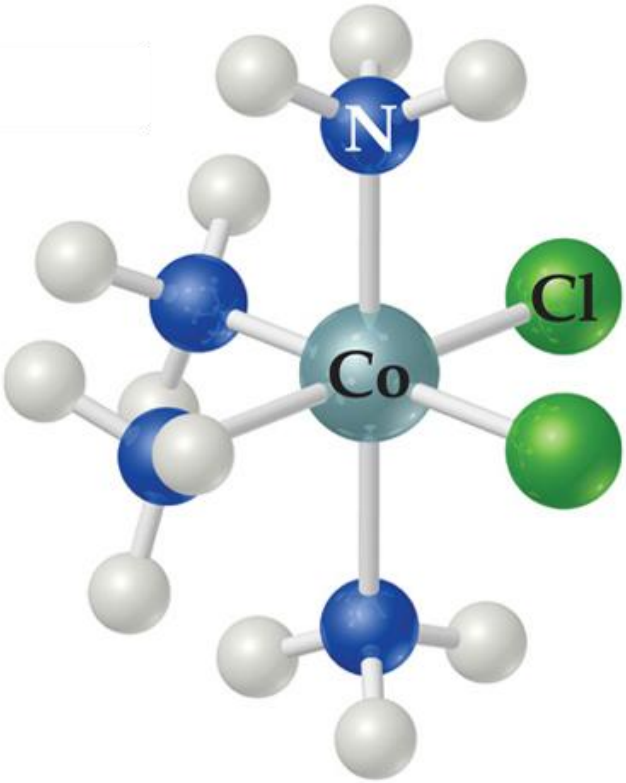
# INTRODUCTION TO

## Coordination Chemistry

**Dr. Sujit Kr. Bera**
**Department of Chemistry**

Chemistry of Coordination Compounds

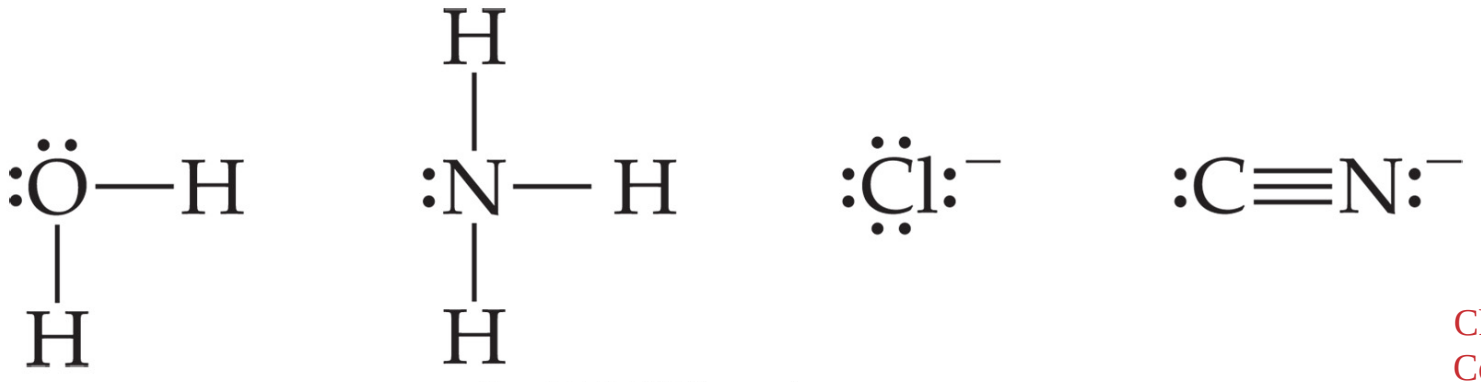
# Complexes




- 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 or electron cloud to interact with metal



# A chemical mystery:

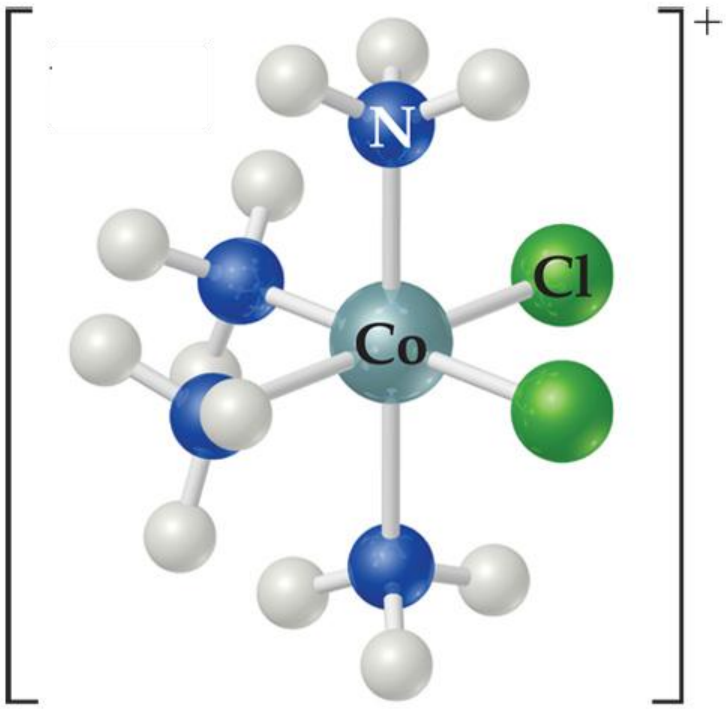
## Same metal, same ligands, different number of ions when dissolved

**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 # 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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# 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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| Original Formulation | Color | Ions per Formula Unit | "Free" $Cl^-$ Ions per Formula Unit | Modern Formulation |
|---|---|---|---|---|
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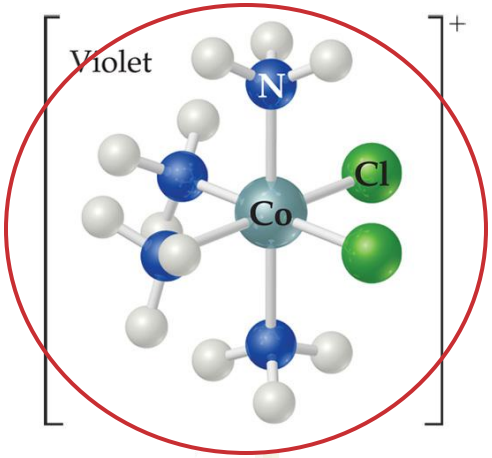
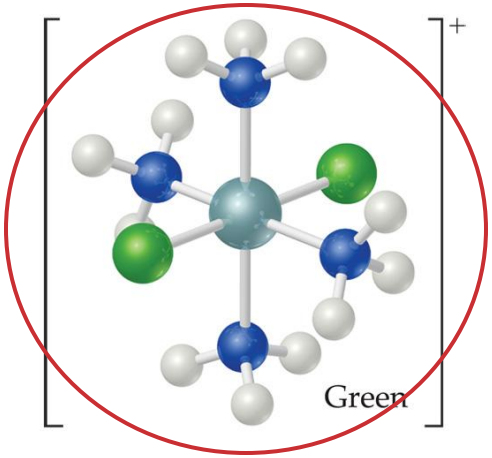
# Werner's Theory

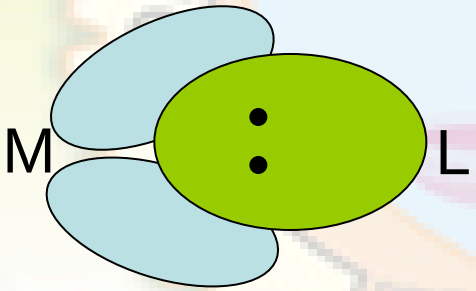



- This approach correctly predicts there would be two forms of $CoCl_3 \cdot 4\ NH_3$.
  - The formula would be written $[Co(NH_3)_4Cl_2]Cl$.
  - One of the two forms has the two chlorines next to each other.
  - The other has the chlorines opposite each other.

