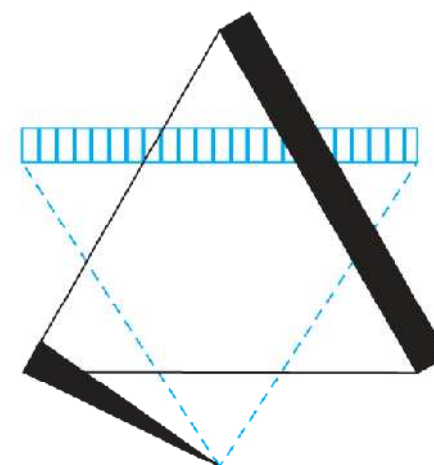
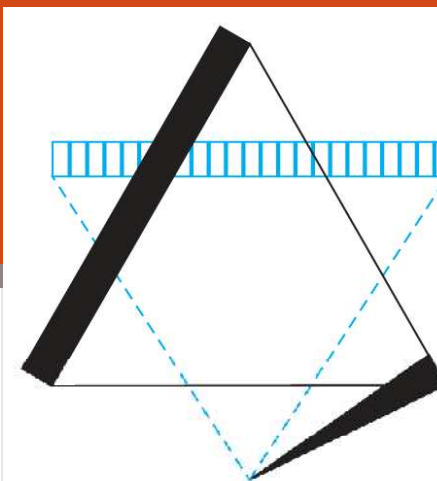


# Coordination Chemistry I: Structures and Isomers

Based on “Inorganic Chemistry”, Miessler and Tarr,  
4<sup>th</sup> edition, 2011, Pearson Prentice Hall



# Coordination compounds

- Term usually used in inorganic chemistry to include compounds composed of a metal atom or ion and one or more ligands
- Ligands are atoms, ions or molecules that formally donate electrons to the metal
- This definition includes compounds with metal-carbon bonds, or organometallic compounds

## Coordination compounds (cont.)

- The term coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another
- The donors are usually the ligands, and the acceptors are the metals
- Coordination compounds are also acid-base adducts, frequently called complexes or, if charged, complex ions

# History

- Prussian blue, aureolin and alizarin were pigments / dyes known since antiquity
- Advances in analytical methodology allowed for the determination of formulas, and theories of structure and bonding became possible
- But organic chemistry bonding theory was not adequate to account for the experimentally determined formulas of some coordination compounds
  - Hexaamminecobalt(III) chloride – only three other atoms were “allowed” to attach to cobalt

**TABLE 9.1** Comparison of Blomstrand's Chain Theory and Werner's Coordination Theory

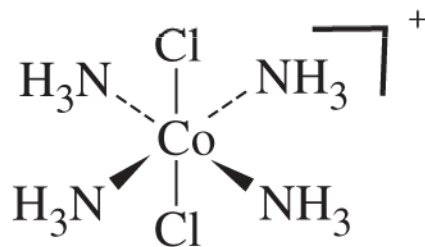
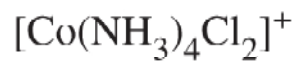
Werner Formula (Modern Form)	Number of Ions Predicted	Blomstrand Chain Formula	Number of Ions Predicted
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	4	$\begin{array}{c} \text{NH}_3-\textit{Cl} \\ \diagdown \quad \diagup \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\textit{Cl} \\ \diagup \quad \diagdown \\ \text{NH}_3-\textit{Cl} \end{array}$	4
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	3	$\begin{array}{c} \text{NH}_3-\textit{Cl} \\ \diagdown \quad \diagup \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\textit{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array}$	3
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	2	$\begin{array}{c} \text{Cl} \\ \diagdown \quad \diagup \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\textit{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array}$	2
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	0	$\begin{array}{c} \text{Cl} \\ \diagdown \quad \diagup \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\textit{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array}$	2

NOTE: The italicized chlorides dissociate in solution, according to the two theories.

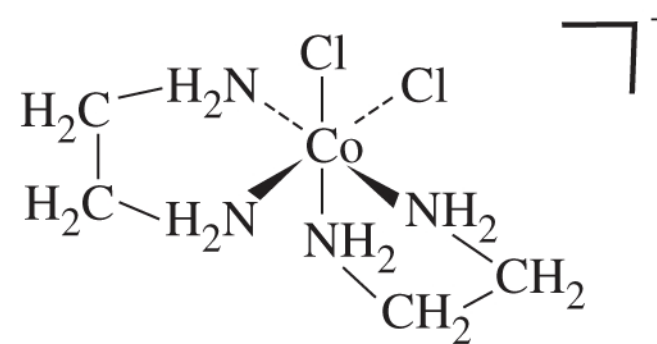
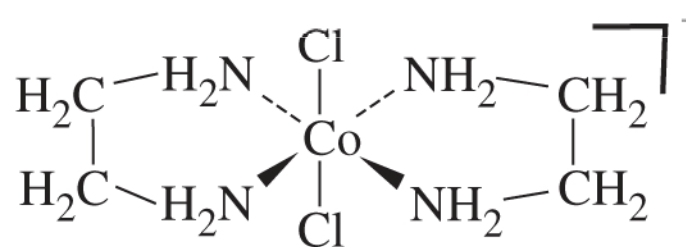
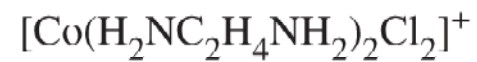
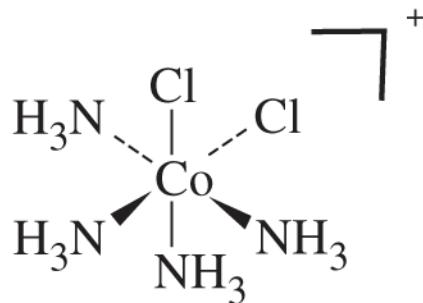
<sup>3</sup> A. Werner, *Z. Anorg. Chem.*, **1893**, 3, 267; *Berichte*, **1907**, 40, 4817; **1911**, 44, 1887; **1914**, 47, 3087; A. Werner and A. Miolati, *Z. Phys. Chem.*, **1893**, 12, 35; **1894**, 14, 506; all translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 1*, New York, 1968.

