Coordination Chemistry Part -1

Asst. Prof. Dr. Abbas A. S. Al-Hamdani

Lecture : Complexes & Introducing the Ligands

Lewis Model of coordinate Bonding

Neutral and Anionic Ligands

Mono- and bidentate ligands

Multidentate ligands

Inner and outer sphere coordination

Definition the Complex:

A complex or coordination compound is a compound in which an atom (called “central atom”) is bound to more groups (called “ligands”) than expected with respect to its charge and position in the periodic table.

The number of ligands around a central atom is called the “coordination number”.

Coordination Chemistry

- Transition metals act as Lewis acids
  - Form complexes/complex ions

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow Fe(CN)_6^{3-}(aq)$$

Lewis acid — Lewis base — Complex ion

$$Ni^{2+}(aq) + 6NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}(aq)$$

Lewis acid — Lewis base — Complex ion

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = metal = center of coordination

Lewis base = ligand = molecules/ions covalently bonded to metal in complex

Coordination Chemistry

- Transition metals act as Lewis acids
  - Form complexes/complex ions

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$

Lewis acid Lewis base Complex ion

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

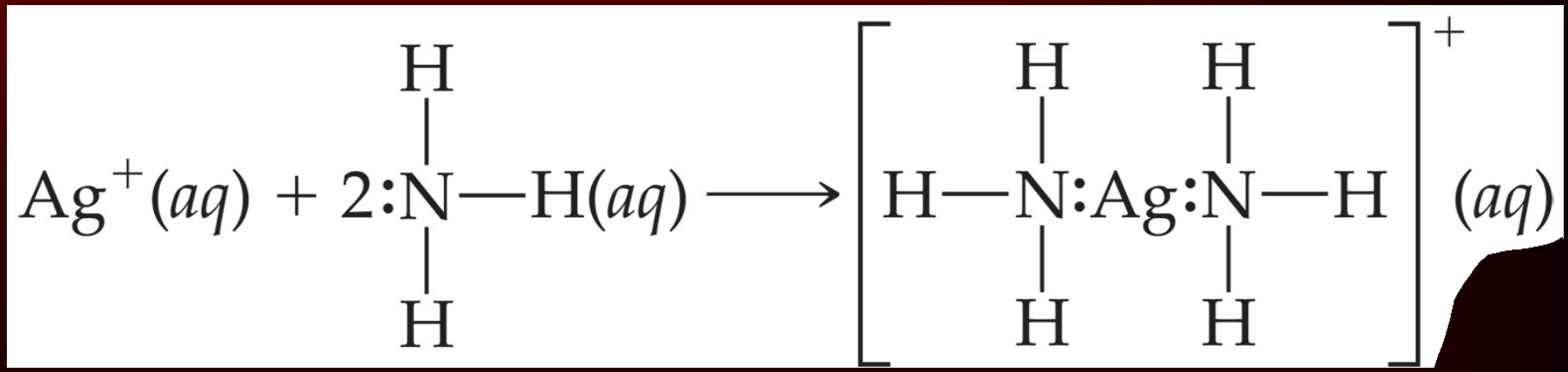
Lewis acid Lewis base Complex ion

Complex with a net charge = complex ion

Complexes have distinct properties

Metal-Ligand Bond

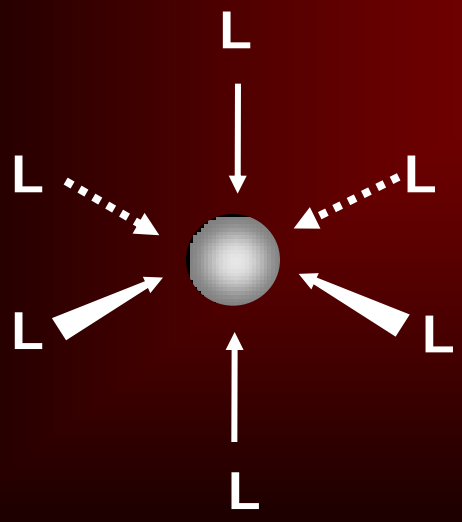
- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have nonbonding electrons.
  - The metal (Lewis acid) has empty orbitals.