# What is Coordination?

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

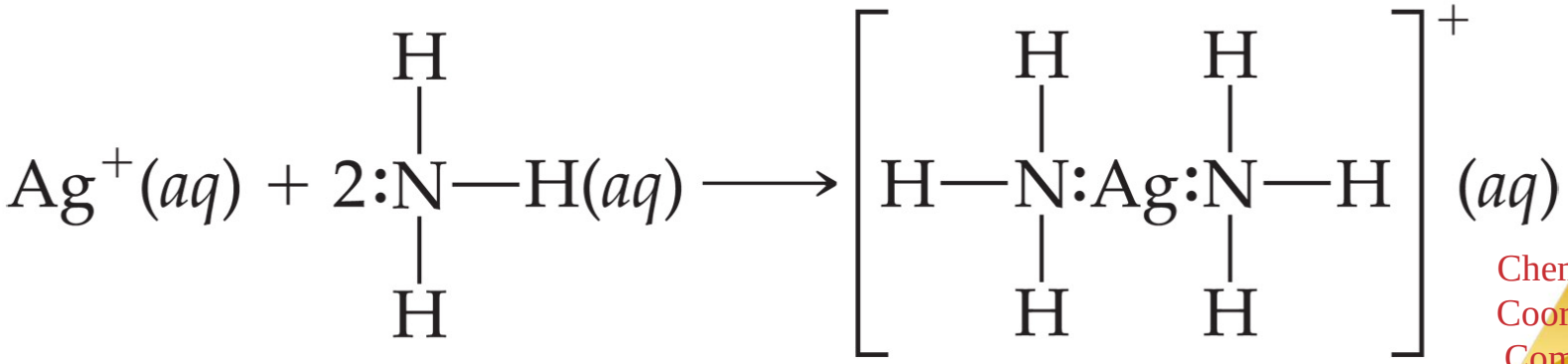



**Sometimes called a coordinate covalent bond**

**So ligands *must* have lone pairs of electrons or electron cloud.**

# Metal-Ligand Bond

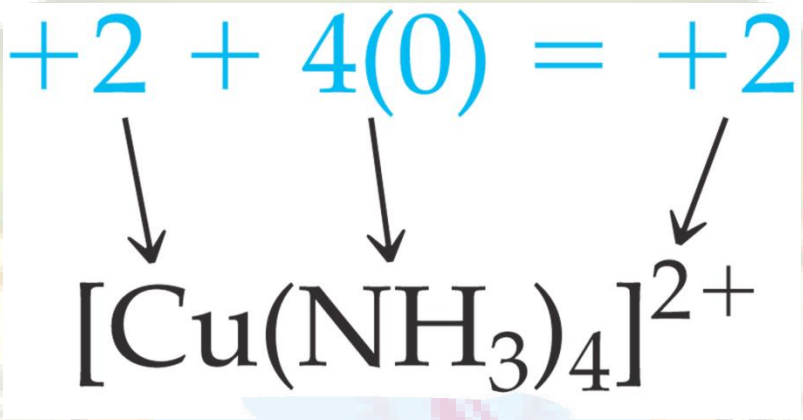
- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have nonbonding electrons.
  - The metal (Lewis acid) has empty orbitals.



# Metal-Ligand Bond

The metal's coordination ligands and geometry can greatly alter its properties, such as color, or 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

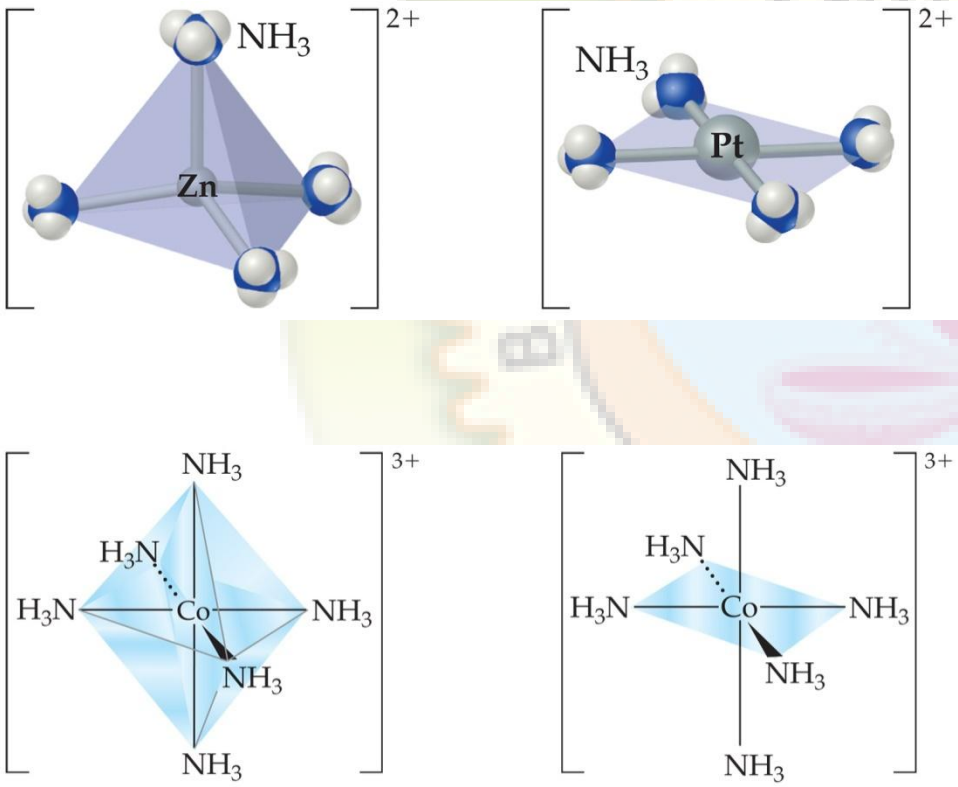
Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

**Example: $Cr(III)(H_2O)_4Cl_2$**

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

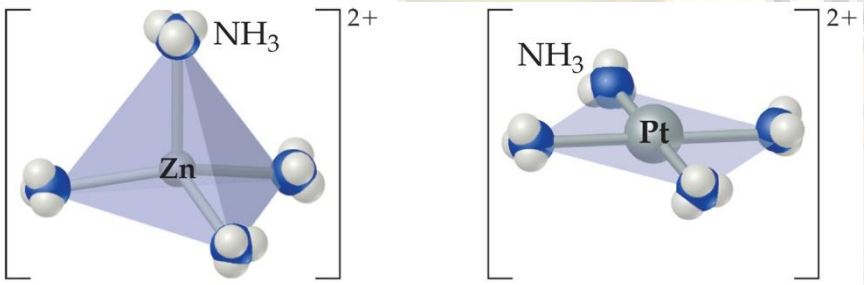
$$Cr(H_2O)_4Cl_2$$

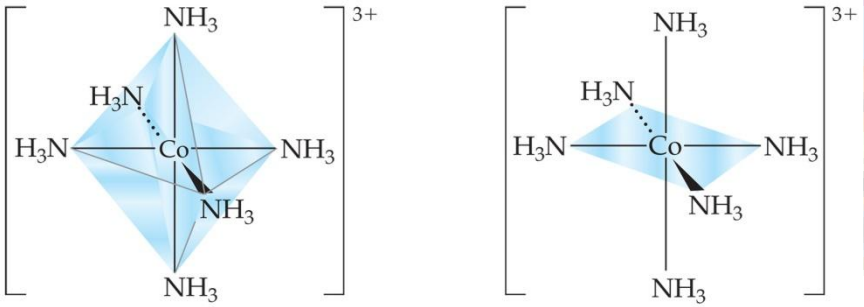
# Coordination Number




- 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

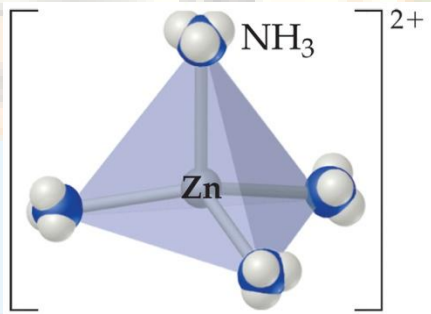


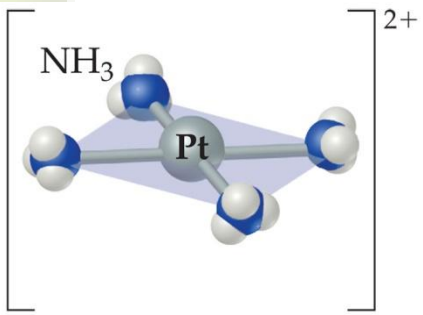




- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).
- The most commonly encountered numbers are 4 and 6.

