C1403 Lecture 19 Monday, November 14, 2005

Chapter 19 **Coordination Complexes**

19.1	The Formation of Coordination Complexes
19.2	Structures of Coordination Complexes
19.3	Crystal-Field Theory and Magnetic Properties
19.4	The Colors of Coordination Complexes
19.5	Coordination Complexes in Biology

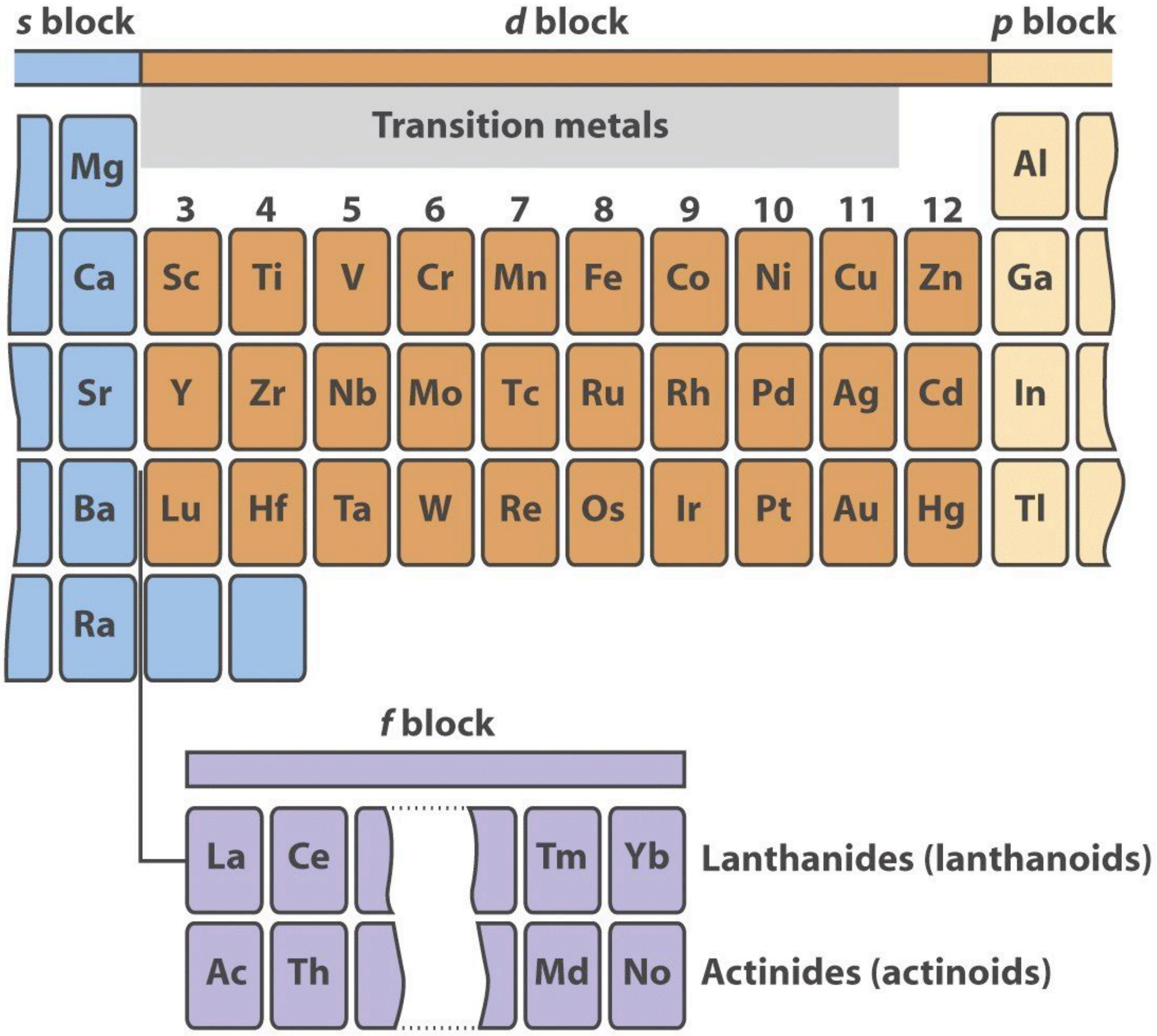
Chapter 24 **From Petroleum to Pharmaceuticals**

24.1	Petroleum Refining and the Hydrocarbons
24.2	Functional Groups and Organic Synthesis
24.3	Pesticides and Pharmaceuticals

Chapter 25 **Synthetic and Biological Polymers**

25.1	Making Polymers
25.2	Biopolymers
25.3	Uses for Polymers

The d block metal for coordination complexes with molecules and ions



19.1 Coordination complexes

The electronic basis of the color of metal complexes

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Coordination complex: A structure containing a **metal** (usually a metal ion) bonded (coordinated) to a group of surrounding **molecules or ions**.

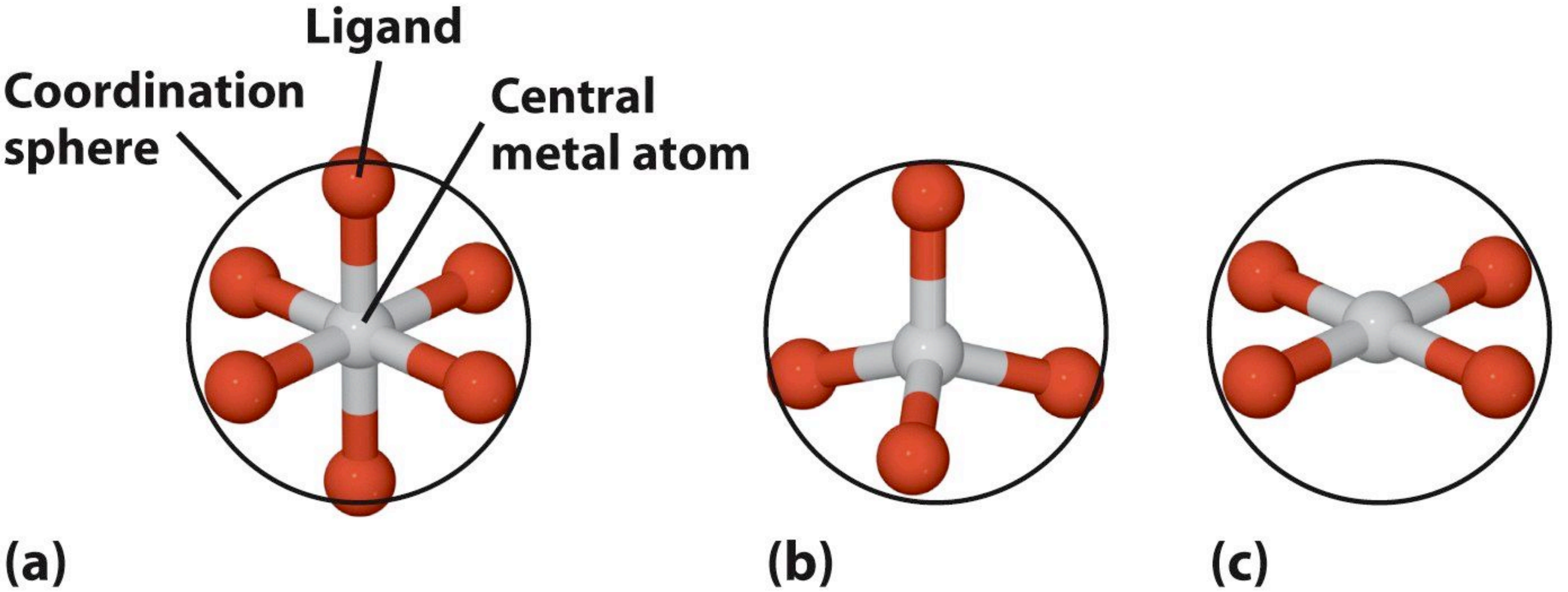
Ligand (ligare is Latin, to bind): A ligand is a molecule or ion that is directly bonded to a metal ion in a coordination complex

A ligand uses a **lone pair of electrons** (Lewis base) to bond to the metal ion (Lewis acid)

Coordination sphere: A metal and its surrounding ligands

Note: religare is Latin, to bind tightly

Complex ions: Three common structural types



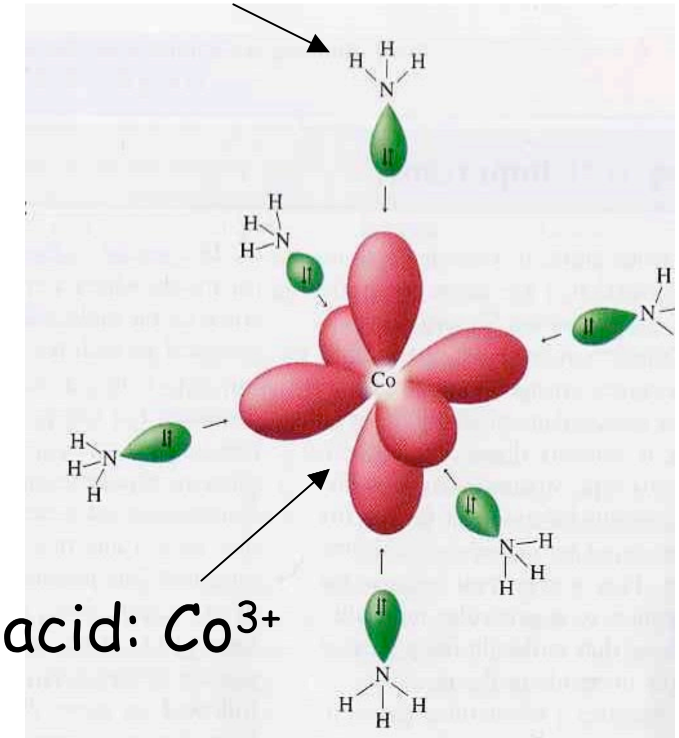
Octahedral:
Most important

Tetrahedral

Square planar

The formation of a coordinate complex is a ***Lewis acid-base*** reaction

Lewis base: $:NH_3$



Lewis acid: Co^{3+}

Coordination complex:
Lewis base coordinated
to a Lewis acid

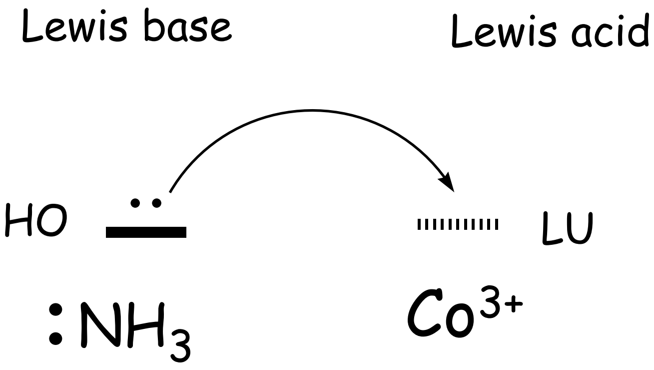
Coordination complex:
Ligand (electron donor)
coordinated to a metal
(electron acceptor)

The number of ligand bonds to the central metal atom is termed the coordination number

The basic idea is that the ligand (Lewis base) is providing electron density to the metal (Lewis acid)

The bond from ligand to metal is covalent (shared pair), but both electrons come from the ligand (coordinate covanent bond)

In terms of MO theory we visualize the coordination as the transfer of electrons from the HO of the Lewis base to the LU of the Lewis acid



