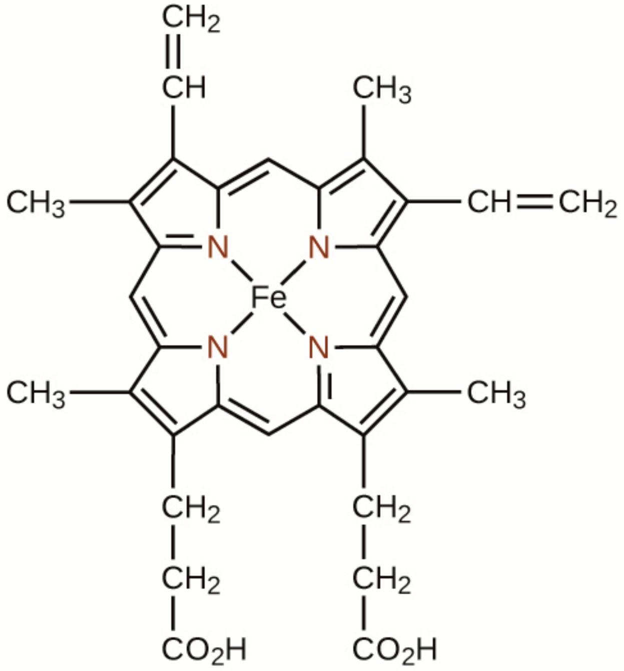
Coordination Chemistry

Metal ions that contain partially filled *d* subshell usually form colored complex ions; ions with empty *d* subshell (d^0) or with filled *d* subshells (d^{10}) usually form colorless complexes.

This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with M = $Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$.

Heme is composed of a ringlike organic compound known as a porphyrin, to which an iron atom is attached. It is the iron atom that reversibly binds oxygen as the blood travels between the lungs and the tissues.

Hemoglobin is a very large, complex protein, but the active site is actually a non-protein group called heme. The heme consists of a flat organic ring surrounding an iron atom. The organic part is a porphyrin ring based on porphin (a tetrapyrrole ring) which contains a large number of conjugated double bonds, which allows the molecule to absorb light in the visible part of the spectrum. The iron atom and the attached protein chain modify the wavelength of the absorption and gives hemoglobin its characteristic color. Oxygenated hemoglobin (found in blood from arteries) is bright red, but without oxygen present (as in blood from veins), hemoglobin turns a darker red. Venous blood is often depicted as blue in color in medical diagrams, and veins sometimes look blue when seen through the skin. The appearance of blood as dark blue is a wavelength phenomenon of light, having to do with the reflection of blue light away from the outside of venous tissue if the vein is ~0.02 inches deep or more.



Both O_2 and CO_2 bind *reversibly* to hemoglobin, but certain other molecules, like carbon monoxide, are small enough to fit into the protein crevice, but form such strong bonds with the iron that the process is *irreversible*. Thus high concentrations of CO rapidly use up the body's limited supply of hemoglobin molecules, and prevent them from binding to oxygen. This is why CO is poisonous - the affected person rapidly dies of asphyxiation because the blood is no longer able to carry enough oxygen to keep the tissues and brain supplied. Hemoglobin binding affinity for CO is 200 times greater than its affinity for oxygen, meaning that small amounts of CO dramatically reduces hemoglobin’s ability to transport oxygen. When hemoglobin combines with CO, it forms a very bright red compound called carboxyhemoglobin. When inspired air contains CO levels as low as 0.02%, headache and nausea occur. If the CO concentration is increased to 0.1%, unconsciousness will follow. In heavy smokers, up to 20% of the oxygen active sites can be blocked by CO. Another poisonous molecule that binds to hemoglobin is hydrogen cyanide (HCN). Once cyanide is taken into the blood stream the majority (92-99%) is found bound to hemoglobin in red blood cells. From there it is taken to the body's tissues where it binds to an enzyme called cytochrome oxidase and stops cells from being able to use oxygen.

Alfred Werner 1866-1919

Alfred Werner was a Swiss chemist who was a student at ETH Zurich and a professor at the University of Zurich. He won the Nobel Prize in Chemistry in 1913 for proposing the octahedral configuration of transition metal complexes. Werner developed the basis for modern coordination chemistry.

Alfred Werner

- Father of Inorganic Stereochemistry and Coordination Chemistry
- Introduced a Revolutionary Theory of "Metal-Centered Coordination Chemistry"
- Saved inorganic chemistry from fading into oblivion in 1893

others such as Blomstrand and Jorgensen thought metal compounds formed chains!

