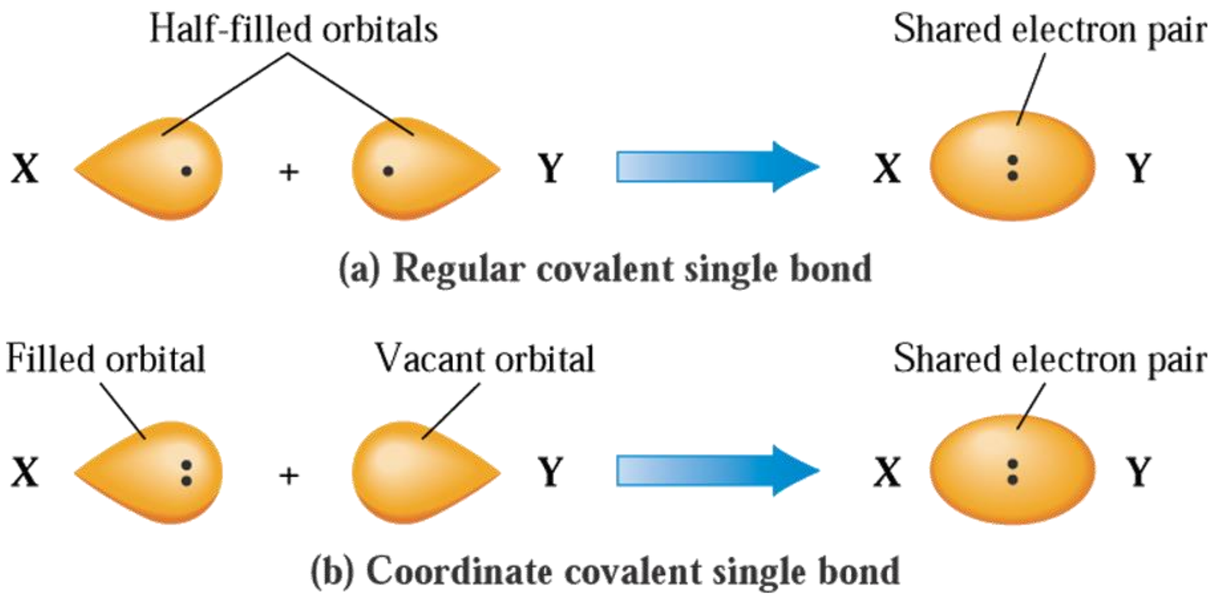
Complexes

Commonly, transition metals can have molecules or ions that bond to them.

These give rise to **complex ions** or **coordination compounds**.

Coordination Compounds

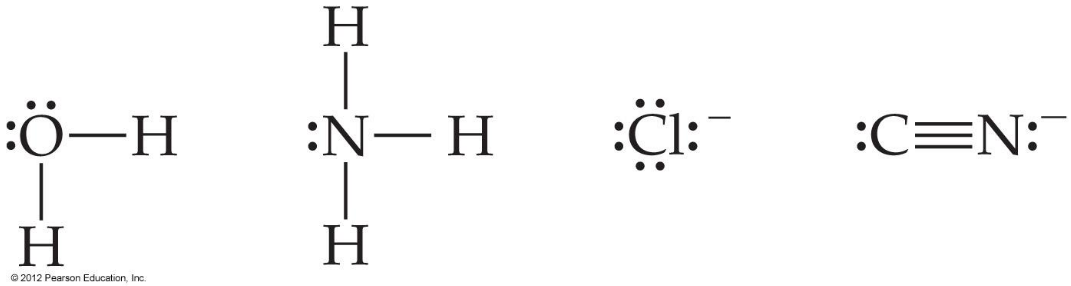
- Coordinate covalent bond – both electrons in a shared pair come from one of the two atoms



TM have vacant *d*-orbitals

Ligands

The molecules or ions that bind to the central metal are called **ligands** (from the Latin *ligare*, meaning “to bind”).



Coordination Chem – Werner's Theory

TABLE 23.3 • 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*-$[Co(NH_3)_4Cl_2]Cl$

One of the properties that has led to the fascination with complexes and transition metals is the wide range of stunning colors found in them.

Werner's Theory

The Swiss chemist Alfred Werner deduced that there was a difference between the oxidation number of a metal and the number of ligands it took on, which he called the **coordination number**.

Alfred Werner (1913 Nobel prize) & complex ions

orange	$CoCl_3 \cdot 6NH_3 + 3\,Ag^+ \rightarrow 3\,AgCl(s)$
purple	$CoCl_3 \cdot 5NH_3 + 3\,Ag^+ \rightarrow 2\,AgCl(s)$
green	$CoCl_3 \cdot 4NH_3 + 3\,Ag^+ \rightarrow 1\,AgCl(s)$
blue/green	$CoCl_3 \cdot 3NH_3 + 3\,Ag^+ \rightarrow 0\,AgCl(s)$ i.e. no rxn

not all Cl^- in the compounds are equal orange $CoCl_3 \bullet 6NH_3 + 3\ Ag^+ \rightarrow 3\ AgCl(s)$

$[Co(NH_3)_6]^{3+}\ (Cl^-)_3$

green $CoCl_3 \bullet 4NH_3 + 3\ Ag^+ \rightarrow 1\ AgCl(s)$

$[Co(NH_3)_4Cl_2]^+\ Cl^-$

NH_3 and Cl^- inside brackets are ligands and are part of the complex ion

Cl^- outside brackets are just plain ions (spectators)

$$[Co(NH_3)_6]^{3+}(Cl^-)_{\mathbf{3}} + 3\,Ag^+ \longrightarrow \mathbf{3}\,AgCl(s)$$

$$[Co(NH_3)_5Cl]^{2+}(Cl^-)_{\mathbf{2}} + 3\,Ag^+ \longrightarrow \mathbf{2}\,AgCl(s)$$

$$[Co(NH_3)_4Cl_2]^{+}(Cl^-)_{\mathbf{1}} + 3\,Ag^+ \longrightarrow \mathbf{1}\,AgCl(s)$$

$$[Co(NH_3)_3Cl_3] + 3\,Ag^+ \longrightarrow 0\,AgCl(s)\ \text{ i.e. no rxn}$$

Werner Theory

TABLE 23.3 • Properties of Some Ammonia Complexes of Cobalt(III)

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

Thus, although the first two complexes in the table above each have 3 chlorines, in the first all three serve as anions, while in the second one of the chlorines is tightly bound to the cobalt and the other two are counterions.

