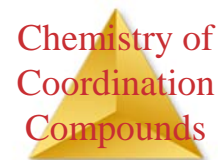


Chemistry, The Central Science, 11th edition
Theodore L. Brown; H. Eugene LeMay, Jr.;
and Bruce E. Bursten

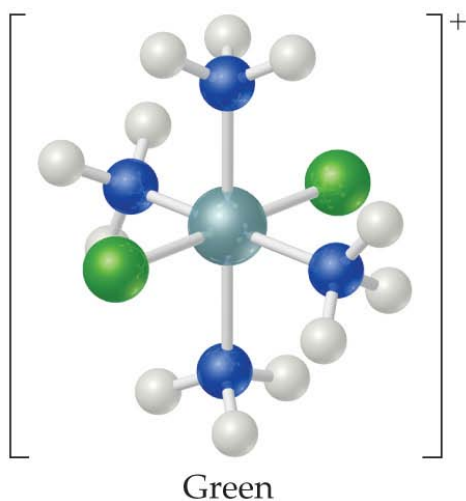
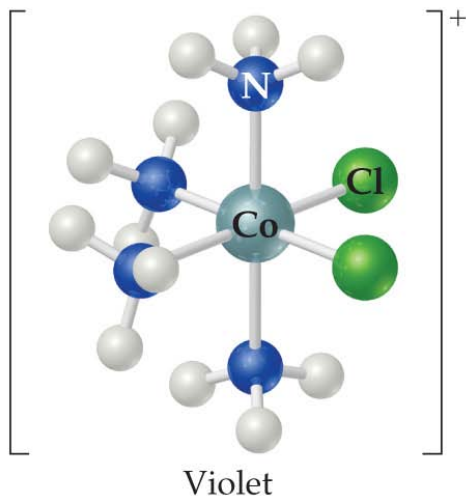
Chapter 24

Chemistry of Coordination Compounds

John D. Bookstaver
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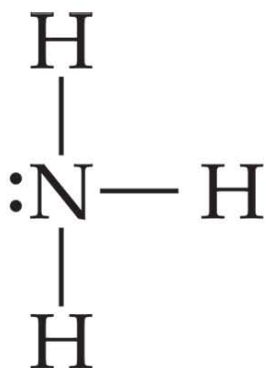
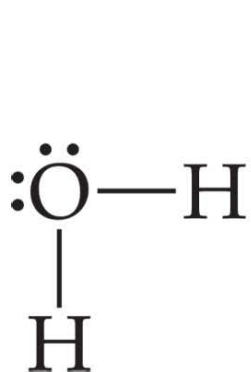
Complexes



- A central metal atom bonded to a group of molecules or ions is a **metal complex**.
- If the complex bears a charge, it is a **complex ion**.
- Compounds containing complexes are **coordination compounds**.

Complexes

- The molecules or ions coordinating with the metal are the **ligands**.
- They are usually anions or polar molecules.

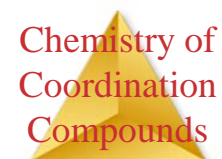


Coordination Compounds

Properties of Some Ammonia Complexes of Cobalt(III)

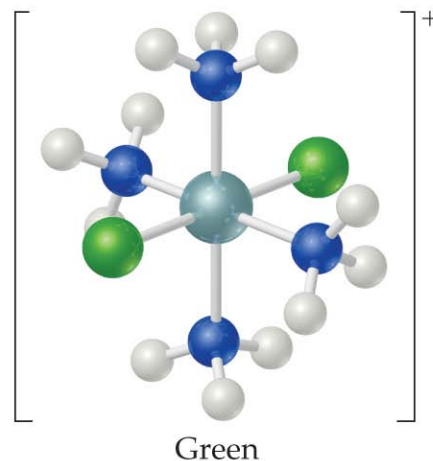
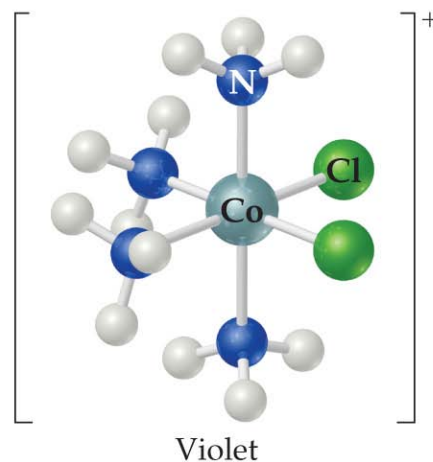
Original Formulation	Color	Ions per Formula Unit	"Free" Cl ⁻ Ions per Formula Unit	Modern Formulation
CoCl ₃ · 6 NH ₃	Orange	4	3	[Co(NH ₃) ₆]Cl ₃
CoCl ₃ · 5 NH ₃	Purple	3	2	[Co(NH ₃) ₅ Cl]Cl ₂
CoCl ₃ · 4 NH ₃	Green	2	1	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂]Cl
CoCl ₃ · 4 NH ₃	Violet	2	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂]Cl

- Many coordination compounds are brightly colored.
- Different coordination compounds from the same metal and ligands can give quite different numbers of ions when they dissolve.



Werner's Theory

- Alfred Werner suggested in 1893 that metal ions exhibit what he called *primary* and *secondary* valences.
 - Primary valences were the oxidation number for the metal (+3 on the cobalt at the right).
 - Secondary valences were the coordination number, the number of atoms directly bonded to the metal (6 in the complex at the right).

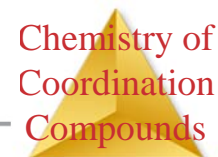


Werner's Theory

- The central metal and the ligands directly bonded to it make up the **coordination sphere** of the complex.
- In $\text{CoCl}_3 \cdot 6 \text{NH}_3$, all six of the ligands are NH_3 and the 3 chloride ions are outside the coordination sphere.

Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6 \text{NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5 \text{NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$



Werner's Theory

In $\text{CoCl}_3 \cdot 5 \text{NH}_3$ the five NH_3 groups and one chlorine are bonded to the cobalt, and the other two chloride ions are outside the sphere.

Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6 \text{NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5 \text{NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

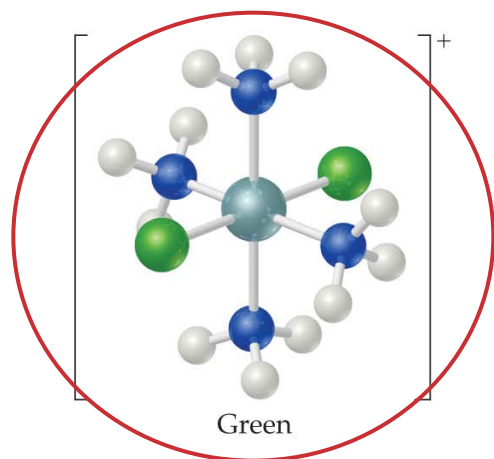
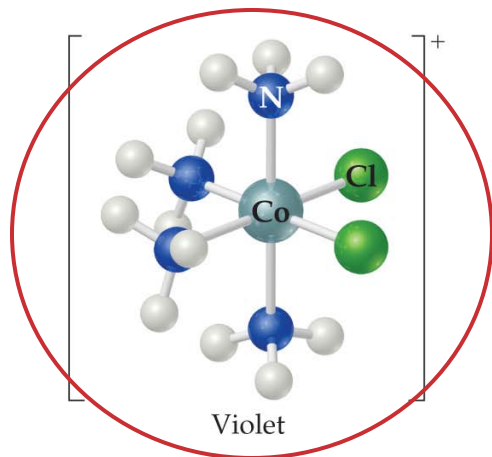
Werner's Theory

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.