Lewis base

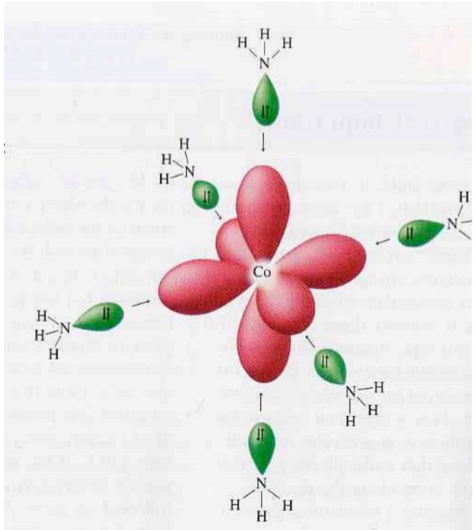
Lewis acid

HO

LU

$:NH_3$

Co^{3+}



Types of Ligands: Monodentate (one tooth) Ligands

Latin: “mono” meaning one and “dens” meaning tooth

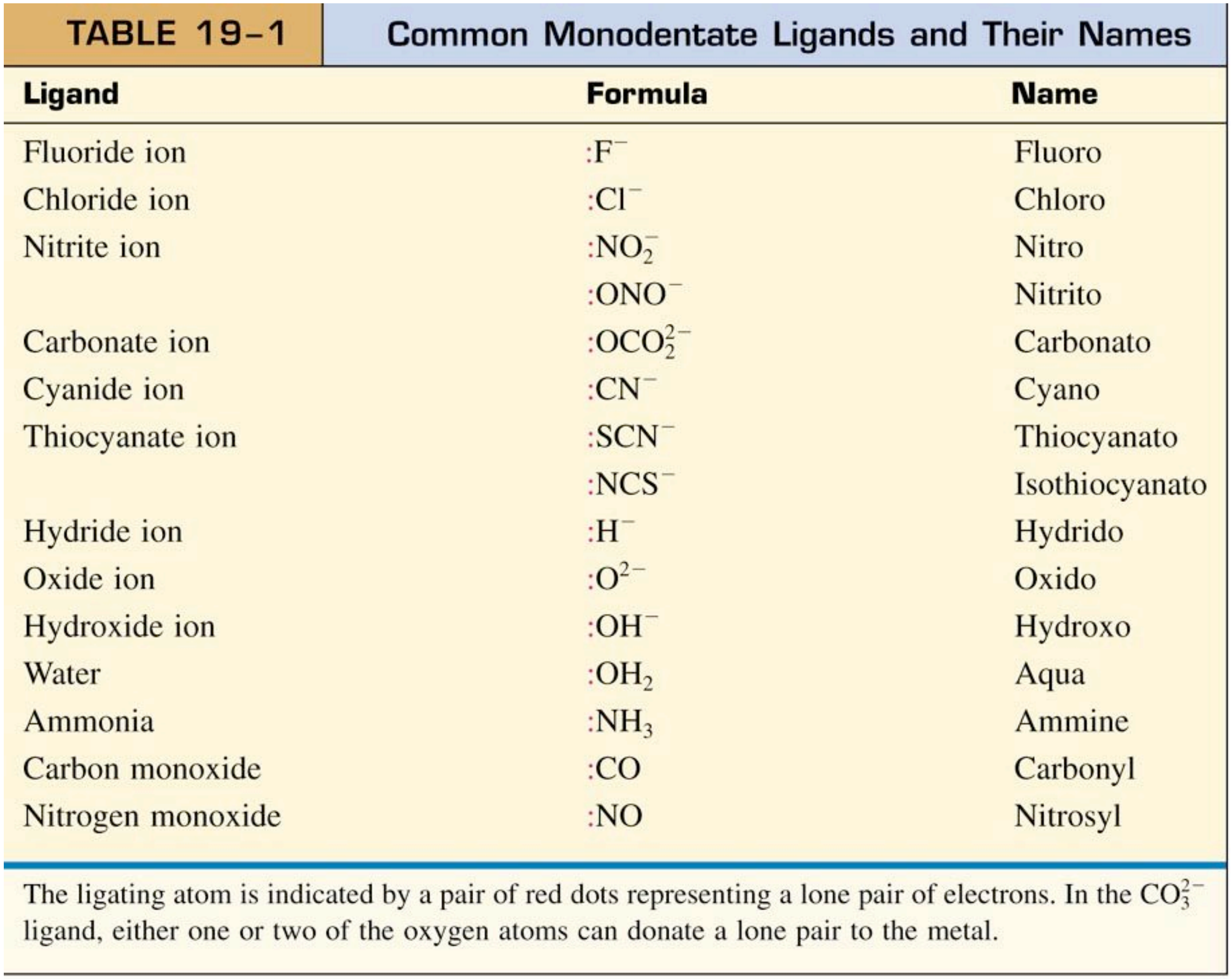


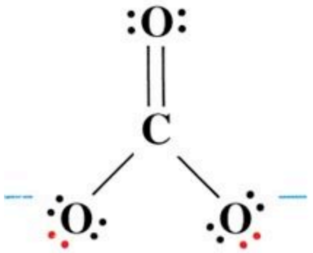
TABLE 19–1 Common Monodentate Ligands and Their Names

Ligand	Formula	Name
Fluoride ion	$:F^-$	Fluoro
Chloride ion	$:Cl^-$	Chloro
Nitrite ion	$:NO_2^-$	Nitro
	$:ONO^-$	Nitrito
Carbonate ion	$:OCO_2^{2-}$	Carbonato
Cyanide ion	$:CN^-$	Cyano
Thiocyanate ion	$:SCN^-$	Thiocyanato
	$:NCS^-$	Isothiocyanato
Hydride ion	$:H^-$	Hydrido
Oxide ion	$:O^{2-}$	Oxido
Hydroxide ion	$:OH^-$	Hydroxo
Water	$:OH_2$	Aqua
Ammonia	$:NH_3$	Ammine
Carbon monoxide	$:CO$	Carbonyl
Nitrogen monoxide	$:NO$	Nitrosyl

The ligating atom is indicated by a pair of red dots representing a lone pair of electrons. In the CO_3^{2-} ligand, either one or two of the oxygen atoms can donate a lone pair to the metal.

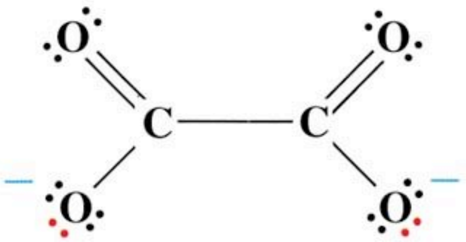
Types of Ligands: Bidentate (two tooth) Ligands

Bidentate (chelates):



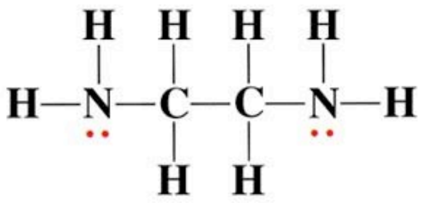
Carbonate ion, CO_3^{2-}

(a)



Oxalate ion, $C_2O_4^{2-}$

(b)

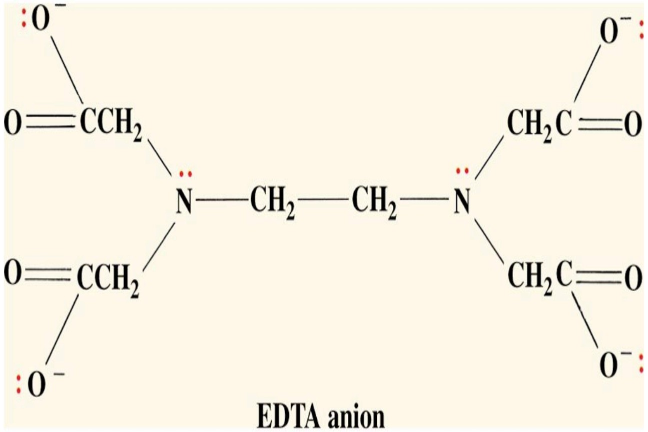


Ethylenediamine, $NH_2\,CH_2\,CH_2\,NH_2$

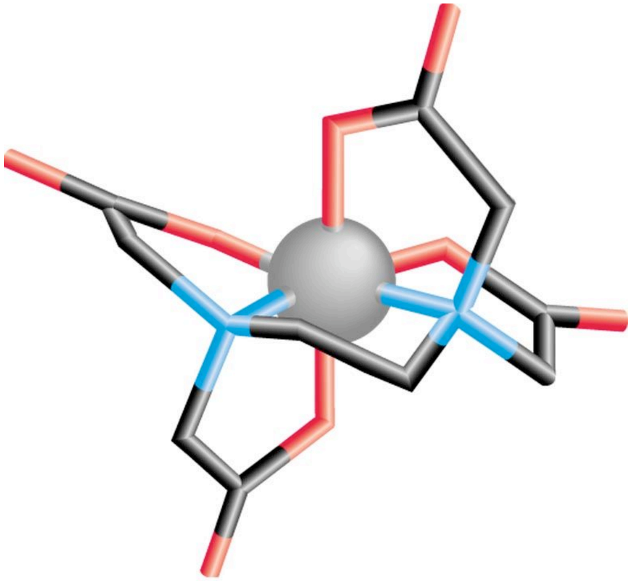
(c)

Types of Ligands: Ethylenediaminetetraacetate ion (EDTA): a polydentate chelating ligand

Chelate from
Greek *chela*, "claw"



EDTA anion



EDTA wraps around the metal ion at all 6 coordination sites producing an exceedingly tight binding to the metal

Alfred Werner: the father of the structure of coordination complexes

Alfred Werner
Switzerland
University of Zurich
Zurich, Switzerland
b. 1866
(in Mulhouse, then Germany)
d. 1919

The Nobel Prize in Chemistry 1913
"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry"

Lewis acids and bases

A Lewis base is a molecule or ion that donates a lone pair of electrons to make a bond

Examples: $:NH_3$ $:OH_2$ $:Cl^-$ $:F^-$

Electrons in the highest occupied orbital (HO) of a molecule or anion are the best Lewis bases

A Lewis acid is a molecule of ion that accepts a lone pair of electrons to make a bond

Examples: H^+ Co^{3+} Co^{2+} M^{n+}

Molecules or ions with a low lying unoccupied orbital (LU) of a molecule or cation are the best Lewis acids

Conventions in writing the structure of coordination compounds:

A coordination compounds is a neutral species consisting of a coordinate complex and uncoordinated ions required to maintain the charge balance

Brackets [] are used to indicate all of the composition of the coordinate complex

The symbol for the central atom metal of the complex is first within the brackets

Species outside of the [] are not coordinated to the metal but are require to maintain a charge balance

Ligand substitution reactions

For some complex ions, the coordinated ligands may be substituted for other ligands

Complexes that undergo very rapid substitution of one ligand for another are termed *labile*

Complexes that undergo very slow substitution of one ligand for another are termed *inert*

$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6\ H_2O$ (aqueous)

Werner's explanation of coordination complexes

Metal ions exhibit two kinds of valence: primary and secondary valences

The primary valence is the oxidation number (positive charge) of the metal (usually 2+ or 3+)

The secondary valence is the number of atoms that are directly bonded (coordinated) to the metal

The secondary valence is also termed the "coordination number" of the metal in a coordination complex

Example of a coordination complex: $[Co(NH_3)_6]Cl_3$

What is the atomic composition of the complex?	$[Co(NH_3)_6]$
What is the net charge of the complex?	$[Co(NH_3)_6]^{3+}$
How do we know the charge is 3+ on the metal?	3+ is required to balance the three Cl^- ions

The primary valence of $[Co(NH_3)_6]Cl_3$ is 3 (charge on Co)
The secondary valence of $[Co(NH_3)_6]Cl_3$ is 6 (ligands)

19.2 Structures of Coordination Complexes: The ammonia complexes of Co(III) = Co^{3+}

How did Werner deduce the structure of coordination complexes?

Composition	Ions released	Color
$CoCl_3 \cdot 6NH_3$	3 “free” Cl^- ions	Orange-Yellow
$CoCl_3 \cdot 5NH_3$	2 “free” Cl^- ions	Purple
$CoCl_3 \cdot 4NH_3$	1 “free” Cl^- ions	Green
$CoCl_3 \cdot 3NH_3$	0 “free” Cl^- ions	Green

In all of these complexes there is no free NH_3
(No reaction with acid)

Logic: Cl^- is not in coordination sphere; NH_3 is in sphere

Compound 1: $CoCl_3 \cdot 6NH_3 = [Co(NH_3)_6]^{3+}(Cl^-)_3 = [Co(NH_3)_6](Cl)_3$

Conclude: 3 free Cl^- ions, $[Co(NH_3)_6]^{3+}$

Compound 2: $CoCl_3 \cdot 5NH_3 = [Co(NH_3)_5Cl]^{2+}(Cl^-)_2 = [Co(NH_3)_5Cl](Cl)_2$

Conclude: 2 free Cl^- ions, $[Co(NH_3)_5Cl]^{2+}$

Compound 3: $CoCl_3 \cdot 4NH_3 = [Co(NH_3)_4Cl_2]^{1+}(Cl^-) = [Co(NH_3)_4Cl_2](Cl)$

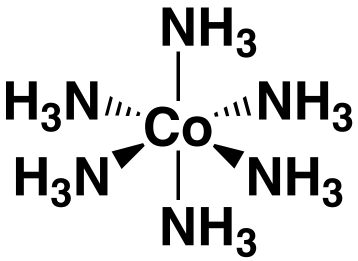
Conclude: 1 free Cl^- ion, $[Co(NH_3)_4Cl_2]^{1+}$

Compound 4: $CoCl_3 \cdot 3NH_3 = [Co(NH_3)_3Cl_3]$

No free Cl^- ions

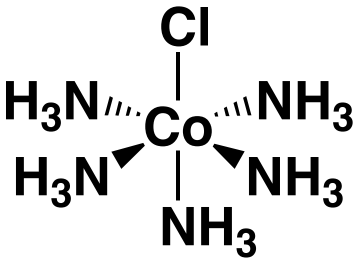
Coordination complexes: Three dimensional structures

$CoCl_3 \cdot 6NH_3$



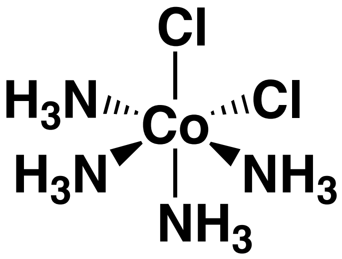
Cl^- Cl^- Cl^-

$CoCl_3 \cdot 5NH_3$

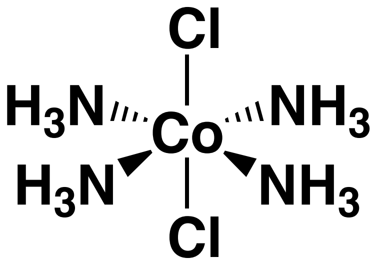


Cl^- Cl^-

$CoCl_3 \cdot 4NH_3$

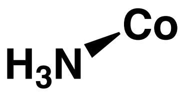


Cl^-



Cl^-

Isomers!