Coordinate bonding

Each ligand donates both electrons to the bond with the metal centre

NH_3 BF_3 $H_3N \rightarrow BF_3$



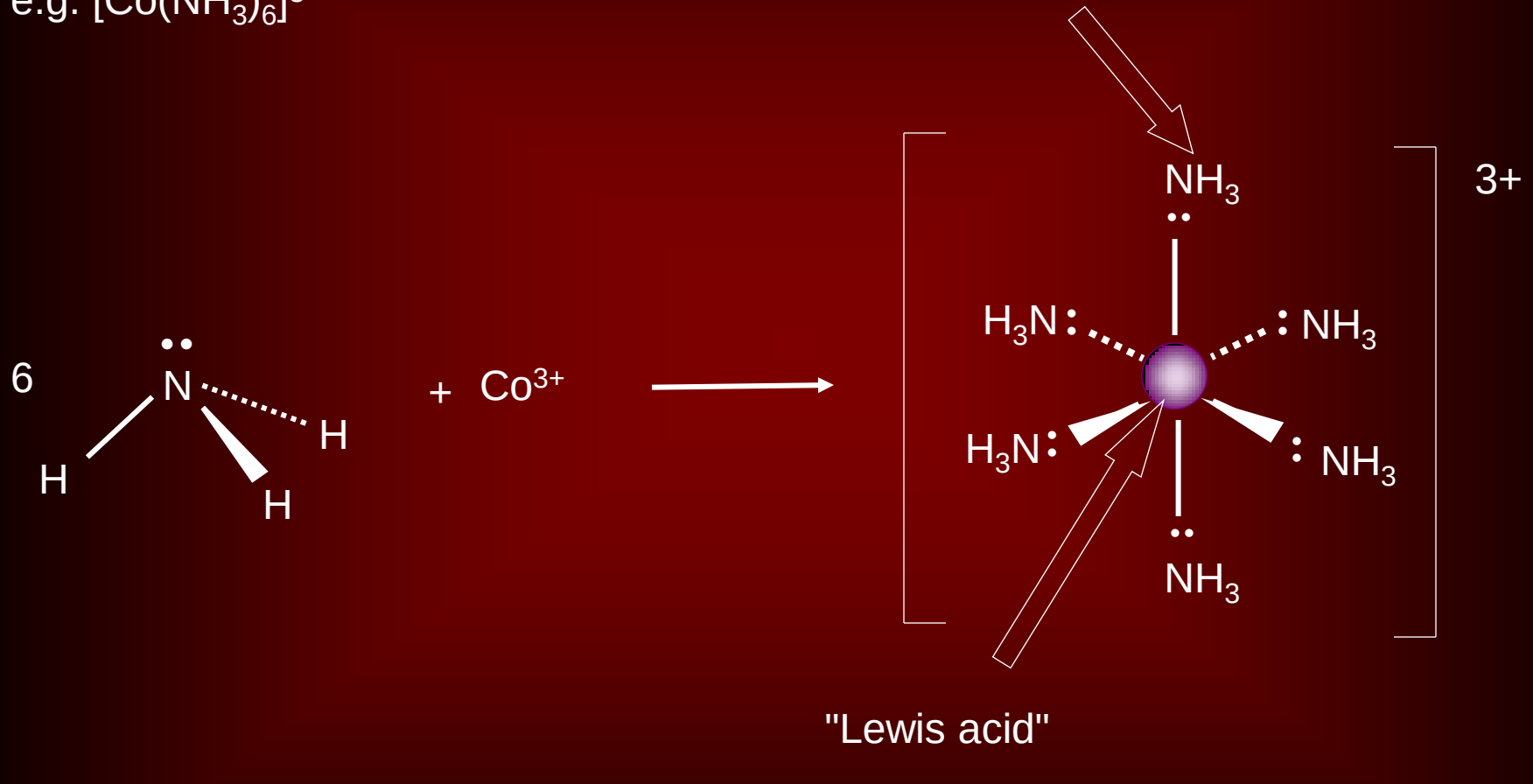
→ = coordinate or dative bond

Metal-Ligand Bond

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

Lewis Model of Bonding

e.g. $[Co(NH_3)_6]^{3+}$

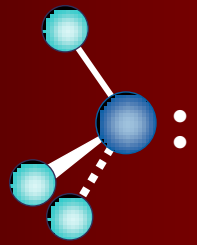


Neutral ligands containing Lone pairs of electrons

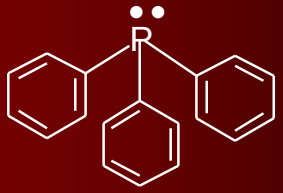
Group 14

CO
carbon monoxide

Group 15

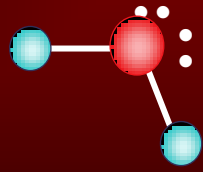


NH_3
ammonia

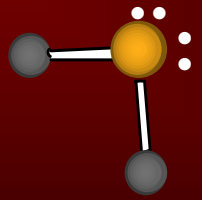


PPh_3
phosphine

Group 16



H_2O
water



SR_2
thioether

Ligands are bonded to the metal centre *via* a donor atoms

Hard donor atoms

e.g. NH_3, H_2O, OH^-, CO_3^{2-}

Small donor atoms

Electronegative

Not very polarisable

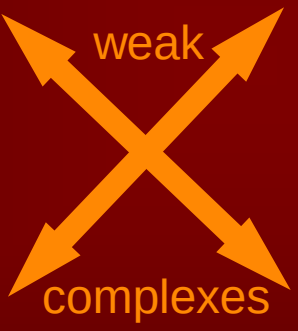
strong complexes

"Hard" metals

e.g. Fe(III), Mn(II), Cr(III)

Small metals (1st row)

High oxidation state



Soft donor atoms

CO, PPh_3, C_2H_4, SRH, CN^-, SCN^-

Larger donor atoms

Less electronegative

Easlily polarisable

strong complexes

Soft metals

e.g. Ag(I), Cu(I)

Larger metals (2nd + 3rd row)

Low oxidation state

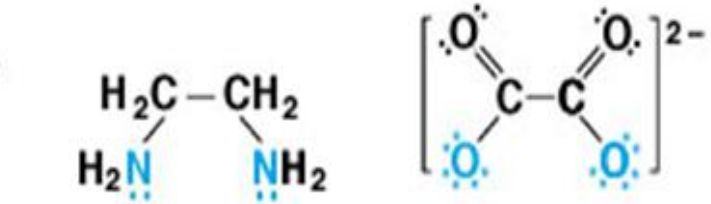
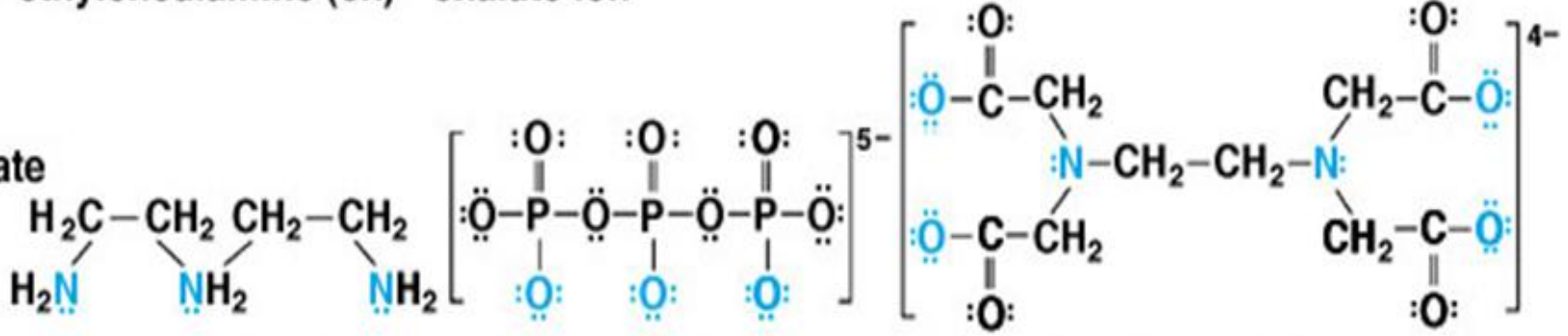
Anionic ligands containing Lone pairs of electrons

Group 14		CN^- cyanide		Ph^- phenyl
Group 15		NO^- nitrous		NCS^- isocyanate
Group 16		OH^- hydroxide		SCN^- thiocyanate
Group 17	X^-	halide	H^-	hydride