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 · 6 NH ₃	Orange	4	3	[Co(NH ₃) ₆]Cl ₃
CoCl ₃ · 5 NH ₃	Purple	3	2	[Co(NH ₃) ₅ Cl]Cl ₂
CoCl ₃ · 4 NH ₃	Green	2	1	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂]Cl
CoCl ₃ · 4 NH ₃	Violet	2	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂]Cl

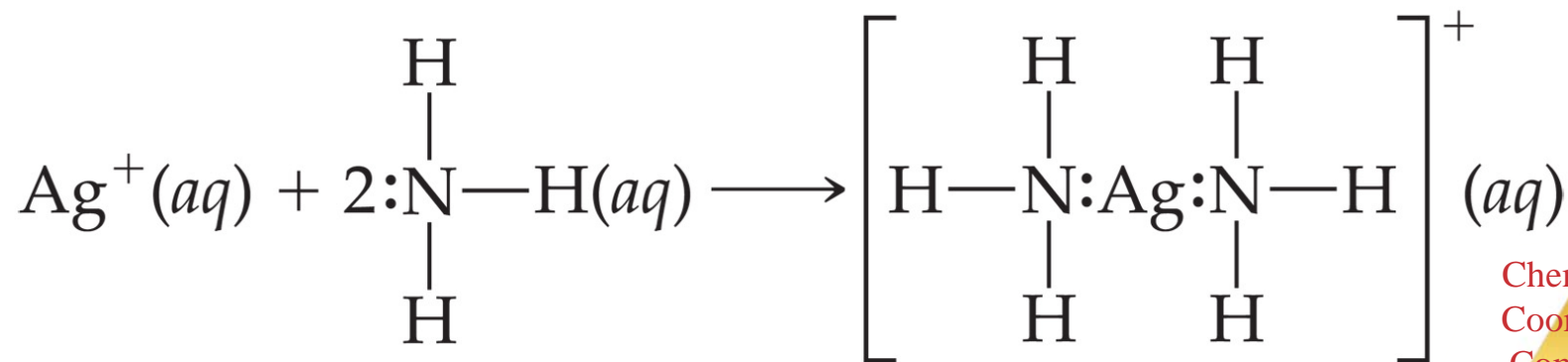
Werner's Theory



- This approach correctly predicts there would be two forms of $\text{CoCl}_3 \cdot 4 \text{NH}_3$.
 - The formula would be written $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.
 - One of the two forms has the two chlorines next to each other.
 - The other has the chlorines opposite each other.

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.

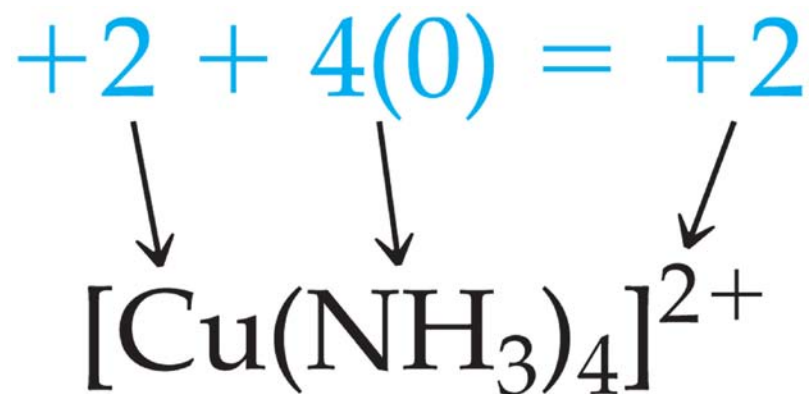


Metal-Ligand Bond

The coordination of the ligand with the metal can greatly alter its physical properties, such as color, or chemical properties, such as ease of oxidation.



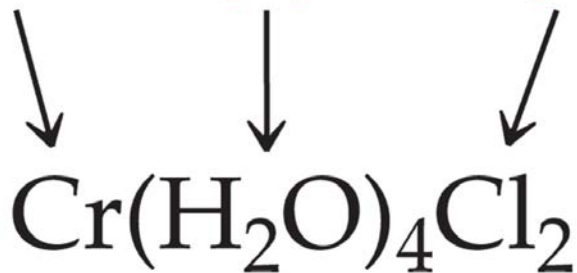
Oxidation Numbers



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

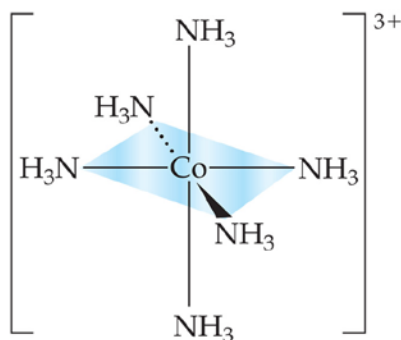
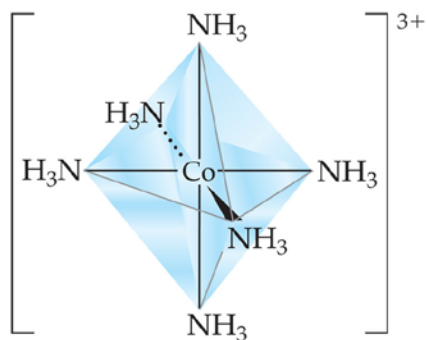
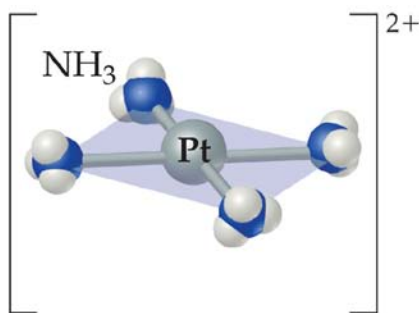
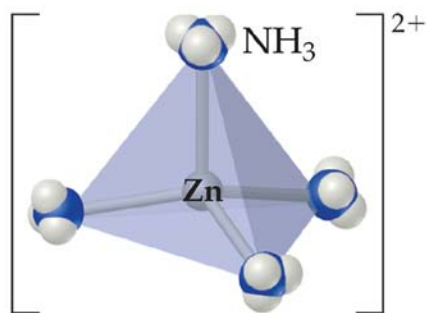
Oxidation Numbers

$$+3 + 4(0) + 2(-1) = +1$$



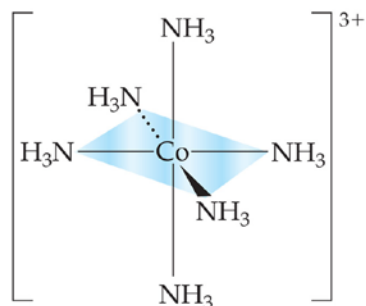
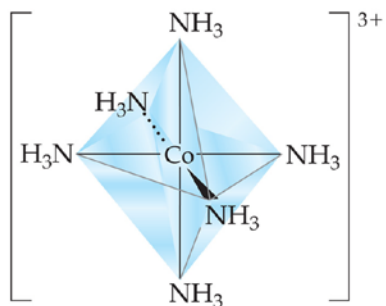
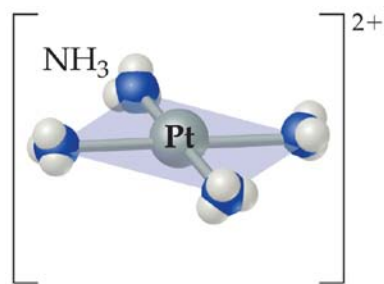
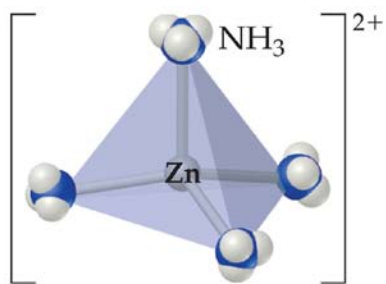
Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