# Geometries

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

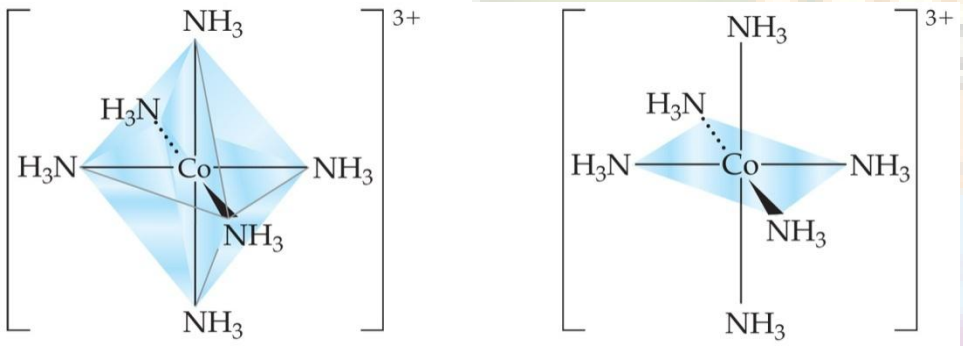



**Tetrahedral** **Square planar**

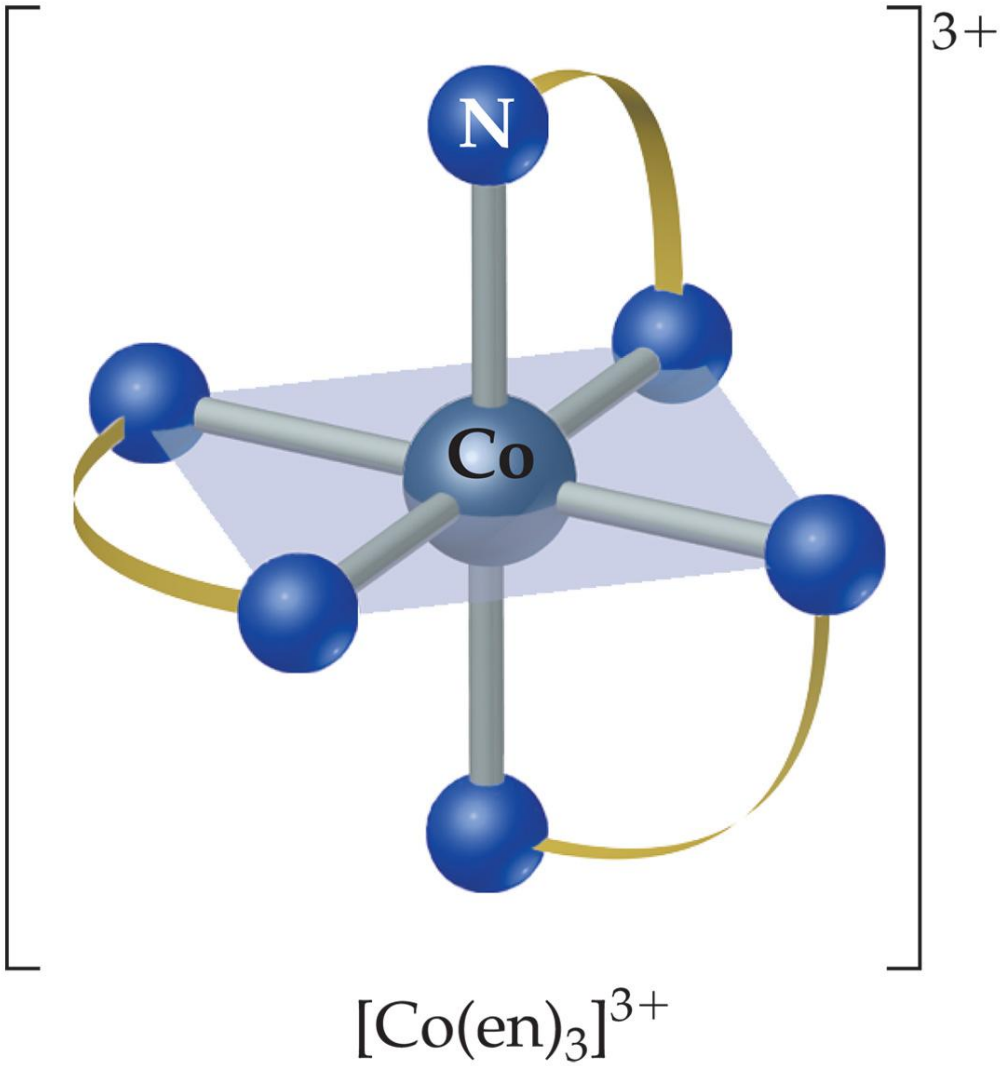
Why square planar? We'll get to that

# Geometries




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

# Polydentate Ligands

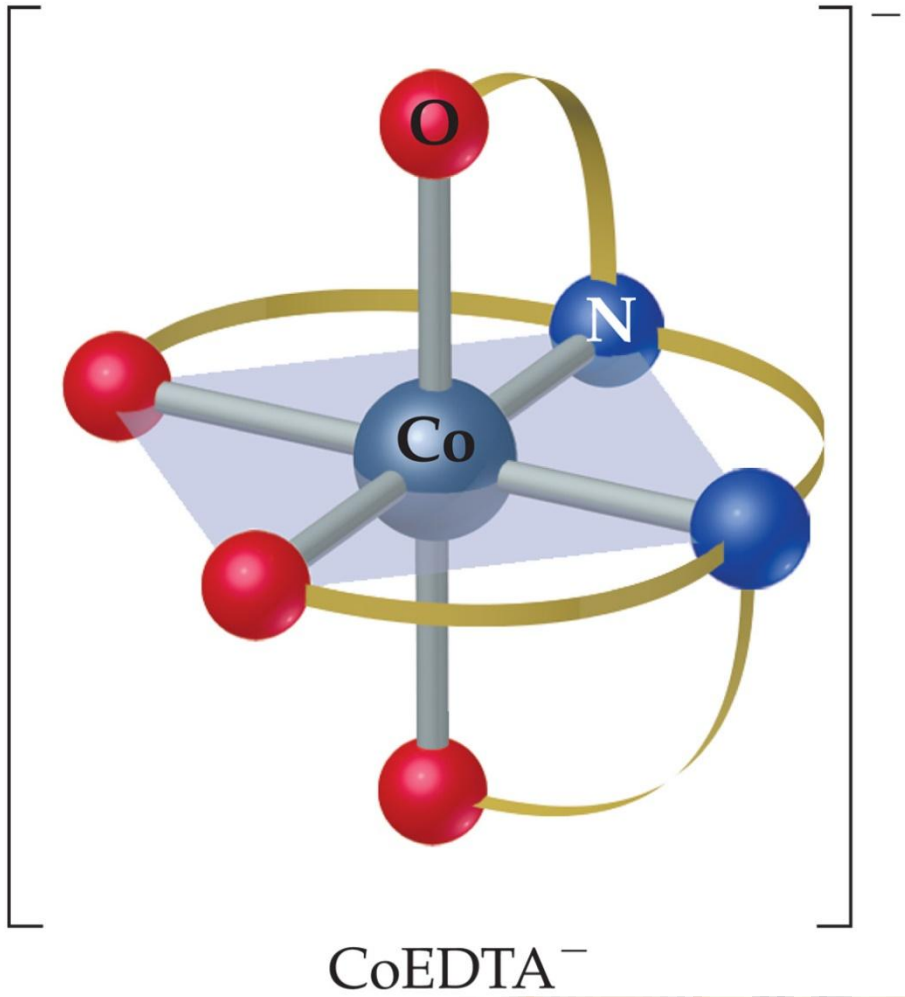



$[Co(en)_3]^{3+}$

- 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.