Werner proposed

- metal ion exhibits both primary and secondary valence

  - primary valence : oxidation state

    Co^{3+}

  - secondary valence : coordination #

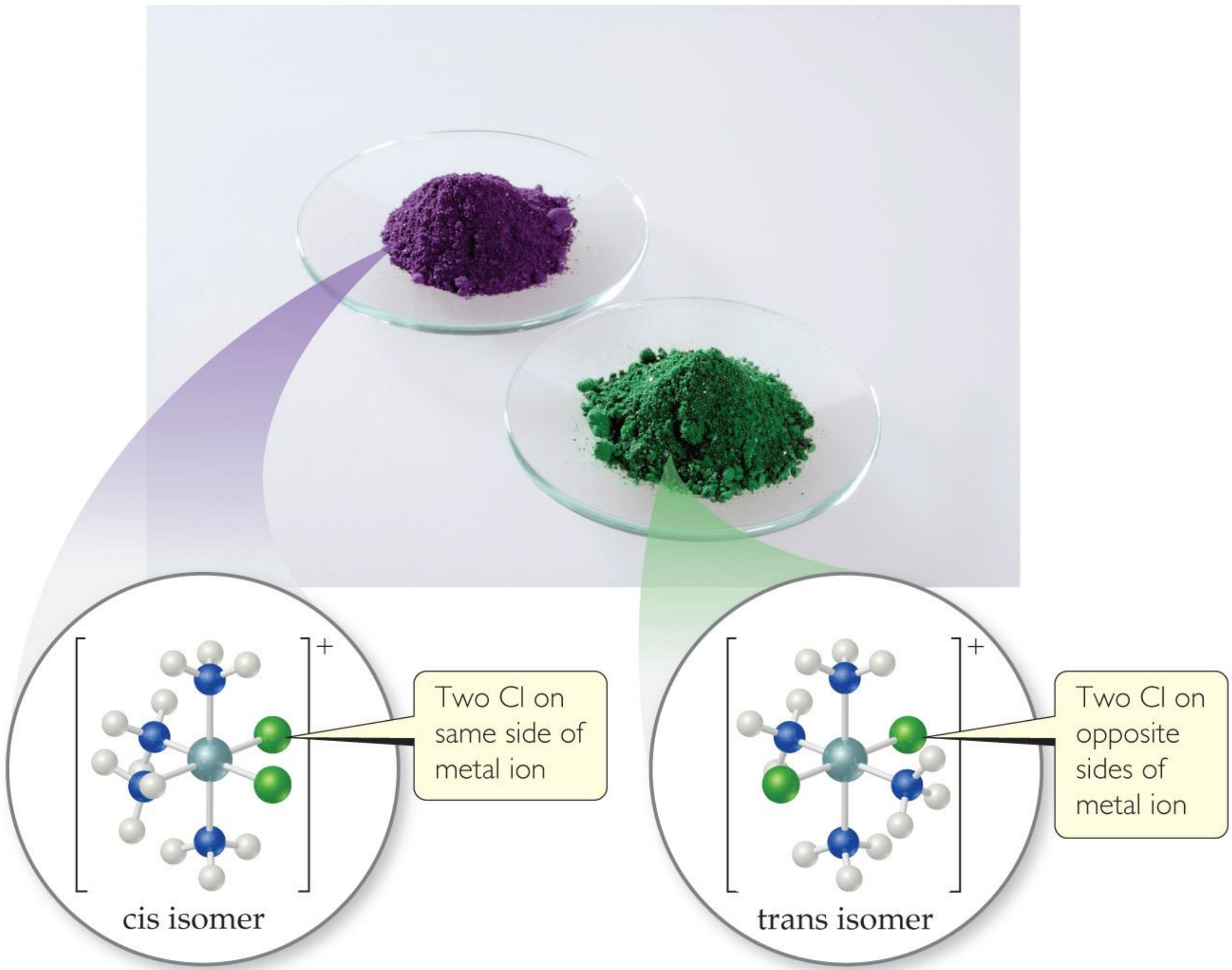
    number of atoms bonded to metal ion

    - 6 for these cobalt complexes

  - explained the two forms of

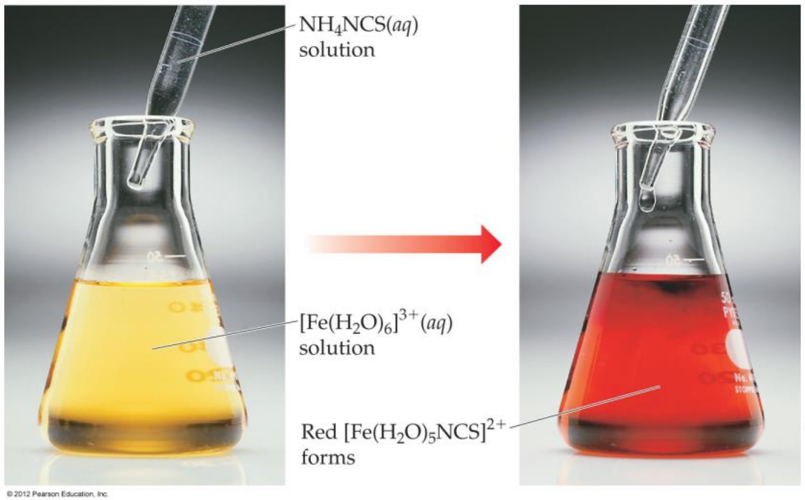
    $[Co(NH_3)_4Cl_2]^+$ complexes

    cis and trans


+
Two Cl on
same side of
metal ion
cis isomer
+
Two Cl on
opposite
sides of
metal ion
trans isomer

The Metal–Ligand Bond

- The reaction between a metal and a ligand is a reaction between a Lewis acid (the metal) and Lewis base (the ligand).
- The new complex has distinct physical and chemical properties.



