



Courtesy, Fräulein Charlotte Werner

ALFRED WERNER, *ca.* 1893.

Alfred Werner 1866-1919

- Father of Inorganic Stereochemistry and Coordination Chemistry
- Nobel Prize in 1913
- 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!





Courtesy, Mr. Victor R. King; Reproduction by Photographic Service, Laidlaw Laboratories Division, American Cyanamid Co., Pearl River, N. Y.

ALFRED WERNER, WITH ASSISTANTS AND DOCTORAL CANDIDATES, ca. 1911.

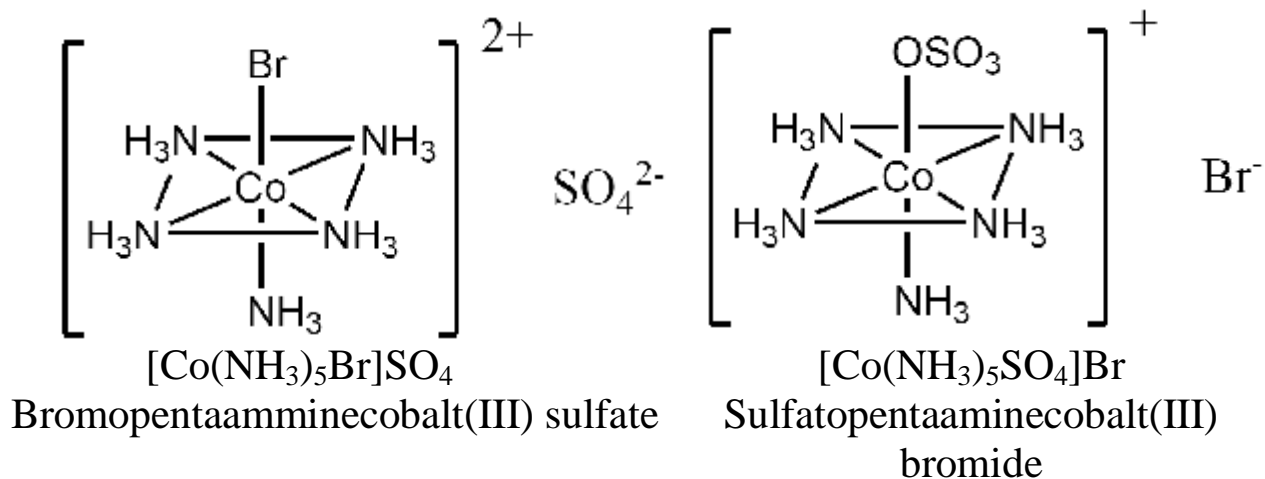
1. Victor L. King *see Paper 5*; 2. Alexander Fraenkel; 3. Siegfried Prager; 4. Gustav Töcpke;
5. Alfred Werner; 6. Sophie Matissen *see Paper 6*; 7. Yoji Shibata *see Paper 5*; 8. Hugh Watts;
9. Thomas P. McCutcheon.

Wernerian Chemistry (main discoveries)

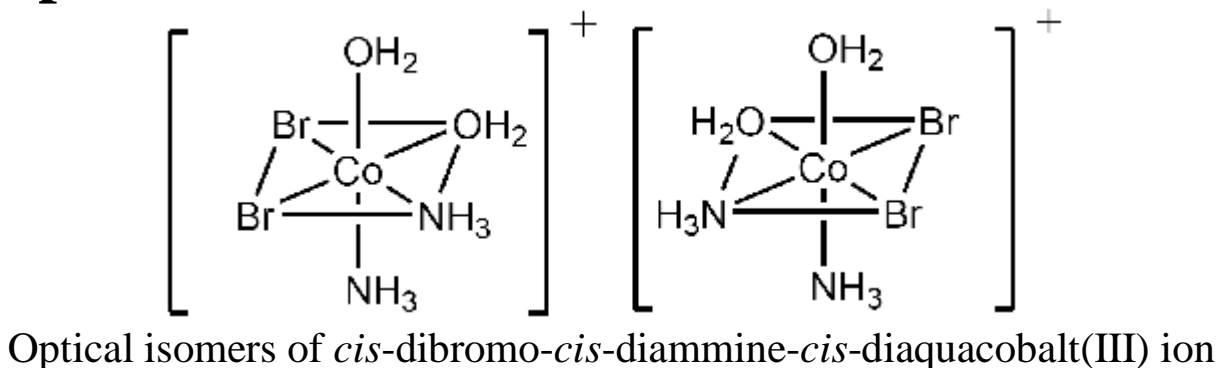
Structural Isomers

Ionization Isomers

These isomers result from the interchange of ions inside and outside the coordination sphere. For example, the red violet $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and the red $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ are ionization isomers.



