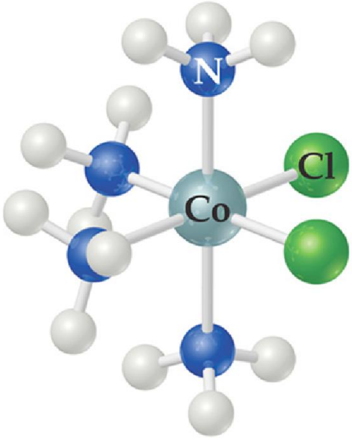
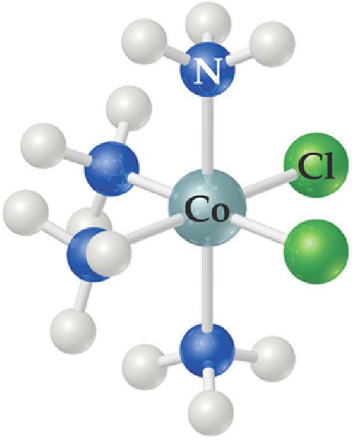


Coordination Compounds

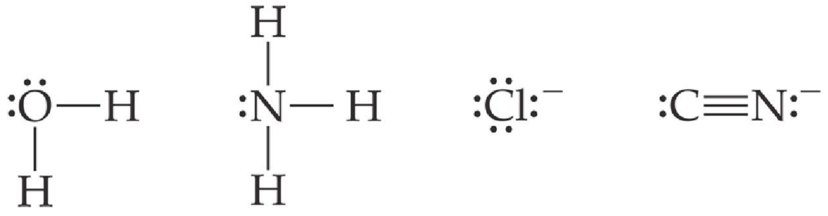
Complexes



- A central metal atom bonded to a group of molecules or ions is a metal complex.
- Compounds containing complexes are coordination compounds.

Complexes

- The molecules or ions coordinating to the metal are the ligands.
- They are usually anions or polar molecules.
- The must have lone pairs to interact with metal



A chemical mystery:

Same metal, same ligands, different number of ions when dissolved

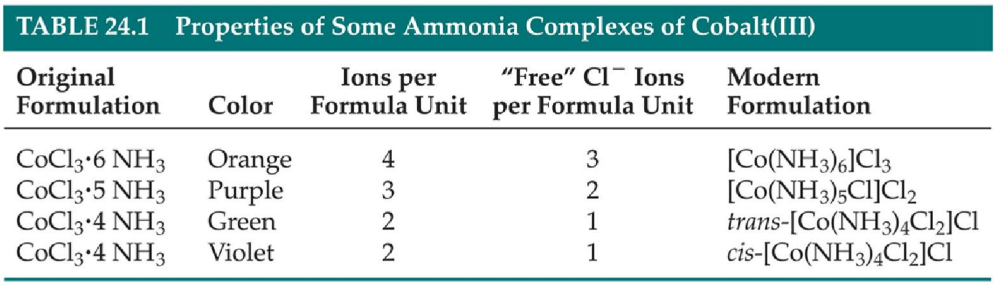
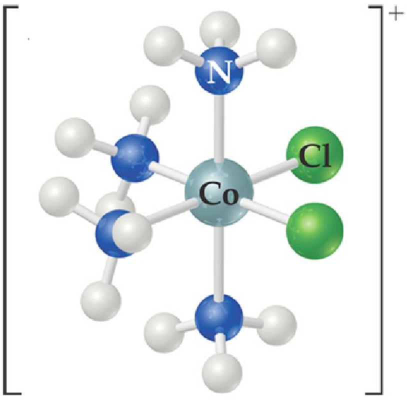


TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\ NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\ NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\ NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\ NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

Many coordination compounds are brightly colored, but again, same metal, same ligands, different colors.

Werner's Theory



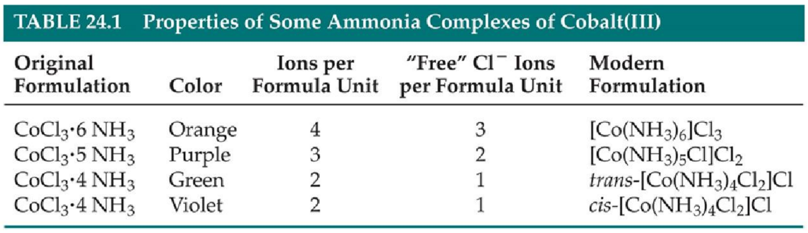
Co(III) oxidation state

Coordination number is 6

- suggested in 1893 that metal ions have ***primary*** and ***secondary*** valences.
  - Primary valence equal the metal's oxidation number
  - Secondary valence is the number of atoms directly bonded to the metal (coordination number)

Werner’s Theory

- The central metal and the ligands directly bonded to it make up the coordination sphere of the complex.
- In $CoCl_3 \cdot 6\ NH_3$, all six of the ligands are NH_3 and the 3 chloride ions are outside the coordination sphere.



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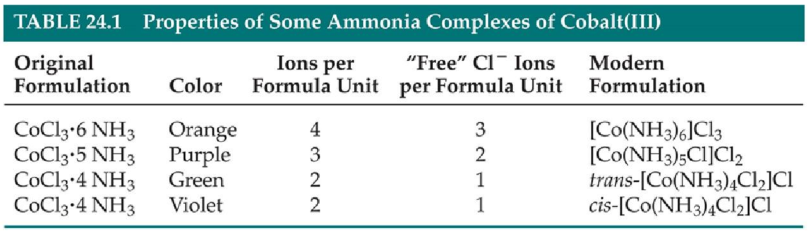
$CoCl_3 \cdot 4\ NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

Werner's Theory

In $CoCl_3 \cdot 5\ NH_3$ the five NH_3 groups and one chlorine are bonded to the cobalt, and the other two chloride ions are outside the sphere.



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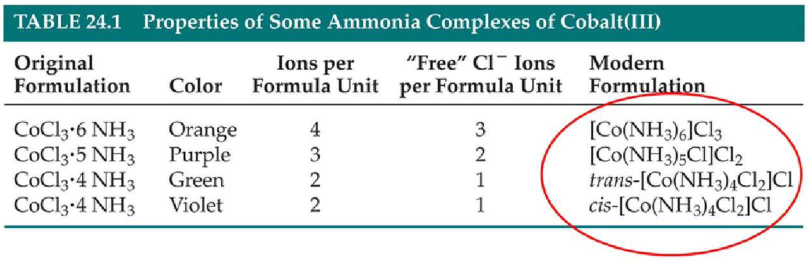
$CoCl_3 \cdot 4\ NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

Werner's Theory

Werner proposed putting all molecules and ions within the sphere in brackets and those "free" anions (that dissociate from the complex ion when dissolved in water) outside the brackets.



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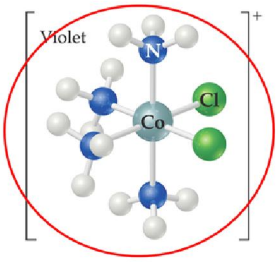
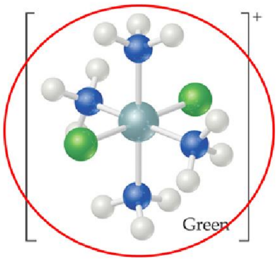
Werner's Theory

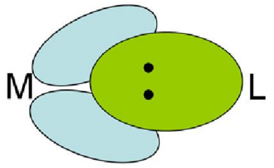




- This approach correctly predicts there would be two forms of $CoCl_3 \cdot 4\ NH_3$.
  - The formula would be written $[Co(NH_3)_4Cl_2]Cl$.
  - One of the two forms has the two chlorines next to each other.
  - The other has the chlorines opposite each other.

What is Coordination?

- When an orbital from a ligand with lone pairs in it overlaps with an empty orbital from a metal

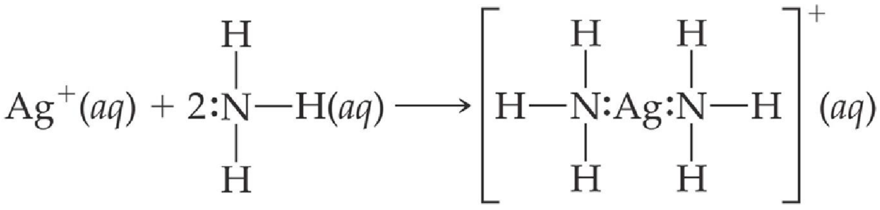


Sometimes called a coordinate covalent bond

So ligands *must* have lone pairs of electrons.

Metal-Ligand Bond

- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have nonbonding electrons.
  - The metal (Lewis acid) has empty orbitals.

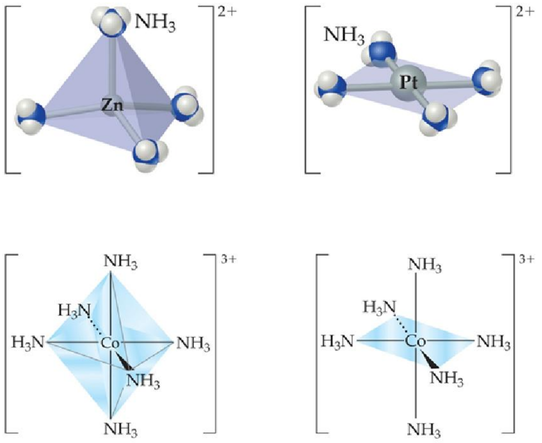


$$\mathrm{Ag}^{+}(aq) + 2\,\mathrm{:NH_3}(aq) \longrightarrow \left[\mathrm{H_3N\!:\!Ag\!:\!NH_3}\right]^{+}(aq)$$

Metal-Ligand Bond

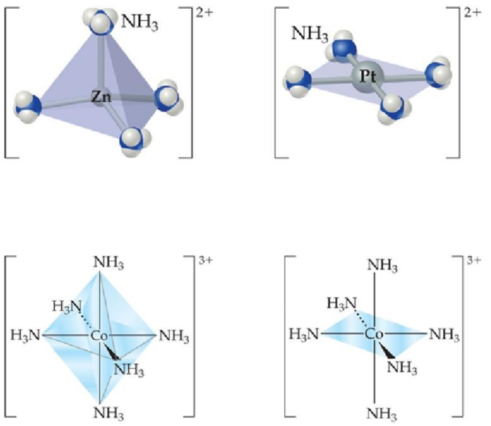
The metal’s coordination ligands and geometry can greatly alter its properties, such as color, or ease of oxidation.

Coordination Number



- The atom that supplies the lone pairs of electrons for the metal-ligand bond is the donor atom.
- The number of these atoms is the coordination number.

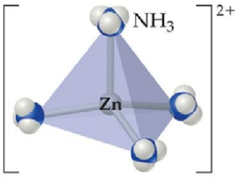
Coordination Number



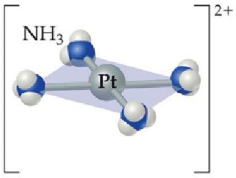
- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.

Geometries

- There are two common geometries for metals with a coordination number of four:
  - Tetrahedral
  - Square planar



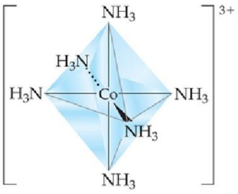
Tetrahedral

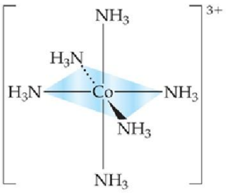


Square planar

Why square planar? We'll get to that

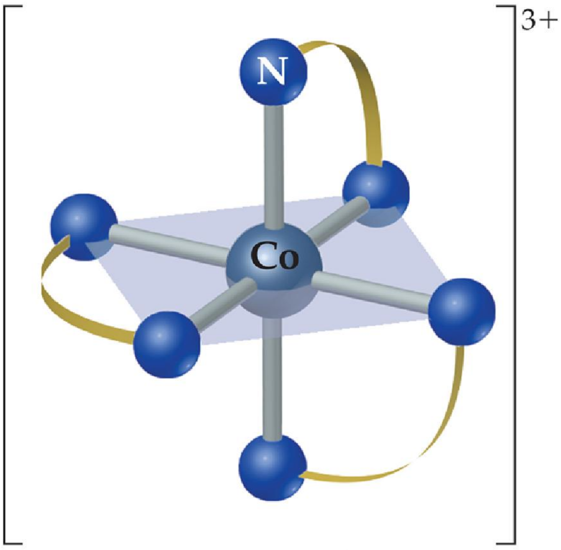
Geometries





By far the most-encountered geometry, when the coordination number is six, is octahedral.

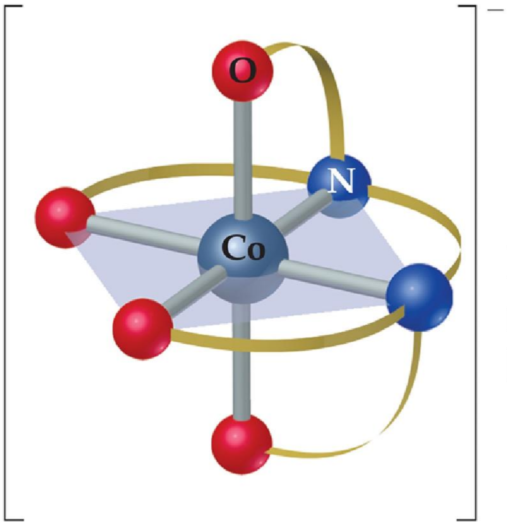
Polydentate Ligands



$[Co(en)_3]^{3+}$

- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylenediamine, $NH_2CH_2CH_2NH_2$, represented here as en, each N is a donor atom.
- Therefore, en is bidentate.

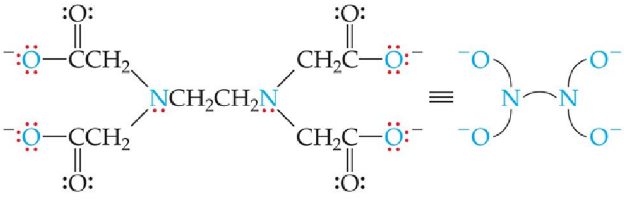
Polydentate Ligands



CoEDTA$^-$

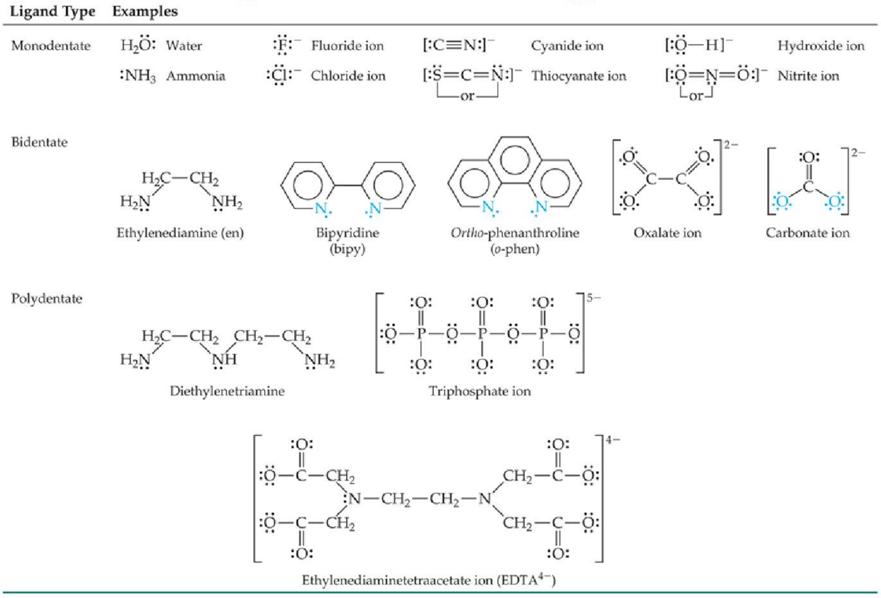
Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.