Coordination Number



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

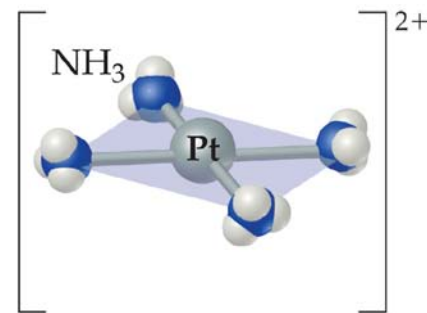
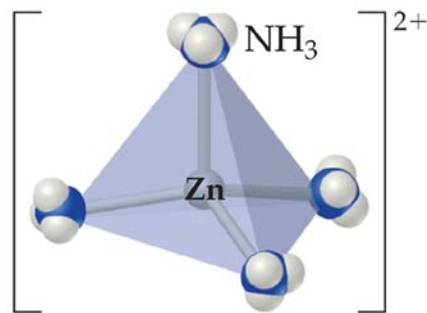
Coordination Number



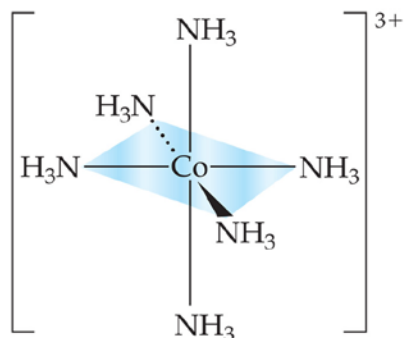
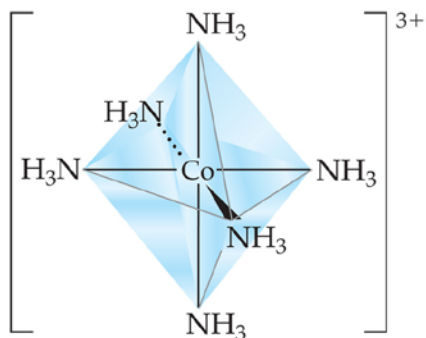
- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.

Geometries

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



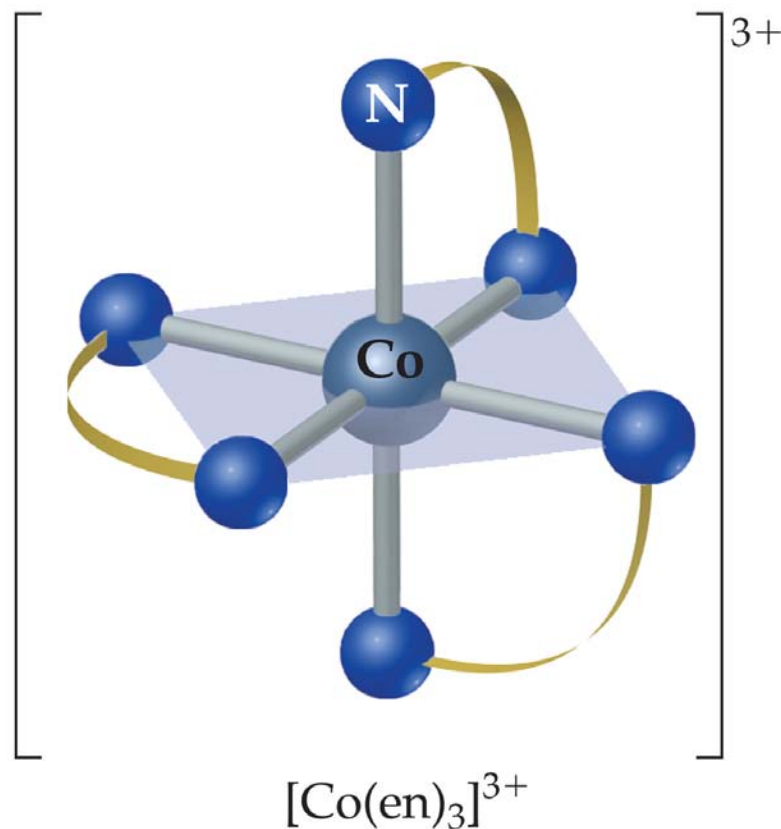
Geometries



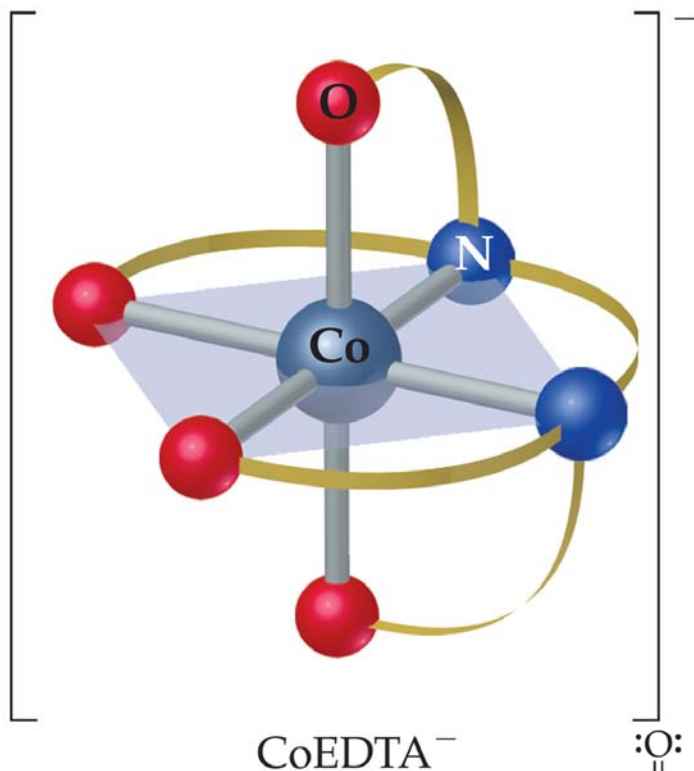
By far the most-encountered geometry, when the coordination number is six, is octahedral.

Polydentate Ligands

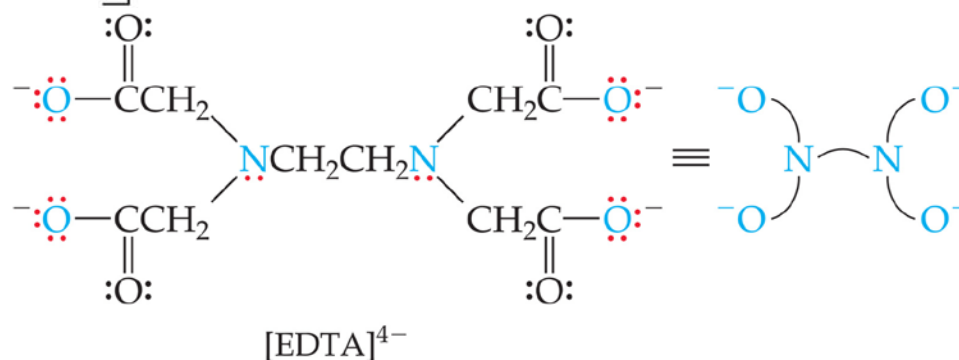
- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, represented here as en, each N is a donor atom.
- Therefore, en is bidentate.