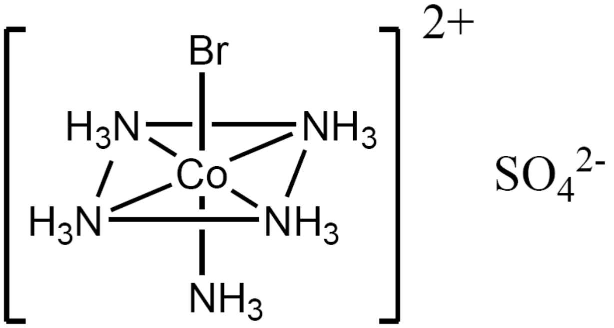
$M\text{-}X\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}X$, *etc*., Beyond this scientific inheritance, Alfred Werner’s personality also reflects the societal challenges which accompanied the transitional and revolutionary time. For instance, the picture of Alfred Werner and co-workers in 1911 strikingly highlights one of the societal challenges in modern science, namely that of enhancing the role of women in science (three women out of 17 people can be seen in this picture). Very unusual at the beginning of the 20th century, Werner’s research group was not only international, one of the reasons for the success of the best research groups of his time, but was also marked by its high proportion of women students. Alfred Werner supervised 230 doctoral students, 22 women among them.

Wernerian Chemistry (main discoveries)

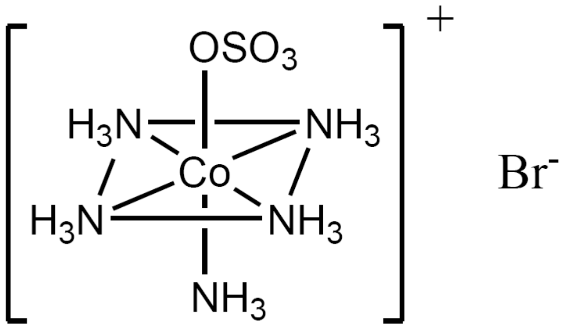
Structural Isomers

Ionization Isomers

These isomers result from the interchange of ions inside and outside the coordination sphere. For example, the red violet $[Co(NH_3)_5Br]SO_4$ and the red $[Co(NH_3)_5(SO_4)]Br$ are ionization isomers.

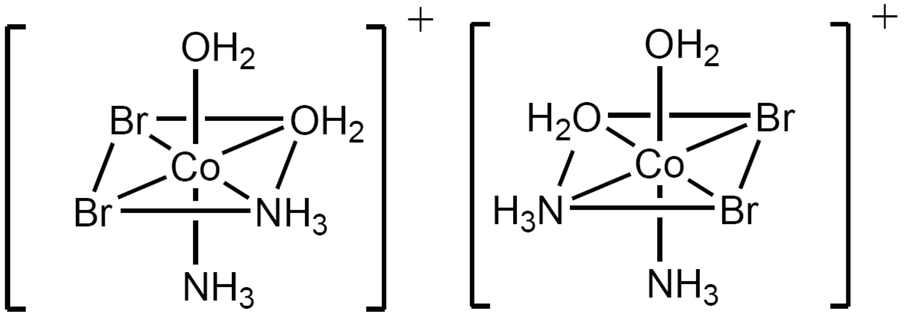


$[Co(NH_3)_5Br]SO_4$
Bromopentaamminecobalt(III) sulfate



$[Co(NH_3)_5SO_4]Br$
Sulfatopentaaminecobalt(III) bromide

Optical Isomers



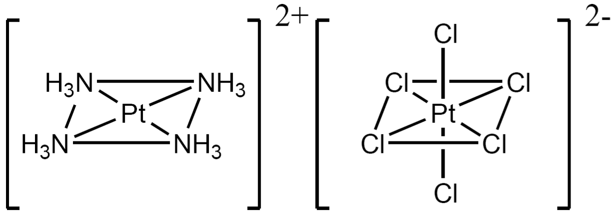
Optical isomers of *cis*-dibromo-*cis*-diammine-*cis*-diaquacobalt(III) ion

The *cis*-dibromo-*cis*-diammine-*cis*-diaquacobalt(III) geometric isomer exists in two forms that bear the same relationship to each other as left and right handed isomers. They are *non-superimposable* mirror images of each other and are called **optical isomers** or **enantiomers**.

Optical isomers have identical physical and chemical properties except that they interact with polarized light in different ways.

