Lecture 1.
COORDINATION COMPOUNDS

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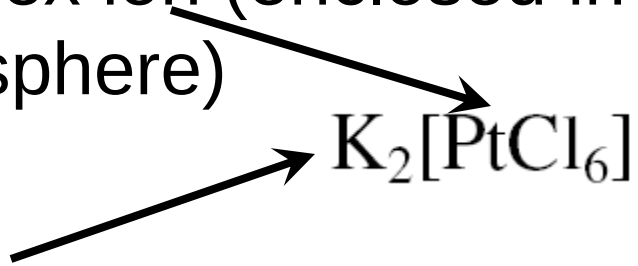
Coordination Chemistry

- ***Coordination compounds*** contain *coordinate covalent* bonds formed between metal ions with groups of *anions* or *polar molecules.*
- ***Complex ion*** – ion in which a metal cation is covalently bound to one or more molecules or ions
  - – Compound that contains 1 or more complexes

  Example
    - $[Co(NH_3)_6]Cl_3$
    - $[Cu(NH_3)_4][PtCl_4]$
    - $[Pt(NH_3)_2Cl_2]$

- Components of a coordination compound
  - Complex ion (enclosed in square brackets- inner sphere)



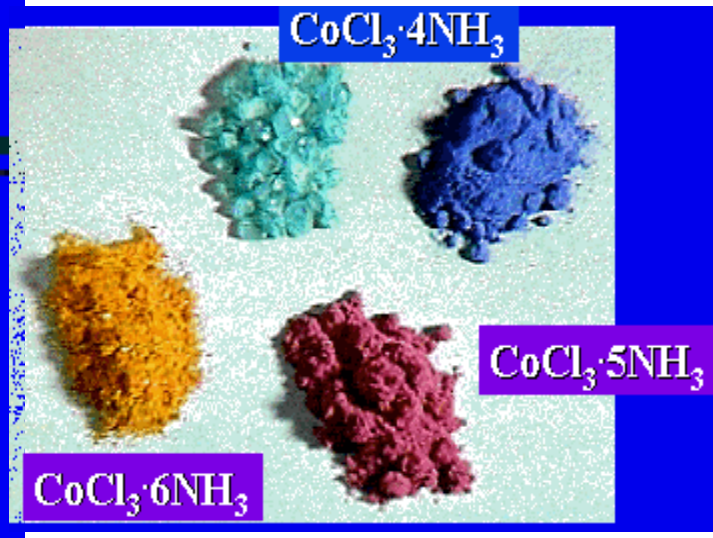
  - Outer sphere
  - Some coordination compounds do not contain a complex ion $Fe(CO)_5$
  - Most of the metals in complexes are transition metals

Coordination complexes

The electronic basis of the color of metal complexes

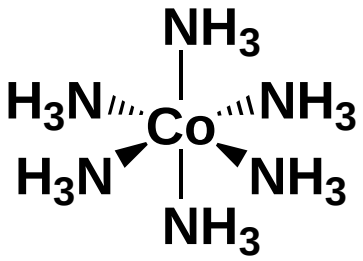
$CoCl_3 \cdot nNH_3$

Composition	Color	No. Cl^- pptd	Formula
$CoCl_3 \cdot 6NH_3$	yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	green	1	$[Co(NH_3)_4Cl_2]Cl$



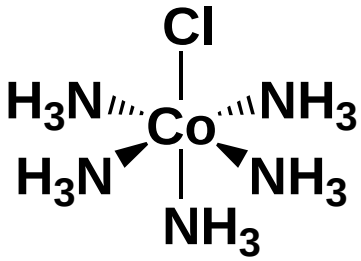
Coordination complexes: Three dimensional structures

$CoCl_3 \cdot 6NH_3$



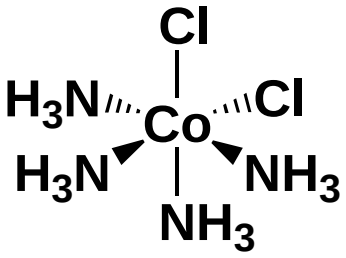
Cl^- Cl^- Cl^-

$CoCl_3 \cdot 5NH_3$

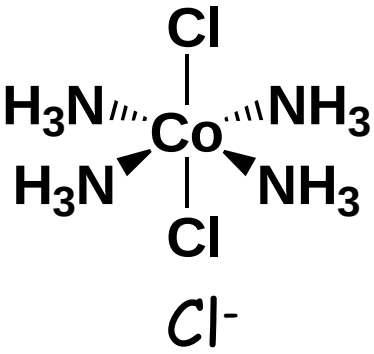


Cl^- Cl^-

$CoCl_3 \cdot 4NH_3$

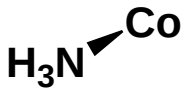


Cl^-



Cl^-

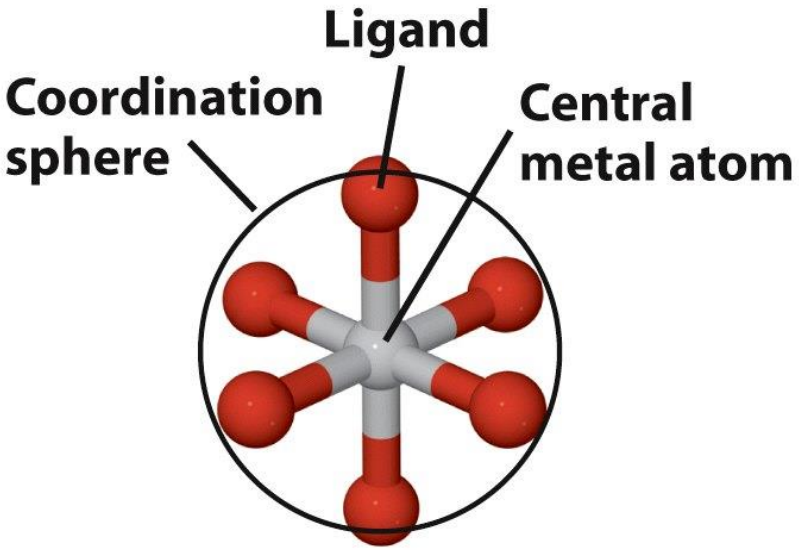
Isomers!



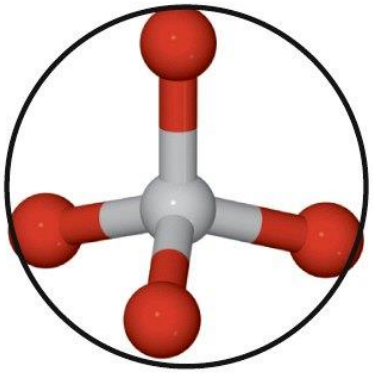
Bond toward you

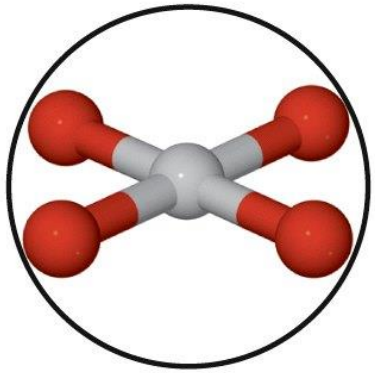
Bond away from you

Complex ions: Three common structural types



$[Co(NH_3)_6]Cl_3$





(a) Octahedral: Most important

(b) Tetrahedral

(c) Square planar

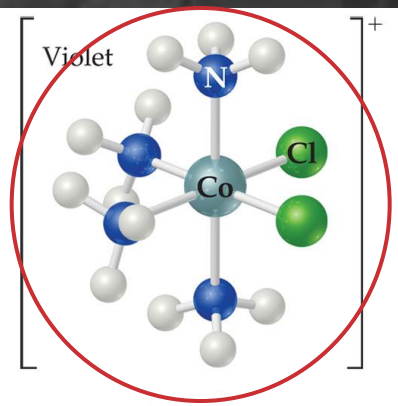
Coordination complex: A structure containing a **metal** (usually a metal ion) bonded (coordinated) to a group of surrounding **molecules or ions**.

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

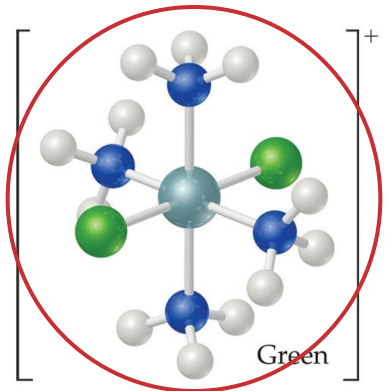
Coordination sphere: A metal and its surrounding ligands

Alfred Werner: the father of the structure of coordination complexes

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"



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.



