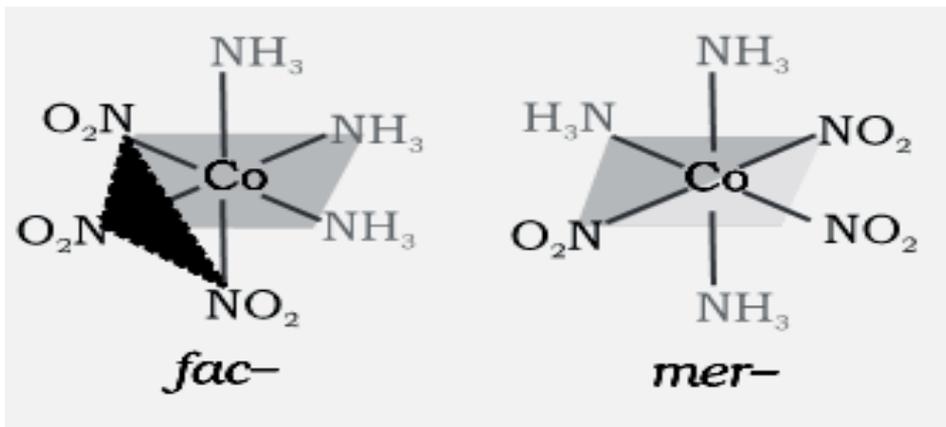
cis- $[CoCl_2(en)_2]$



trans- $[CoCl_2(en)_2]$

Geometrical isomerism in Octahedral complex

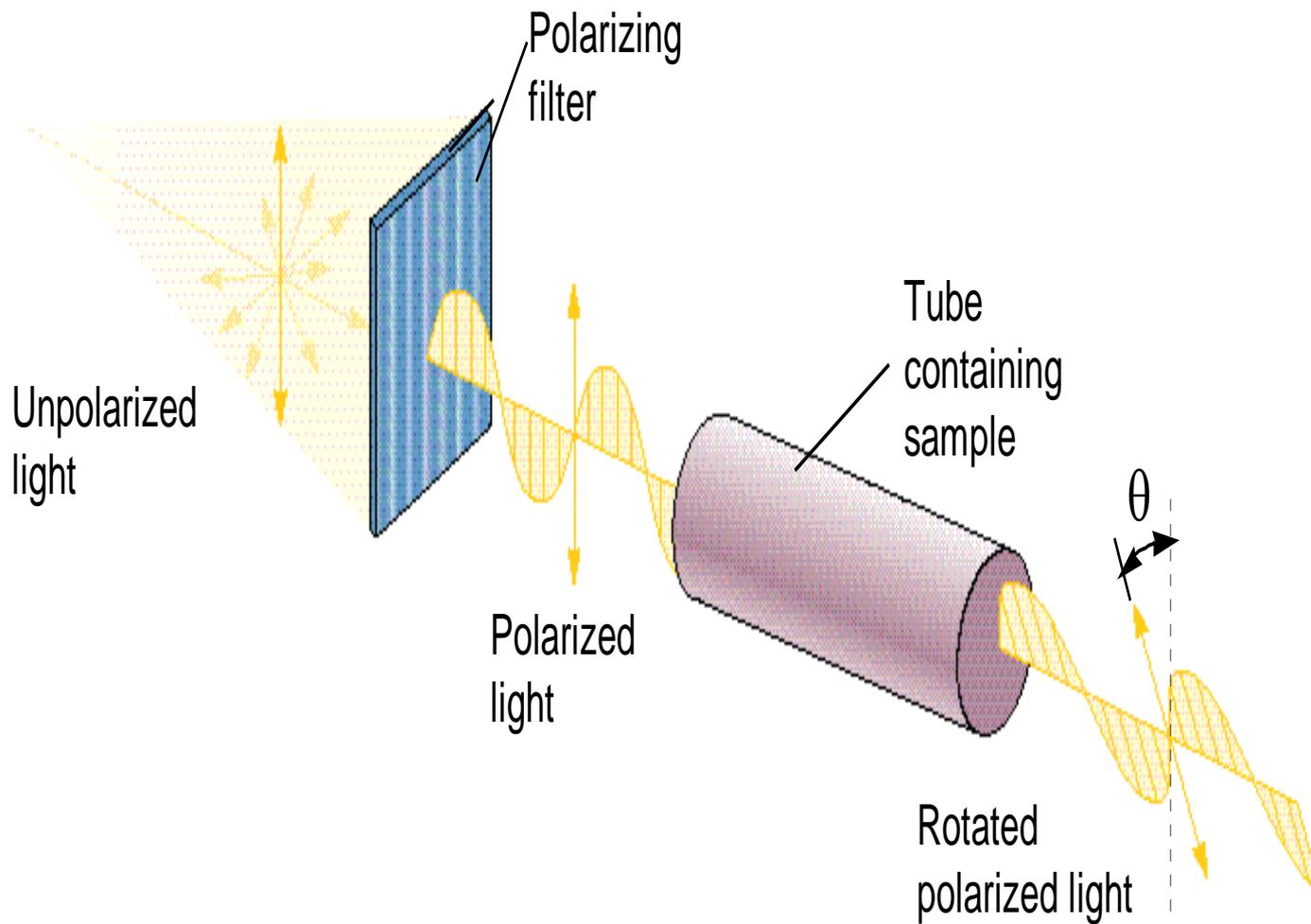
Ma_3b_3 type $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$



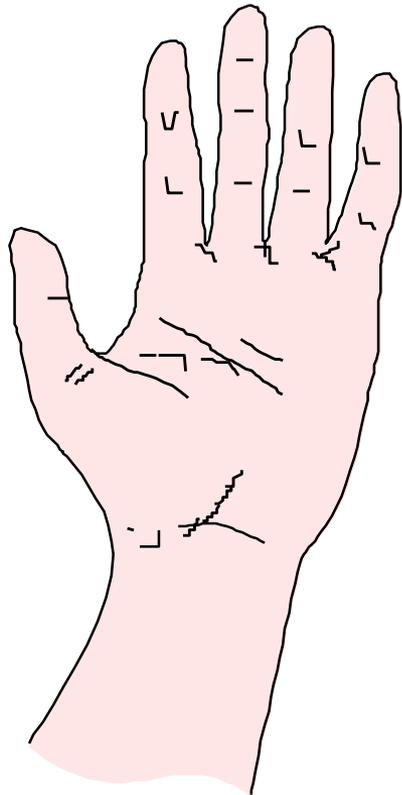
b) Optical isomerism

- ❖ Optical isomers are mirror images that cannot be superimposed on one another.
- ❖ The molecules or ions that cannot be superimposed are called chiral.

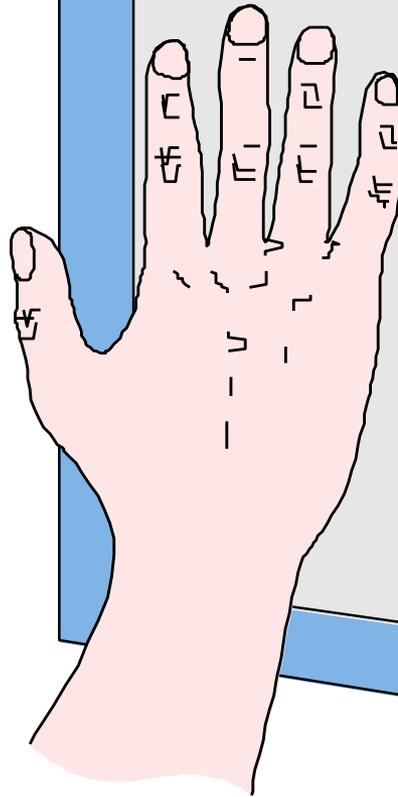
Optical Isomerism



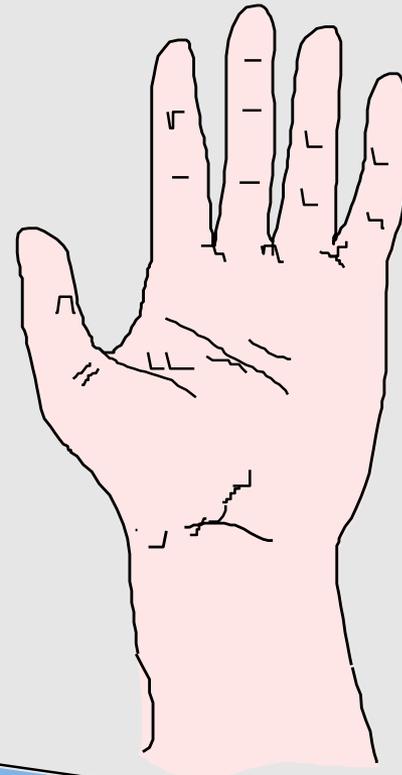
Left hand

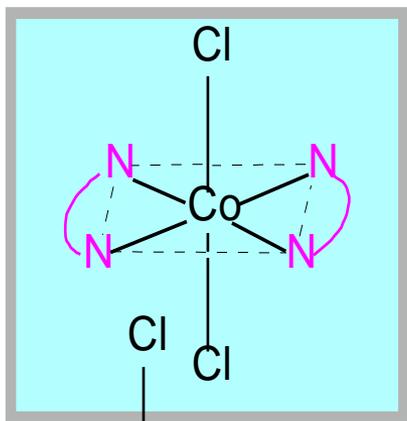


Right hand

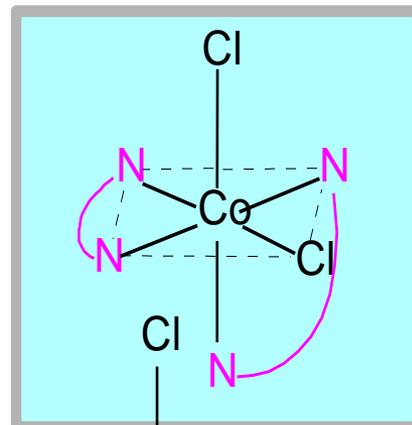


Mirror image
of right hand

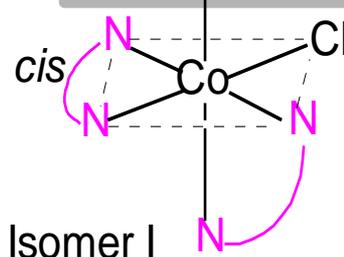
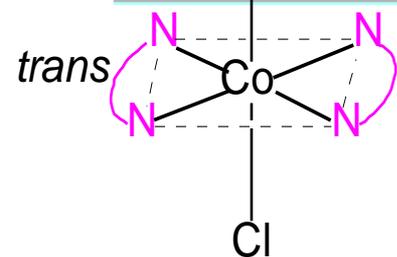




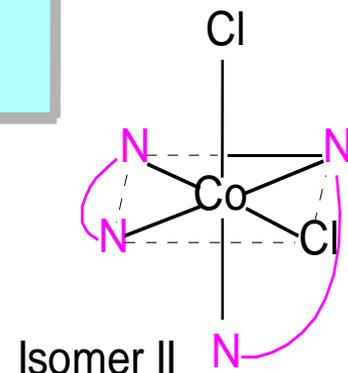
The *trans* isomer and its mirror image are identical. They are not isomers of each other.



Isomer II cannot be superimposed exactly on isomer I. They are not identical structures.



Isomer I



Isomer II

(a)

(b)

Isomer II has the same structure as the mirror image of isomer I.

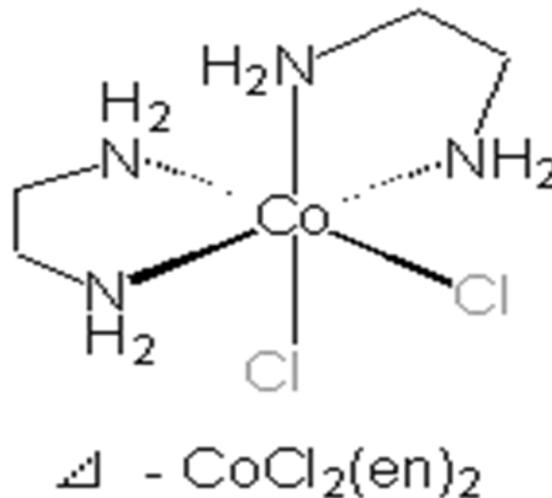
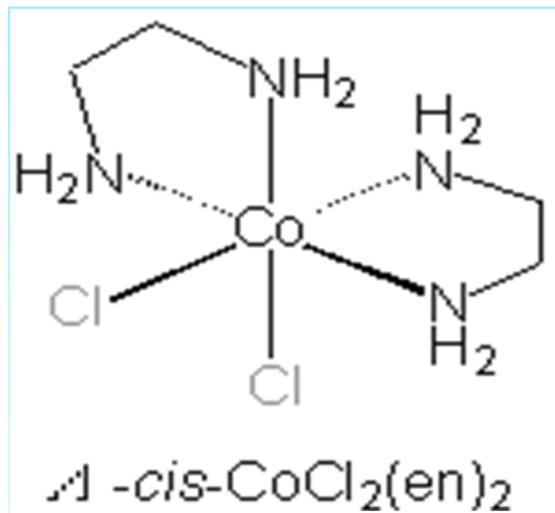
Optical Isomerism

The absolute configuration be designated Lambda Λ (left-handed)

and Delta Δ (right-handed)

❖ cis-isomers of octahedral complexes with 2 bidentate ligands and 2 monodentate ligands

❖ Example : cis-[CoCl₂(en)₂] complex (cis-bis chel.ates)



Bonding in coordination Complexes

- **Valence Bond Theory** predicts metal complex bonding arises from overlap of filled ligand orbitals and vacant metal orbitals.
- Resulting bond is a *coordinate covalent bond*.



Bonding in coordination Complexes

- Complex geometry can be linked to five main orbital hybridization processes.

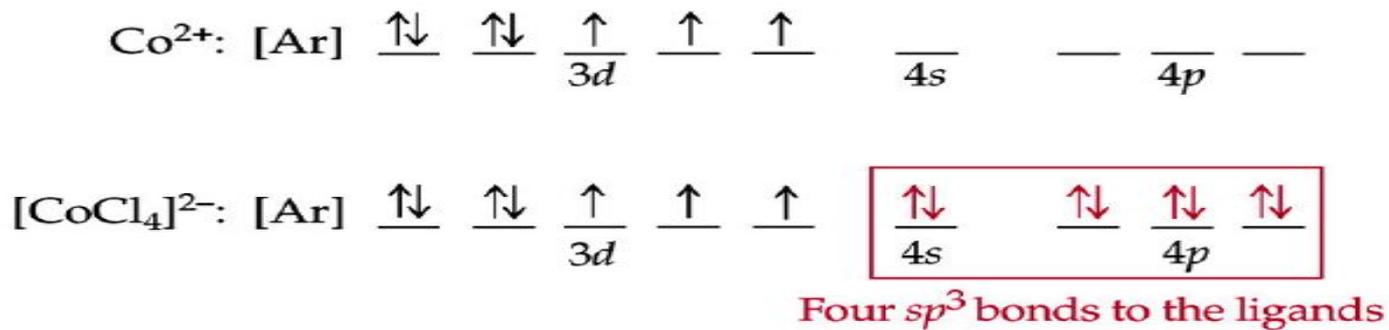
TABLE 20.7 Hybrid Orbitals for Common Coordination Geometries

| Coordination Number | Geometry | Hybrid Orbitals | Example |
|---------------------|---------------|------------------------|---|
| 2 | Linear | sp | $[\text{Ag}(\text{NH}_3)_2]^+$ |
| 4 | Tetrahedral | sp^3 | $[\text{CoCl}_4]^{2-}$ |
| 4 | Square planar | dsp^2 | $[\text{Ni}(\text{CN})_4]^{2-}$ |
| 6 | Octahedral | d^2sp^3 or sp^3d^2 | $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ |

Bonding in coordination Complexes

- Tetrahedral Geometry:

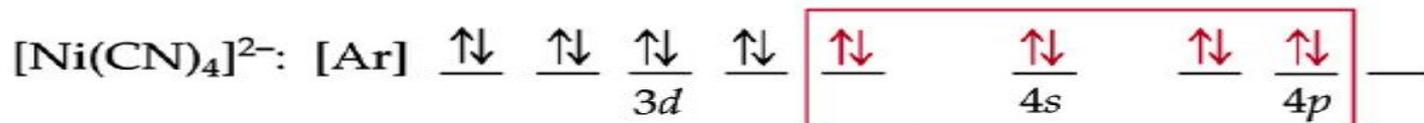
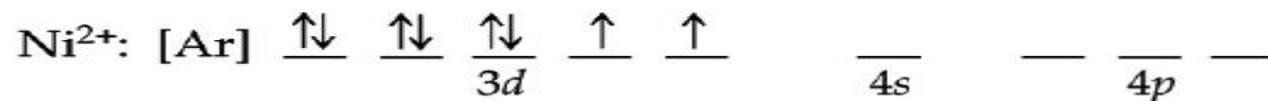
Gives $[\text{CoCl}_4]^{2-}$ three unpaired electrons, which makes it paramagnetic and attracted by magnets. Bonding in Complexes.