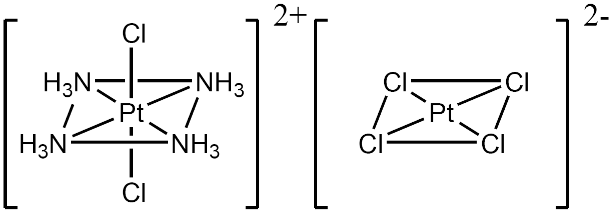
Coordination Isomers

Coordination isomerism can occur in compounds containing both complex cations and complex anions. Such isomers involve exchange of ligands between cation and anion, i.e., between coordination spheres



$[Pt(NH_3)_4][PtCl_6]$

tetraammineplatinum(II) hexachloroplatinate(IV)

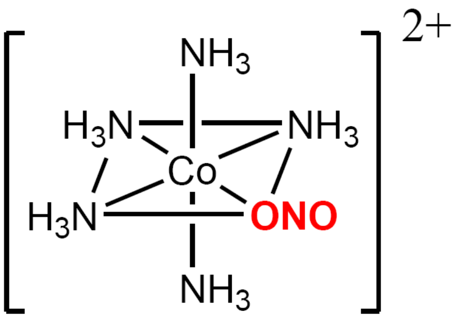


$[Pt(NH_3)_4Cl_2][PtCl_4]$

trans-dichlorotetraammine platinum(IV) tetrachloroplatinate(II)

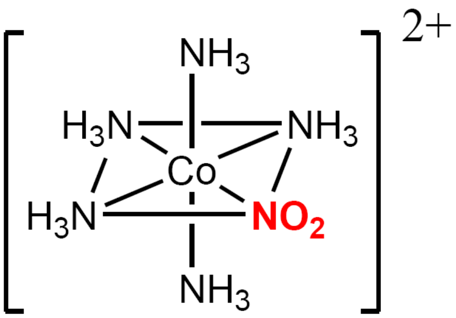
Linkage Isomers

Certain ligands can bind to a metal ion in more than one way. Examples of such ligands are cyano, $-CN^-$, and isocyano, $-NC^-$; nitro, $-NO_2^-$, and nitrite, $-ONO^-$. The donor atoms are on the left in these representations. Examples of linkage isomers are given below.



$2Cl^-$

$[Co(NH_3)_5ONO]Cl_2$
pentaamminenitritocobalt(III) chloride

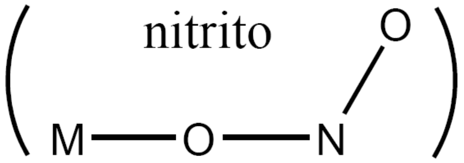


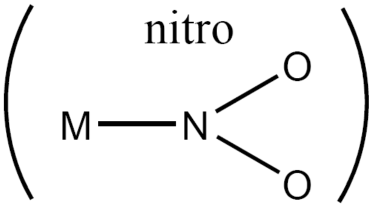
$2Cl^-$

$[Co(NH_3)_5NO_2]Cl_2$
pentaamminenitrocobalt(III) chloride

red, decomposes in acids

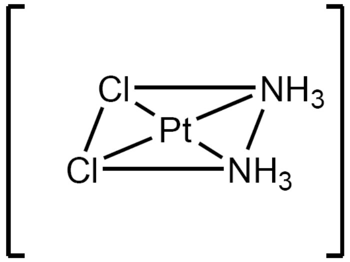
yellow, stable in acids



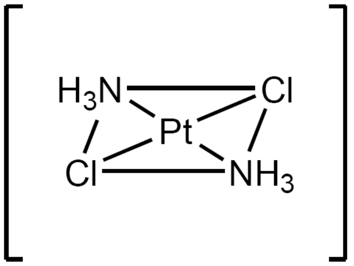


Geometrical Isomers

These are stereoisomers that are not optical isomers (see p. 806) but are geometrical isomers or positional isomers. *Cis-trans* isomerism is one kind of geometrical isomerism. *Cis* means "adjacent to" and *trans* means "on the opposite side of". *Cis*- and *trans*-diamminedichloroplatinum(II) are shown below.



cis
pale yellow

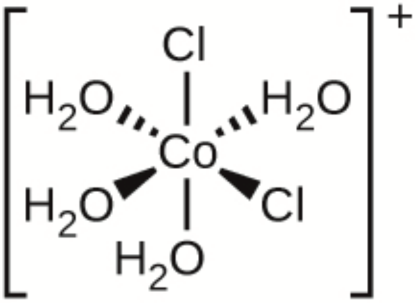


trans
dark yellow

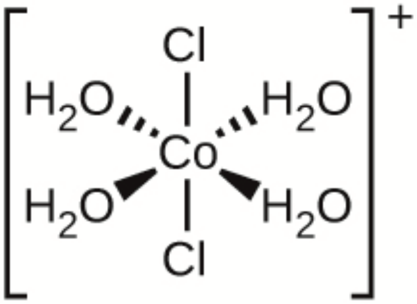
often different physical properties

In the *cis* complex, the chloro groups are closer to each other (on the same side of the square) then they are in the *trans* complex. the amine groups are also closer together in the *cis* complex.