Optical Isomers

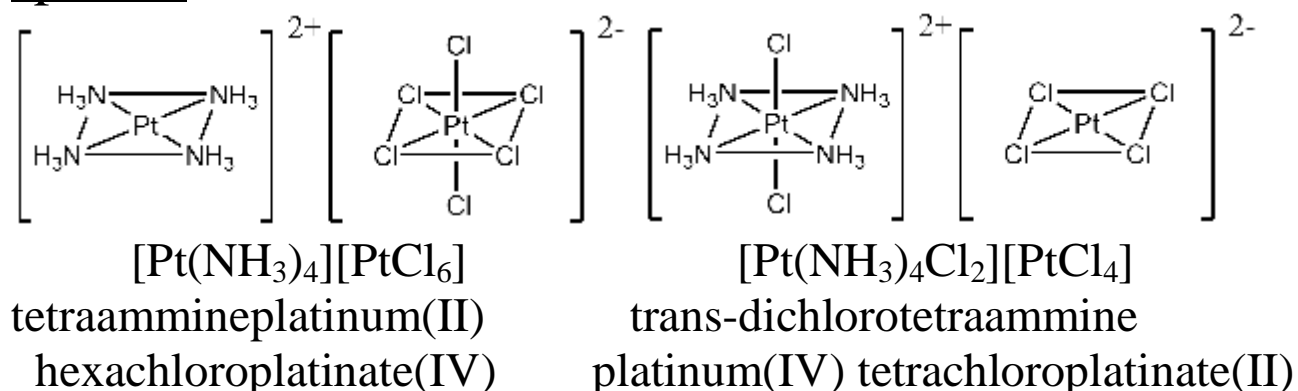


The *cis*-dibromo-*cis*-diammine-*cis*-diaquacobalt(III) geometric isomer exists in two forms that bear the same relationship to each other as left and right handed isomers. They are *non-superimposable* mirror images of each other and are called **optical isomers** or **enantiomers**.

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

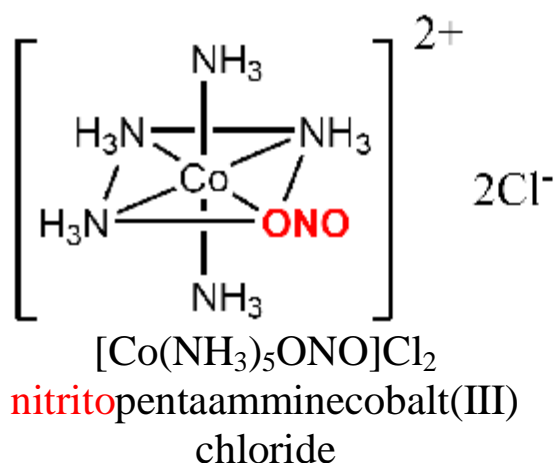
Coordination Isomers

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

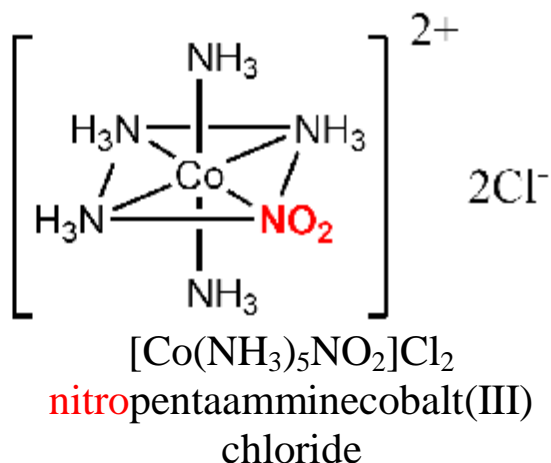
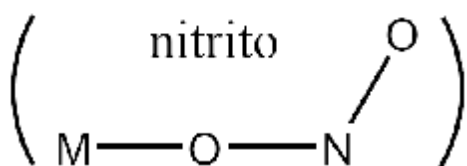


Linkage Isomers

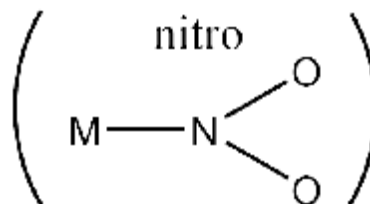
Certain ligands can bind to a metal ion in more than one way. Examples of such ligands are cyano, -CN^- , and isocyano, -NC^- ; nitro, -NO_2^- , and nitrite, -ONO^- . The donor atoms are on the left in these representations. Examples of linkage isomers are given below.