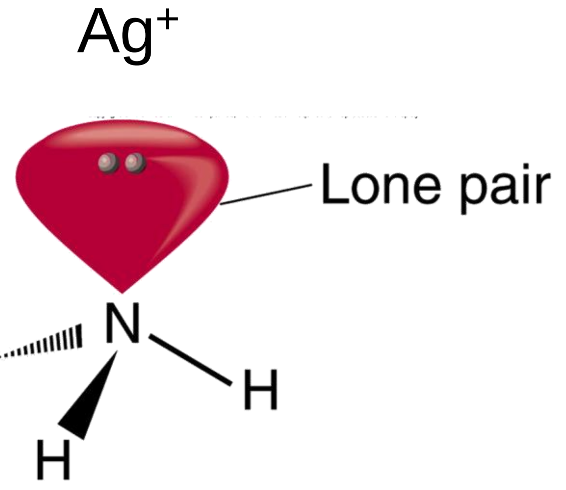
Think Lewis Acid-Base Theory

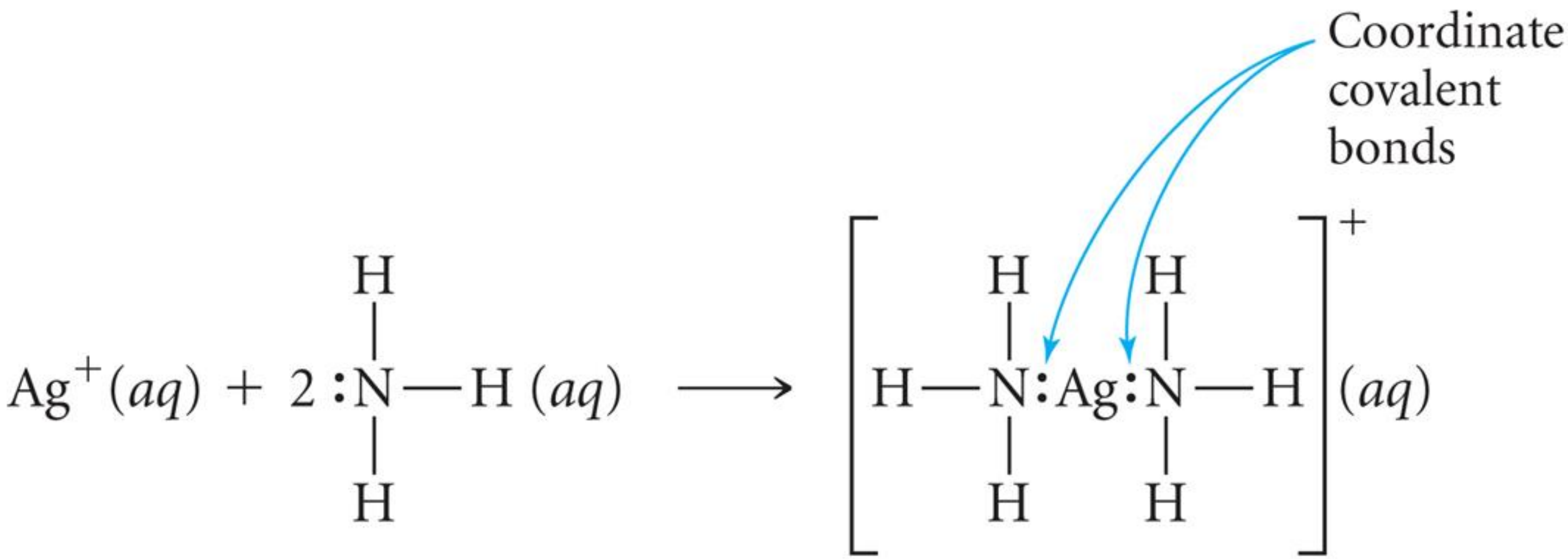
Lewis acid: e^- pair acceptor (metal cation)

Lewis base : e^- pair donor (ligand)

Lewis Acid

Lewis Base




Coordinate covalent bonds
Ag+(aq) + 2 :NH3 (aq) → [H3N:Ag:NH3]+(aq)

Charges, Coord. Numbers & Geometries

Given a coordination complex, it is important to determine the oxidation state, coordination number, and coordination geometry of the central metal atom.

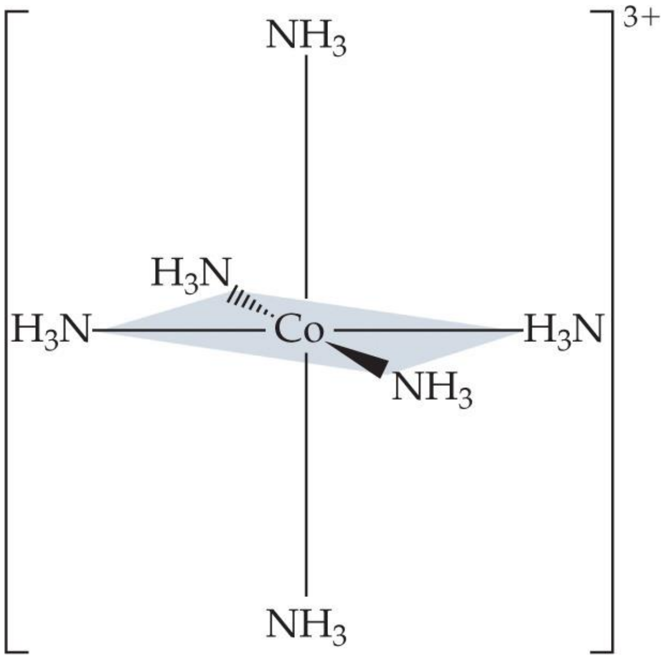
Oxidation State

Charge on Cluster = Metal Oxidation state + (Number of Ligands * Charge of Ligands)

Ex. $K_3[Co(CN)_6]$

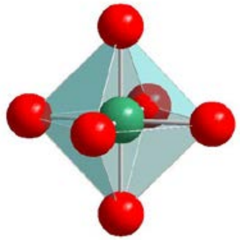
Coordination Numbers

- The coordination number of a metal depends upon the size of the metal and the size of the ligands.
- While iron(III) can bind to 6 fluorides, it can only accommodate 4 of the larger chlorides.
- Only count ligands inside square brackets. (Watch for polydentate ligands - donor atoms).