# Jorgensen vs Werner

*trans*  
green

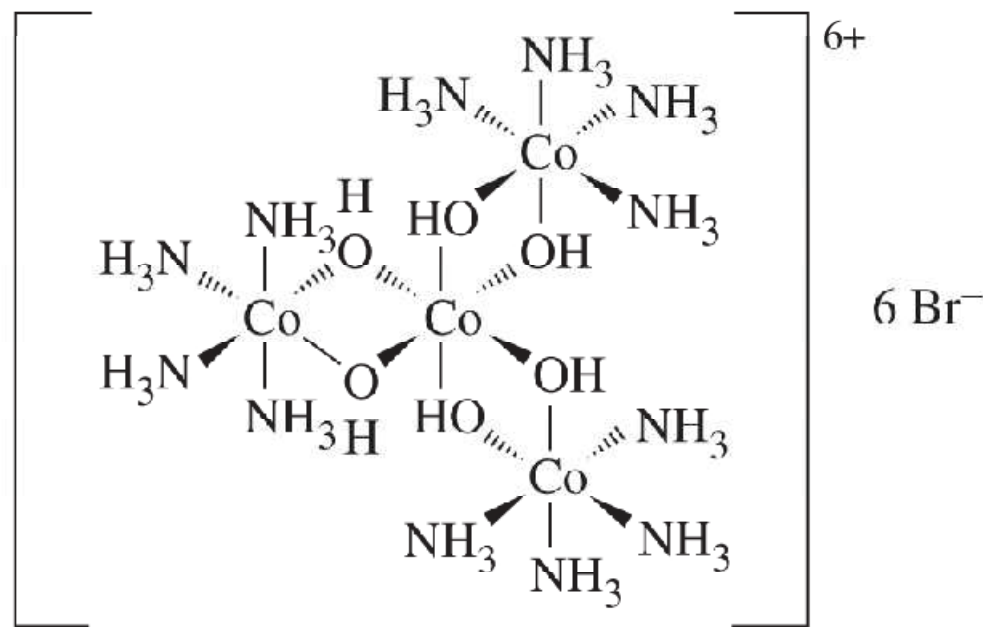


*cis*  
violet



# Werner vs other chemists

- This complex was originally prepared by Jorgensen and Werner was able to resolve it into its two optically active forms
- This complex does not has carbon atoms

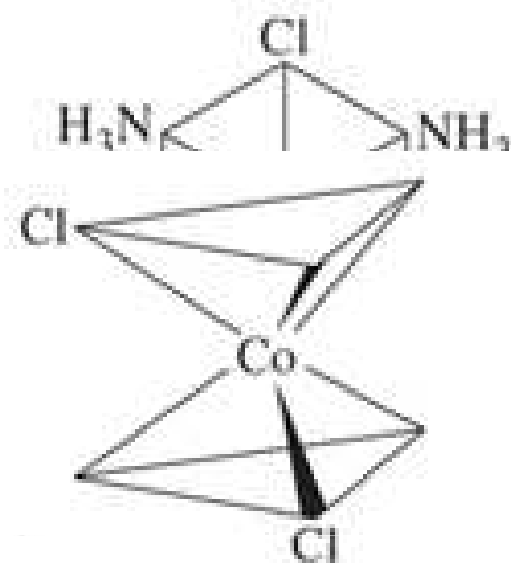
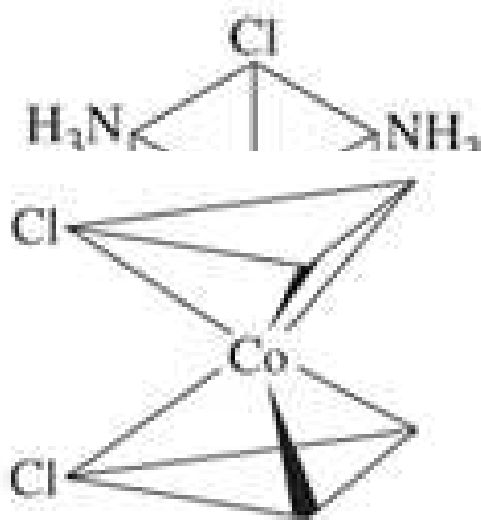
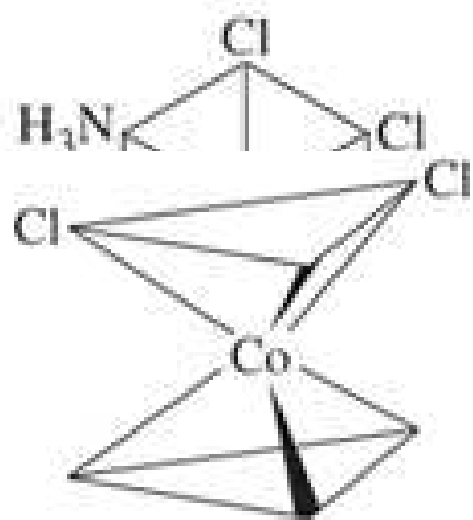