These ligands are σ-bonded to the metal centre

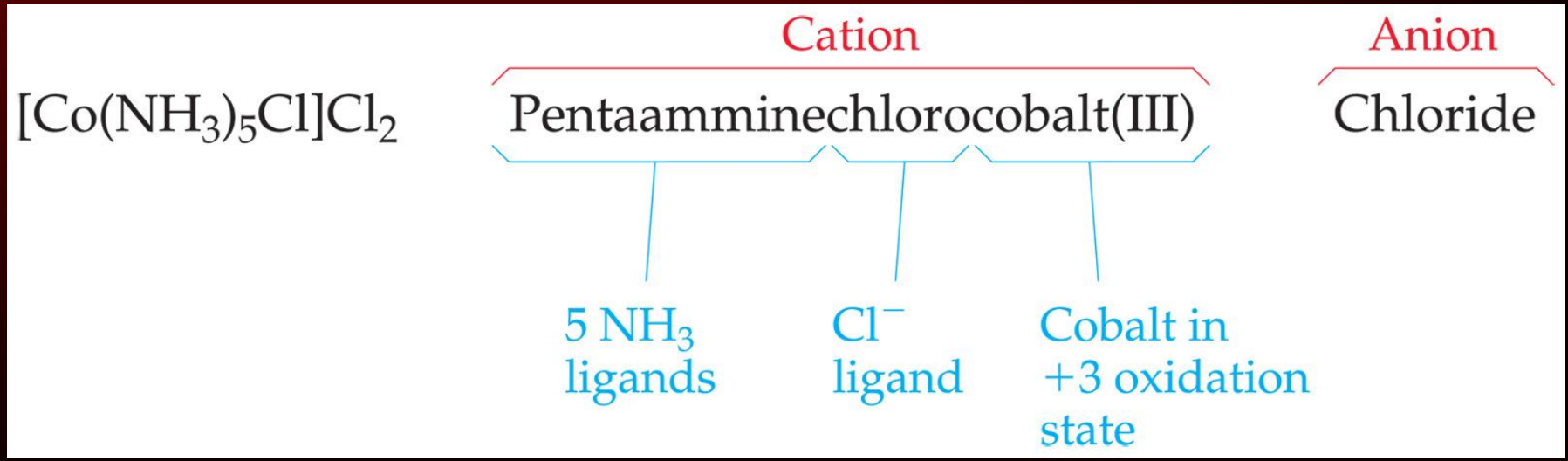
Ligands in Coordination Compounds

Some Common Ligands in Coordination Compounds

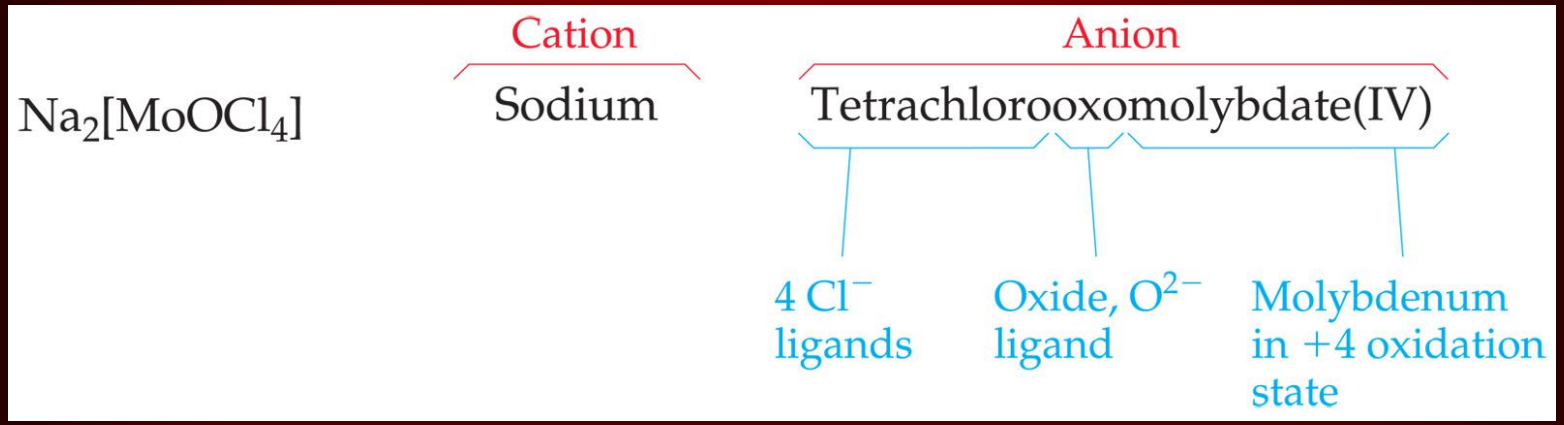
Ligand Type	Examples
Unidentate	H_2O: water; F^- fluoride ion; $C\equiv N^-$ cyanide ion; $[O-H]^-$ hydroxide ion; NH_3 ammonia; Cl^- chloride ion; $[S=C=N]^-$ (or $[C\equiv N-S]^-$) thiocyanate ion; $[O-N=O]^-$ (or $[O-N=O]^-$) nitrite ion
Bidentate	 ethylenediamine (en); oxalate ion
Polydentate	 diethylenetriamine; triphosphate ion; ethylenediaminetetraacetate (EDTA) ion

Nomenclature of Coordination Compounds

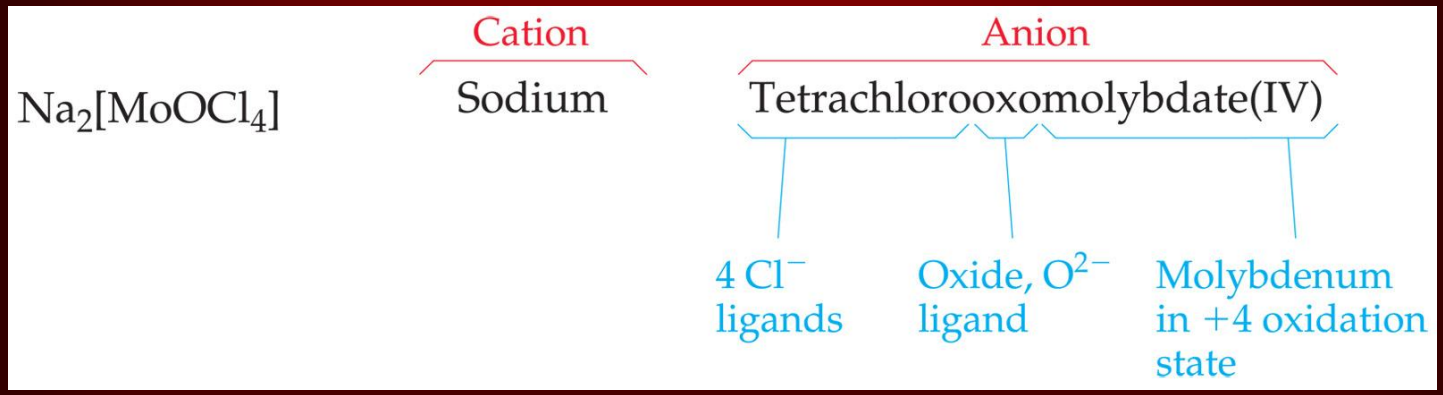
- As always the name of the **cation** appears first; the **anion** is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.



- 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.



- 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.



Names of Some Ligands

Names of Some Neutral and Anionic Ligands

Name	Formula
A. Neutral	
Aqua	H_2O
Ammine	NH_3
Carbonyl	CO
Nitrosyl	NO
B. Anionic	
Fluoro	F^-
Chloro	Cl^-
Bromo	Br^-
Iodo	I^-
Hydroxo	OH^-
Cyano	CN^-

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.

Metal Ions in Complex Anions

Names of Some Metal Ions in Complex Anions

Metal	Name in Anion
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

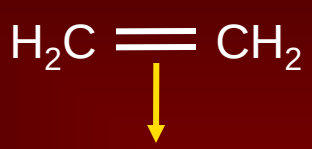
Examples

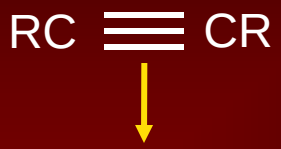
- $K_2[Co(NH_3)_2Cl_4]$
- Potassium diamminetetrachloroCobaltate(II)

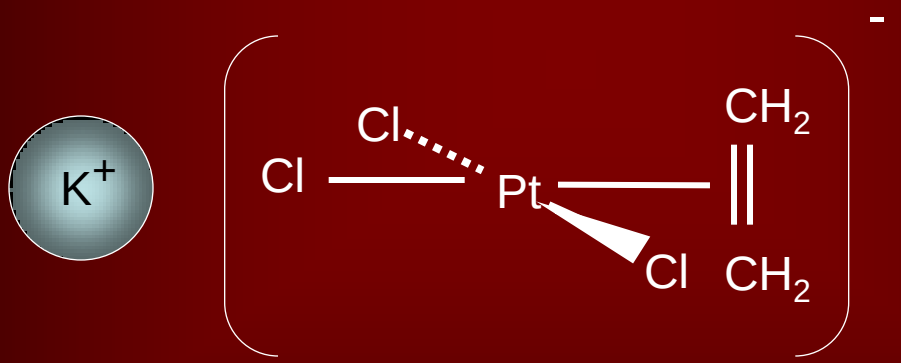
- $[Co(NH_3)_4Cl_2]Cl$
- Tetraamminedichloro Cobalt(III) chloride
- $Na_2[Ni\ (NH_3)\ Br_2\ (py)\ (OH)_2]$
- $Ca\ [Fe\ (C_2O_4)\ Br\ (CO)\ (OH)_2]$
- $[Cr\ (H_2O)_4\ Br\ (py)\ (NO)]\ (SO_4)$

π - bonded ligands

The electrons in multiple bonds can act as a lone pair of electrons







$[PtCl_3(\eta^2\text{-}C_2H_4)]^-$

eta-two ethene means the C_2H_4 is bonded *via* two atoms to the metal

Ligand Denticity

Denticity = number of donor atoms with which a ligand can bind to a metal centre

Monodentate	one donor atom per ligand
Bidentate	two donor atoms per ligand
Tridentate	three donor atoms per ligand
Multidentate	many donor atoms per ligand

Denticity refers to the number of "teeth" a ligand has

Chelating ligand: a ligand which binds to the same metal centre with more than one donor atom

- Ligands
  - classified according to the number of donor atoms
  - Examples
    - monodentate = 1
    - bidentate = 2
    - tetradentate = 4
    - hexadentate = 6
    - polydentate = 2 or more donor atoms