red, decomposes in acids

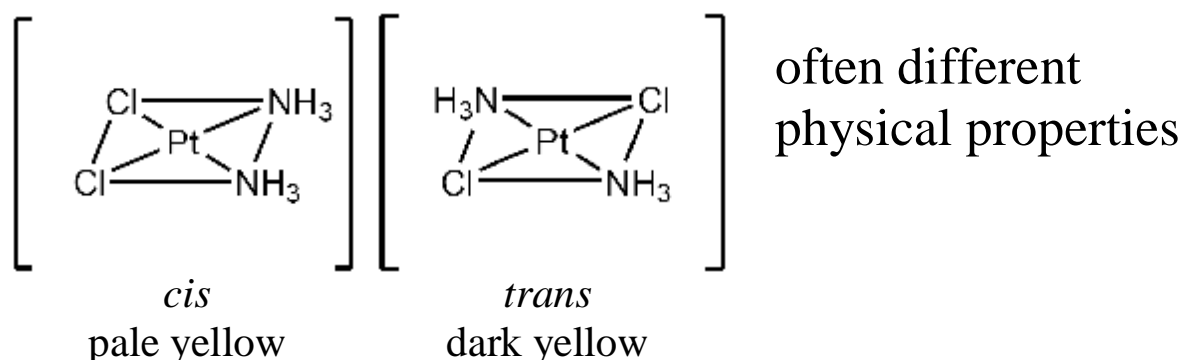


yellow, stable in acids



Geometrical Isomers

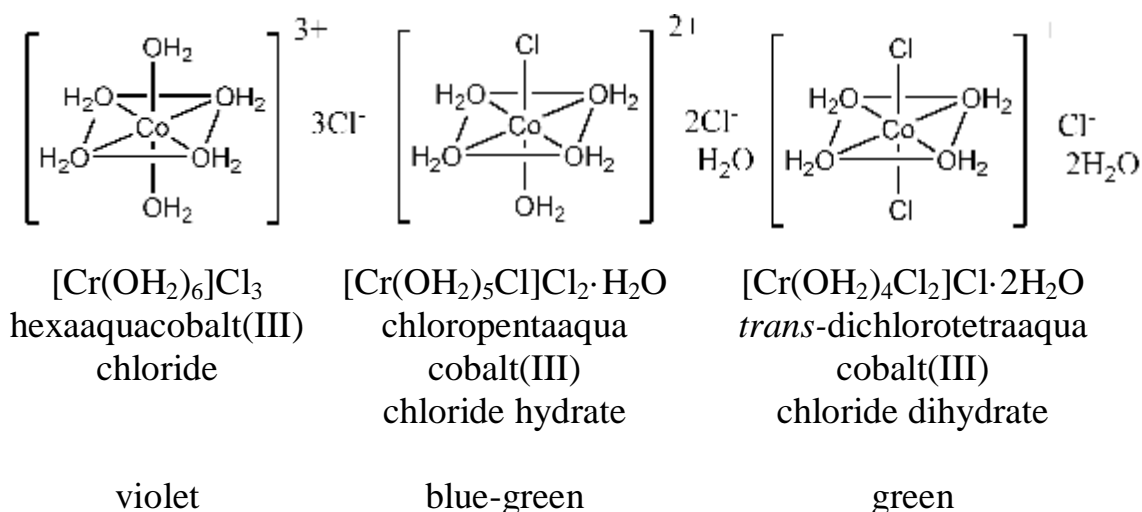
These are stereoisomers that are not optical isomers (see p. 806) but are geometrical isomers or positions isomers. *Cis-trans* isomerism is one kind of geometrical isomerism. *Cis* means “adjacent to” and *trans* means “on the opposite side of”. *Cis-* and *trans*-dichlorodiammineplatinum(II) are shown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



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

Other Isomers

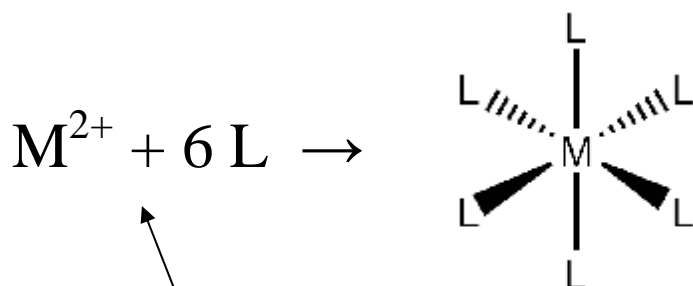
Hydration isomerism and ionization isomerism are quite similar. In some crystalline complexes, water can occur in more than one way, inside and outside the coordination sphere. For example, solutions of the three hydrate isomers given below yield three, two, and one mole of silver chloride precipitate,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



Definitions

Coordination Complex- The defining characteristic of a coordination compounds 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.



This cation can exist in solution

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 chem. \rightarrow nucleophiles)

Lewis Acids Metal Ions
(in organic chemistry \rightarrow 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. number of bonds they make to a metal ion through different atoms

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 $C\equiv O$

carbon monoxide can accept electrons into any empty π^* symmetry molecular orbital

Types of Ligands

monodentate

bidentate

tridentate

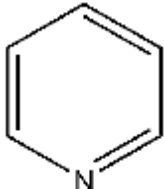
tetradentate

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

literally

“one-toothed”, “two-toothed”, etc.