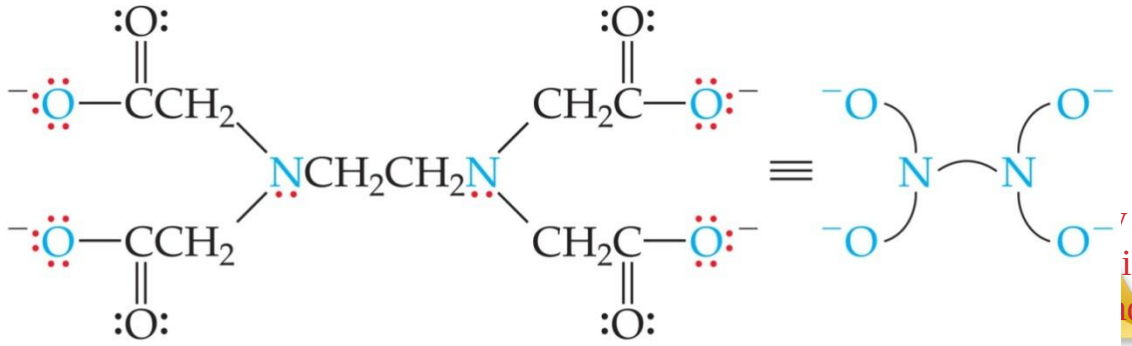
# Polydentate Ligands

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.




$CoEDTA^-$

Wraps around the central atom like an octopus



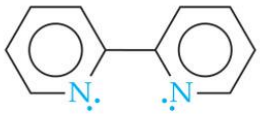
$[EDTA]^{4-}$

# Polydentate Ligands

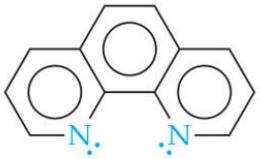
| Ligand Type | Examples | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Monodentate | $H_2\ddot{O}:$ Water | $:\ddot{F}:^-$ Fluoride ion | $[:C\equiv N:]^-$ Cyanide ion | $[:\ddot{O}-H]^-$ Hydroxide ion |
| | $:NH_3$ Ammonia | $:\ddot{Cl}:^-$ Chloride ion | $[:\ddot{S}=C=\ddot{N}:]^-$ (or) Thiocyanate ion | $[:\ddot{O}=N=\ddot{O}:]^-$ (or) Nitrite ion |

Bidentate

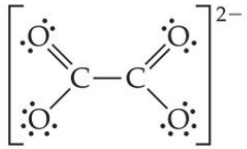
Ethylenediamine (en)



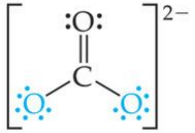
Bipyridine (bipy)



*Ortho*-phenanthroline (*o*-phen)

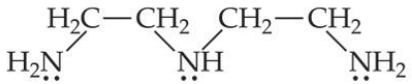


Oxalate ion

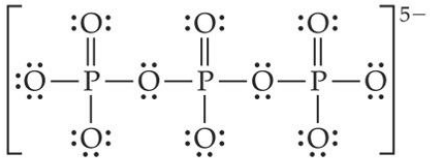


Carbonate ion

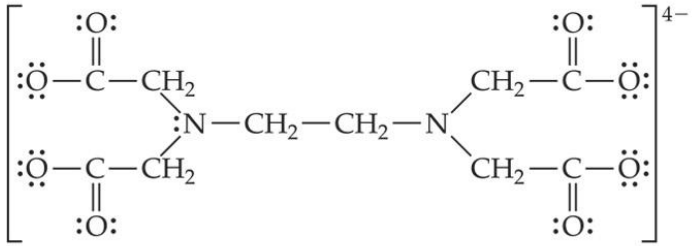
Polydentate



Diethylenetriamine



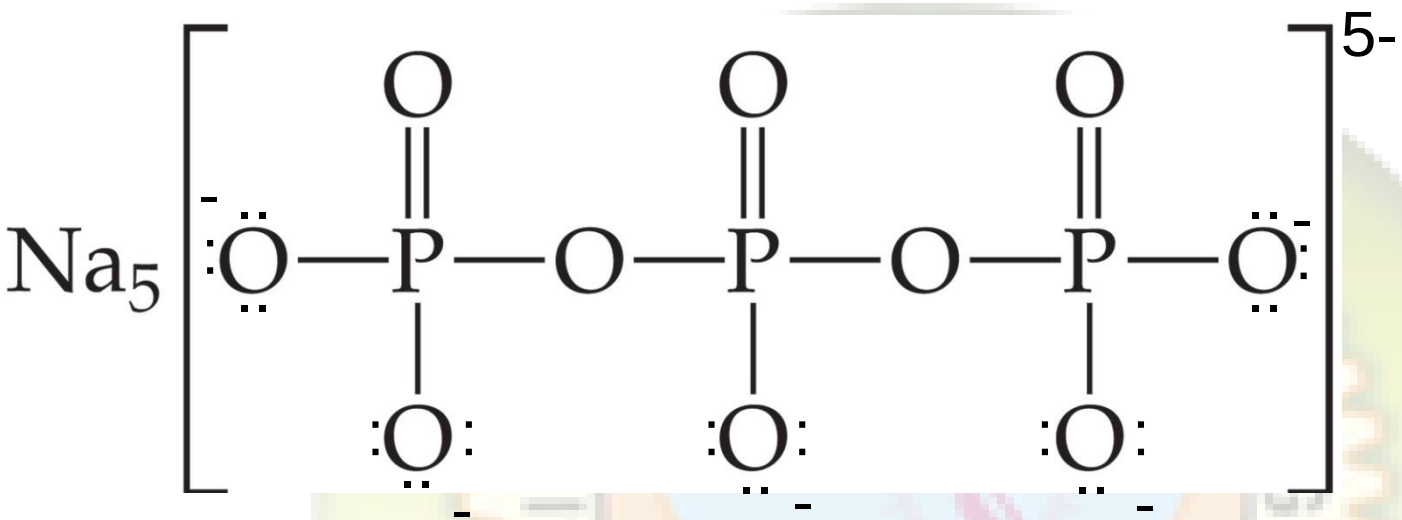
Triphosphate ion



Ethylenediaminetetraacetate ion ($EDTA^{4-}$)