Polydentate Ligands

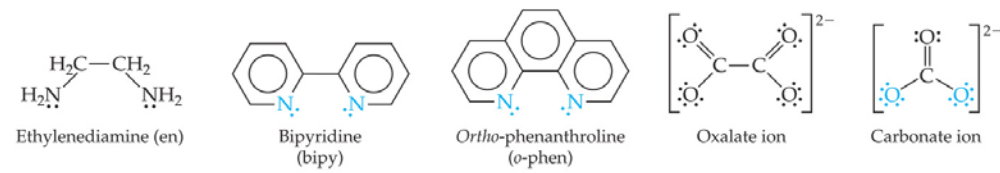
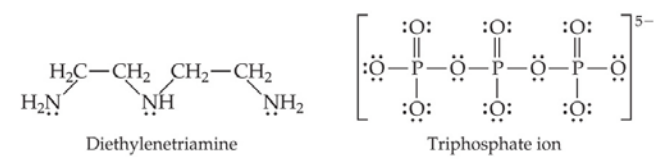
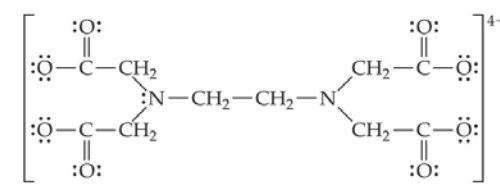


Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.

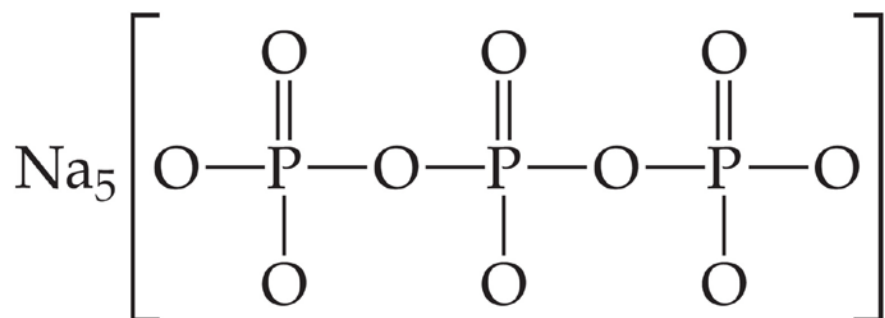


Polydentate Ligands

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

Ligand Type	Examples
Monodentate	$\text{H}_2\ddot{\text{O}}:$ Water $:\text{NH}_3$ Ammonia $:\ddot{\text{F}}:^-$ Fluoride ion $:\ddot{\text{Cl}}:^-$ Chloride ion $[\text{C}\equiv\text{N}:]^-$ Cyanide ion $[\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ Thiocyanate ion $[\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion $[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion
Bidentate	 Ethylenediamine (en) Bipyridine (bipy) Ortho-phenanthroline (o-phen) Oxalate ion Carbonate ion
Polydentate	 Diethylenetriamine Triphosphate ion
	 Ethylenediaminetetraacetate ion (EDTA^{4-})

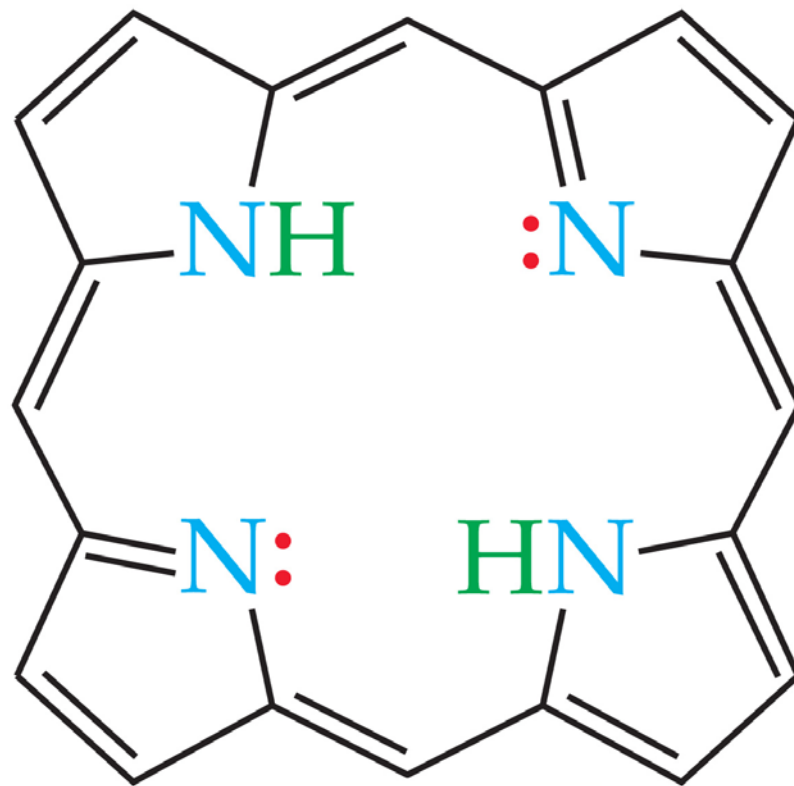
Chelating Agents



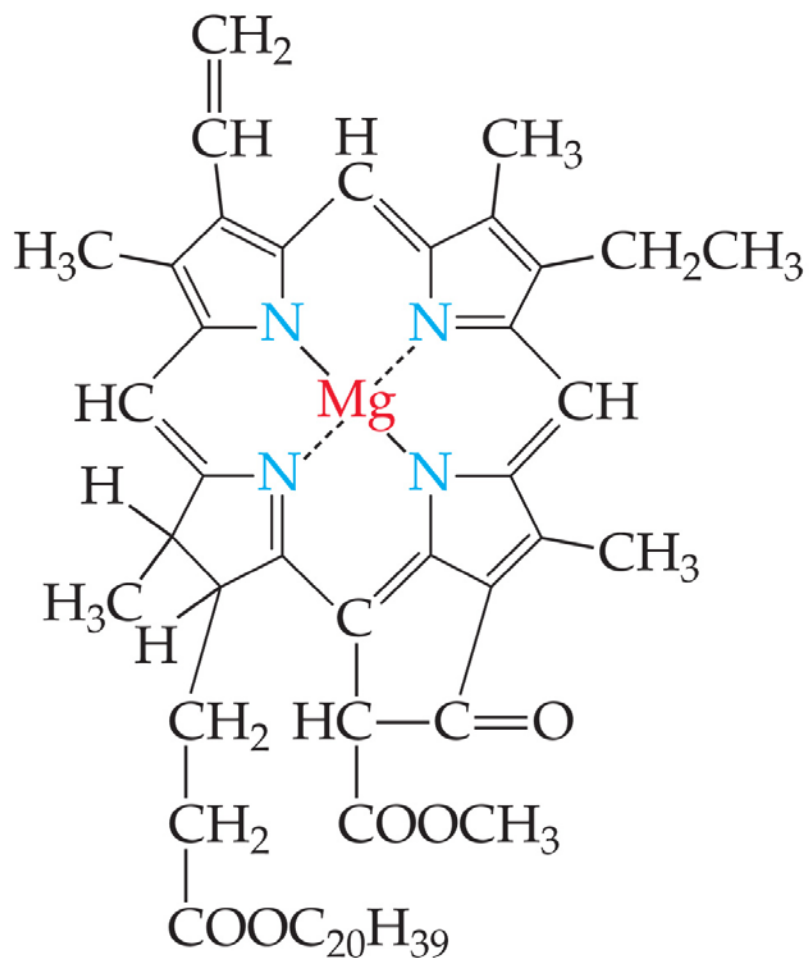
- Therefore, they can render metal ions inactive without actually removing them from solution.
- Phosphates are used to tie up Ca^{2+} and Mg^{2+} in hard water to prevent them from interfering with detergents.

