

Coordination Chemistry I: Structures and Isomers

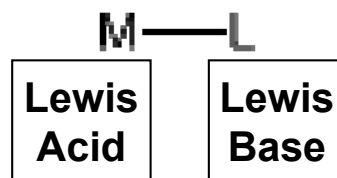
Chapter 9

Friday, November 13, 2015

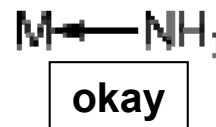
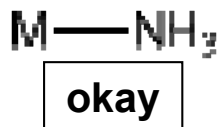
Coordination Chemistry

Coordination compounds

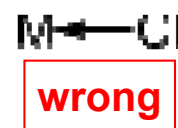
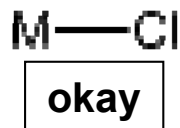
- compounds that include one or more metal atoms or ions and one or more *ligands* that formally donate electrons to the metal



- *coordinate covalent bond* – sometimes used to emphasize that a neutral ligand is acting as a Lewis base towards the metal
 - a neutral ligand is one that has no charge when the donor atom has a full octet



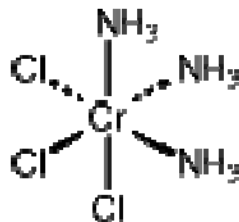
- an anionic ligand is one that has a formal negative charge when the donor atom has a full octet



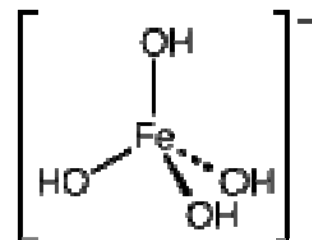
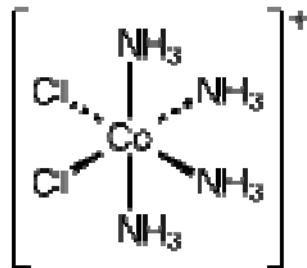
Coordination Chemistry

Coordination compounds

- neutral coordination compounds include the metal and its bound ligands



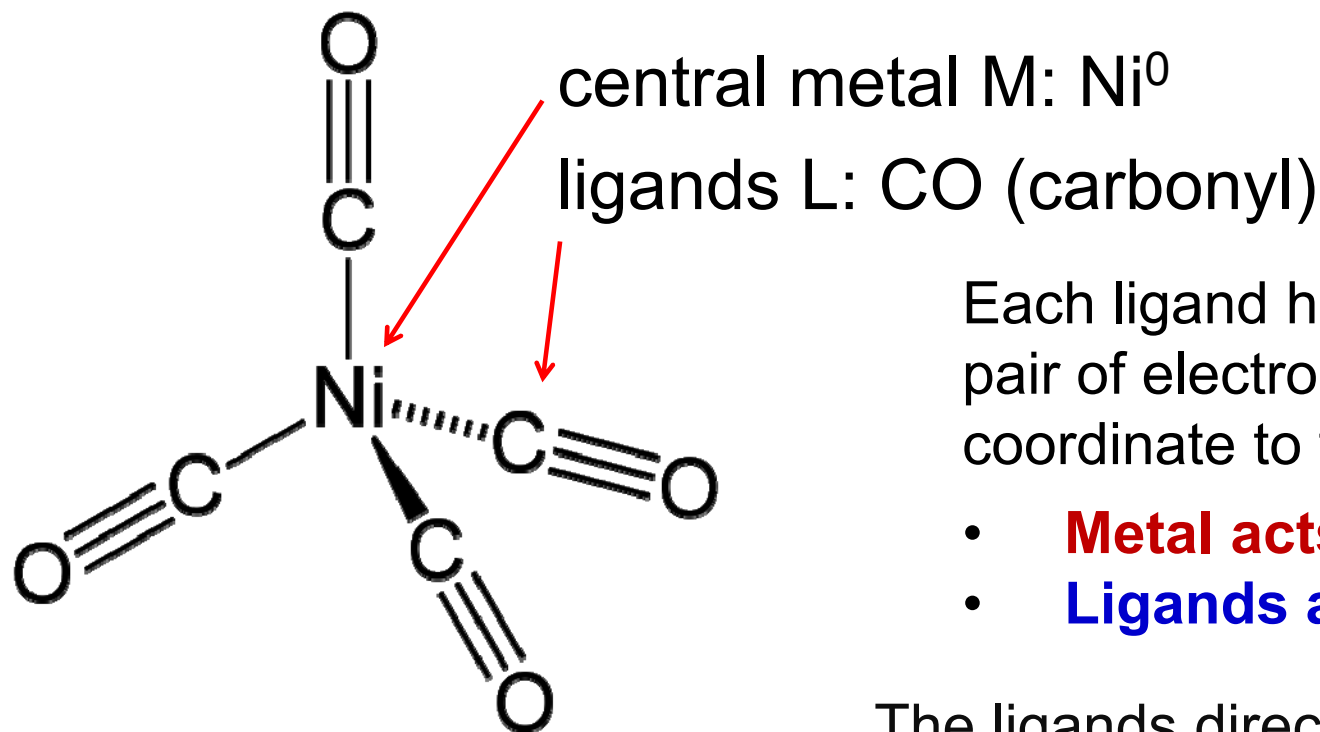
- the number of bonds in a coordination complex does not correlate with the formal oxidation state of the metal
- coordination complexes can also be charged – complex cations or complex anions