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

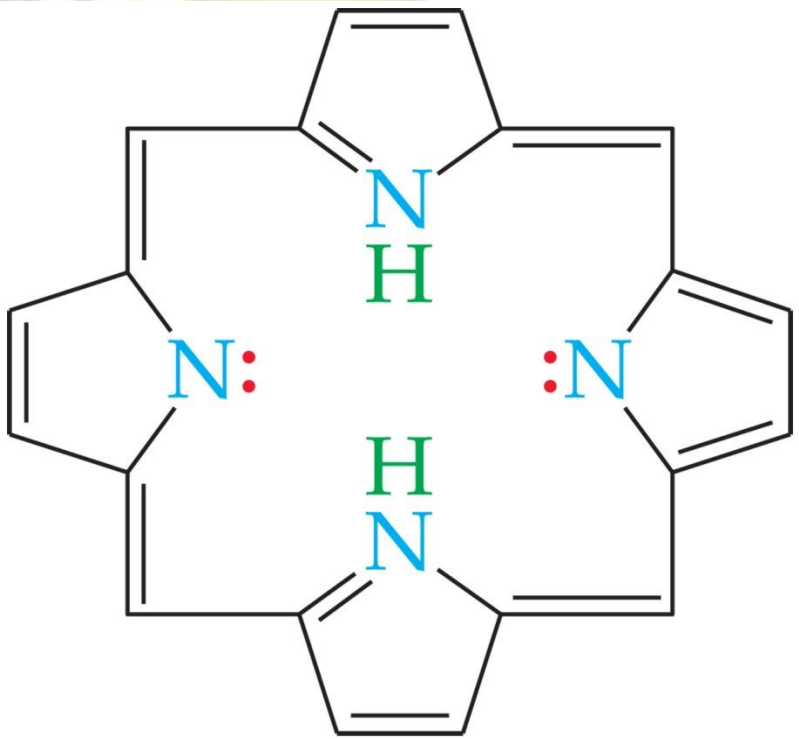
# Chelating Agents



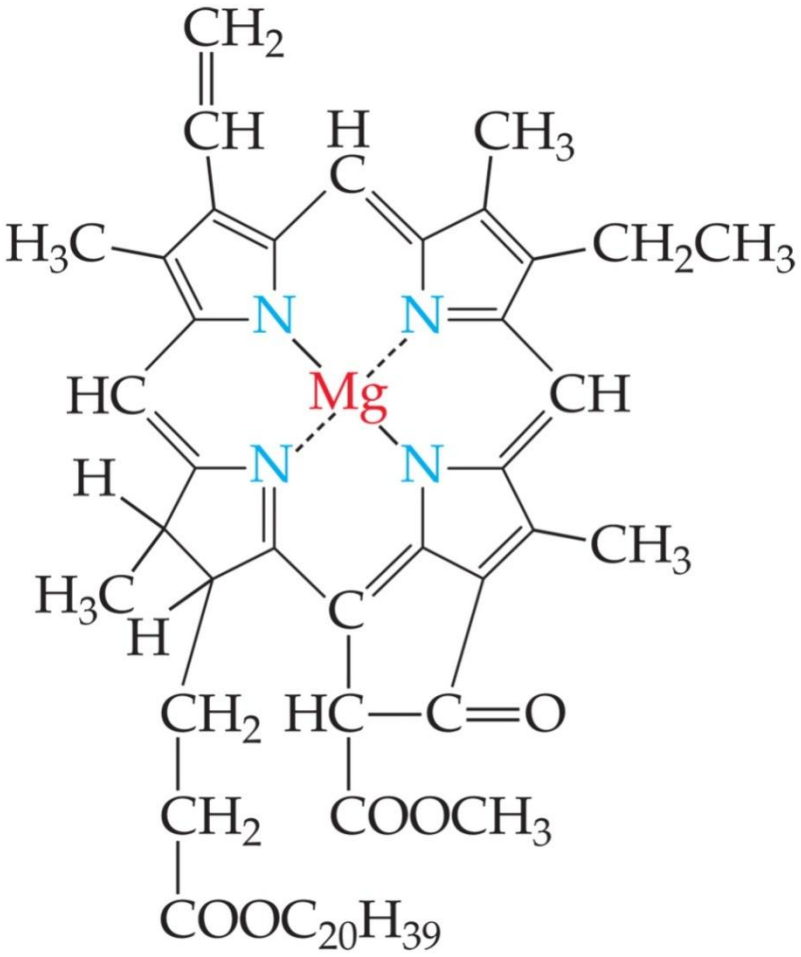

- Bind to metal ions removing them from solution.
- Phosphates are used to tie up $Ca^{2+}$ and $Mg^{2+}$ in hard water to prevent them from interfering with detergents.

# Chelating Agents

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



# Chelating Agents




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

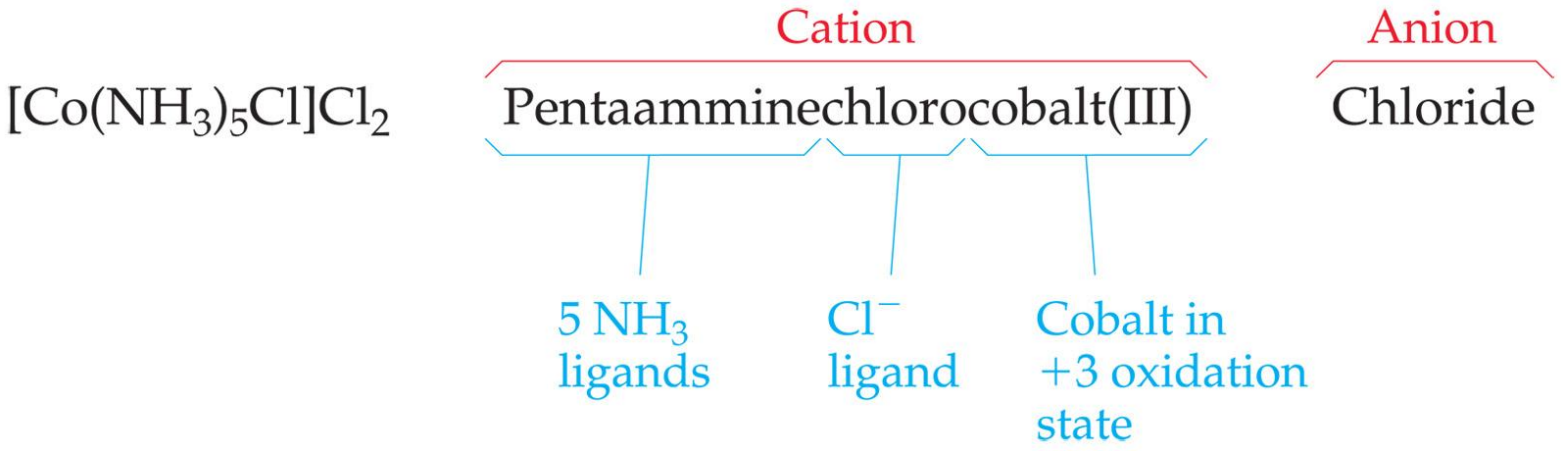
# Nomenclature of Coordination Compounds

| 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.

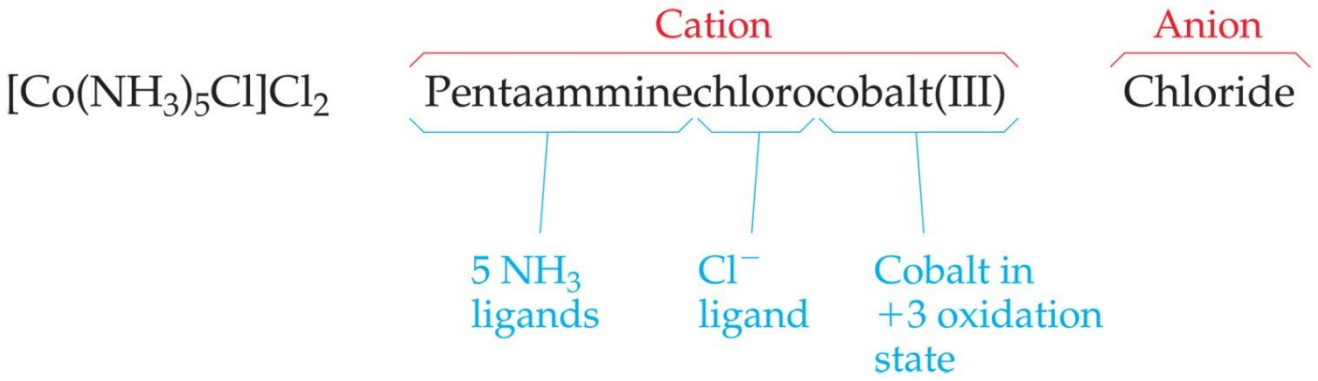
# Nomenclature of Coordination Compounds

- 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.



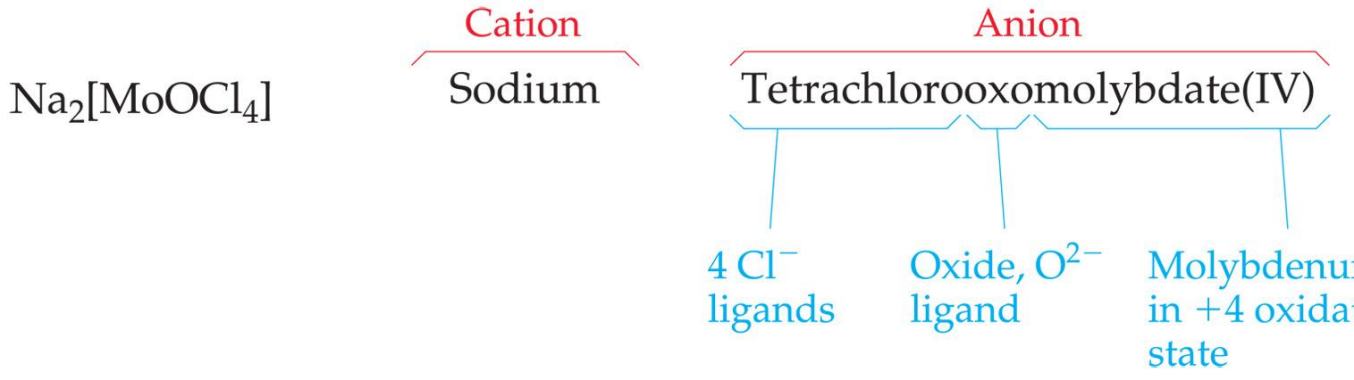
# Nomenclature of Coordination Compounds

- 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.