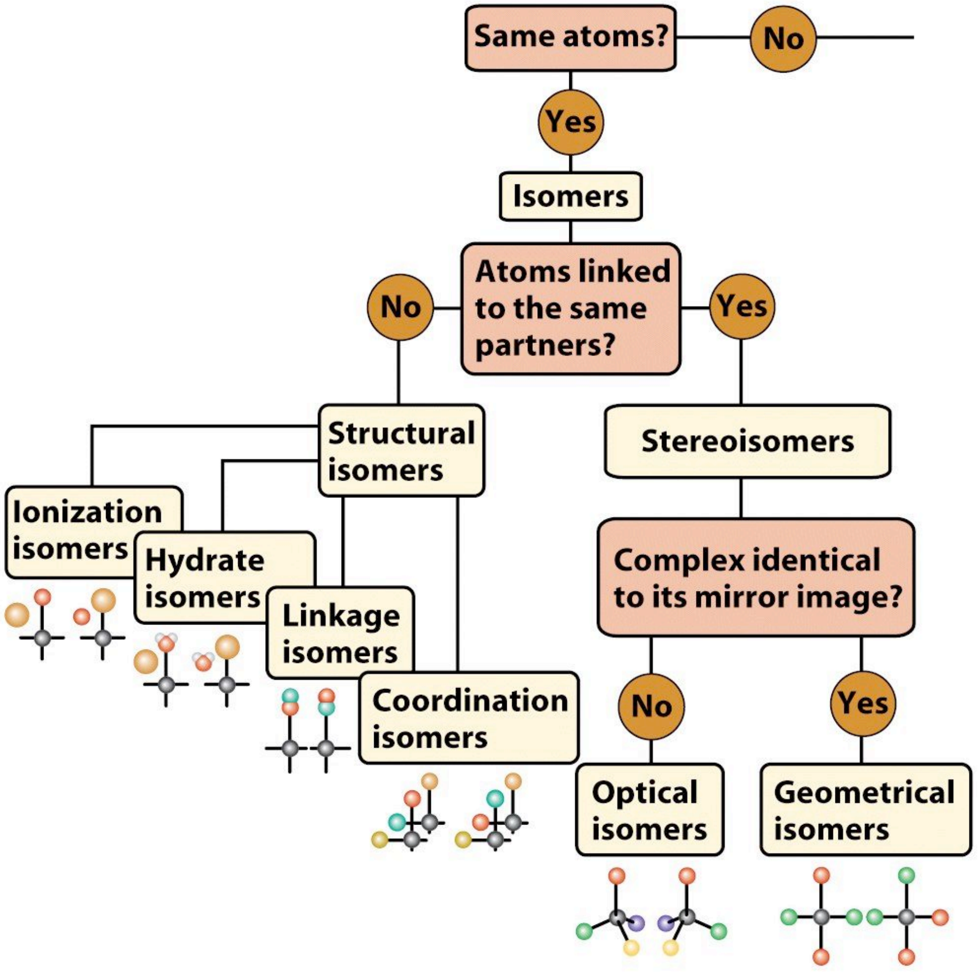


Bond toward you

Bond away from you

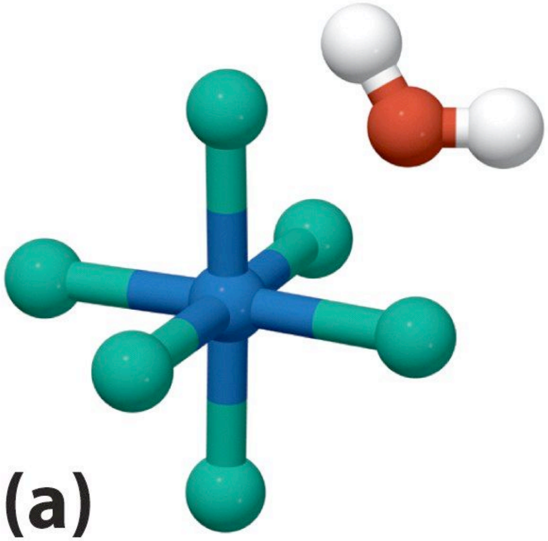
Coordination complexes: isomers

Isomers: same atomic composition, different structures

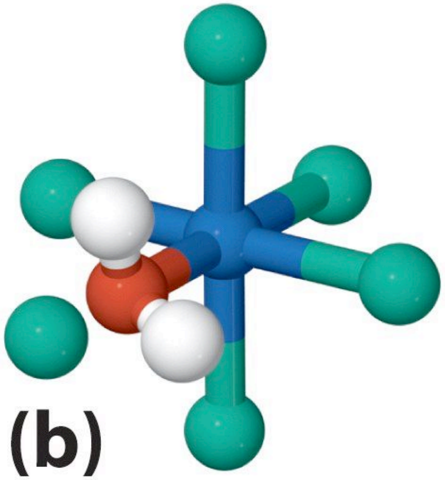


We'll discuss the following types of isomers:
Hydrate
Linkage
Cis-trans
Optical (Enantiomers)

Hydrate isomers:


(a)

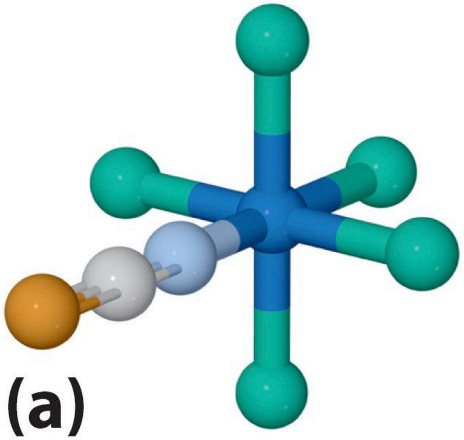
Water in outer sphere (water that is part of solvent)


(b)

Water in the inner sphere water (water is a ligand in the coordination sphere of the metal)

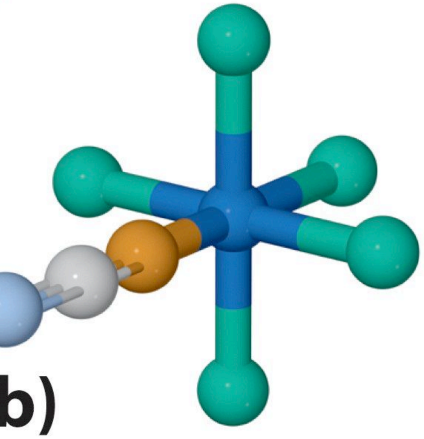
Linkage isomers

Example: ⊖S—C≡N Bonding to metal may occur at the S or the N atom



(a)

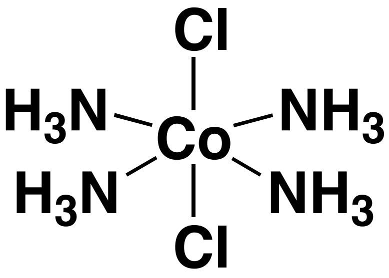
Bonding occurs from N atom to metal



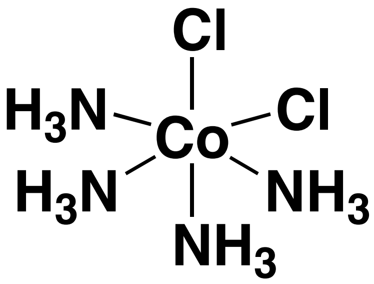
(b)

Bonding occurs from S atom to metal

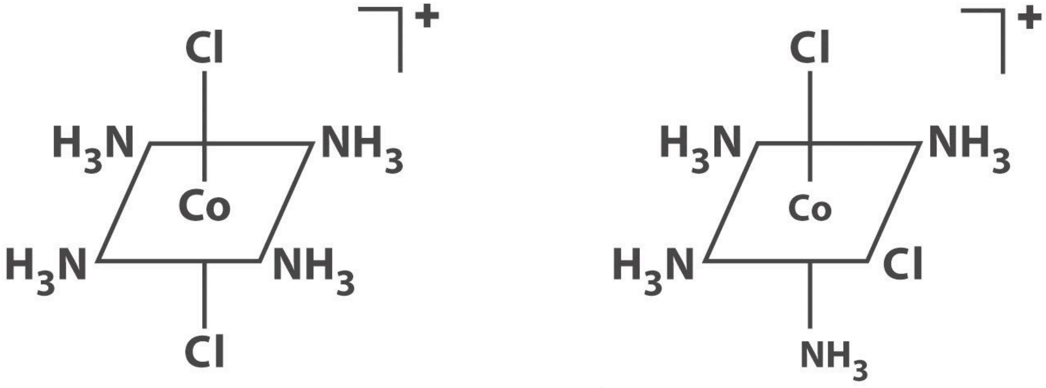
Stereoisomers: geometric isomers (cis and trans)



Cl^-



Cl^-



(a) *trans*-$[CoCl_2(NH_3)_4]^+$ (b) *cis*-$[CoCl_2(NH_3)_4]^+$

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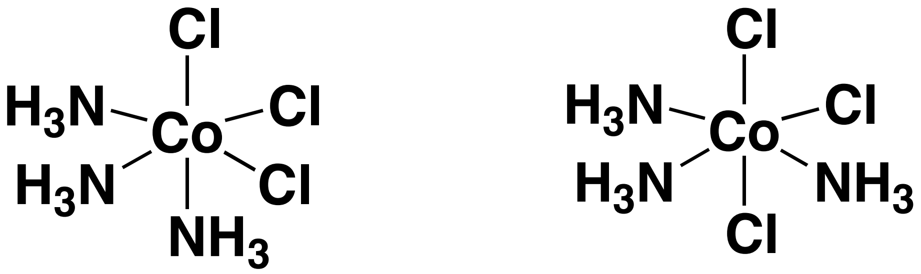
Cis-trans isomers and beyond

Beyond cis and trans isomers

$CoCl_3 \cdot 3NH_3$



Optical isomers: enantiomers

Enantiomers are mirror images which are **not** superimposable

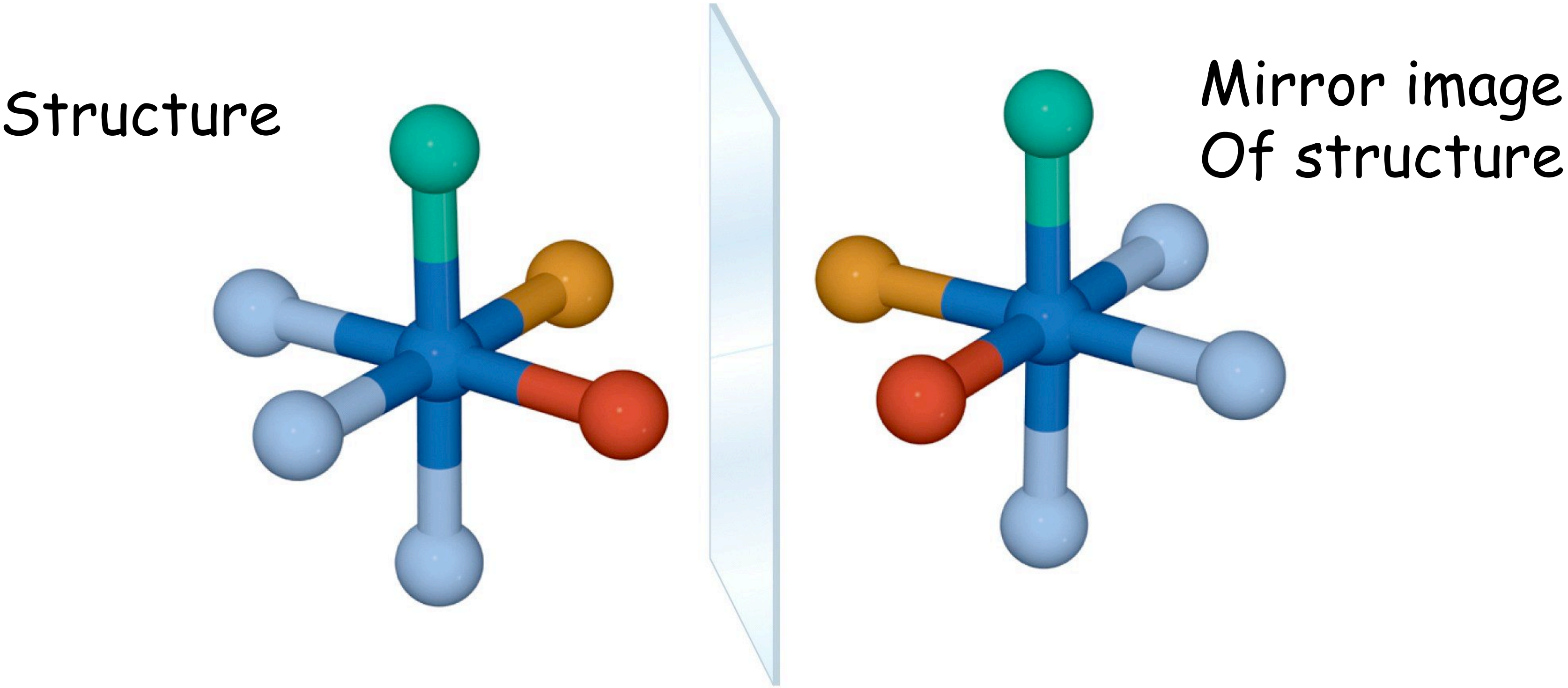
Enantiomers do not have a plane of symmetry