Violet, *cis* form

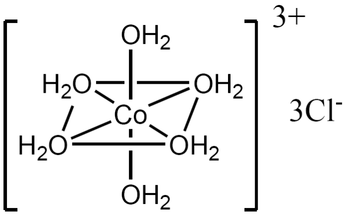


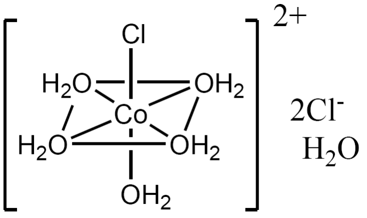
Green, *trans* form

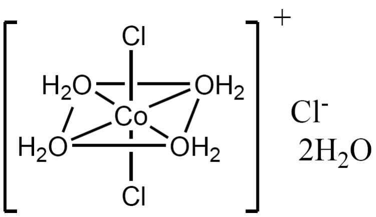


Other Isomers

Hydration isomerism and ionization isomerism are quite similar. In some crystalline complexes, water can occur in more than one way, <u>inside and outside the coordination sphere</u>. For example, solutions of the three hydrate isomers given below yield three, two, and one mole of silver chloride precipitate, respectively, per mole of complex when treated with excess silver nitrate.





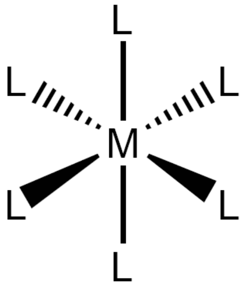


$[Cr(OH_2)_6]Cl_3$ hexaaquachromium(III) chloride	$[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$ chloropentaaqua chromium(III) chloride hydrate	$[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$ trans-dichlorotetraaqua chromium(III) chloride dihydrate
violet	blue-green	green

Definitions

Coordination Complex- The defining characteristic of a coordination compound or “complex” is that a metal ion is surrounded by atoms or molecules (either neutral or ionic) in a particular geometry. Furthermore, these ions and molecules are capable of existing independently of each other.

$M^{2+} + 6\,L \rightarrow$



This cation can exist in solution as a solvated cation

Outline of Coordination Chemistry

1. Alfred Werner
   father of coordination chemistry
2. Metal is at the center of a group of ligands
   → called a complex
3. Structural Isomers
   (realized by Werner)

   a. Ionization Isomers
   b. Optical Isomers
   c. Coordination Isomers
   d. Linkage Isomers
   e. Geometrical Isomers
   f. Hydrate Isomers
4. Geometries
   coordination numbers
   2, 3, 4, 5, 6, > 6
5. Ligands
   a. donor type/names
   b. number of donor sites
   c. chelate effect
6. Nomenclature
   a. abbreviations
   b. rules
7. Reactivity Patterns
   a. octahedral complexes
   b. square planar complexes
   c. associative (A) versus dissociative (D) substitution
   d. solution stabilities
      thermodynamic versus kinetic stability

8. Electron Transfer Reactions
    “inner-sphere” versus “outer-sphere” mechanisms
9. Stereochemical non-rigidity
    “fluxional” behavior
    interconversion of geometries

Ligand

Any molecule or ion that has at least one electron pair that can be donated to a metal atom or ion.

Lewis Bases Ligands
(in organic chemistry → nucleophiles)

Lewis Acids Metal Ions
(in organic chemistry → electrophiles)

Classifications of Ligands

1. type of bonding they engage in
    π-donation, σ-donation, π-accepting

2. number of electrons that they donate

3. The “denticity” of a ligand refers to how many total donor sites for binding

Discussion of Ligands

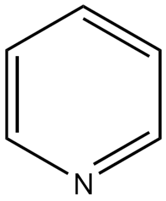
1. Classical σ-donors
   these form bonds by donating an e^- to a σ-bond
   e.g $:NH_3$ $:PR_3$ $:R^-$ (alkyl)

2. **Non-classical** π-donors and π-acceptors
   π-donors $:X^-$ halides can form π-bonds
   π-acceptor C≡O
   carbon monoxide can accept electrons into any empty π* symmetry molecular orbital

Types of Ligands
monodentate
bidentate
tridentate
tetradentate

literally “one-toothed”, “two-toothed”, etc.

Monodentate

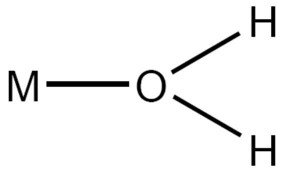
NH_3, RNH_2,  amines

H_2O, OH^-, ROH, R_2O, R_2CO, R_2SO

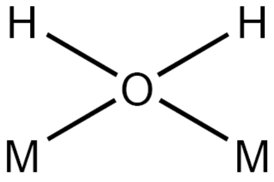
R_3PO, PR_3, X^-

(Note, some can bridge as well)

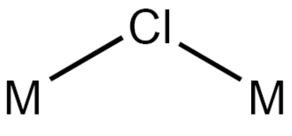
e.g.