- in a complex ion, the ligands coordinated to the metal make up the primary coordination sphere
- there will also be counterions and other ions (and possibly neutral molecules) that make up the secondary coordination sphere

Coordination Complexes

Species consisting of a central metal atom/ion bound to a number of molecules or ions (called **ligands**) by coordinate covalent bonds.



tetracarbonylnickel: Ni(CO)₄

- pale yellow liquid (m.p. -17°C, b.p. 43°C)
- tetrahedral compound
- synthesized in 1890 by Mond
- extremely poisonous

Each ligand has at least one lone pair of electrons with which to coordinate to the metal.

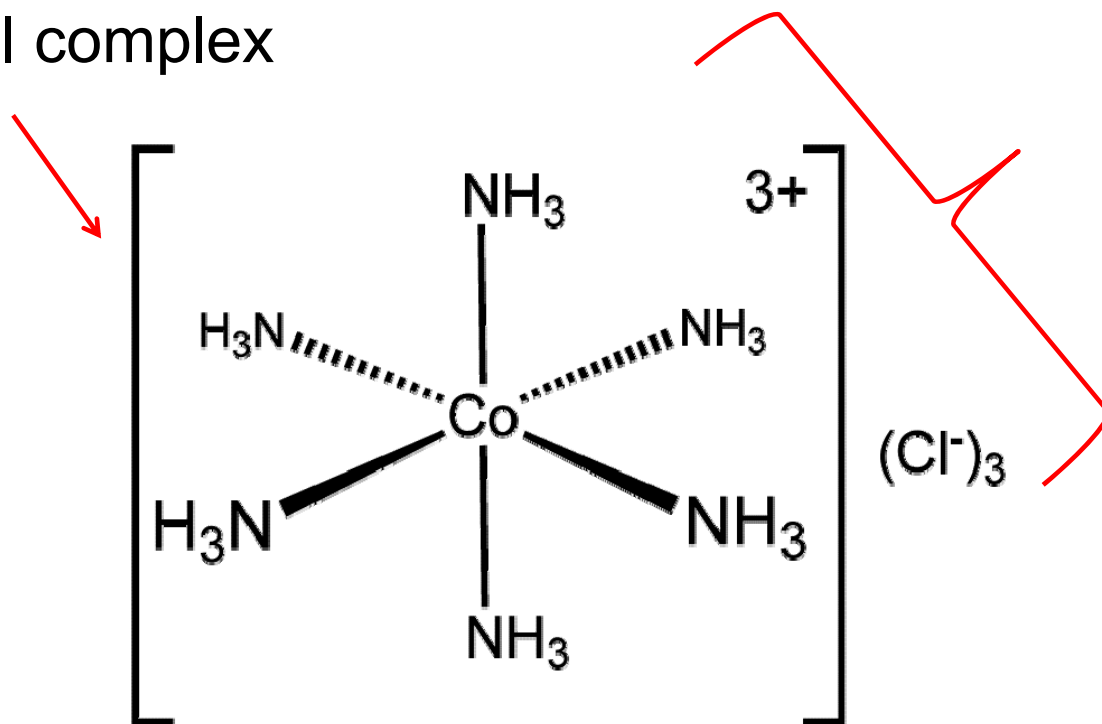
- **Metal acts as Lewis acid.**
- **Ligands act as Lewis bases.**

The ligands directly attached to the metal are its **first coordination sphere**.