Any molecule which possesses a plane of symmetry is superimposable on its mirror image

Enantiomers rotate polarized light in different directions; therefore, enanotiomers are also termed "optical isomers"

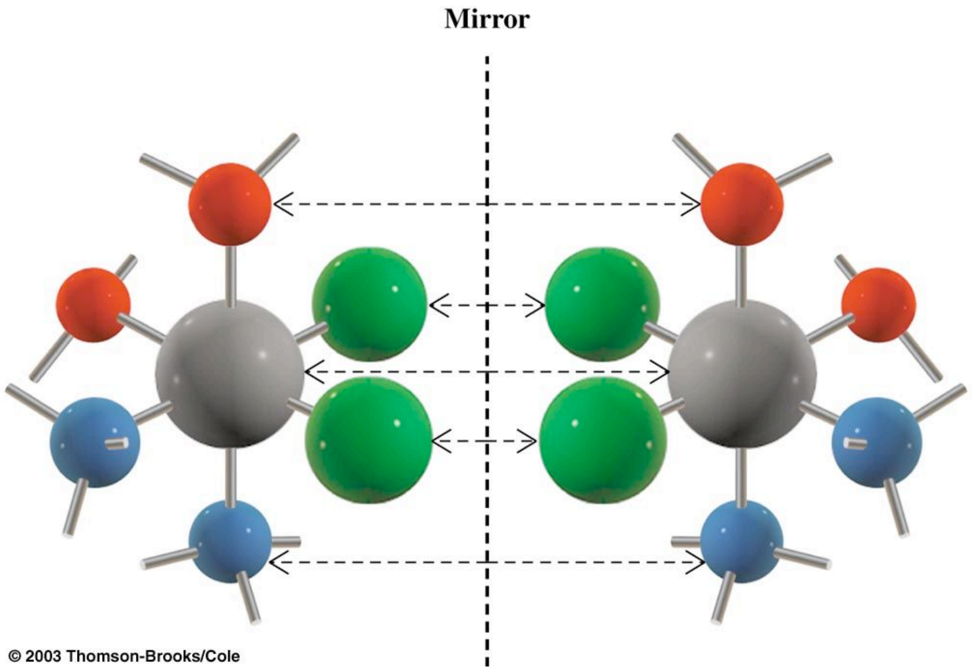
Enantiomers: non superimposable mirror images

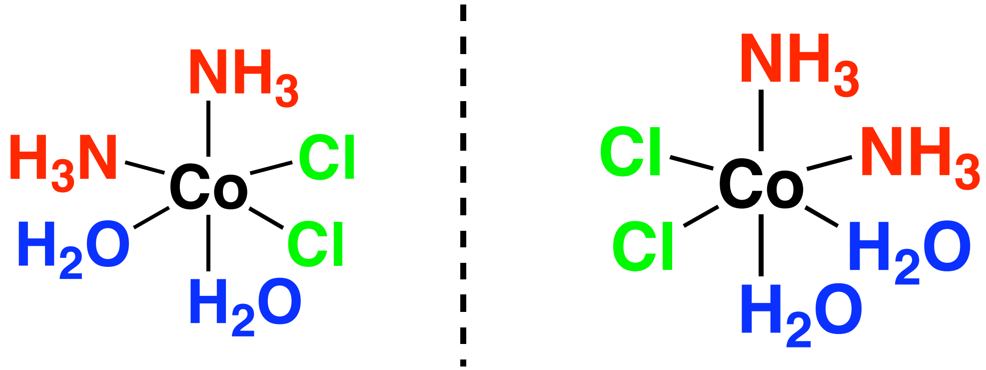
A structure is termed ***chiral*** if it is not superimposable on its mirror image



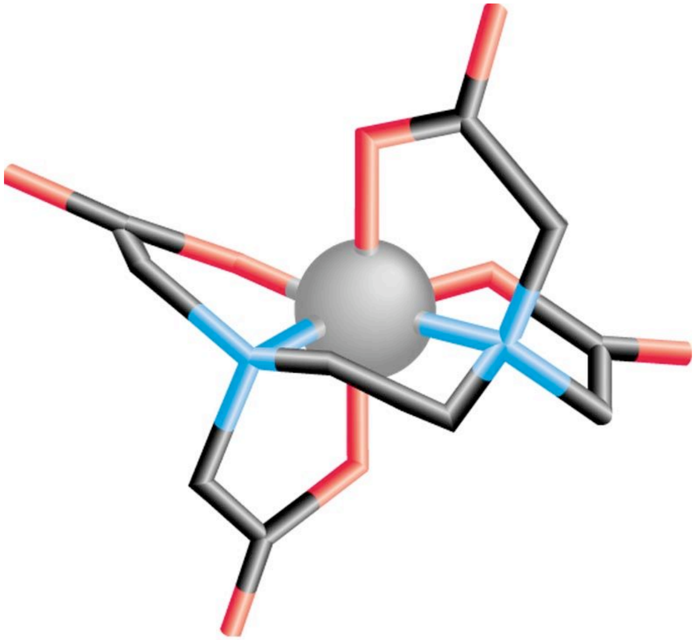
Two chiral structures: non superimposable mirror images

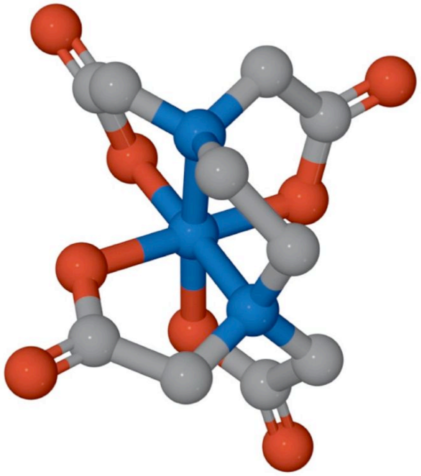
Examples of enantiomers



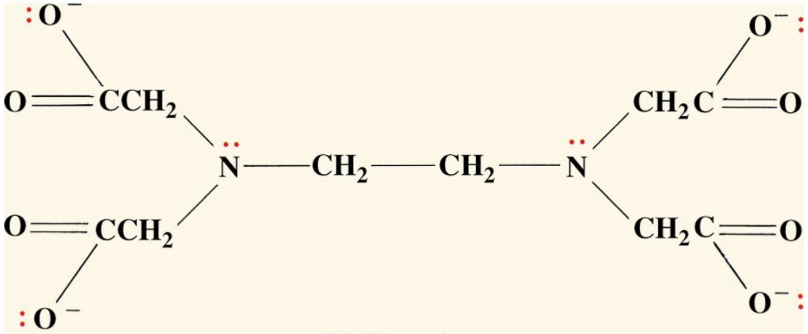


EDTA complexes are optically active





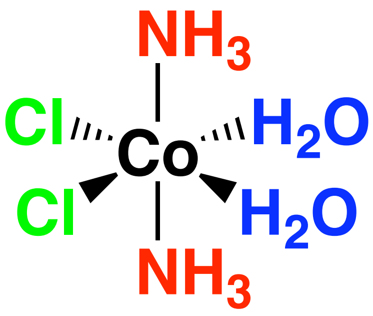
10 An edta complex

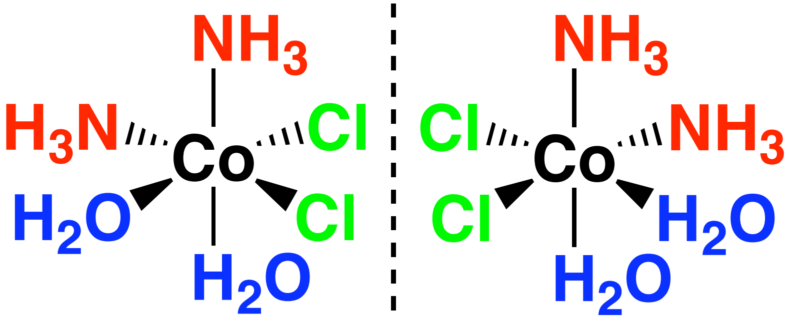


EDTA anion

Chirality: the absence of a plane of symmetry
Enantiomers possible

If a molecule possess a plane of symmetry it is achiral
and is superimposible on its mirror image
Enantiomers NOT possible

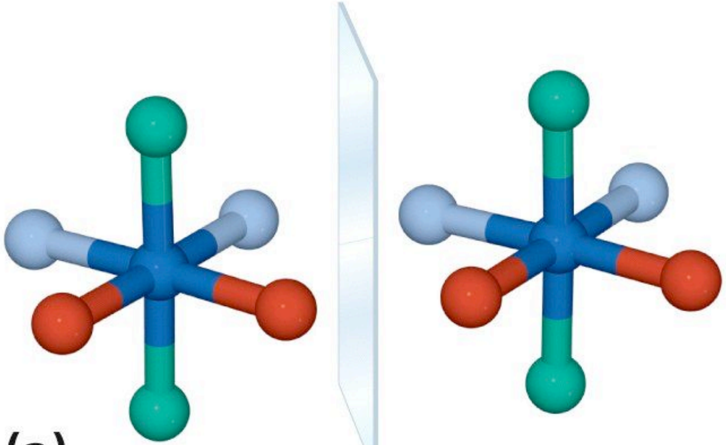


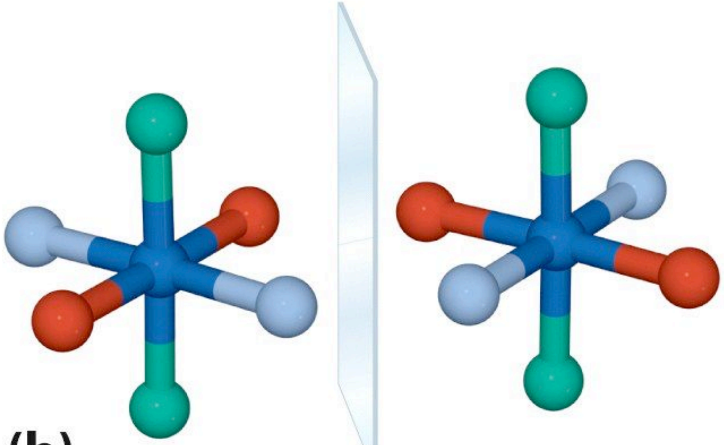


Plane of symmetry
Achiral (one structure)

No plane of symmetry
Chiral (two enantiomer)

Which are enantiomers (non-superimposable mirror images) and which are identical (superimposable mirror images)?


(a)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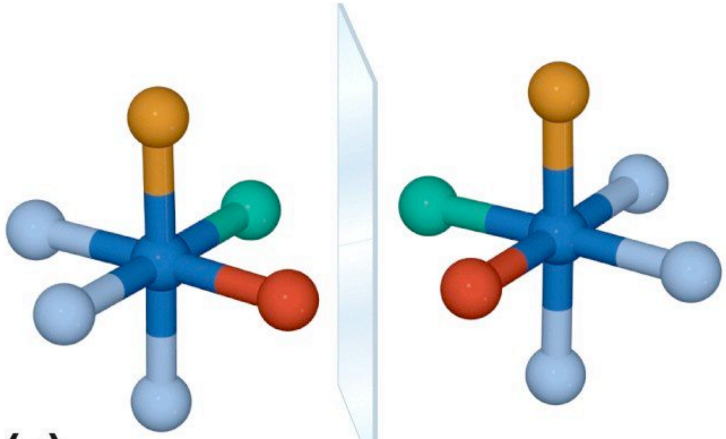
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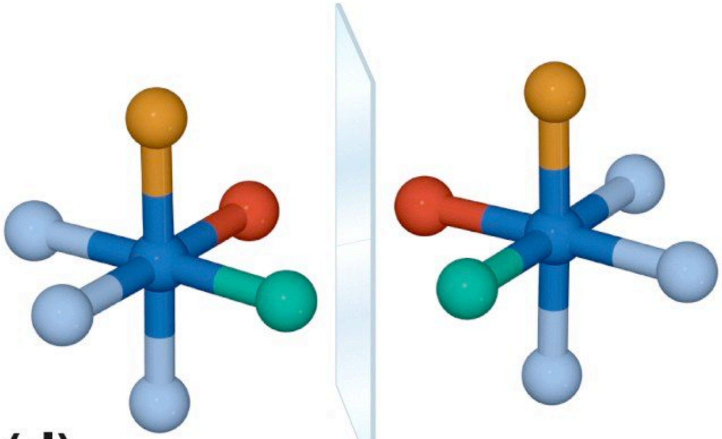
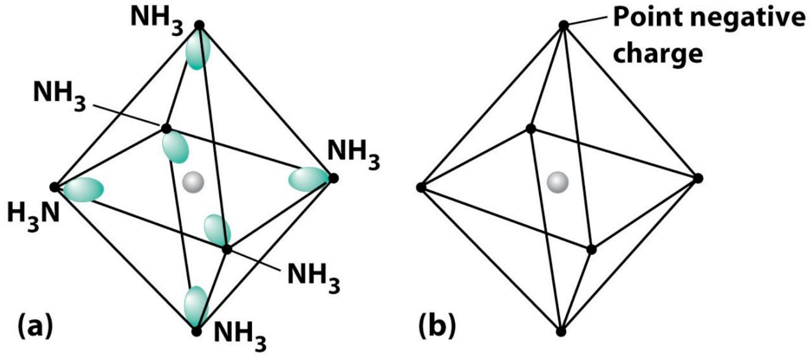