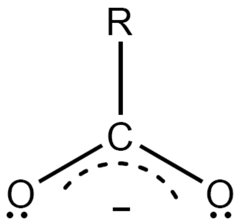
or



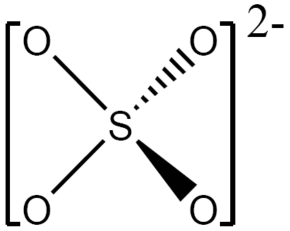
or



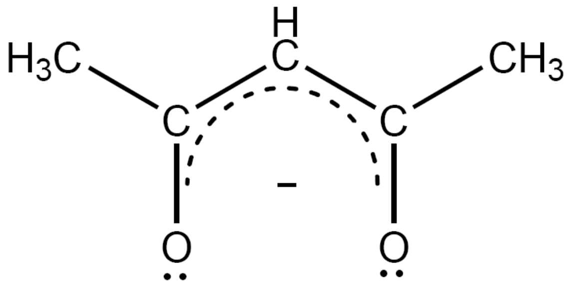
Bidentate



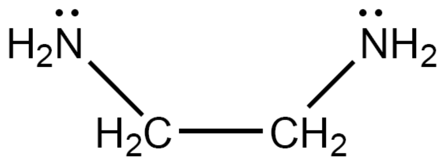
carboxylate



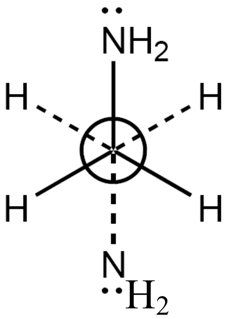
sulfate



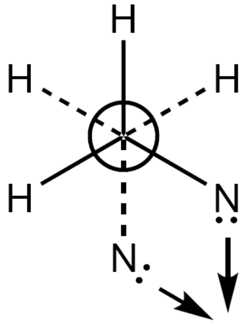
acetylacetonate (general class is β-diketones)



ethylenediamine (en)

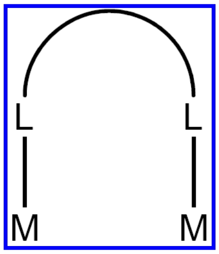


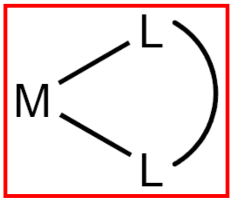
anti-conformer would give a bridge between two metals



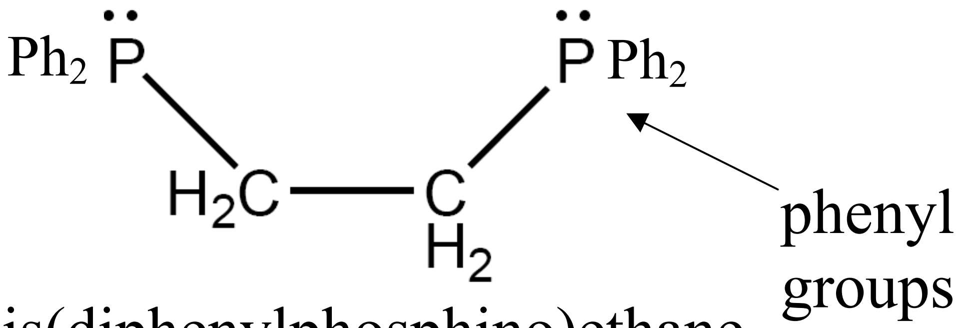
gauche conformer would chelate

bridging versus chelating for a bidentate L-L ligand





2



Bis(diphenylphosphino)ethane

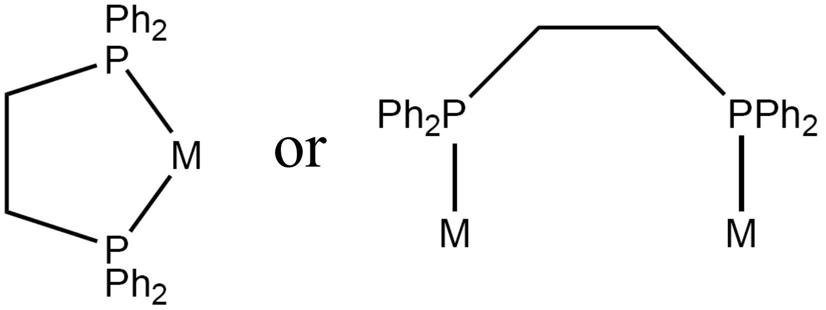
two

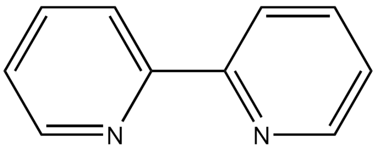
PPh_2

$-CH_2CH_2-$

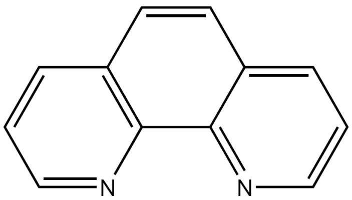
also called “dppe” for short

dppe can chelate and bridge

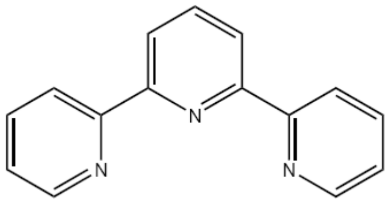




2,2’-bipyridine
(or bpy)



