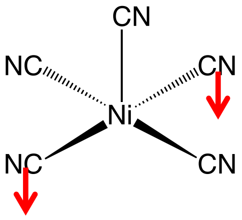
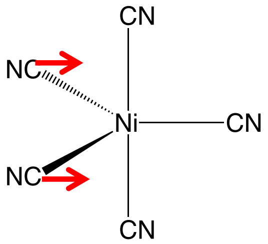
Week 2

- Coordination number of 5

For 5-coordinate complexes, the two most common geometries are **trigonal bipyramidal** and **square pyramidal**. These are less common than 4 and 6. Trigonal bipyramial: minimizes ligand-ligand repulsions, but often polydentate ligands will prefer square pyramidal.

Example: $[Ni(CN)_5]^{3-}$ Can exist as both in the solid state.





Some 5-coordinate complexes have geometries in between ideal trigonal bipyramidal and square pyramidal. We often designate their geometries as either distorted trigonal bipyramidal or distorted square pyramidal, depending on which geometry is closet to theirs.

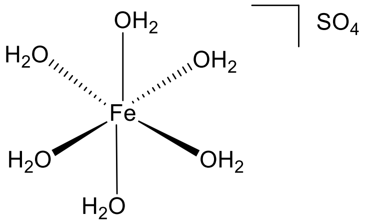
In the absence of polydentate ligands that force a specific geometry; often the energies between the two complexes is so similar that when dissolved in solutions, they undergo what is known as a **Berry pseudorotation** where they interconvert from one to another. In this case the axial ligands become equatorial and vice versa. See the red arrows above.

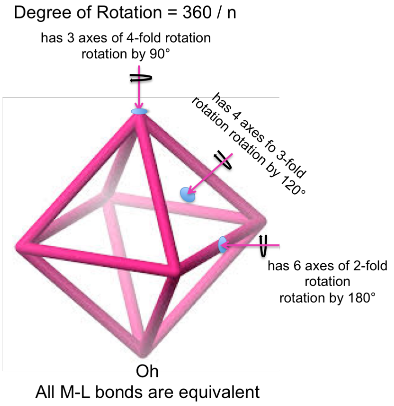
CN^-: cyano, anionic ligand

Exercise: What are the oxidation states of the two metal ions here? Answer: 2+

- Coordination number of 6

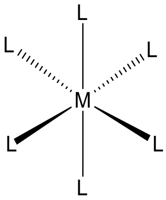
For 6-coordinate complexes, the most common Coordination Geometry is **Octahedral.** For examples, the Fe complex below has an octahedral geometry. We can identify several rotational axes shown below.



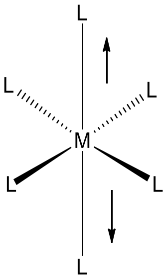


Some 6-coordinate complexes have a structure that is slightly deviated from the ideal octahedral geometry, so we call them distorted octehdra. However, there are some common distortions that have more specific names. The most common deviations are tetragonal and trigonal distortions. **Tetragonal distortion**: elongation or compression along the 4-fold axis of the original octahedron. This distortion is commonly seen for complexes with non-equivalent ligands and also there are examples where all ligands are the same as in **Jahn Teller ions** like Cu^{2+}, this is common for instance for d^9 complexes. All you need to know currently is that a Jahn Teller distortion to lower the energy of d-orbitals. We will go over this to a greater extent later.

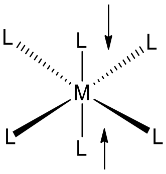
Compression is along the 4-fold axis of the octahedron.