# Primary vs secondary bonding

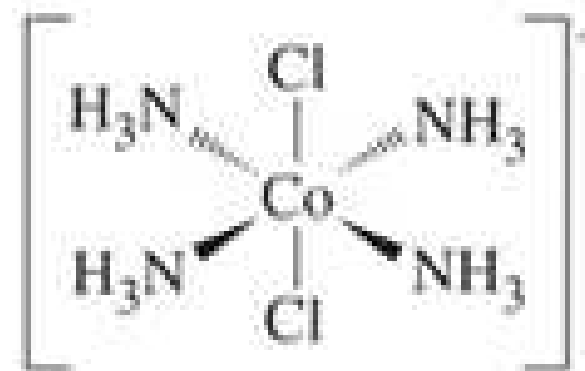
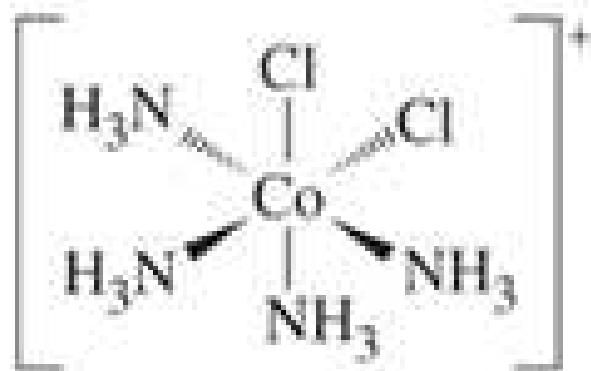
- Primary bonding required counterbalance ions
- Secondary bonding were that of the ligands – now known as coordination sphere
- Current practice considers the coordination sphere more important so the words primary and secondary exchanged the significance



*cis* - and *trans* - Tetramminedichlorocobalt (III),  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$



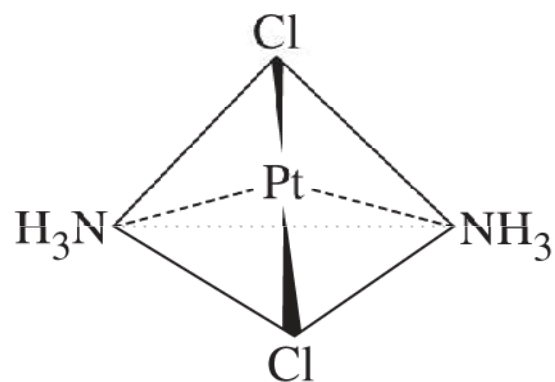
Trigonal prismatic (three isomers)



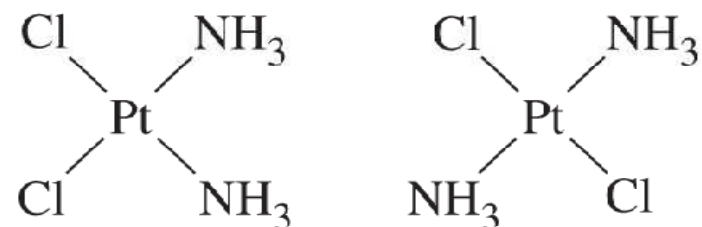
Octahedral (two isomers)

# Tetrahedral vs square planar

*cis*- and *trans*- Diamminedichloroplatinum(II),  $[\text{PtCl}_2(\text{NH}_3)_2]$



Tetrahedral (one isomer)



Square planar (two isomers)

# Some facts

- Werner's theory required more bonds than that commonly accepted
- 18-electron-rule is useful to account the number of valence electrons around the central atom
- Pauling used his **valence bond** approach to explain differences in magnetic behavior by use of either 4s or 3d orbitals
- Griffith and Orgel developed and popularized the use of **ligand field theory** derived from the **crystal field theory** of Bethe and Van Vleck

# Nomenclature

- Organic and some inorganic ligands are frequently named using older trivial names rather than IUPAC names, although IUPAC names are preferred
- Ligands can be **monodentated** (one point of attachment), **ambidentated** (two mutually exclusive points of attachment), **bidentated** (two points of attachment), **tridentated**, etc.
- Bidentated and multidentated ligands usually are called **chelating ligands** because they can form rings