The **coordination number** of the metal is the number of coordinate bonds to the metal (CN = 4 in this case).

Coordination Compounds

The metal complex



The electrically neutral compound (complex plus counter ions) is the **coordination compound**.

Counter ions are not ligands. They are part of the **second coordination sphere**.

hexamminecobalt(III) chloride: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$



- solid yellow salt
- octahedral complex (CN = 6)
- fairly inert

Common Ligands

TABLE 9.2 Classic Monodentate Ligands

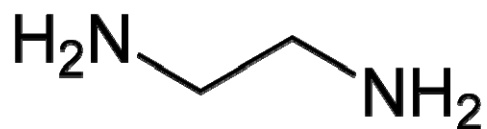
Common Name	IUPAC Name	Formula
hydrido	hydrido	H^-
fluoro	fluoro	F^-
chloro	chloro	Cl^-
bromo	bromo	Br^-
iodo	iodo	I^-
nitrido	nitrido	N^{3-}
azido	azido	N_3^-
oxo	oxido	O^{2-}
cyano	cyano	CN^-
thiocyano	thiocyanato- <i>S</i> (S-bonded)	SCN^-
isothiocyano	thiocyanato- <i>N</i> (N-bonded)	NCS^-
hydroxo	hydroxo	OH^-
aqua	aqua	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO^+
nitro	nitrito- <i>N</i> (N-bonded)	NO_2^-
nitrito	nitrito- <i>O</i> (O-bonded)	ONO^-
methyl isocyanide	methylisocyanide	CH_3NC
phosphine	phosphane	PR_3
pyridine	pyridine (abbrev. py)	$\text{C}_5\text{H}_5\text{N}$
ammine	ammine	NH_3
methylamine	methylamine	MeNH_2
amido	azanido	NH_2^-
imido	azandiido	NH^{2-}

Polydentate Ligands

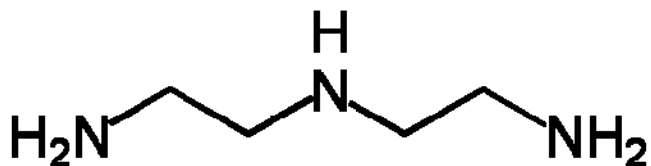
“Many toothed” ligands. Ligands with lone pairs on more than one atom, capable of binding to a metal at multiple sites.

- The number of sites by which a ligand binds is called its **denticity**.
- Ligands that bind via more than one atom are called **chelating ligands**. They make **chelate (“claw”) complexes**.

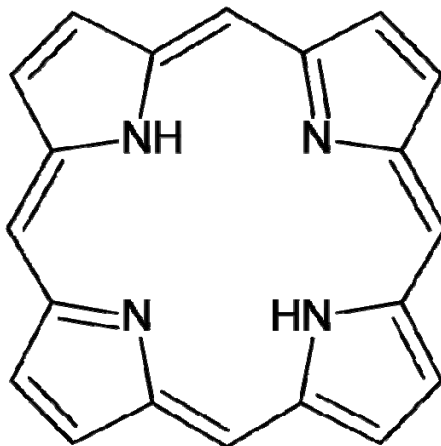
bidentate: **en**



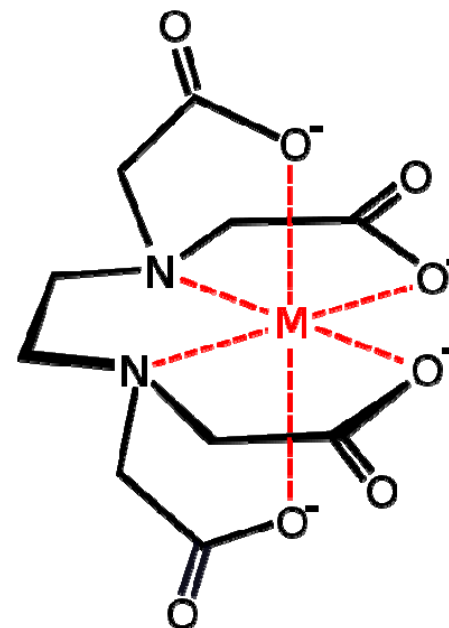
tridentate: **dien**



tetradentate:
porphyrin



hexadentate: **EDTA**



Polydentate Ligands

The denticity of a ligand is its number of donor atoms that coordinate to the metal:

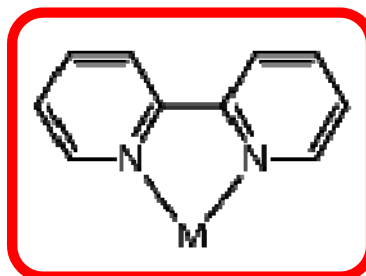
- monodentate – one donor atom, e.g.,



py

- bidentate – two donors, e.g.,

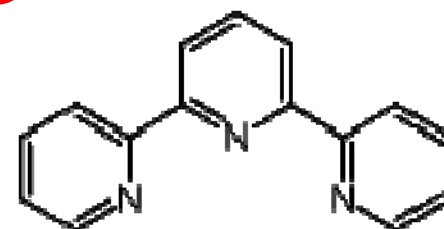
en



bpy

- tridentate – three donors, e.g.,

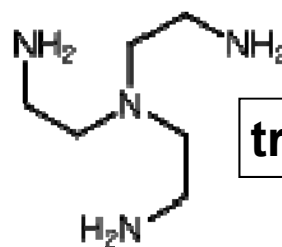
dien



terpy

- tetradentate – four donors, e.g.,

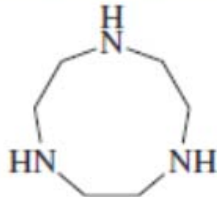
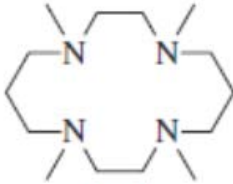
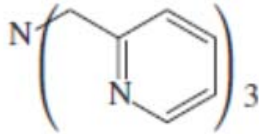
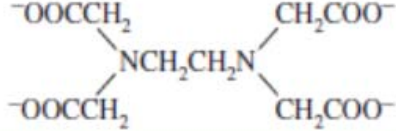
trien



tren

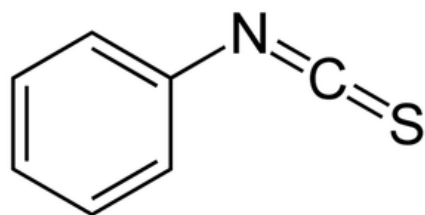
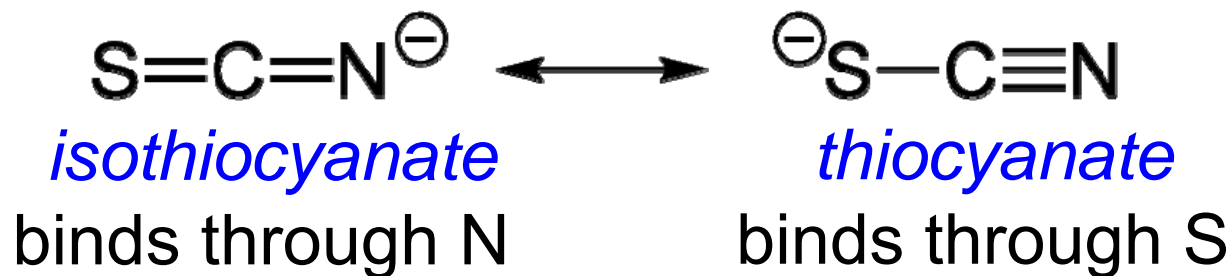
Polydentate Ligands

TABLE 9.3 Chelating Amines

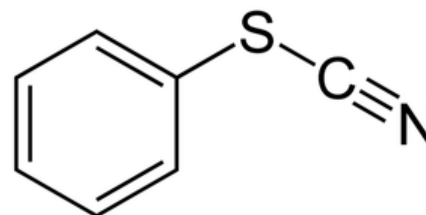
Chelating Points	Common Name	IUPAC Name	Abbrev.	Formula
bidentate	ethylenediamine	1,2-ethanediamine	en	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
tridentate	diethylenetriamine	1,4,7-triazaheptane	dien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
		1,3,7-triazacyclononane	tacn	
tetradentate	triethylenetetraamine	1,4,7,10-tetraazadecane	trien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
	β, β', β'' -triaminotriethylamine	β, β', β'' -tris(2-aminoethyl)amine	tren	$\begin{array}{c} \text{NH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$
	tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC	
	tris(2-pyridylmethyl)amine	tris(2-pyridylmethyl)amine	TPA	
pentadentate	tetraethylene-pentamine	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	ethylenediamine-tetraacetate	1,2-ethanediyl (dinitrilo) tetraacetate	EDTA	

Ambidentate Ligands

Ambidentate ligands can bind to a metal using either of several atoms.