Wraps around the central atom like an octopus



[EDTA]$^{4-}$

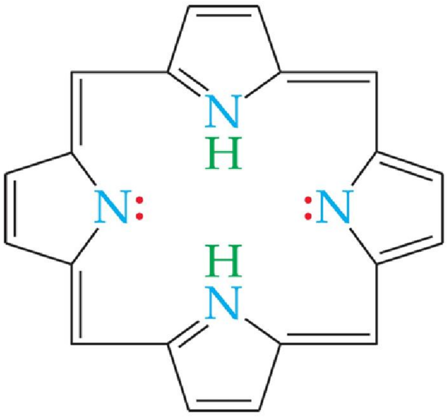
Polydentate Ligands



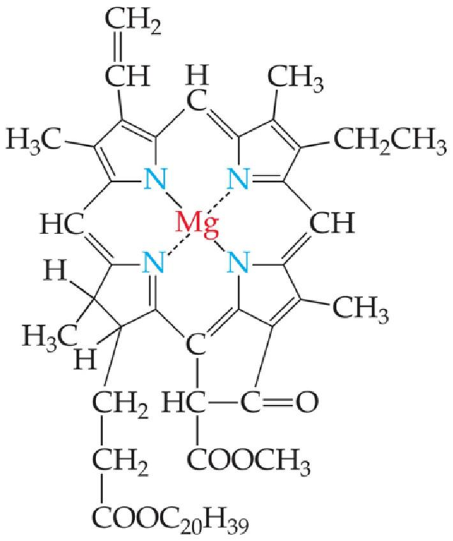
Chelating agents generally form more stable complexes than do monodentate ligands.

Chelating Agents

- Porphyrins are complexes containing a form of the porphine molecule shown at right.
- Important biomolecules like heme and chlorophyll are porphyrins.



Chelating Agents



Porphines (like chlorophyll *a*) are tetradentate ligands.

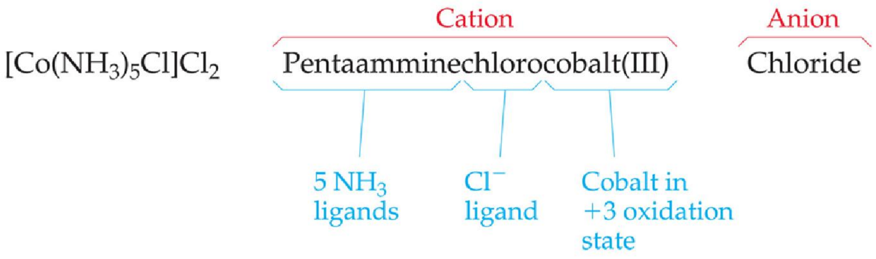
Nomenclature of Coordination Compounds

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-	Hydroxo	Pyridine, C_5H_5N	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

- The basic protocol in coordination nomenclature is to name the ligands attached to the metal as prefixes before the metal name.
- Some common ligands and their names are listed above.

Nomenclature of Coordination Compounds

- As always the name of the **cation** appears first; the **anion** is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.



$[Co(NH_3)_5Cl]Cl_2$

Cation: Pentaamminechlorocobalt(III)

Anion: Chloride

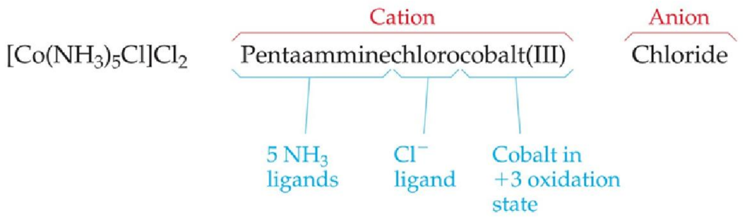
$5\ NH_3$ ligands

Cl^- ligand

Cobalt in +3 oxidation state

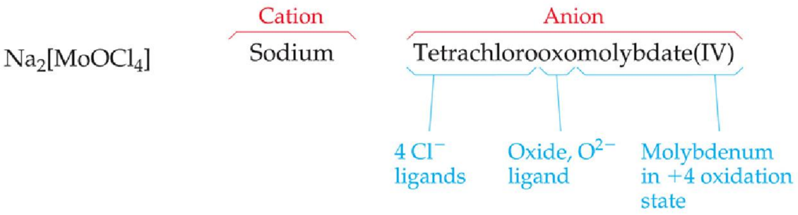
Nomenclature of Coordination Compounds

- The names of anionic ligands end in “o”; the endings of the names of neutral ligands are not changed.
- Prefixes tell the number of a type of ligand in the complex. If the name of the ligand itself has such a prefix, alternatives like *bis*-, *tris*-, etc., are used.



Nomenclature of Coordination Compounds

- If the complex is an anion, its ending is changed to *-ate*.
- The oxidation number of the metal is listed as a Roman numeral in parentheses immediately after the name of the metal.



$Na_2[MoOCl_4]$

Cation: Sodium

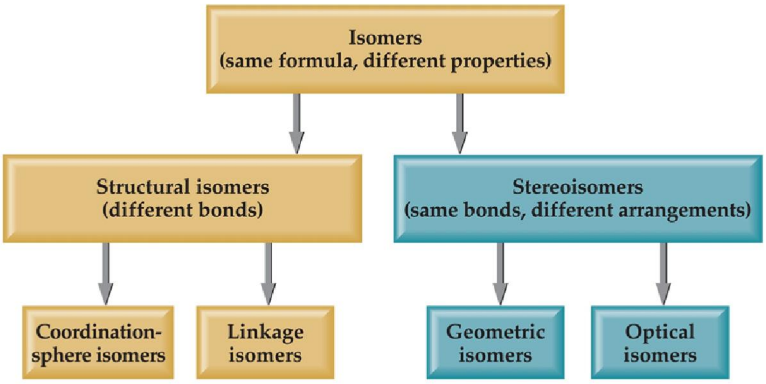
Anion: Tetrachlorooxomolybdate(IV)

4 Cl^- ligands

Oxide, O^{2-} ligand

Molybdenum in +4 oxidation state

Isomers



Isomers (same formula, different properties)

Structural isomers (different bonds)

Stereoisomers (same bonds, different arrangements)

Coordination-sphere isomers

Linkage isomers

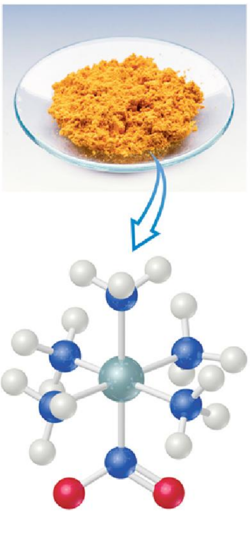
Geometric isomers

Optical isomers

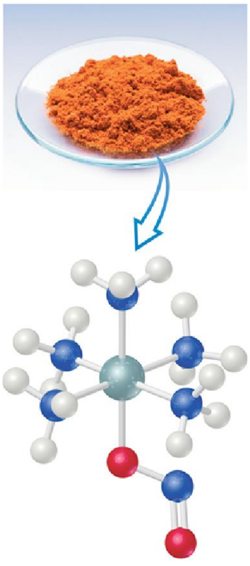
Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

Structural Isomers

If a ligand (like the NO_2 group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, linkage isomers are formed.



Nitro isomer

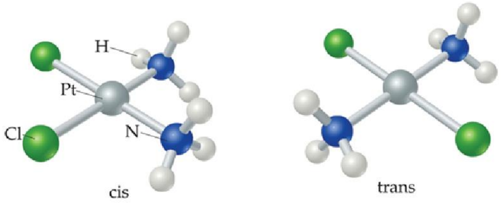


Nitrito isomer

Structural Isomers

- Some isomers differ in what ligands are bonded to the metal and what is outside the coordination sphere; these are coordination-sphere isomers.
- Three isomers of $CrCl_3(H_2O)_6$ are
  - The violet $[Cr(H_2O)_6]Cl_3$,
  - The green $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and
  - The (also) green $[Cr(H_2O)_4Cl_2]Cl \cdot 2\,H_2O$.

Geometric isomers

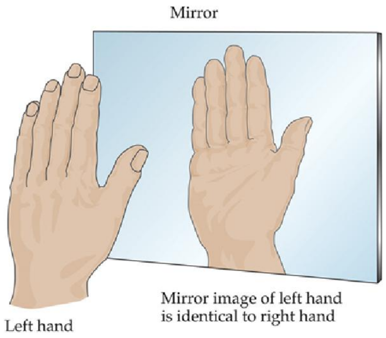


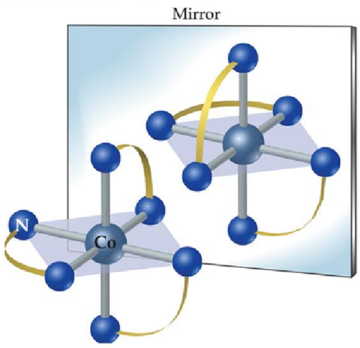
- With these geometric isomers, two chlorines and two NH_3 groups are bonded to the platinum metal, but are clearly different.

- *cis*-Isomers have like groups on the same side.
- *trans*-Isomers have like groups on opposite sides.

# of each atom the same
Bonding the same
Arrangement in space different

Stereoisomers

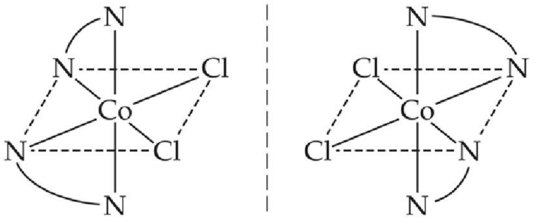




- Other stereoisomers, called optical isomers or enantiomers, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

Enantiomers

A molecule or ion that exists as a pair of enantiomers is said to be chiral.



Stability of coordination compounds

$[M(H_2O)_x]^{z+}{}_{(aq)} + L_{(aq)} \rightleftharpoons [M(H_2O)_{(x-1)}(L)]^{z+}{}_{(aq)} + H_2O_{(aq)}$

$M + L \rightleftharpoons ML$

$$K_1 = [ML]/[M][L]$$

$ML + L \rightleftharpoons ML_2$

$$K_2 = [ML_2]/[ML][L]$$

Stability of coordination compounds

for $M + L \rightleftharpoons ML$ $\quad \beta_1 = [ML]/[M][L]$

for $M + 2L \rightleftharpoons ML_2$ $\quad \beta_2 = [ML_2]/[M][L]^2$

Stepwise stability constants

$M + nL \rightleftharpoons ML_n$ $\quad \beta_n = [ML_n]/[M][L]^n$

$$\beta_j = K_1 K_2 \dots K_j \quad \text{or} \quad \beta_j = \prod_{i=1}^{i=j} K_j$$

Overall stability constants

Chelate & Macrocyclic Effect

$$\mathrm{Cd^{2+}}_{(aq)} + 4\mathrm{MeNH}_{2(aq)} \rightleftharpoons [\mathrm{Cd(MeNH_2)_4}]^{2+}_{(aq)}$$

$\Delta G^{\ominus} = -37.2\ \mathrm{kJ\ mol^{-1}}$ and $\log_{10}\beta_n = 6.52$

$$\mathrm{Cd^{2+}}_{(aq)} + 2\mathrm{en}_{(aq)} \rightleftharpoons [\mathrm{Cd(en)_2}]^{2+}_{(aq)}$$

$\Delta G^{\ominus} = -60.7\ \mathrm{kJ\ mol^{-1}}$ and $\log_{10}\beta_n = 10.6$

$$[\mathrm{Cd(MeNH_2)_4}]^{2+}_{(aq)} + 2\mathrm{en}_{(aq)} \rightleftharpoons [\mathrm{Cd(en)_2}]^{2+}_{(aq)} + 4\mathrm{MeNH}_{2(aq)}$$

$$\log_{10}K = 10.6 - 6.52 = 4.08$$

- This is due to a combination of enthalpic and entropic effects.
- Enhanced whe the ligand in a macrocyclic molecule.

Hard & Soft Model

Hard metals

Strongest complexes
with oxygen donor atoms

Hard bases

Contain the smaller
electronegative atoms (F, O, N)

Soft metals

Strongest complexes
with sulfur of phosphorus
donor atoms

Soft metals

Contain the larger more polarizable
and less electronegative atoms
(S, Se, P or As)

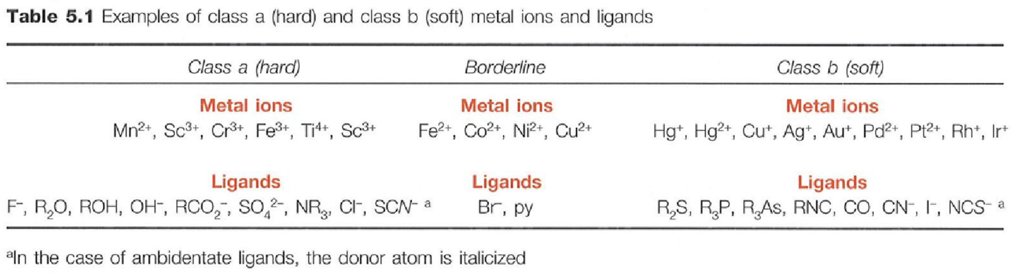


Table 5.1 Examples of class a (hard) and class b (soft) metal ions and ligands

Class a (hard)	*Borderline*	*Class b (soft)*
Metal ions	**Metal ions**	**Metal ions**
Mn^{2+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Ti^{4+}, Sc^{3+}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	Hg^+, Hg^{2+}, Cu^+, Ag^+, Au^+, Pd^{2+}, Pt^{2+}, Rh^+, Ir^+
Ligands	**Ligands**	**Ligands**
F^-, R_2O, ROH, OH^-, RCO_2^-, SO_4^{2-}, NR_3, Cl^-, $\mathrm{SC}N^-$ [a]	Br^-, py	R_2S, R_3P, R_3As, RNC, CO, CN^-, I^-, $\mathrm{NC}S^-$ [a]

[a] In the case of ambidentate ligands, the donor atom is italicized

Explaining the properties of transition metal coordination complexes

1. Magnetism
2. Color

Metal complexes and color

The ligands of a metal complex effect its color

Addition of NH_3 ligand to $Cu(H_2O)_4^{2+}$ changes its color

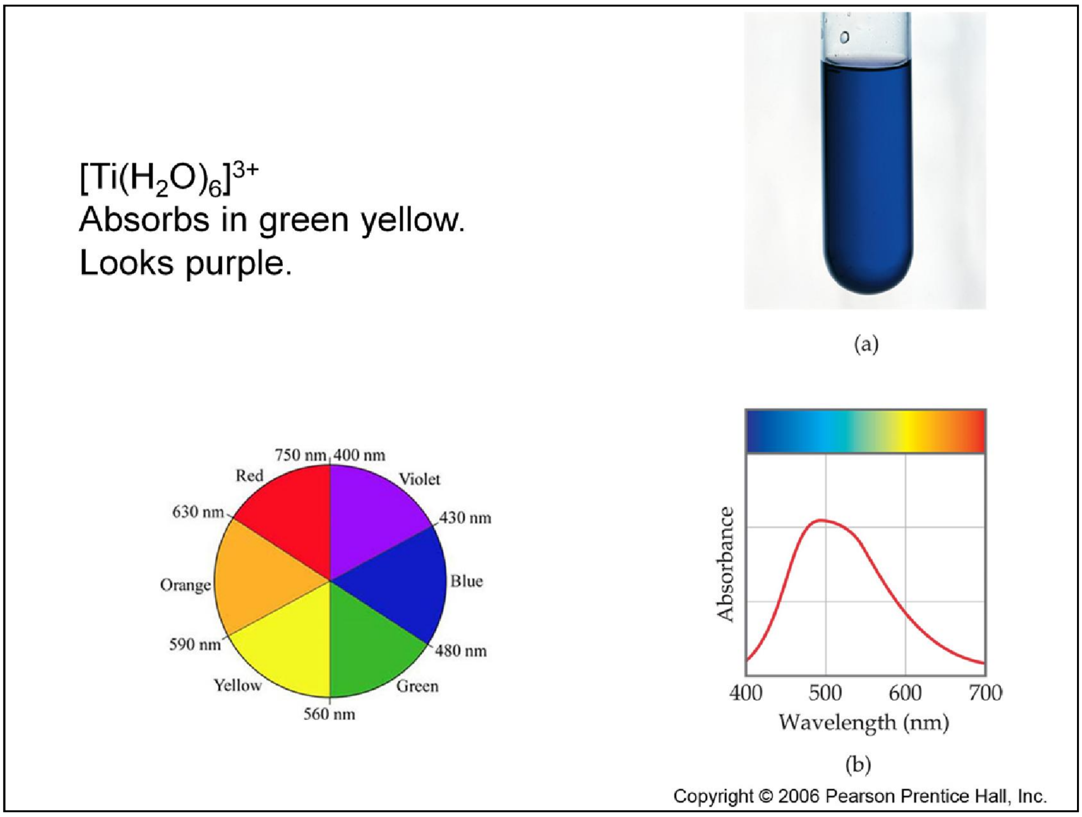
Figure: 24-22

Title:

Effect of ligands on color.