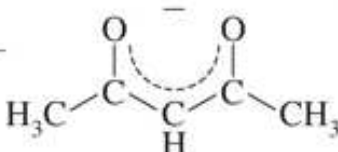
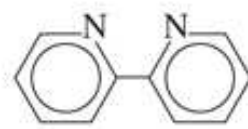
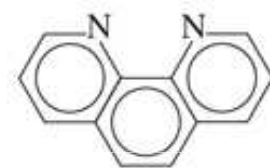
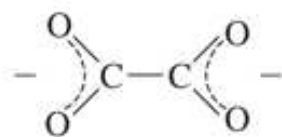
**TABLE 9.2 Common Monodentate Ligands**

Common Name	IUPAC Name	Formula
hydrido	hydrido	$\text{H}^-$
nitrido	nitrido	$\text{N}^{3-}$
azido	azido	$\text{N}_3^-$
oxo	oxido	$\text{O}^{2-}$
cyano	cyano	$\text{CN}^-$
thiocyano	thiocyanato- <i>S</i> ( <i>S</i> -bonded)	$\text{SCN}^-$
isothiocyano	thiocyanato- <i>N</i> ( <i>N</i> -bonded)	$\text{NCS}^-$
hydroxo	hydroxo	$\text{OH}^-$
aqua	aqua	$\text{H}_2\text{O}$
carbonyl	carbonyl	$\text{CO}$

**TABLE 9.3 Common Chelating Amines**

Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
monodentate	ammine, methylamine	ammine, methylamine		$\text{NH}_3, \text{CH}_3\text{NH}_2$
bidentate	ethylenediamine	1,2-ethanediamine	en	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
tridentate	diethylenetriamine	2,2'-diaminodiethylamine or 1,4,7-triazaheptane	dien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
tetradentate	triethylenetetraamine	1,4,7,10-tetraazadecane	trien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
	$\beta, \beta', \beta''$ - triaminotriethylamine	$\beta, \beta', \beta''$ -tris(2- aminoethyl)amine	tren	$\begin{array}{c} \text{NH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \\   \\ \text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$
pentadentate	tetraethylenepentamine	1,4,7,10,13- pentaazatridecane		$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
hexadentate	ethylenediaminetetraacetate	1,2-ethanediyl (dinitrilo) tetraacetate	EDTA	$\begin{array}{c} ^-\text{OOCCH}_2 \qquad \qquad \text{CH}_2\text{COO}^- \\ \diagdown \qquad \qquad \diagup \\ \text{NCH}_2\text{CH}_2\text{N} \\ \diagup \qquad \qquad \diagdown \\ ^-\text{OOCCH}_2 \qquad \qquad \text{CH}_2\text{COO}^- \end{array}$

**TABLE 9.4 Common Multidentate (Chelating) Ligands**

Common Name	IUPAC Name	Abbreviation	Formula and Structure
acetylacetonato	2,4-pentanediono	acac	$\text{CH}_3\text{COCHCOCH}_3^-$ 
2,2'-bipyridine	2,2'-bipyridyl	bipy	$\text{C}_{10}\text{H}_8\text{N}_2$ 
1,10-phenanthroline, o-phenanthroline	1,10-diaminophenanthrene	phen, o-phen	$\text{C}_{12}\text{H}_8\text{N}_2$ 
oxalato	oxalato	ox	$\text{C}_2\text{O}_4^{2-}$ 

# Nomenclature rules

- Positive ion comes first, then the negative ion
  - Potassium hexacyanoferrate(III)
  
- Ion negativo se escribe primero, luego el positivo
  - Hexacianoferrato(III) de potasio



# Nomenclature rules

- Inner coordination sphere is enclosed in square brackets in the formula, the metal is written first in the formula but last in the name
  - Hexamminecobalt(III) chloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- La esfera de coordinación interna se coloca en “brackets”, el metal se escribe primero en la fórmula, pero último en el nombre
  - Cloruro de hexaaminocobalto(III),  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

# Nomenclature rules

- The number of ligands is given with prefixes
- If the ligand name is complicated or it includes a prefix, the second prefix is used (the one ending with “is”)

Dichlorobis(ethylenediamine)cobalt(III)

Tris(bipyridine)iron(III)

Diclorobis(etilendiamina)cobalto(III)

Tris(bipiridina)hierro(III)

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis
8	octa	octakis
9	nona	nonakis
10	deca	decakis

# Nomenclature rules

- Ligands are named in alphabetical order, according to the name of the ligand, not the prefix
- Earlier rule gave anionic ligands first, then neutral ligands
- Tetraamminedichlorocobalt(III)
- Amminebromochloromethylamineplatinum(II)

# Nomenclature rules

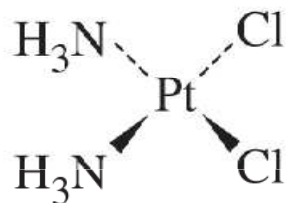
- Anionic ligands are given an *o* suffix
  - Chloro
  - Bromo
  - Sulfato
- Neutral ligands retain their usual name
- Coordinated water is called aqua
- Coordinated ammonia is called ammine