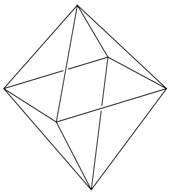
6 M-L bonds are equal

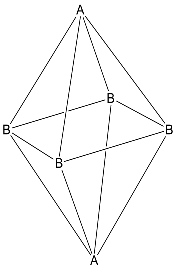


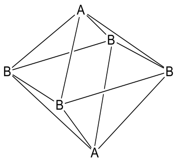
two M-L bonds are elongated



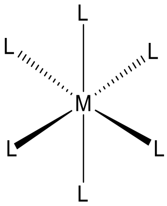
two M-L bonds are compressed



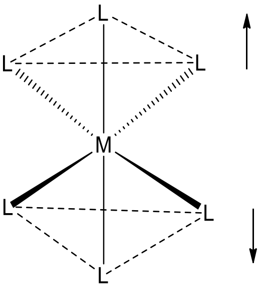




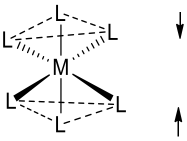
Trigonal distortion: elongation or compression along the 3-fold axis of the original octahedron. This distortion is favored by ligands with strong intermolecular interactions or those that are weak sigma donor ligands. The trigonal distortion gives rise to a number of different structures between octahedral and **trigonal prismatic geometry**, a second type of 6-coordinate geometry.



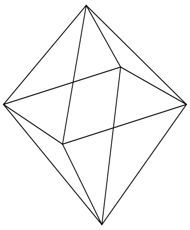
6 M-L bonds are equal

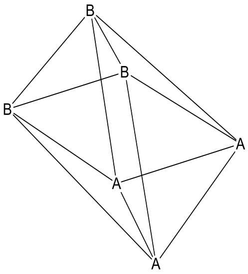


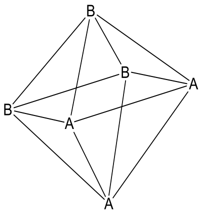
elongation along the 3-fold axis



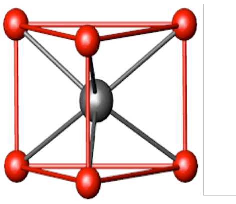
compression along the 3-fold axis



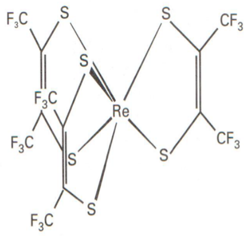




Examples of trigonal prismatic geometry: While rare, this geometry is very common for sulfur containing compounds and weak σ-donors. The reason is that sulfur atoms often form covalent bonds to each other. There are also several d^0 complexes like Zr and Hf.