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*-$[Co(NH_3)_4Cl_2]Cl$

Werner's explanation of coordination complexes

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

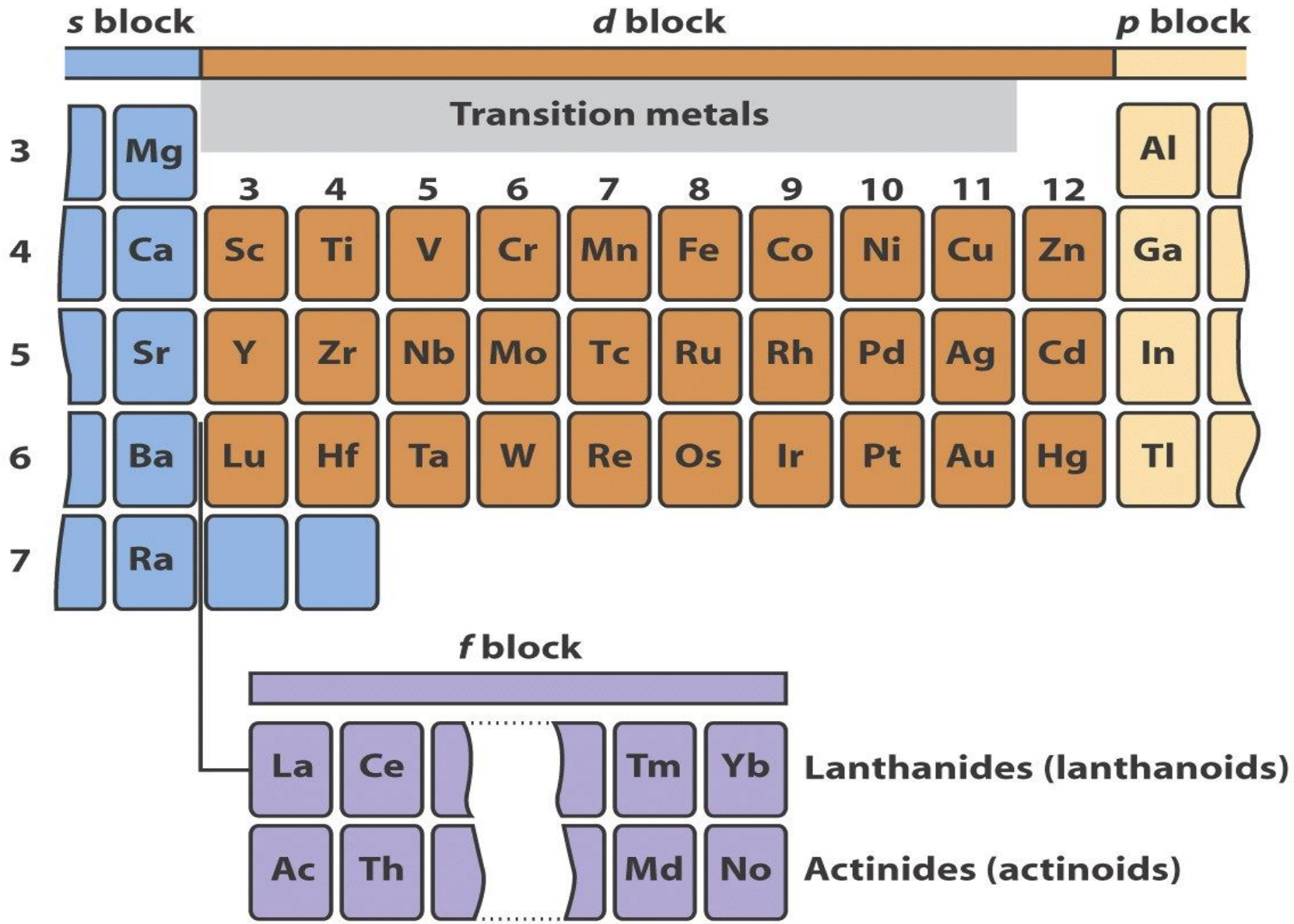
$[Co(NH_3)_6]Cl_3$

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

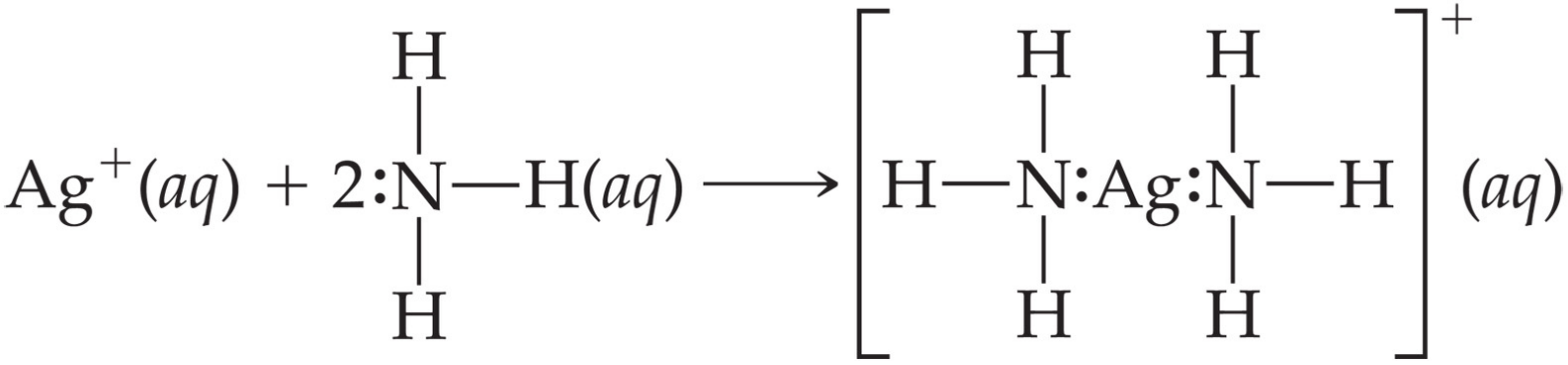
The d block metal for coordination complexes with molecules and ions



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

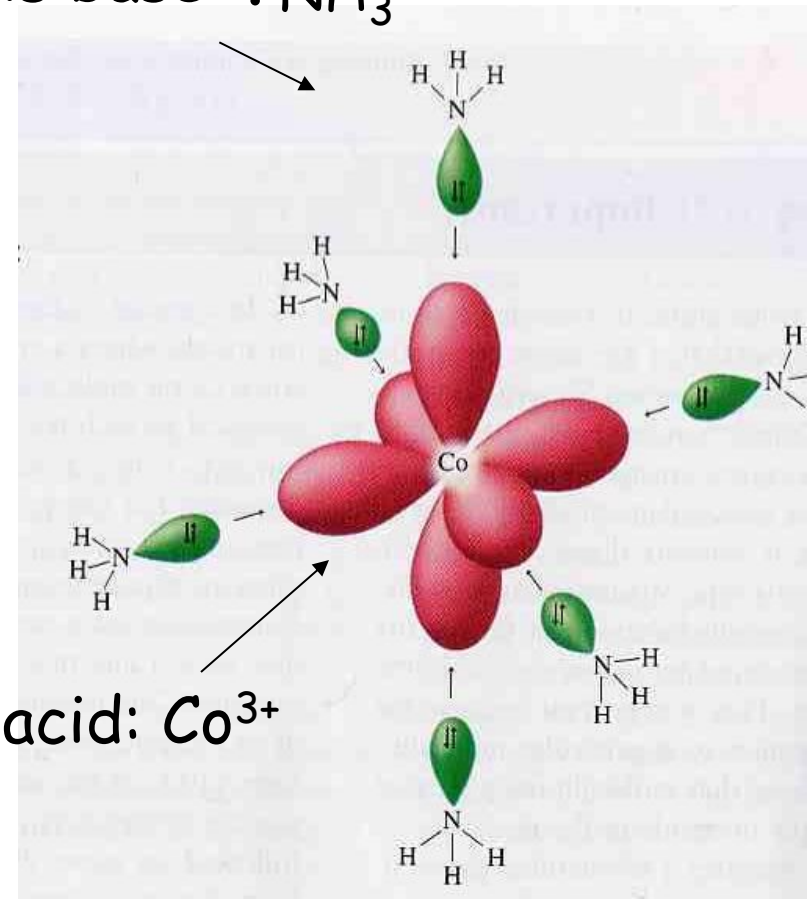
A Lewis acid is a molecule of ion that accepts a lone pair of electrons to make a bond

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

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***

Oxidation number of the central metal ion

$[Co(NH_3)_4\ Cl\ (NO_2)]$

$x + 4(o) + 1\ (-1) + 1\ (-1) = 0$

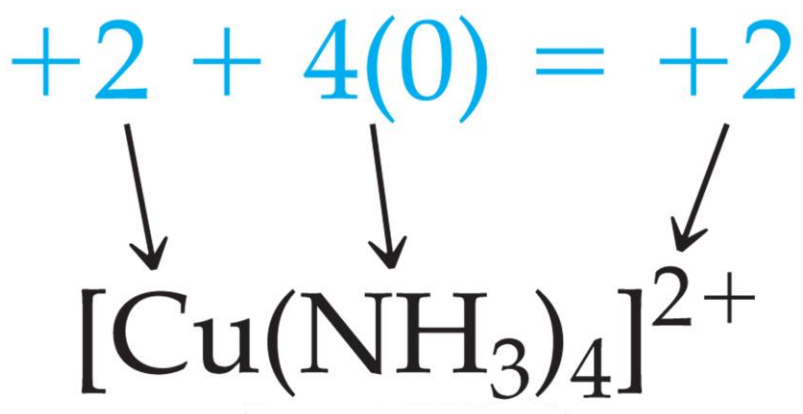
$x = +2$

$K_3[Fe(CN)_6]$

$3(1) + x + 6(-1) = 0$

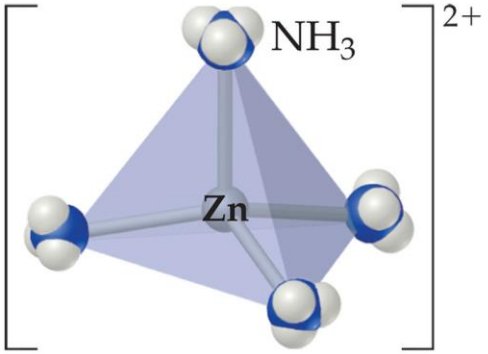
$x = +3.$

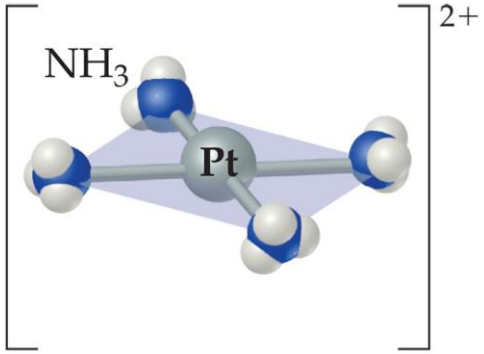
Central atom/ion: in a coordination entity the atom/ion to which are bound a fixed number of ligands in a definite geometrical arrangement around it.
For example: Ni^{2+} in $[NiCl_2(OH_2)_4]$, Fe^{3+} in $[Fe(CN)_6]^{3-}$.

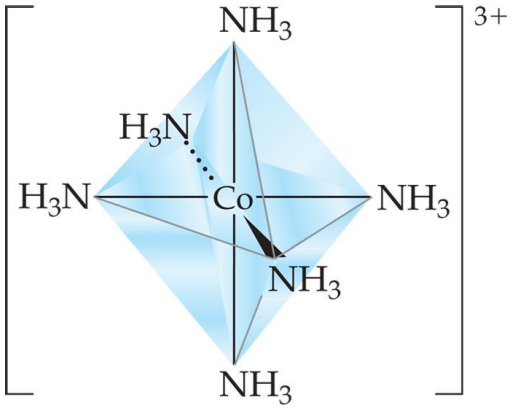


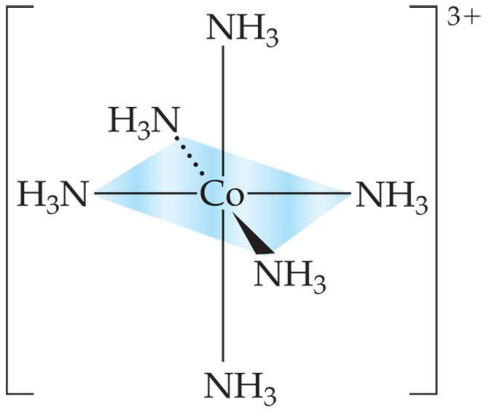
Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.