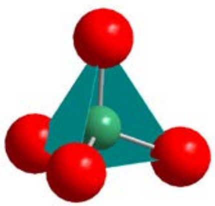


Coordination Geometries

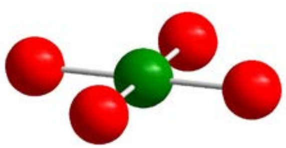
Coordination geometry   Determined by number of ligands



C.N. = 6 → Octahedron



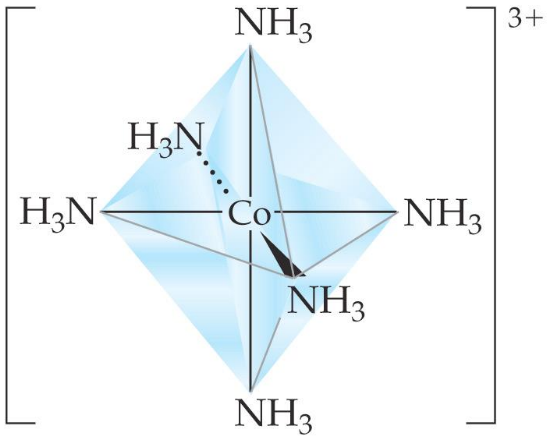
C.N. = 4 → Tetrahedron (normally)



C.N. = 4 → Square Planar = *Non Euclidian*

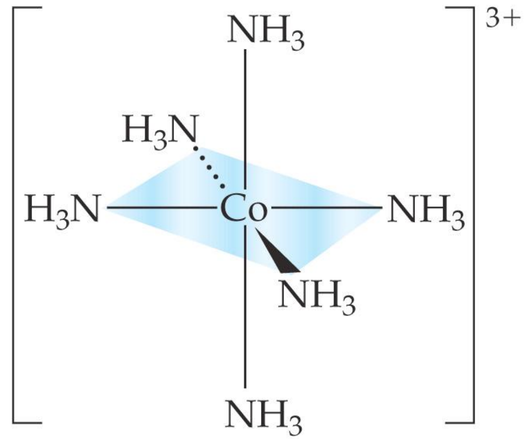
Must be a d^8 or d^9, and a 4d or 5d metal.

C.N. = 2 → Linear (usually d^{10})



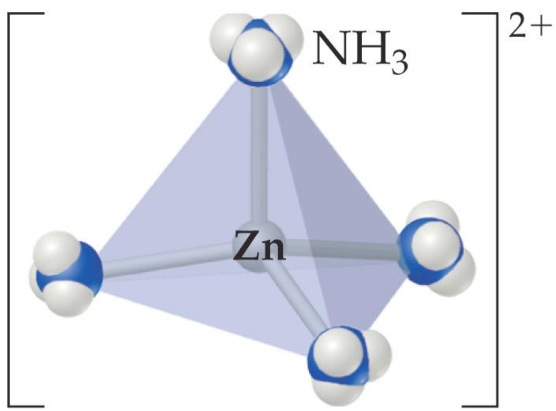
NH_3
H_3N
H_3N
Co
NH_3
NH_3
NH_3
3+

(a)



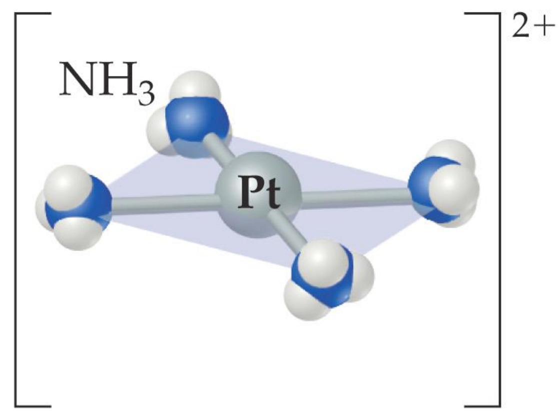
NH_3
H_3N
H_3N
Co
NH_3
NH_3
NH_3
3+

(b)



NH_3
Zn
2+

(a)



NH_3
Pt
2+

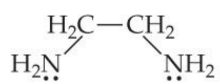
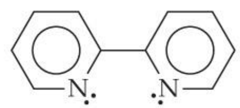
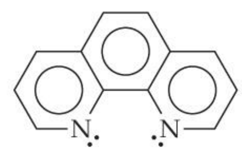
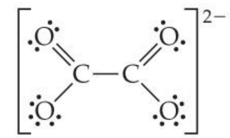
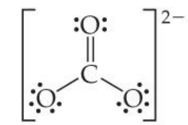
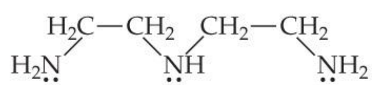
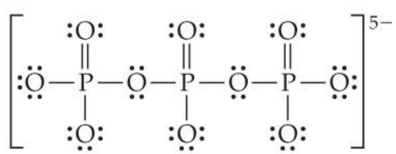
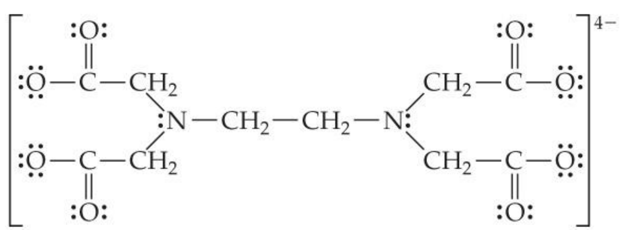
(b)