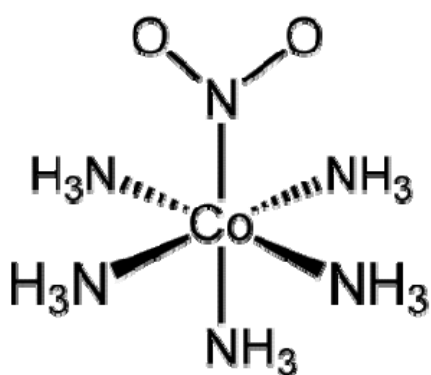


phenyl isothiocyanate



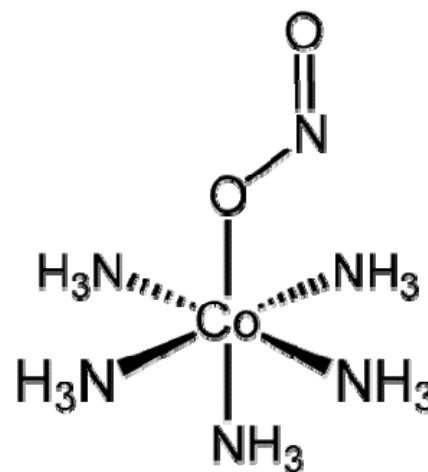
phenyl thiocyanate

nitro NO_2^-
binds through N



yellow

2+



red

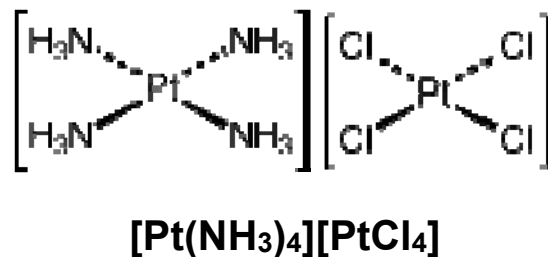
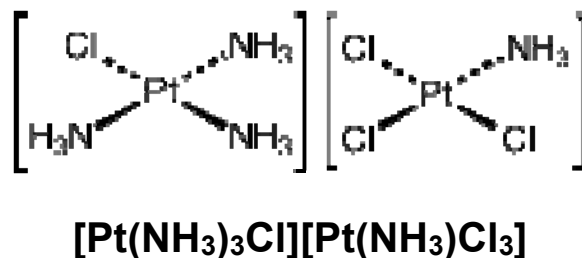
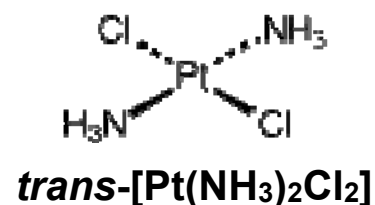
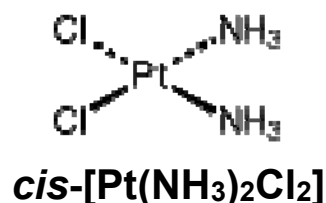
2+

nitrito ONO^-
binds through O

Formulae & Nomenclature

The complexity of coordination complexes demands strict adherence to a formal and detailed naming system.

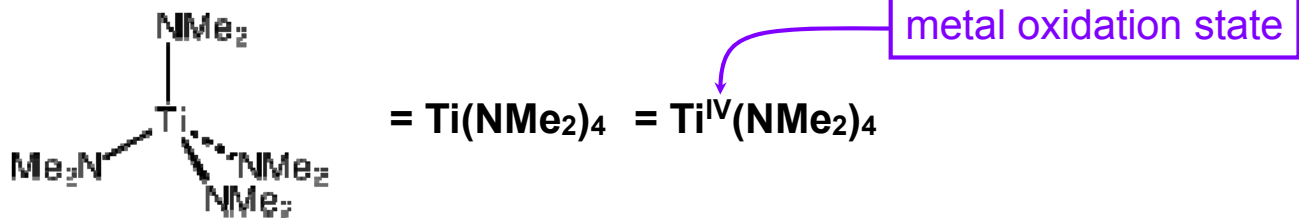
- consider a coordination compound with the empirical formula $\text{PtCl}_2(\text{NH}_3)_2$, which could mean any of the following known compounds