Caption:

An aqueous solution of $CuSO_4$ is pale blue because of $[Cu(H_2O)_4]^{2+}$ (left). When NH_3(*aq*) is added (middle and right), the deep blue $[Cu(NH_3)_4]^{2+}$ ion forms.



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

Absorbs in green yellow.

Looks purple.

(a)

(b)

Figure: 24-26

Title:

The color of $[Ti(H_2O)_6]^{3+}$.

Caption:

(a) A solution containing the $[Ti(H_2O)_6]^{3+}$ ion. (b) The visible absorption spectrum of the $[Ti(H_2O)_6]^{3+}$ ion.

Crystal Field Model

Model of ligand/metal bonding.

Electron pair comes from ligand

Bond very polarized.

Assumption: interaction pure electrostatic.

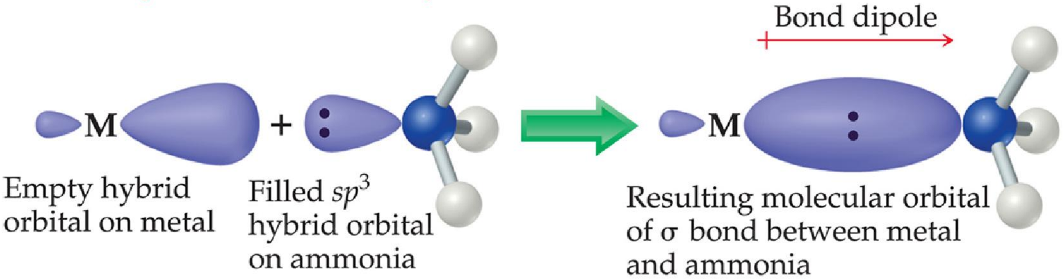


Figure: 24-27

Title:

Metal-ligand bond formation.

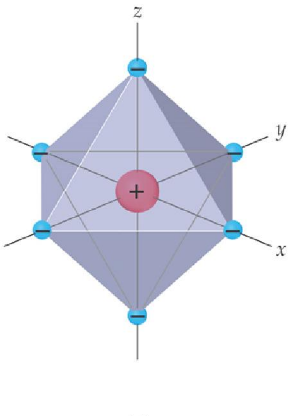
Caption:

The ligand, which acts as a Lewis base, donates charge to the metal via a metal hybrid orbital. The bond that results is strongly polar, with some covalent character. It is often sufficient to assume that the metal-ligand interaction is entirely electrostatic in character, as is done in the crystal-field model.

Octahedral complexes

Ligands will interact with some d orbitals more than others

Depends on relative orientation of orbital and ligand



(a)

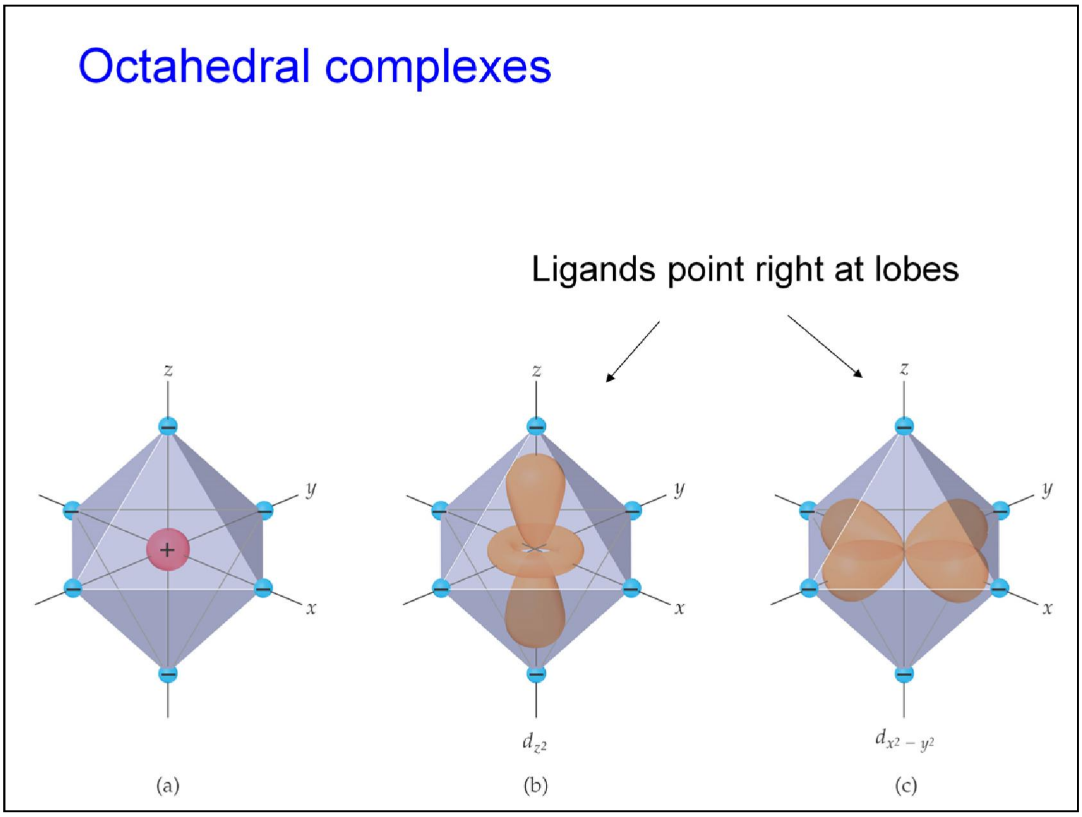
Figure: 24-29abc

Title:

The five *d* orbitals in an octahedral crystal field.

Caption:

(a) An octahedral array of negative charges approaching a metal ion. (b) The orientations of the *d* orbitals relative to the negative charges. Notice that the lobes of the d_{z2} and d_{x2-y2} orbitals (b and c) point toward the charges, whereas the lobes of the d_{xy}, d_{yz}, and d_{xz} orbitals (d–f) point between the charges.



Octahedral complexes

Ligands point right at lobes

Figure: 24-29abc

Title:

The five *d* orbitals in an octahedral crystal field.

Caption:

(a) An octahedral array of negative charges approaching a metal ion. (b) The orientations of the *d* orbitals relative to the negative charges. Notice that the lobes of the d_{z2} and d_{x2-y2} orbitals (b and c) point toward the charges, whereas the lobes of the d_{xy}, d_{yz}, and d_{xz} orbitals (d–f) point between the charges.

Octahedral complexes

In these orbitals, the ligands are between the lobes

Interact less strongly

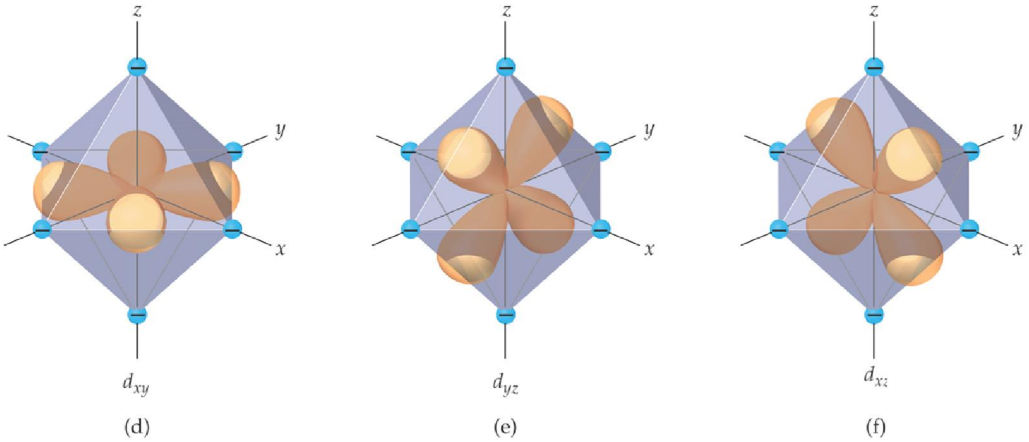


Figure: 24-29def

Title:

The five *d* orbitals in an octahedral crystal field.

Caption:

(a) An octahedral array of negative charges approaching a metal ion. (b) The orientations of the *d* orbitals relative to the negative charges. Notice that the lobes of the d_{z2} and d_{x2-y2} orbitals (b and c) point toward the charges, whereas the lobes of the d_{xy}, d_{yz}, and d_{xz} orbitals (d–f) point between the charges.

What about electrons in d orbitals?

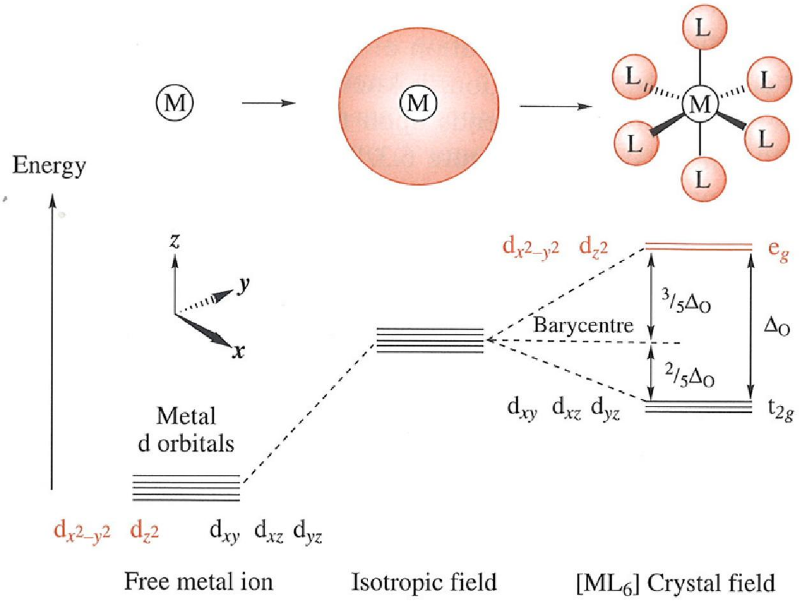


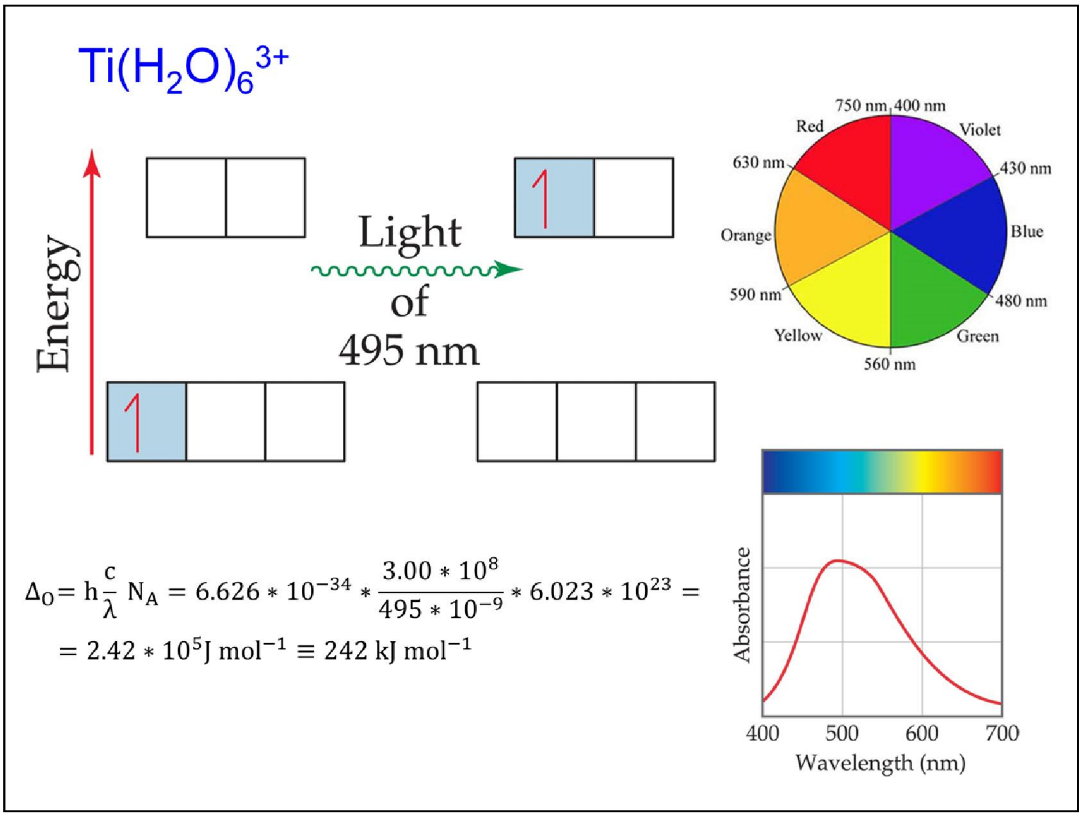
Figure: 24-28

Title:

Energies of *d* orbitals in an octahedral crystal field.

Caption:

On the left the energies of the *d* orbitals of a free ion are shown. When negative charges are brought up to the ion, the average energy of the *d* orbitals increases (center). On the right the splitting of the *d* orbitals due to the octahedral field is shown. Because the repulsion felt by the d_{z2} and d_{x2-y2} orbitals is greater than that felt by the d_{xy}, d_{xz}, and d_{yz} orbitals, the five *d* orbitals split into a lower-energy set of three (the t_2 set) and a higher-energy set of two (the *e* set).



$Ti(H_2O)_6^{3+}$

$$\Delta_O = h\frac{c}{\lambda}\,N_A = 6.626 * 10^{-34} * \frac{3.00 * 10^{8}}{495 * 10^{-9}} * 6.023 * 10^{23} =$$

$$= 2.42 * 10^{5}\,\mathrm{J\,mol^{-1}} \equiv 242\ \mathrm{kJ\,mol^{-1}}$$

Figure: 24-30

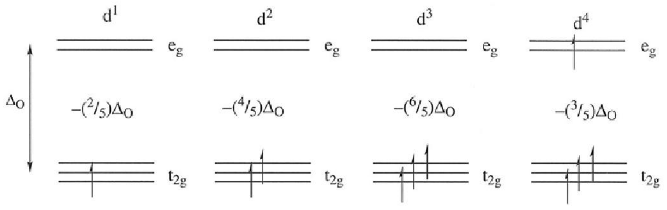
Title:

Electronic transition accompanying absorption of light.

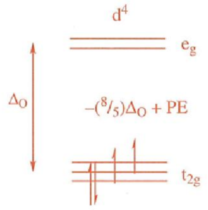
Caption:

The 3*d* electron of $[Ti(H_2O)_6]^{3+}$ is excited from the lower-energy *d* orbitals to the higher-energy ones when irradiated with light of 495-nm wavelength.