Ligands

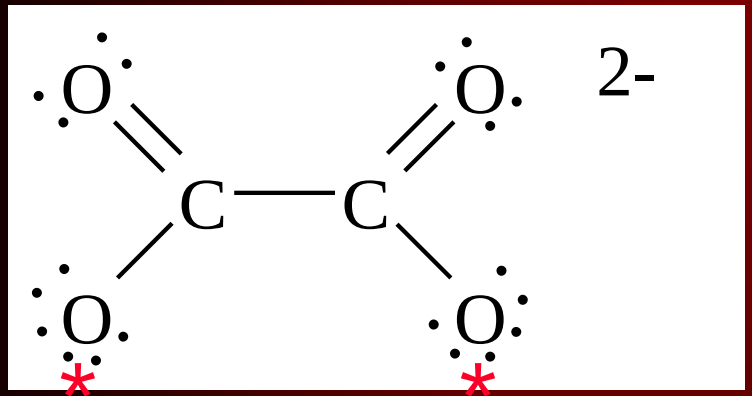
- Monodentate
  - Examples:
    - H_2O, CN^-, NH_3, NO_2^-, SCN^-, OH^-, X^- (halides), CO, O^{2-}
  - Example Complexes
    - $[Co(NH_3)_6]^{3+}$
    - $[Fe(SCN)_6]^{3-}$

Ligands

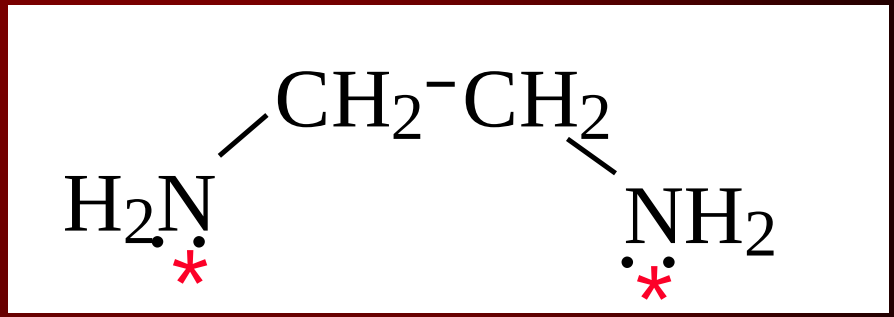
- Bidentate
  - Examples
    - oxalate ion = $C_2O_4^{2-}$
    - ethylenediamine (en) = $NH_2CH_2CH_2NH_2$
    - ortho-phenanthroline (o-phen)
  - Example Complexes
    - $[Co(en)_3]^{3+}$
    - $[Cr(C_2O_4)_3]^{3-}$
    - $[Fe(NH_3)_4(o\text{-}phen)]^{3+}$