Bonding in coordination Complexes

- **Square Planar Geometry:**

Gives $[\text{Ni}(\text{CN})_4]^{2-}$ all paired electrons, which makes it diamagnetic and weakly repelled by magnets.

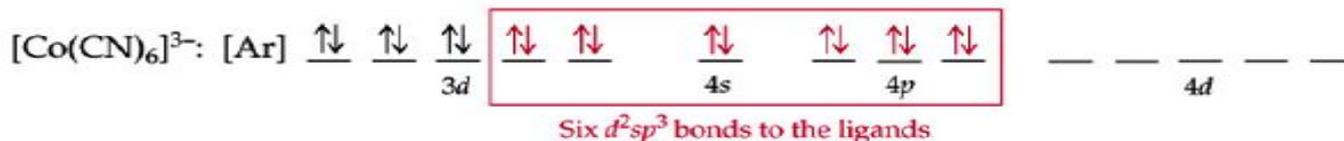
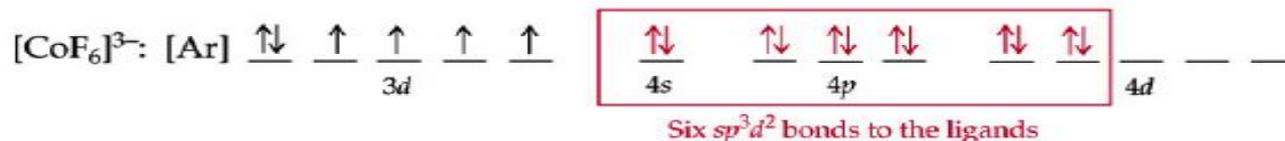
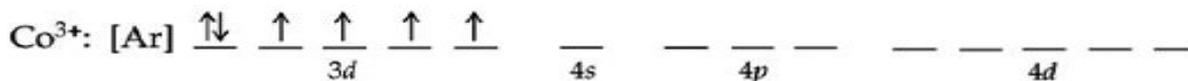


Four dsp^2 bonds to the ligands

Bonding in coordination Complexes

- Octahedral sp^3d^2 Geometry:

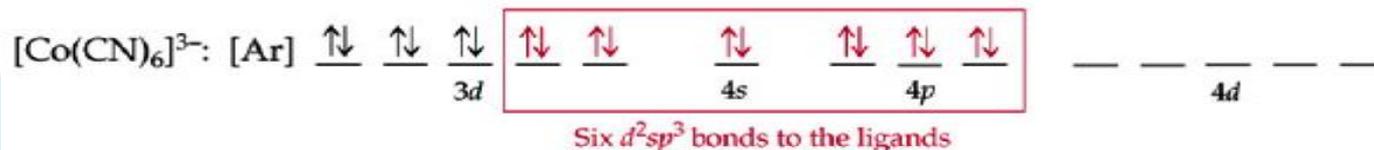
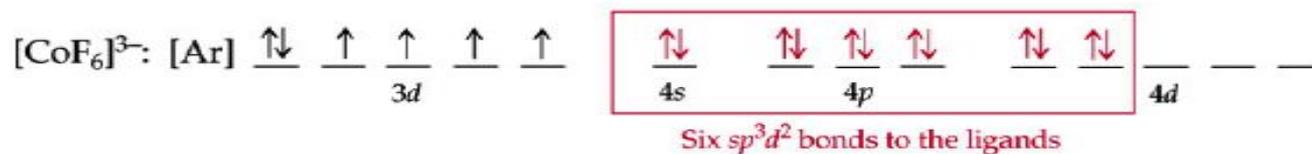
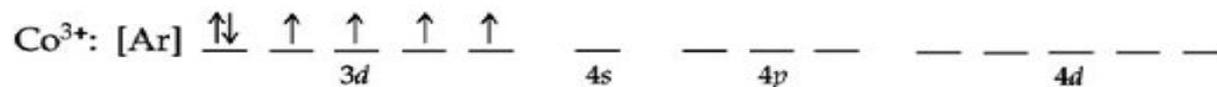
Gives $[CoF_6]^{3-}$ four unpaired electrons, which makes it paramagnetic and is called a *high-spin complex*.



Bonding in coordination Complexes

- Octahedral d^2sp^3 Geometry:

Gives $[\text{Co}(\text{CN})_6]^{3-}$ paired electrons, which makes it diamagnetic and is called a *low-spin complex*.



Bonding in coordination Complexes

- The difference between *sp³d²* and *d²sp³* hybrids lies in the principal quantum number of the *d* orbital.
- In *sp³d²* hybrids, the *s*, *p*, and *d* orbitals have the same principal quantum number—High Spin.
- In *d²sp³* hybrids, the principal quantum number of the *d* orbitals is one less than *s* and *p* orbitals—Low Spin.
- A complex's magnetic properties determine which hybrid is being used.

Positive of Valence bond theory

- ▶ Present a simple description of metal ligand bonding
- ▶ Predicts the geometry of the complexes correctly
- ▶ Account for the magnetic properties of the coordination complexes

Negatives of valence bond theory

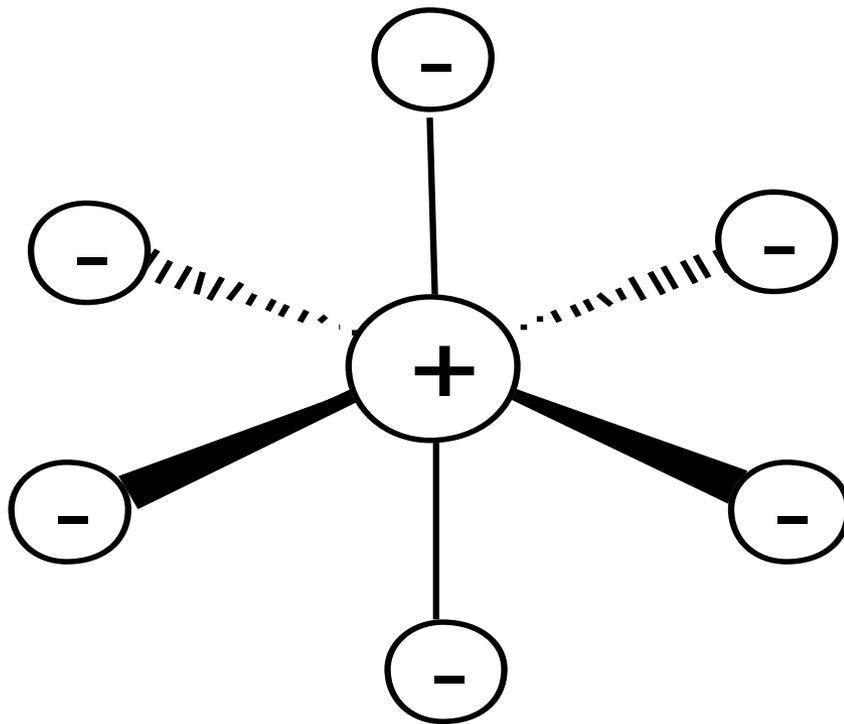
- ▶ It offers no explanation for the colors of the complexes.
- ▶ It doesn't explain the spectra of complexes.
- ▶ It fails to give a satisfactory explanation for the formation of $[\text{Cu}(\text{NH}_3)_4]^{+2}$.

Crystal field theory: an electrostatic model

Crystal Field Theory is a model that helps explain

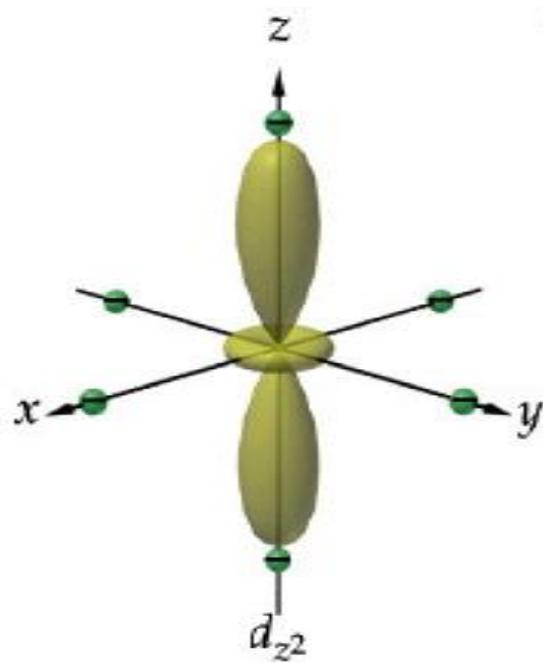
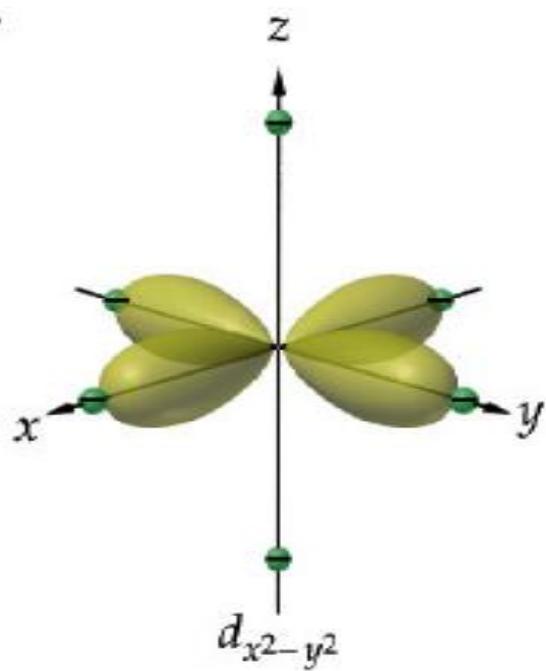
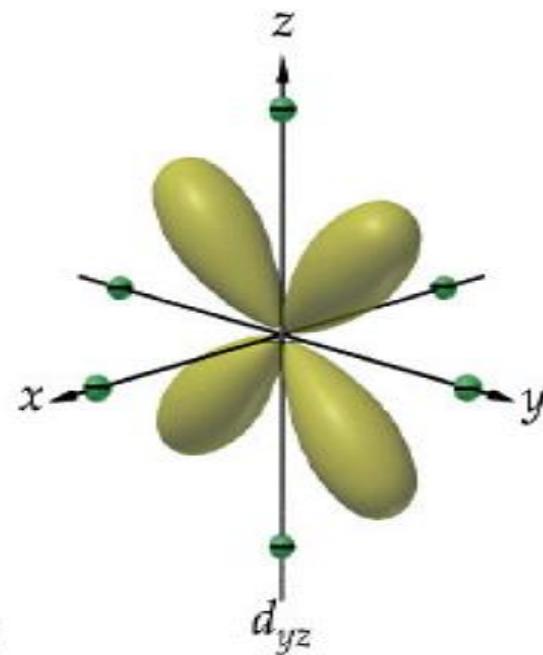
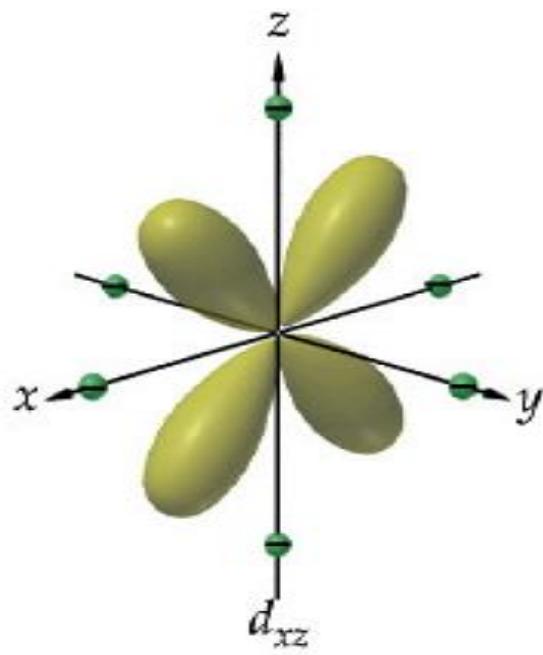
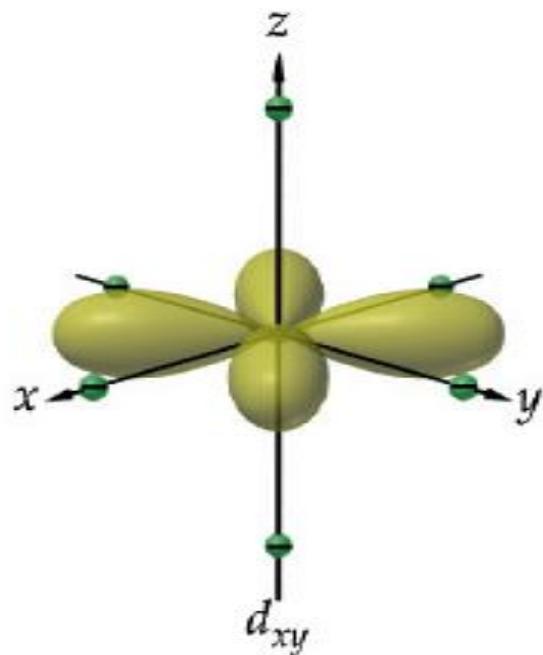
why some complexes are *high spin* and some are *low spin*.

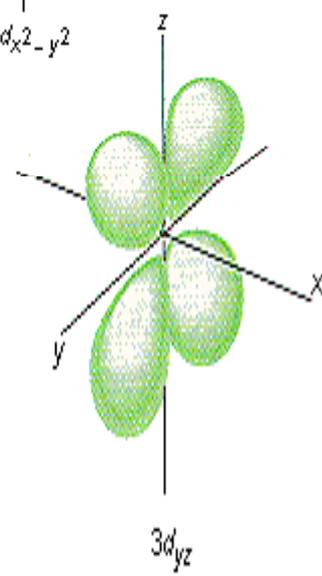
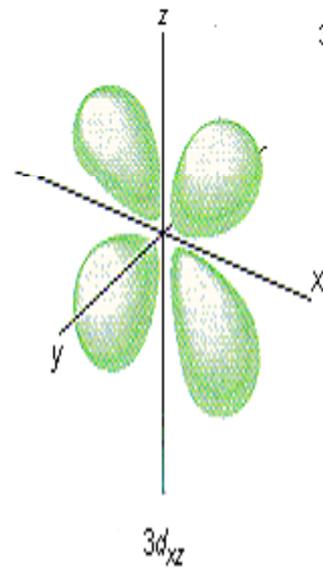
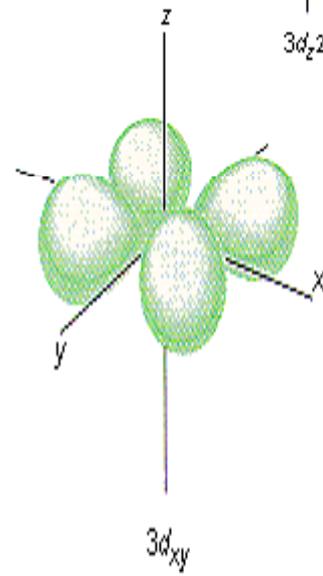
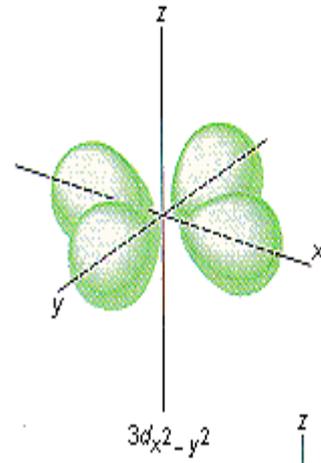
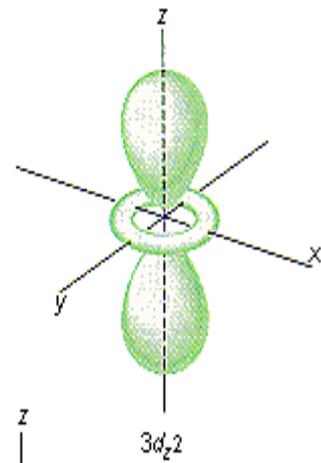
- Crystal Field Theory views bonding in complexes as the result of *electrostatic interactions* and considers the *effect of ligand charges on energies of metal ion d orbitals*.
- Crystal Field Theory uses *no covalent bonds*.