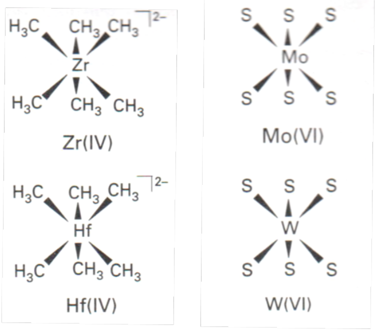


Dithiolene ligand



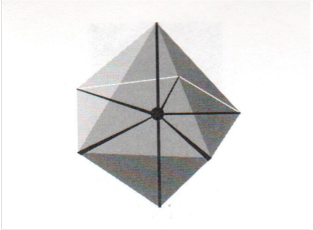
$[Re(S_2C_2(CF_3)_2)_3]$

d^0 complexes S-complexes

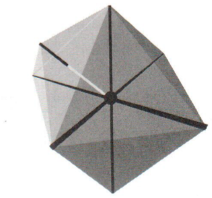


- Coordination number of 7

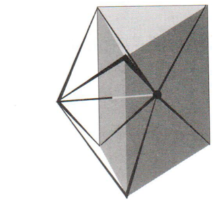
Pentagonal-bipyramidal



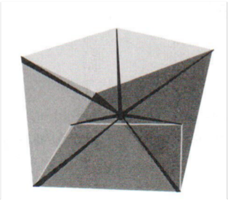
Capped octahedral



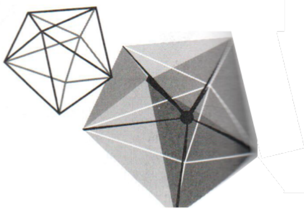
Capped trigonal prism



- Coordination number of 8



Square-antiprism

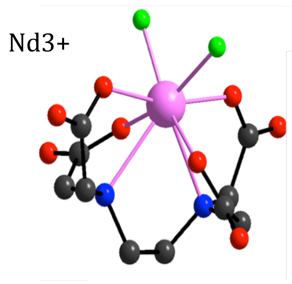


Dodecahedral

- Coordination number of 8 and higher

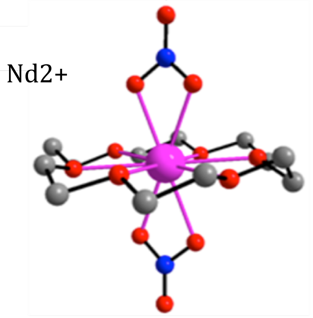
Complexes with a coordination number of 7 or higher exist, but they are less frequent. Most of these complexes have lanthanide or main group metal ions. Here I show you two examples.

$[Nd(edta)(F_2)]^{3-}$



CN = 8

$[Nd(NO_3)_2(18C6)]$



CN = 10

The Nd (Neodymium) ion has a coordination number of 8. Green balls represent F; Red balls represent O; Blue balls represent N. This is a so-called ball-stick drawing of the structure of a complex.
The Nd (Neodymium) ion has a coordination number of 10. The abbreviation 18C6 stands for 18-Crown-6, a crown ether ligand.

- ***For your information.*** If you are interested seeing more examples of coordination compounds, read pages 325-333 of the reference book.

4. Examples of some common ligands

Now that you know what coordination compounds are, know about the coordination geometries and coordination numbers, let's see some common ligands. There are a number of common ligands in coordination chemistry that have a number of different species responsible for the connectivity these include but are not limited to

-Type of connection points - O, N, C, S, halides, etc.

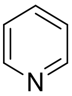
You can also have ligands with a number of different connecting points
- **Terminal** ligands – cap metals

- Some ligands are **bridging** – go between metals and can lead to the formation of coordination polymers
- Some ligands, known as **chelates**, connect to the same metal forming rings.

- **Mono-dentate ligands** - ligands with only one point of attachment to the metal center.

Charged ligands:
F^-: fluoro; Cl^-: chloro; Br^-; bromo; I^-: iodo.
CN^-: cyano; HO^-: hydroxo; N_3^-: azido; SCN^-: thiocyano; NH_2^-: amido. Many negative ligands end in o!

Neutral ligands:

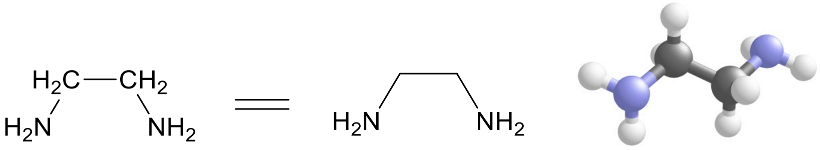
CO: carbonyl; H_2O: aqua; PR_3: phosphine; NH_3: ammine;  : pyridine

- **Chelating ligands** -Ligands with two or more points of attachment to a single metal atoms are called chelating ligands.

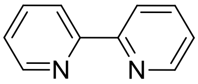
Dentate is a Latin term that literally means "tooth" and refers to the number of connecting points a ligand has.

Bidentate: a ligand has *two* points of attachment.
Tridentate: a ligand has *three* points of attachment.
Tetradentate: a ligand has *four* points of attachment.
Pentadentate: a ligand has *five* points of attachment.
Hexadentate: a ligand has *six* points of attachment.
Polydentate: a ligand has *more than two* points of attachment.

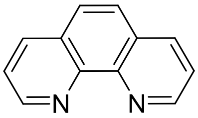
Examples.



Common name: ethylenediamine; Abbreviation: en
"en" is a very popular **bidentate** ligand. It coordinates to a metal center by its two nitrogen atoms.



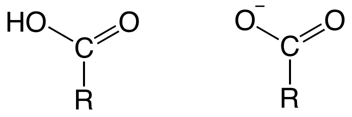
Common name: 2,2-bipyridine; Abbreviation: bipy.



Common name: 1,10-phenanthroline; Abbreviation: phen.