Monodentate

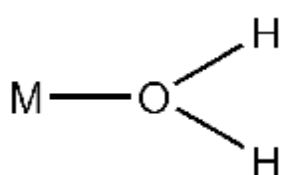
NH_3 , RNH_2 ,  amines

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

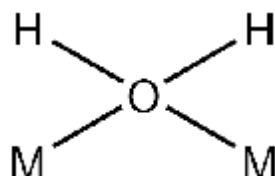
R_3PO , PR_3 , X^-

(Note, some can bridge as well)

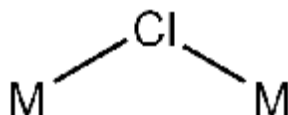
e.g.



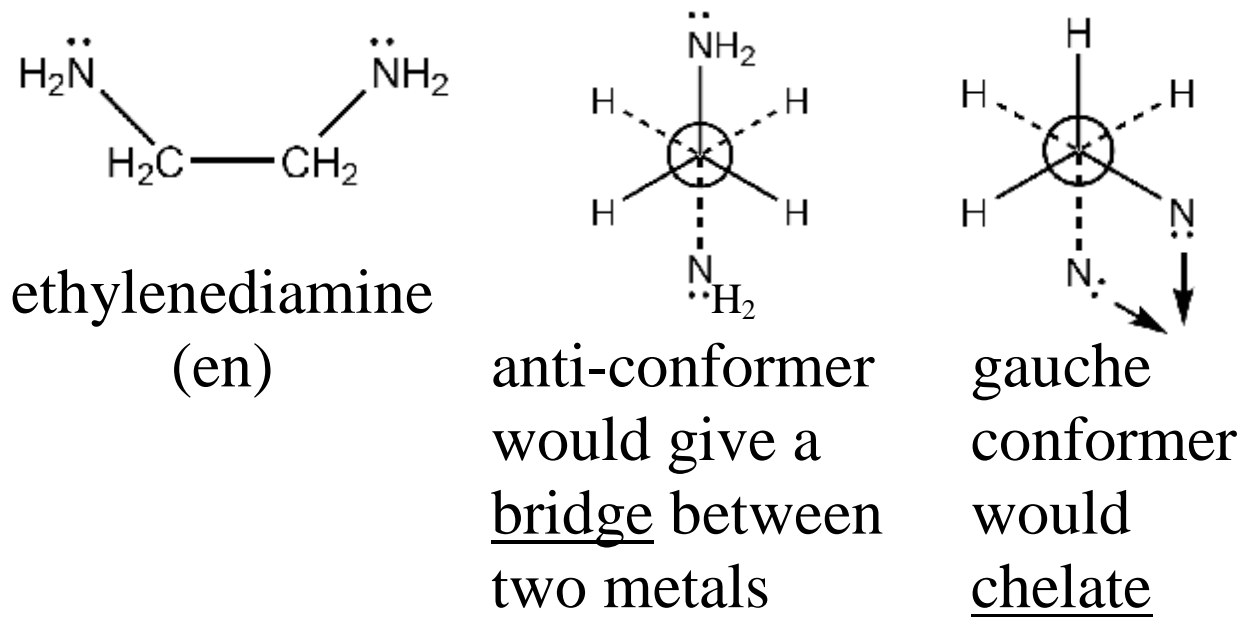
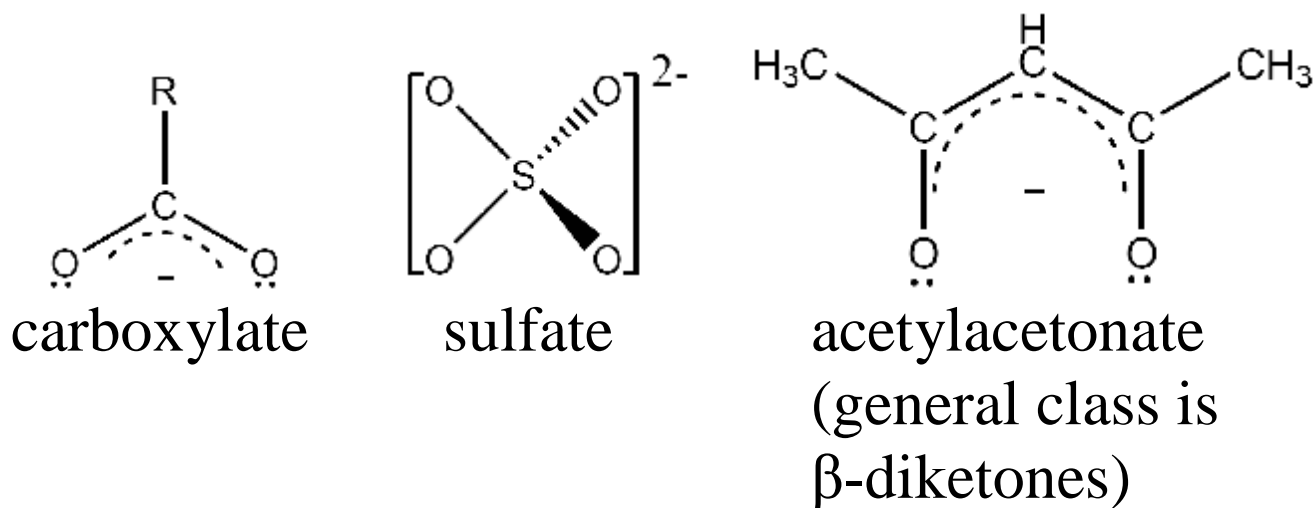
or