1,10-phenanthroline
(phen)

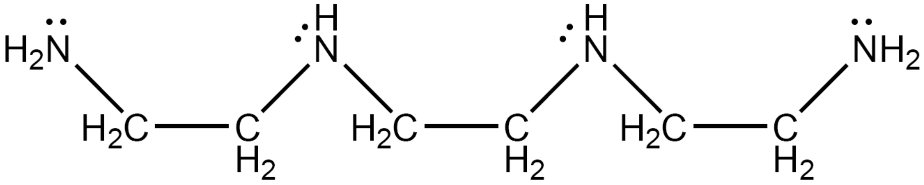


terpyridine
(terpy)

Bidentate **Tridentate**

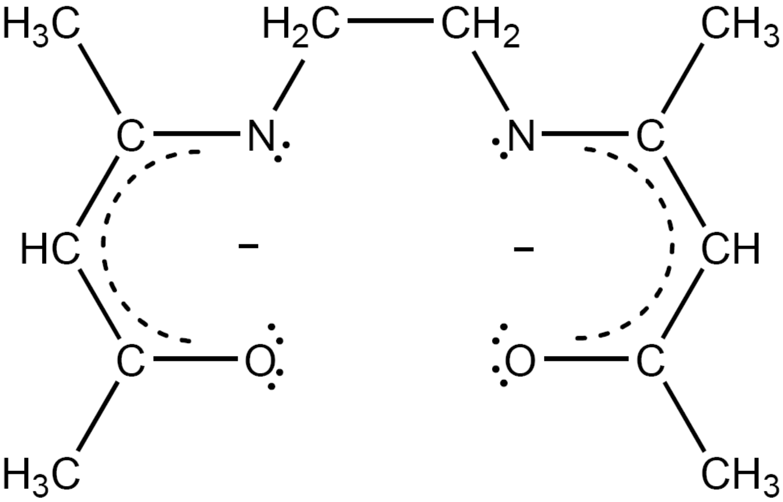
(forms meridonal isomers)

Tetradentate



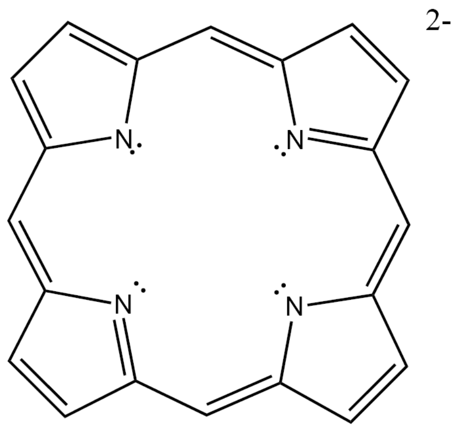
Triethylenetetramine (trien)

acac + en → acacen (condensation product)

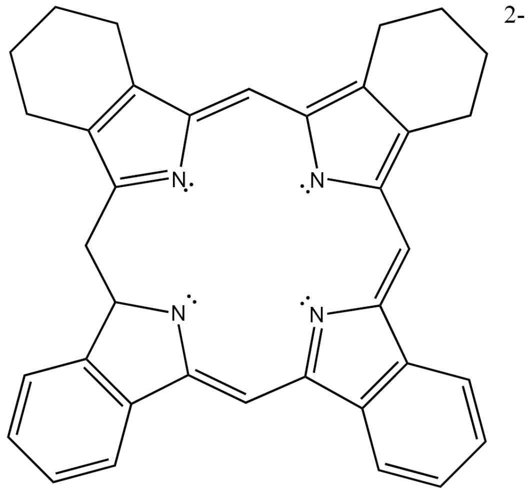


known as a Schiff Base

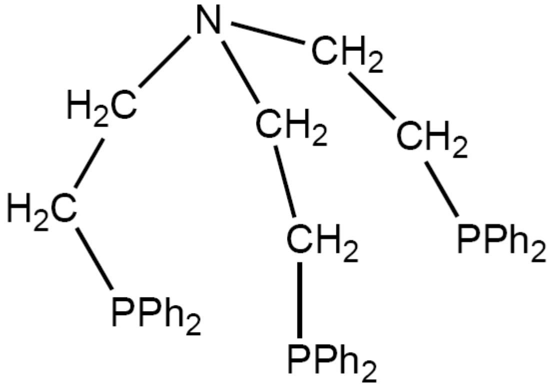
Biologically Relevant Ligands that chelate metals in the body