**It should be noted that carboxylato is a very common ligand, which has several modes of binding after deprotonation. Please see the image below. The R groups can vary significantly.

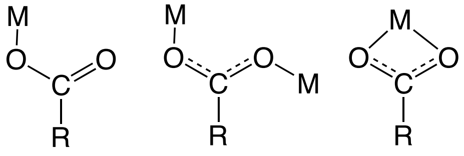
Deprotonation



free carboxylic acid

deprotonated the ligand has 1- charge

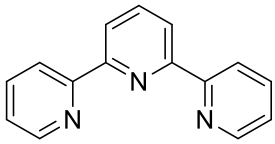
Different binding modes for carboxylate ligands:



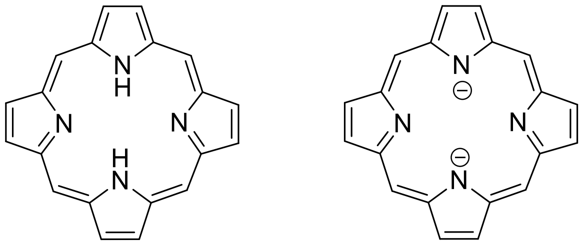
monodentate

bidentate bridging

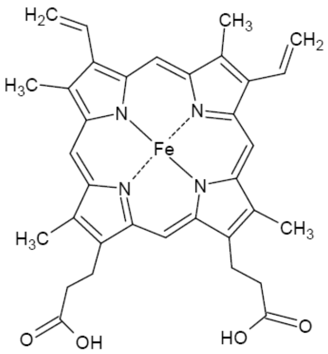
bidentate chelating

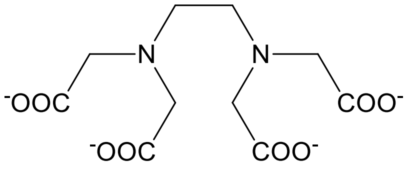


Common name: terpyridine; Abbreviation: terpy.

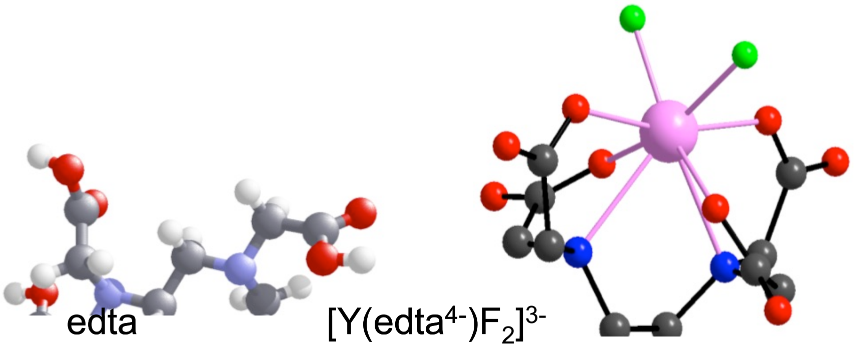


Common name: **porphyrin** (left). When it coordinates to a metal ion, it normally loses 2 protons, to form porphyrinate (right). These can be defined as heterocyclic macrocycles that have 4 pyrrole subunits attached at their alpha carbon and bridged by methine units. The porphyrin is an important biological ligand. One of the best-known porphyrin is heme, present in your blood. Heme (below) is a Fe porphyrinate complex that carries oxygen. Also present in plants are Mg porphyrins in chlorophyll, which is responsible for converting light energy into chemical energy for plants to thrive. So the porphyrin absorbs light that is then used to convert CO_2 into sugar and oxygen.

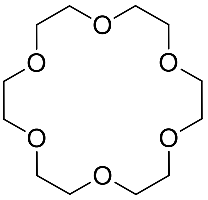




Common name: enthylenediaminetetraacetato; Abbreviation: EDTA



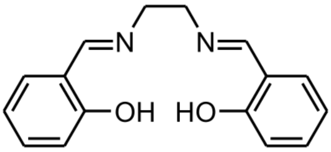
EDTA is a very strong chelating ligand. It is often used in biological studies to extract trace amount of metal ions. Further, it is quite cheap and often used to regenerate adsorbent materials used to extract for instance heavy metal ions from solution.