Chelating Agents

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



Chelating Agents



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

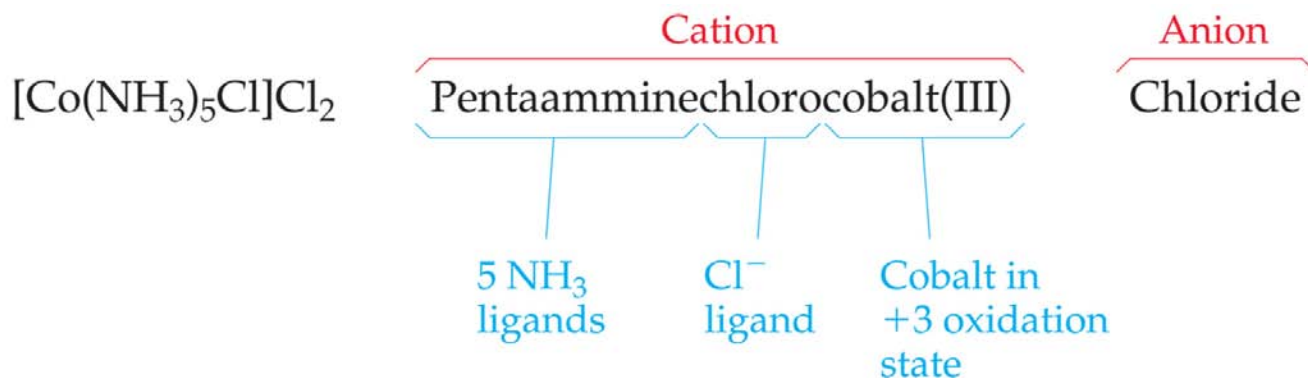
Nomenclature of Coordination Compounds

Some Common Ligands			
Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $\text{C}_2\text{O}_4^{2-}$	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, $\text{C}_5\text{H}_5\text{N}$	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.

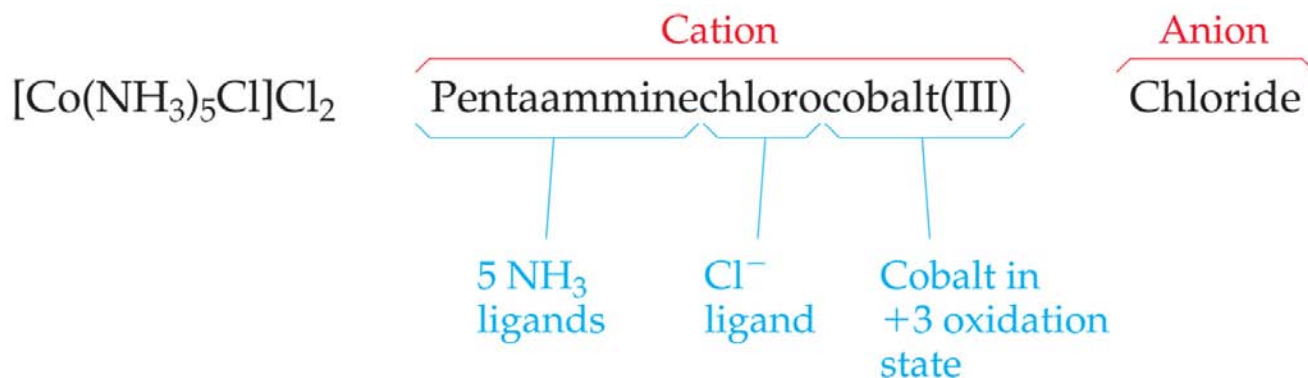
Nomenclature of Coordination Compounds

- As is the case with ionic compounds, 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.



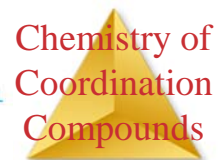
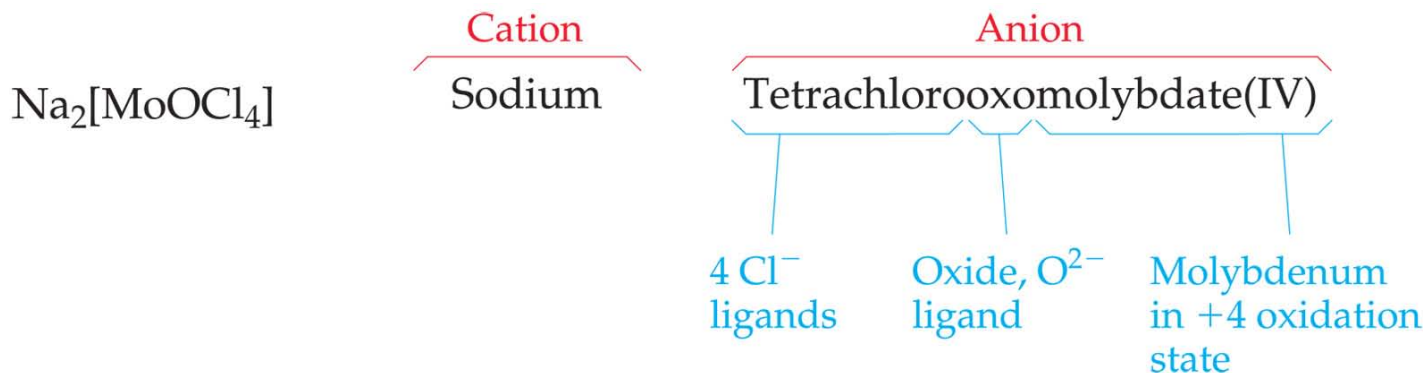
Nomenclature of Coordination Compounds

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

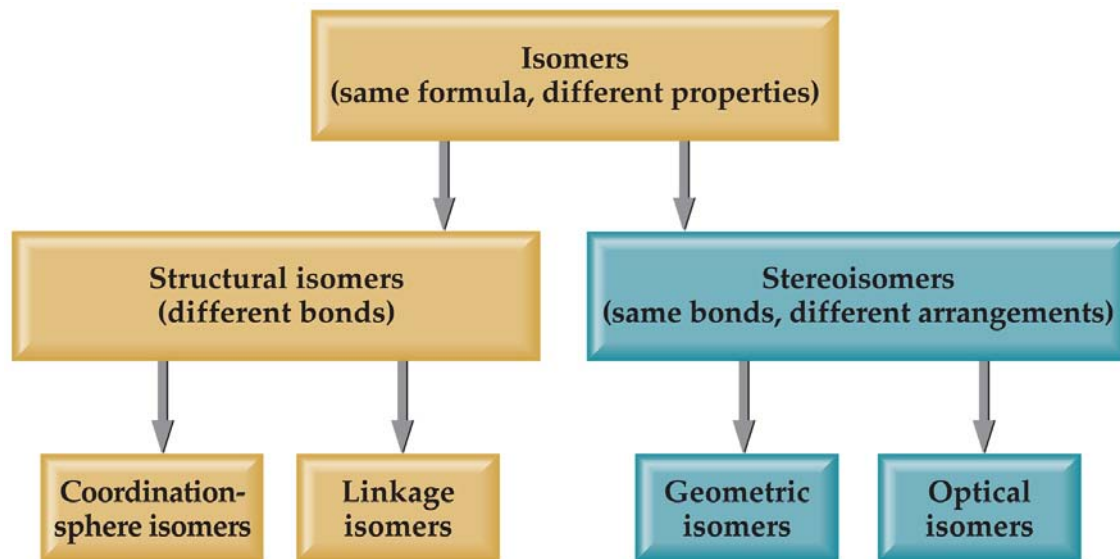


Nomenclature of Coordination Compounds

- 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.