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.

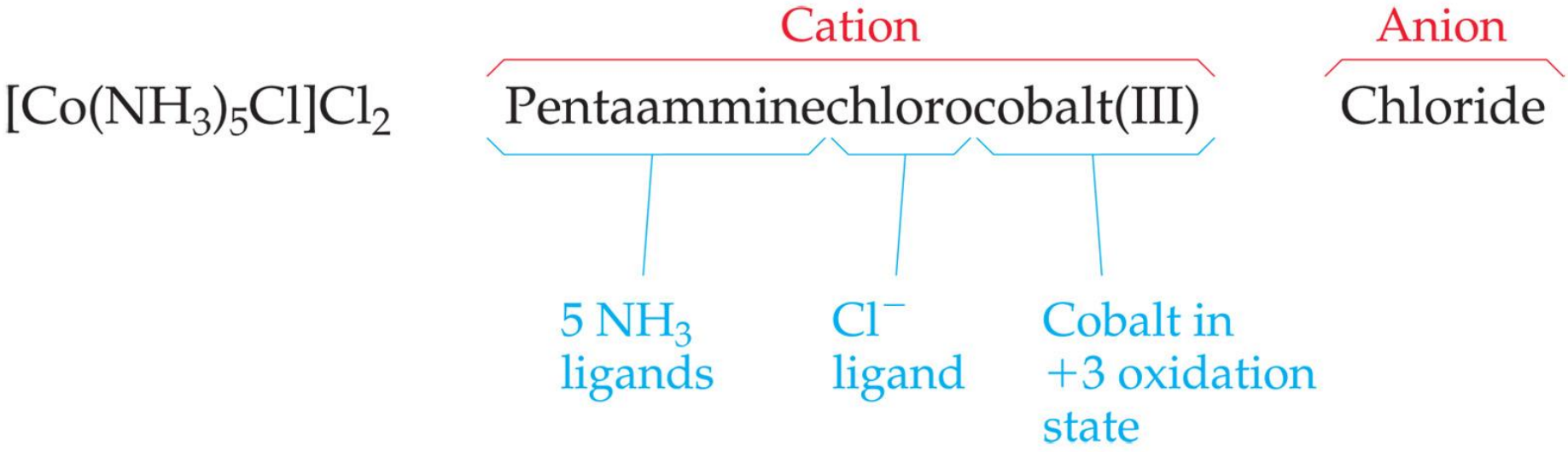
Nomenclature of Coordination Compounds

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.



Nomenclature of Coordination Compounds

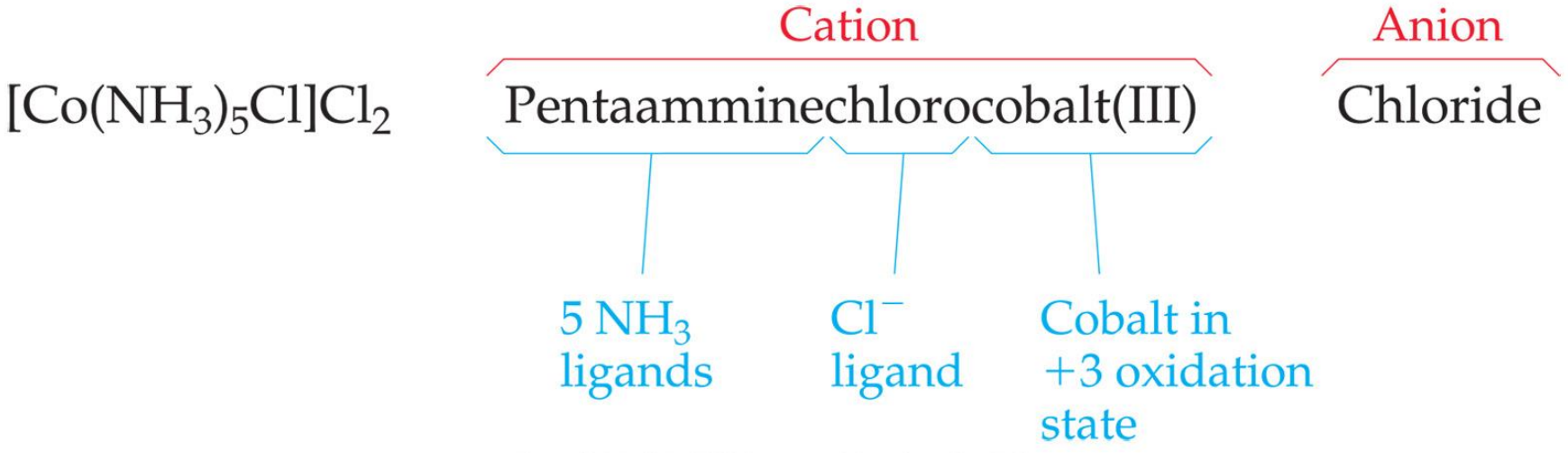
- The names of anionic ligands end in "**o**"; the endings of the names of neutral ligands are not changed.

-ide suffix changed to **-o**

-**ite** suffix changed to **–ito**

-ate suffix changed to **-ato**

- 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: IUPAC Rules

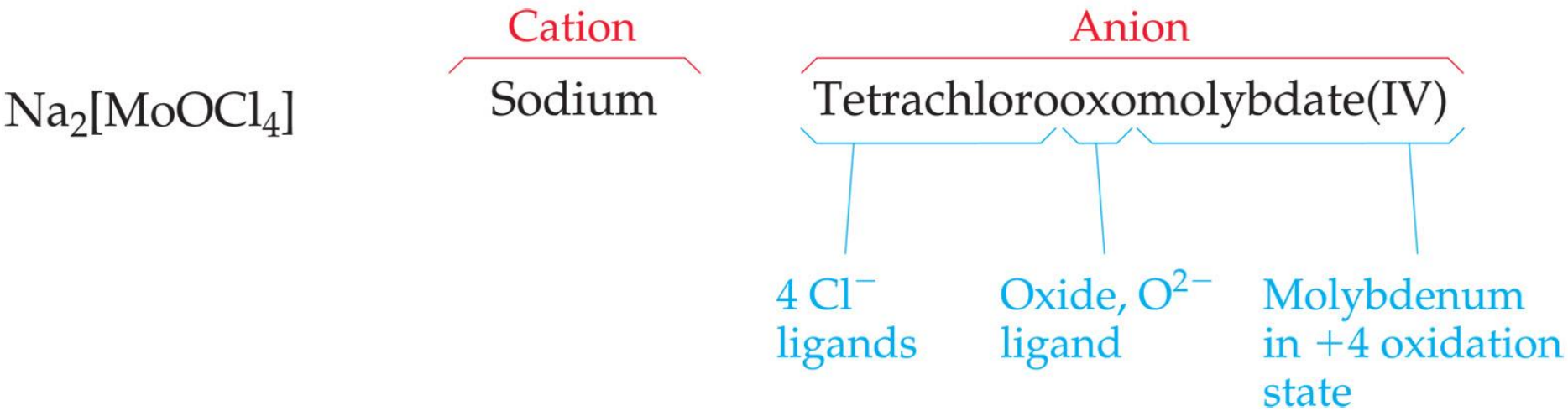
Transition Metal	Name if in Cationic Complex	Name if in Anionic Complex
Sc	Scandium	Scandate
Ti	titanium	titanate
V	vanadium	vanadate
Cr	chromium	chromate
Mn	manganese	manganate
Fe	iron	ferrate
Co	cobalt	cobaltate
Ni	nickel	nickelate
Cu	Copper	cuprate
Zn	Zinc	zincate

Nomenclature

- Ligands are named in alphabetical order (name of ligand, not prefix)
  - $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)BrCl(CH_3NH_2)]^{+2}$
- Anionic ligands are given an ‘o’ suffix. Neutral ligands retain the usual name.
  - Coordianted water is called ‘aqua’.
  - Chloro, Cl^-
  - Sulfato, SO_4^{2-}

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.



IUPAC nomenclature

$[Co(NH_3)_5(NCS)]Cl_2$ Pentaammineisothiocyanatocobalt (III) chloride

$[Cr(H_2O)_4Cl_2]^+$ Tetraaquadichlorochromium (III) ion

$K_2[HgI_4]$ Potassium tetraiodomercurate (II)

$Na_2[CrOF_4]$ Sodium tetrafluorooxochromate (IV)

- complexes are enclosed in square brackets.
- first the name of the central atom is given.
- followed by first the anionic ligand and then the neutral ligands; within each group they are alphabetically ordered according to the first character of their formula.

Examples: $[PtCl_2(C_2H_4)(NH_3)]$

$K_2[PdCl_4]$

Illustrative Example

Write IUPAC name of the following compounds:

(i) $K_2[Zn(OH)_4]$

(ii) $[CoCl(CN)(NO_2)(NH_3)_3]$

(iii) $[Cr(CN)_2(H_2O)_3NH_3]Cl$

.

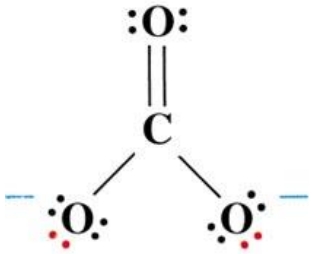
Types of Ligands: Monodentate (one tooth) Ligands

Latin: "mono" meaning one and "dens" meaning tooth

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

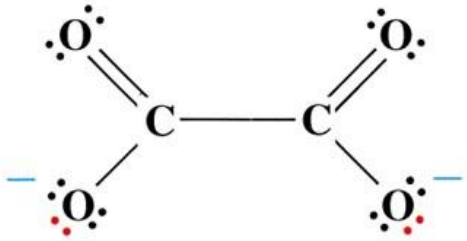
The ligating atom is indicated by a pair of red dots representing a lone pair of electrons. In the CO_3^{2-} ligand, either one or two of the oxygen atoms can donate a lone pair to the metal.