Crystal Field Stabilization Energy

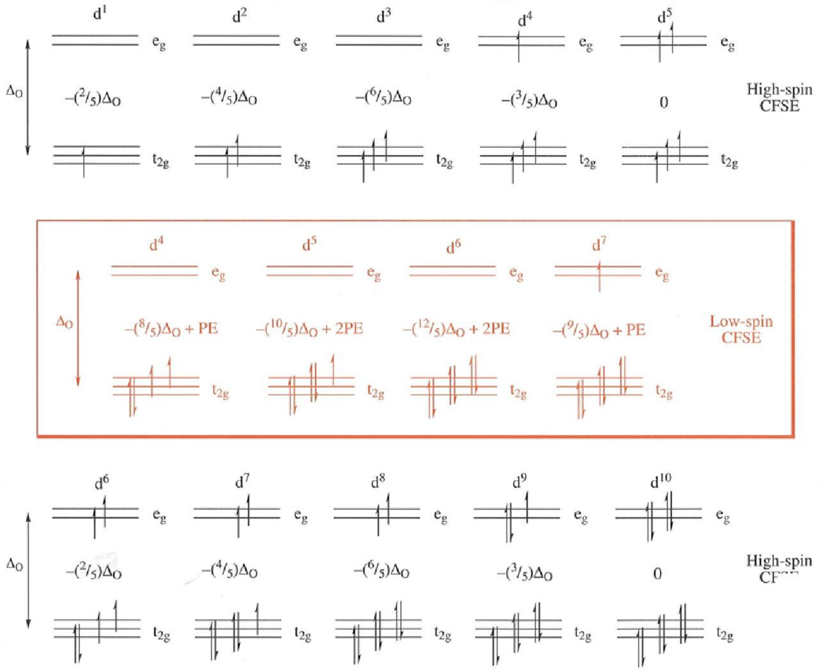


$$\mathrm{CFSE_H} = \left\{\frac{3}{5}\mathrm{y} - \frac{2}{5}\mathrm{x}\right\}\Delta_O$$



$$\mathrm{CFSE_L} = \left\{\frac{3}{5}\mathrm{y} - \frac{2}{5}\mathrm{x}\right\}\Delta_O + \Pi(\mathrm{PE})$$

Crystal Field Stabilization Energy

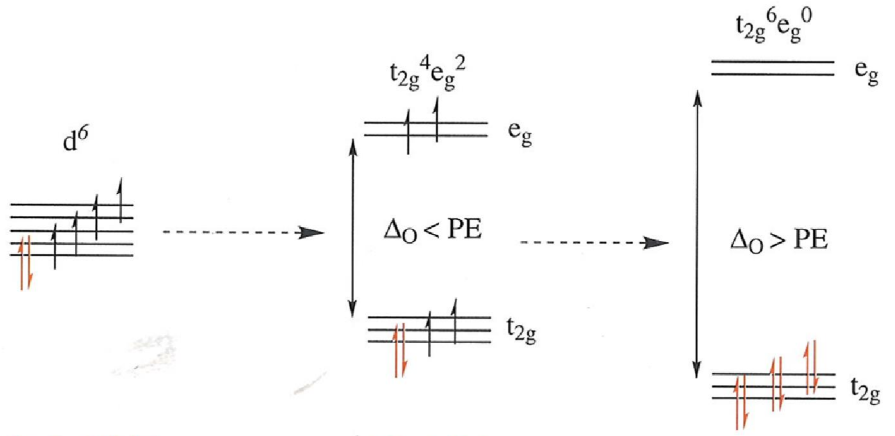


d¹	d²	d³	d⁴	d⁵	
$-({}^{2}/_{5})\Delta_O$	$-({}^{4}/_{5})\Delta_O$	$-({}^{6}/_{5})\Delta_O$	$-({}^{3}/_{5})\Delta_O$	0	High-spin CFSE

d⁴	d⁵	d⁶	d⁷	
$-({}^{8}/_{5})\Delta_O + PE$	$-({}^{10}/_{5})\Delta_O + 2PE$	$-({}^{12}/_{5})\Delta_O + 2PE$	$-({}^{9}/_{5})\Delta_O + PE$	Low-spin CFSE

d⁶	d⁷	d⁸	d⁹	d¹⁰	
$-({}^{2}/_{5})\Delta_O$	$-({}^{4}/_{5})\Delta_O$	$-({}^{6}/_{5})\Delta_O$	$-({}^{3}/_{5})\Delta_O$	0	High-spin CF

Crystal Field Stabilization Energy



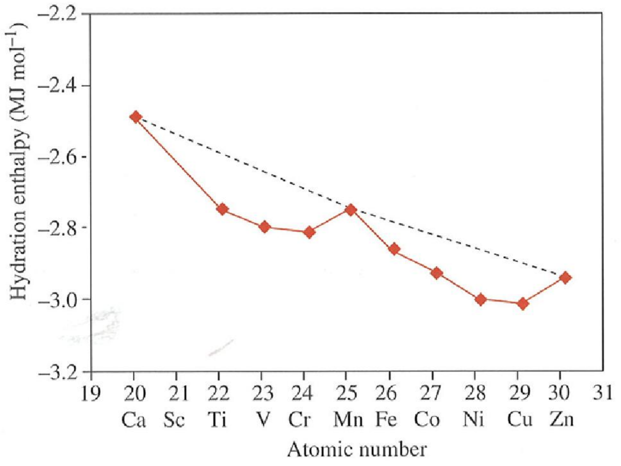
Spherical field
One pair

Weak field
One pair
CFSE $= -(2/5)\Delta_O$

Strong field
Three pairs
CFSE $= -(12/5)\Delta_O + 2PE$

Effect of splitting of d orbitals

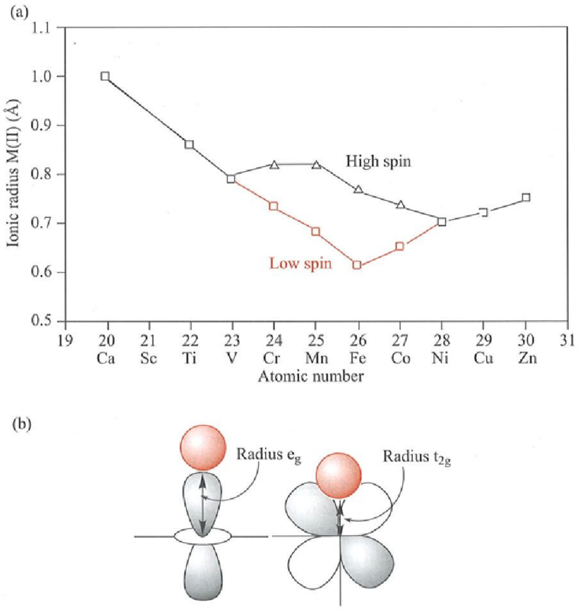
Hydration enthalpy



- All HS

Effect of splitting of d orbitals

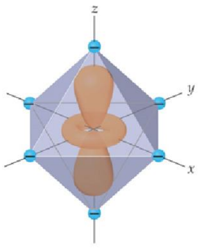
Ionic radii in complexes



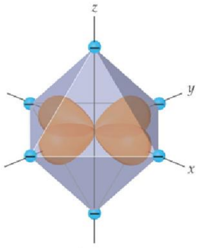
Jahn-Teller effect

Theorem:

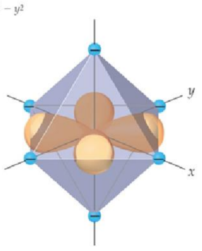
A nonlinear polyatomic system in a spatially degenerate electronic state distorts spontaneously in such a way that the degeneracy is lifted and a new equilibrium structure of lower symmetry is attained.



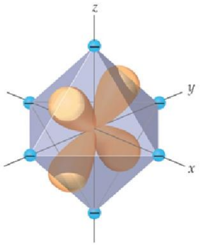
d_{z^2}



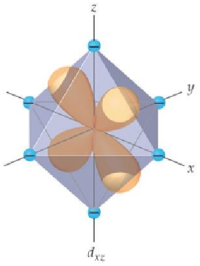
$d_{x^2-y^2}$



d_{xy}

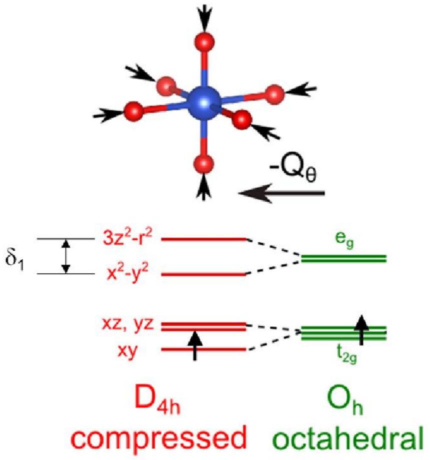


d_{yz}

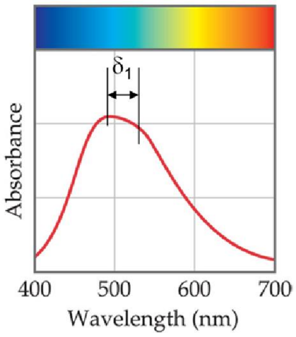


d_{xz}

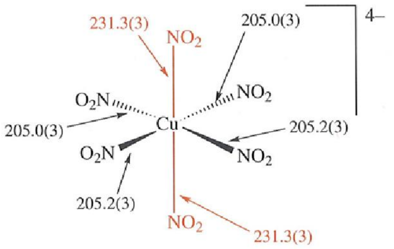
Jahn-Teller effect

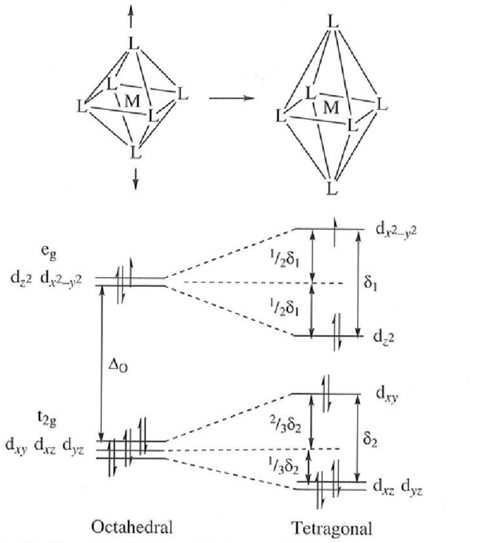


$Ti(H_2O)_6^{3+}$



Jahn-Teller effect

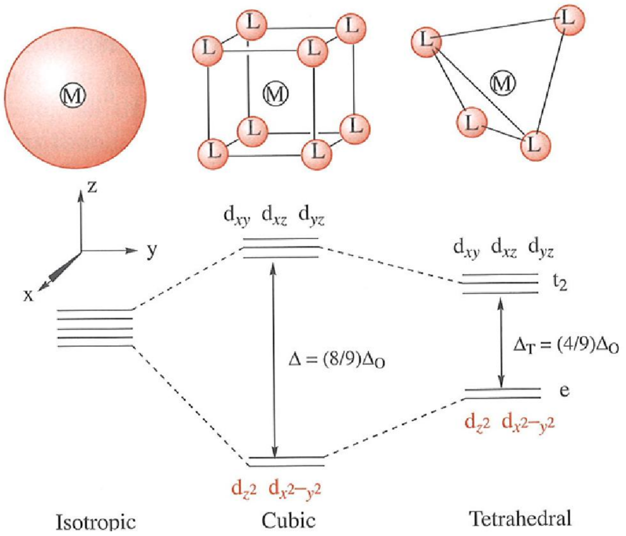




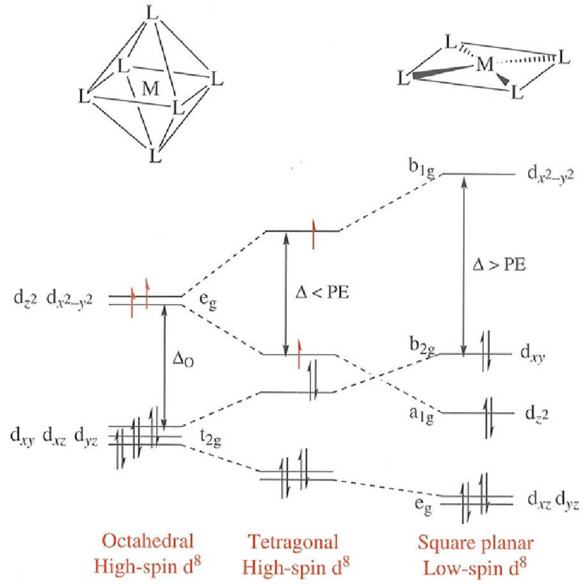
Octahedral CFSE $= (3 \times {}^3/_5 - 6 \times {}^2/_5)\Delta_O = -({}^3/_5)\Delta_O$

Tetragonal CFSE $= -({}^3/_5)\Delta_O + (2 \times {}^2/_3)\delta_2 - (4 \times {}^1/_3)\delta_2 + ({}^1/_2)\delta_1 - (2 \times {}^1/_2)\delta_1$
$= -({}^3/_5)\Delta_O - ({}^1/_2)\delta_1$

Tetrahedral complexes



Square Planar complexes



Factors affecting Δ

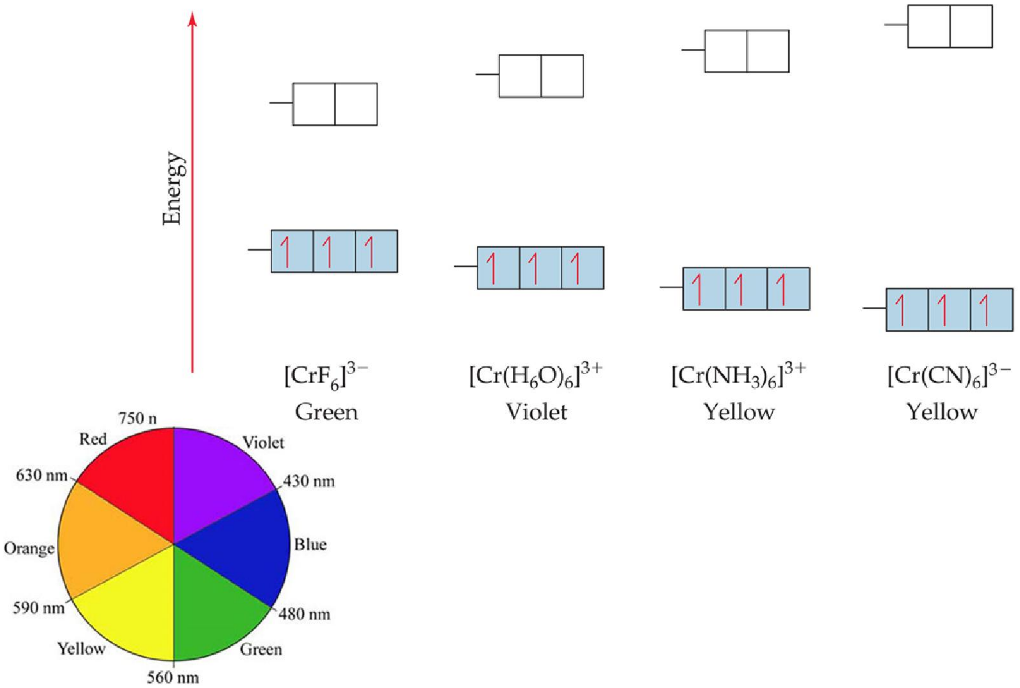


Figure: 24-31

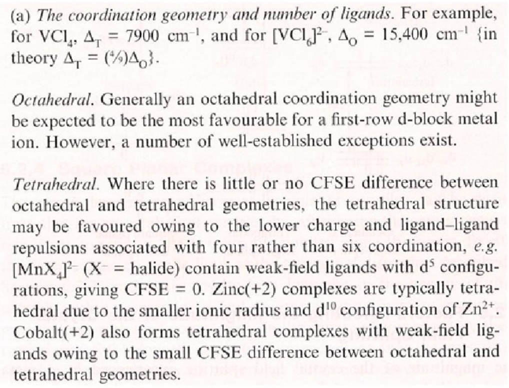
Title:

Effect of ligand on crystal-field splitting.

Caption:

This series of octahedral chromium(III) complexes illustrates how Δ, the energy gap between the t_2 and *e* orbitals, increases as the field strength of the ligand increases.