# Nomenclature rules

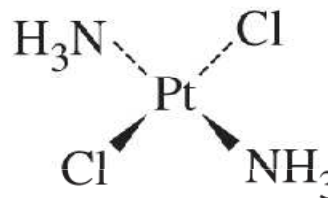
- Two systems exist for designating the charge or oxidation number: Stock system (oxidation number of metal ion as a Roman numeral) and Ewing-Basset system (charge of coordination sphere as a “normal” numeral)
- Ewing-Basset is used in Chemical Abstracts
- In either case, if the charge is negative, the suffix –ate (–ato in Spanish) is used
- Tetrachloroplatinate(II) or tetrachloroplatinate (2-) for the  $[\text{PtCl}_4]^{2-}$  ion
- Tetraammineplatinum(II) or tetraammineplatinum (2+) for the  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  ion

# Nomenclature rules

- Cis and trans designate adjacent and opposite geometric locations (as in organic chemistry)



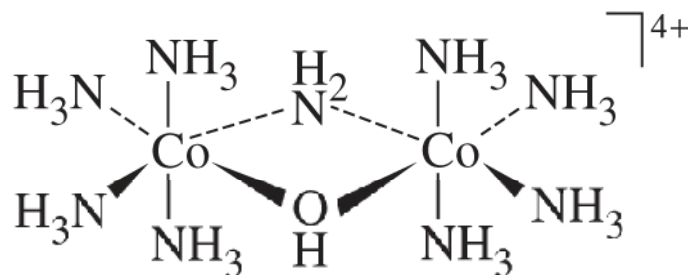
*cis*



*trans*

# Nomenclature rules

- Bridging ligands between two metal ions have the prefix  $\mu$ - as in  $\mu$ -amido- $\mu$ -hydroxobis(tetraamminecobalt) (4+)



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# Nomenclature rules

- When the complex is negatively charged, the names for some metals are derived from the sources of their symbols
- Tetrachloroferrate(III) for the  $[\text{FeCl}_4]^-$  ion
- Tetracloroferrato(III) para el ión  $[\text{FeCl}_4]^-$

iron (Fe)

ferrate

lead (Pb)

plumbate

silver (Ag)

argentate

tin(Sn)

stannate

gold (Au)

aurate

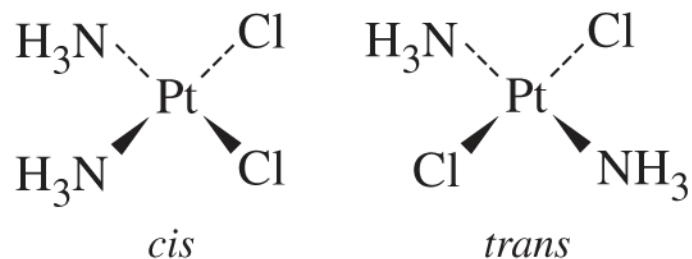


# Isomerism

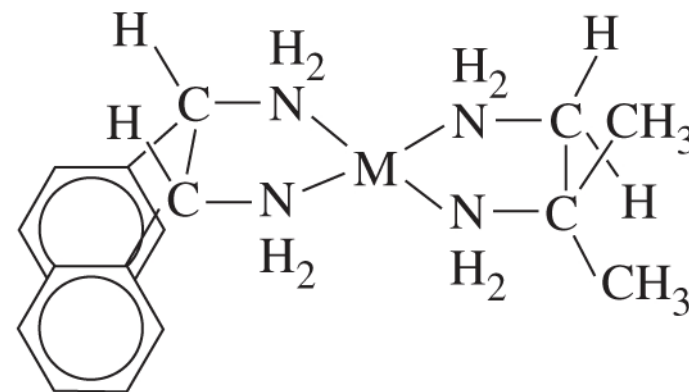
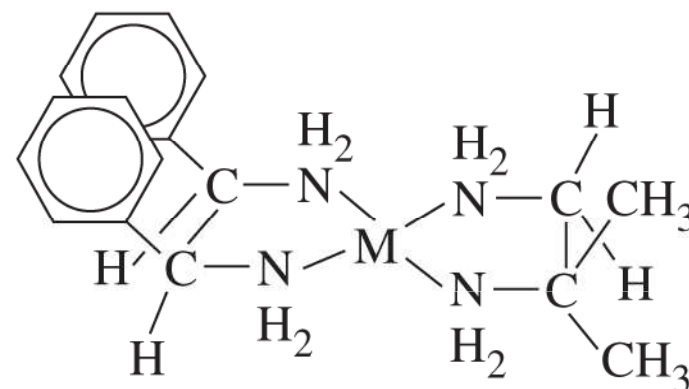
- The variety of coordination numbers in coordination compounds provides with a large number of isomers, the number of which increases with coordination number
- Our discussion will be limited to isomers with the same ligands arranged in different geometries; types are:
  - Hydrate or solvent isomerism
  - Ionization isomerism
  - Coordination isomerism
  - Linkage (or ambidentate) isomerism
  - Stereoisomerism