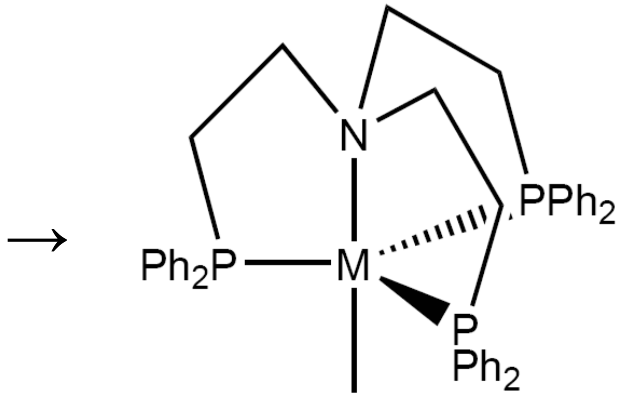
porphyrin
ligand



phthalocyanine
ligand

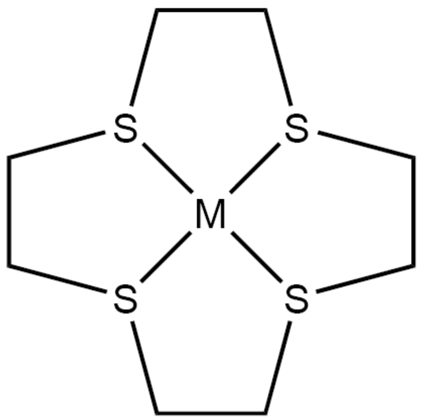


“tripod” ligands

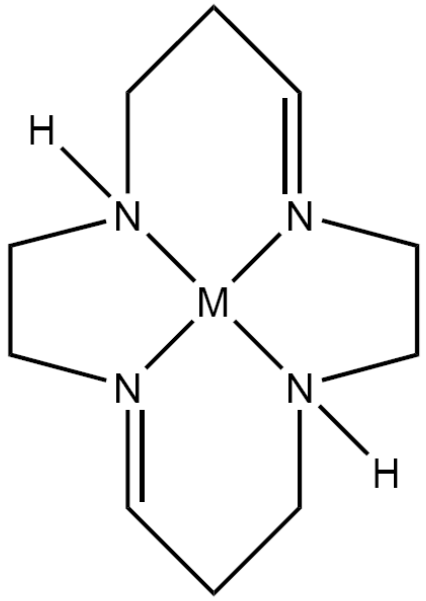


stabilizes
trigonal bipyramidal
geometry

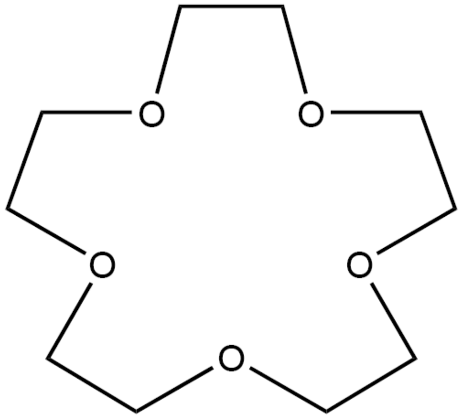
other polydentate ligands



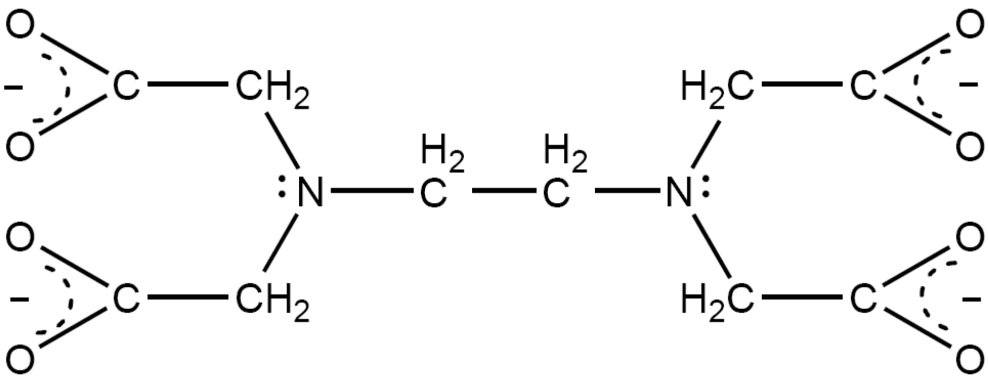
cyclic thioether



cyclic polyamine



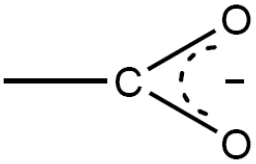
cyclic polyether
(crown ether)