Ex: $Na_2[CdBr_4]$

Ex: $[PtCl_2(NH_3)_2]$

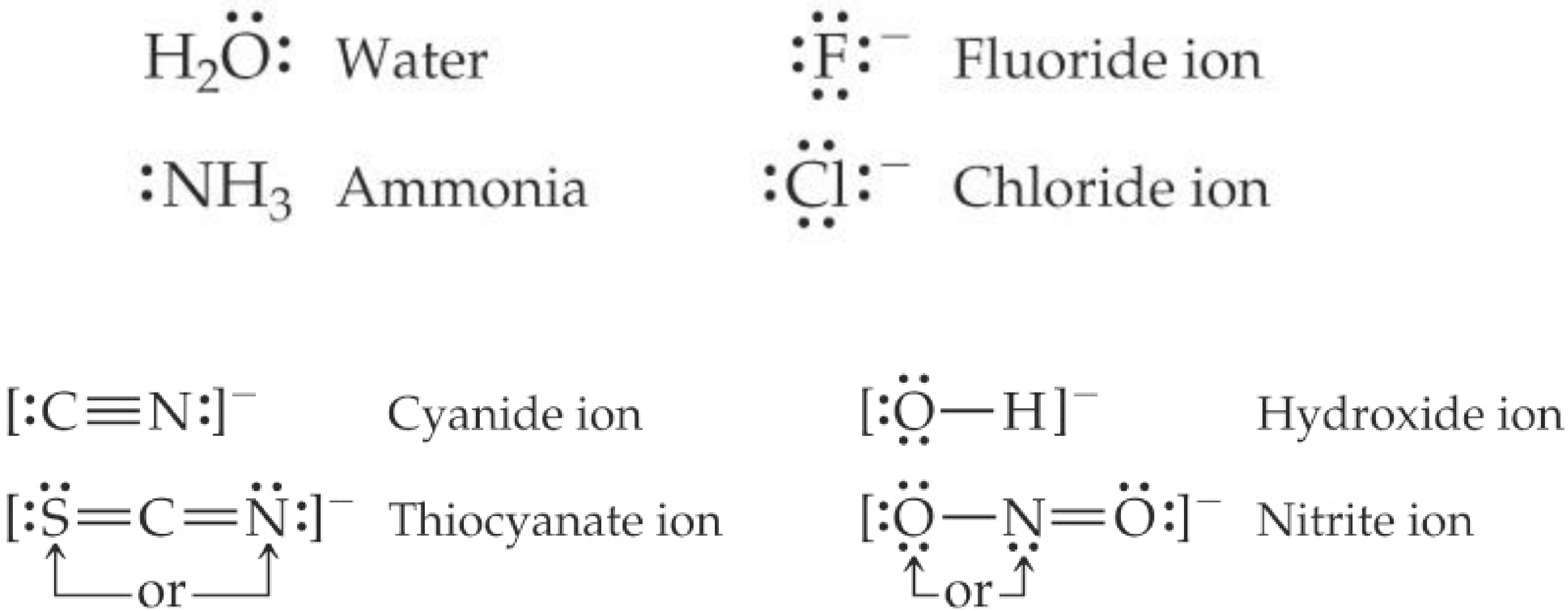
Common Ligands

TABLE 23.4 • Some Common 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	$[:\ddot{S}=C=\ddot{N}:]^-$ (bonds through S or N)	Thiocyanate ion	$[:\ddot{O}-\ddot{N}=\ddot{O}:]^-$ (bonds through O or N)	Nitrite ion
Bidentate	 Ethylenediamine (en)		 Bipyridine (bipy or bpy)		 *Ortho*-phenanthroline (*o*-phen)		 Oxalate ion	 Carbonate ion
Polydentate	 Diethylenetriamine			 Triphosphate ion				
			 Ethylenediaminetetraacetate ion ($EDTA^{4-}$)					

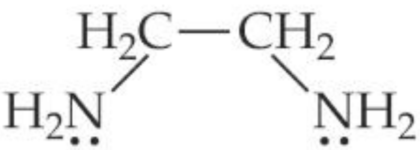
Monodentate Ligands

Coordinate to one site on metal

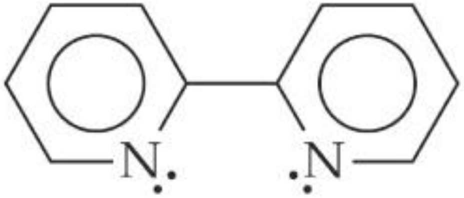


Bidentate Ligands

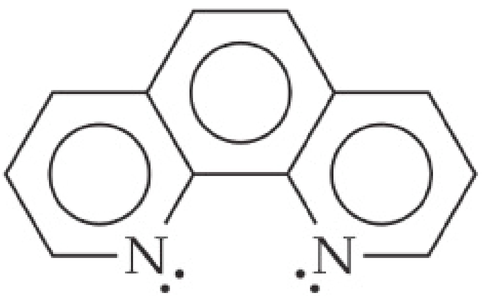
Ligands with 2 donor atoms



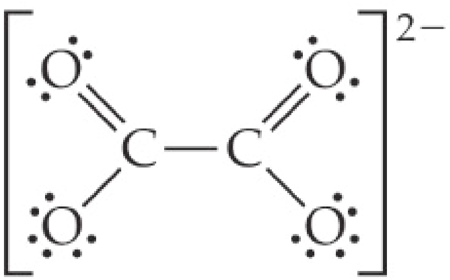
Ethylenediamine (en)



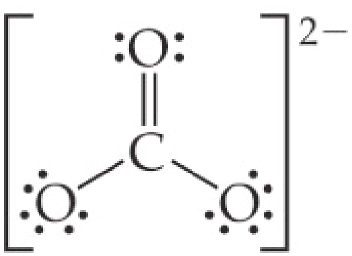
Bipyridine
(bipy)



Ortho-phenanthroline
(*o*-phen)