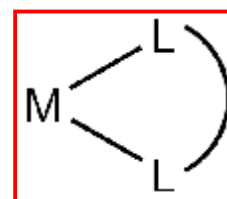
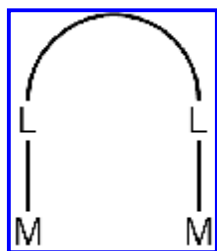
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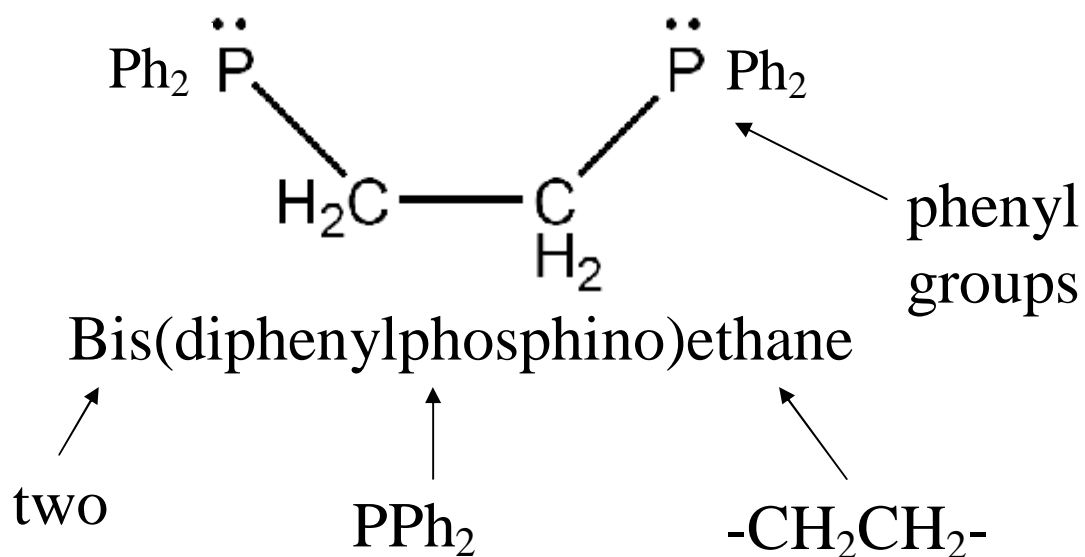


Bidentate



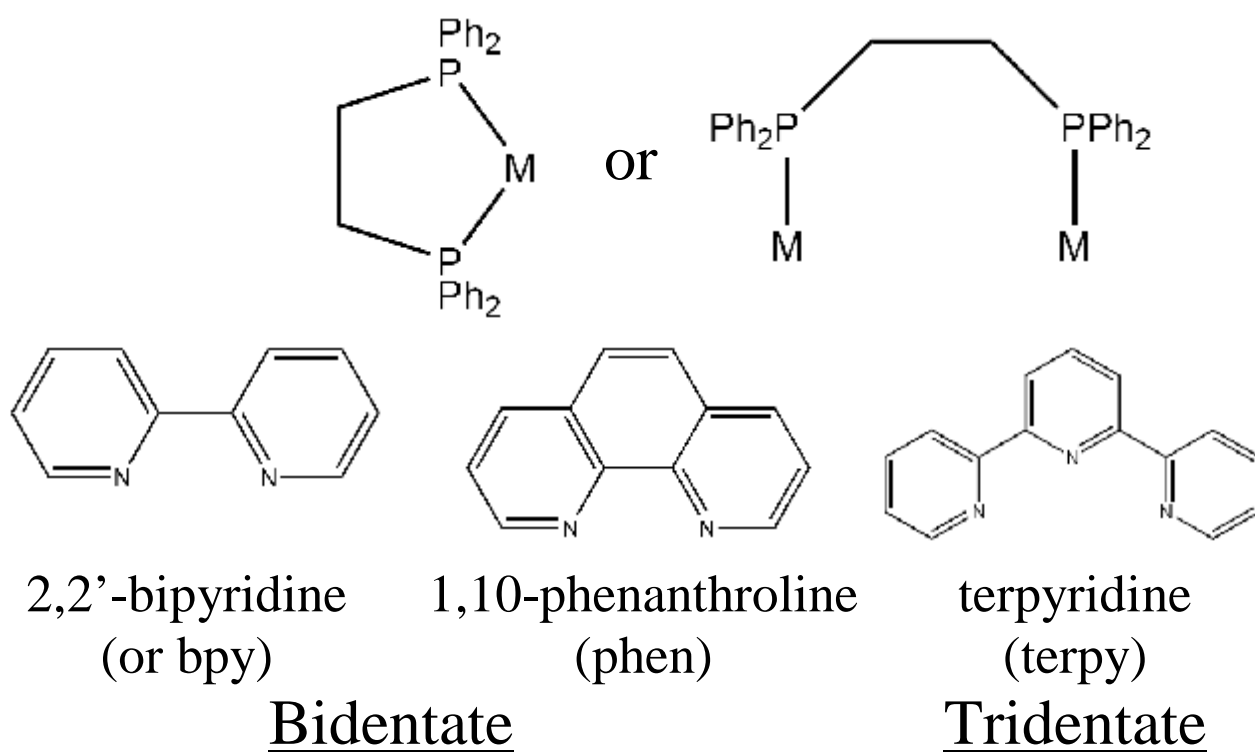
bridging versus
chelating for a
bidentate
L-L ligand