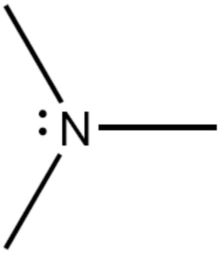


[EDTA]$^{4-}$

<u>e</u>thylene<u>d</u>iamine<u>t</u>etra<u>a</u>cetic acid

has both bidentate and monodentate binding sites





It is a <u>Hexadentate Ligand</u>

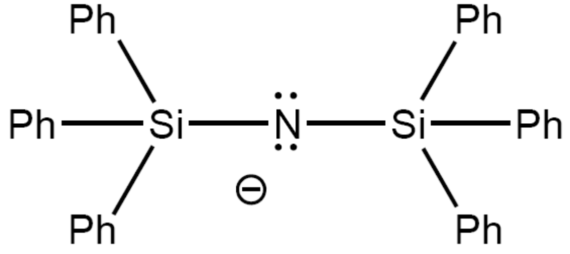
Coordination Numbers and Geometries

Coordination Number Two

rare - usually found with Cu^+, Ag^+, Au^+, Hg^{2+}

linear $[Cl\text{-}Au\text{-}Cl]^-$

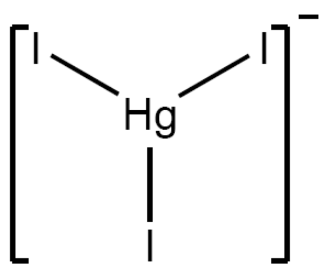
or when one uses very bulky ligands

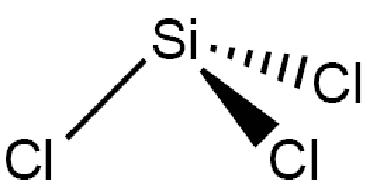


→ forms two-coordinate Fe(II) complex $Fe[N(SiPh_3)_2]_2$

Coordination Number Three

trigonal planar and
trigonal pyramidal

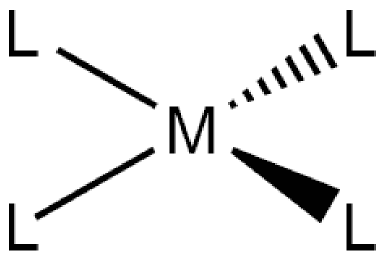




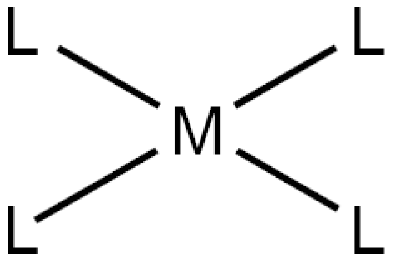
Coordination Number Four

tetrahedral	and	square planar
$[CoBr_4]^{2-}$		$[PtCl_4]^{2-}$
ReO_4^-		$RhCl(L)_3$
$Ni(CO)_4$		$[Ni(CN)_4]^{2-}$
most common		d^8 complexes primarily (also some d^9)

Why? d^8 complexes would prefer square planar geometry



vs



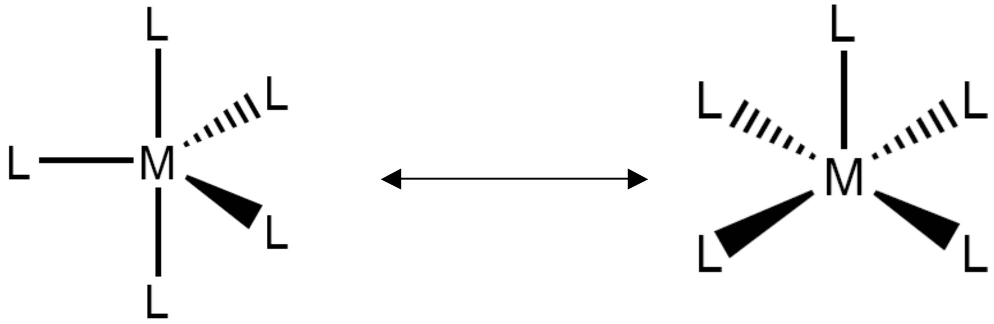
What are the orbitals involved in M-L bonding?

→ in the case of the tetrahedral geometry, it is a linear combinations of d orbitals.

→ in the case of square planar, the only d orbital that needs to be used is the $d_{x^2-y^2}$ which points directly at the ligands. The remaining electron pairs are in orbitals (non-bonding) that don't experience any repulsion from the ligand lone pair.

Coordination Number Five

trigonal bipyramidal **square pyramidal**



can be interconverted
(often low energy difference)