Types of Ligands: Bidentate (two tooth) Ligands



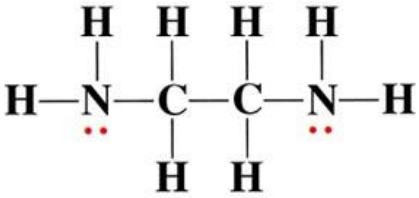
Carbonate ion, CO_3^{2-}

(a)



Oxalate ion, $C_2O_4^{2-}$

(b)

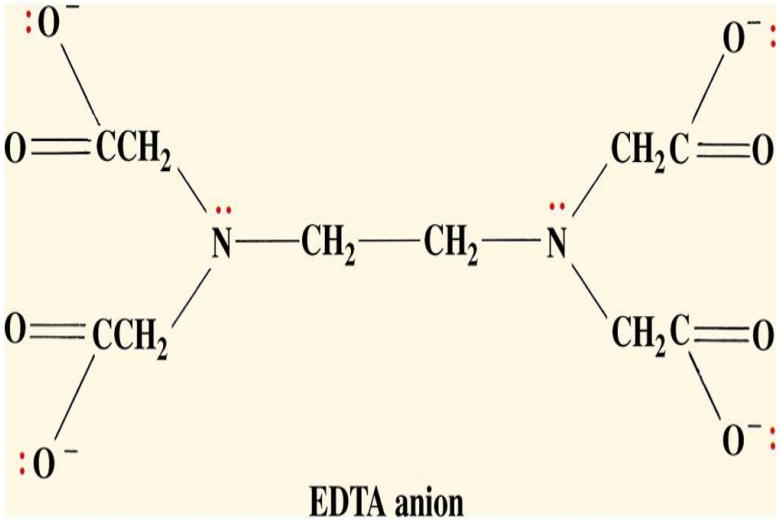


Ethylenediamine, $NH_2CH_2CH_2NH_2$

(c)

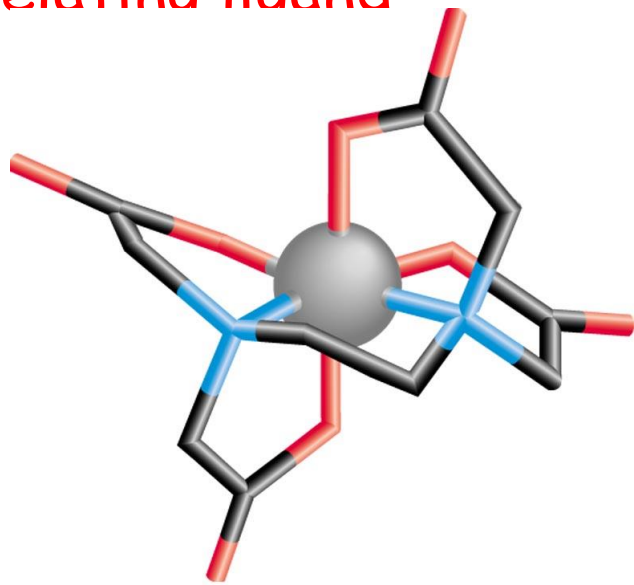
Bidentate (chelates)

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



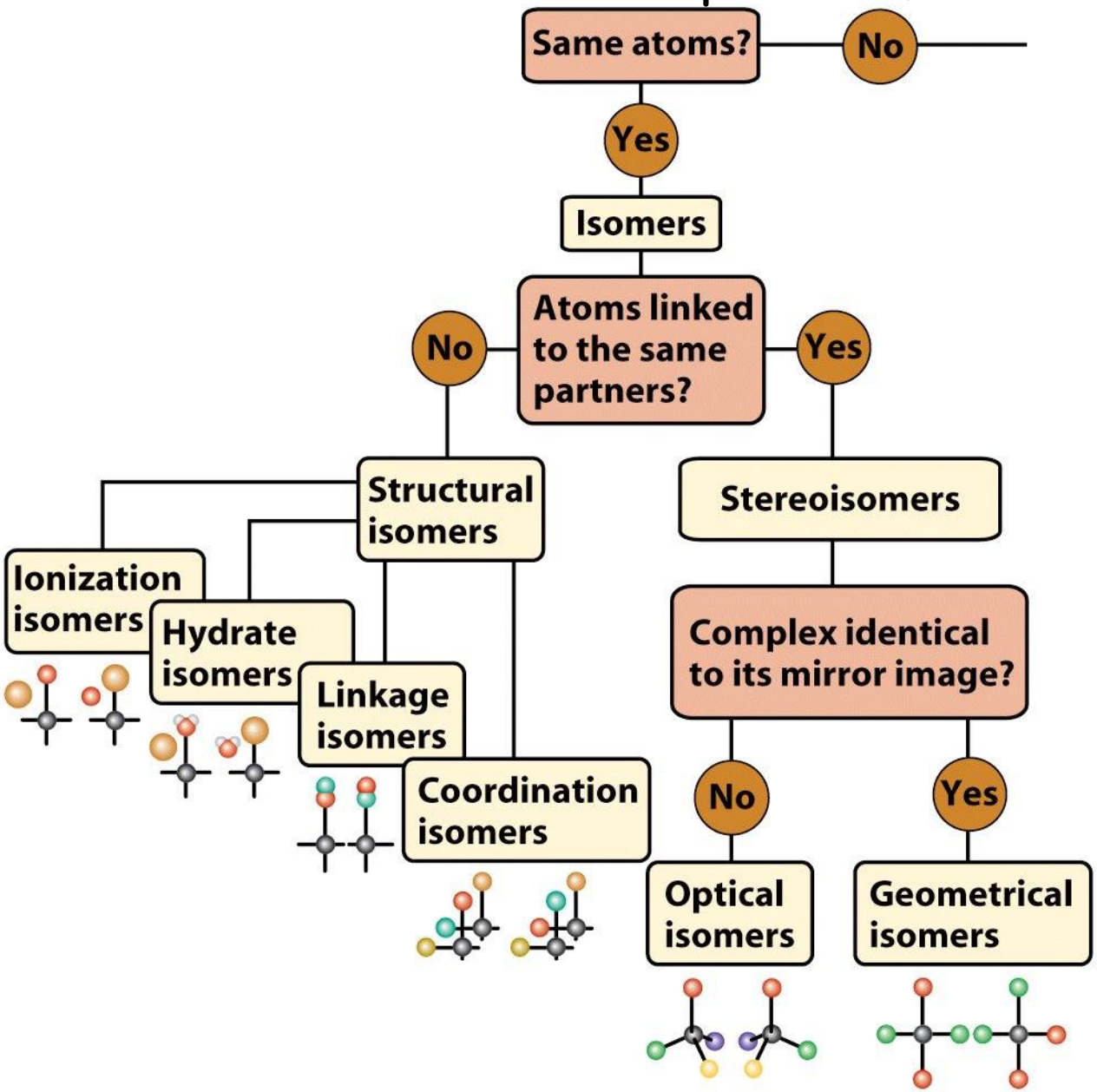
EDTA anion

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



Coordination complexes: isomers

Isomers: same atomic composition, different structures



We'll discuss the following types of isomers:

Hydrate

Linkage

Cis-trans

Optical (Enantiomers)

Isomerism in Coordination Compounds

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

Structural isomerism

Ionization isomerism

(i) Structural isomerism
(ii) Stereo-isomerism

$[Co(NH_3)Br]\ SO_4$ $[Co(NH_3)_5Br]^{2+}\ SO_4^{2-}$

$[Co(NH_3)_5SO_4]\ Br$ $[Co(NH_3)_5SO_4]^{+} + Br^{-}$

Isomerism

Hydrate isomerism

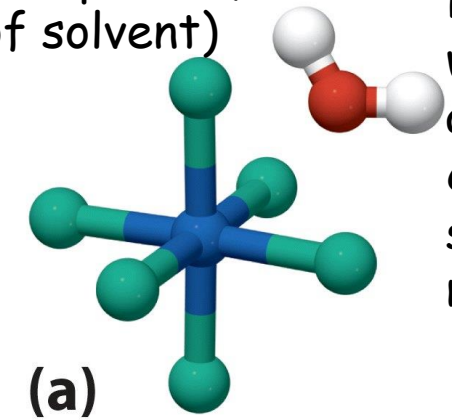
$[Cr(H_2O)_6]Cl_3$ (Violet)

$[Cr(H_2O)_5Cl]Cl_2.H_2O$ (Green)

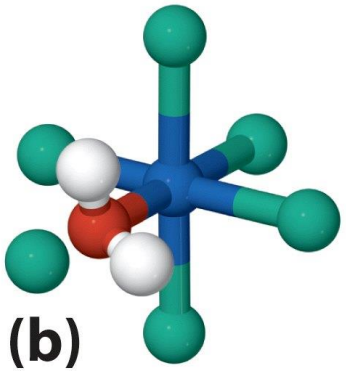
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (Green)

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

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



(a)



(b)

Coordination isomerism

$[Co(NH_3)_6]\ [Cr\ (CN)_6]$ and $[Cr(NH_3)_6]\ [Co\ (CN)_6]$

Isomerism

Linkage isomerism

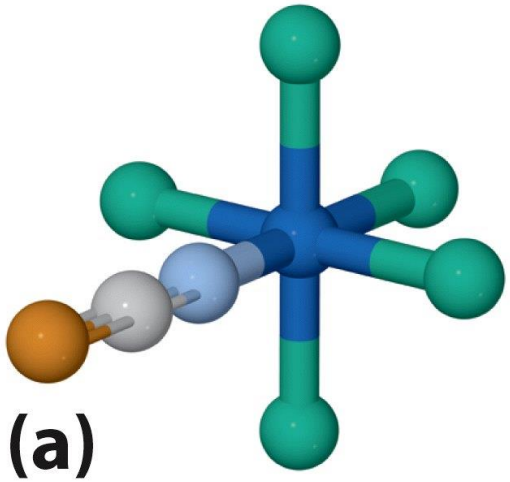
This type of isomerism occurs in ambidentate ligands like CO, NO_2^-, SCN^-, CN^-, $S_2O_3^{2-}$

Example

$[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

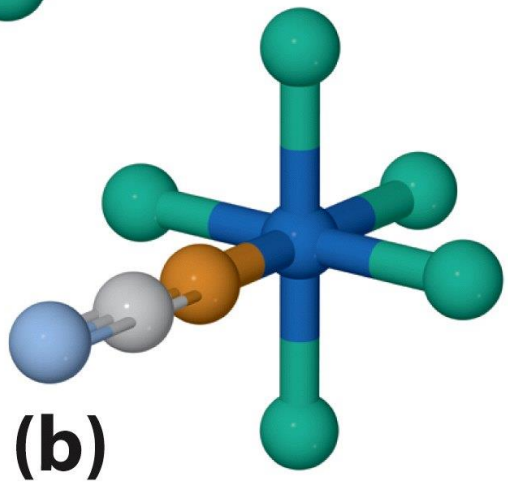
Example: $\ominus S—C\equiv N$

Bonding to metal may occur at the S or the N atom



(a)