Ligands

oxalate ion

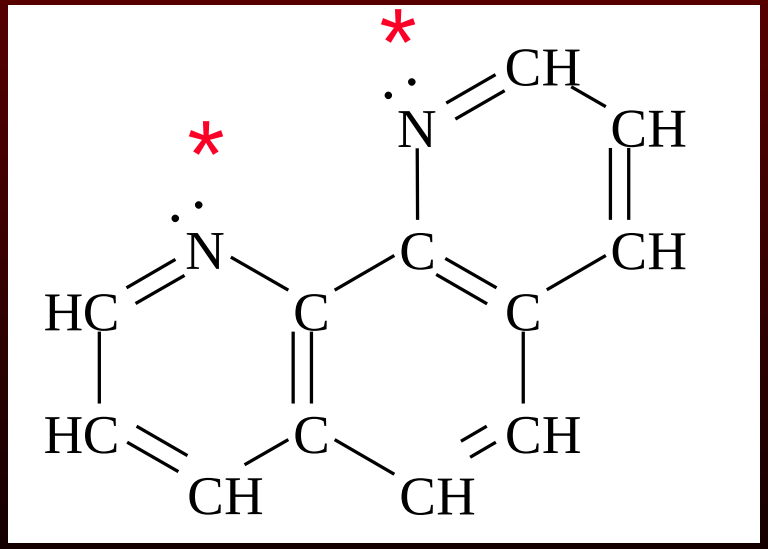


ethylenediamine



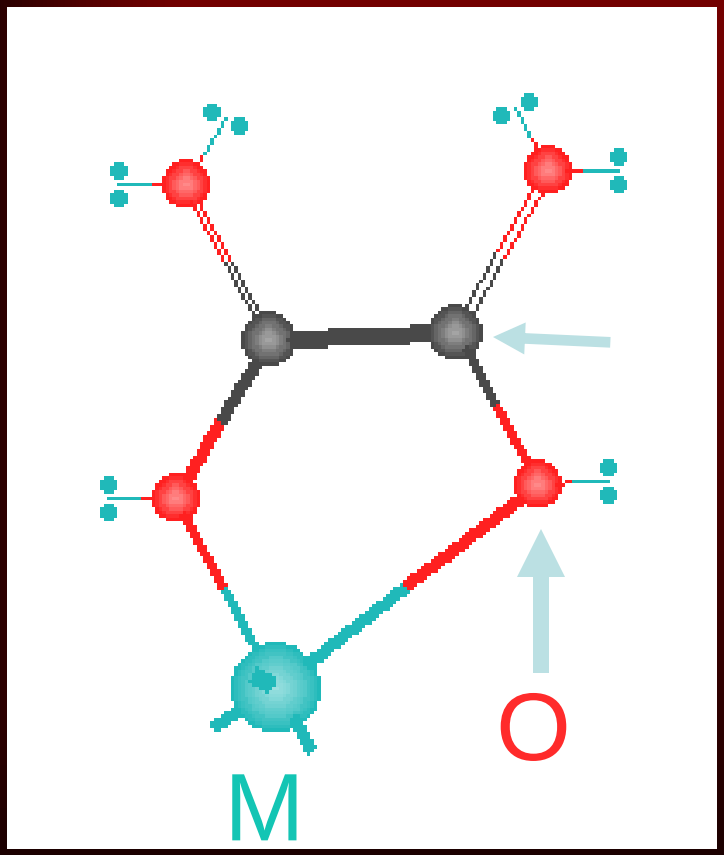
Donor Atoms

ortho-phenanthroline

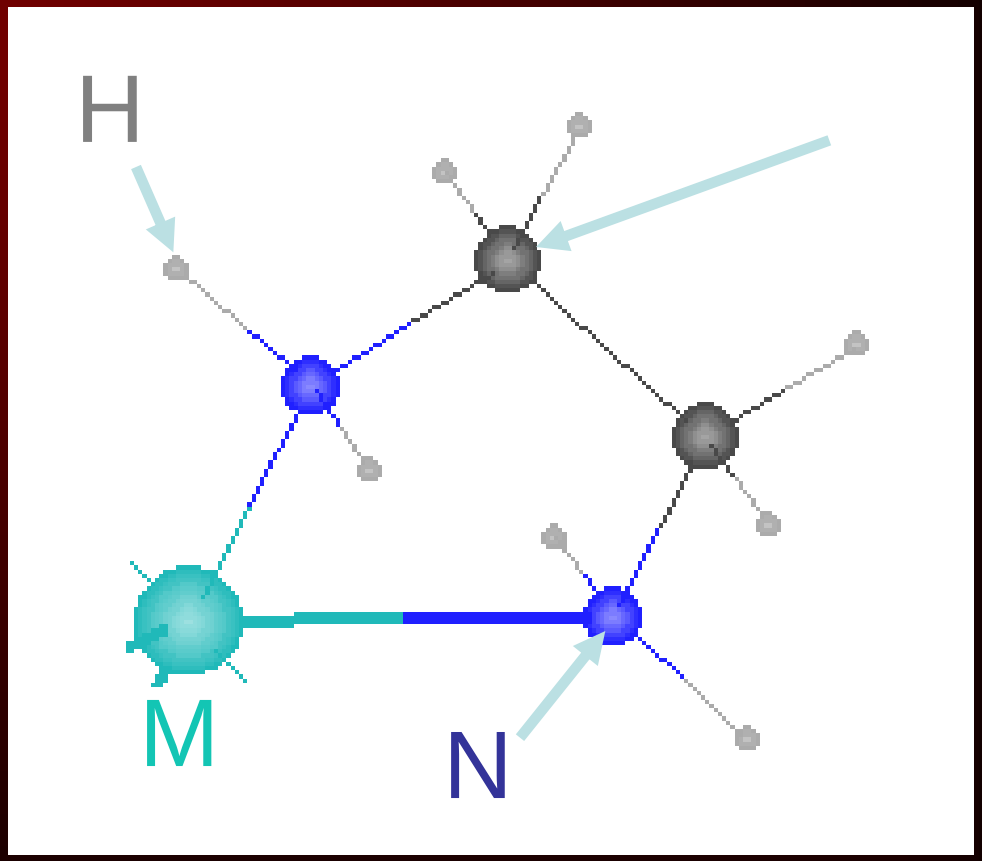


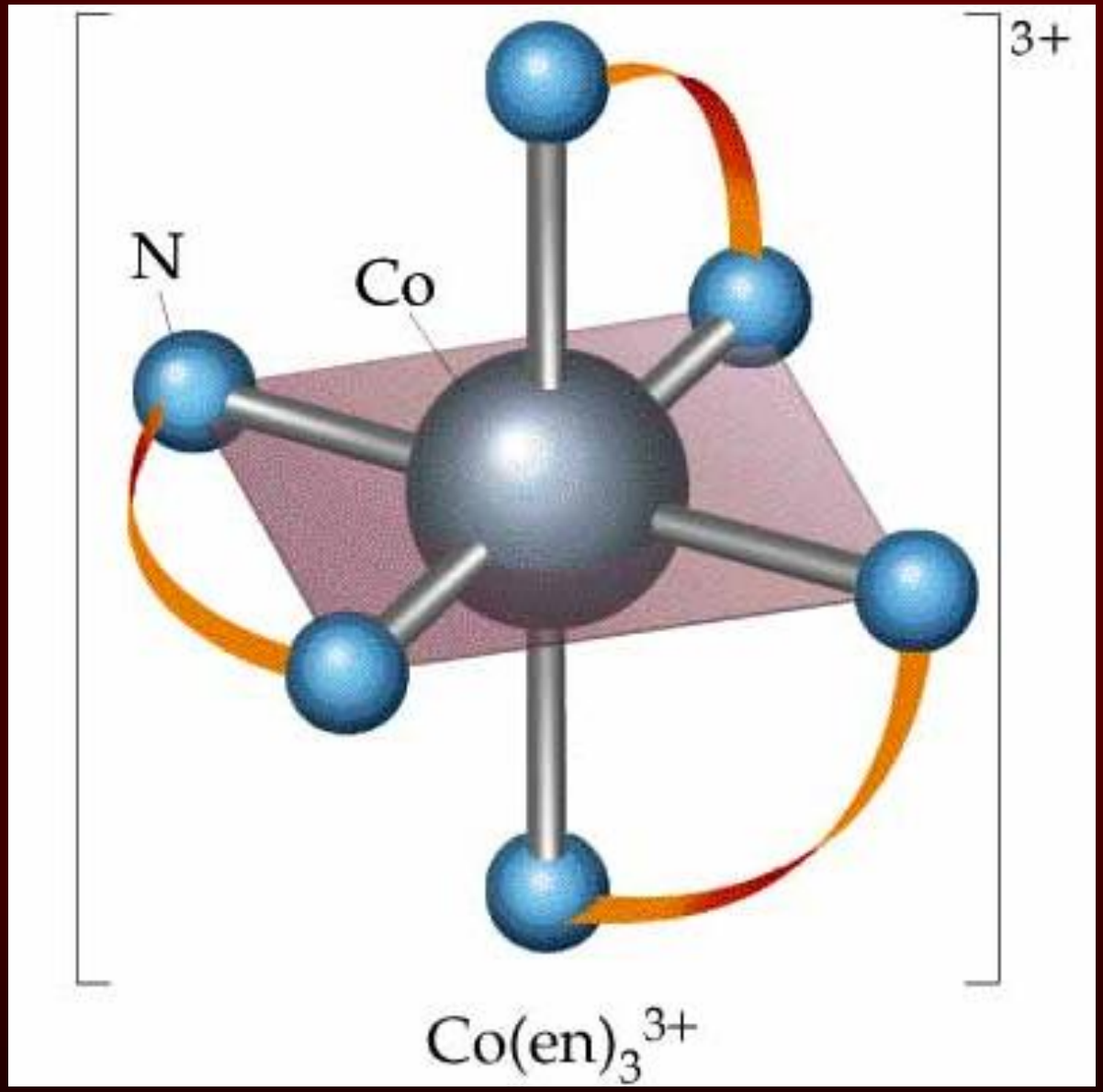
Ligands

oxalate



ethylenediamine

