

## 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:**  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  inner coordination sphere is positive and so it would come first

**Example:** For  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , the inner coordination sphere is negative and so it would come second, after Potassium

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

**Example:**  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  So, the ammine would come before silver

**Example:**  $\text{K}_3[\text{Fe}(\text{CN})_6]$  Potassium comes first, then cyano, then iron when naming.

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

**Example:**  $[\text{Ag}(\text{NH}_3)(\text{H}_2\text{O})]\text{Cl}$

Ammine aqua silver.... ammine comes before aqua.

**Example:** for  $\text{NaK}_2[\text{Fe}(\text{CN})_6]$

Name the two cations first.

Potassium would come before sodium

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( $\mu$ -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)  $\text{NaK}_2[\text{Fe}(\text{CN})_6]$  then you would use a prefix to give the number of potassium. This rule also applies to charge balancing anions. Dipotassium sodium hexacyano.....

**Example:**  $(\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O})$  would be called Potassium hexacyano.....here you do not need a prefix before potassium, because when you finish the naming you will know the complex charge and this will automatically tell you how many potassium you are meant to have.

\*\*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:**

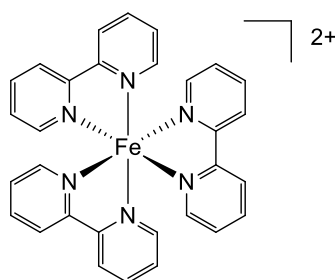


5. There are two possibilities for designating the charge or the oxidation state.

(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

**Example:**



= tris(bipyridine)iron(II)

=tris(bipyridine)iron (2+)

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

**Example:**  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  = tetraammineplatinum(II) = tetraammineplatinum(2+)

$[\text{PtCl}_6]^{2-}$  = hexachloroplatinate(IV) = hexachloroplatinate(2-)

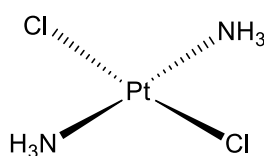
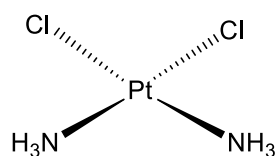
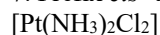
metal	changed to
cobalt	cobaltate
aluminium	aluminate
chromium	chromate
vanadium	vanadate
copper	cuprate
iron	ferrate
platinum	platinate
silver	argentate
gold	Aurate

**Exercise:** (A)  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

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.



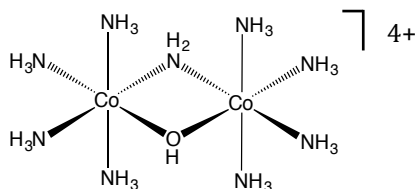
*cis*-diamminedichloroplatinum(II)

*trans*-diamminedichloroplatinum(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  $\Delta$  and  $\Lambda$  later in the course, which denotes different enantiomers of octahedral complexes. These are used in front of the name of coordination compound.

8. Bridging ligands between metal ions have the prefix " $\mu$ -"



$\mu$ -amido- $\mu$ -hydroxobis(tetraamminecobalt)(4+)

### Exercise to be done in groups:

Give chemical names for the following.

a.  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

tetraamminecopper(II) sulfate

b.  $[\text{PtCl}_4]^{2-}$

tetrachloroplatinate(II)

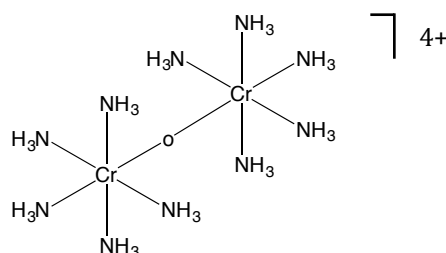
c.  $[\text{Co}(\text{en})_3]^{3+}$

tris(ethylenediamine)cobalt(III)

d.  $[\text{Cr}_2(\mu\text{-O})(\text{NH}_3)_{10}]^{4+}$  draw it and name it...