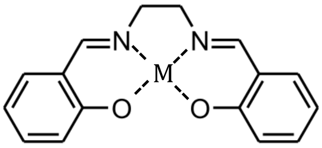


Common name: 18-crown-6; Abbreviation: 18C6.

Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide $-CH_2$-CH_2O- units however sometimes they have other functionality for instance amines.

Salen ligands are very common building blocks used in coordination chemistry and also used in homogeneous catalysis. Given this, I wanted you to see it. It is formed through a condensation reaction between ethylenediamine and salicylaldehyde. These are tetradentate and form square planar type metal complexes.



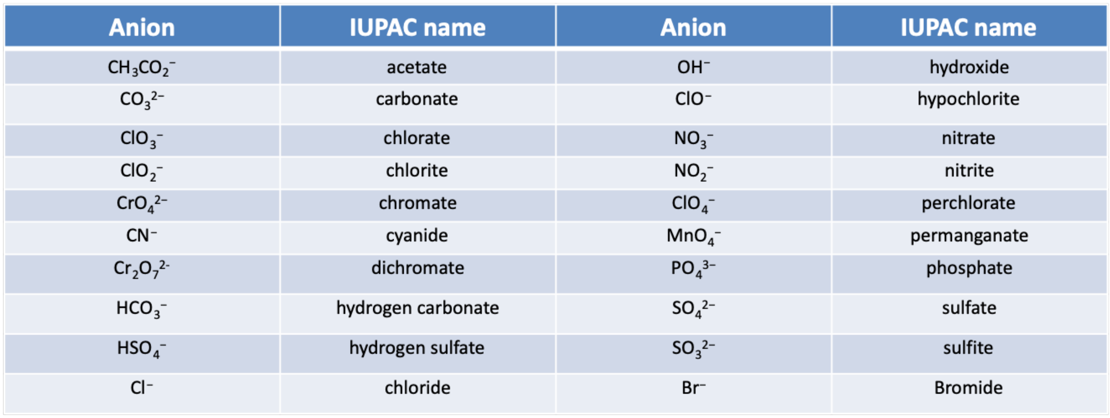


In addition to the aforementioned ligands I have shown you, I have made you a table of some of the most common ligands that you should also be familiar with are the following. The ones I have highlighted in yellow are known as **ambidentate**. This means they can bind through multiple atoms and we will discuss this a bit more in the next section.

Common Name	Abbreviation	Formula	Classification
hydrido		H^-	M(H)
fluoro		F^-	
chloro		Cl^-	
bromo		Br^-	

iodo		I^-	
nitrido		N^{3-}	
azido		N_3^-	
oxo		O^{2-}	
cyano		CN^-	
thiocyano (S-bonded)		SCN^-	
Isothiocyano (N-bonded)		NCS^-	
hydroxo		OH^-	
aqua		H_2O	
carbonyl		CO	
thiocarbonyl		CS	
nitrosyl		NO^+	
nitro (N-bonded)		NO_2^-	
nitrito (O-bonded)		ONO^-	
phosphine		PR_3	
pyridine	py	C_5H_5N	
ammine		NH_3	
methylamine		$MeNH_2$	
amido		NH_2^-	
imido		NH^{2-}	
ethylenediamine	en	$C_2H_8N_2$	
18-crown-6	18C6	$C_{12}H_{24}O_6$	
2,2-bipyridine	bipy	$C_{10}H_8N_2$	
1,10-phenanthroline	phen	$C_{12}H_8N_2$	
terpyridine	terpy	$C_{15}H_{11}N_3$	
enthylenediaminetetraacetato	edta	$C_{10}H_{12}N_2O_8$	
porphyrinate		$C_{20}H_{12}N_4$	
tetraazacyclotetradecane	cyclam	$C_{16}H_{16}N_2O_2$	
2,2′Ethylenebis(nitrilomethylidene)diphenolato	salen	$C_{16}H_{14}N_2O_2$	

Exercise: Go through and classify ligands in your spare time.
M= monodentate, B = bidentate, T = tridentate, H = hexadentate
You should also indicate the atoms the ligands bind through.