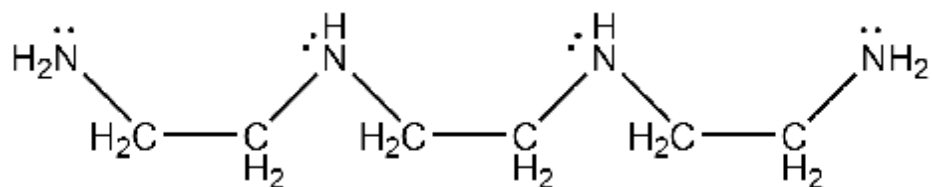
also called “dppe” for short

dppe can chelate and bridge



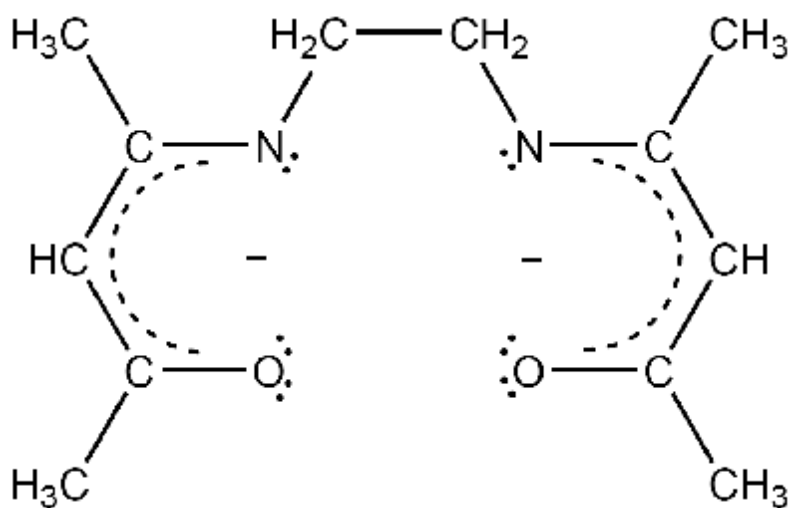
(forms meridonal isomers)

Tetradentate



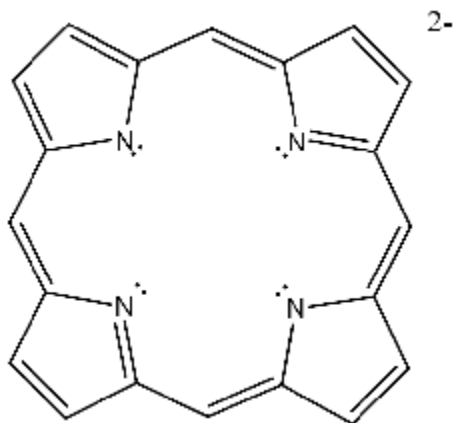
Triethylenetetramine (trien)

acac + en \rightarrow acacen (condensation product)