$\mu$ -oxo-bis(pentaamminechromium (III))

or  $\mu$ -oxo-bis(pentaamminechromium) (4+)



e.  $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$

$[\text{Ag}(\text{NH}_3)_2]$  is the cation +1 and  $[\text{Ag}(\text{CN})_2]$  is the anion -1.

diamminesilver(I)dicyanoargentate(I)

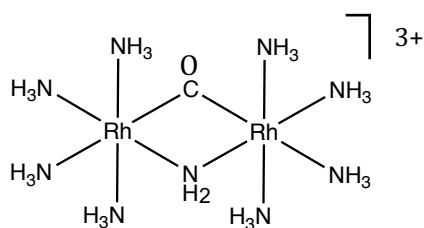
f.  $[\text{Fe}(\text{CO})_5]$

pentacarbonyliron(0)

g.  $[\text{Rh}_2(\mu\text{-CO})(\mu\text{-NH}_2)(\text{NH}_3)_8]^{3+}$  Draw it and name it.

$\mu$ -amido- $\mu$ -carbonylbis(tetraamminerhodium)(3+) or

$\mu$ -amido- $\mu$ -carbonylbis(tetraamminerhodium(II))



## 6. Isomers

Due to the vast number of coordination environments, there are a large number of isomers. As the coordination number goes up so does the number of possible isomers. For this course, we will focus on isomers related to coordination compounds and mostly those related to 4-coordinate and 6-coordinate complexes as these are in deed the most common. I would like for you to know the different types of isomers and also be able to identify the isomers for a selected chemical formula. You should be able to draw the complexes and then draw the isomers. Hopefully in the coming practice sessions you will get a bit of experience with this.

**Isomers** are two or more complexes having the same chemical compositions but different chemical and physical properties.

Isomers can be classified as constitutional isomers and stereoisomers. For two or more coordination compounds with identical chemical formula.

if all the chemical bonds are the same between the M and L, then they are **stereoisomers**. Stereoisomers have the same ligands but different geometric arrangements.

If not all the chemical bonds are between the same atoms, then they are **constitutional isomers (aka structural isomers)**.

**Constitutional or structural Isomers:** There are 4 kinds in coordination chemistry

### (a) **Hydrate or solvent isomer**

Hydrate isomers exist for complexes that have water either as a ligand or as an added part of the crystal structure. The standard example is  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . Three distinct crystalline compounds exist with the same formula. They are:

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet)

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (blue-green)

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green)

These are hydration isomers.

These complexes have optical properties that vary significantly.

**\*\***The ions in the outer sphere of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  are much more easily exchanged than those in the inner sphere. If you had these dissolved in water you could perform a precipitation reaction with silver nitrate you would see different results for these compounds. So silver(I)chloride, which has minimal solubility in water, precipitates out. In the first compound, 3 moles of silver chloride precipitates, in the second 2 moles of silver chloride precipitates, and in the 3<sup>rd</sup> 1 mole of silver chloride precipitates.

**\*\***complexes with varying number of hydration are not considered to be hydration isomers.  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  are known, but their chemical formulas are different.

### (b) **Ionization isomers**

Compounds with the same formula but give different ions in solution, exhibit ionization isomerization. The difference is in which ion is included as a ligand and which is presented to balance the overall charge.

Examples.

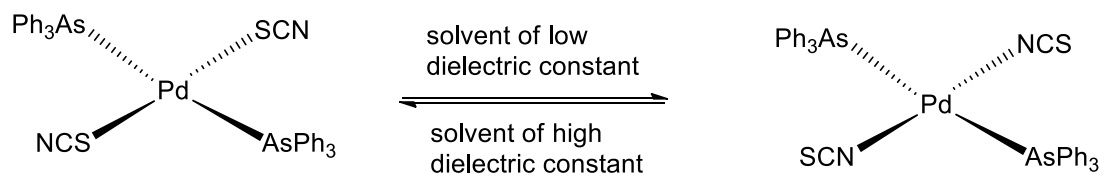
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{Cl}$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$