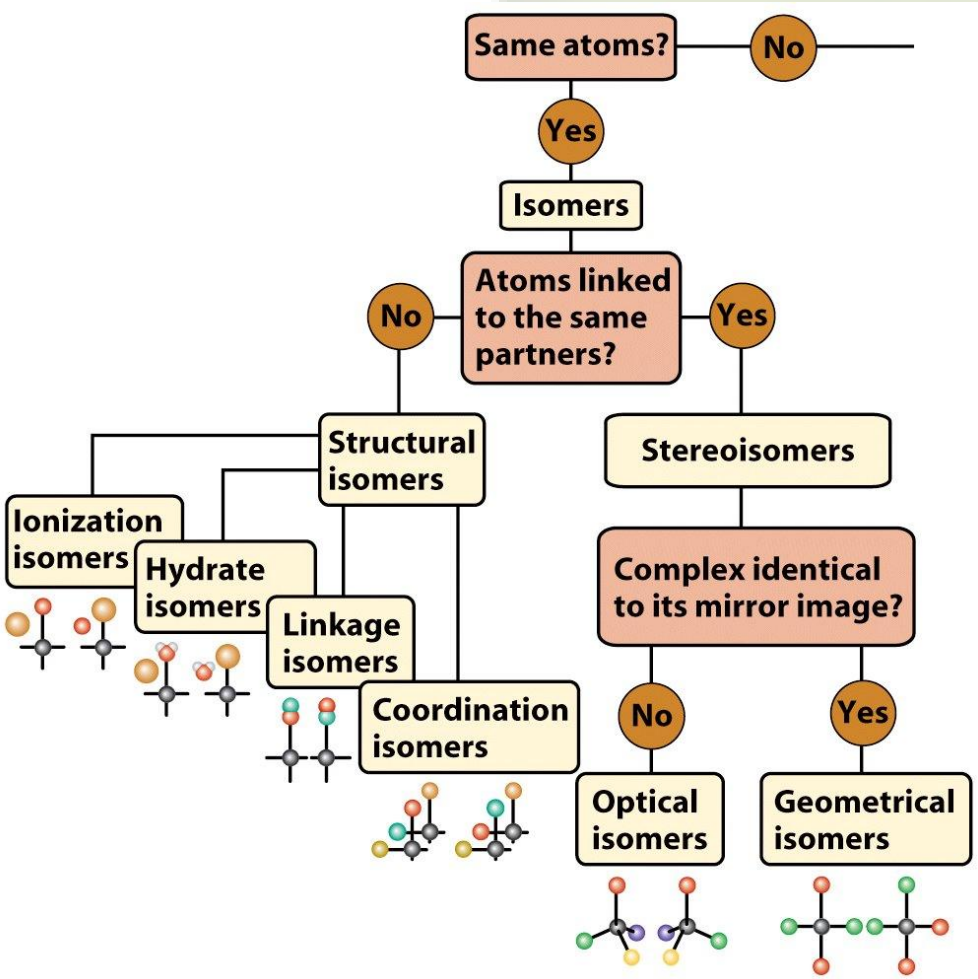
# Nomenclature of Coordination Compounds

- 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.



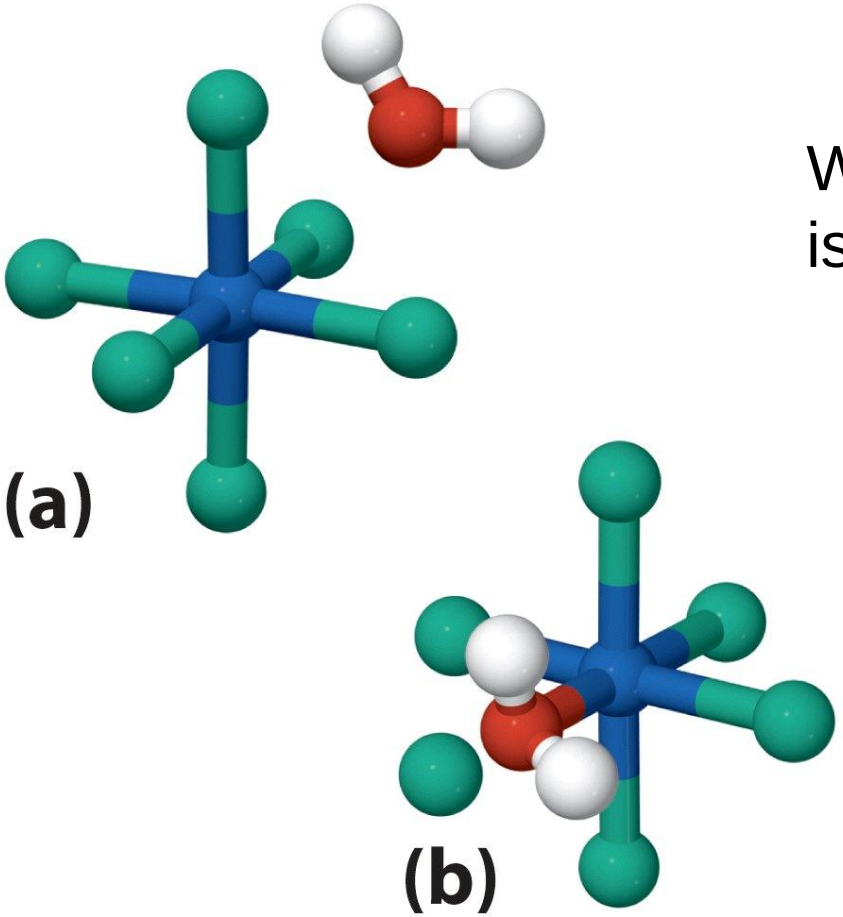
# Coordination complexes: isomers

Isomers: same atomic composition, different structures




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

# Hydrate isomers:

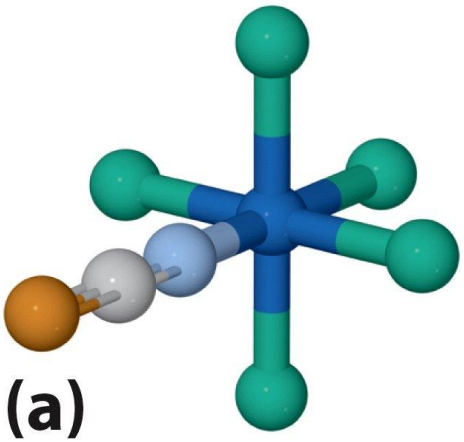



Water in outer sphere (water that is part of solvent)

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

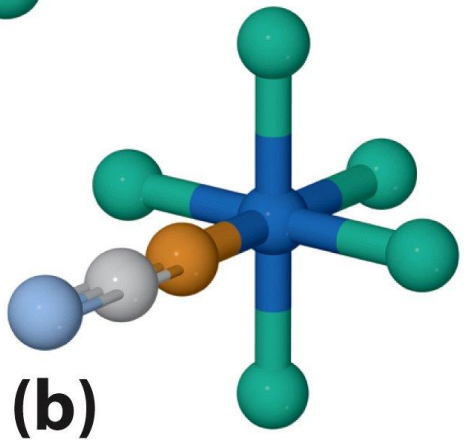
# Linkage isomers

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



(a)

Bonding occurs from N atom to metal



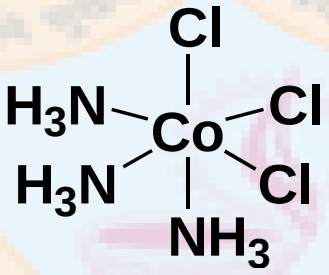
(b)