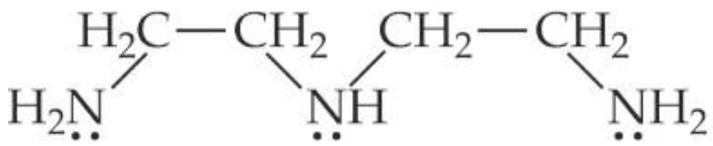
Oxalate ion



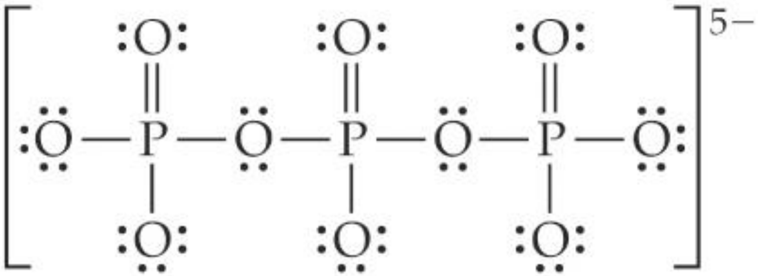
Carbonate ion

Polydentate Ligands

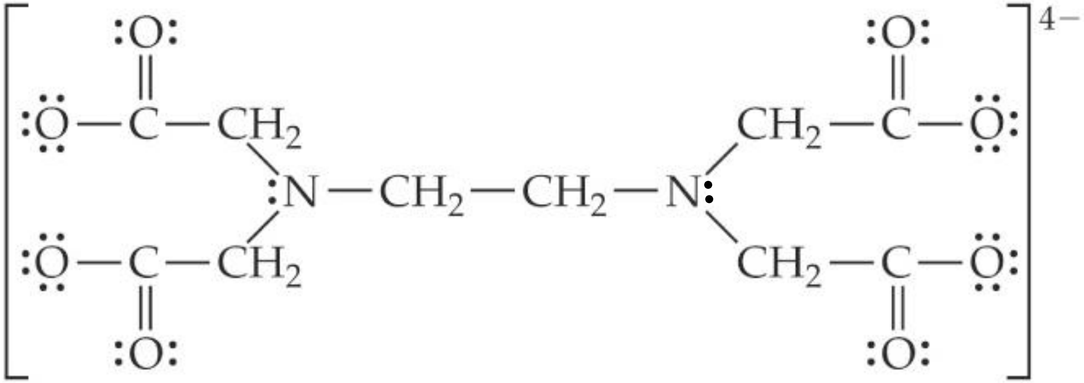
Ligands with 3 or more donor atoms



Diethylenetriamine



Triphosphate ion



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

Chelating Agents

Bidentate and Polydentate Ligands

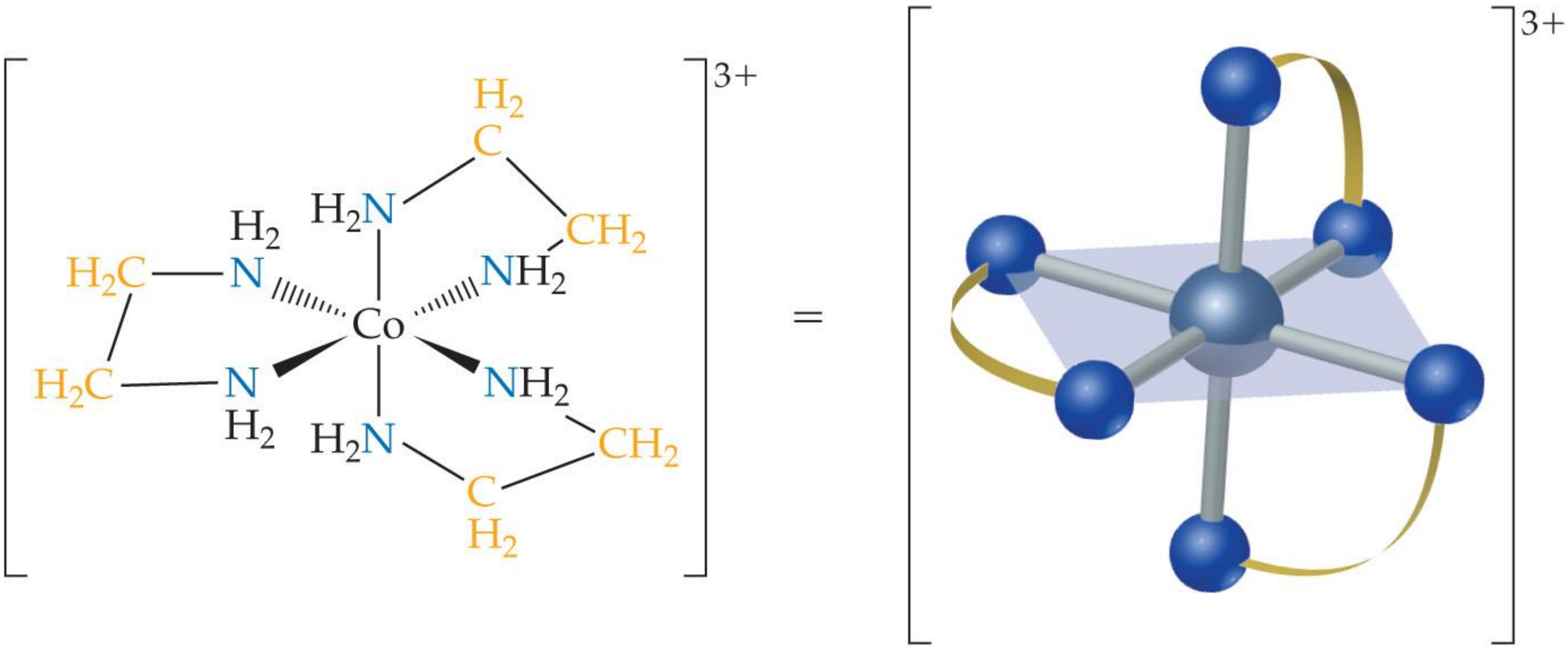
ethylene diamine, en

$(NH_2CH_2CH_2NH_2)$

ethylenediaminetetraacetate ion,

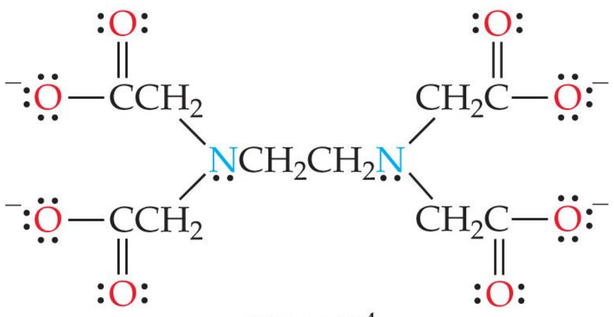
$[EDTA]^{4-}$

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

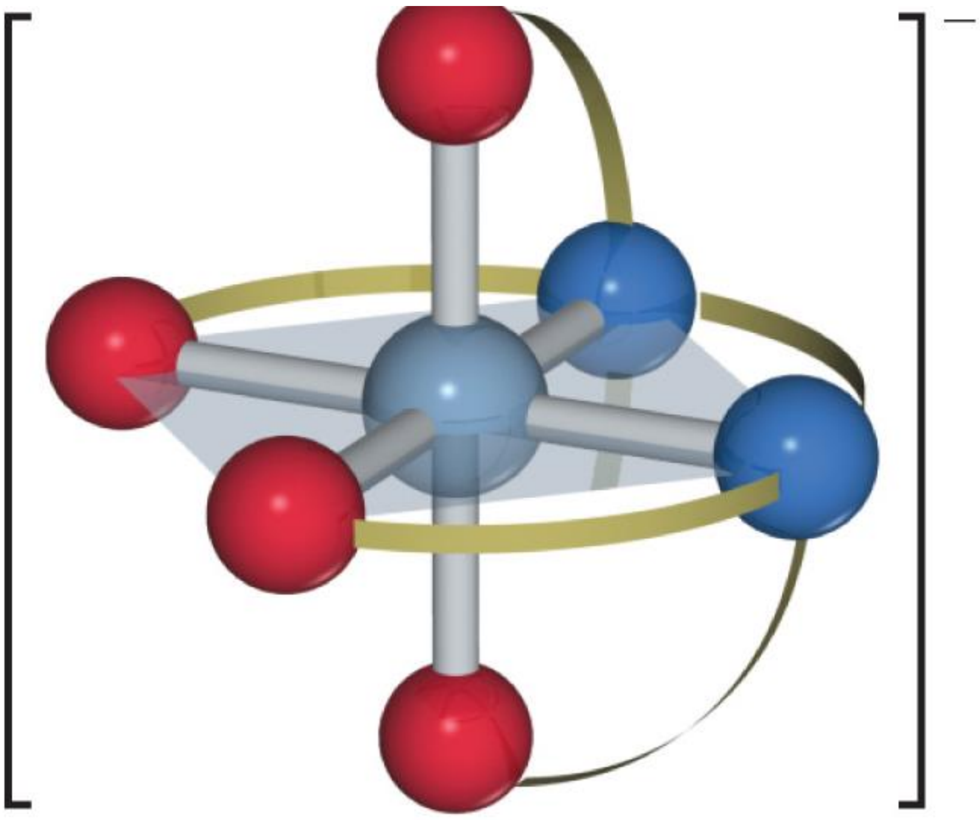


$[Co(en)_3]^{3+}$

EDTA and an EDTA complex



$[EDTA]^{4-}$



Chelate Effect

- Form more stable cmpds than monodentate ligands

$$Ni(H_2O)_6^{2+}(aq) + 6\ NH_3(aq) \leftrightarrows [Ni(NH_3)_6]^{2+}(aq) + 6\ H_2O(l)$$

$$K_f = 1.2 \times 10^{9}$$

$$Ni(H_2O)_6^{2+}(aq) + 3\ en(aq) \leftrightarrows [Ni(en)_3]^{2+}(aq) + 6\ H_2O(l)$$