The metal ion will be positive and therefore attract the negatively charged ligands

But there are electrons in the metal orbitals, which will experience repulsions with the negatively charged ligands

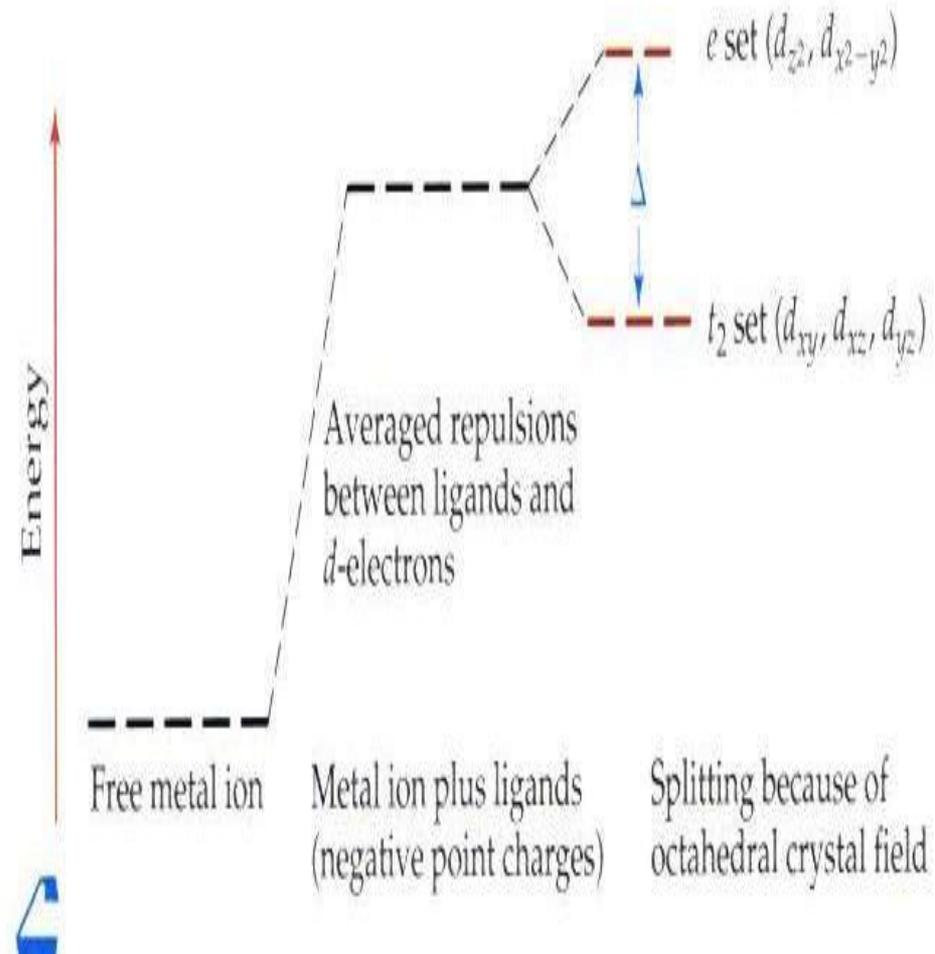




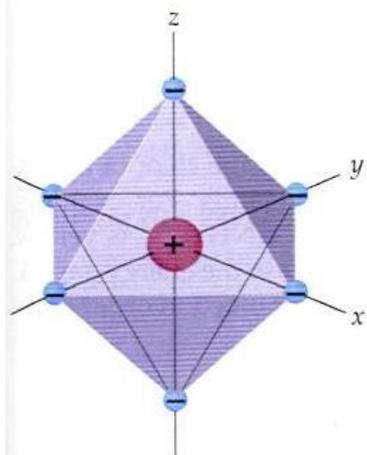
d-electron to ligand-electron repulsions affect d-orbital

energy levels.

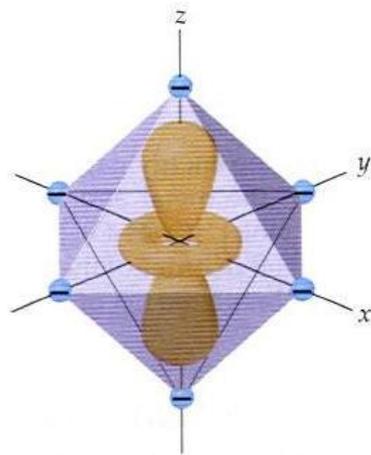
- *dz^2 and $dx^2 - y^2$ orbitals point at the ligands and have higher energies than other d -electrons.*
- This energy gap Δ is called *crystal field splitting*.



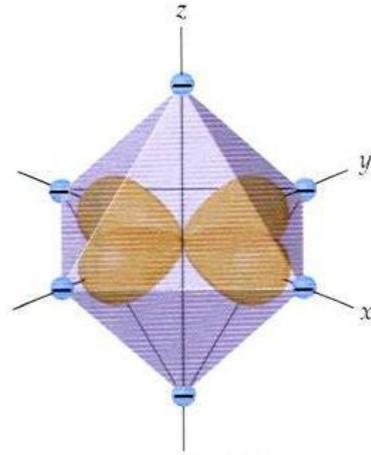
Ligand/*d* orbital interactions for O_h



(a)

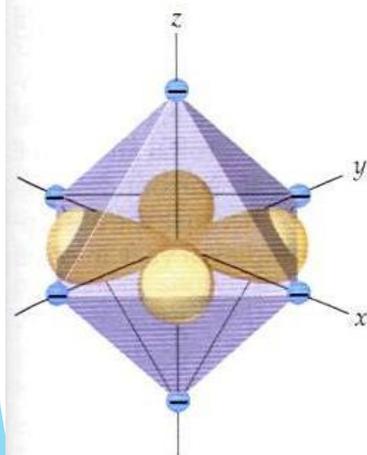


(b)

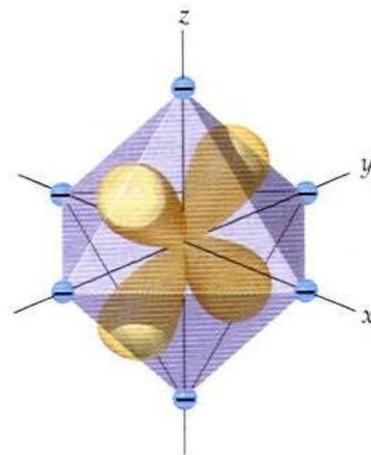


(c)

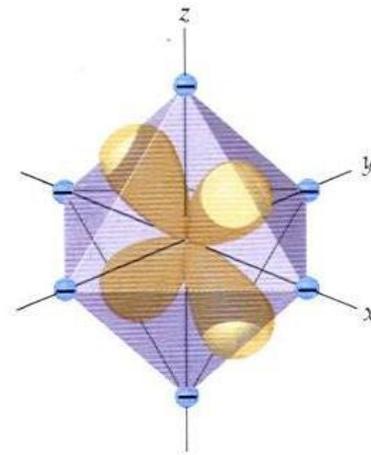
Orbitals point at ligands (maximum repulsion)



(d)



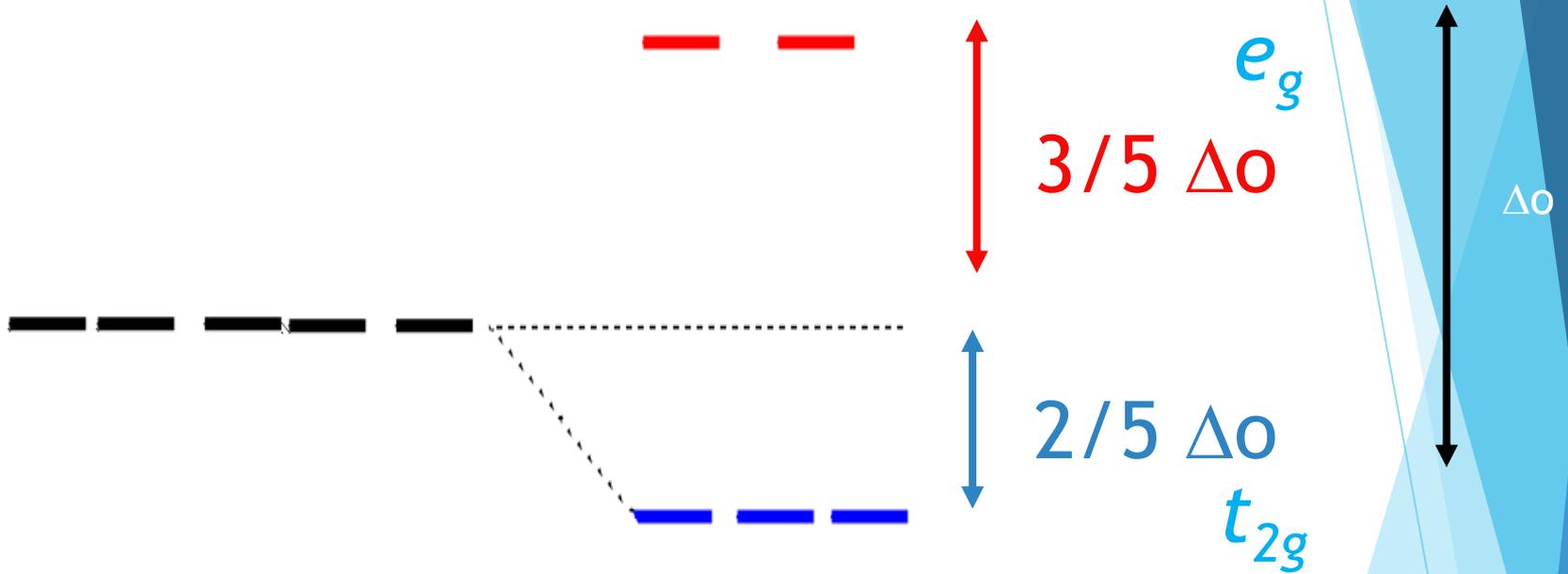
(e)



(f)

Orbitals point between ligands (less pronounced repulsion)

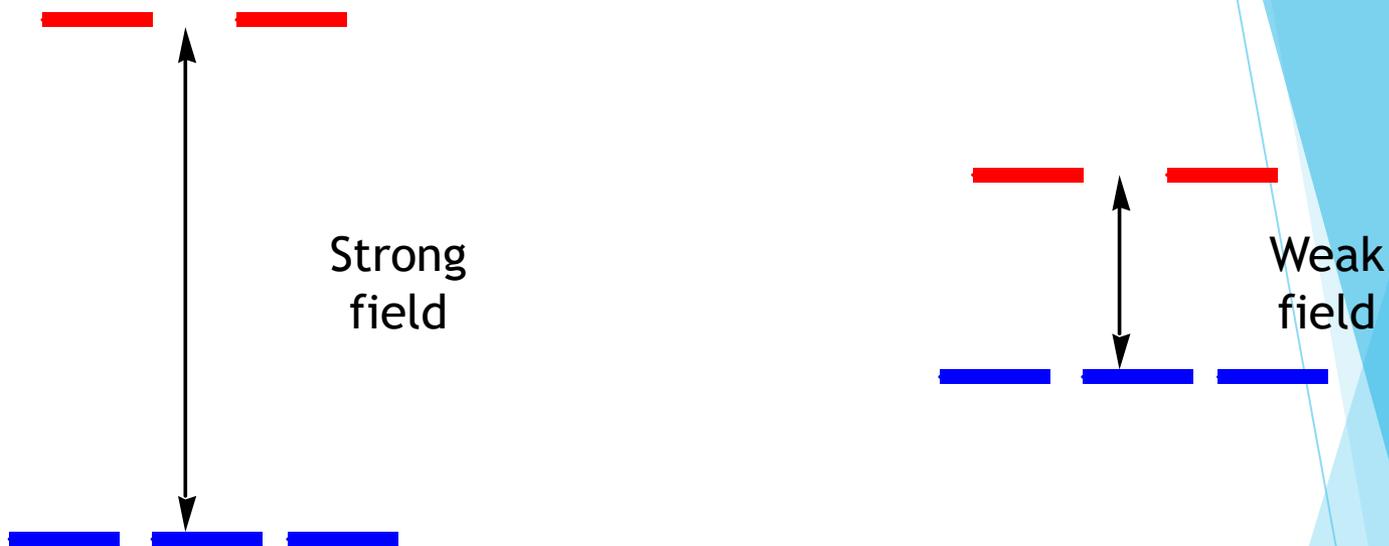
Splitting of d orbitals in an octahedral field



$$E(t_{2g}) = -0.4\Delta_o \times 3 = -1.2\Delta_o$$

$$E(e_g) = +0.6\Delta_o \times 2 = +1.2\Delta_o$$

The magnitude of the splitting (ligand effect)



The spectrochemical series

$\text{CO}, \text{CN}^- > \text{phen} > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{NCS}^- > \text{H}_2\text{O} > \text{F}^- > \text{RCO}_2^- > \text{OH}^- > \text{Cl}^- > \text{Br}^-$

Δ increases with increasing formal charge on the metal ion

Δ increases on going down the periodic table

Placing electrons in d orbitals

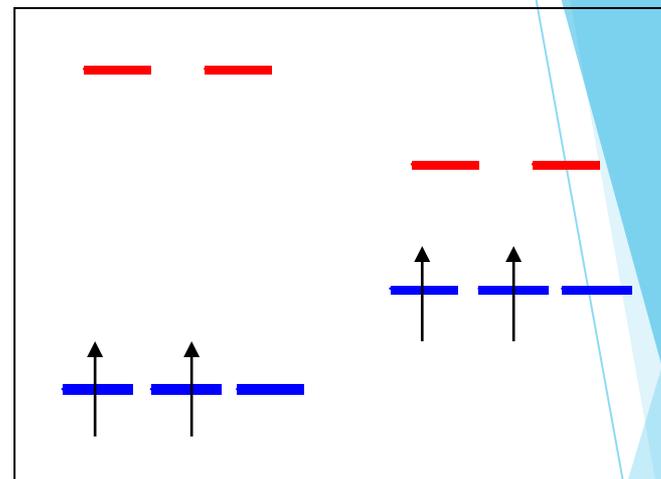
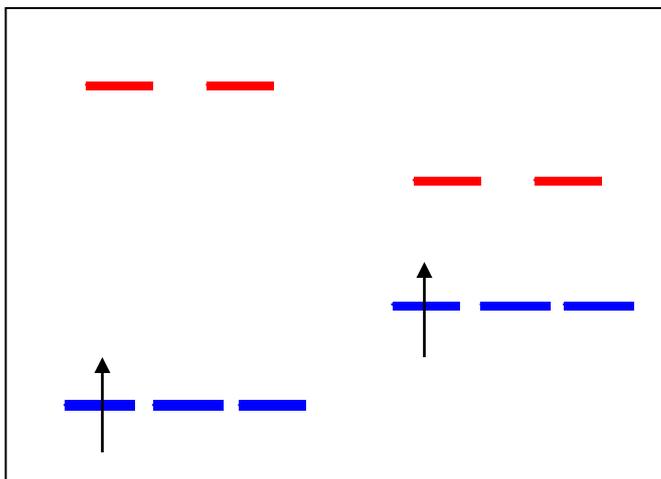
Strong field