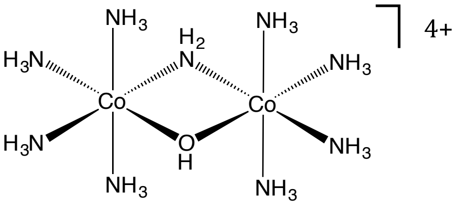
Anion	IUPAC name	Anion	IUPAC name
$CH_3CO_2^-$	acetate	OH^-	hydroxide
CO_3^{2-}	carbonate	ClO^-	hypochlorite
ClO_3^-	chlorate	NO_3^-	nitrate
ClO_2^-	chlorite	NO_2^-	nitrite
CrO_4^{2-}	chromate	ClO_4^-	perchlorate
CN^-	cyanide	MnO_4^-	permanganate
$Cr_2O_7^{2-}$	dichromate	PO_4^{3-}	phosphate
HCO_3^-	hydrogen carbonate	SO_4^{2-}	sulfate
HSO_4^-	hydrogen sulfate	SO_3^{2-}	sulfite
Cl^-	chloride	Br^-	Bromide

A common cation is NH_4^+ known as ammonium.

Exercise Poll 1.

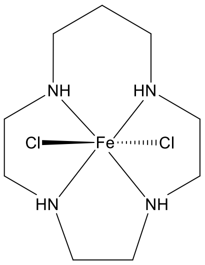
Judge which ligands in the following complexes are chelating ligands. Are they bi-, tri-, tetra-, or hexa-dentate? Coordination number? Oxidation state? Coordination Geometry?

1)



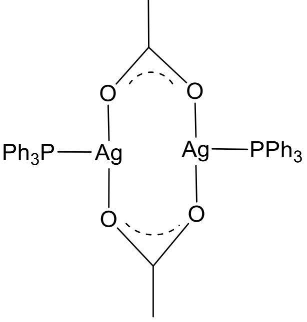
Answer: All ligands are monodentate and there are no chelating ligands here. There are two monodentate, bridging ligands….amido NH_2^- and hydroxo OH^-. The NH_3 ligands are monodentate, terminal. It is likely cobalt (III) because this is a common oxidation state for this metal, whereas cobalt (IV) is not so common (see your table above). Likely if it were cobalt (II) and (IV) the environment around the two cobalt metals would be significantly different from one another as higher oxidation states tend to have shorter bond distances. CN = 6, Geometry = distorted octahedral

Exercise Poll 2.



Answer: The tetraza or cyclam ligand is chelating and tetradentate, CN of the complex is = 6, the Geometry is distorted octahedral and the oxidation state must be Fe(II). The two chloro ligands are terminal monodentate.

Exercise Poll 3.



Answer: Here the acetate ligands, $CH_3CO_2^-$, are bidentate, but are not chelating and instead are bridging. The CN = 3 and the coordination geometry is trigonal planar. The oxidation state of silver is +1 because the carboxylate is -1 and the phosphine is neutral. The phosphine ligands are monodentate.

5. Nomenclature of coordination compounds.

The International Union of Pure and Applied Chemistry (IUPAC) has set up rules for the nomenclature of coordination compounds. In practice, many common names and abbreviation are widely used. (***For your information***. See pages 317-321 of the reference book if you are interested in knowing the complete rules.) Here I list the most important rules.

1. The cation comes before the anion. If the complex is +, it comes first. If the complex is –, it goes second.

Example: $[Ag(NH_3)_2]Cl$ inner coordination sphere is positive and so it would come first but for $K_3[Fe(CN)_6]$, the inner coordination sphere is negative and so it would come second.

2. The names of the ligands in the inner coordination sphere come before the metal

3. Ligand or ion names are placed in alphabetical order. Use ligand names in the table I provided you in the table.

Example: $[Ag(NH_3)(H_2O)]Cl$ if you have the ammine and aqua ligand, the ammine would come first in the name.