$$K_f = 6.8 \times 10^{17}$$

Chelate Effect

- Why is K_f for the second compound so high?

- Both complexes contain 6 Ni-N bonds, so ΔH_{rxn} values are very similar.

- In order to remove one (*en*), you have to break the exact two, 2 Ni – NH_2R bonds corresponding to the same en, and not just two random Ni – NH_3 in $[Ni(NH_3)_6]^{2+}$. It is usually favorable for polydentate ligands to replace monodentate ligands.

Entropy and the Chelate Effect

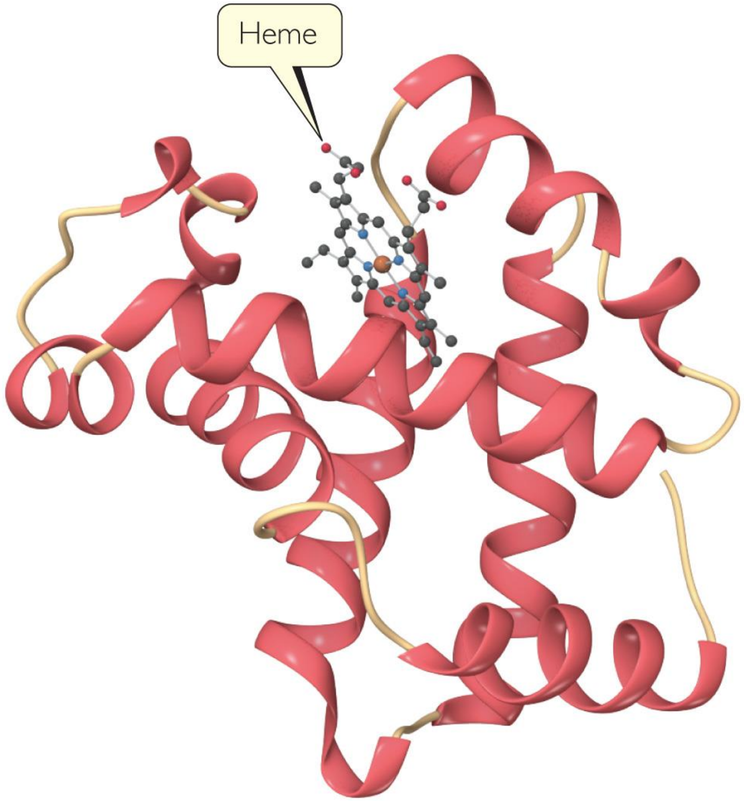
- $Cu^{2+} + 2\ NH_3$
- $Cu^{2+} + 1$ en

$[Cu(OH_2)_4]^{2+}$(aq) to

	ΔH^0	ΔS^0	ΔG^0	K
$Cu(OH_2)_2(NH_3)_2]^{2+}$	-46 kJ	-8.4 J/K	-43 kJ	3.1×10^7
$Cu(OH_2)_2(en)]^{2+}$	-54 kJ	+23 J/K	-61 kJ	4.2×10^{10}

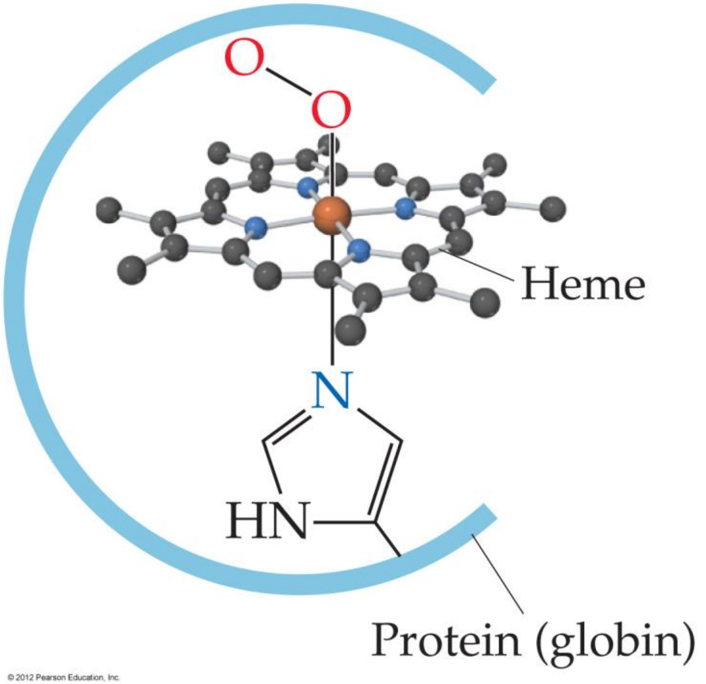
Chelates in Biological Systems

- There are many transition metals that are vital to human life.
- Several of these are bound to chelating agents.