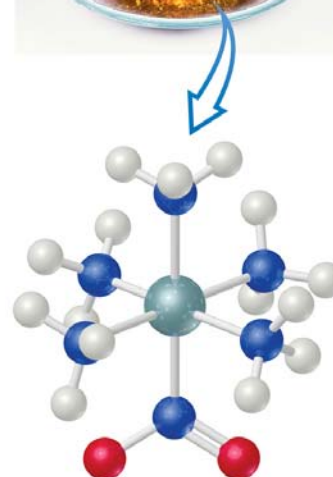
Isomers



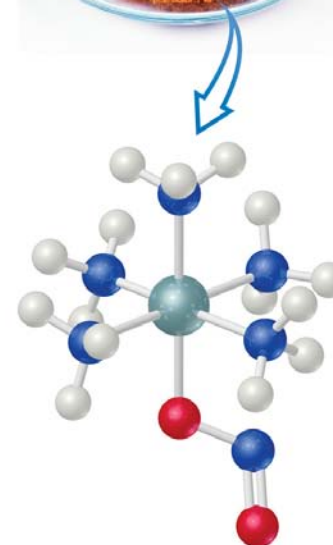
Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

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

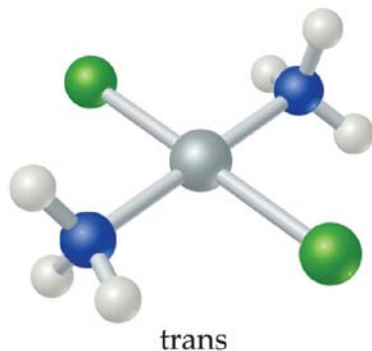
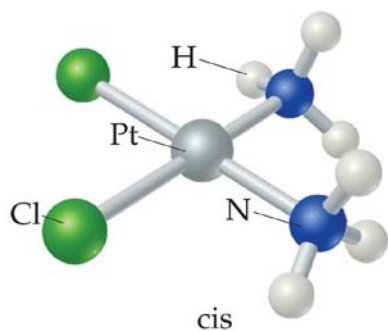


Nitrito isomer

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 $\text{CrCl}_3(\text{H}_2\text{O})_6$ are
 - The violet $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$,
 - The green $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and
 - The (also) green $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$.

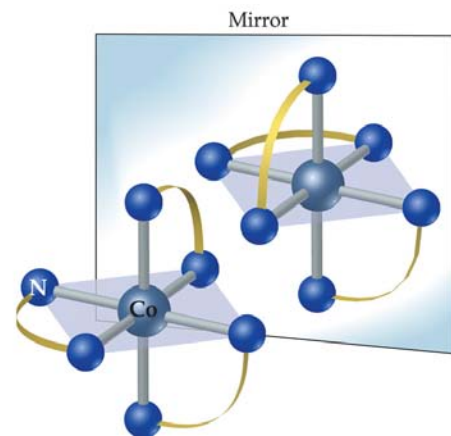
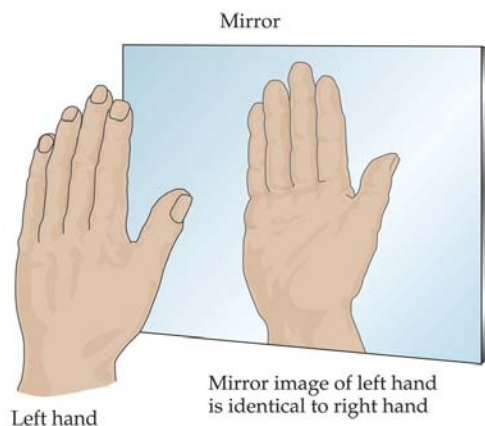
Stereoisomers



- 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.

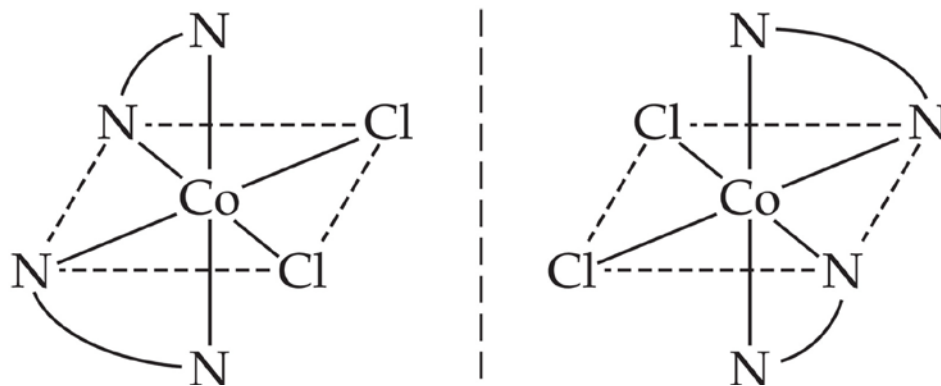
Stereoisomers



- 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.