Formulae & Nomenclature

Formulae

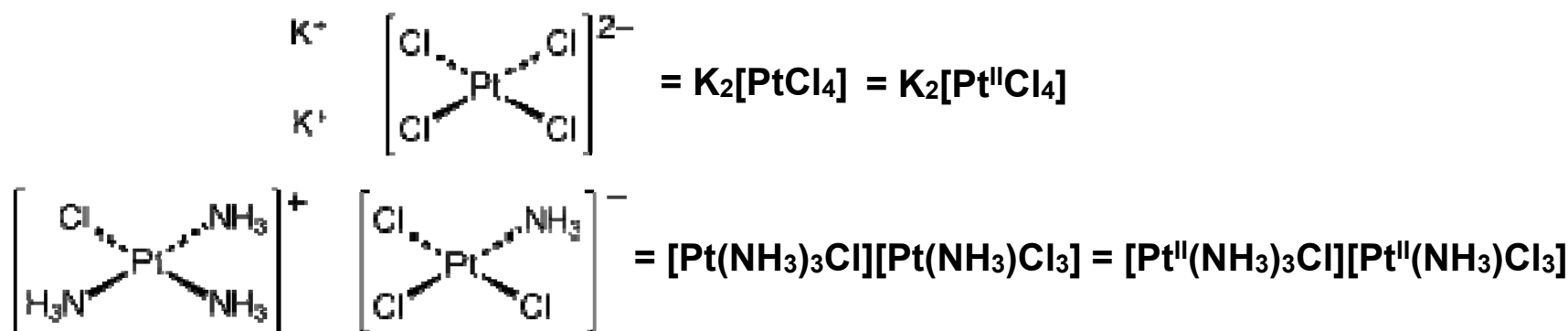
- When writing the formulae of coordination complexes the metal comes first followed by the ligands in alphabetical order (by the ligand name).
- If the complex is simple, brackets are not needed, for example



- If the complex needs a prefix or is ionic, it is enclosed in square brackets



- When both the cation and anion are given, the cation always comes first in the formula



Formulae & Nomenclature

Names

1. When writing the names of coordination complexes, the cation always comes before the anion
2. The ligands are listed alphabetically (by name, not abbreviation or prefix) and come *before* the metal
3. The number of simple ligands is given by the 'simple prefix' below, for complex ligands the 'complex' prefix is used

Number	Simple Prefix	Complex Prefix
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

Formulae & Nomenclature

Names

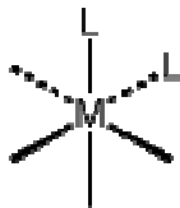
4. Anionic ligands get an -o suffix (e.g., *chloro* for Cl^-). Neutral ligands keep their normal name except for H_2O (*aqua*) and NH_3 (*ammine*)
5. There are two ways to deal with charge when naming complexes
 - a. *Stock system* – the formal oxidation state of the metal is given by Roman numerals in parenthesis after the metal name – more commonly used but sometimes problematic
 - b. *Ewing-Bassett system* – the charge of the complex is given by regular numbers in parenthesis after the metal name – less common but always correct
6. Metals in complex cations keep their normal name. Metals in complex anions get an -ate suffix, except for the following metals which use their Latin names:

Metal	Anionic Name
Fe	ferrate
Ag	argenate
Pb	plumbate
Sn	stannate
Au	aurate

Formulae & Nomenclature

Names

7. Prefixes are used to designate the geometric arrangement of ligands when needed.



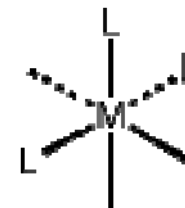
cis-



trans-



fac-



mer-

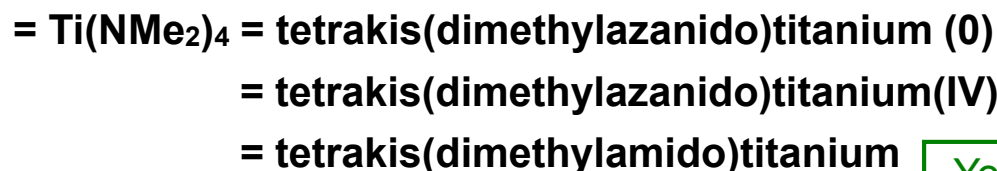
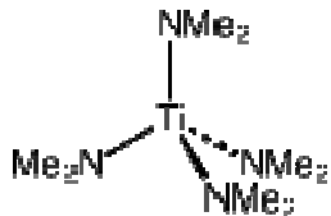
8. Ligands that bridge two or more metals get a prefix μ^n -, where n is the number of metals bridged