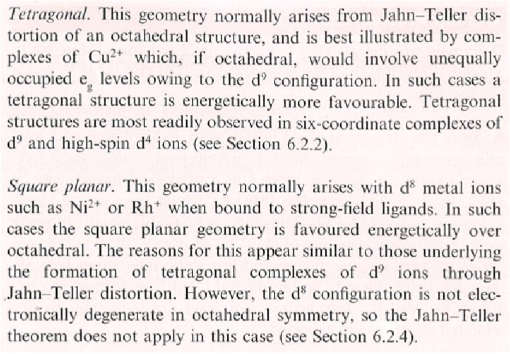
Factors affecting Δ



(a) *The coordination geometry and number of ligands.* For example, for VCl_4, $\Delta_T = 7900\ cm^{-1}$, and for $[VCl_6]^{2-}$, $\Delta_O = 15{,}400\ cm^{-1}$ {in theory $\Delta_T = (4/9)\Delta_O$}.

Octahedral. Generally an octahedral coordination geometry might be expected to be the most favourable for a first-row d-block metal ion. However, a number of well-established exceptions exist.

Tetrahedral. Where there is little or no CFSE difference between octahedral and tetrahedral geometries, the tetrahedral structure may be favoured owing to the lower charge and ligand–ligand repulsions associated with four rather than six coordination, *e.g.* $[MnX_4]^{2-}$ (X^- = halide) contain weak-field ligands with d^5 configurations, giving CFSE = 0. Zinc(+2) complexes are typically tetrahedral due to the smaller ionic radius and d^{10} configuration of Zn^{2+}. Cobalt(+2) also forms tetrahedral complexes with weak-field ligands owing to the small CFSE difference between octahedral and tetrahedral geometries.



Tetragonal. This geometry normally arises from Jahn–Teller distortion of an octahedral structure, and is best illustrated by complexes of Cu^{2+} which, if octahedral, would involve unequally occupied e_g levels owing to the d^9 configuration. In such cases a tetragonal structure is energetically more favourable. Tetragonal structures are most readily observed in six-coordinate complexes of d^9 and high-spin d^4 ions (see Section 6.2.2).

Square planar. This geometry normally arises with d^8 metal ions such as Ni^{2+} or Rh^+ when bound to strong-field ligands. In such cases the square planar geometry is favoured energetically over octahedral. The reasons for this appear similar to those underlying the formation of tetragonal complexes of d^9 ions through Jahn–Teller distortion. However, the d^8 configuration is not electronically degenerate in octahedral symmetry, so the Jahn–Teller theorem does not apply in this case (see Section 6.2.4).

Figure: 24-31

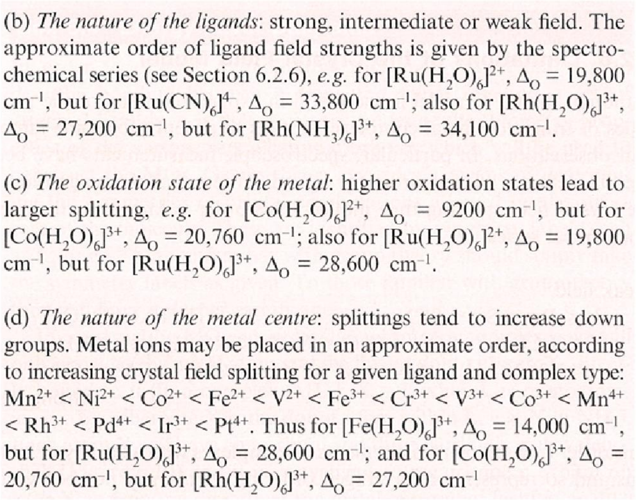
Title:

Effect of ligand on crystal-field splitting.

Caption:

This series of octahedral chromium(III) complexes illustrates how Δ, the energy gap between the t_2 and e orbitals, increases as the field strength of the ligand increases.

Factors affecting Δ



(b) *The nature of the ligands*: strong, intermediate or weak field. The approximate order of ligand field strengths is given by the spectrochemical series (see Section 6.2.6), *e.g.* for $[Ru(H_2O)_6]^{2+}$, $\Delta_O = 19,800$ cm^{-1}, but for $[Ru(CN)_6]^{4-}$, $\Delta_O = 33,800$ cm^{-1}; also for $[Rh(H_2O)_6]^{3+}$, $\Delta_O = 27,200$ cm^{-1}, but for $[Rh(NH_3)_6]^{3+}$, $\Delta_O = 34,100$ cm^{-1}.

(c) *The oxidation state of the metal*: higher oxidation states lead to larger splitting, *e.g.* for $[Co(H_2O)_6]^{2+}$, $\Delta_O = 9200$ cm^{-1}, but for $[Co(H_2O)_6]^{3+}$, $\Delta_O = 20,760$ cm^{-1}; also for $[Ru(H_2O)_6]^{2+}$, $\Delta_O = 19,800$ cm^{-1}, but for $[Ru(H_2O)_6]^{3+}$, $\Delta_O = 28,600$ cm^{-1}.

(d) *The nature of the metal centre*: splittings tend to increase down groups. Metal ions may be placed in an approximate order, according to increasing crystal field splitting for a given ligand and complex type: $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Rh^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$. Thus for $[Fe(H_2O)_6]^{3+}$, $\Delta_O = 14,000$ cm^{-1}, but for $[Ru(H_2O)_6]^{3+}$, $\Delta_O = 28,600$ cm^{-1}; and for $[Co(H_2O)_6]^{3+}$, $\Delta_O = 20,760$ cm^{-1}, but for $[Rh(H_2O)_6]^{3+}$, $\Delta_O = 27,200$ cm^{-1}

Figure: 24-31

Title:

Effect of ligand on crystal-field splitting.

Caption:

This series of octahedral chromium(III) complexes illustrates how Δ, the energy gap between the t_2 and e orbitals, increases as the field strength of the ligand increases.

Limitation of Crystal Field Model

Spectrochemical series (strength of ligand interaction)

Weak field

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- < (NH_2)_2C{=}O, OH^-$
$< O_2CCO_2^{2-} < O^{2-} < H_2O < NCS^- < NC_5H_5$ (py) $< NH_3$
$< 2,2'\text{-}NC_5H_5C_5H_5N$ (bpy) $< NO_2^- < CH_3^- < CN^- < CO$

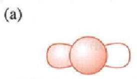
Strong field

- Based on experimental measurements
- Crystal Field Model is an electrostatic model: it is surprising that anionic ligands are weaker-field than neutral ligands.

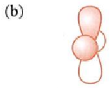
Molecular Orbital Model

Linear combination of atomic/molecular orbitals to generate new orbitals in the complex.

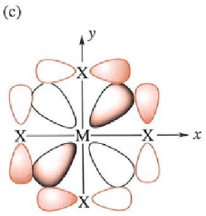
X = O, halogens



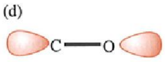
Filled σ-type s and p orbitals on X



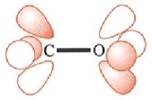
Filled π-type p orbitals on X



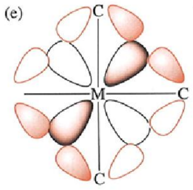
The set of filled donor atom p orbitals in the *xy* plane showing the possibility of overlap with a metal d_{xy} orbital



Filled σ orbitals on CO



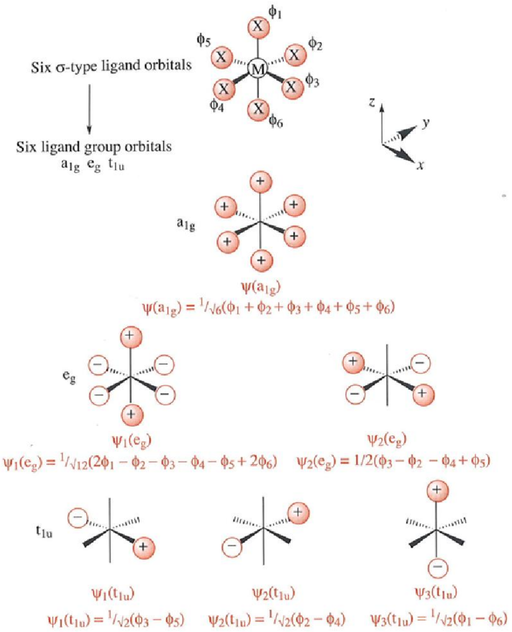
Empty π* orbitals on CO



The set of empty CO carbon atom π* orbitals in the *xy* plane showing the possibility of overlap with a metal d_{xy} orbital

Molecular Orbital Model

Ligand Group Orbitals (LGOs)



$\psi(a_{1g}) = {}^1/\sqrt{6}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$

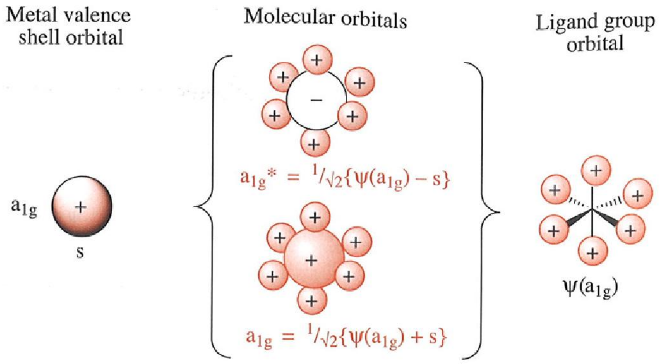
$\psi_1(e_g) = {}^1/\sqrt{12}(2\phi_1 - \phi_2 - \phi_3 - \phi_4 - \phi_5 + 2\phi_6)$ $\psi_2(e_g) = 1/2(\phi_3 - \phi_2 - \phi_4 + \phi_5)$

$\psi_1(t_{1u}) = {}^1/\sqrt{2}(\phi_3 - \phi_5)$ $\psi_2(t_{1u}) = {}^1/\sqrt{2}(\phi_2 - \phi_4)$ $\psi_3(t_{1u}) = {}^1/\sqrt{2}(\phi_1 - \phi_6)$

- Construct, from the six σ-type ligand donor atomic orbitals, six new combination orbitals known as LGOs.
- LGOs must have symmetry allowed by the structure of the molecule.
- In the metal ion, atomic orbitals with the same symmetry are present.

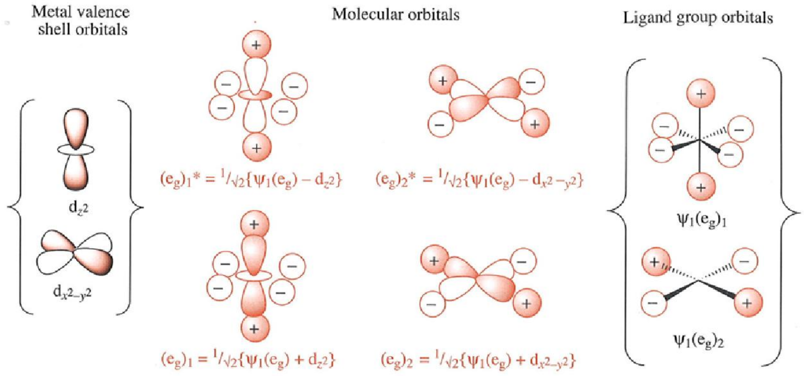
Molecular Orbital Model

Ligand Group Orbitals (LGOs)



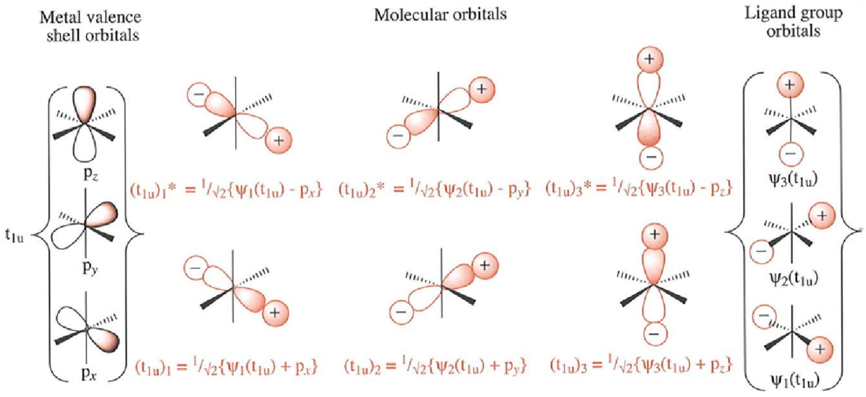
Molecular Orbital Model

Ligand Group Orbitals (LGOs)



Molecular Orbital Model

Ligand Group Orbitals (LGOs)

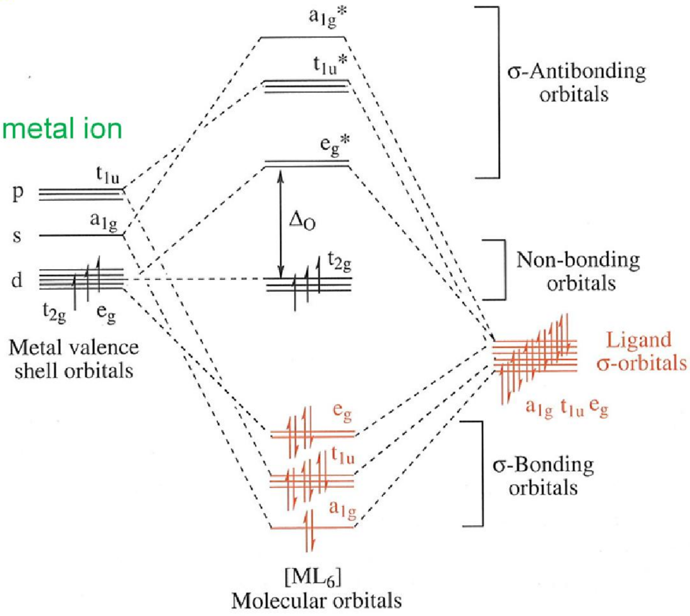


Molecular Orbital Model

σ donor ligands

Metal d^3

Naked metal ion

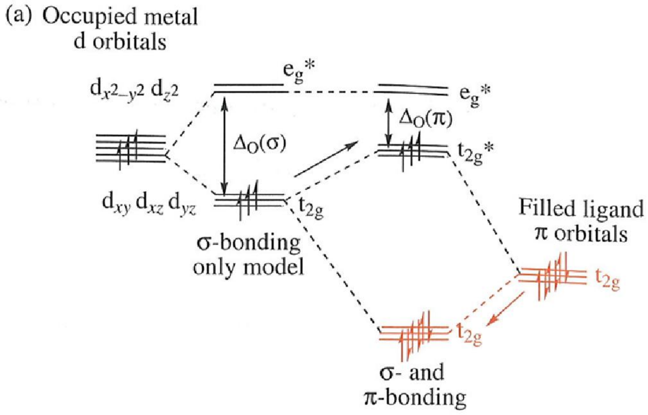


Molecular Orbital Model

σ donor + π donor ligands

Metal d^3

π orbitals of the ligands generate LGOs with t_{2g} symmetry.



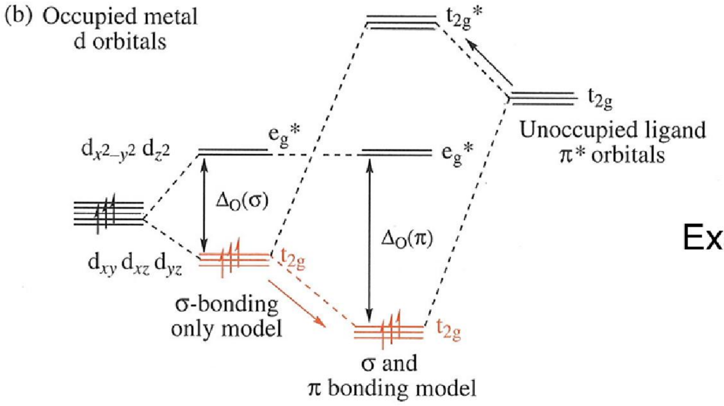
Example: **F^-**

Molecular Orbital Model

σ donor + π acceptor ligands

Metal d^3

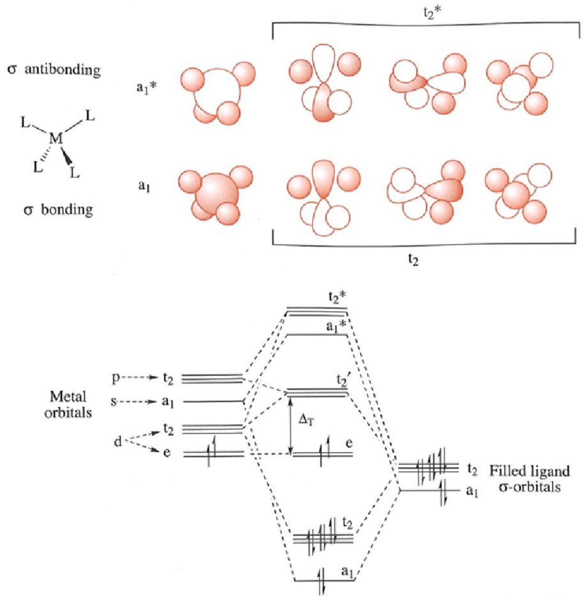
π orbitals of the ligands generate LGOs with t_{2g} symmetry.