# Stereoisomerism

- cis/trans isomers
- Chiral isomers
- Different conformation of chelate rings
- Other isomers that differ only in the geometry of attachment to the metal atom



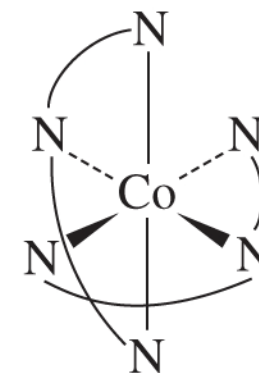
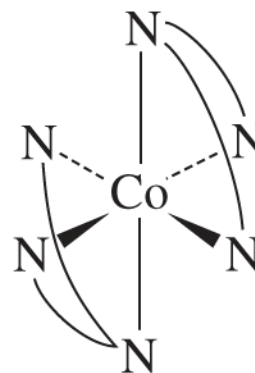
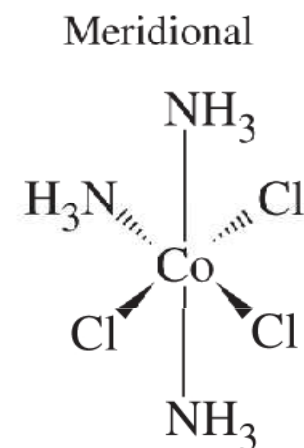
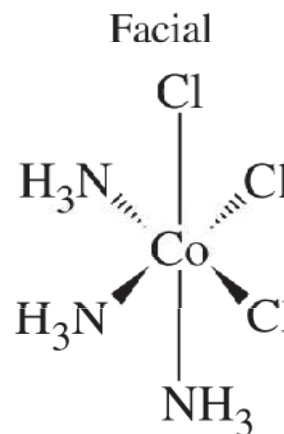
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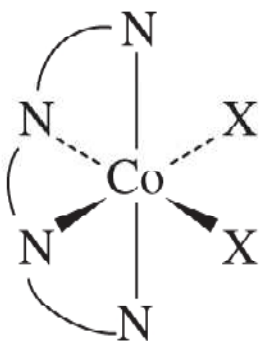
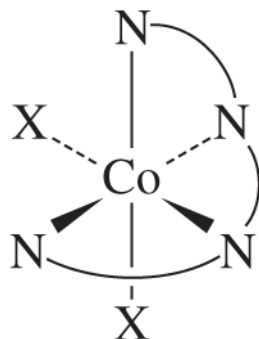
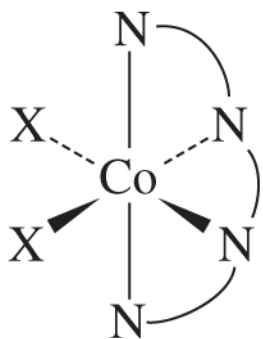
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# fac/mer Isomerism in 6-coordinate complexes