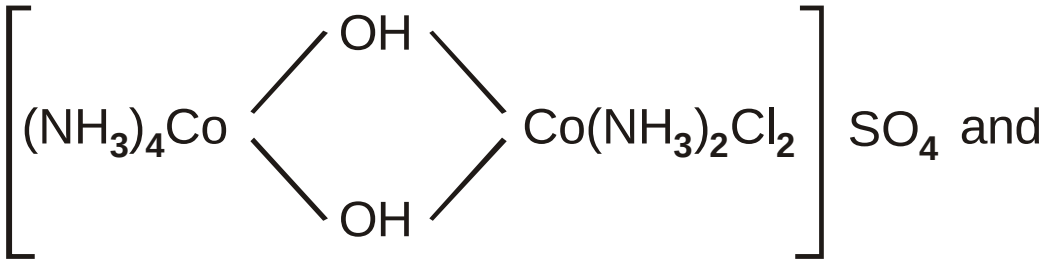
Bonding occurs from N atom to metal



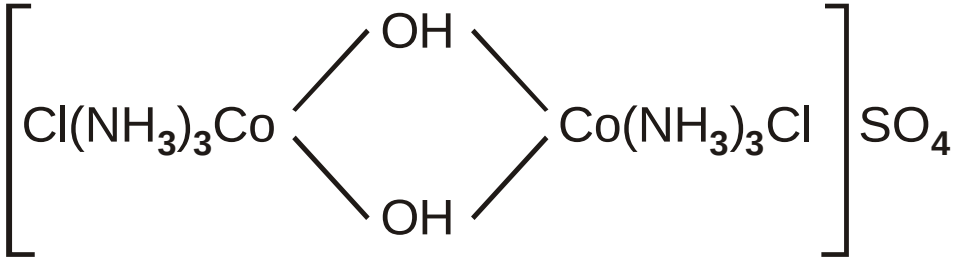
(b)

Bonding occurs from S atom to metal

Coordination position isomerism



and



- Example

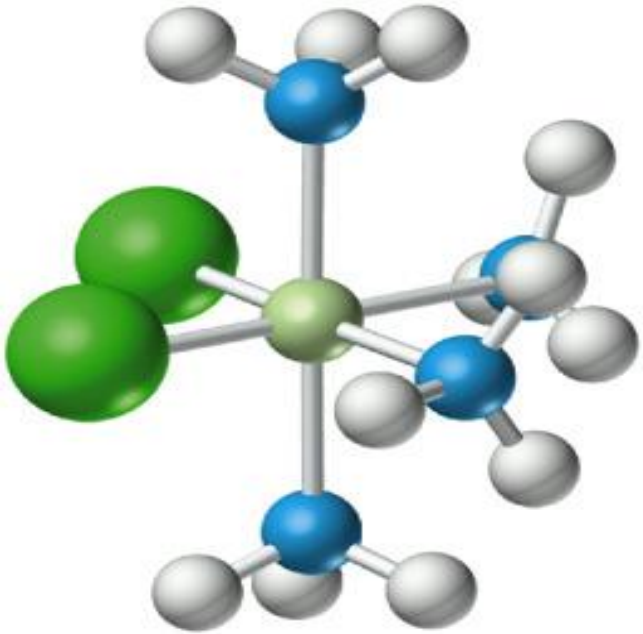
  $[Co(NH_3)_5Cl]Br$ vs. $[Co(NH_3)_5Br]Cl$

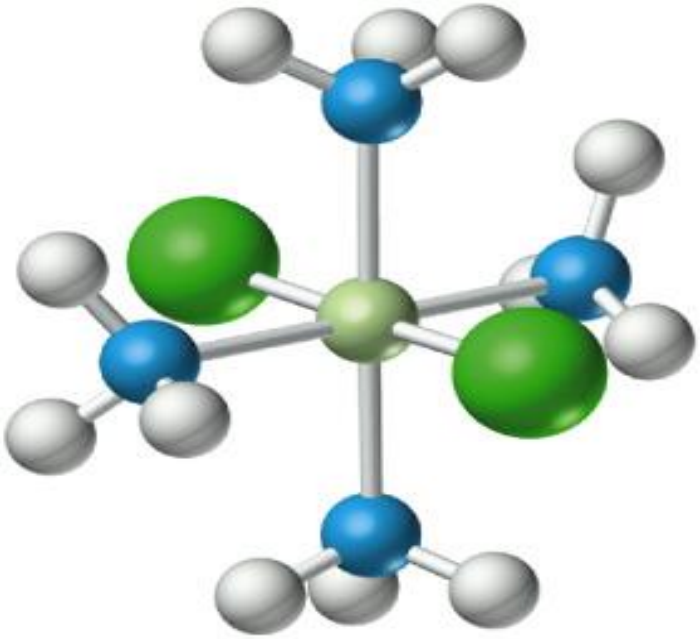
- Consider ionization in water

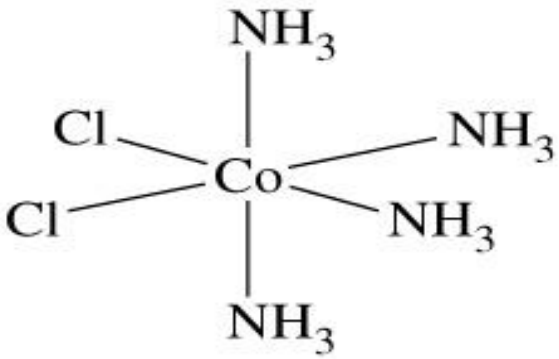
  $[Co(NH_3)_5Cl]Br \rightarrow [Co(NH_3)_5Cl]^+ + Br^-$

  $[Co(NH_3)_5Br]Cl \rightarrow [Co(NH_3)_5Br]^+ + Cl^-$

Geometrical isomerism



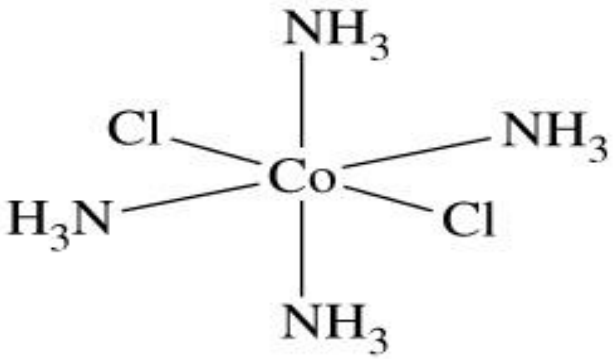




cis-$[CoCl_2(NH_3)_4]^+$

(purple)

(a)

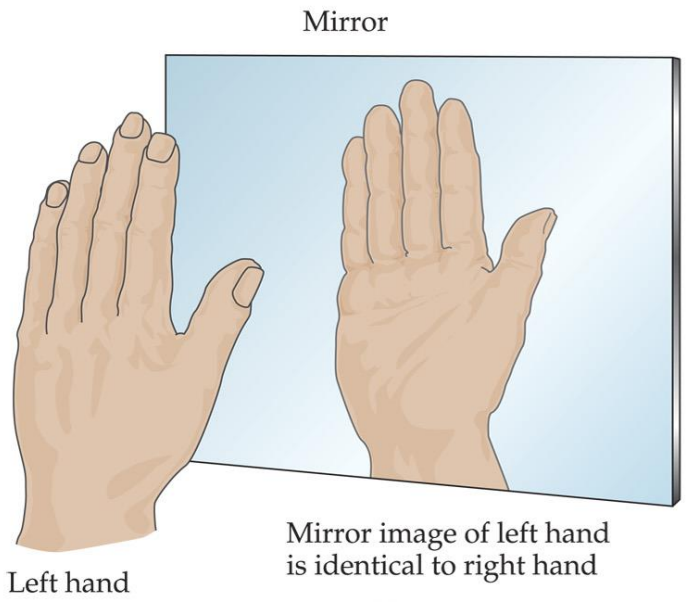


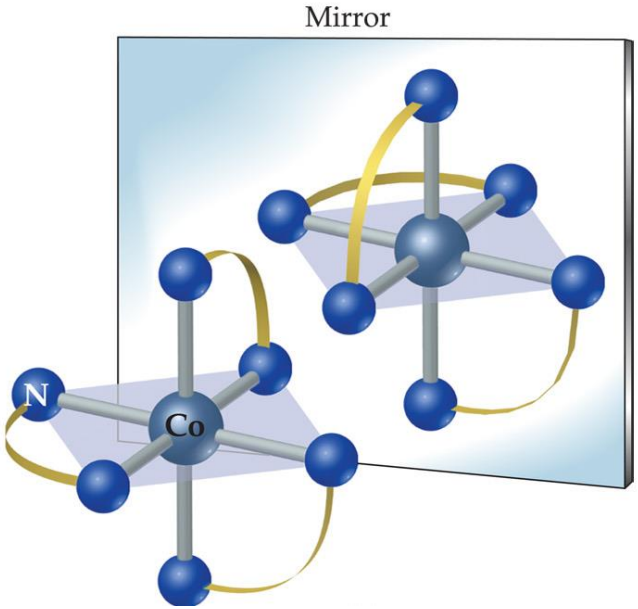
trans-$[CoCl_2(NH_3)_4]^+$

(green)

(b)