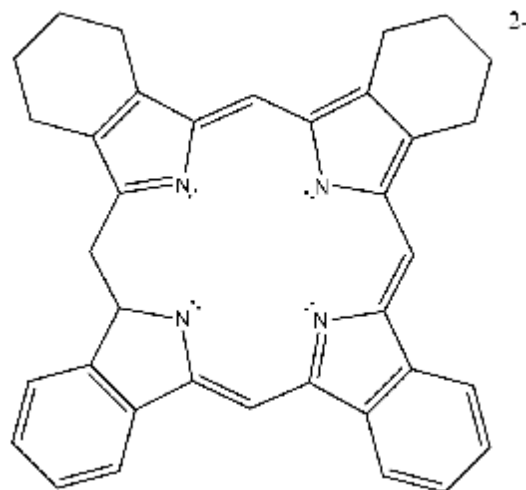


known as a Schiff Base

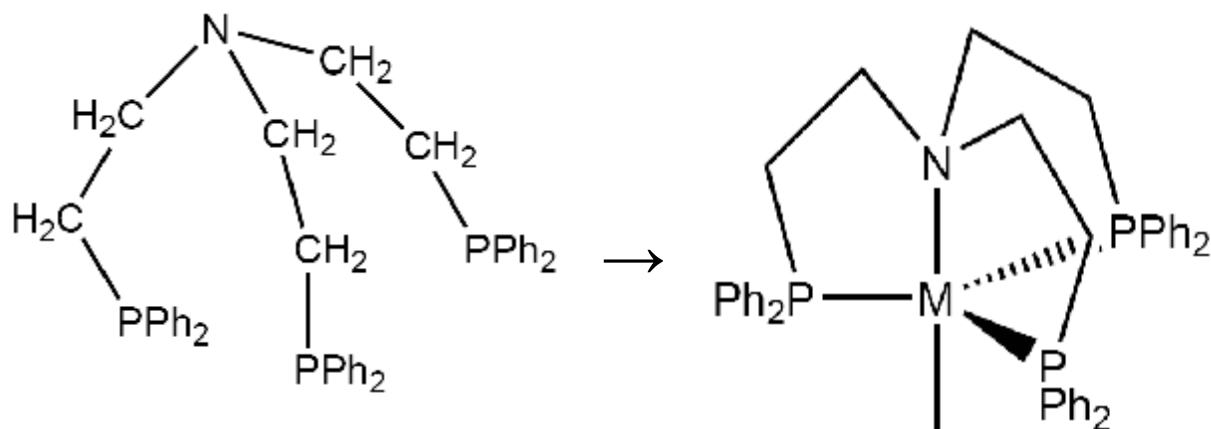
Biologically Relevant Ligands that chelate metals in the body