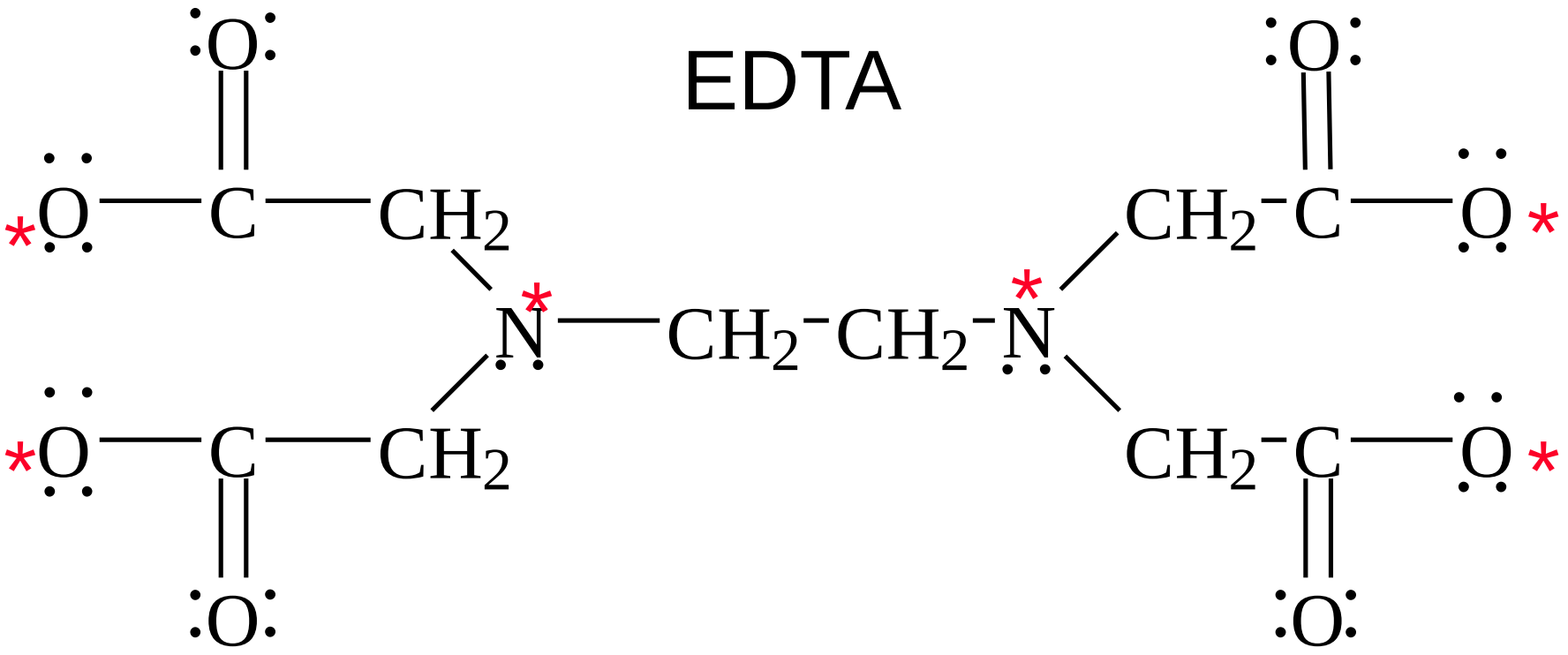



3+
N
Co
Co(en)3 3+

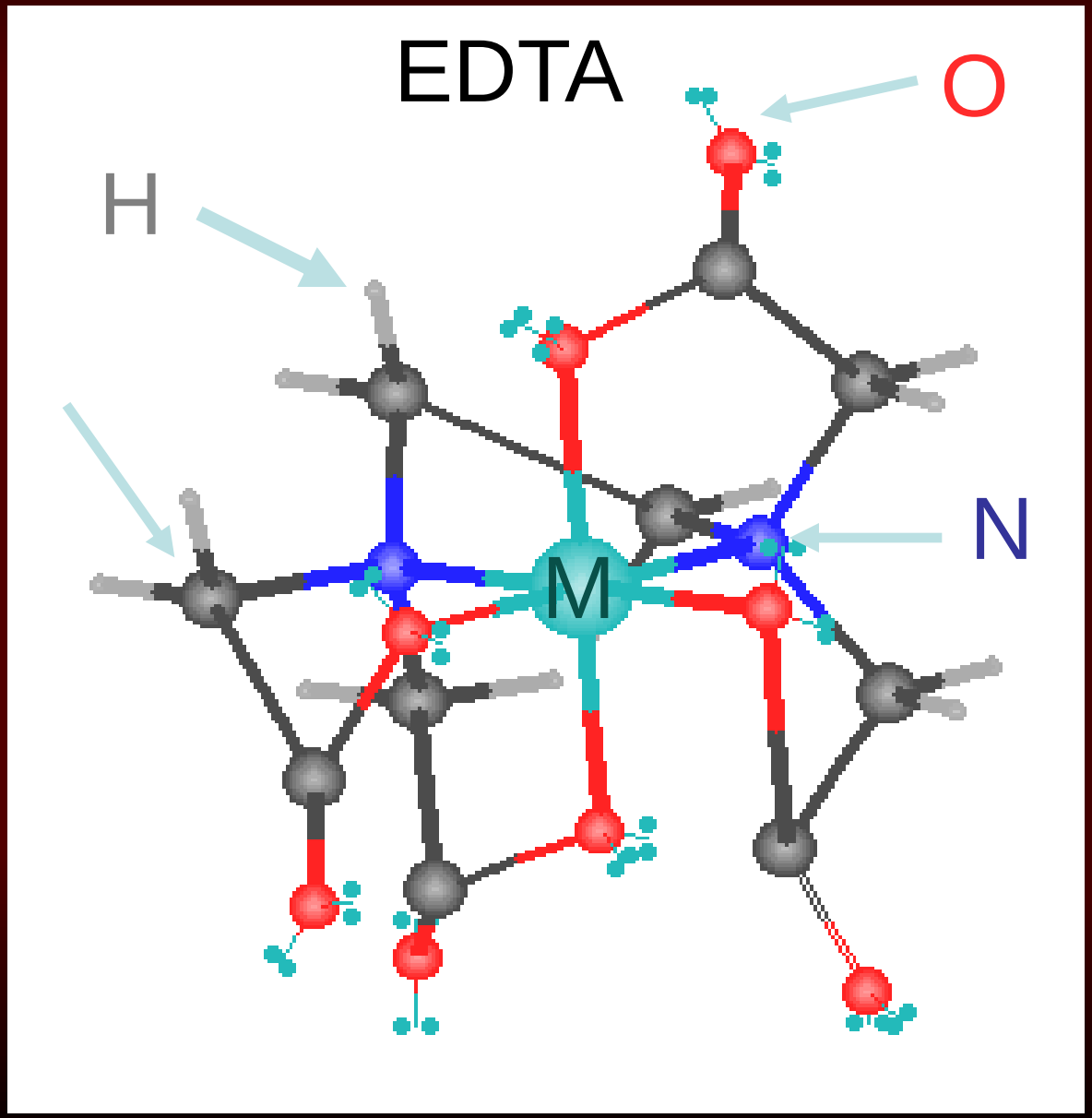
Ligands

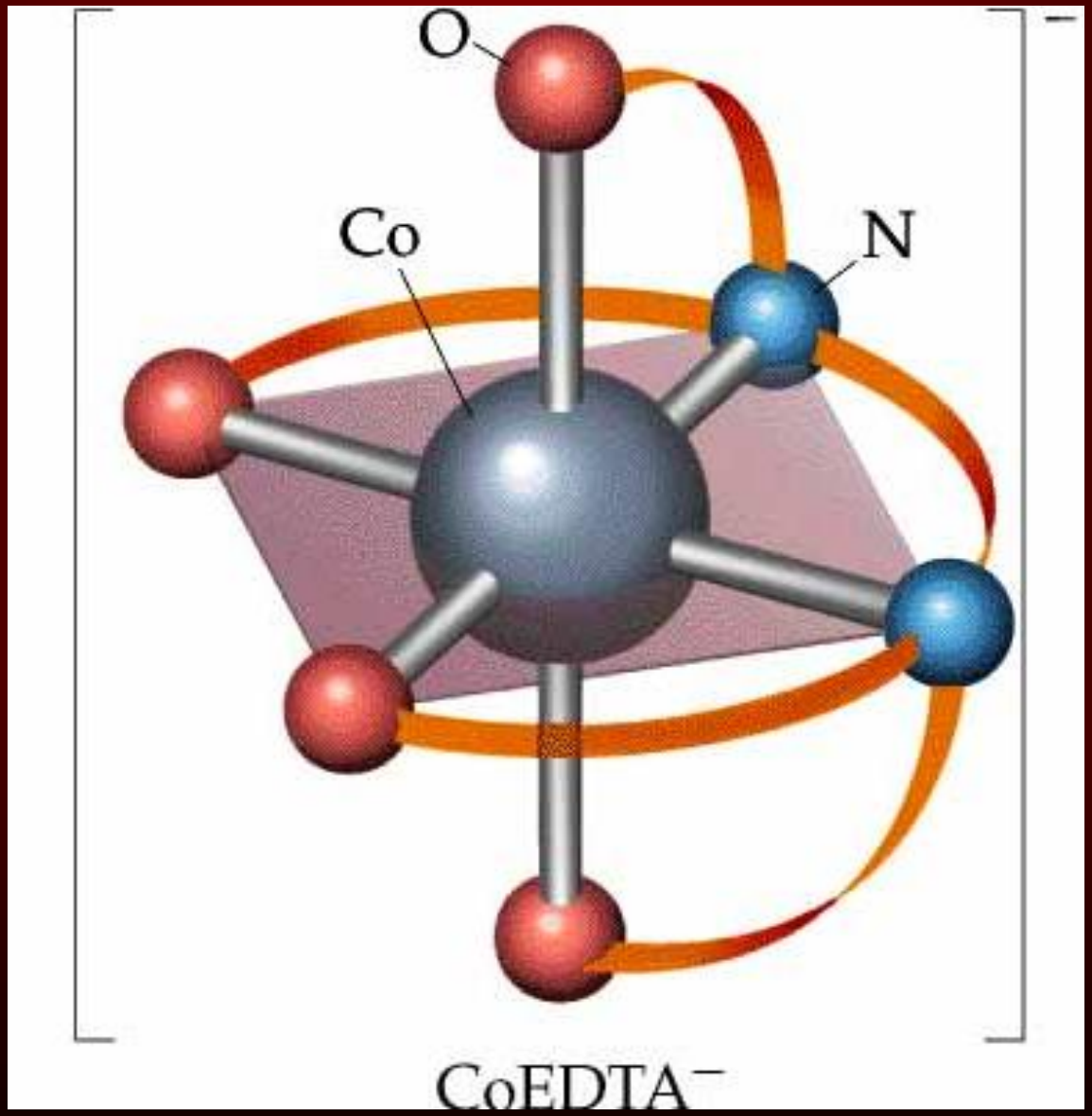
- Hexadentate
  - ethylenediaminetetraacetate (EDTA) = $(O_2CCH_2)_2N(CH_2)_2N(CH_2CO_2)_2^{4-}$
  - Example Complexes
    - $[Fe(EDTA)]^{-1}$
    - $[Co(EDTA)]^{-1}$