Example: for $NaK_2[Fe(CN)_6]$ Sodium would come after potassium

4. The number of species of one kind is often given by two set of prefixes. The second set of prefixes is used in conjunction with parenthesis for the name of the ligand.

Always use the first set of prefixes unless:

a. If the name includes already the first set of prefixes
b. If the ligand is polydentate
c. If there are multiple bridges of the same kind (i.e bis(μ-oxo)…)

Number of ligands	First set of prefixes	Second set of prefixes
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis

*It should be noted that these prefixes are not typically used for charge balancing cations or anions unless absolutely needed. Considering that the metal oxidation state or complex charge is reflected in the name, it is not common to use the prefix in front of the cation unless needed. See examples below.

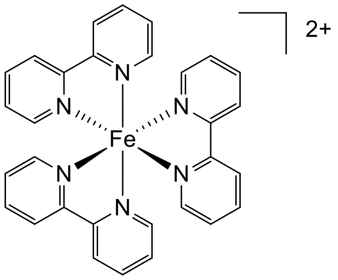
Example: (A) $NaK_2[Fe(CN)_6]$ then you would use a prefix to give the number of potassium. This rule also applies to charge balancing anions. Dipotassium sodium hexacyanoferrate(III)

Example: ($K_3[Fe(CN)_6]\cdot 6H_2O$ would be called Potassium hexacyanoferrate(III) hexahydrate.

**If there is solvent, then prefixes are often used to give the number of solvent molecules as this cannot be determined from the metal oxidation state or the charge of the complex.

Example:
$[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$ = dichlorobis(ethylenediamine)...cobalt(III)

Example:



= tris(bipyridine)iron(II)
=tris(bipyridine)iron (2+)

5. There are two possibilities for designating the charge or the oxidation state.
(a) Put the oxidation state as a Roman numeral in parenthesis after the name of the metal.
(b) Put the charge of the coordination sphere in parenthesis after the name of the metal

6. If complex charge is negative, the suffix –ate is added to the name of the metal name.

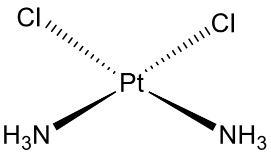
Example: $[Pt(NH_3)_4]^{2+}$ = tetraammineplatinum(II) = tetraammineplatinum(2+)
$[PtCl_6]^{2-}$ = hexachloroplatinate(IV) = hexachloroplatinate(2-)

metal	**changed to**
cobalt	cobaltate
aluminium	aluminate
chromium	chromate
vanadium	vanadate
copper	cuprate
iron	ferrate
platinum	platinate
silver	argentate
gold	Aurate

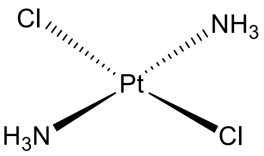
Exercise: (A) $[Ag(NH_3)_2]Cl$

The coordination sphere is enclosed in square brackets in the formula.
Diamminesilver(I) chloride or Diamminesilver(1+) chloride

7. Prefix *cis*- and *trans*- designate adjacent and opposite geometric locations.
$[Pt(NH_3)_2Cl_2]$



cis-diamminedichloroplantium(II)

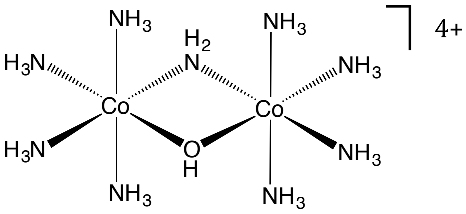


trans-diamminedichloroplantium(II)

These two platinum complexes are *cis/trans* isomers. There are also *fac* and *mer* isomers that we will cover in the later section.

You will also learn Δ and Λ later in the course, which denotes different entantiomers of octahedral complexes. These are used in front of the name of coordination compound.

8. Bridging ligands between metal ions have the prefix "μ-"



μ-amido-μ-hydroxobis(tetraamminecobalt)(4+)