- Ligands can occupy the face of the octahedron or a meridian line

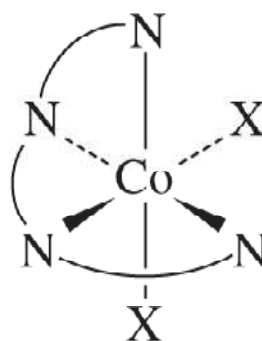


# Stereoisomerism



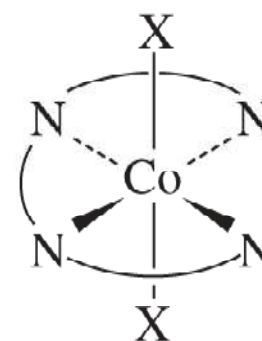
$\alpha$

No coplanar rings



$\beta$

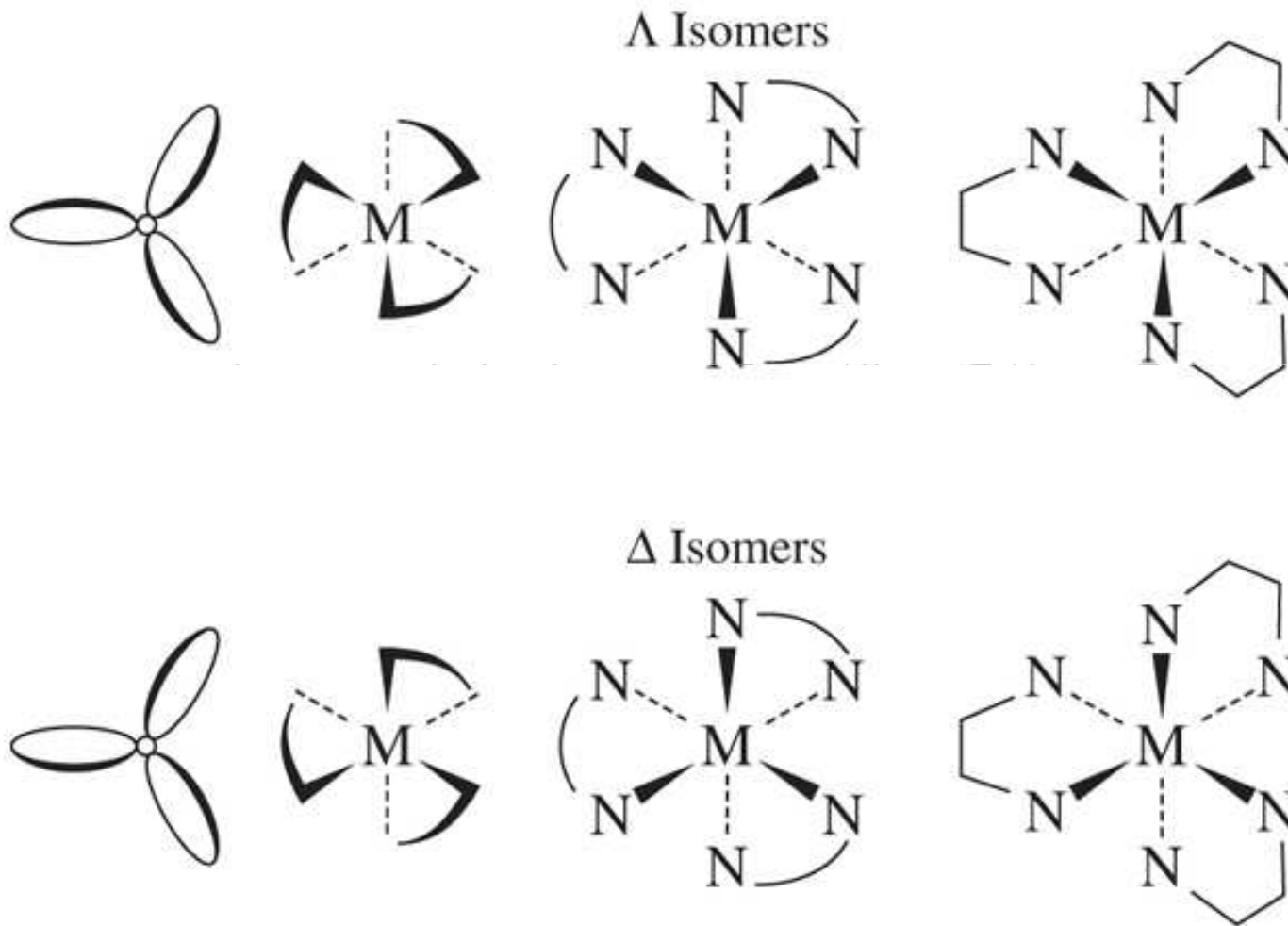
Two coplanar rings



*trans*

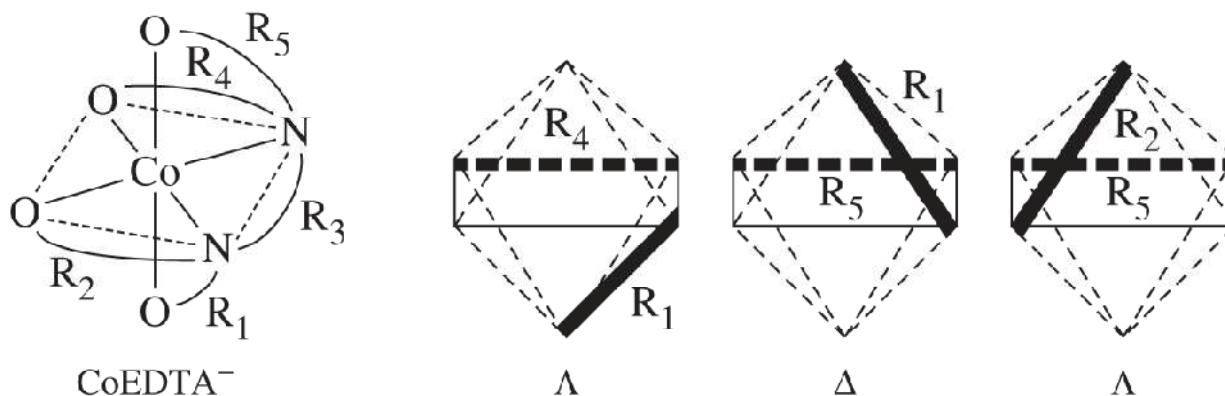
Three coplanar rings

# Isomerism – combination of chelate rings – propellers – $\Delta$ and $\Lambda$ isomers



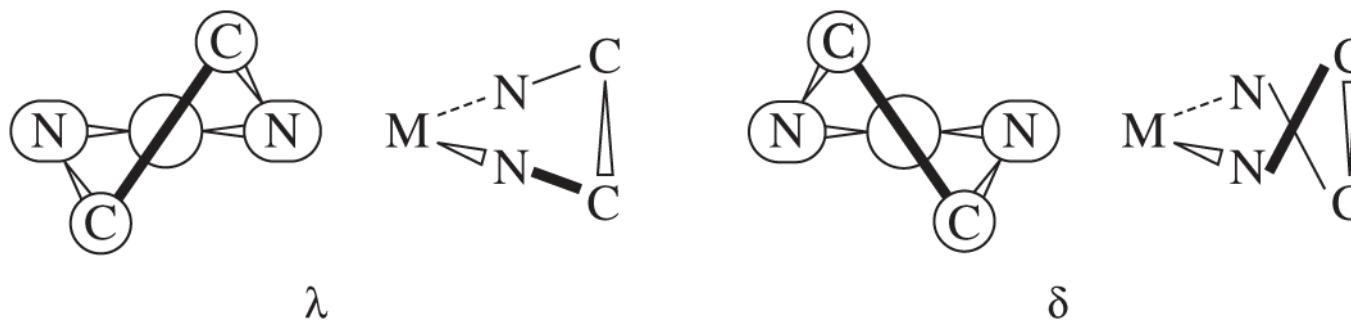
# Multiple $\Delta$ and $\Lambda$ rings and ring conformation

- Ligands such as EDTA will form multiple rings



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- Chelate rings can also adopt different conformations (designated  $\delta$  and  $\lambda$ ) - we will not focus on them



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# Constitutional isomerism

- Hydrate (or solvent) isomerism



- Ionization isomerism



- Coordination isomerism



- Linkage (ambidentate) isomerism

Ligands such as  $\text{NCS}^-$  or  $\text{NO}_2^-$  which have two attachment points

# Experimental separation and identification of isomers

- Geometric isomers are separated with fractional crystallization
- Chiral isomers requires chiral counterions
- Best identification method, when crystallization allows it, is X-ray diffraction
- Measurement of optical activity is useful for assigning absolute configuration to chiral isomers



# Coordination number and structures

- Overall shape of a coordination compound is the product of several factors:
  - Number of bonds
  - VSEPR considerations