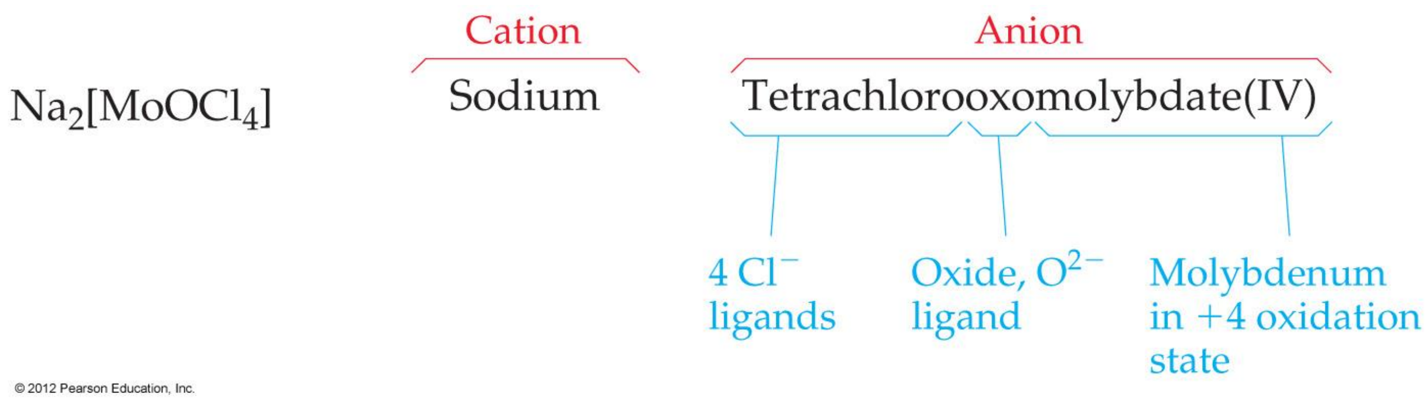


Chelates in Biological Systems

- For instance, the iron in hemoglobin carries O_2 and CO_2 through the blood.
- Carbon monoxide and cyanide are poisonous because they will bind more tightly to the iron than will oxygen.

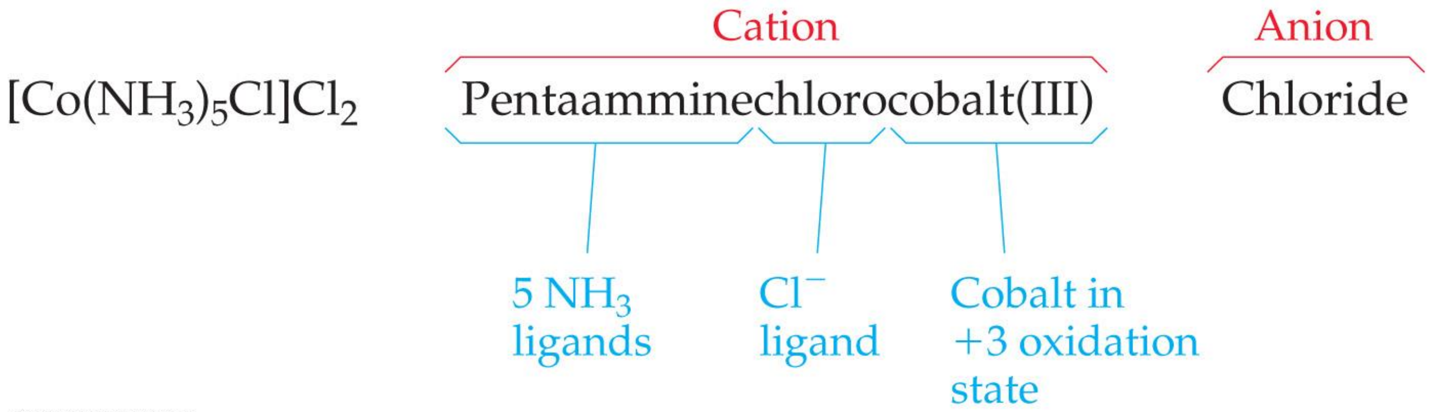


Nomenclature in Coordination Chemistry



1. Naming complexes that are salts:

   name of cation before name of anion.



2. Naming complex ions or molecules:

ligands named before the metal.

- Ligands listed in name in alphabetical order, regardless of their charges.

- Prefixes used to indicate # ligands
    - not used in alphabetical ordering

3. Names of anionic ligands end in the letter *o*, but electrically neutral ligands ordinarily bear the name of the molecules.

TABLE 23.5 • Some Common Ligands and Their Names

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

$[Fe(CN)_2(NH_3)_2(H_2O)_2]^+$

Diamminediaquadicyanoiron(III) ion

4. Greek prefixes used to indicate number of each kind of ligand when more than one is present.

2 = di-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-

4a. If ligand contains a Greek prefix or is polydentate, the prefixes below are used w. the ligand name in parentheses.

2 = bis-, 3 = tris-, 4 = tetrakis-, etc.

$[Co(en)_3]Br_3$

tris(ethylenediamine)cobalt(III) bromide

5. If complex is an anion, name ends in -ate. Some use the Latin name as the root.

Metal	Name of Metal in Anionic Complex
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Silver	Argentate
Tin	Stannate

6. The oxidation number of the metal is given in parentheses in Roman numerals following the name of the metal.

Examples

$[Mo(NH_3)_3Br_3]NO_3$

$[Cr(en)_3]Br_3$

$[Ni(NH_3)_6]^{2+}$

Examples

$(NH_4)_2[PtCl_4]$

$[Ru(H_2O)_2(C_2O_4)_2]^-$