Weak field

Strong field

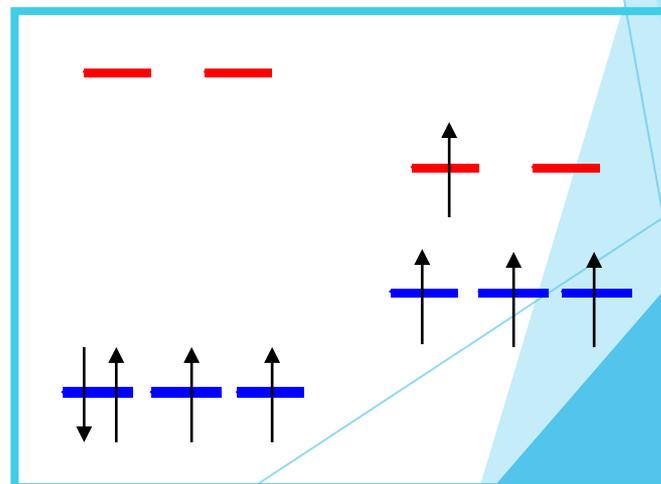
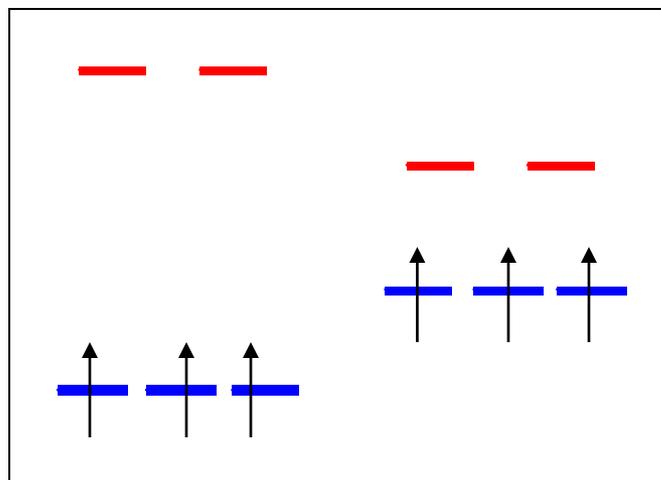
Weak field

d^1



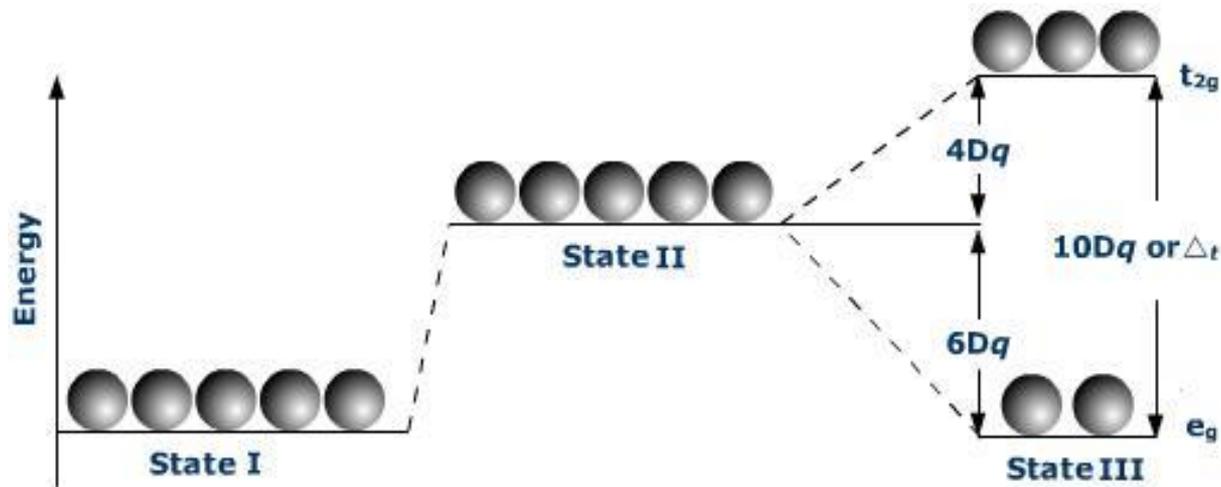
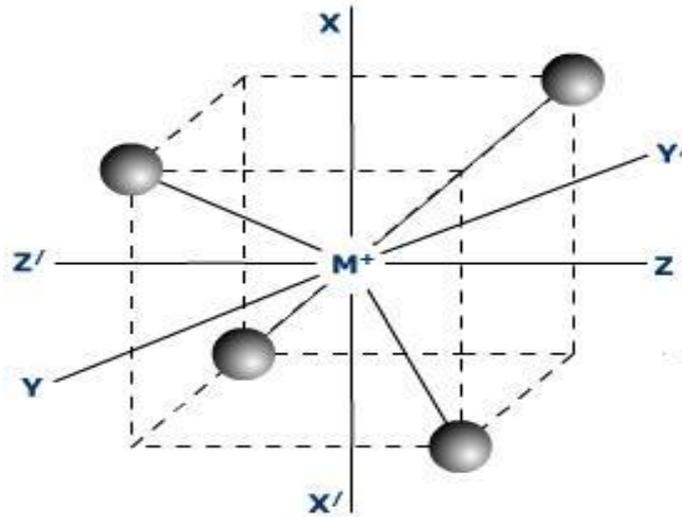
d^2

d^3



d^4

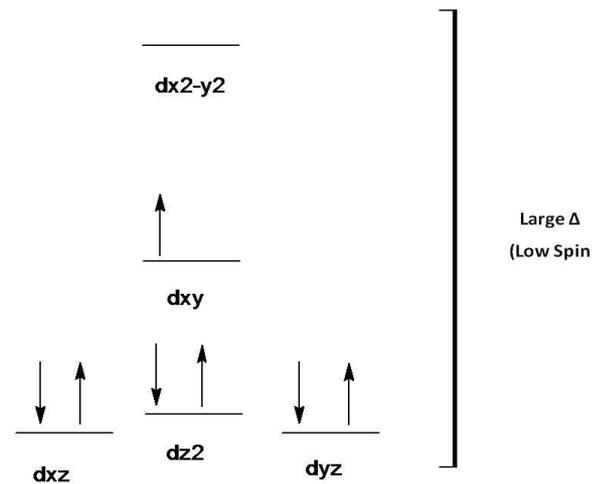
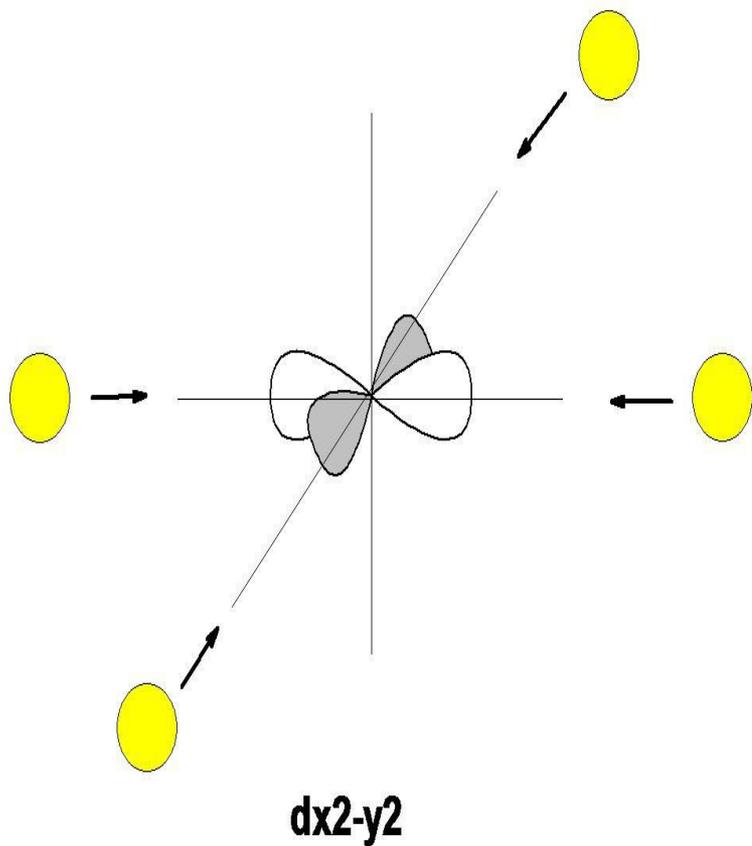
Tetrahedral complexes



Tetrahedral complexes

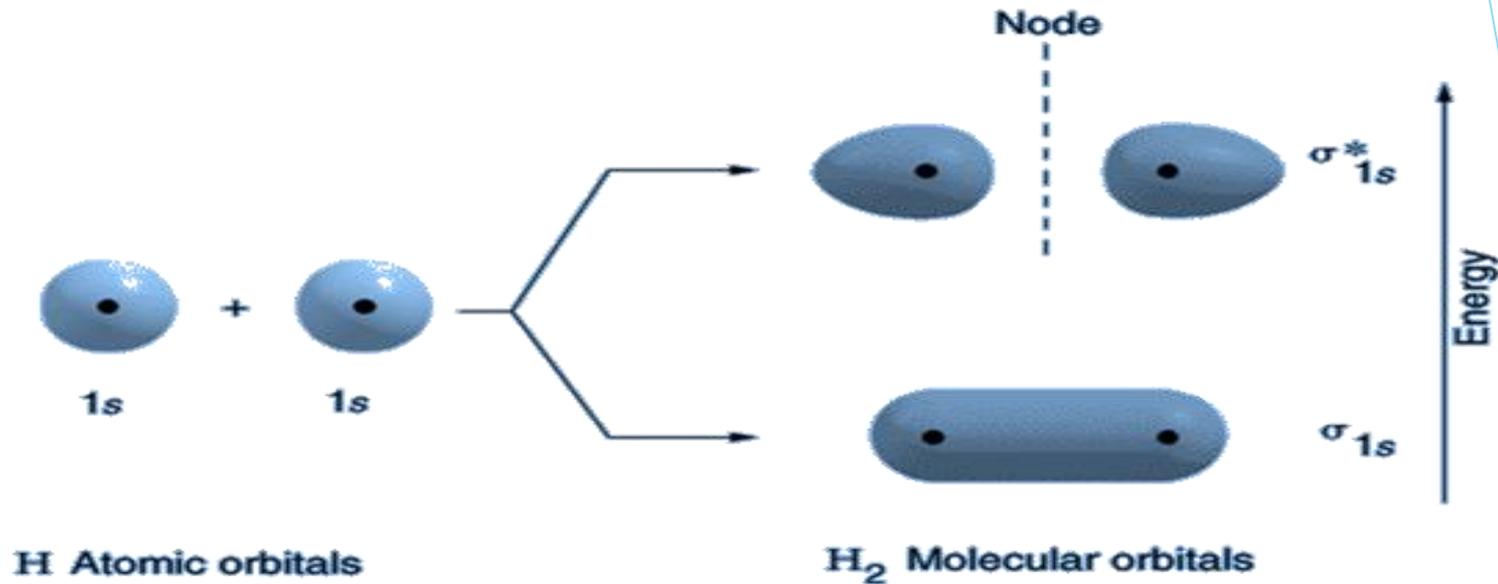
- In a tetrahedral complex, Δ is relatively small even with strong-field ligands as there are fewer ligands to bond with.
- It is rare for the Δ of tetrahedral complexes to exceed the pairing energy.
- Usually, electrons will move up to the higher energy orbitals rather than pair.
- Because of this, most tetrahedral complexes are high spin.

Square Planar Complexes



In square planar complexes Δ will almost always be large, even with a weak-field ligand. Electrons tend to be paired rather than unpaired because pairing energy is usually much less than Δ . Therefore, square planar complexes are usually low spin.

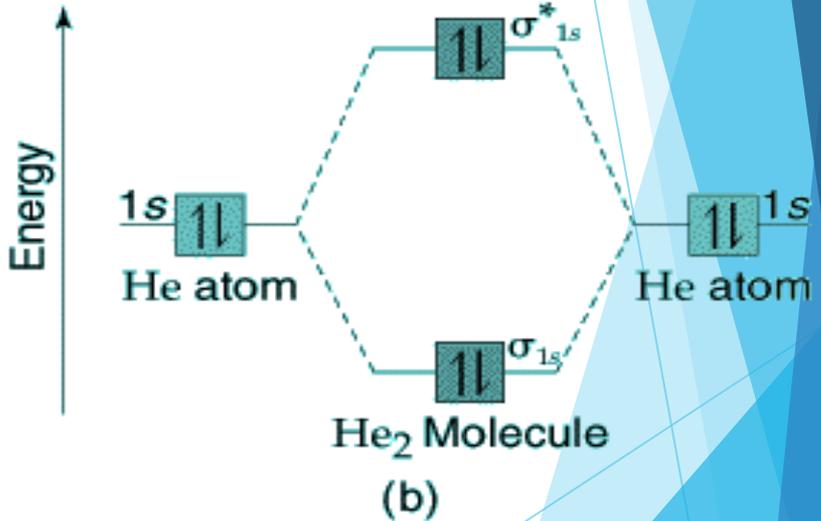
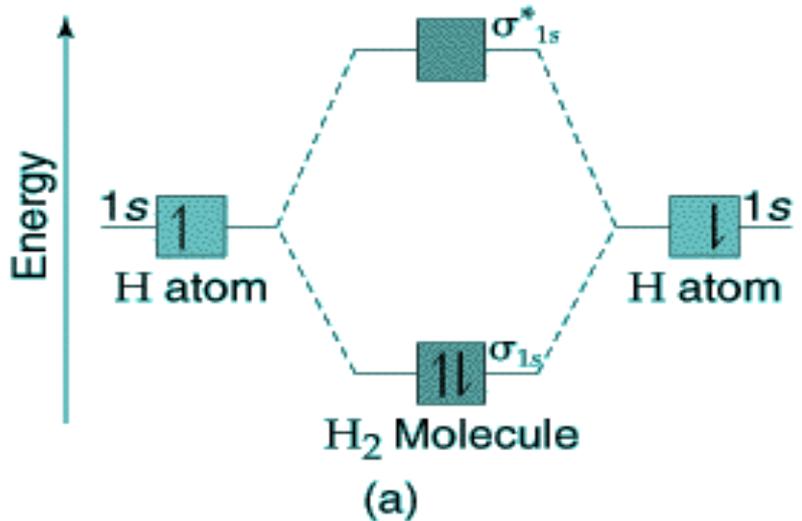
Molecular Orbital (MO) Theory



The one that is lower in energy is called the **bonding orbital**,

The one higher in energy is called an **antibonding orbital**.