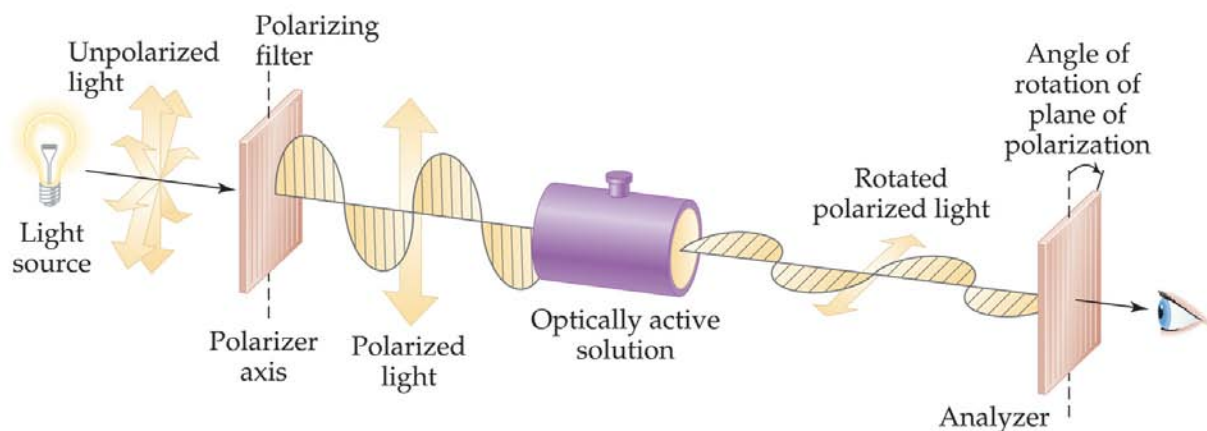
Enantiomers

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



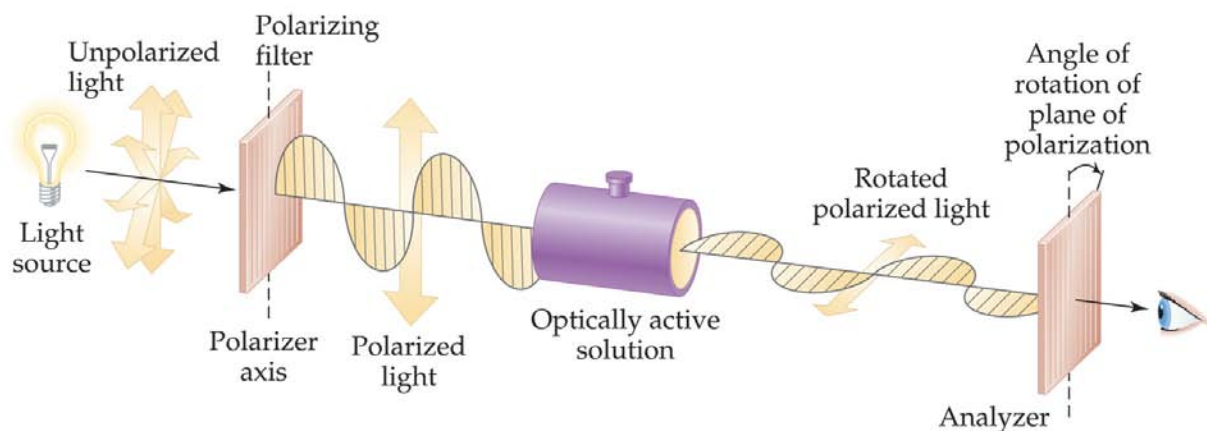
Enantiomers

- The physical properties of chiral molecules are the same *except* in instances where the spatial placement of atoms matters.
- One example is the interaction of a chiral molecule with plane-polarized light.



Enantiomers

- If one enantiomer of a chiral compound is placed in a polarimeter and polarized light is shone through it, the plane of polarization of the light will rotate.
- If one enantiomer rotates the light 32° to the right, the other will rotate it 32° to the left.



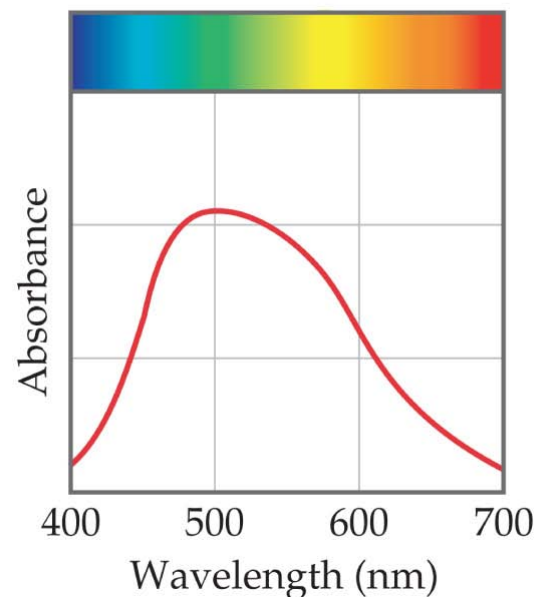
Complexes and Color



- Many complexes are richly colored.
- The color arises from the fact that the complex absorbs some wavelengths of visible light and reflects others.

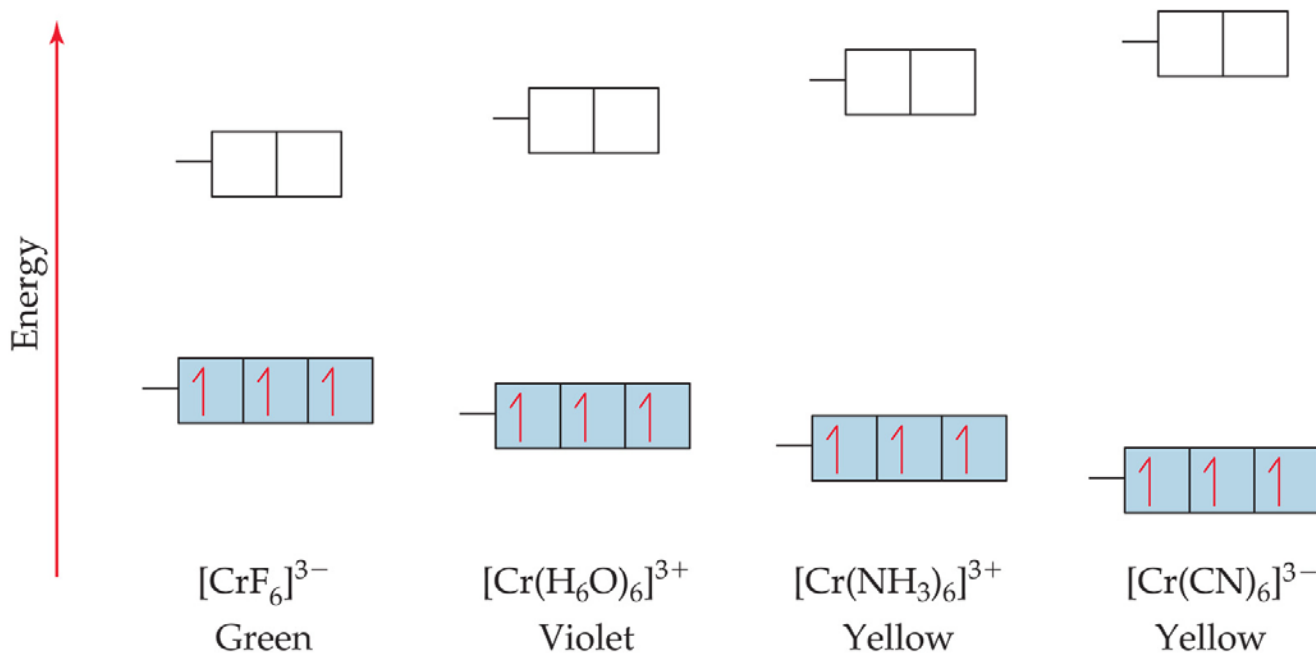
Complexes and Color

This complex ion appears violet in color because it absorbs light at the center of the visible spectrum.