Stereoisomers

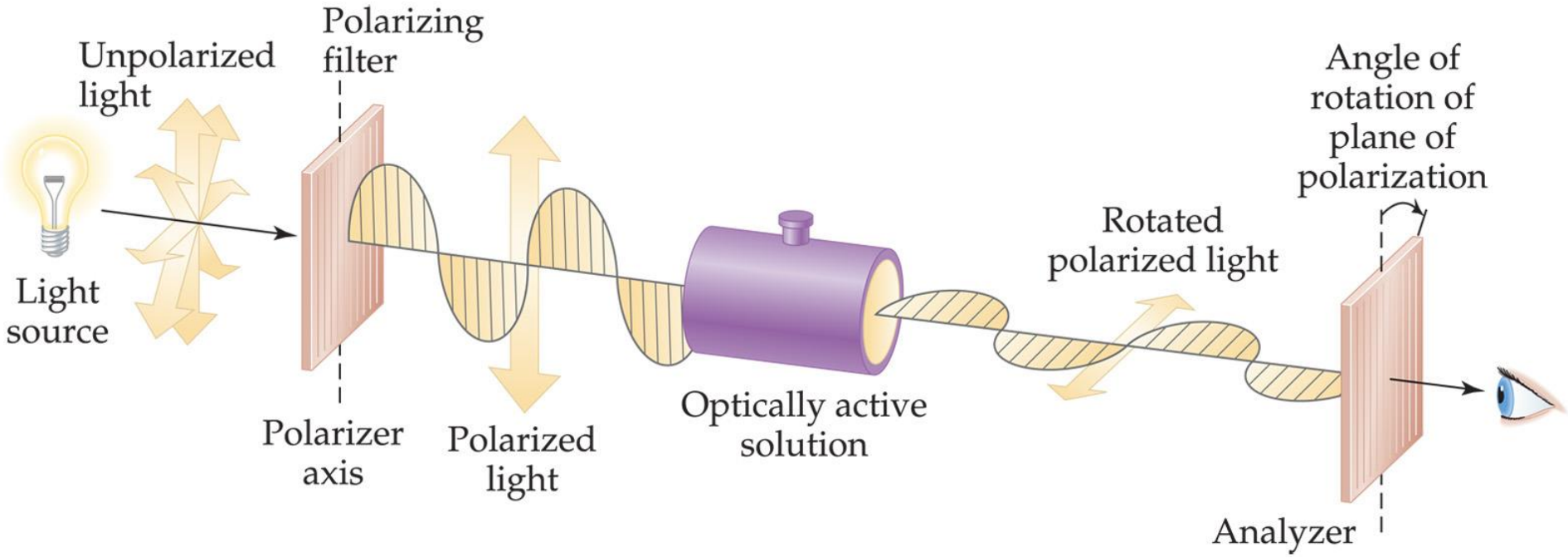




- Other stereoisomers, called optical isomers or enantiomers, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

Enantiomers

- Most of the physical properties of chiral molecules are the same, boiling point, freezing point, density, etc.
- One exception is the interaction of a chiral molecule with plane-polarized light.

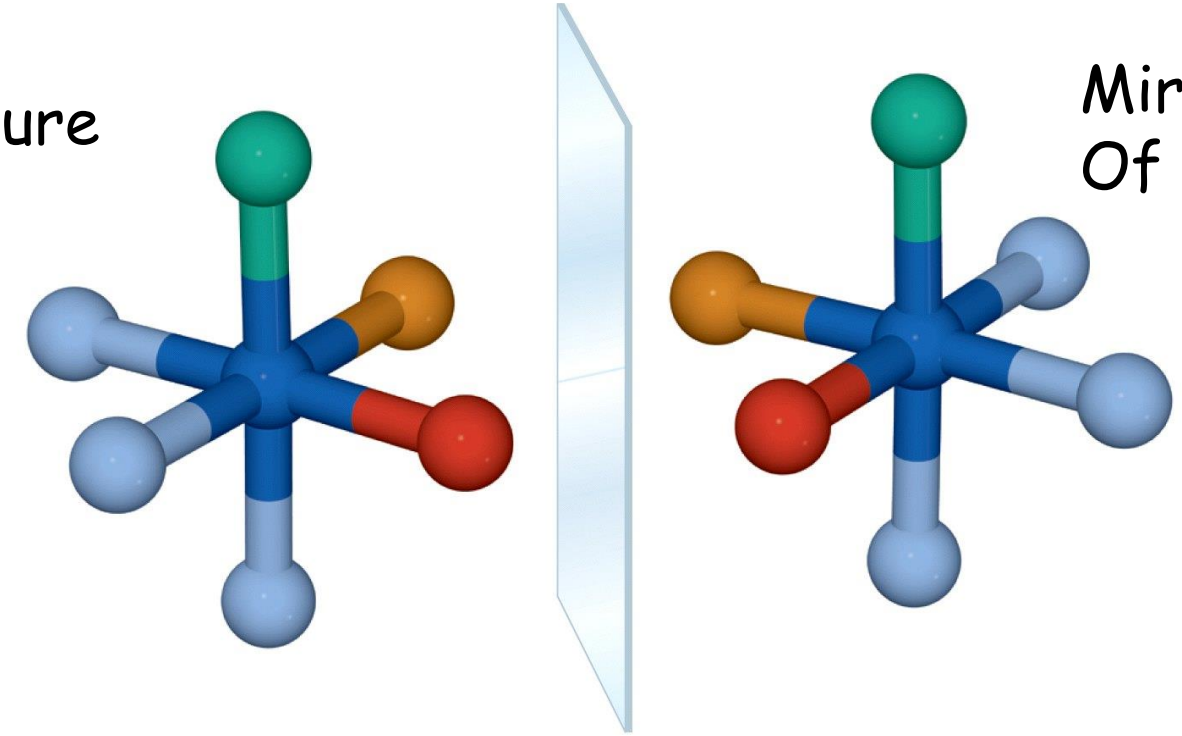


Stereoisomerism

Enantiomers: non superimposable mirror images

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

Structure

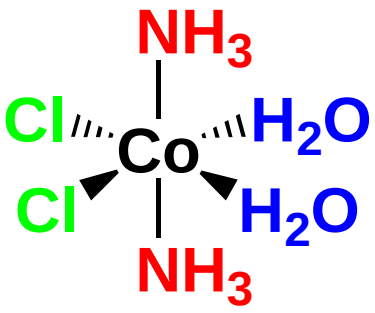


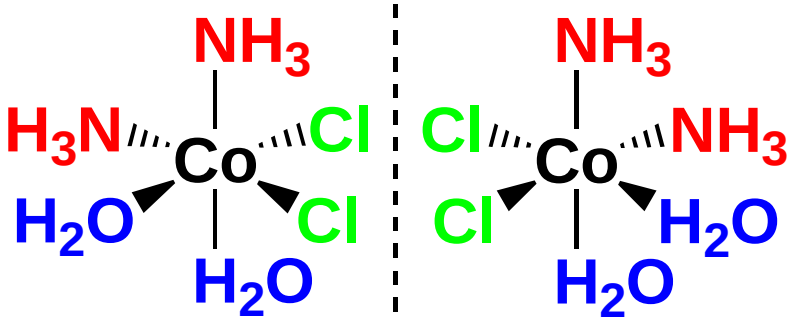
Mirror image
Of structure

Two chiral structures: non superimposable mirror images

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

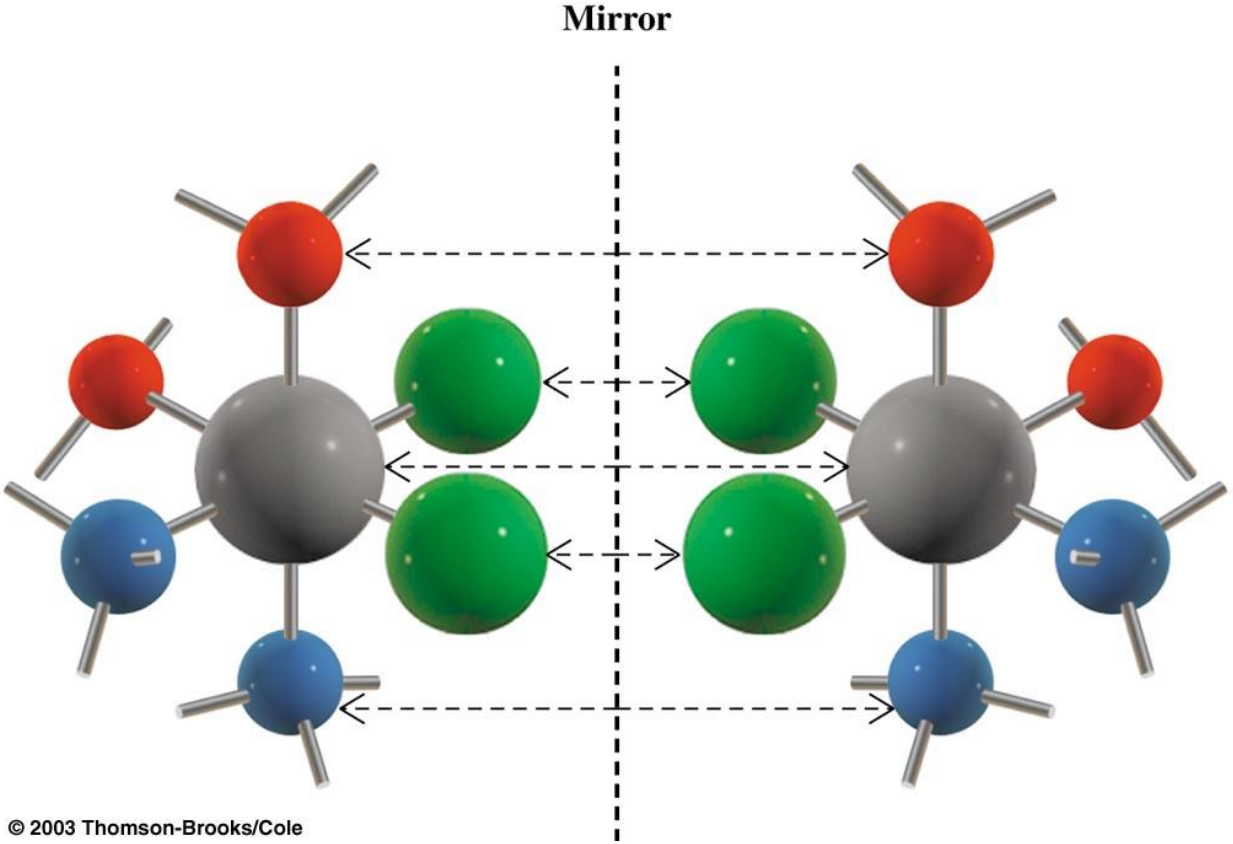


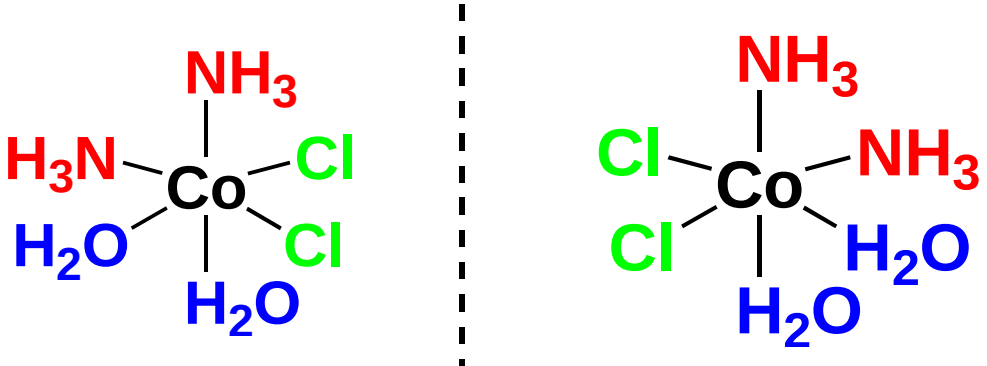


Plane of symmetry
Achiral (one structure)