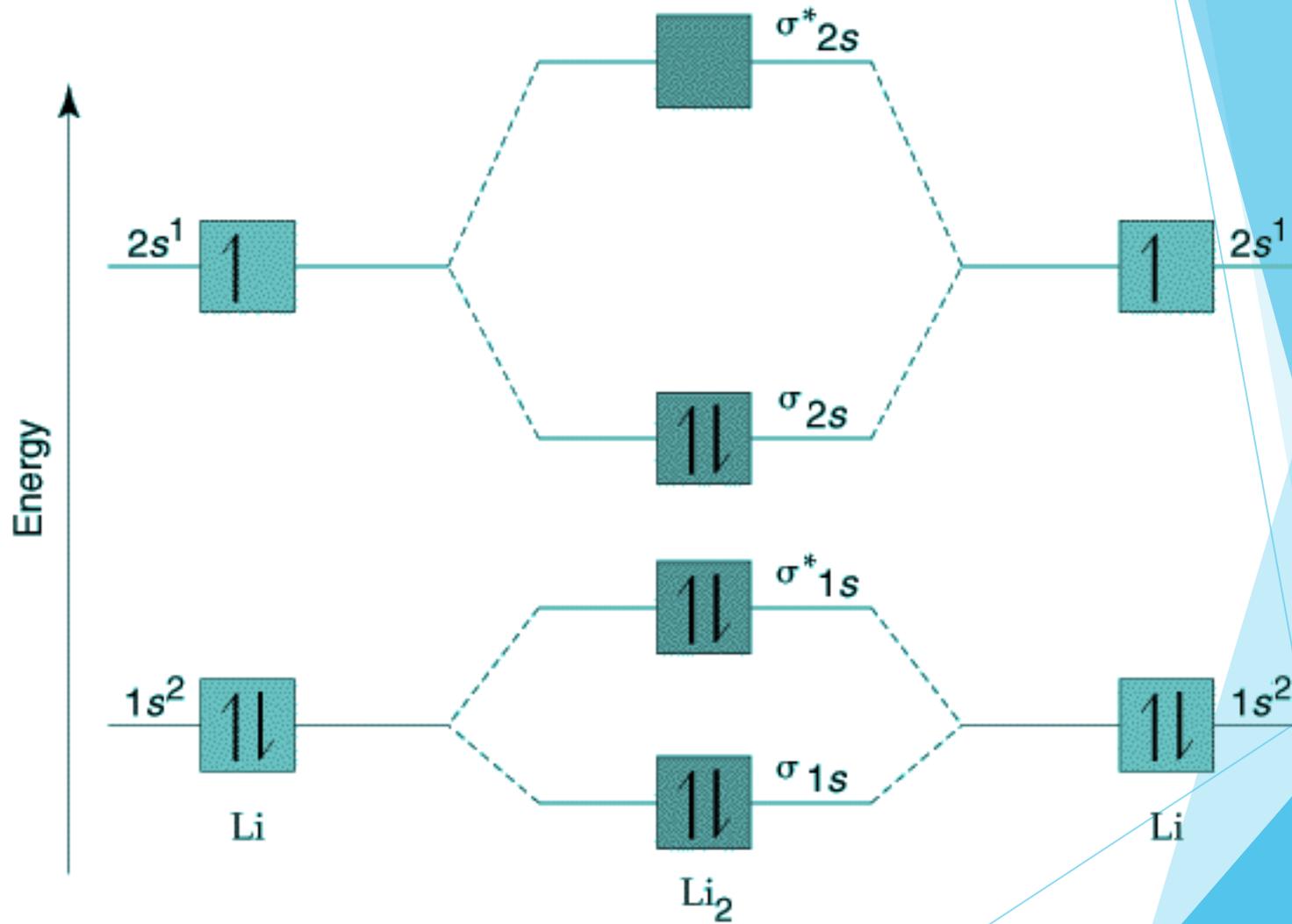
Energy level diagrams / molecular orbital diagrams

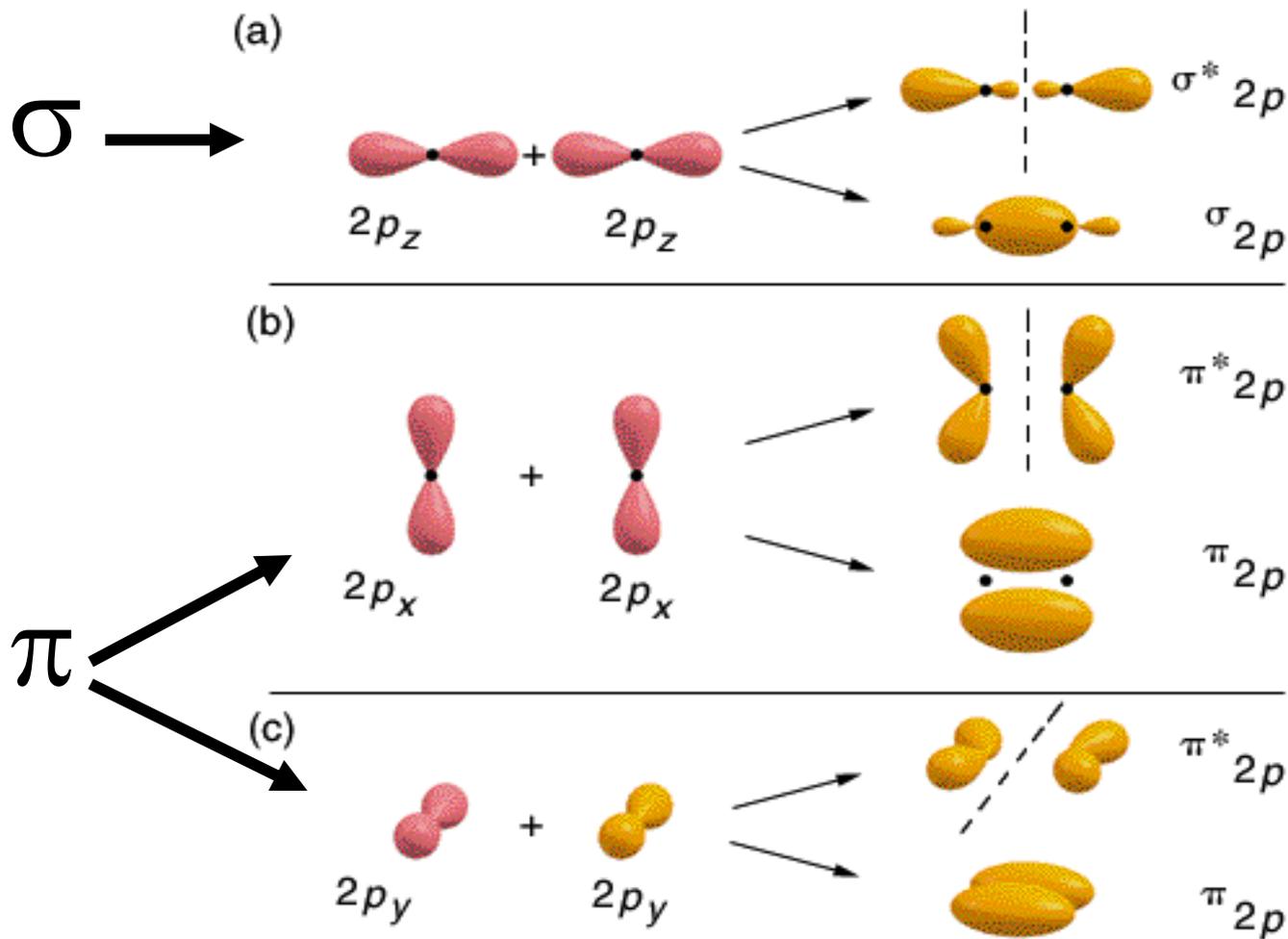


Molecular Orbitals (MO's) from Atomic Orbitals (AO's)

1. # of Molecular Orbitals = # of Atomic Orbitals
2. The number of electrons occupying the Molecular orbitals is equal to the sum of the valence electrons on the constituent atoms.
3. When filling MO's the Pauli Exclusion Principle Applies (2 electrons per Molecular Orbital)
4. For degenerate MO's, Hund's rule applies.
5. AO's of similar energy combine more readily than ones of different energy
6. The more overlap between AOs the lower the energy of the bonding orbital they create and the higher the energy of the antibonding orbital.

Example: Li_2

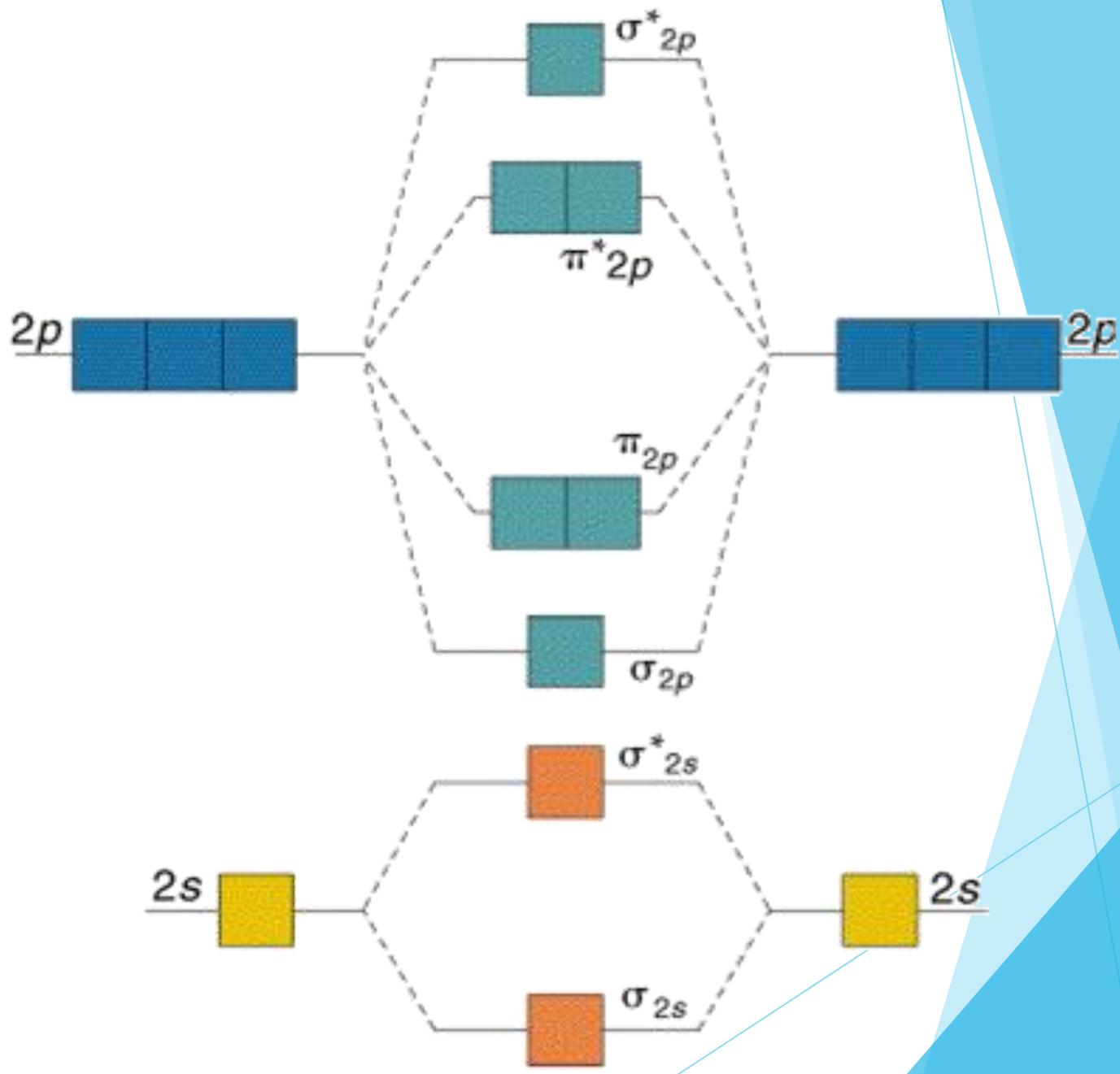




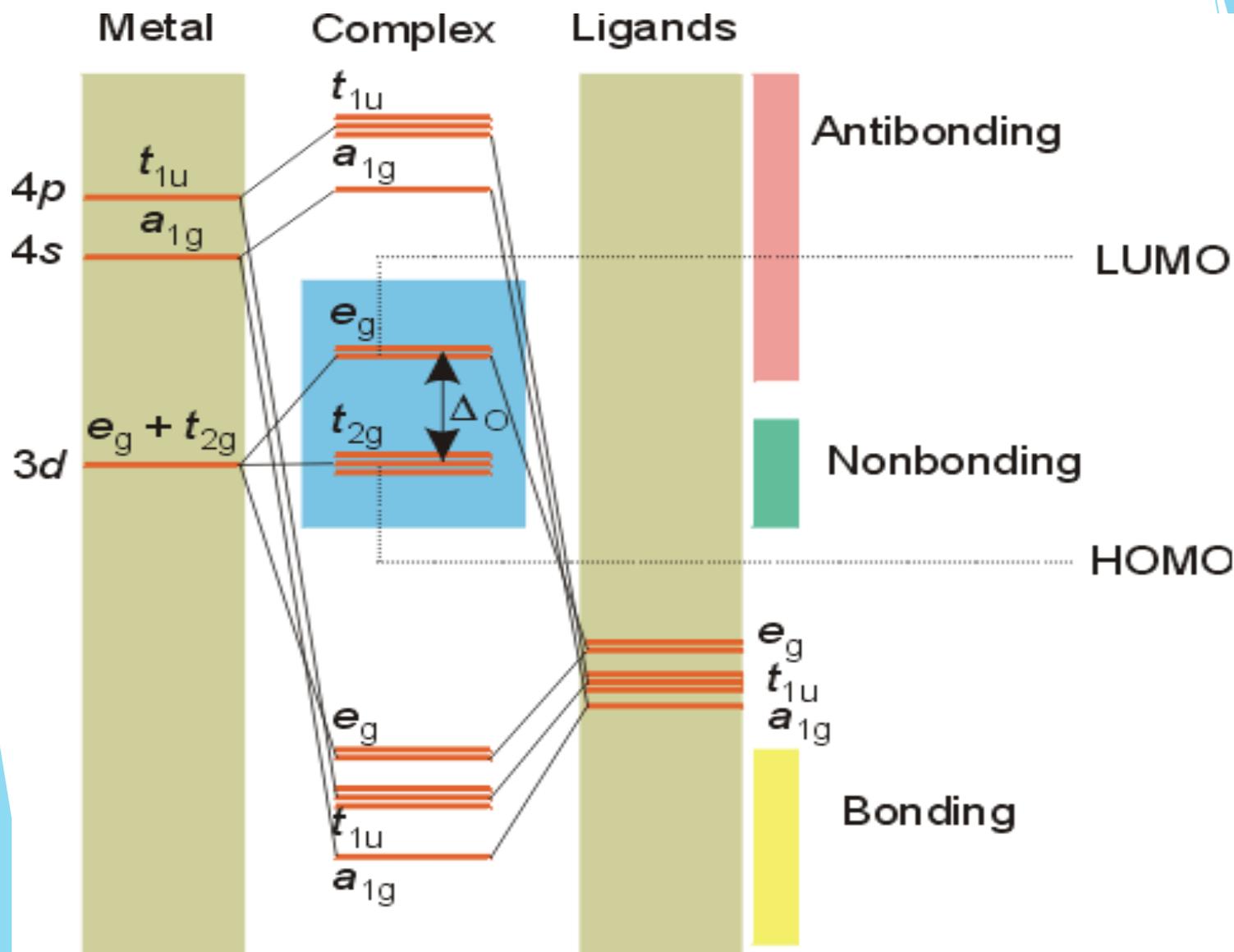
1) 1 sigma bond through overlap of orbitals along the internuclear axis.

2) 2 pi bonds through overlap of orbitals above and below (or to the sides) of the internuclear axis.