Example: **CO, CN^-**

Molecular Orbital Model

Tetrahedral symmetry

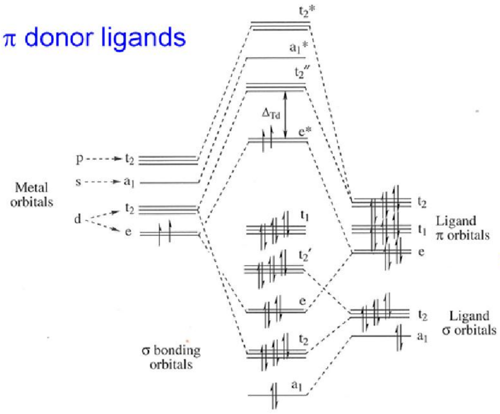


$\Delta_T < \Delta_O$

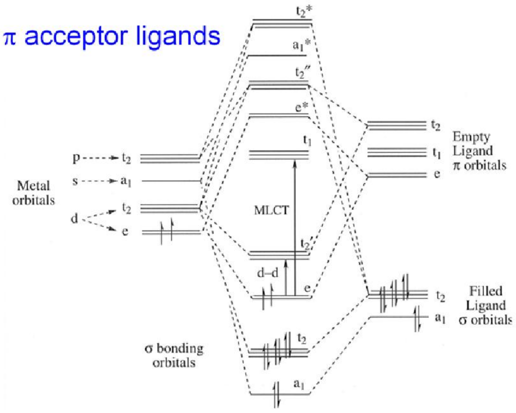
Molecular Orbital Model

Tetrahedral symmetry

π donor ligands



π acceptor ligands



Molecular Orbital Model

Square planar symmetry

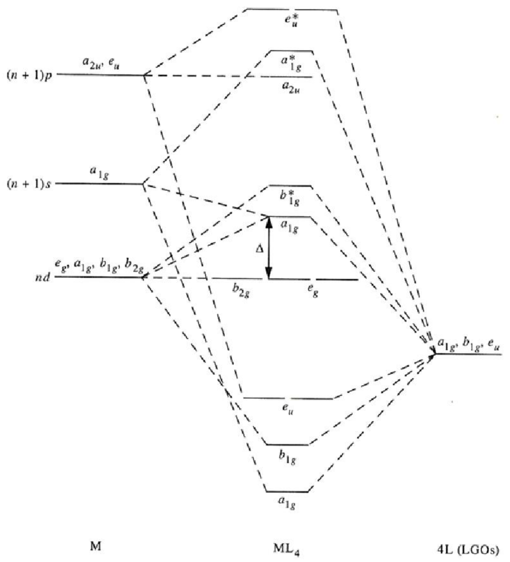
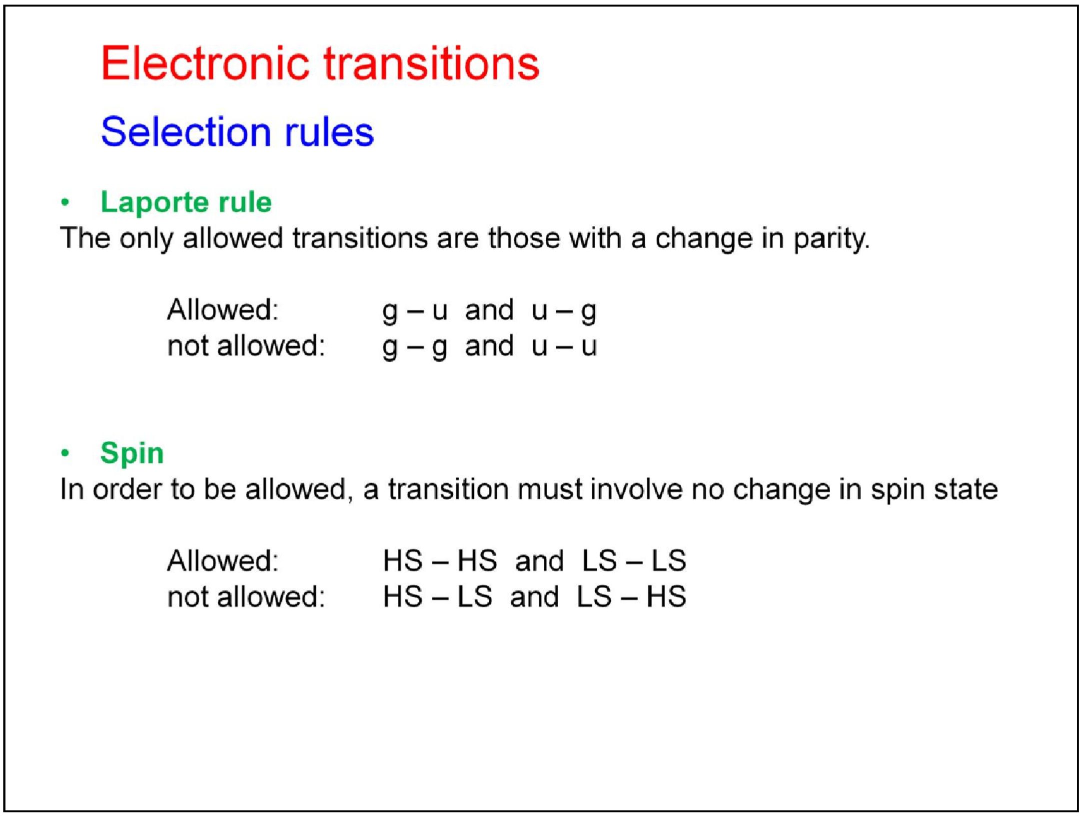


Fig. 11.22 A σ MO diagram for a square planar ML_4 complex (D_{4h} symmetry).



Electronic transitions

Selection rules

- **Laporte rule**

The only allowed transitions are those with a change in parity.

Allowed: g – u and u – g
not allowed: g – g and u – u

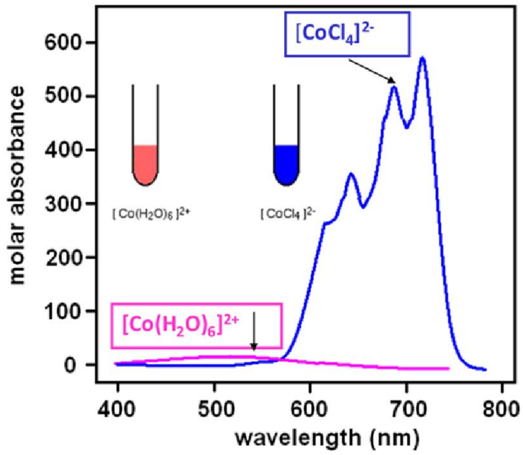
- **Spin**

In order to be allowed, a transition must involve no change in spin state

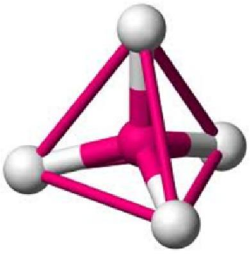
Allowed: HS – HS and LS – LS
not allowed: HS – LS and LS – HS

Electronic transitions

The spectra of octahedral $[Co(H_2O)_6]^{2+}$ and tetrahedral $[CoCl_4]^{2-}$ ions:



Intense d-d bands in the blue tetrahedral complex $[CoCl_4]^{2-}$, as compared with the much weaker band in the pink octahedral complex $[Co(H_2O)_6]^{2+}$. This difference arises because the T_d complex has no center of symmetry, helping to overcome the g→g Laporte selection rule.



Electronic transitions

Relaxation of selection rules

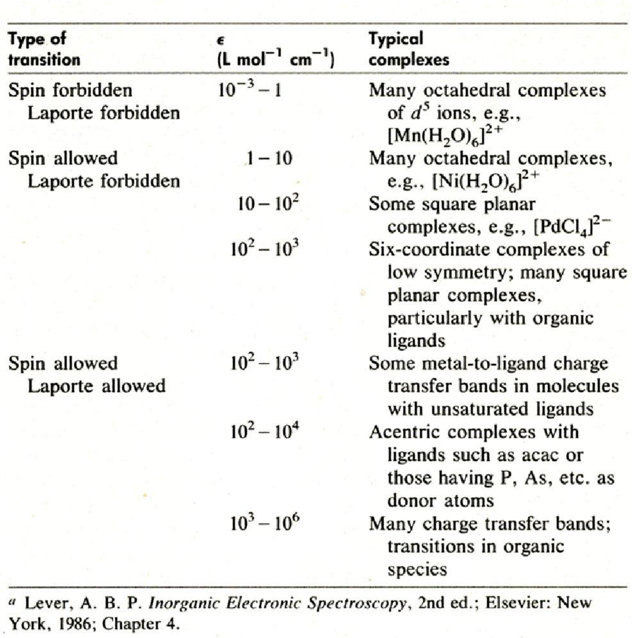
- **Vibronic Coupling:** During some unsymmetrical vibrations of a molecule there an be a temporary/transient loss of the centre of symmetry. Loss of center of symmetry helps to overcome the Laporte selection rule. Also time required for an electronic transition to occur (lifetime 10^{-18} sec) is much less than the time required for a vibration to occur (lifetime 10^{-13} sec).

- **Mixing of states:** The states in a complex are never pure, and so some of the symmetry properties (g or u) of neighboring states become mixed into those of the states involved in a ‘forbidden’ transition. For example mixing of d (gerade) and p (ungerade) orbitals results in partial breakdown of the Laporte rule.

- **Spin orbit coupling:** Partial lifting of the spin selection ruleis possible when there is coupling of the spin and orbital angular momentum, known as the spin-orbit coupling (common in heavier transition metals).

Electronic transitions

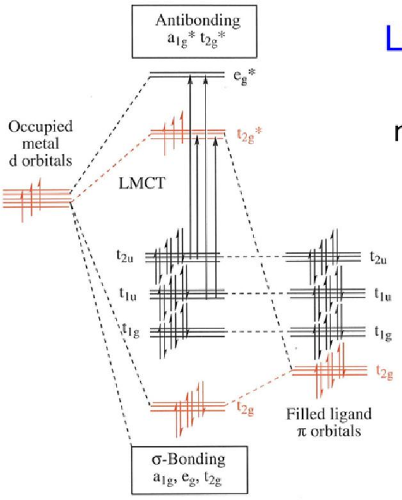
Selection rules



Type of transition	ϵ (L mol^{-1} cm^{-1})	Typical complexes
Spin forbidden Laporte forbidden	$10^{-3}-1$	Many octahedral complexes of d^5 ions, e.g., $[Mn(H_2O)_6]^{2+}$
Spin allowed Laporte forbidden	$1-10$	Many octahedral complexes, e.g., $[Ni(H_2O)_6]^{2+}$
	$10-10^2$	Some square planar complexes, e.g., $[PdCl_4]^{2-}$
	10^2-10^3	Six-coordinate complexes of low symmetry; many square planar complexes, particularly with organic ligands
Spin allowed Laporte allowed	10^2-10^3	Some metal-to-ligand charge transfer bands in molecules with unsaturated ligands
	10^2-10^4	Acentric complexes with ligands such as acac or those having P, As, etc. as donor atoms
	10^3-10^6	Many charge transfer bands; transitions in organic species

[a] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1986; Chapter 4.

Charge transfer

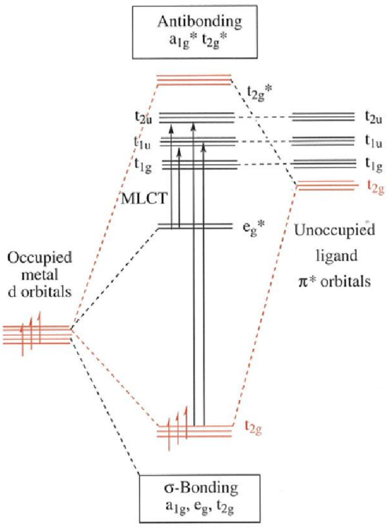


Ligand-to-Metal Charge Transfer

From an orbital that has mainly a metal character to an orbital that has mainly a ligand character.

$PbCrO_4$
$BaCrO_4$

Charge transfer



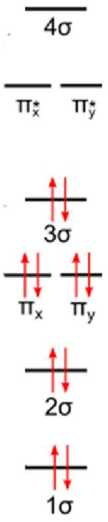
Metal-to-Ligand Charge Transfer

From an orbital that has mainly a ligand character to an orbital that has mainly a metal character.

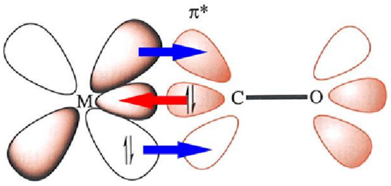
$Fe_4[Fe(CN)_6]_3$

Synergic bonding

CO molecule



σ donation
L to M

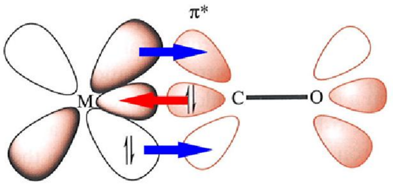


Synergic bonding
filled CO to empty M σ donation
filled M d to empty CO π* back-donation
(for clarity the second out-of-plane
π interaction is not shown)

π back-donation
M to L

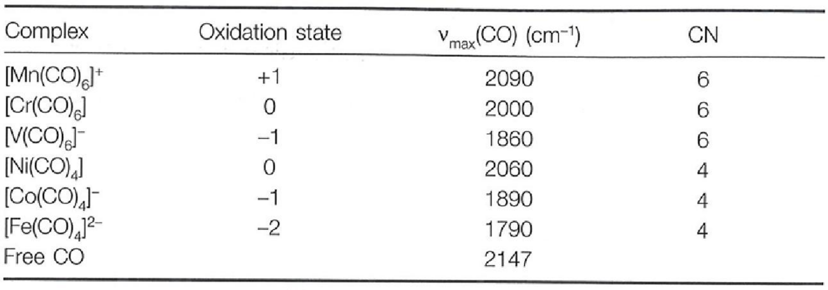
Stable with metals in low oxidation state

Metal carbonyl



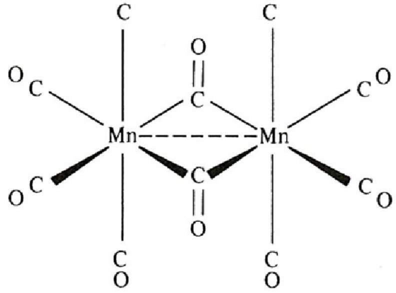
- π back-donation increases electron density in antibonding orbitals of CO
- C-O bond is weaker
- C-O length increases and ν_{CO} decreases

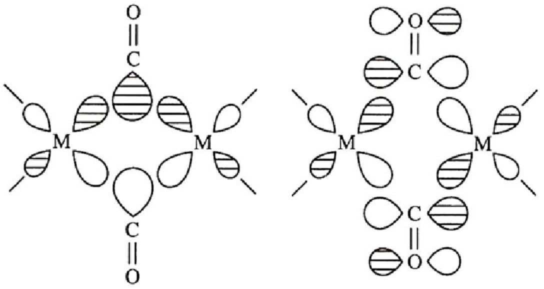
Table 6.1 CO stretching frequencies in some binary metal carbonyls