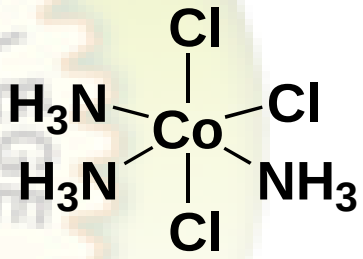
Bonding occurs from S atom to metal

# 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

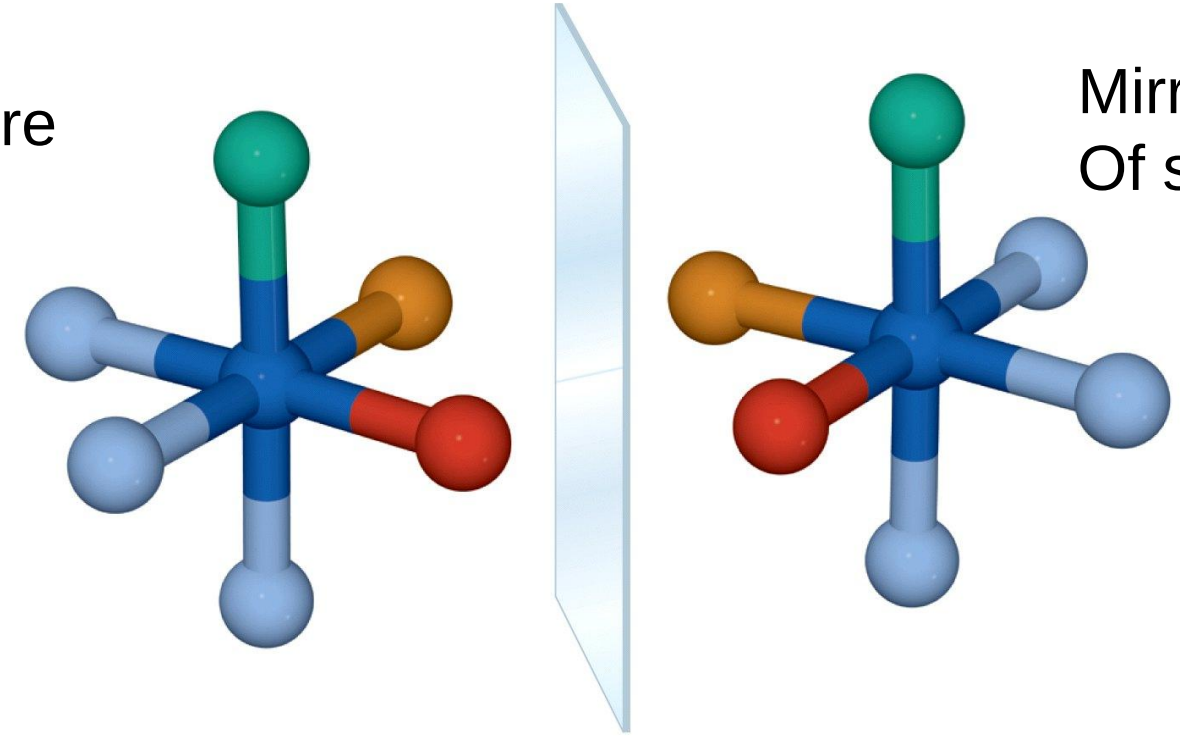
Any molecule which possesses a plane of symmetry is superimposable on its mirror image

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

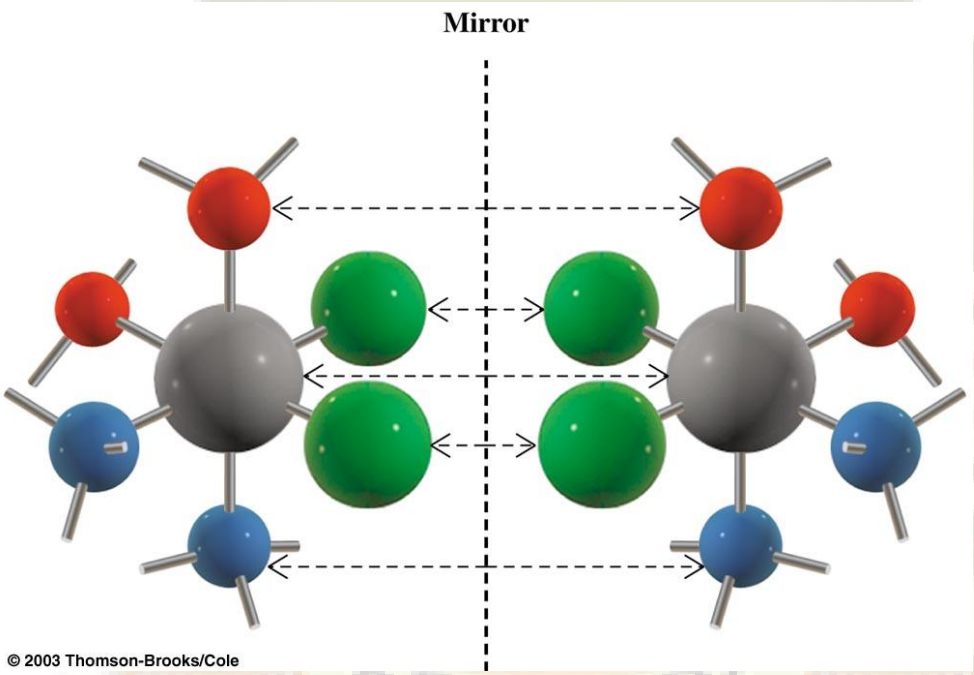
Structure



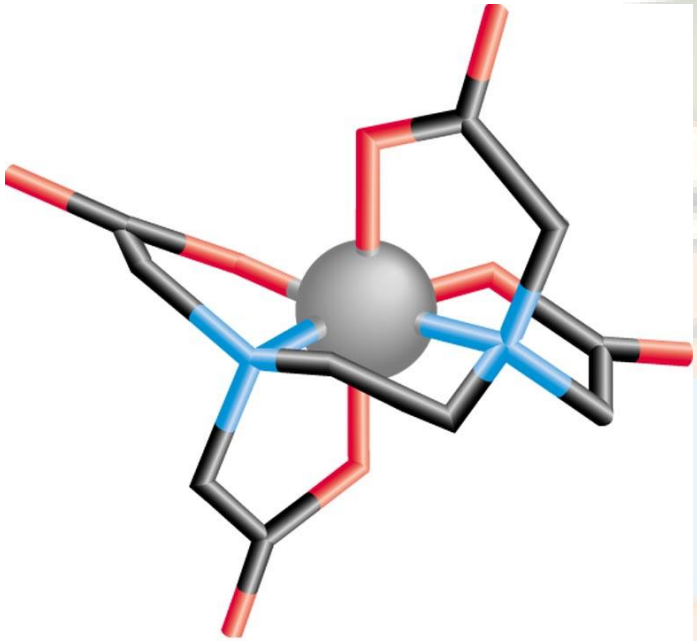
Mirror image
Of structure

Two chiral structures: non superimposable mirror images

# Examples of enantiomers




# EDTA complexes are optically active



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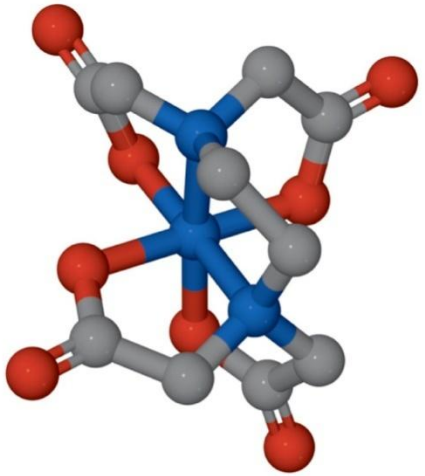
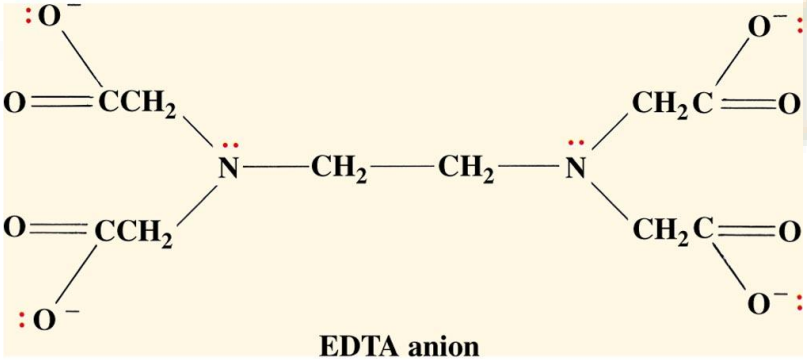