(d)

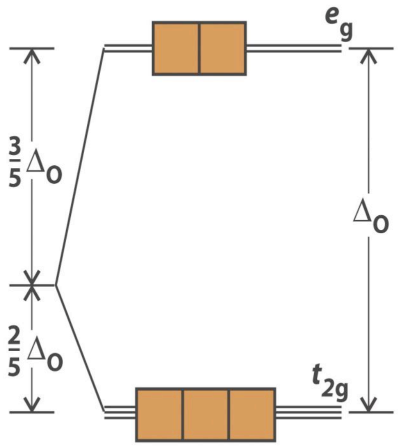
19.3 Crystal Field Theory: Splitting of the 5 d orbitals

Consider the response of the energy of the d orbitals to the approach of 6 negatively charged ligands (a "crystal field") along the x, y and z axes of the metal



The two d orbitals (d_{x2-y2} and d_{z2}) that are directed along the x, y and z axes are affected more than the other three d orbitals (d_{xy}, d_{xz} and d_{yz})

e_g orbitals

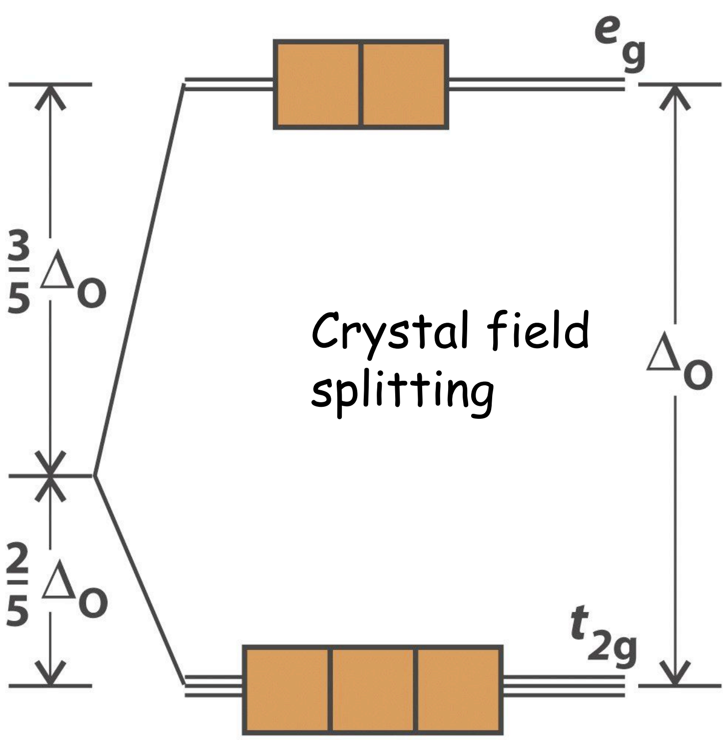


t_{2g} orbitals

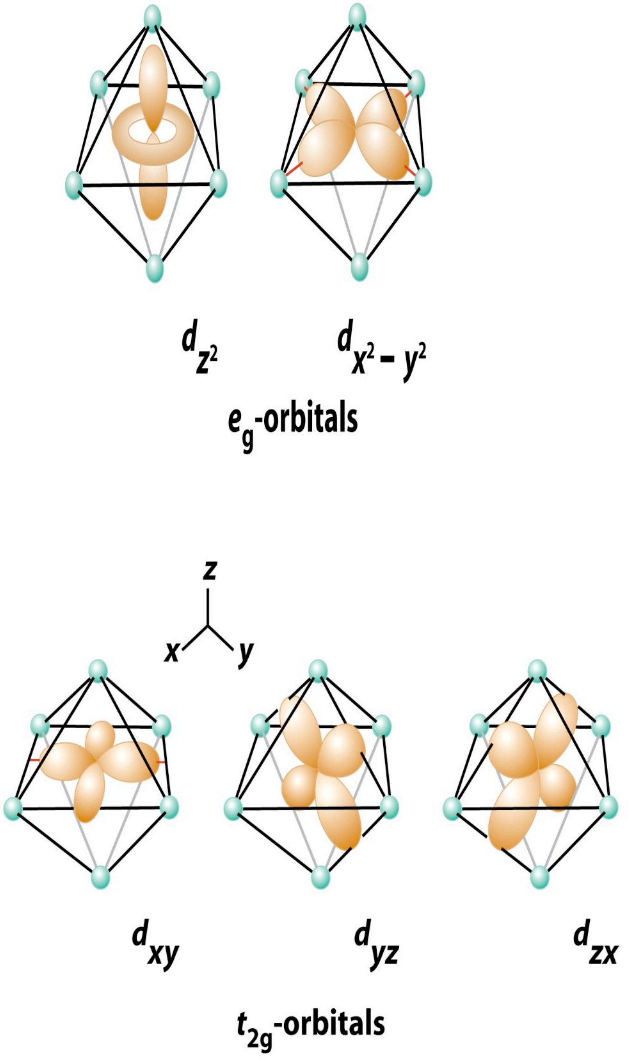
The result is that the d_{x2-y2} and d_{z2} orbital increase in energy relative to the d_{xy}, d_{xz} and d_{yz} orbitals (D_0 is called the "crystal field energy splitting

Crystal field splitting of the 5 d orbitals by the “crystal field” of 6 ligands

e_g orbitals

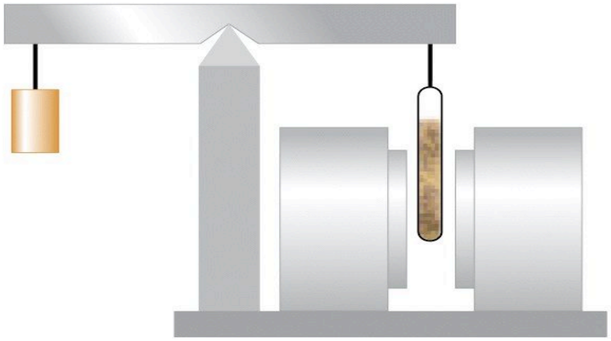


t_{2g} orbitals



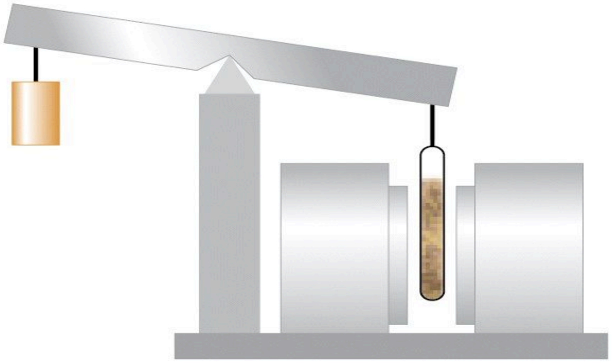
Paramagnetism and diamagnetism

Magnet off

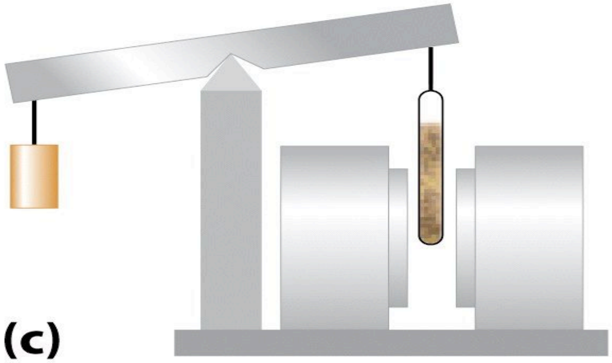


(a)

Magnet on
Paramagnetic



(b)

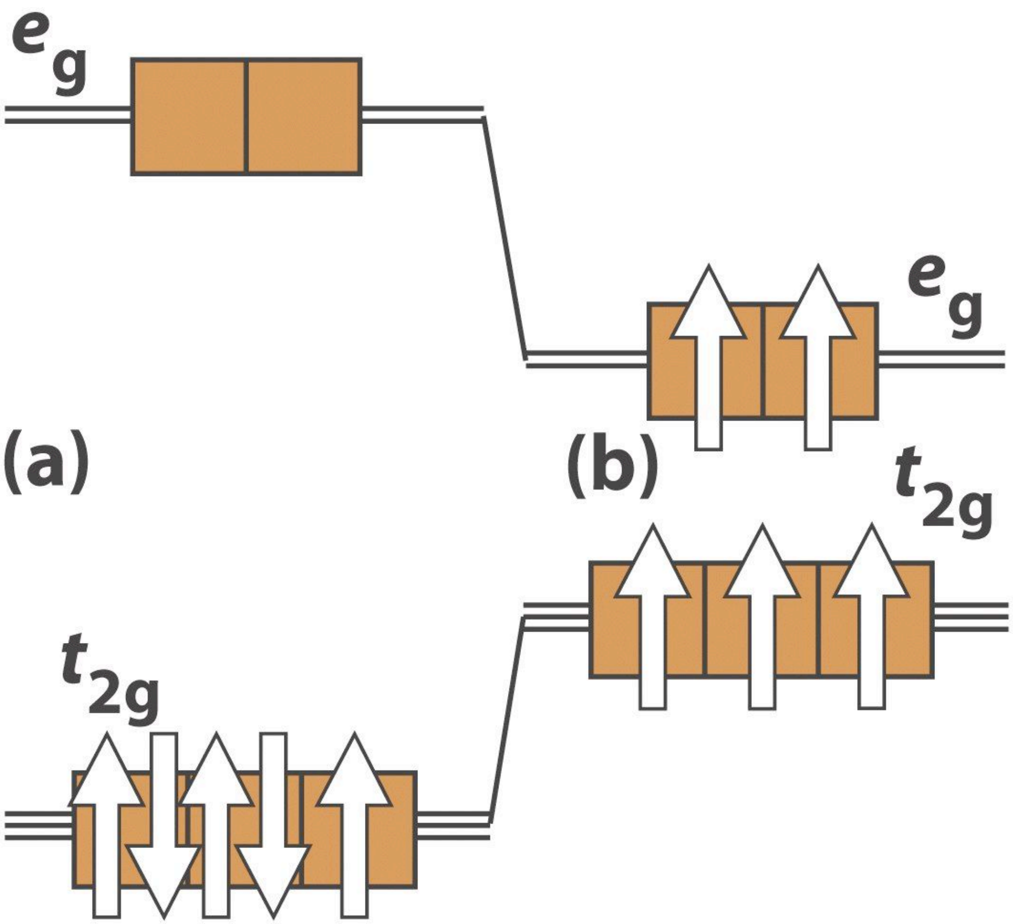


(c)

Magnet on
diamagnetic

Crystal Field Splitting of d orbitals: high spin and low spin situations for a d^5 metal (draw the diagrams for high and low spin)

Large splitting:
Low spin



Small splitting:
High spin

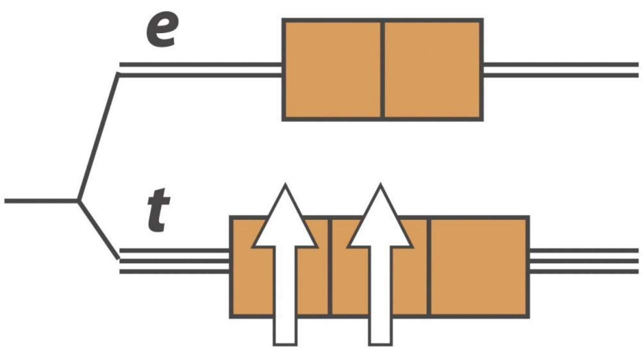
Net spin = 0 spins
Diamagnetic

Net spin = 5 spins
Paramagnetic

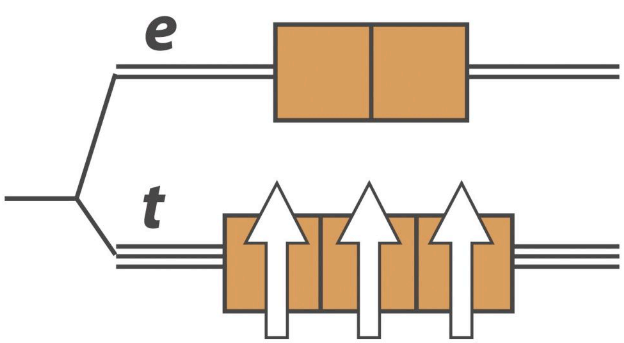
The d electron configurations of M(II) cations of the transition metals

Metal	Atom Configuration	Cation (II) Configuration Valence electrons only
Sc	[Ar]$4s^2 3d^1$	$3d^1$
Ti	[Ar]$4s^2 3d^2$	$3d^2$
V	[Ar]$4s^2 3d^3$	$3d^3$
Cr	[Ar]$4s^1 3d^5$	$3d^4$
Mn	[Ar]$4s^2 3d^5$	$3d^5$
Fe	[Ar]$4s^2 3d^6$	$3d^6$
Co	[Ar]$4s^2 3d^7$	$3d^7$
Ni	[Ar]$4s^2 3d^8$	$3d^8$
Cu	[Ar]$4s^2 3d^9$	$3d^9$
Zn	[Ar]$4s^2 3d^{10}$	$3d^{10}$

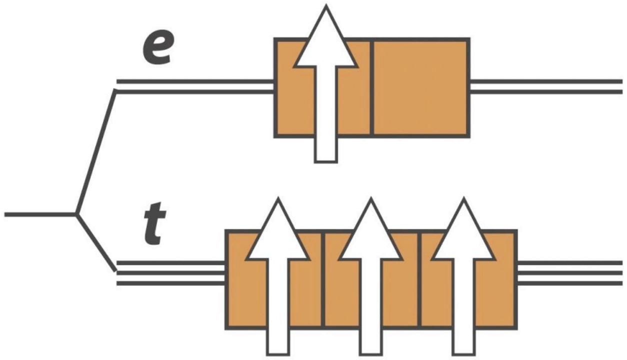
Building of weak field, high spin electron configurations



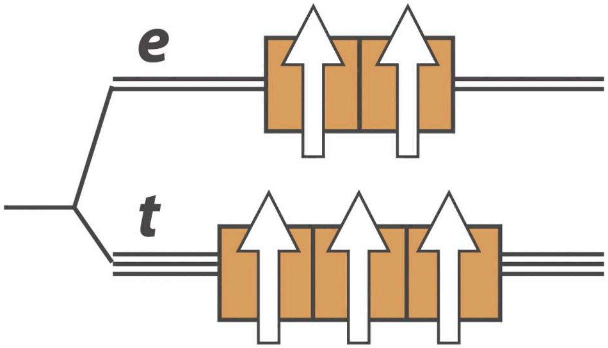
15 t_{2g}^{2}



16 t_{2g}^{3}



18 $t_{2g}^{3}e_{g}^{1}$



20 $t_{2g}^{3}e_{g}^{2}$

How many unpaired spins in $Fe(CN)_6^{4-}$ and in $Fe(H_2O)_6^{2+}$?