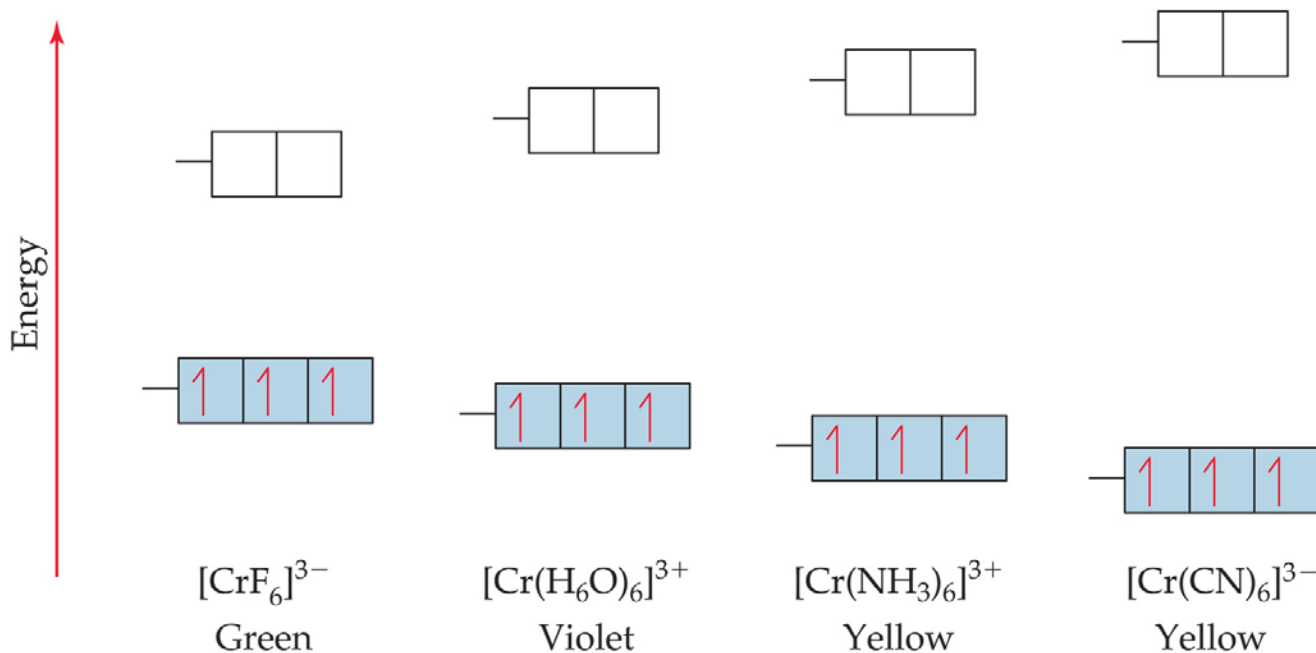
Complexes and Color

Interactions between electrons on a ligand and the orbitals on the metal cause differences in energies between orbitals in the complex.



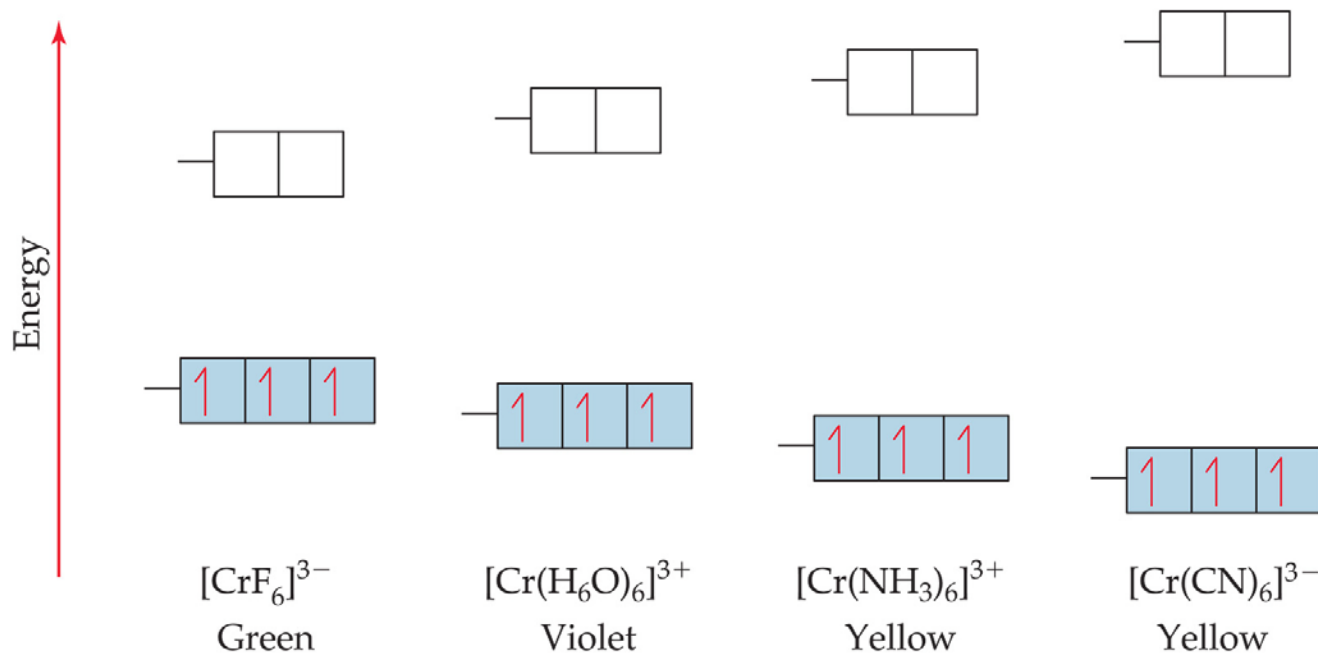
Complexes and Color

Some ligands (such as fluoride) tend to make the gap between orbitals larger, some (like cyano groups) tend to make it smaller.



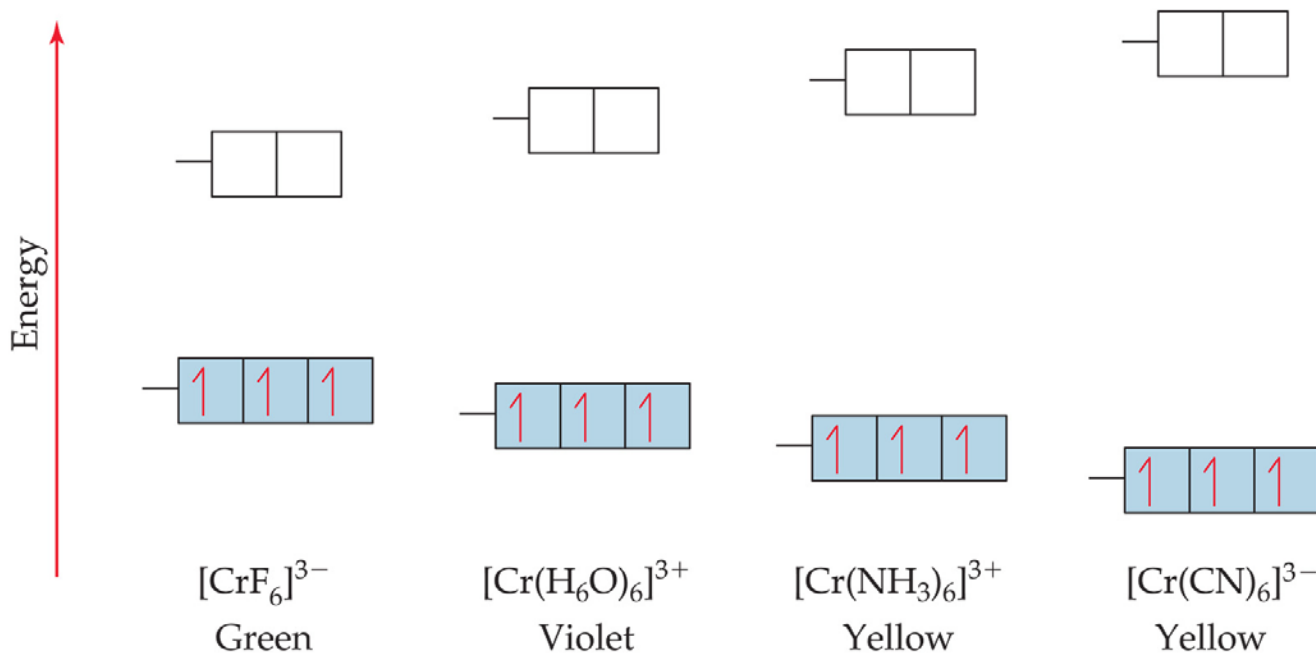
Complexes and Color

The larger the gap, the shorter the wavelength of light absorbed by electrons jumping from a lower-energy orbital to a higher one.



Complexes and Color

Thus, the wavelength of light observed in the complex is longer (closer to the red end of the spectrum).



Complexes and Color

As the energy gap gets smaller, the light absorbed is of longer wavelength, and shorter-wavelength light is reflected.