porphyrin
ligand



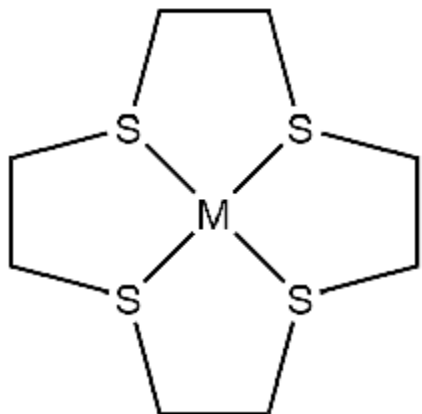
phthalocyanine
ligand



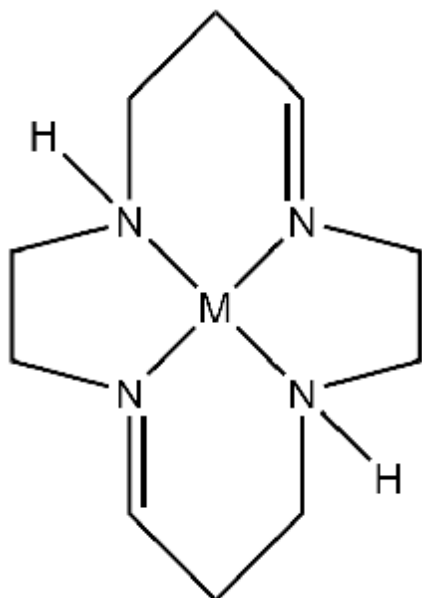
“tripod” ligands

stabilizes
trigonal bipyramidal
geometry

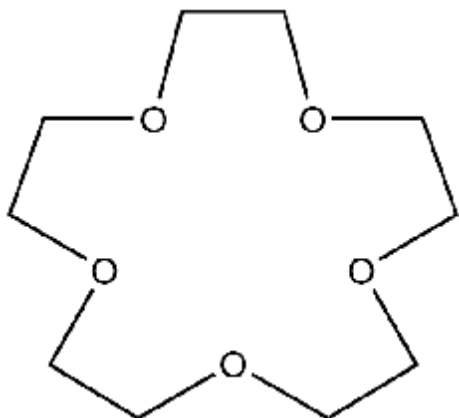
other polydentate ligands



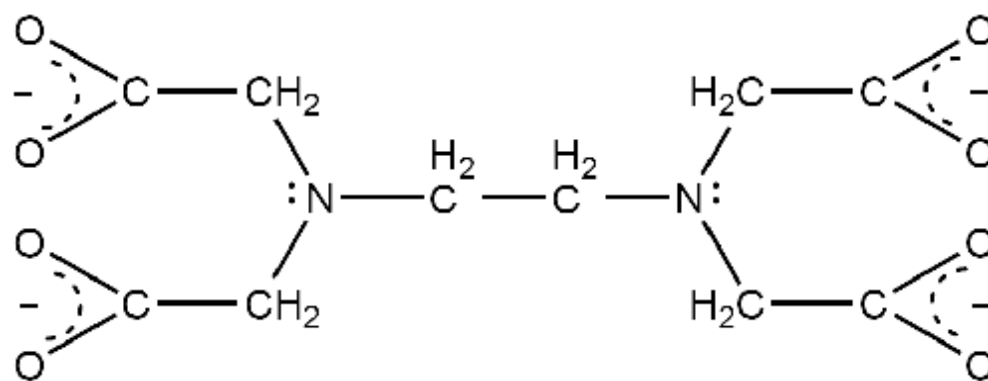
cyclic
thioether



cyclic
polyamine

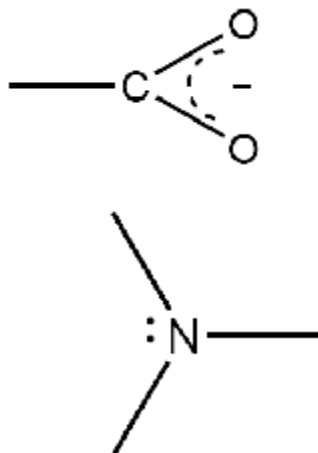


cyclic
polyether
(crown ether)



ethylenediaminetetraacetic acid

has both bidentate and
monodentate binding
sites



It is a Hexadentate Ligand

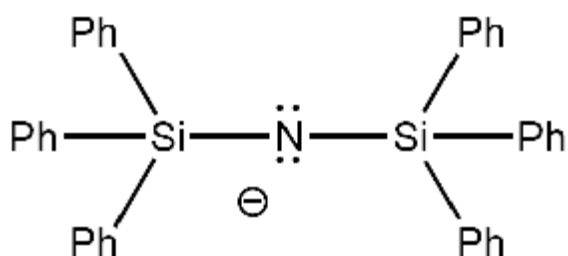
Coordination Numbers and Geometries

Coordination Number Two

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

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

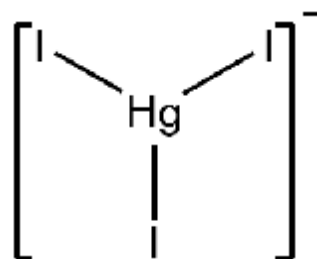
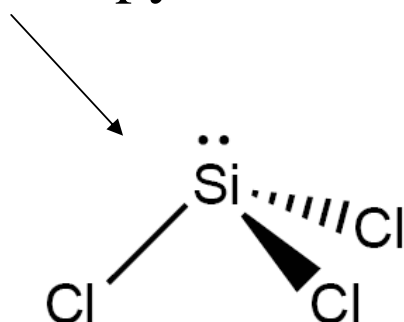
or when one uses very bulky ligands



→ forms two-coordinate
Fe(II) complex
 $\text{Fe}[\text{N}(\text{SiPh}_3)_2]_2$

Coordination Number Three

trigonal planar and
trigonal pyramidal



Coordination Number Four

tetrahedral

and

square planar



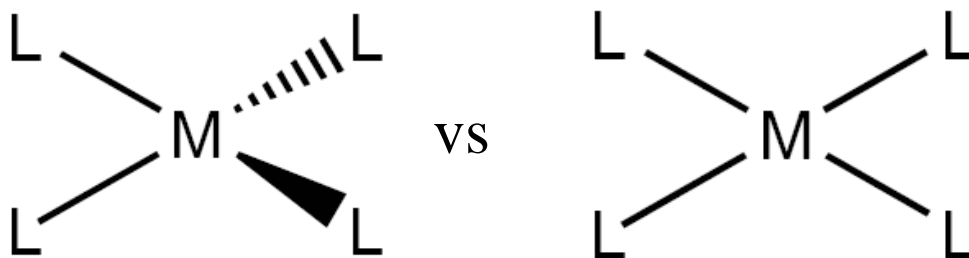
most common

d⁸ complexes

primarily

(also some d⁹)

Why? \leftarrow d⁸ complexes would prefer square planar geometry



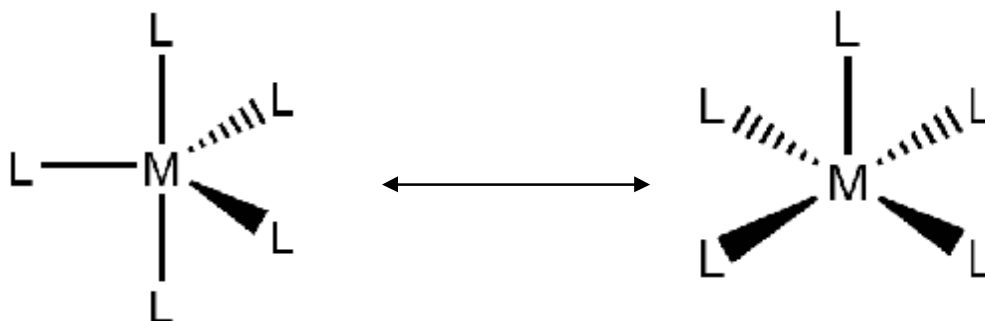
What are the orbitals involved in M-L bonding?

- in the case of the tetrahedral geometry, it is 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)