**10 An edta complex**




EDTA anion

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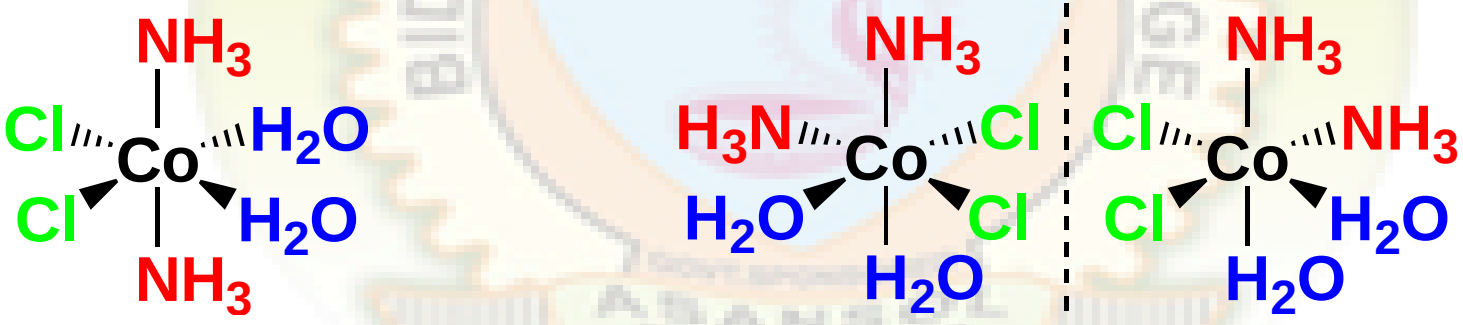
Chemistry of Coordination Compounds

Chirality: the absence of a plane of symmetry
Enantiomers possible

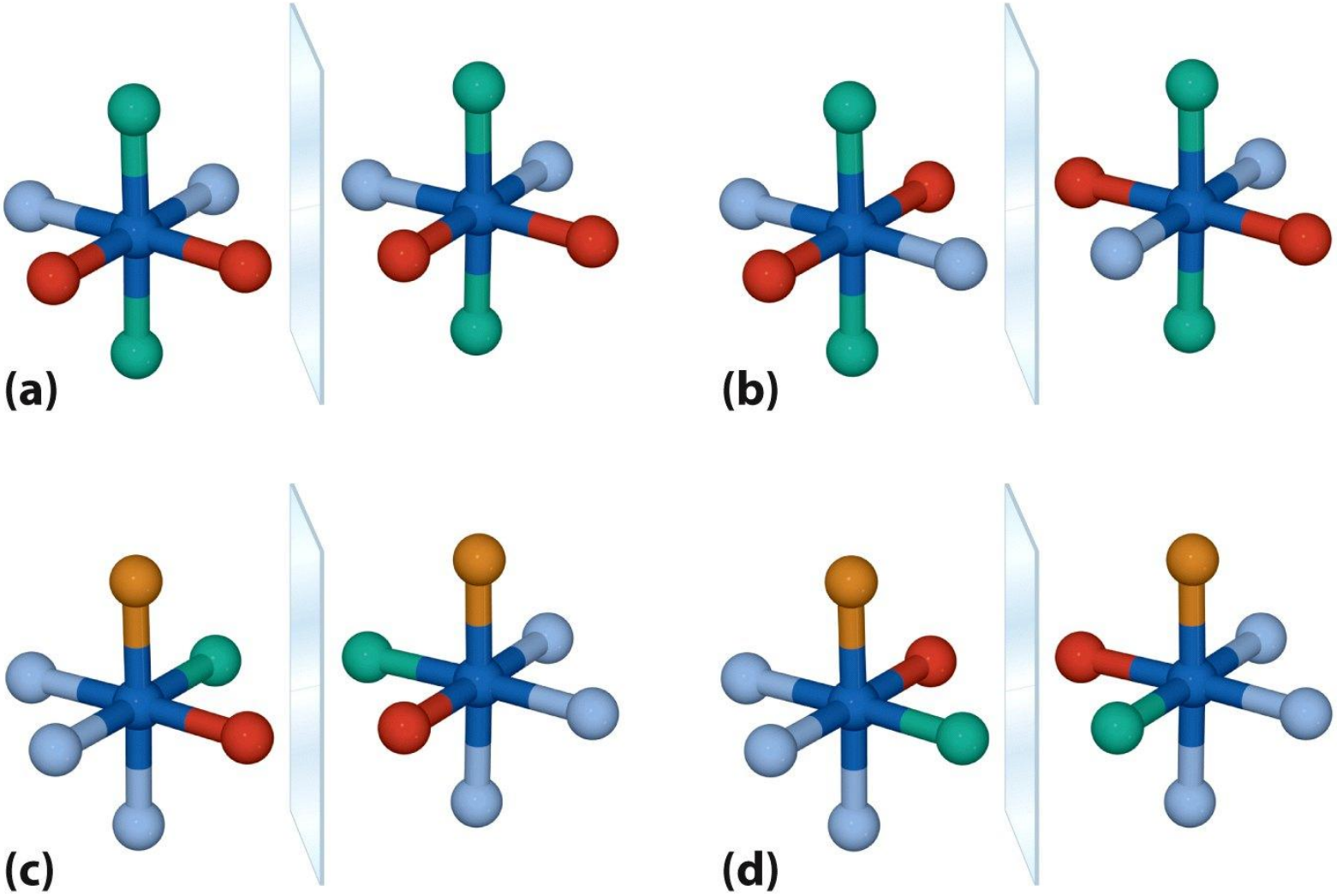
If a molecule possess a plane of symmetry it is achiral and is superimposible on its mirror image
Enantiomers NOT possible



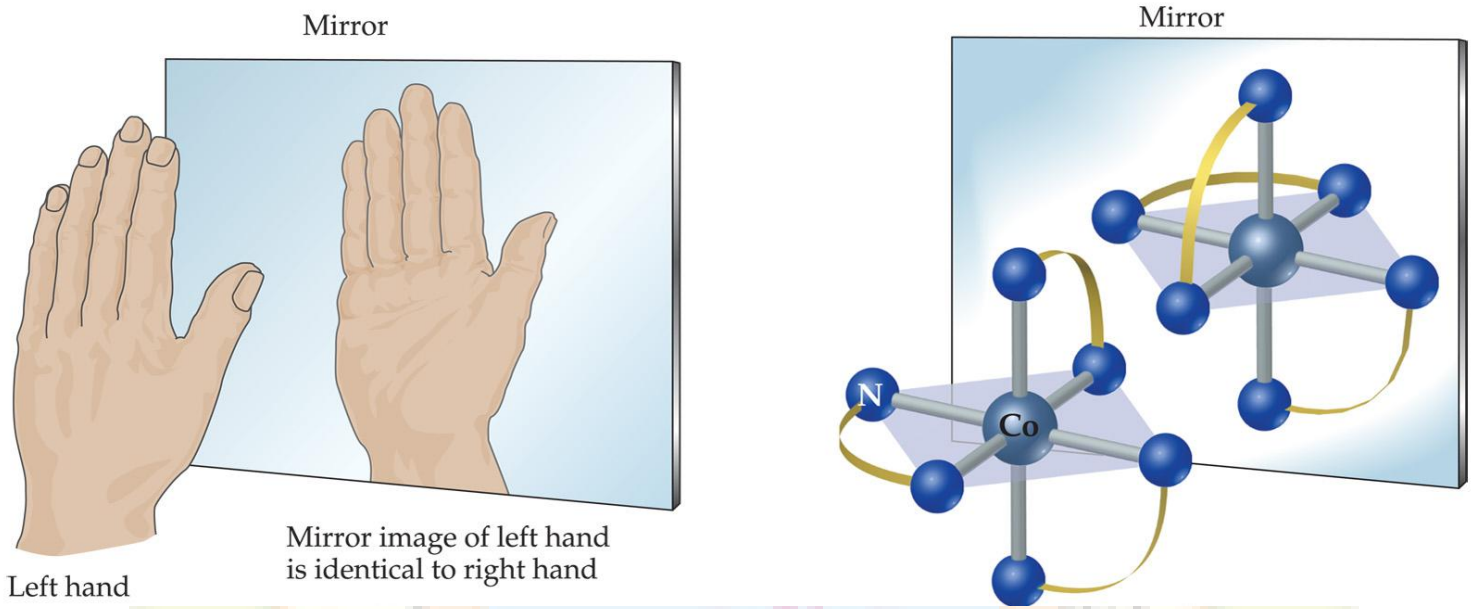

Plane of symmetry
Achiral (one structure)

No plane of symmetry
Chiral (two enantiomer)

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



# Stereoisomers




- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

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  The material has been developed with the help of different text books, journal material and web help.For details contact through author mail (sujitkbera@gmail.com)