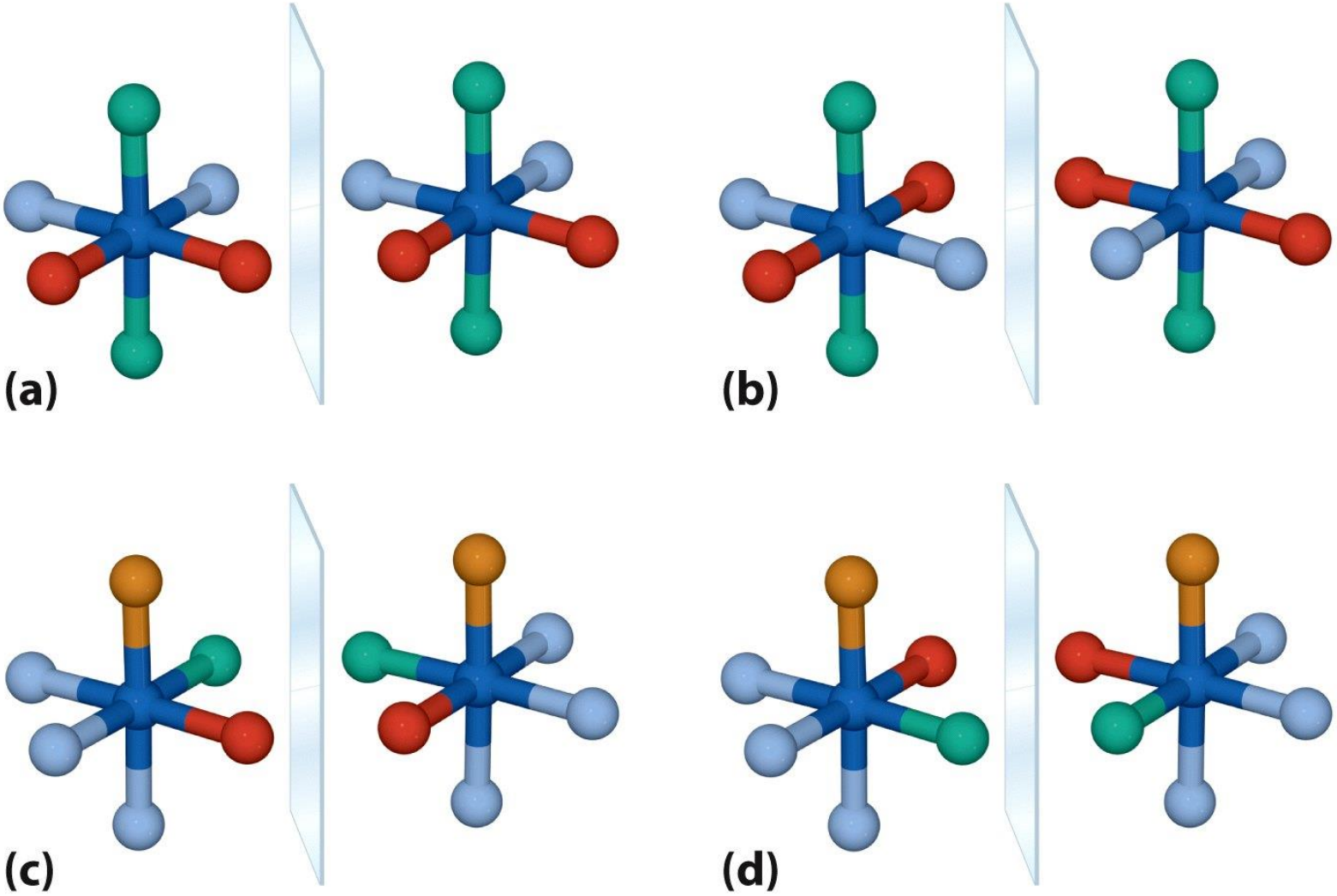
No plane of symmetry
Chiral (two enantiomer)

Examples of enantiomers





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



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)

Coordination Complexes in Living Systems

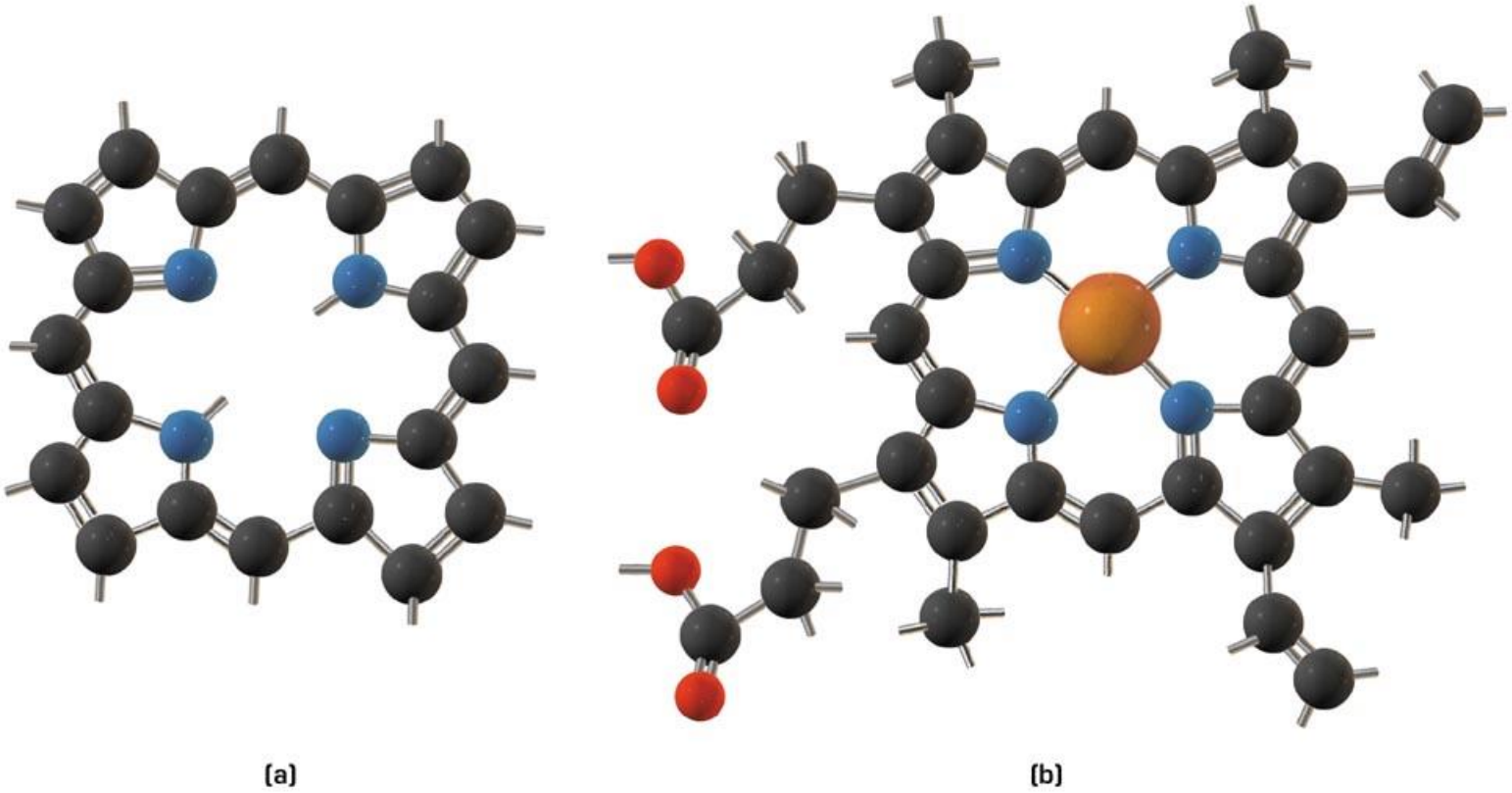
Porphines, hemes, hemoglobin

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



(a) (b)

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

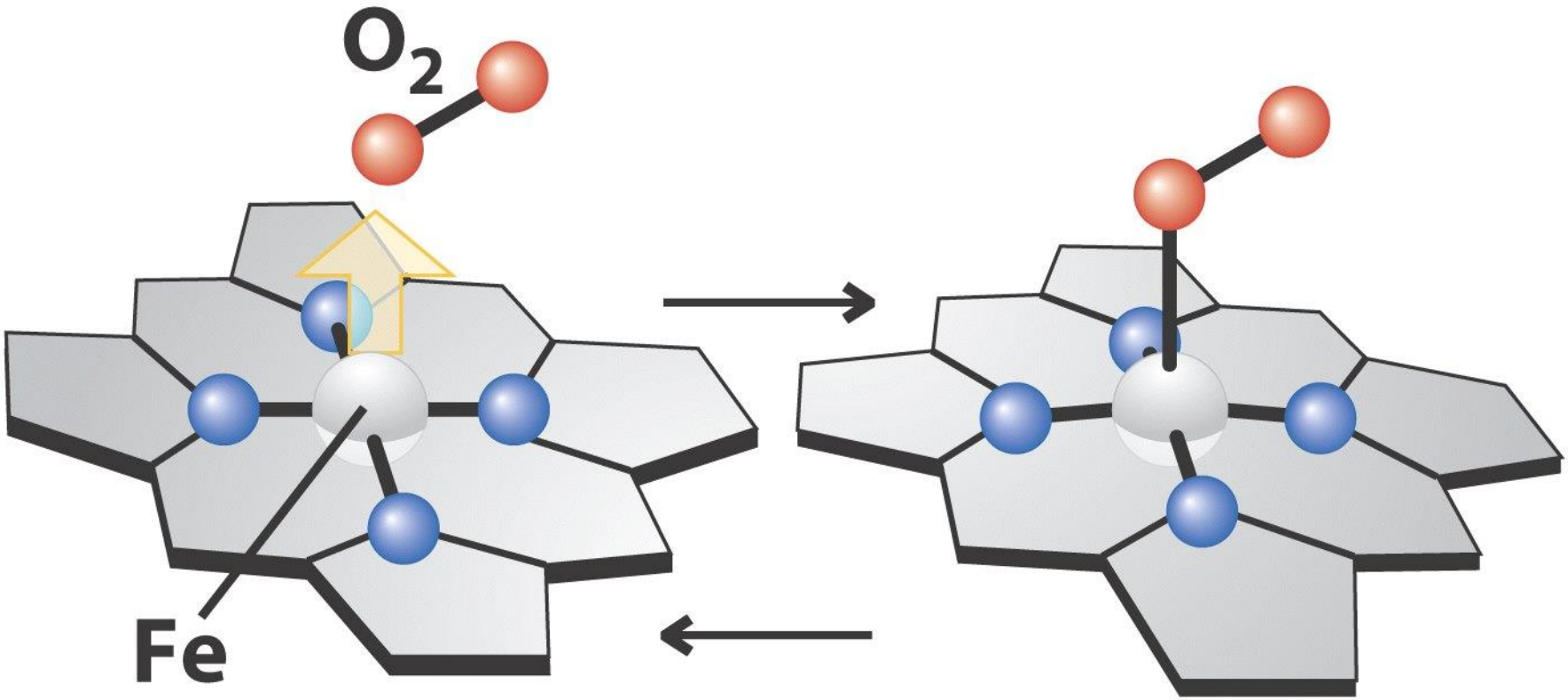
22.4 Reactions of Coordination Compounds