9. Many ligands have commonly-used names that differ from the IUPAC name, leading to more confusion:

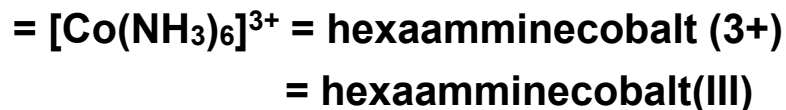
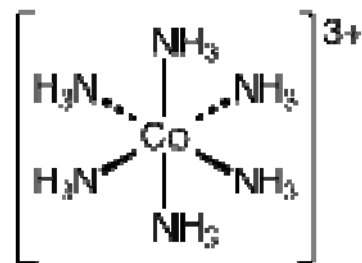
Ligand	Common Name	IUPAC Name
O^{2-}	oxo	oxido
PR_3	phosphine	phosphane
NR_2^-	amido	azanido
NR_2^-	imido	azanedido
$-SCN^-$	thiocyano	thiocyanato-S
$-NCS^-$	isothiocyano	thiocyanato-N

Formulae & Nomenclature

Examples



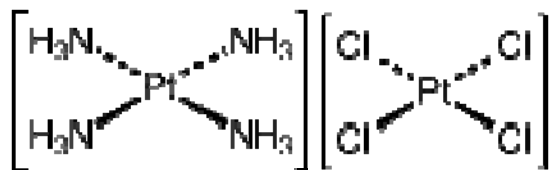
In cases where the overall charge on the complex is zero, this number is usually not included for the Ewing-Bassett system



You'll see amido much more often than azanido to describe NR_2^-

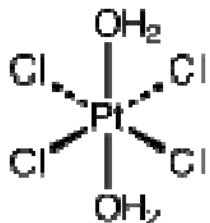


because the entire geometry is defined by a single *cis* prefix, a second one is not needed

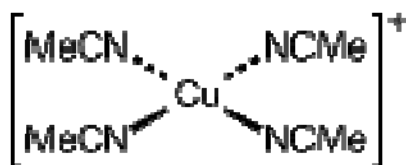


Formulae & Nomenclature

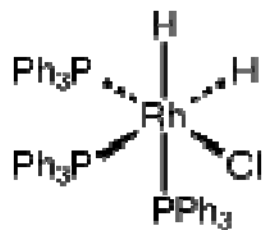
Examples



= *trans*-[Pt(H₂O)₂Cl₄] = *trans*-diaquatetrachloroplatinum
 = *trans*-diaquatetrachloroplatinum(IV)

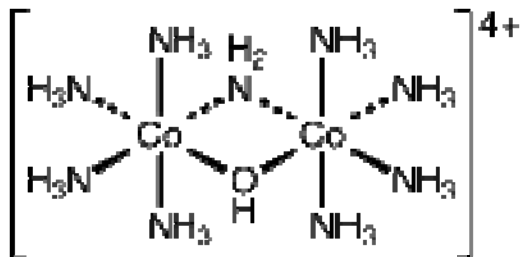


[BF₄]⁻ = [Cu(CH₃CN)₄][BF₄] = tetrakis(acetonitrile)copper tetrafluoroborate
 = tetrakis(acetonitrile)copper(I) tetrafluoroborate



= *cis, fac*-[RhClH₂(PPh₃)₃]
 = *cis, fac*-chlorodihydridotris(triphenylphosphane)rhodium
 = *cis, fac*-chlorodihydridotris(triphenylphosphane)rhodium(III)
 = *cis, fac*-chlorodihydridotris(triphenylphosphine)rhodium

According to IUPAC, it should be triphenylphosphane, but triphenylphosphine is much, much more common



= [(NH₃)₄Co(μ²-NH₂)(μ²-OH)Co(NH₃)₄]⁴⁺
 = μ²-azanido-μ²-hydroxobis(tetraamminecobalt) (4+)
 = μ²-azanido-μ²-hydroxobis{tetraamminecobalt(III)}