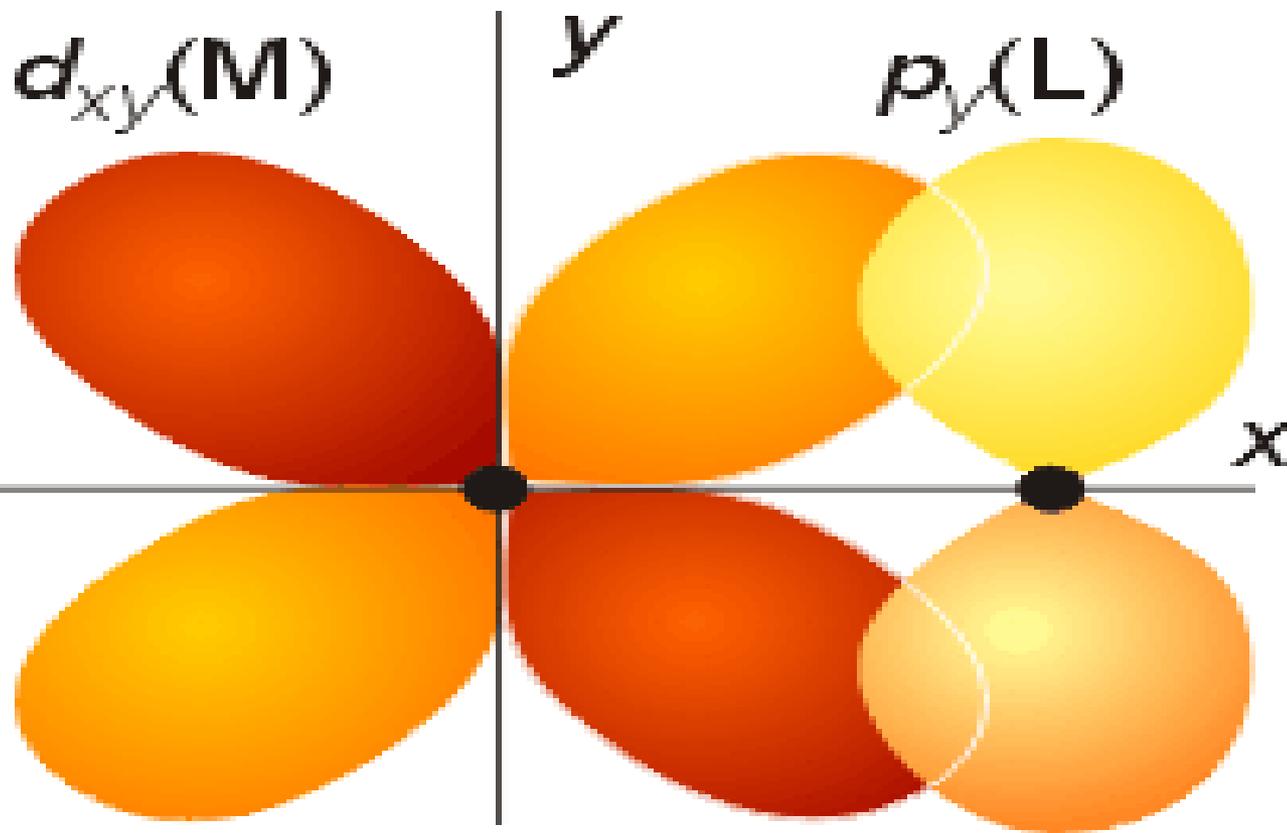
Energy



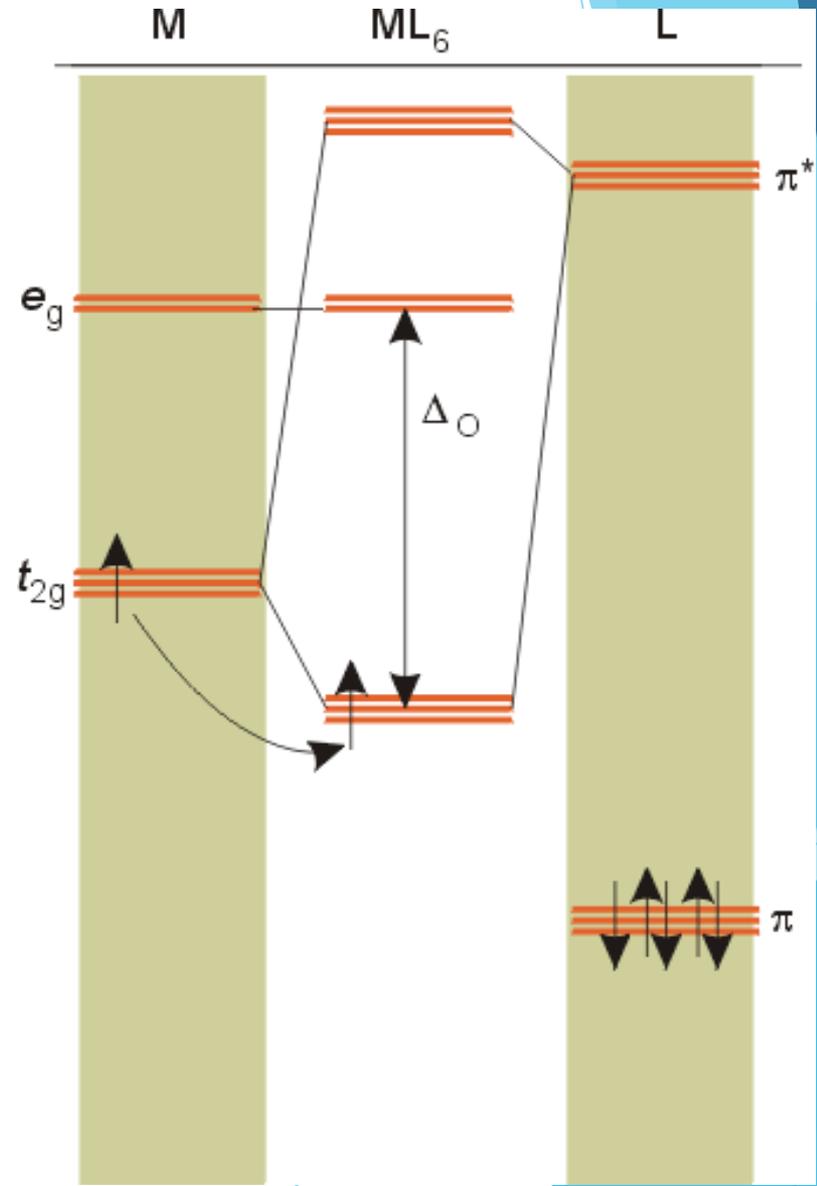
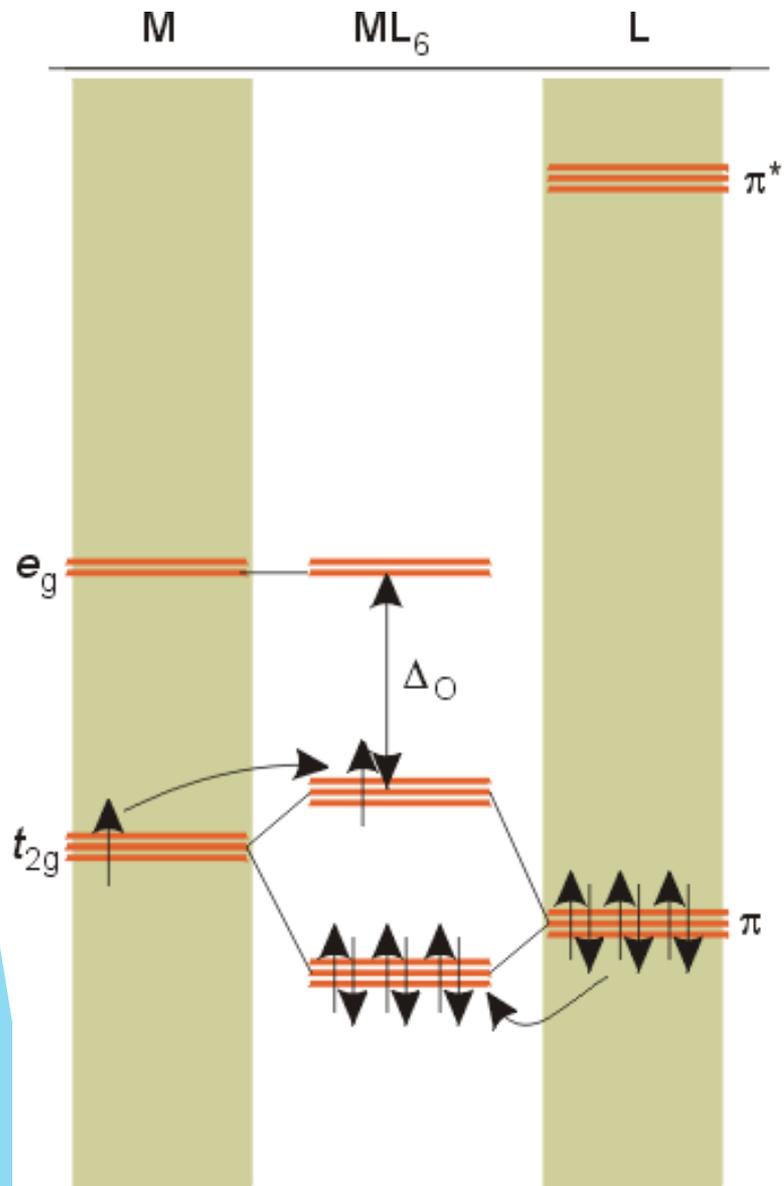
Molecular orbital diagram of σ bonds in O_h



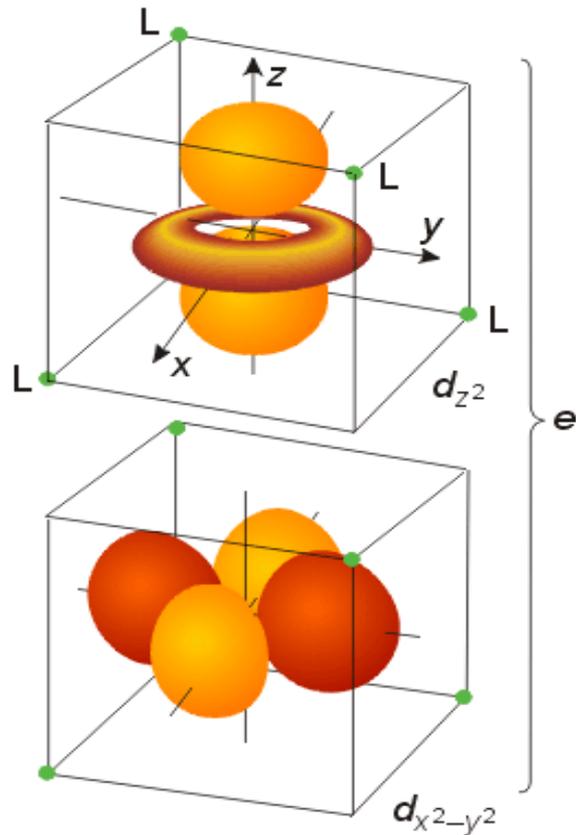
π bonding



Molecular orbital diagram of π in O_h

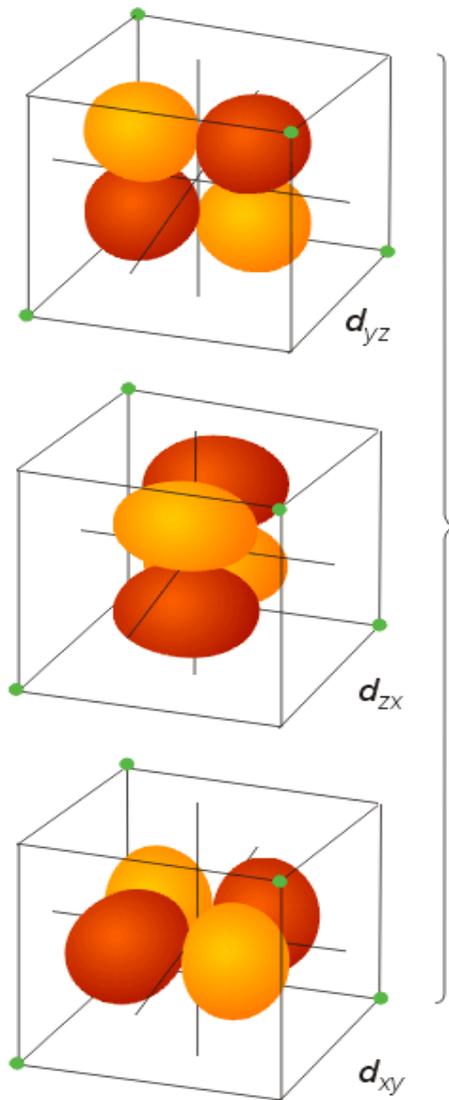


Tetrahedral Complexes



The d_{z^2} and $d_{x^2-y^2}$ orbitals point directly between the ligands in a tetrahedral arrangement. As a result, these two orbitals, designated as e in the point group T_d , are lower in energy.

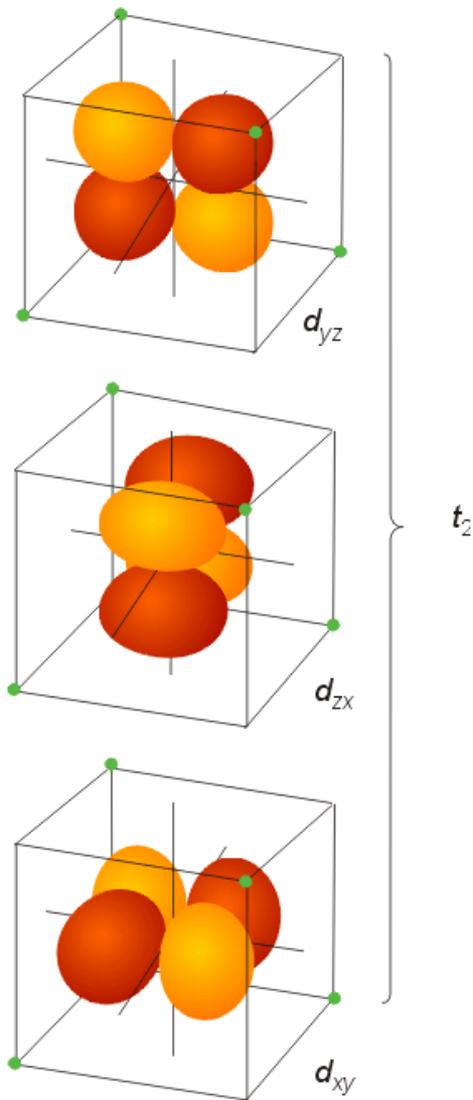
Tetrahedral Complexes



▶ The t_2 set of orbitals, consisting of the d_{xy} , d_{yz} , and d_{xz} orbitals, are directed more in the direction of the ligands.

▶ These orbitals will be higher in energy in a tetrahedral field due to repulsion with the electrons on the ligands.

Tetrahedral Complexes

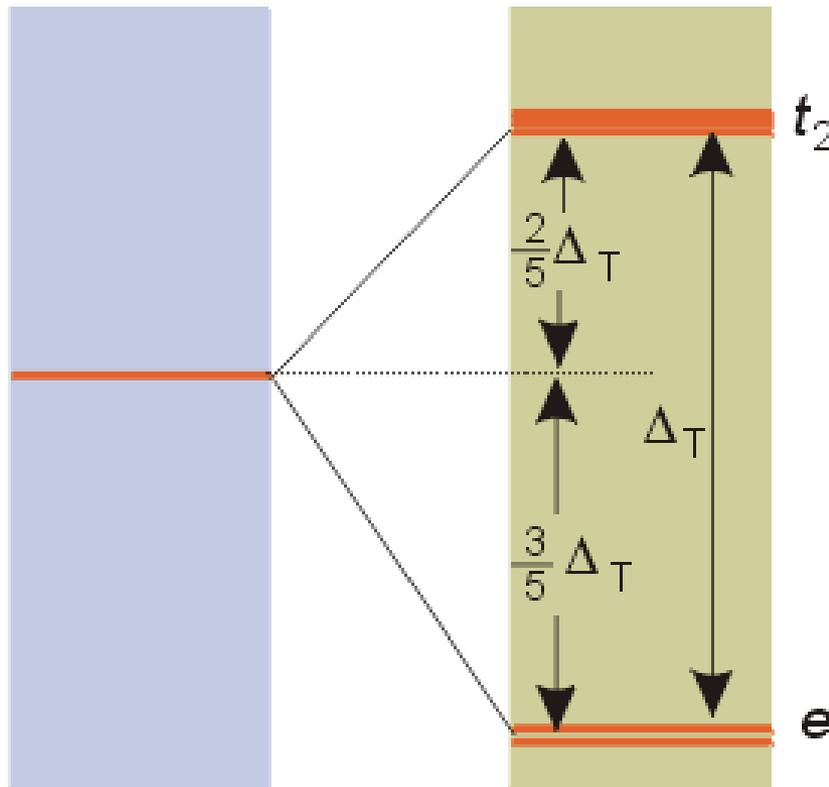


The size of the splitting, Δ_T , is considerably smaller than with comparable octahedral complexes. This is because only 4 bonds are formed, and the metal orbitals used in bonding don't point right at the ligands as they do in octahedral complexes.