What is the charge of Fe in $Fe(CN)_6^{4-}$ and in $Fe(H_2O)_6^{2+}$?

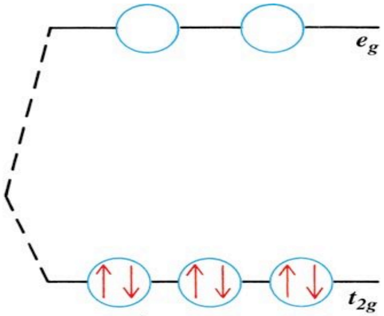
Fe^{2+} in both cases

$Fe = [Ar]3d^64s^2$; $Fe^{2+} = [Ar]3d^6$

What kind of ligands are CN^- and H_2O?

CN^- is a strong field ligand and H_2O is a weak field ligand

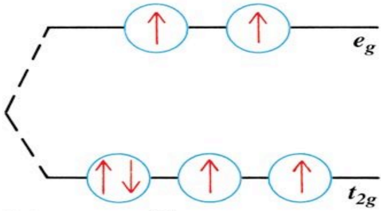
Large splitting
Low spin



(a) $Fe(CN)_6^{4-}$ (low spin)

Energy gap larger than advantage due to Hund's rule

Small splitting
High spin

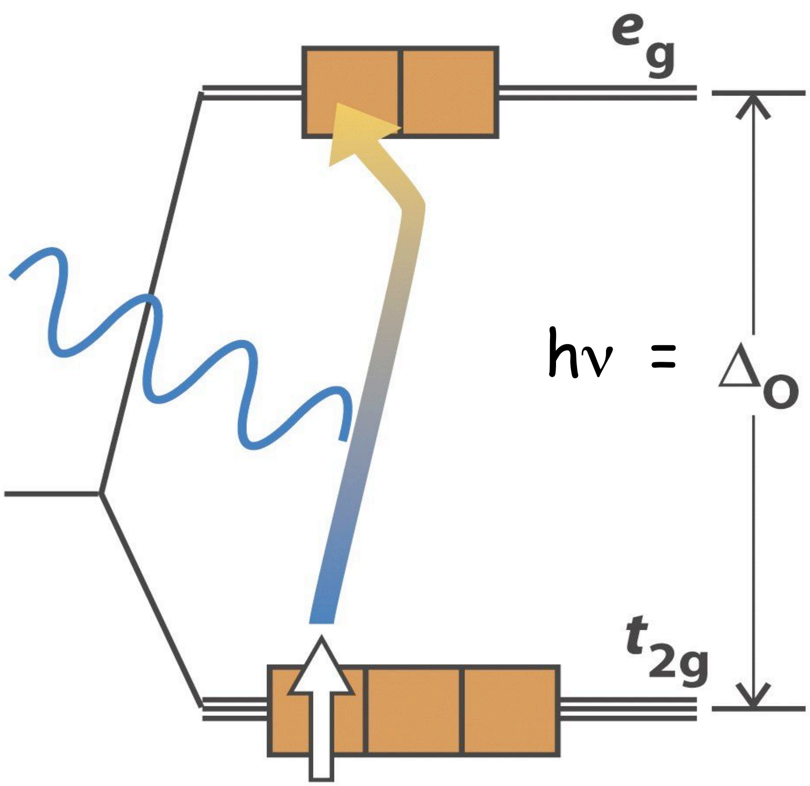


(b) $Fe(H_2O)_6^{2+}$ (high spin)

Energy gap small; Hund's rule applies

Complex	Valence electrons	Unpaired electrons	Electron configuration	Spin configuration
$Ti(H_2O)_6^{3+}$	$3d^1$	1	$(t_{2g})^1$	$(\uparrow)^1$
$Cr(H_2O)_6^{3+}$	$3d^3$	3	$(t_{2g})^3$	$(\uparrow\uparrow\uparrow)^3$
$Fe(H_2O)_6^{3+}$	$3d^5$	5	$(t_{2g})^3(e_g)^2$	$(\uparrow\uparrow\uparrow)^3(\uparrow\uparrow)^2$
$Fe(CN)_6^{3-}$	$3d^5$	1	$(t_{2g})^5$	$(\uparrow\downarrow\uparrow\downarrow\uparrow)^5$
$Fe(H_2O)_6^{2+}$	$3d^6$	4	$(t_{2g})^4(e_g)^2$	$(\uparrow\downarrow\uparrow\uparrow)^4(\uparrow\uparrow)^2$
$Fe(CN)_6^{2-}$	$3d^6$	0	$(t_{2g})^6$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6$
$Ni(H_2O)_6^{2+}$	$3d^8$	2	$(t_{2g})^6(e_g)^2$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\uparrow)^2$
$Cu(H_2O)_6^{2+}$	$3d^9$	1	$(t_{2g})^6(e_g)^3$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\downarrow\uparrow)^3$
$Zn(H_2O)_6^{2+}$	$3d^{10}$	0	$(t_{2g})^6(e_g)^4$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\downarrow\uparrow\downarrow)^4$

19.4 Crystal Field Theory: The Color of Coordination Compounds



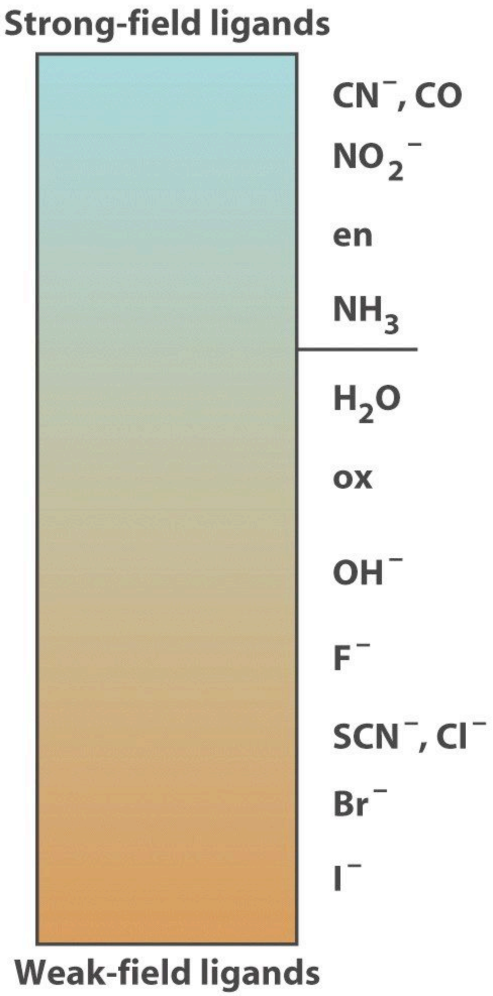
Absorption of a photon causes a jump from a t_{2g} to an e_g orbital

The energy gap between the e_g and t_{2g} orbitals, Δ_0, (the crystal field splitting) equals the energy of a photon:

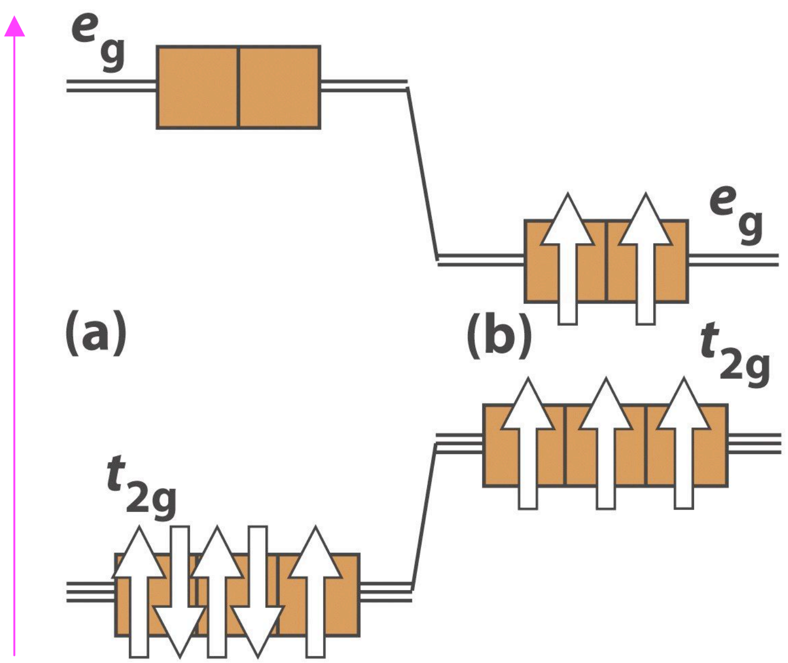
$\Delta_0 = h\nu = \Delta E$

As Δ_0, varies, $h\nu$ will also vary and the color of the compound will change

The spectrochemical series of color and magnetic properties: weak field (red, high spin), strong field (violet, low spin)

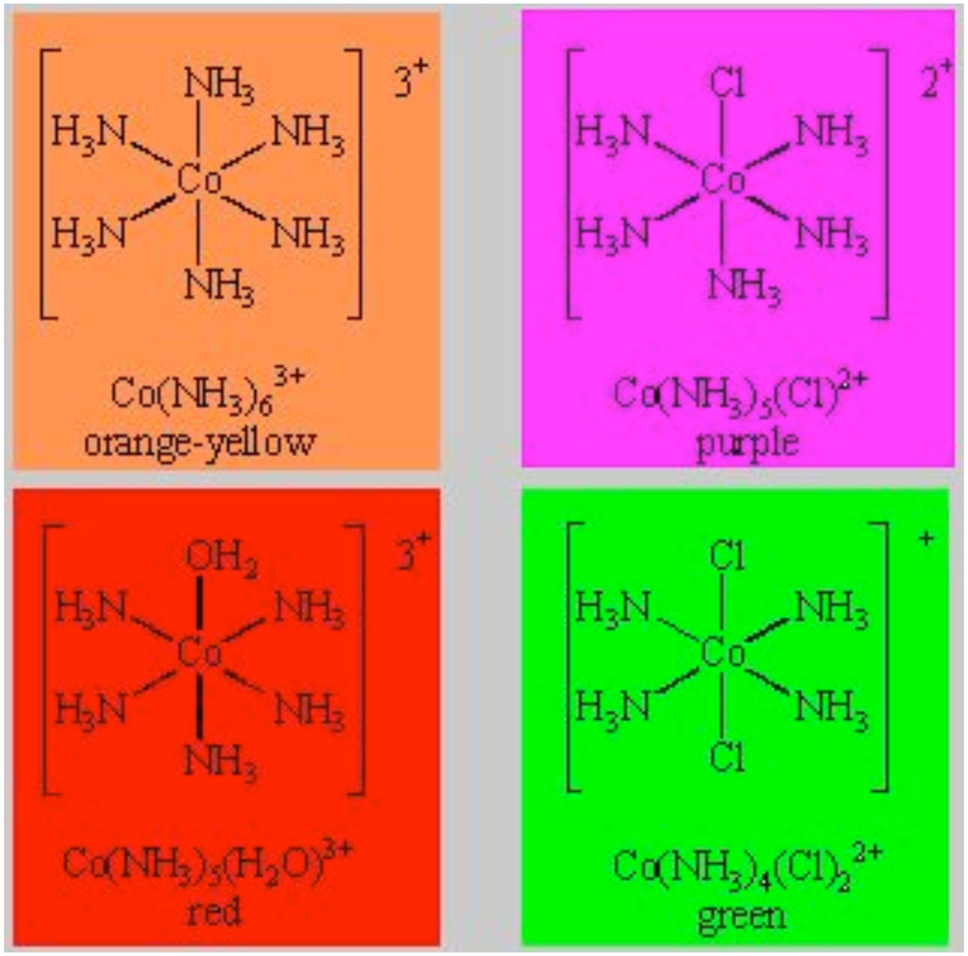


A d^5 electron metal ion

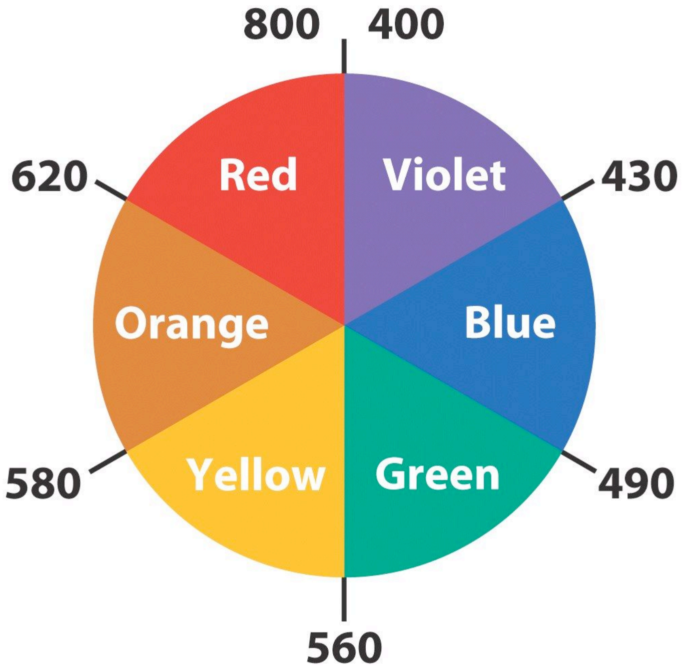


Strong field
Ligands (violet, low spin)