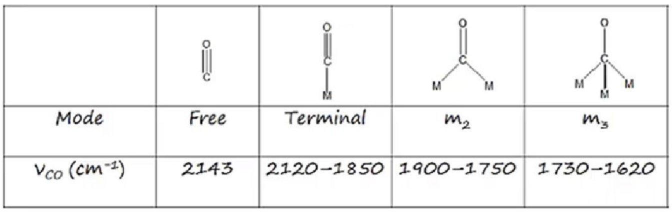
Complex	Oxidation state	ν_{max}(CO) (cm^{-1})	CN
$[Mn(CO)_6]^+$	+1	2090	6
$[Cr(CO)_6]$	0	2000	6
$[V(CO)_6]^-$	−1	1860	6
$[Ni(CO)_4]$	0	2060	4
$[Co(CO)_4]^-$	−1	1890	4
$[Fe(CO)_4]^{2-}$	−2	1790	4
Free CO		2147	

Metal carbonyl clusters

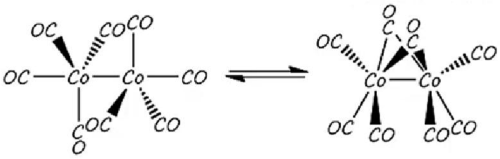




Metal carbonyl clusters



Mode	Free	Terminal	m_2	m_3
ν_{CO} (cm^{-1})	2143	2120–1850	1900–1750	1730–1620

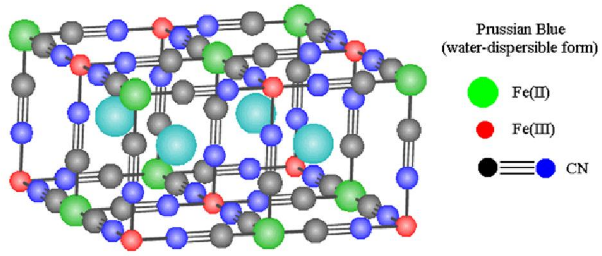


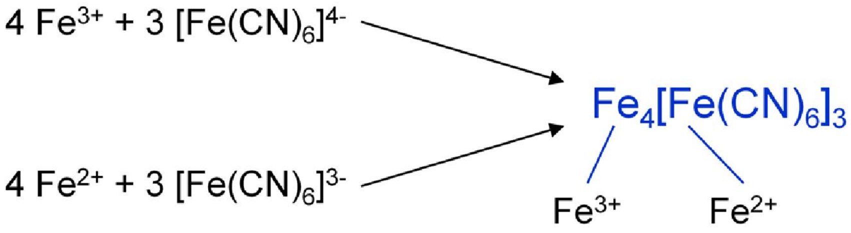
In solution: 2107, 2069, 2042, 2031, 2023, 1991 cm^{-1}

In solid state: 2112, 2071, 2059, 2044, 2031, 2001, 1886, 1857 cm^{-1}

Cyanide complexes

Prussian Blue





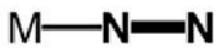
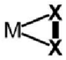
$4\ Fe^{3+} + 3\ [Fe(CN)_6]^{4-}$

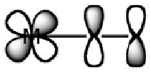
$4\ Fe^{2+} + 3\ [Fe(CN)_6]^{3-}$

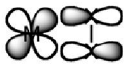
$Fe_4[Fe(CN)_6]_3$

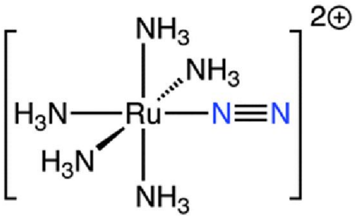
Fe^{3+} Fe^{2+}

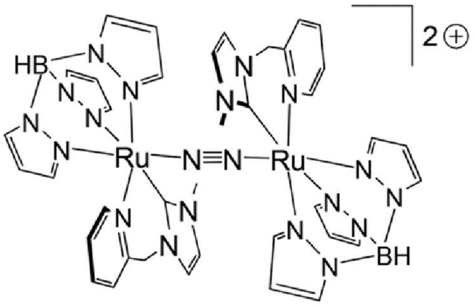
N_2 coordination

	end-on	η^1–X_2
	side-on	η^2–X_2
	end-on/end-on	μ–η^1:η^1–X_2
	side-on/side-on	μ–η^2:η^2–X_2

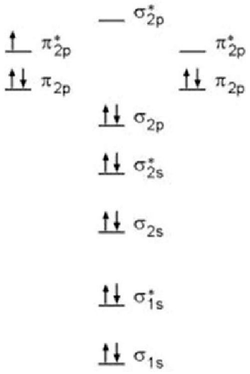
end-on π-interactions: 

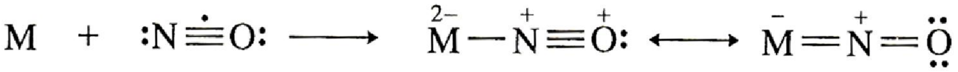
side-on π-interactions: 





NO coordination

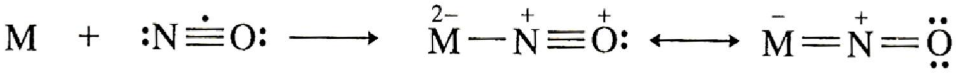




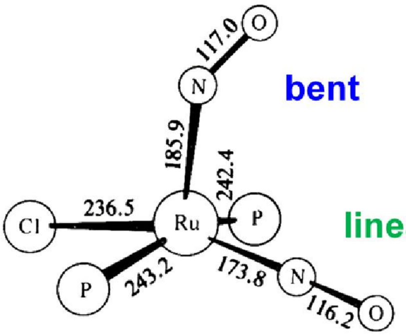
$$\mathrm{M} + :\mathrm{N}\overset{\cdot}{\equiv}\mathrm{O}: \longrightarrow \overset{2-}{\mathrm{M}}-\overset{+}{\mathrm{N}}\equiv\overset{+}{\mathrm{O}}: \longleftrightarrow \overset{-}{\mathrm{M}}=\overset{+}{\mathrm{N}}=\ddot{\underset{\cdot\cdot}{\mathrm{O}}}$$

Coordination by transferring an electron to the metal

NO coordination



$$M + :\dot{N}\equiv O: \longrightarrow \overset{2-}{M}-\overset{+}{N}\equiv\overset{+}{O}: \longleftrightarrow \overset{-}{M}=\overset{+}{N}=\underset{\cdot\cdot}{\ddot{O}}$$



bent

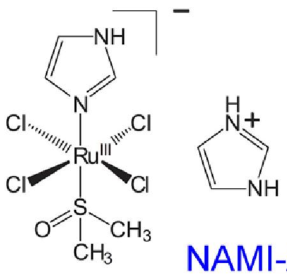
linear

$[Ru(PPh_3)_2(NO)_2Cl]^+$

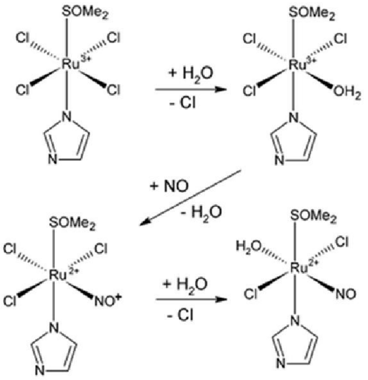
Linear: electron-poor metal (σ donor + π backdonation)

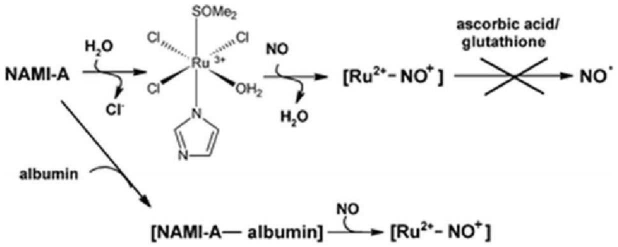
Bent: electron-rich metal (electron in nonbonding orbital, requiring sp^2 hybridization)

NO coordination



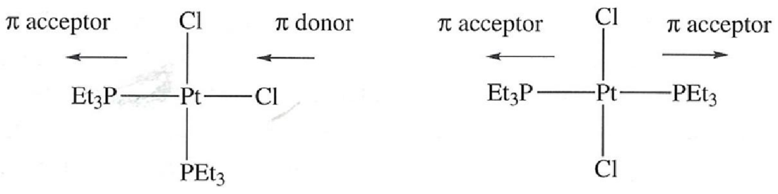
NAMI-A





NAMI-A derivatives coordinate NO stopping cancer growth

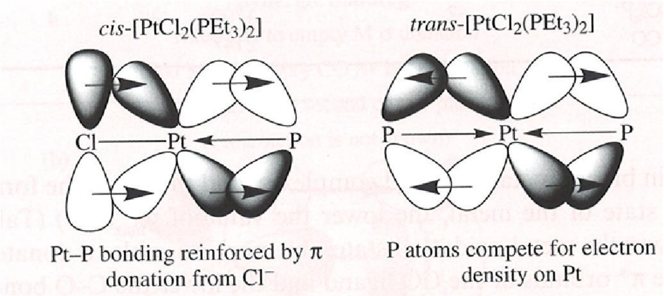
Phosphines coordination



$J(^{195}Pt,^{31}P) = 3520$ Hz

$J(^{195}Pt,^{31}P) = 2400$ Hz

J (Pt, P) depends on the electron density along the Pt-P bond

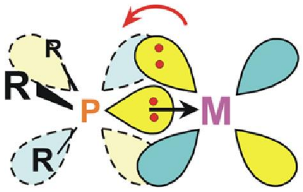


Pt–P bonding reinforced by π donation from Cl$^-$

P atoms compete for electron density on Pt

Phosphines

empty d orbitals on phosphine can act as π-acceptor orbitals } not very important unless R-groups are electron-withdrawing



neutral 2e⁻ donor

Phosphine ligands

excellent soft-donor ligands
with a wide variety of easily adjusted
steric and electronic factors

R = carbon groups

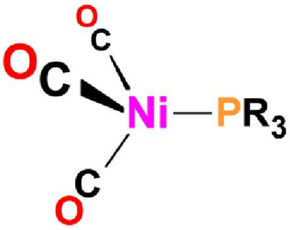
R = OR groups ⟶ phosphite

Phosphines – Electronic vs Cone angle

The electron-donating ability of a phosphine ligand was determined by measuring the ν_{CO} of a $Ni(CO)_3(PR_3)$ complex:

Lowest CO stretching frequency:

most donating phosphine

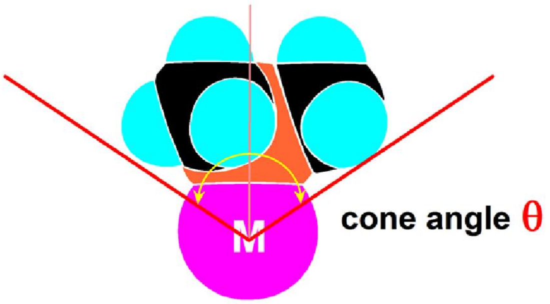


Highest CO stretching frequency:

least donating phosphine

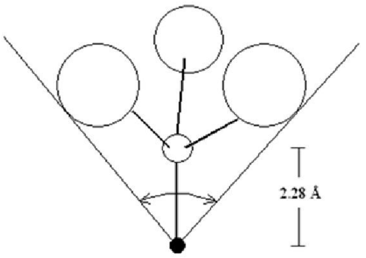
(best π-acceptor)

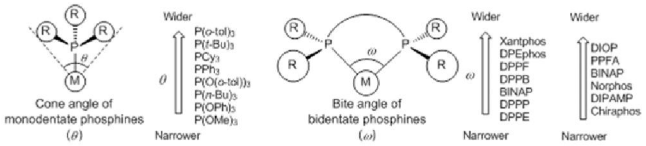
The size or steric bulk of a phosphine ligand was determined from simple 3-D space-filling models of the phosphine ligand coordinated to a Ni atom:



Phosphines – Cone angle

L	θ	L	θ
P(OCH$_2$)$_3$CEt	101	P(*p*-CF$_3$C$_6$H$_4$)$_3$	145
PPhH$_2$	106	PBzlPh$_2$	152
P(OMe)$_3$	107	PCyPh$_2$	153
P(OEt)$_3$	109	P(*i*-Pr)$_3$	160
P(OCH$_2$CH$_2$Cl)$_3$	110	PCy$_2$Ph	162
PMe(OEt)$_2$	112	PBzl$_3$	165
P(CH$_2$CH$_2$CN)$_2$H	117	P(*m*-tol)$_3$	165
PMe$_3$	118	PCy$_3$	170
P(OMe)$_2$Ph	120	P(*t*-Bu)$_2$Ph	170
P(OEt)$_2$Ph	121	P(*t*-Bu)$_3$	182
PMe$_2$Ph	122	NH$_3$	94
PPh$_2$H	126	NH$_2$Me	106
P(OPh)$_3$	128	NH$_2$Et	106
P(O-*i*-Pr)$_3$	130	NH$_2$Ph	111
P(OMe)Ph$_2$	132	NH$_2$Cy	115
PEt$_3$	132	NHMe$_2$	119
PBu$_3$	132	Piperidine	121
P(CH$_2$CH$_2$CN)$_3$	132	NHEt$_2$	125
P(OEt)Ph$_2$	133	NHCy$_2$	133
PMe(*i*-Bu)$_2$	135	NHPh$_2$	136
PEt$_2$Ph	136	NEt$_3$	150
PMePh$_2$	136	NPh$_3$	166
PPh(CH$_2$CH$_2$CN)$_2$	136	NBzl$_3$	210
PEtPh$_2$	140	H	75
P(O-*o*-tol)$_3$	141	Me	90
PPh$_2$(CH$_2$CH$_2$CN)	141	F	92
P(OCy)$_3$	141	CO	95
P(*i*-Bu)$_3$	143	Cl	102
PCy$_2$H	143	Et	102
PPh$_3$	145	Br	105
P(*p*-tol)$_3$	145	Ph	105
P(*p*-MeOC$_6$H$_4$)$_3$	145	I	107
P(*p*-ClC$_6$H$_4$)$_3$	145	*i*-Pr	114
P(*p*-FC$_6$H$_4$)$_3$	145	*t*-Bu	126
P(*p*-Me$_2$NC$_6$H$_4$)$_3$	145		





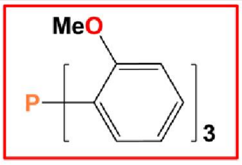
Cone angle of monodentate phosphines (θ)

Bite angle of bidentate phosphines (ω)

Phosphines – Electronic properties

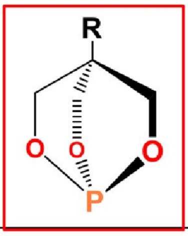
Tolman's Electronic Parameter ν (most donating to least)

PR$_3$	mixed	P(OR)$_3$	PX$_3$	ν, cm^{-1}
P(*t*-Bu)$_3$				2056.1
PCy$_3$				2056.4
P(*o*-OMe-C$_6$H$_4$)$_3$				2058.3
P(*i*-Pr)$_3$				2059.2
PBu$_3$				2060.3
PEt$_3$				2061.7
	PEt$_2$Ph			2063.7
PMe$_3$				2064.1
	PMe$_2$Ph			2065.3
P(*p*-OMe-C$_6$H$_4$)$_3$	PPh$_2$(*o*-OMe-C$_6$H$_4$)			2066.1
PBz$_3$				2066.4
P(*o*-Tol)$_3$				2066.6
P(*p*-Tol)$_3$	PEtPh$_2$			2066.7
	PMePh$_2$			2067.0
P(*m*-Tol)$_3$				2067.2
	PPh$_2$(NMe$_2$)			2067.3
	PPh$_2$(2,4,6-Me-C$_6$H$_2$)			2067.4
	PPhBz$_2$			2067.6
	PPh$_2$(*p*-OMe-C$_6$H$_4$)			2068.2
	PPh$_2$Bz			2068.4
PPh$_3$				**2068.9**