Tetrahedral Complexes

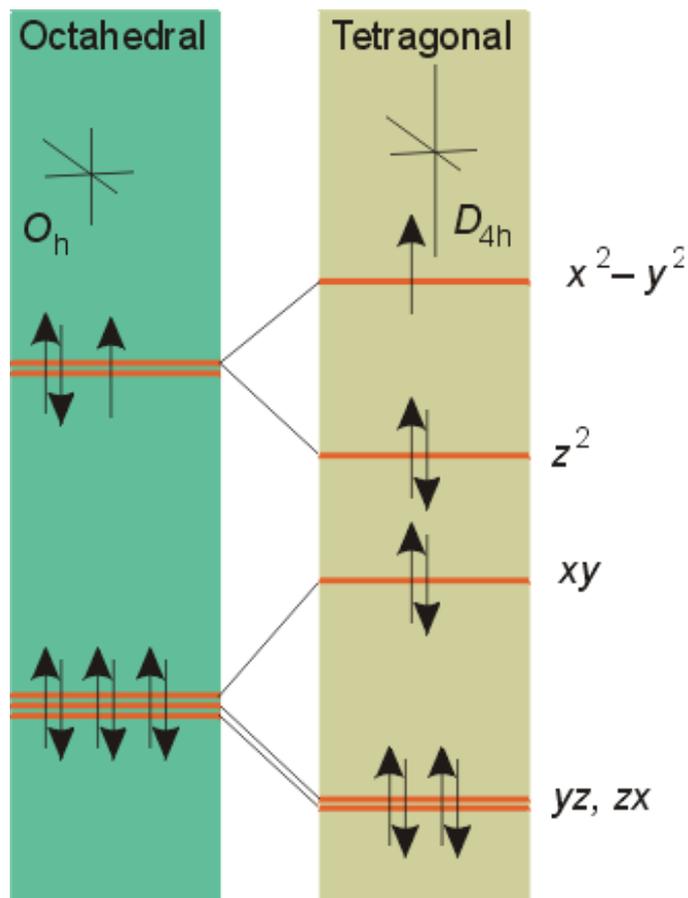
Spherical environment

In tetrahedral crystal field



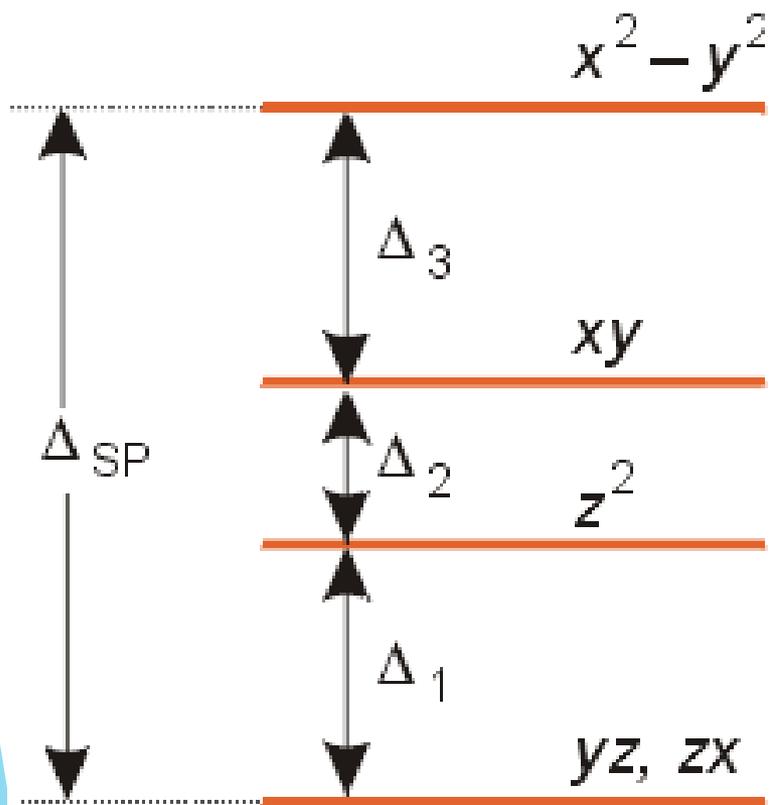
In general, $\Delta_T \approx 4/9 \Delta_o$.
Since the splitting is smaller, all tetrahedral complexes are weak-field, high-spin cases.

Square Planar Complexes



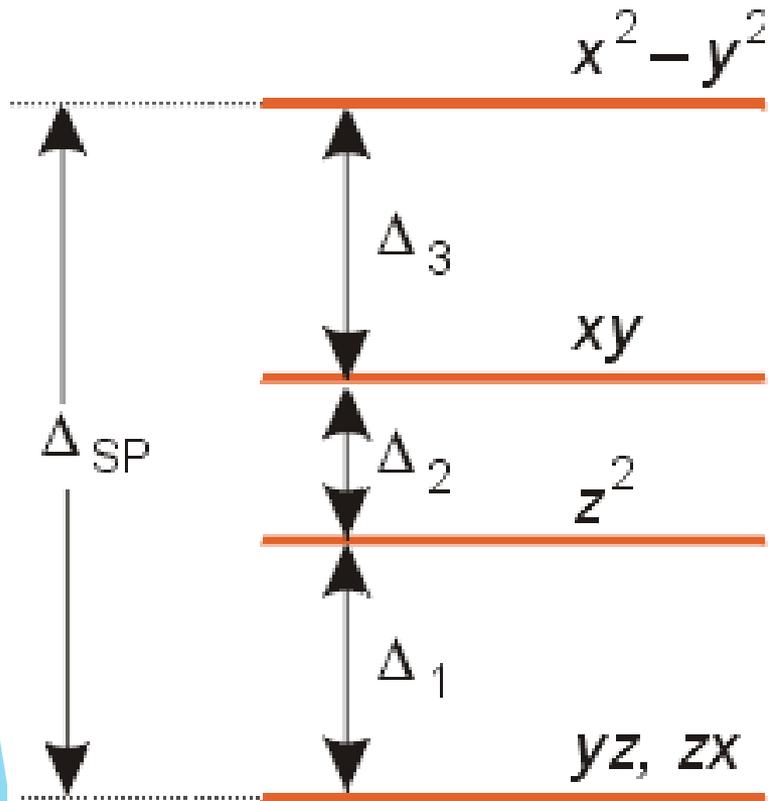
For complexes with 2 electrons in the e_g set of orbitals, a d^8 configuration, a severe distortion may occur, resulting in a 4-coordinate square planar shape, with the ligands along the z axis no longer bonded to the metal.

Square Planar Complexes



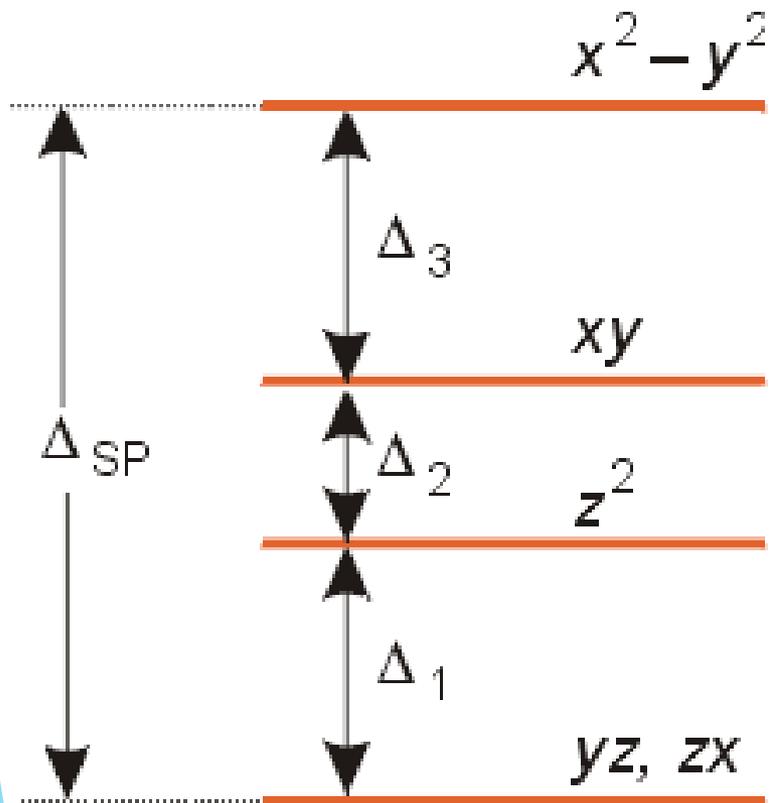
Square planar complexes are quite common for the d^8 metals in the 4th and 5th periods: Rh(I), Ir(I), Pt(II), Pd(II) and Au(III). The lower transition metals have large ligand field stabilization energies, favoring four-coordinate complexes.

Square Planar Complexes



Square planar complexes are rare for the 3rd period metals. Ni(II) generally forms tetrahedral complexes. Only with very strong ligands such as CN^- , is square planar geometry seen with Ni(II).

Square Planar Complexes



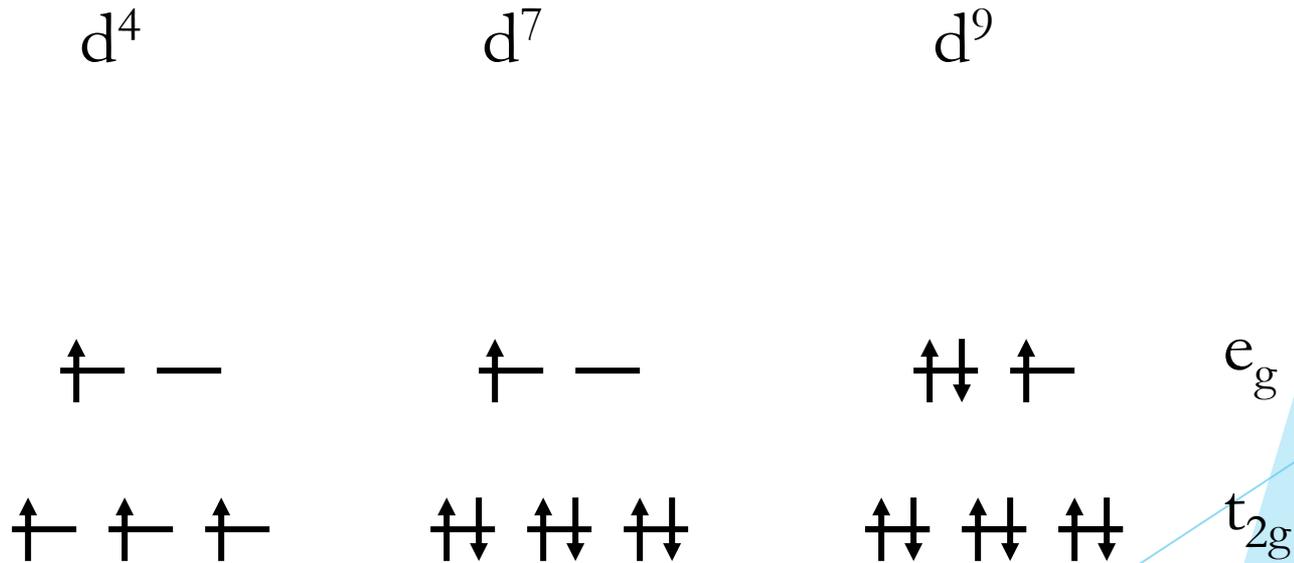
The value of Δ_{sp} for a given metal, ligands and bond length is approximately $1.3(\Delta_o)$.

The Jahn-Teller Effect

- ▶ *If the ground electronic configuration of a non-linear complex is orbitally degenerate, the complex will distort so as to remove the degeneracy and achieve a lower energy.*
- ▶ The Jahn-Teller effect predicts which structures will distort. It does not predict the nature or extent of the distortion. The effect is most often seen when the orbital degeneracy is in the orbitals that point directly towards the ligands.

The Jahn-Teller Effect

In octahedral complexes, the effect is most pronounced in high spin d^4 , low spin d^7 and d^9 configurations, as the degeneracy occurs in the e_g set of orbitals.



The Jahn-Teller Effect

The strength of the Jahn-Teller effect is tabulated below: (w=weak, s=strong)

| <u># e⁻</u> | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> | <u>7</u> | <u>8</u> | <u>9</u> | <u>10</u> |
|------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|
| High spin | * | * | * | s | - | w | w | * | * | * |
| Low spin | w | w | - | w | w | - | s | - | s | - |

- *There is only 1 possible ground state configuration.
- No Jahn-Teller distortion is expected.

Z-OUT(elongation) & Z-IN(compression) JAHN TELLER DISTORTIONS

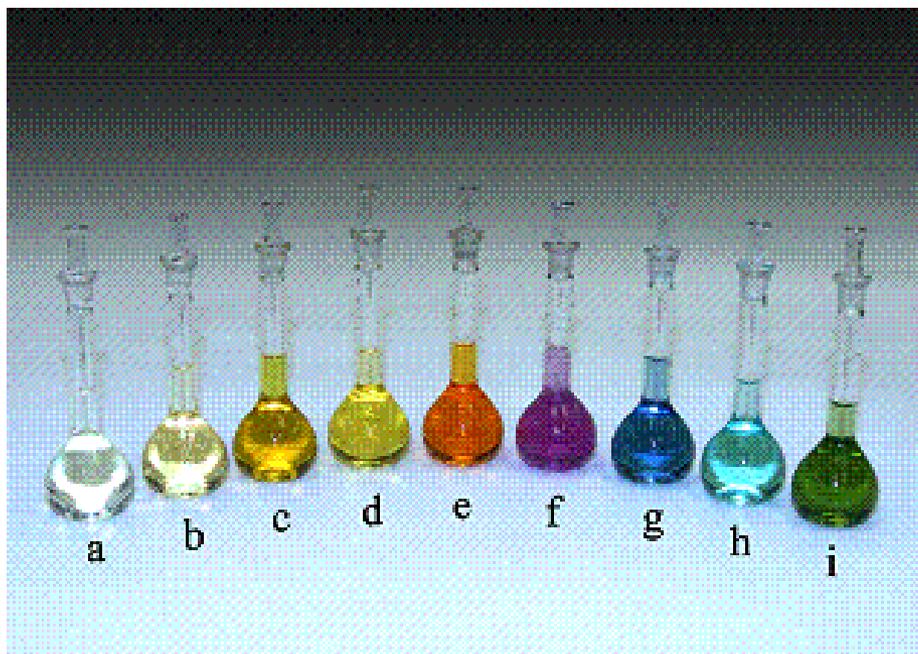
- ▶ **Z-out(Elongation) distortion:** In this case, the energies of d-orbitals with z factor (i.e., d_{z^2} , d_{xz} , d_{yz}) are *lowered* since the bonds along the z-axis are elongated. This is the most preferred distortion and occurs in most of the cases, especially when the degeneracy occurs in e_g level.
- ▶ E.g. Usually the octahedral d^2 , d^4 high spin, d^7 low spin, d^8 low spin & d^9 configurations show the z-out distortion.
- ▶ Theoretically it is not possible to predict the type of distortion occurs when the degeneracy occurs in e_g level. However it is observed that z-out distortion is more preferred.