Weak field
Ligands (red, high spin)



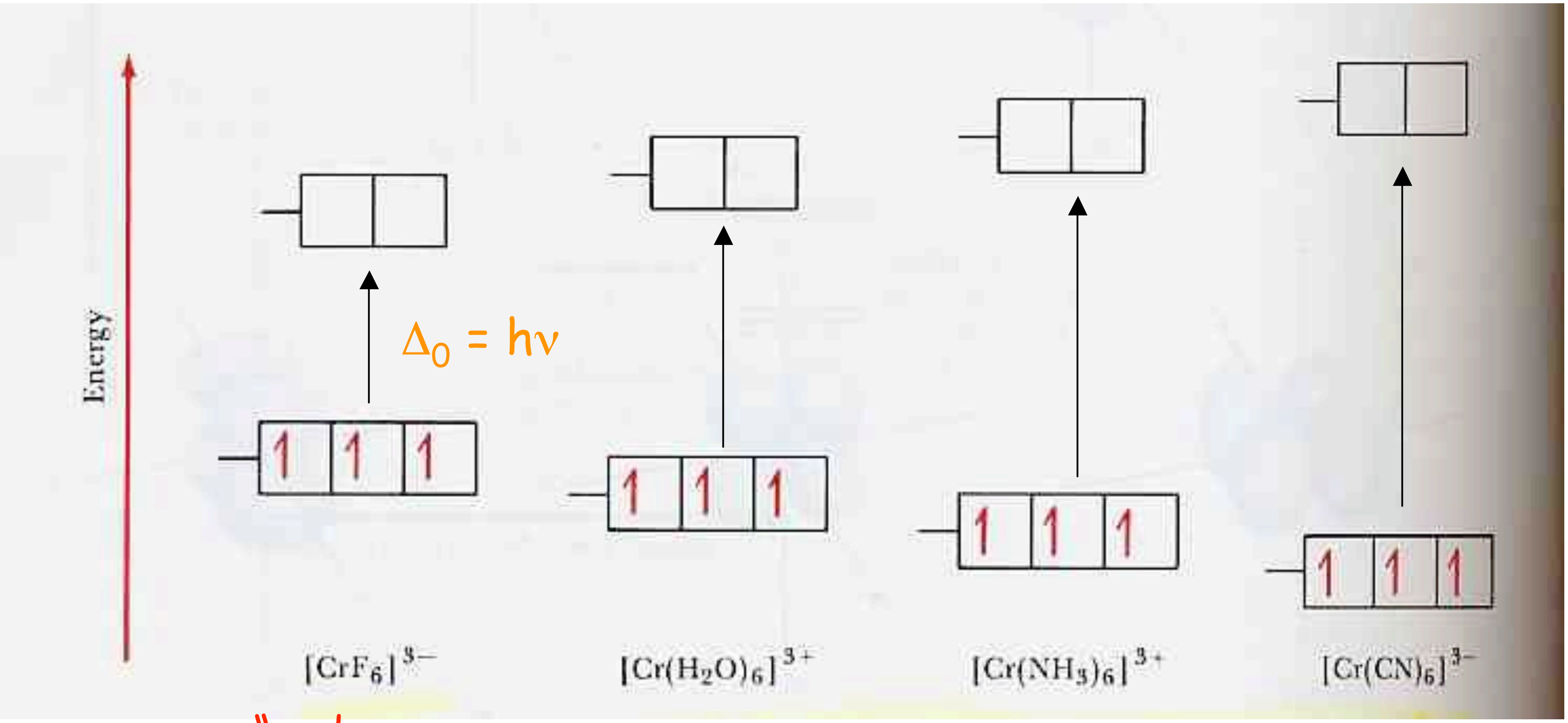
The color that we see is the color that is not absorbed, but is transmitted. The transmitted light is the complement of the absorbed light.



So if red light is mainly absorbed the color is green; if green light is mainly absorbed, the color is red.

Numbers are nm

Color of complexes depend on the value of $\Delta_0 = h\nu = \Delta E$

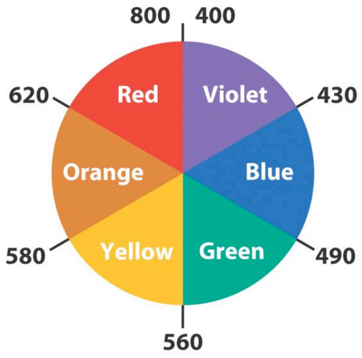


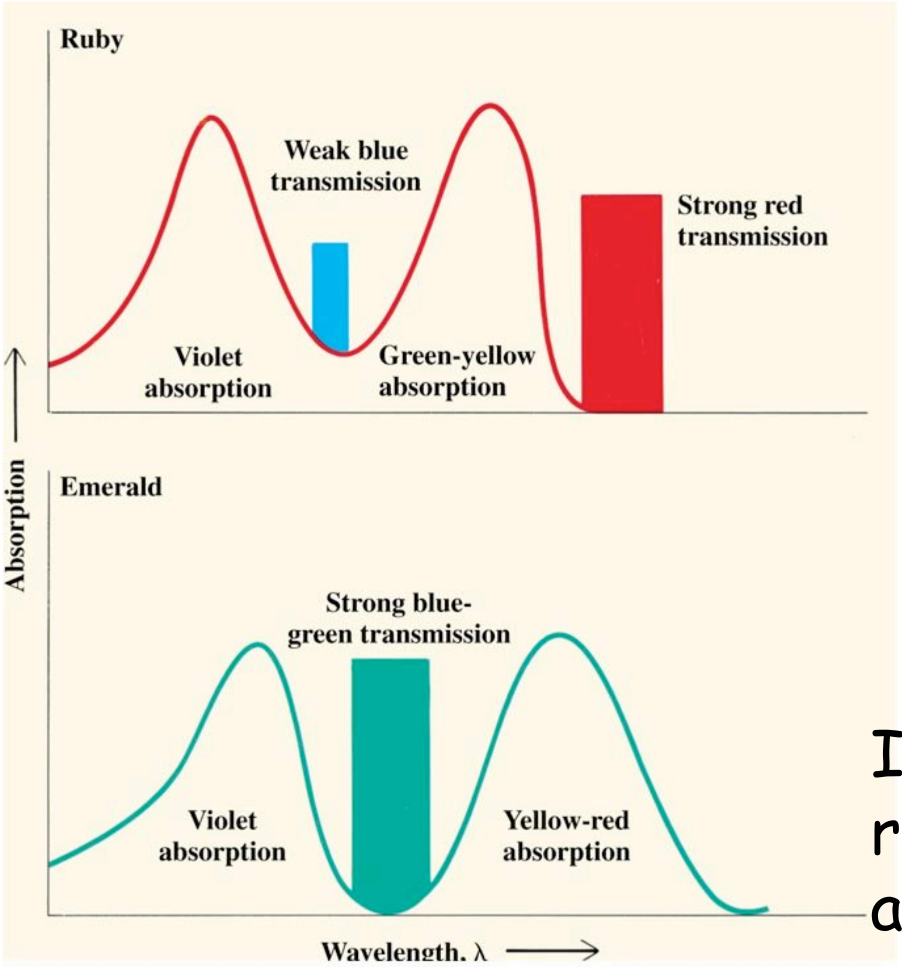
"red absorption"

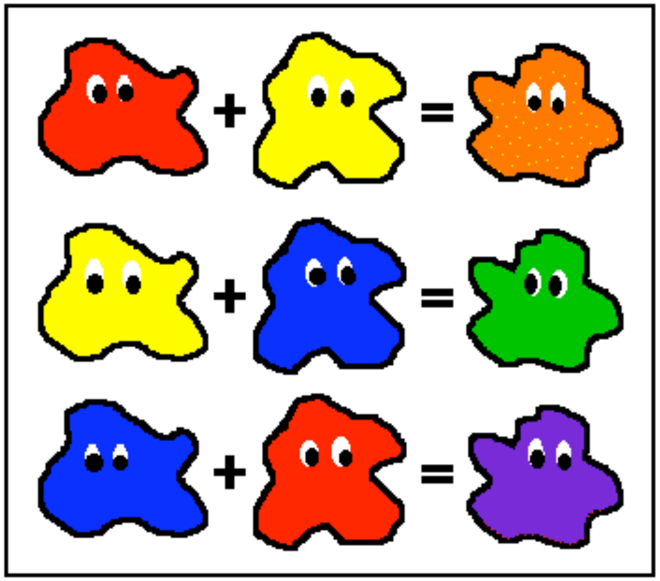
"looks green"

"violet absorption"

"looks yellow







In real systems there are regions of different light absorptions leading to a wide range of colors

19.5 Coordination Complexes in Living Systems

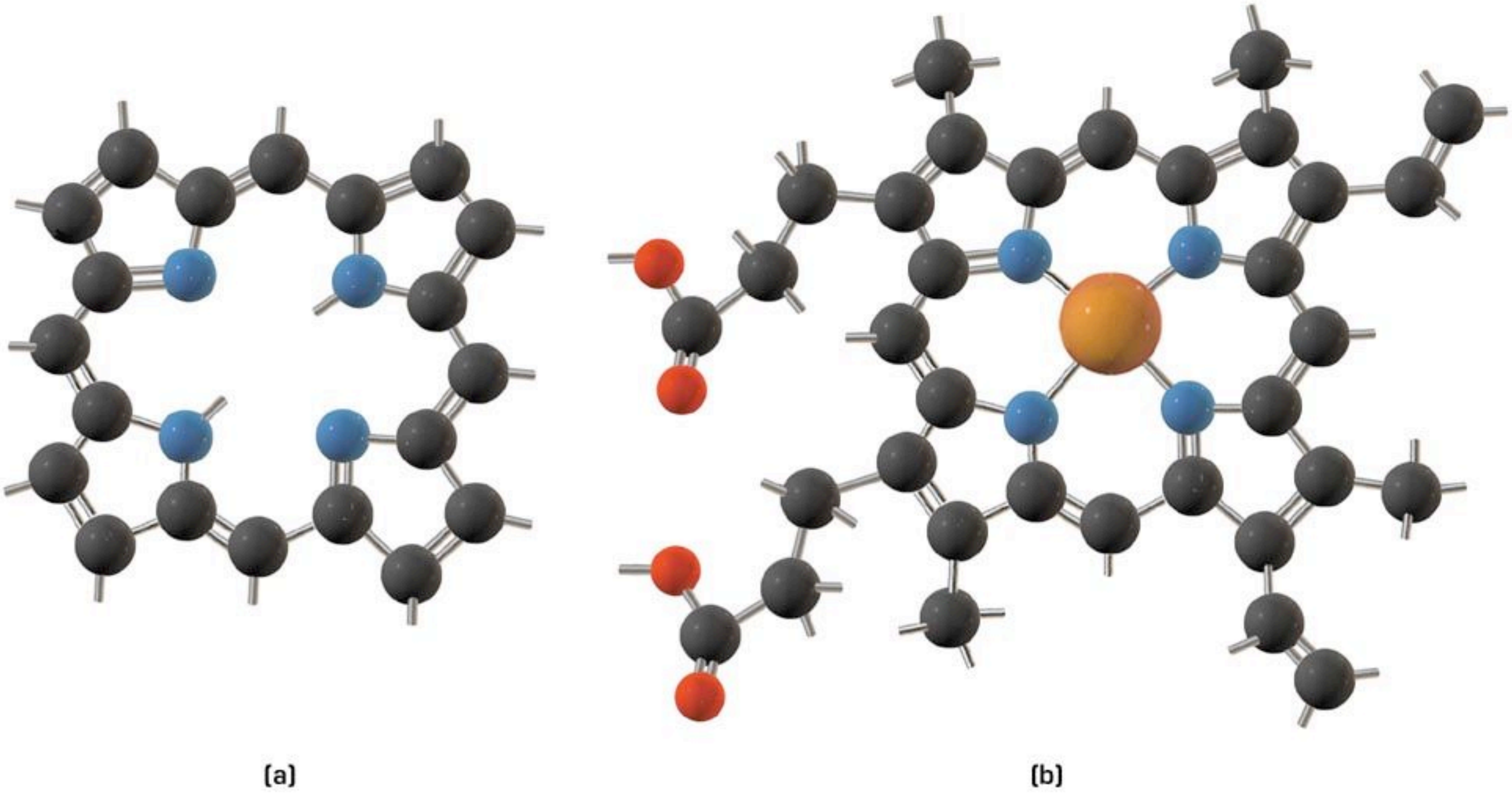
Porphines, hemes, hemoglobin

Photosynthesis: electron transfer

Vitamin B_{12}

Porphines and hemes: important molecules in living systems

These planar molecules have a “hole” in the center which to which a metal can coordinate



Porphine $(C_{20}H_{14}N_4)_{)}$

heme $(C_{34}H_{32}N_4O_4Fe)_{)}$

Why do we need to eat d metals?