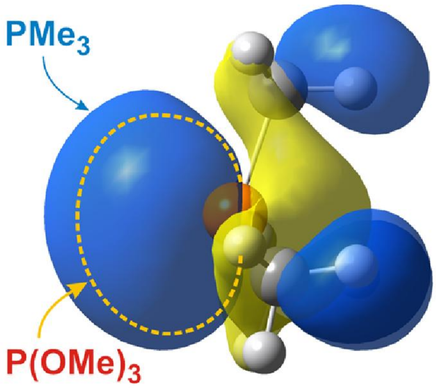
Phosphines – Electronic properties

$P(CH=CH_2)_3$	$PPh_2(p\text{-}F\text{-}C_6H_4)$			2069.5
	$PPh(p\text{-}F\text{-}C_6H_4)_2$			2070.0
$P(p\text{-}F\text{-}C_6H_4)_3$				2071.3
	$PPh_2(OEt)$			2071.6
	$PPh(O\text{-}i\text{-}Pr)_2$			2072.2
$P(p\text{-}Cl\text{-}C_6H_4)_3$				2072.8
	PPh_2H			2073.3
	$PPh(OBu)_2$			2073.4
$P(m\text{-}F\text{-}C_6H_4)_3$				2074.1
	$PPh(OEt)_2$			2074.2
	$PPh_2(C_6F_5)$			2074.8
		$P(O\text{-}i\text{-}Pr)_3$		2075.9
		$P(OEt)_3$		2076.3
	$PPhH_2$			2077.0
		$P(OMe)_3$		2079.5
	$PPh(OPh)_2$			2079.8
		PPh_2Cl		2080.7
		PMe_2CF_3		2080.9
		$P(O\text{-}2,4\text{-}Me\text{-}C_6H_3)_3$	PH_3	2083.2
		$P(OPh)_3$		2085.3
		$P(OCH_2)_3CR$		2086.8
	$P(C_6F_5)_3$			2090.9
			PCl_3	2097.0
			PF_3	2110.8



Phosphines – Electronic properties

PMe_3 vs. $P(OMe)_3$

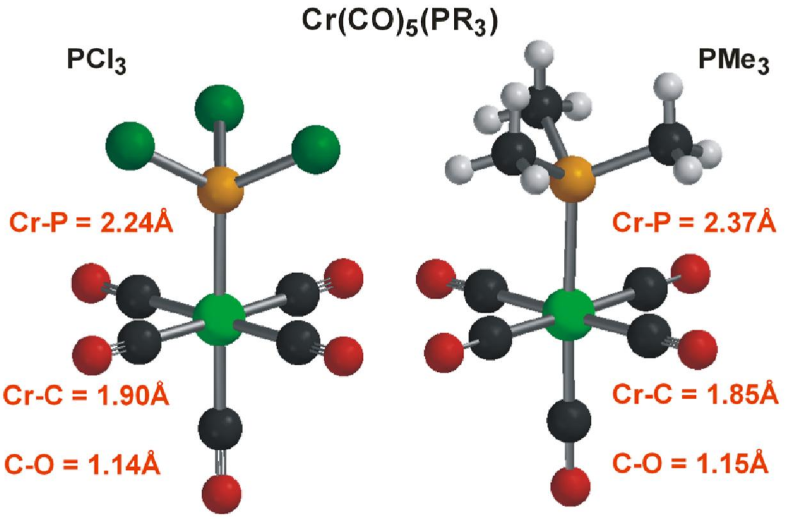


MO plot of the lone pair orbital (HOMO) for PMe_3. Dashed outline indicates the spatial extent of the lone pair for $P(OMe)_3$.

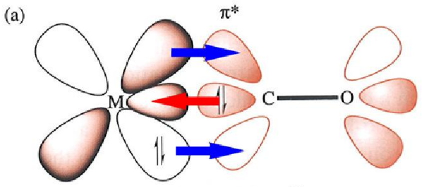
PMe_3
HOMO = –5.03 eV
Charge on P = +0.22

$P(OMe)_3$
HOMO = –7.40 eV
Charge on P = +0.75

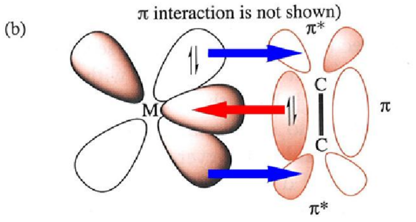
Phosphines


$Cr(CO)_5(PR_3)$
PCl_3
PMe_3
Cr-P = 2.24Å
Cr-C = 1.90Å
C-O = 1.14Å
Cr-P = 2.37Å
Cr-C = 1.85Å
C-O = 1.15Å

Alkenes



Synergic bonding
filled CO to empty M σ donation
filled M d to empty CO π* back-donation
(for clarity the second out-of-plane
π interaction is not shown)

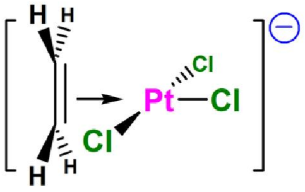


Synergic bonding
C_2H_4 filled π to empty M σ donation
filled M d to empty C_2H_4 π* back-donation

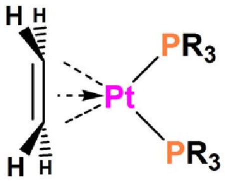
σ donation
L to M

π back-donation
M to L

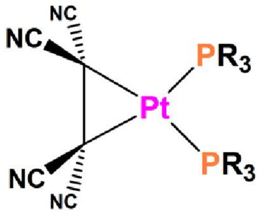
Alkenes



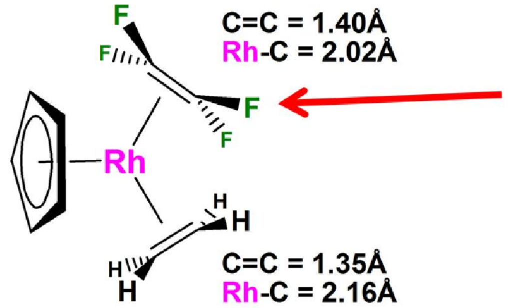
Pt(2+)
C=C = 1.37Å
Zeiss's Salt



Pt(0)
C=C = 1.43Å



Pt(+2)
C--C = 1.49Å
metallocyclopropane



C=C = 1.40Å
Rh-C = 2.02Å

C=C = 1.35Å
Rh-C = 2.16Å

The electron-withdrawing fluorine groups on the $F_2C=CF_2$ alkene makes it a better π-acceptor ligand. This *weakens* the C=C bond, but ***strengthens*** the alkene-metal bond.

Alkenes

Electronic Effects

π acceptor

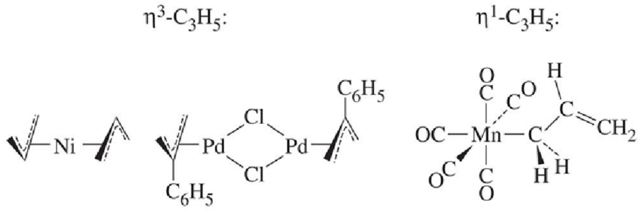
Ethylene Complex	νC=C (cm^{-1})
Free Ethylene	1623
$[Ag(H_2C{=}CH_2)_2]^+$	1584
$Fe(CO)_4(H_2C{=}CH_2)$	1551
$[Re(CO)_4(H_2C{=}CH_2)_2]^+$	1539
$[CpFe(CO)_2(H_2C{=}CH_2)]^+$	1527
$Pd_2Cl_4(H_2C{=}CH_2)_2$	1525
$[PtCl_3(H_2C{=}CH_2)]^-$	1516
$CpMn(CO)_2(H_2C{=}CH_2)$	1508
$Pt_2Cl_4(H_2C{=}CH_2)_2$	1506
$CpRh(H_2C{=}CH_2)_2$	1493

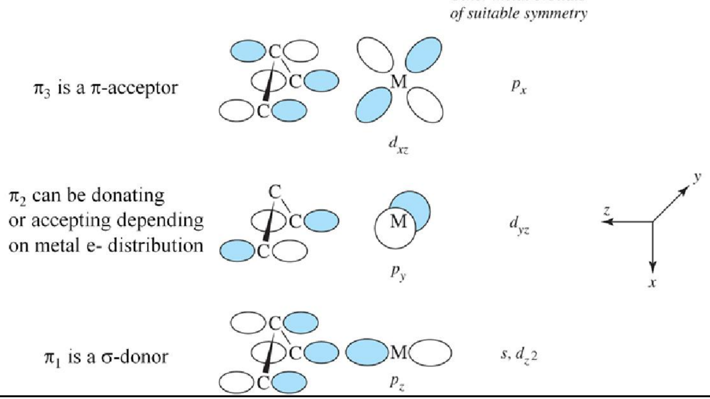
σ and π donor

Alkenes

π-Allyl Complexes

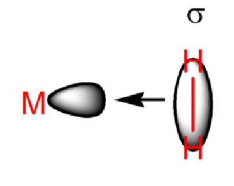
- Can be trihapto: both σ- and π-bonding
- Can be monohapto: σ-bonding only from sp^2 hybrid orbital (120° bond angle)



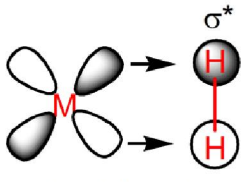


H_2

- $M(H_2)$ = a type of σ-complex
- ν(H-H) = 2300-2900 cm^{-1} but often weak
- ^{1}H NMR = 0 to -10 ppm (often broad)



σ-donation



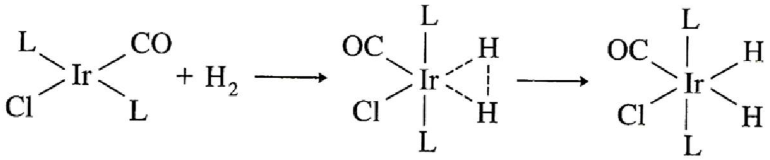
π-backdonation

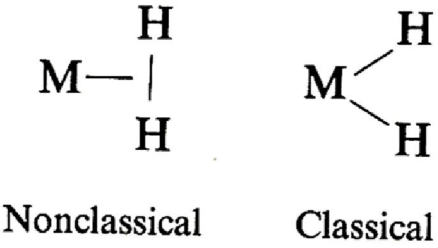
- Both interactions weaken the H-H bond

- Typical H-H distances in M-(H_2) complexes are 84-90 pm (*vs* 74 pm in free H_2)

H_2

Metals capable of strong π-backdonation and with an accessible oxidation state 2 units higher (e.g. $Ir^{I} \rightarrow Ir^{III}$) can break the H-H bond to give a dihydride.





H_2

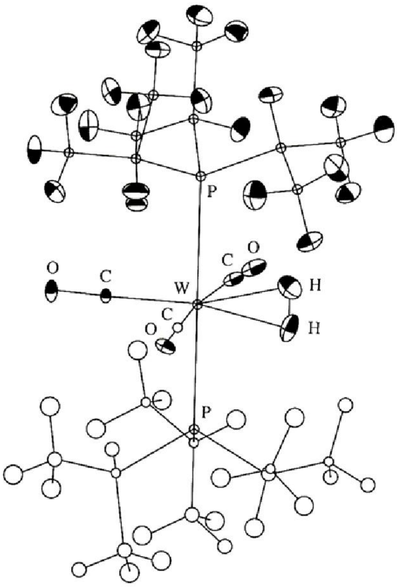
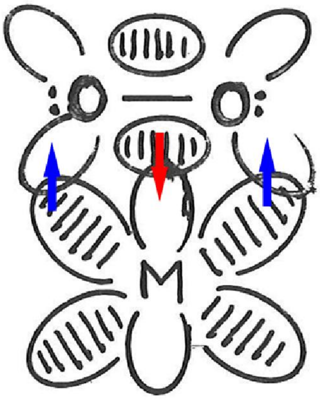
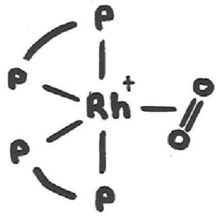


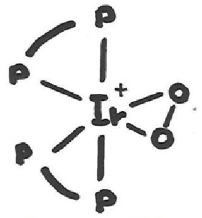
Fig. 15.11 Structure of $Mo(CO)_3(PPr^i_3)_2H_2$, the first nonclassical dihydrogen complex to be discovered. [From Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128. Reproduced with permission.]

O_2





Reversible
O – O = 1.42 Å



Irreversible
O – O = 1.52 Å

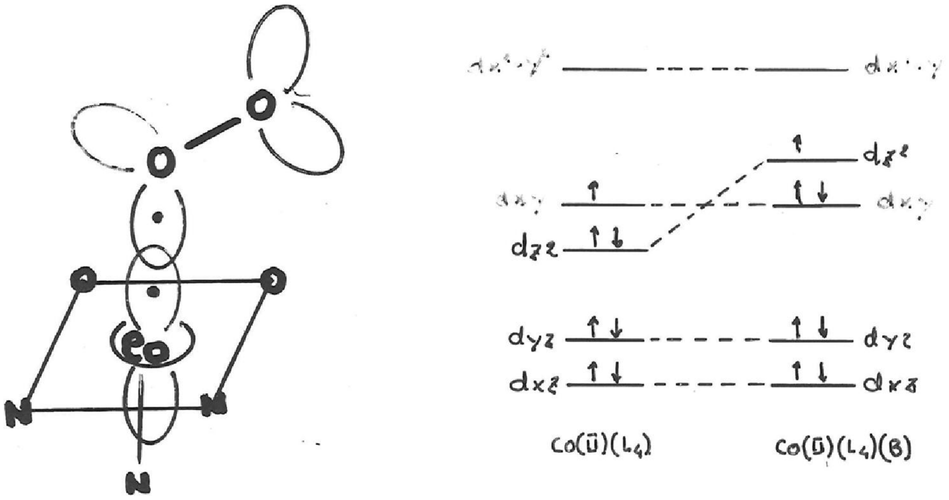
O_2

$\text{Co(II)(acac)}_2\text{en} + O_2 \not\longrightarrow$

paramagn.

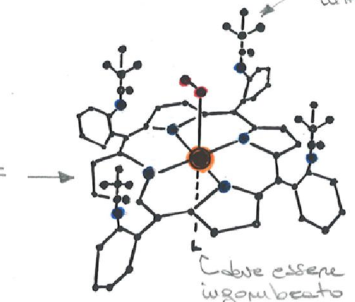
$\text{Co(acac)}_2\text{en Py} + O_2 \rightleftharpoons \text{Co(acac)}_2\text{en Py}(O_2)$

paramagn. paramagn.



O_2

$$2\left[\mathrm{Fe}^{II}(\mathrm{Por})(\mathrm{B})_2\right] + \tfrac{1}{2}\mathrm{O}_2 \longrightarrow \left[(\mathrm{Por})\mathrm{Fe}^{III}-\mathrm{O}-\mathrm{Fe}^{III}(\mathrm{Por})\right] + 4\mathrm{B}$$



gruppi stericamente ingombranti tutti dalla stessa parte.

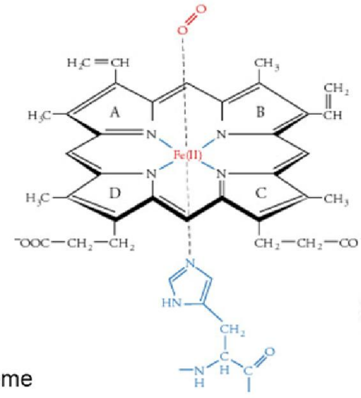
Si forma una cavità in cui si lega O_2 ma non riesce ad avvicinarsi altro Fe(II) per dare Fe(III).

Formazione reversibile

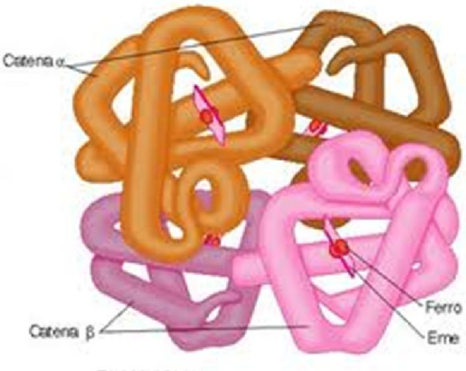
L deve essere stericamente molto ingombrato per non occupare il posto di O_2.

picket-fence porphyrin.

O_2



Gruppo eme



Emoglobina