- ▶ **Z-in(Compression) distortion:** In this case, the energies of d-orbitals with x^2-y^2 factor (i.e., $d_{x^2-y^2}$, d_{xy} , d_{yz}) are *lowered* since the bonds along the x^2-y^2 -axis are elongated. This is the most preferred distortion and occurs in most of the cases, especially when the degeneracy occurs in e_g level.
- ▶ E.g. Usually the octahedral d^2 , d^4 high spin, d^7 low spin, d^8 low spin & d^9 configurations show the z-in distortion.
- ▶ Theoretically it is not possible to predict the type of distortion occurs when the degeneracy occurs in e_g level. However it is observed that z-out distortion is more preferred.

STATIC & DYNAMIC JAHN-TELLER DISTORTIONS

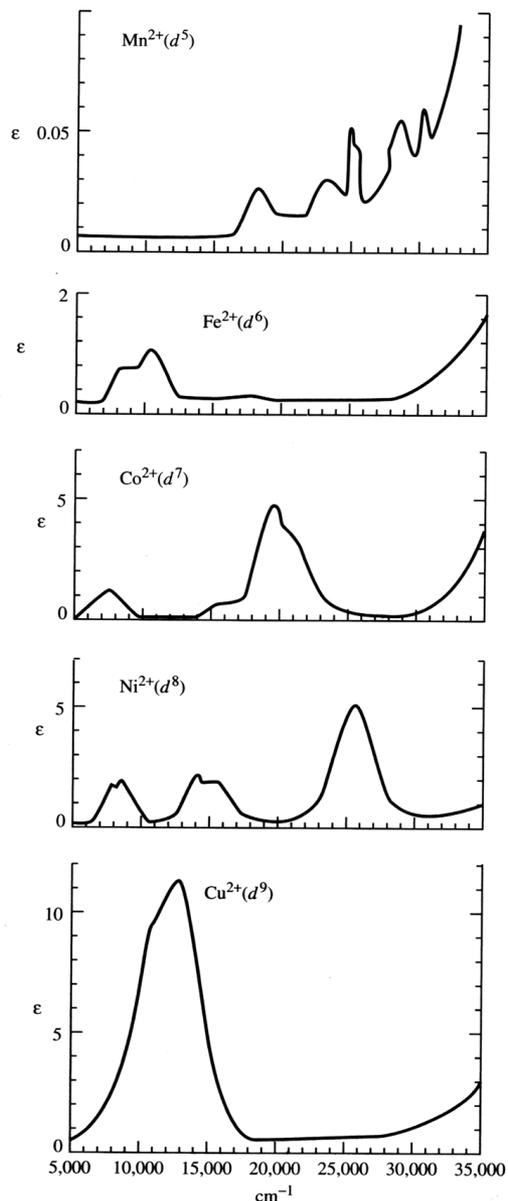
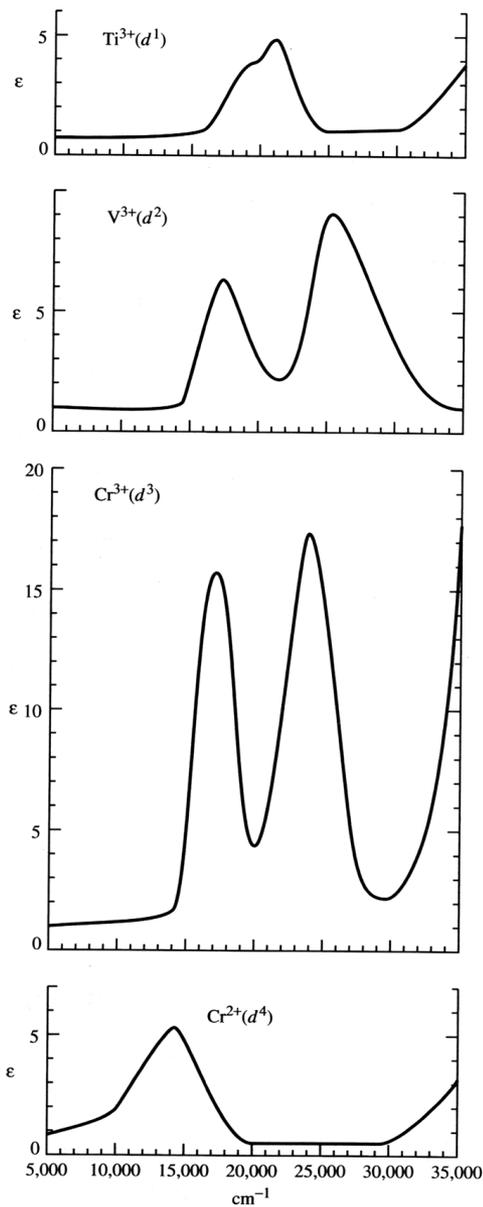
- ▶ **Static Jahn-Teller distortion:** Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. It is observed when the degeneracy occurs in e_g orbitals. Hence the distortion is strong and permanent.
- ▶ **Dynamic Jahn-Teller distortion:** In some molecules, the distortion is not seen either due to random movements of bonds which does not allow the measurement within a time frame or else the distortion is so weak as to be negligible. However the distortion can be seen by freezing the molecule at lower temperatures. This condition is referred to as dynamic Jahn-Teller distortion.

The Electronic Spectra of Coordination Compounds



The UV/Vis spectra of transition metal complexes shows the transitions of the electrons.

Analysis of these spectra can be quite complex.

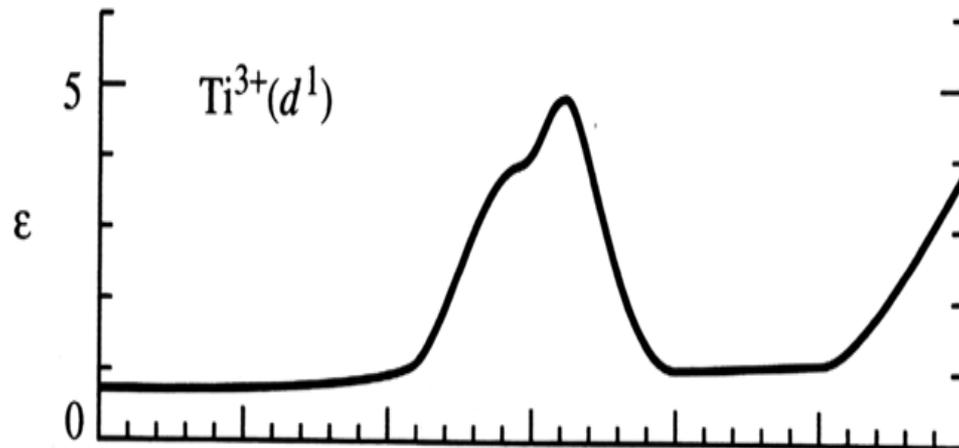


Electron Spectra

- ▶ The UV/Vis spectra are used to determine the value of Δ_o for the complex.
- ▶ The spectra arise from electronic transitions between the t_{2g} and e_g sets of molecular orbitals.
- ▶ Electron-electron interactions can greatly complicate the spectra.
- ▶ Only in the case of a single electron is interpretation of the spectrum straightforward.

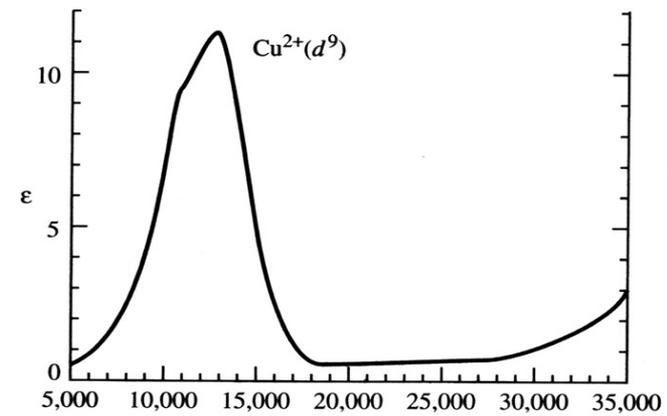
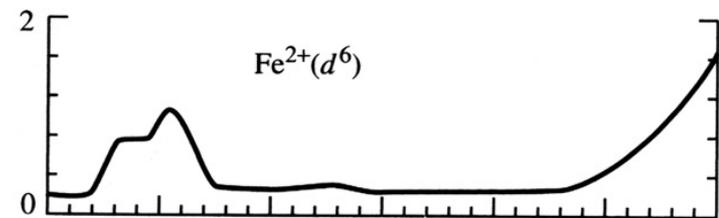
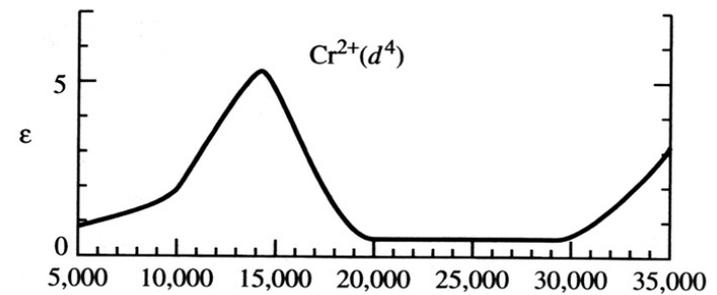
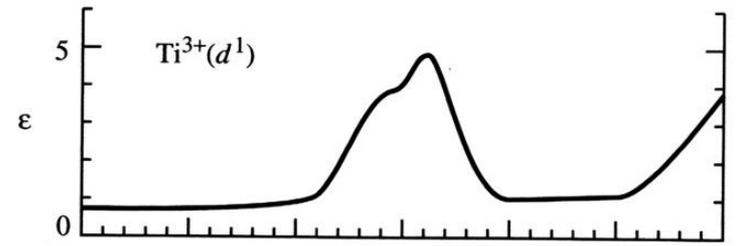
Obtaining Δ_o

For a d^1 configuration, only a single peak is seen. It results from the electron promotion from the t_{2g} orbitals to the e_g orbitals. The “toothed” appearance of the peak is due to a Jahn-Teller distortion of the excited state. The energy of the peak = Δ_o .



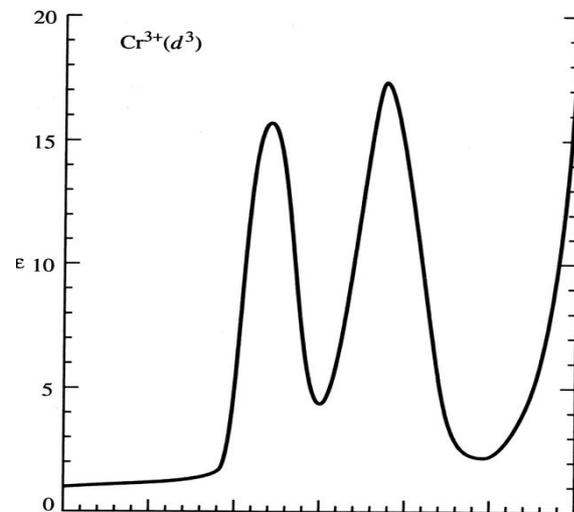
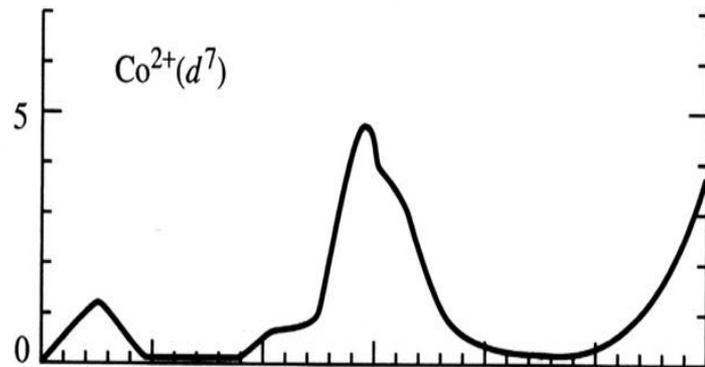
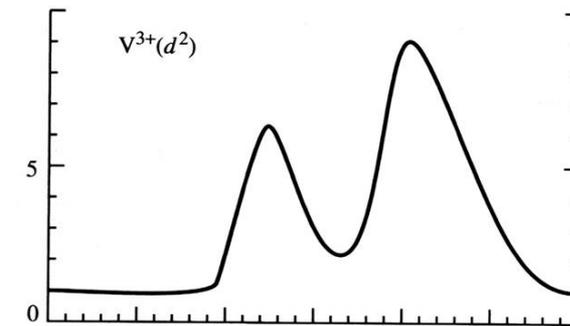
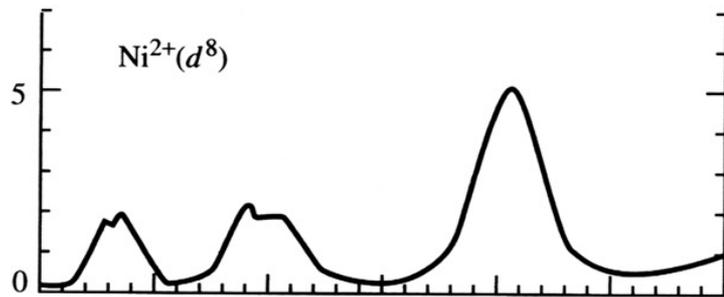
General Observations

d^1 , d^4 , d^6 and d^9 usually have 1 absorption, though a side “hump” results from Jahn-Teller distortions.



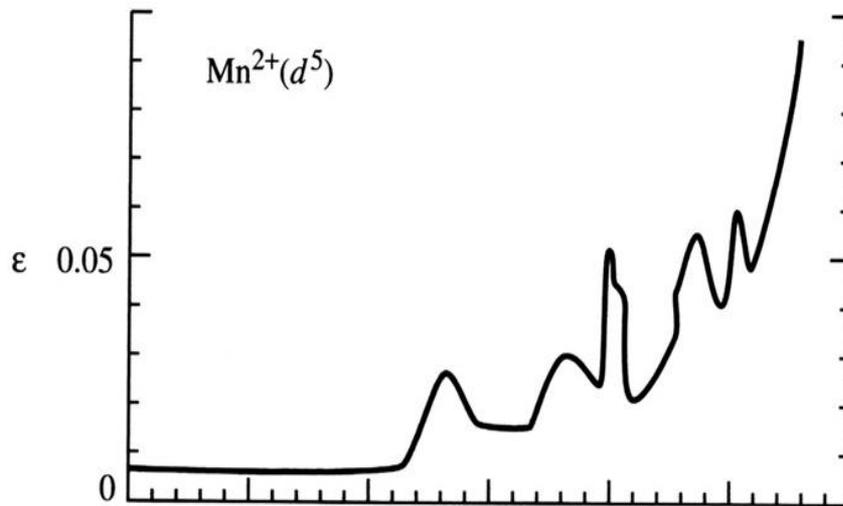
General Observations

d^2 , d^3 , d^7 and d^8 usually have 3 absorptions, one is often obscured by a charge transfer band.



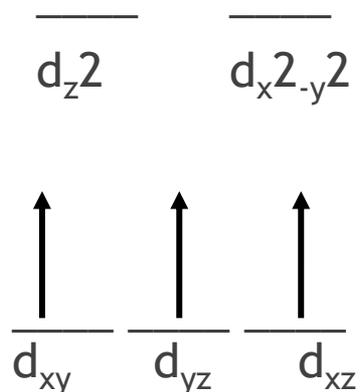
General Observations

d^5 complexes consist of very weak, relatively sharp transitions which are spin-forbidden, and have a very low intensity.



Qualitative Explanation

Consider a Cr(III) complex such as $[\text{Cr}(\text{NH}_3)_6]^{3+}$. The ground state configuration is:



A transition from the d_{xy} to the $d_{x^2-y^2}$, or the d_{yz} or d_{xz} to the d_{z^2}

orbitals involve a relatively minor change in environment.

Qualitative Explanation

Since the promotion of an electron from the t_{2g} set of orbitals to the e_g set can involve differing changes in environment, several peaks will be seen in the spectrum.