Ligands

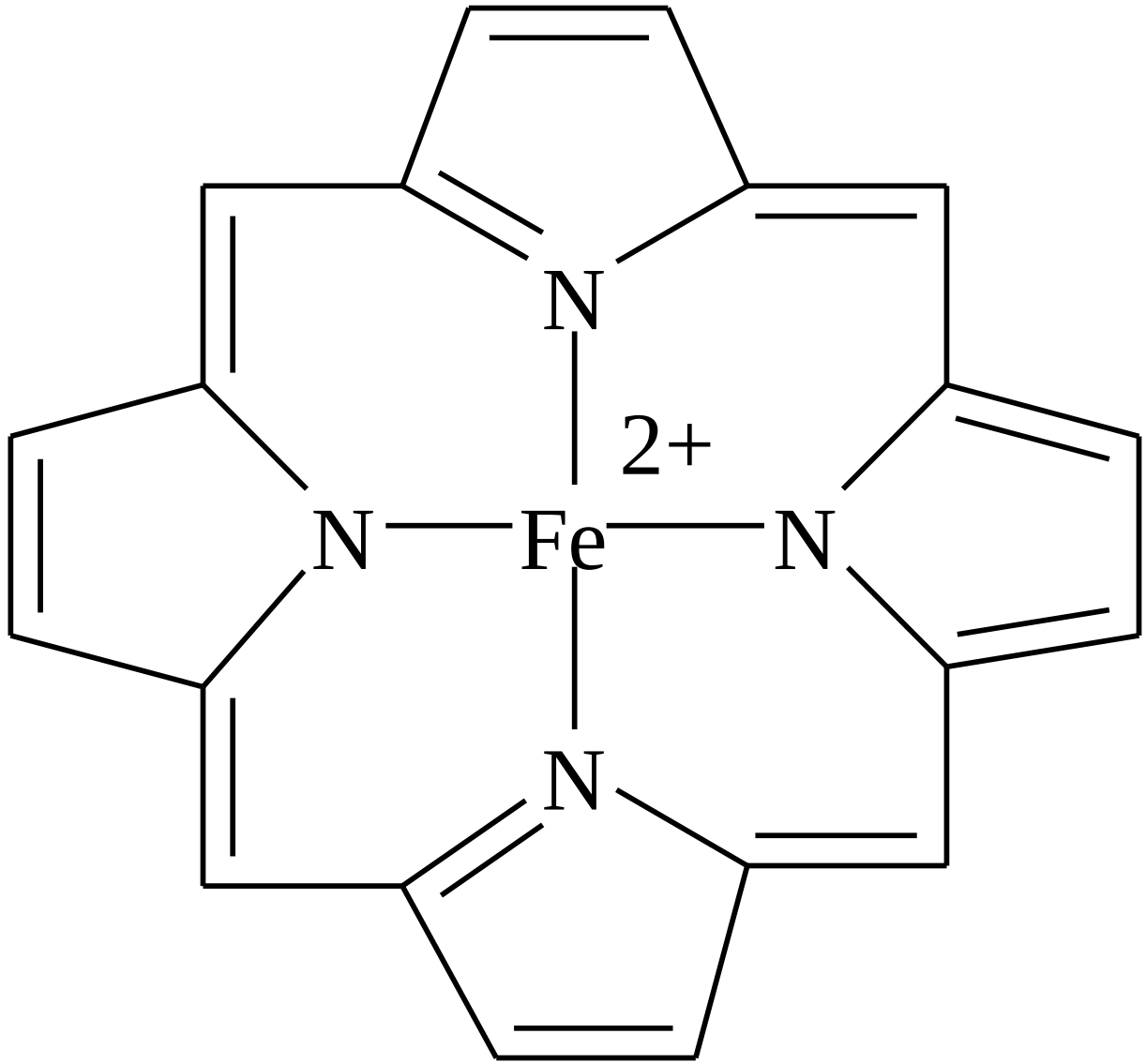


Donor Atoms

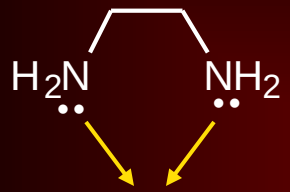

EDTA
O
H
N
M


O
Co
N
−
CoEDTA⁻

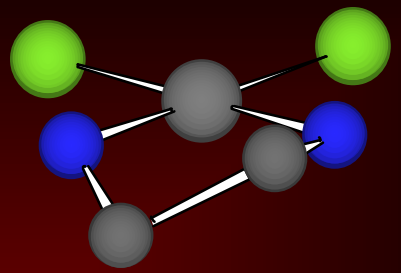
Metalloporphyrin



Neutral bidentate ligands: 2 donor atoms



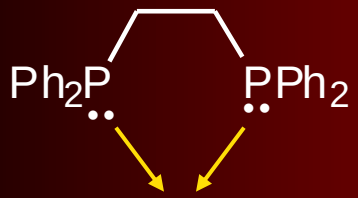
e.g. $[PtCl_2(en)]$



five membered chelate

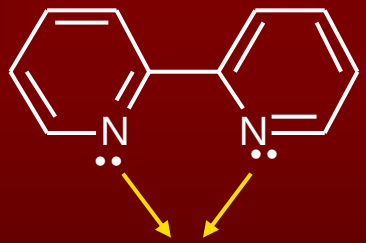
square planar complex

1,2-diaminoethane = ethylene diamine = en



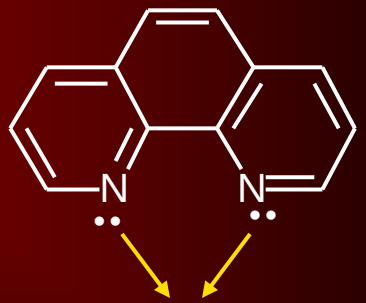
1,2-diphenylphosphineethane

dppe



2,2'-bipyridine

bpy

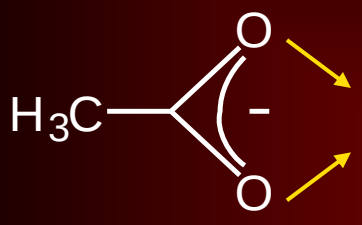


1,10-phenanthroline

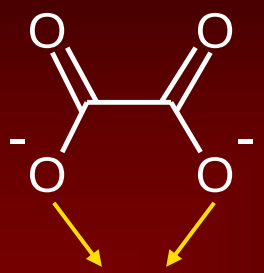
phen

Chelating ligands bind strongly to metal centres

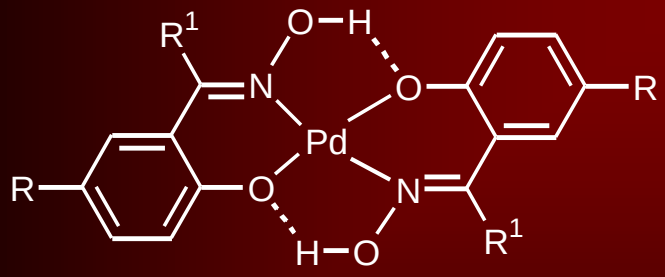
Anionic bidentate ligands



acetate = ac^-

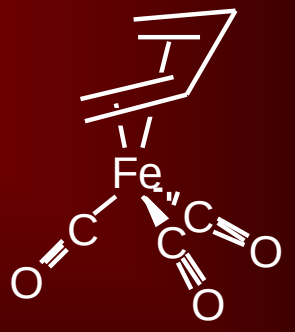


oxalate = ox^{2-}



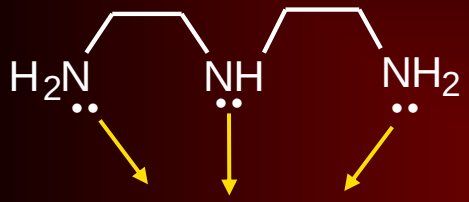
Pd(II)-oxime complex

π-donor bidentate ligand



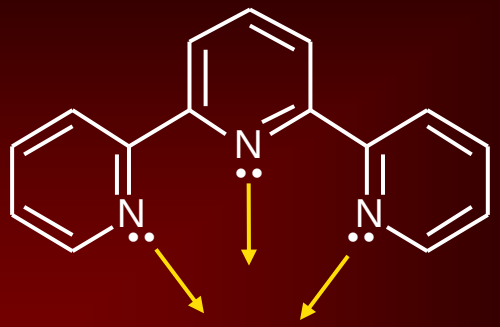
$[Fe(CO)_3(\eta^4\text{-}C_4H_6)]$

Tridentate ligands: three donor atoms



diethylenetriamine

dien

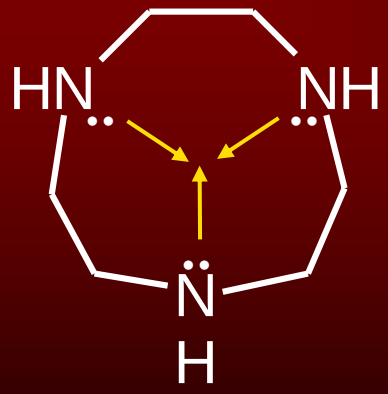


2,2':6',2''-terpyridine

tpy

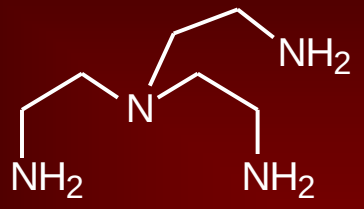
1,2,4-triazacyclonane