- Complex ions undergo *ligand exchange* (or *substitution*) reactions in solution.
  - Example: Exchange of NH_3 with H_2O

$$[Co(NH_3)_6]^{3+} + 6H^+ + 6H_2O \rightleftharpoons [Co(H_2O)_6]^{3+} + 6NH_4^+$$

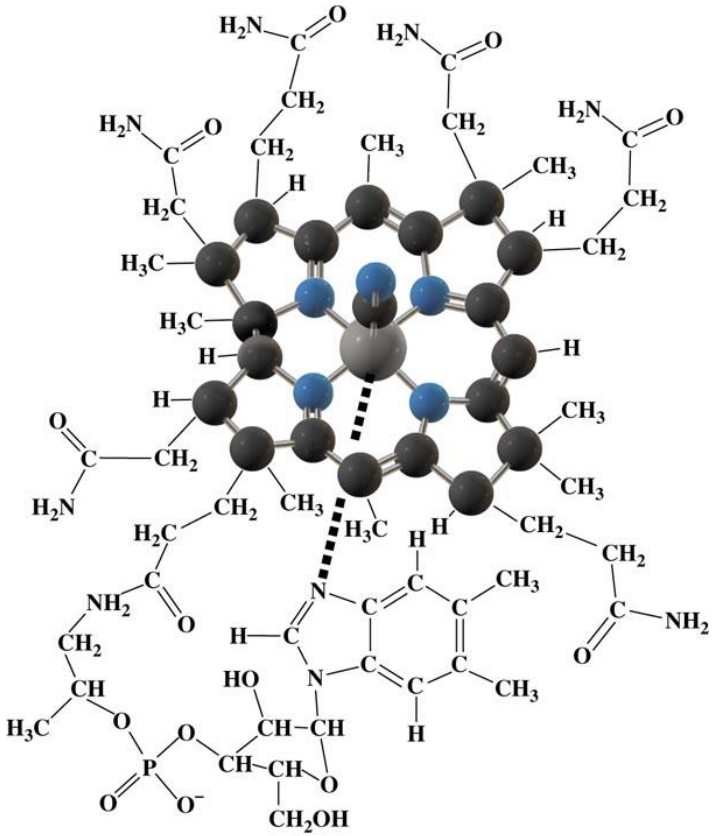
  - Rates of exchange reactions vary widely

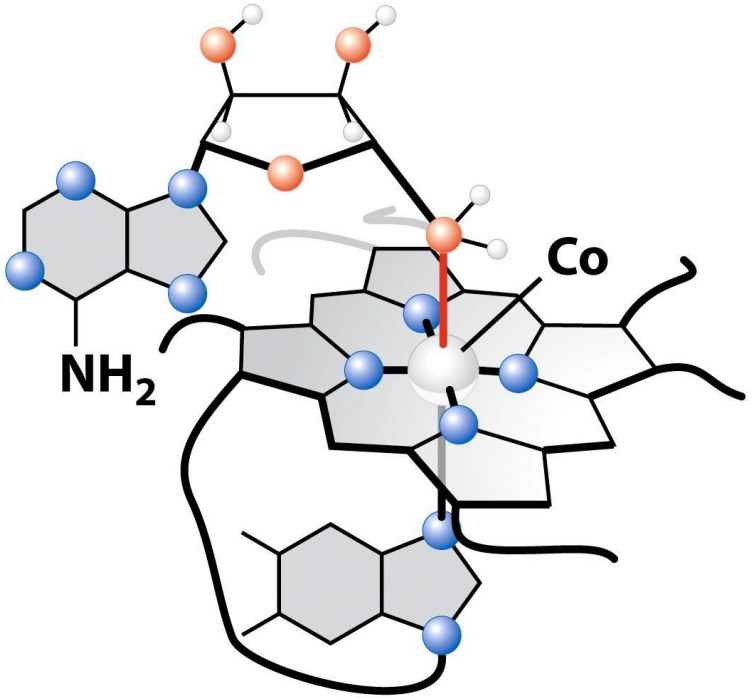
Reversible addition of O_2 to hemoglobin



The mechanism by which oxygen is carried throughout the body

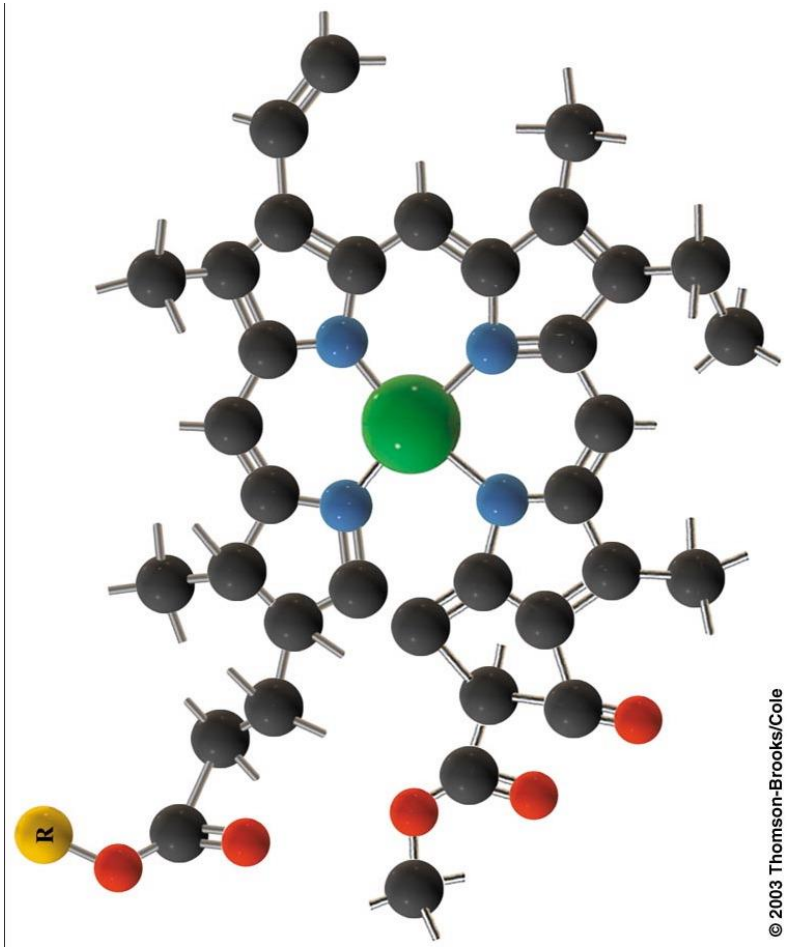
Involved in many important biological processes, including the production of red blood cells

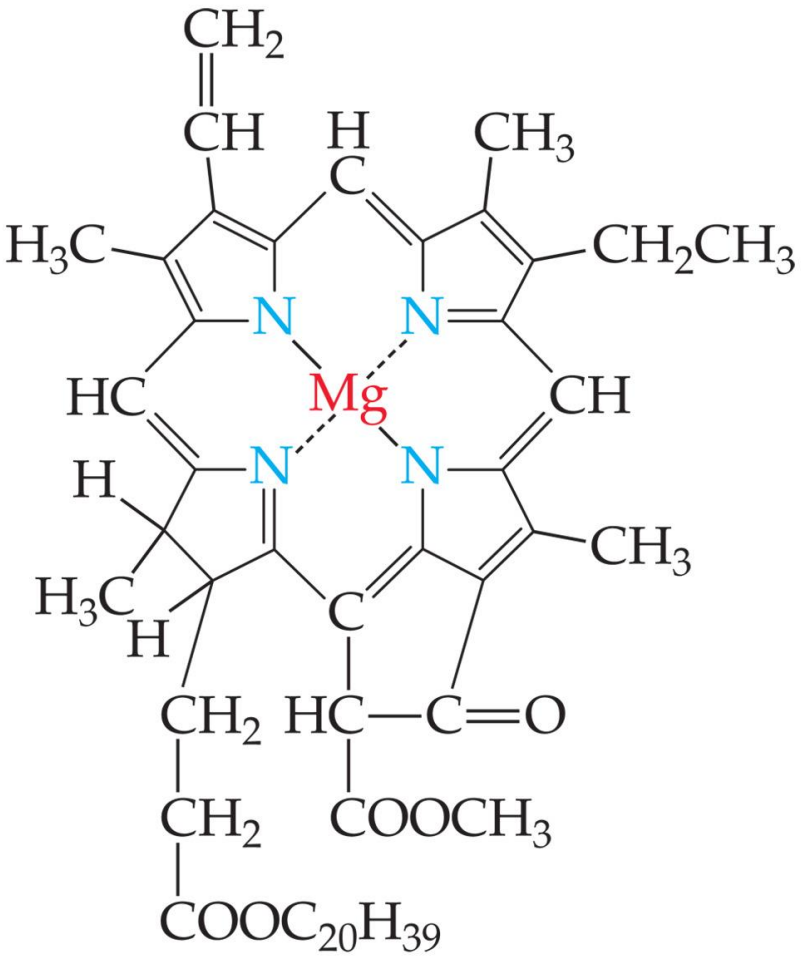




Vitamin B_{12} ($Co[C_{62}H_{88}N_{13}O_{14}P])CN$

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





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

Mechanism of Cisplatin in Chemotherapy