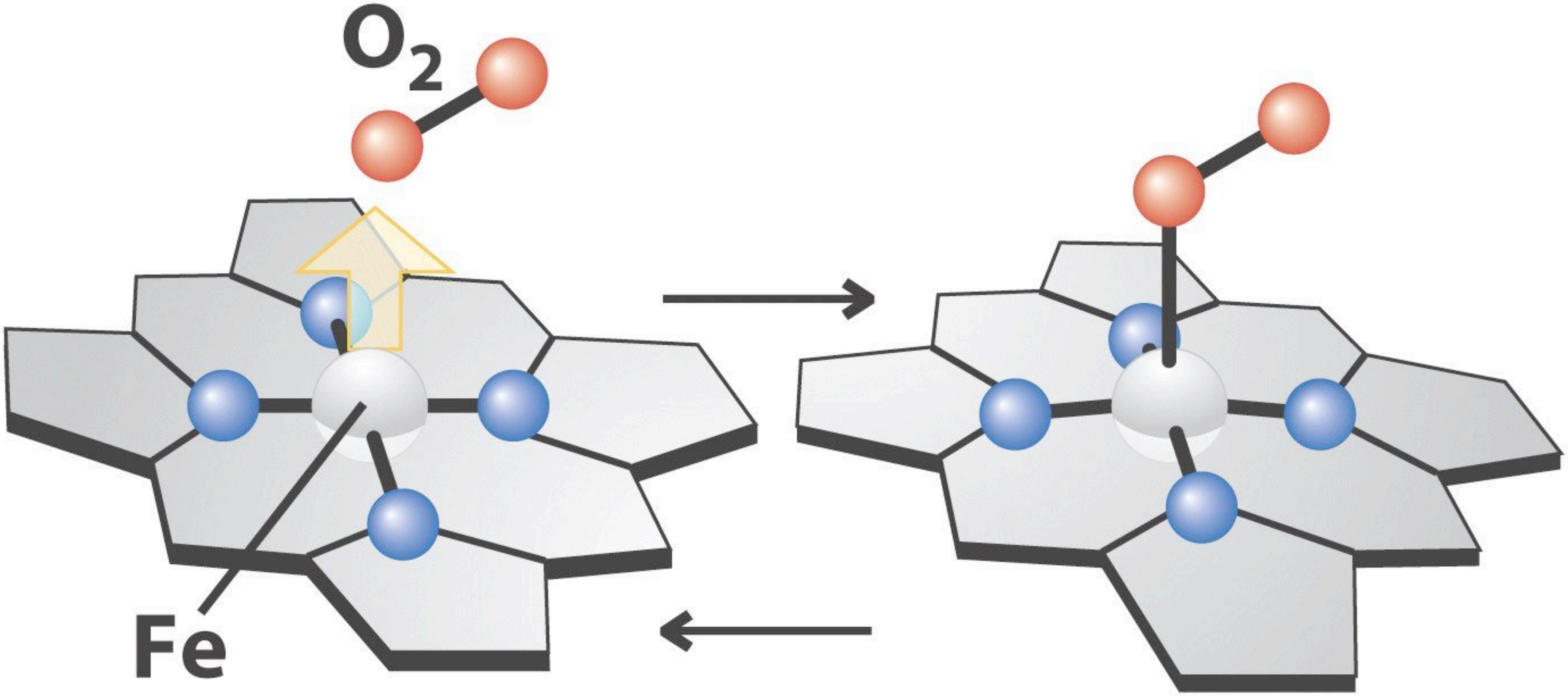
Some critical enzymes in our cells are ***metalloproteins,*** giant biolmolecules which contain a metal atom

These metalloproteins control key life processes such as respiration and protect cells against disease

Hemoglobin is a metalloprotein which contains an iron atom and transports O_2 through out living systems

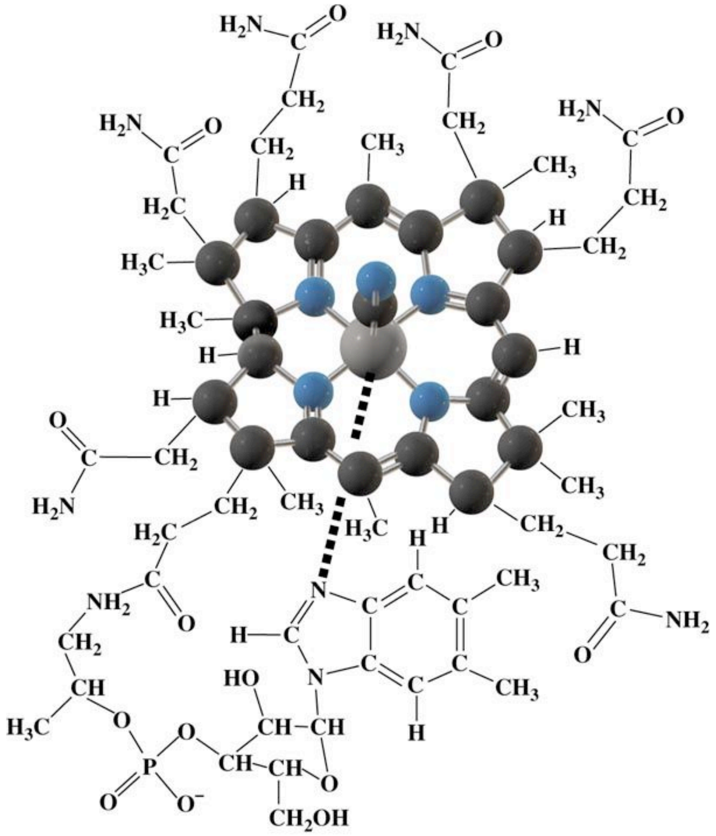
Vitamin B_{12}, which prevents pernicious anemia, contains a Co atom which gives the vitamin a red color

Reversible addition of O_2 to hemoglobin



The mechanism by which oxygen is carried throughout the body

Involved in many important biological processes, including the production of red blood cells



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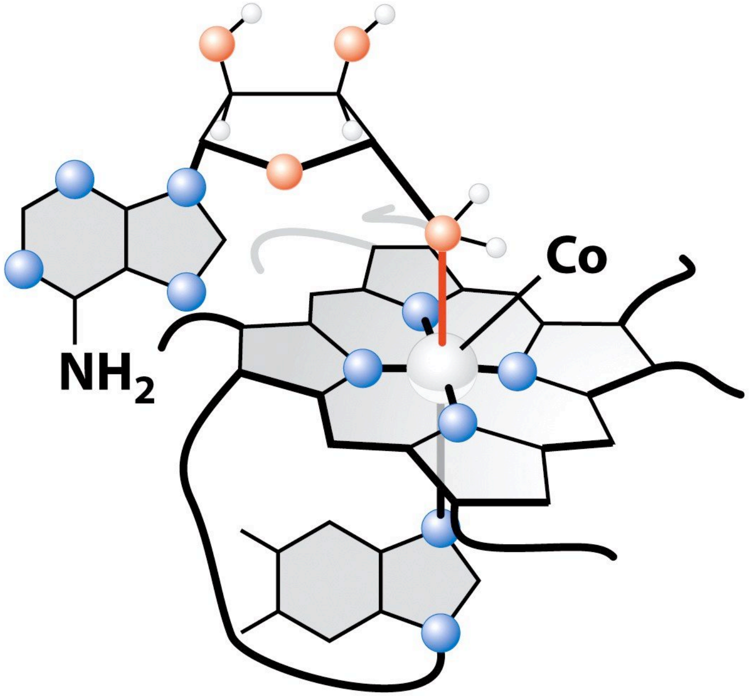
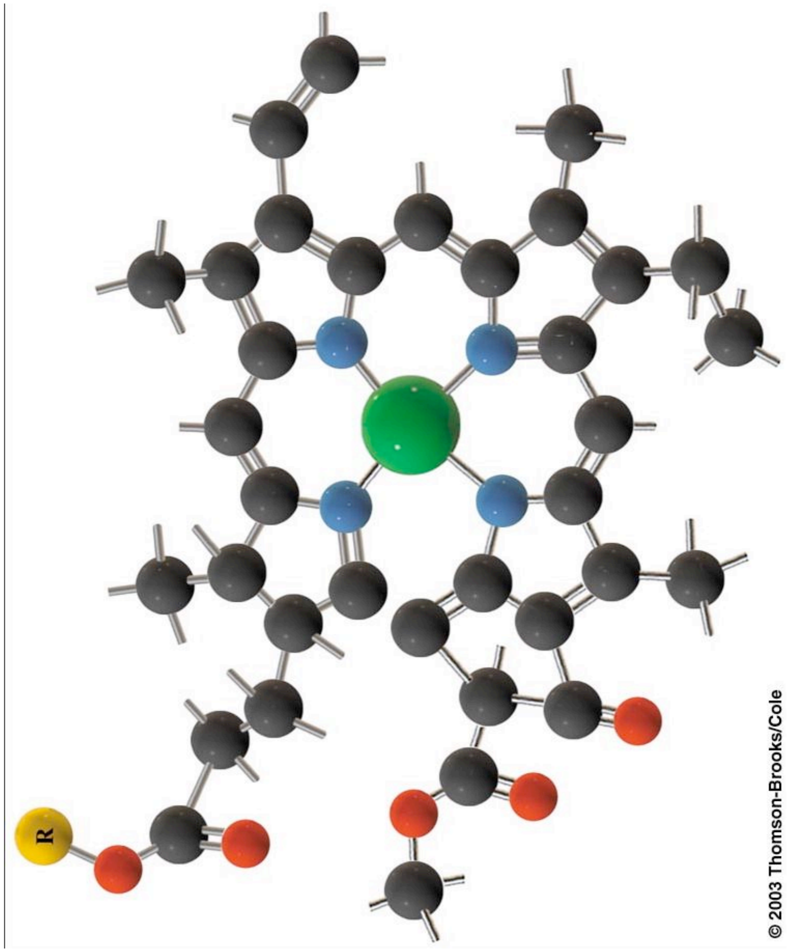


Vitamin B_{12} $(Co[C_{62}H_{88}N_{13}O_{14}P])CN$

A very important porphine that converts solar photons into food energy: chlorophyll



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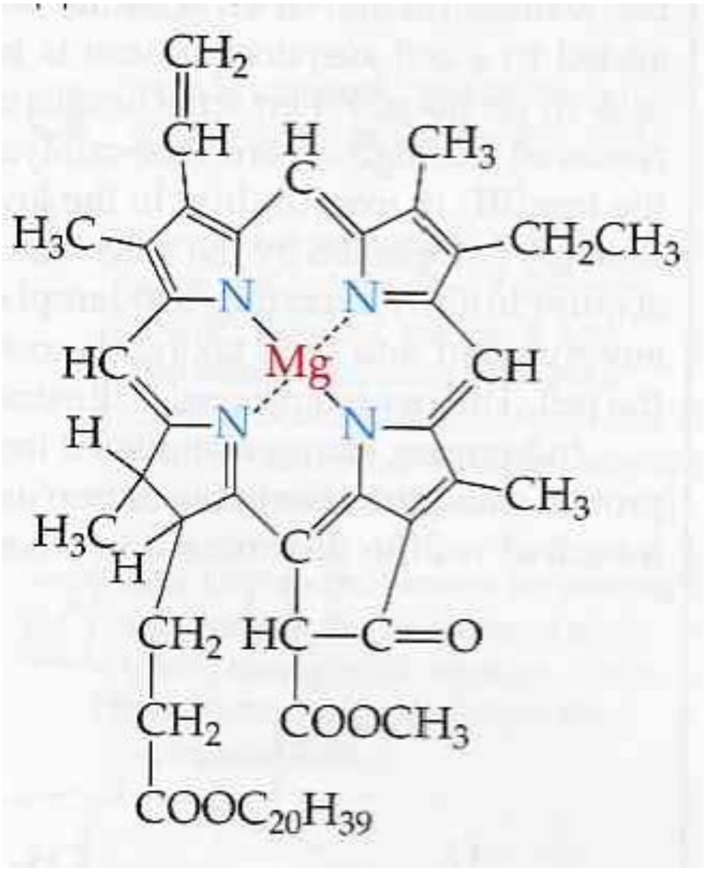

Chlorophyll ($C_{55}H_{72}N_4O_5Mg$)