macrocyclic ligand



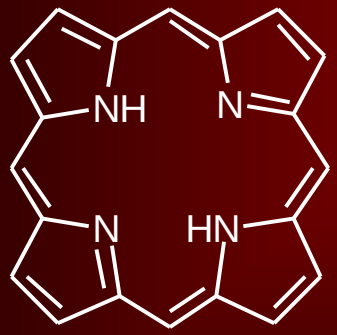
A macrocycle is a ring of at least nine atoms of which at least three are donor atoms

Tetradentate ligands: 4 donor atoms

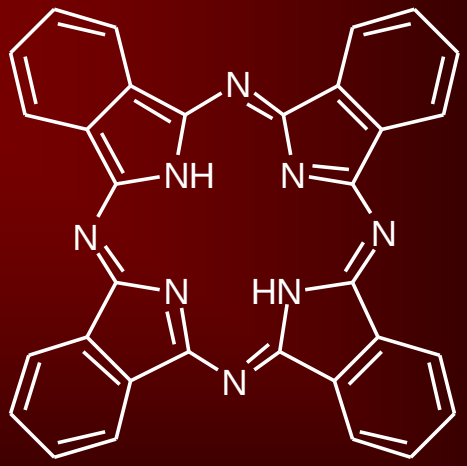


tris(2-aminoethyl)amine

tren



porphyrin

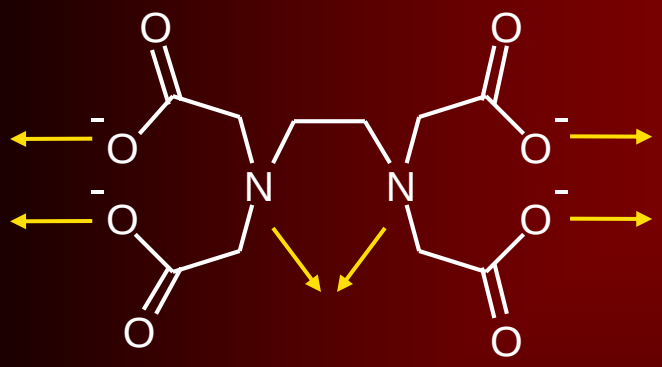


phthalocyanin

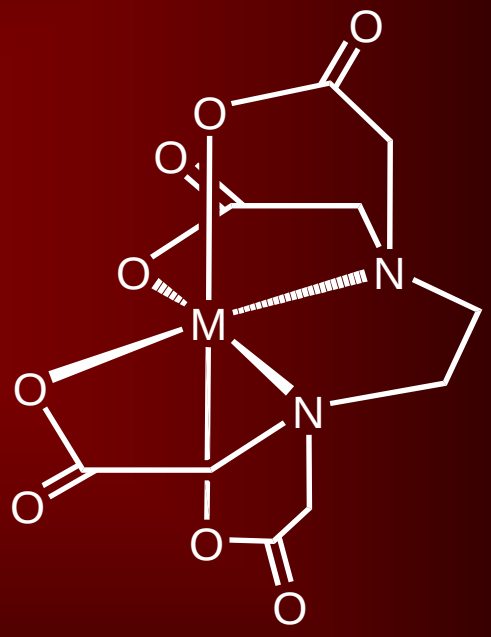
Multidentate ligands

tetraanion of ethylenediaminetetraacetic acid

EDTA

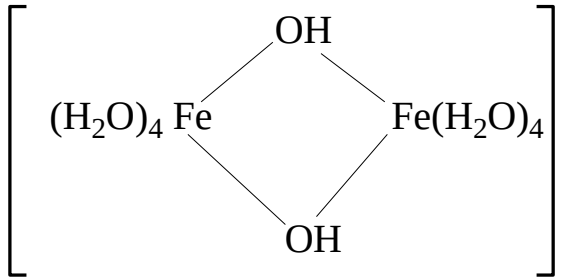


Hexadentate

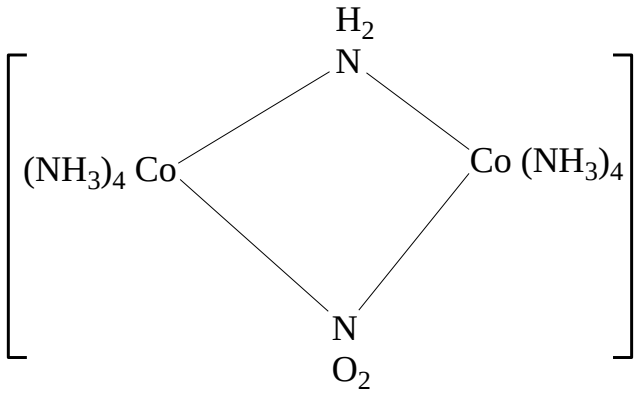


$[Co(NH_3)_6]$

$[Pt(NH_3)_3Br]$



$(SO_4)_2$



$(NO_3)_4$

Coordination Chemistry

- Coordination compound
  - Compound that contains 1 or more complexes
  - Example
    - $[Co(NH_3)_6]Cl_3$
    - $[Cu(NH_3)_4][PtCl_4]$
    - $[Pt(NH_3)_2Cl_2]$

Coordination Chemistry

Complex charge = sum of charges on the metal and the ligands

$[Fe(CN)_6]^{3-}$

Coordination Chemistry

Complex charge = sum of charges on the metal and the ligands

$[Fe(CN)_6]^{3-}$

Coordination Chemistry

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions

$[Co(NH_3)_6]Cl_2$

neutral compound

Coordination Chemistry

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions

$[Co(NH_3)_6]Cl_2$