  - Occupancy of d orbitals
  - Steric interference
  - Crystal packing effects

# Coordination number and structures

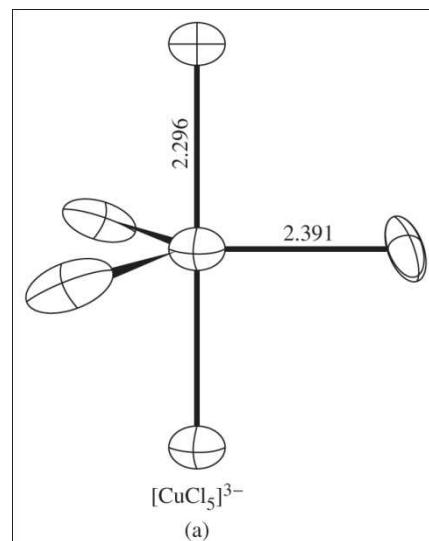
- Coordination number 1 is rare, except in ion pairs in gas phase
- Coordination number 2 is also rare,  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{CuCl}_2]^-$  and  $\text{Hg}(\text{CN})_2$  are well-known examples with a d10 metal ion and are linear
- Coordination number 3 is likely with d10 metal ions, with a trigonal-planar structure being the most common

# Coordination number and structures

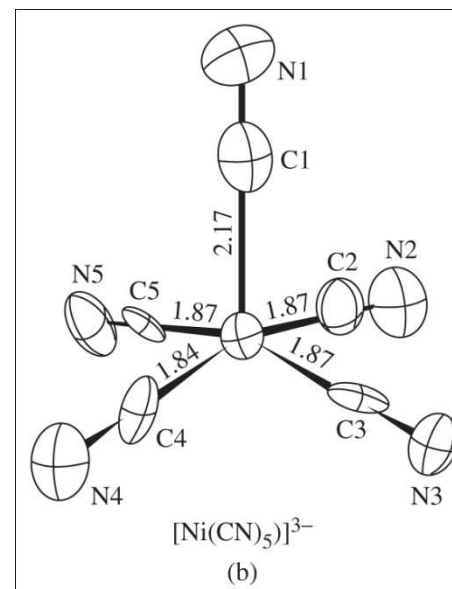
- Coordination number 4 results in a tetrahedral or square-planar structure; tetrahedral is most common
- Square-planar structures, when not imposed by a planar ligand, occur for d8 metal ions

# Coordination number 5 and structures

- Coordination number 5 can result in trigonal bipyramid, square pyramid and pentagonal plane (extremely rare).
- The energy difference is small and structures can interconvert



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# Coordination number and structures

- Coordination number 6 is the most common, with octahedral geometry the most common
- Other structures are trigonal prismatic and antiprismatic
- A regular octahedron can be distorted to tetragonal structures

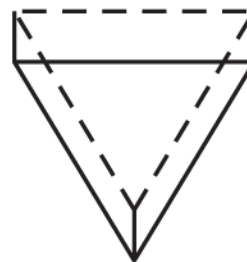


Elongated

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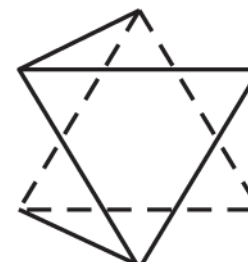


Compressed



(a)

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(b)

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