$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$

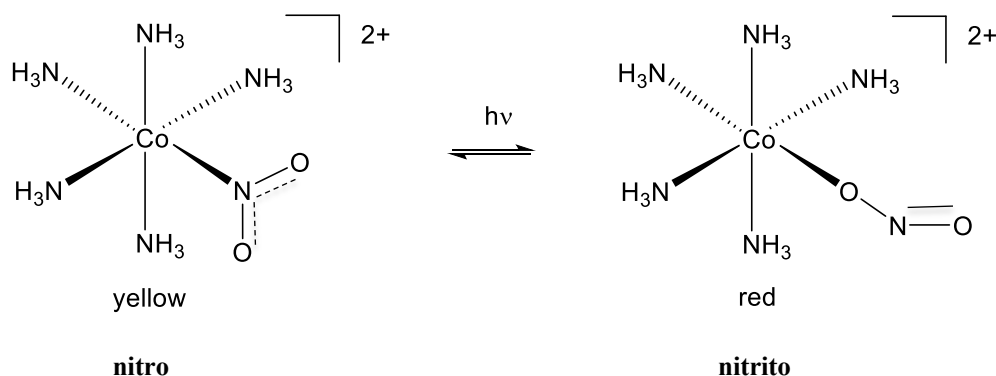
**\*\***These have different ions in their outer sphere. Because the ions in the outer sphere have ionic interactions with the charged complex, if dissolved in solution they will not be attached to the coordination sphere and as such would go off in solution and could be readily precipitated out.

### (c) **Linkage isomers**

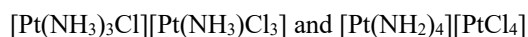
Some ligands can bind to the metal through different atoms. For example, thiocyanate ( $\text{SCN}^-$ ) can bond to metal through either S or N, and are called thiocyno or isothiocyno respectively. Nitrite ( $\text{NO}_2^-$ ) can bond to metal through either N or O called nitro or nitrito, respectively. These ligands which referred to earlier as **ambidentate**.



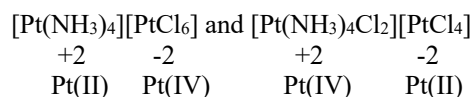
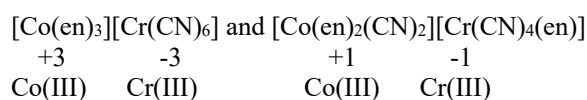
What is the reason the solvent dictates the coordination of the SCN ligand?



**(d) Coordination isomers** - compounds containing complex anionic and cationic parts can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part. To have coordination isomers, the complexes have at least two metal ions. The total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. This is best described by example.



Can be composed of the same metal and oxidation state, different metals (with the same or varying oxidation state), or same metal in different oxidation states. See below for 2 examples:



*In general*, for constitutional isomerism, it is not important to know exactly what kind of isomerism the isomers belong to. It is however important to be able to know whether two or more complexes are isomers, and to draw the structures of possible isomers if you are given a chemical formula.

### Exercise.

Which of the following pairs are isomers and what kind are they?

- $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Br}$  and  $[\text{Co}(\text{H}_2\text{O})_4\text{ClBr}]\cdot\text{H}_2\text{O}$  hydration isomer
- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$  ionization isomer
- $[\text{Co}(\text{NH}_3)_6]\text{ClBr}$  and  $[\text{Co}(\text{NH}_3)_6]\text{BrCl}$  not an isomer...it is the same compound

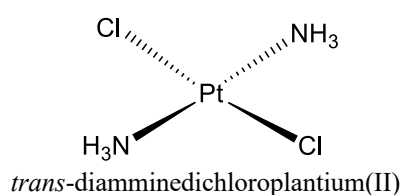
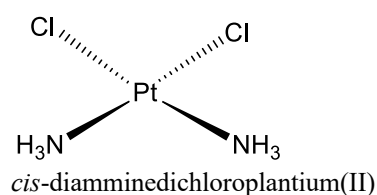
**Stereoisomers** - have the same M-L bonds but different spatial distributions.

Stereoisomers in coordination chemistry are molecules with identical chemical composition and have the same bonds between the atoms. They can be classified as **Diastereomers or geometric isomers** and **enantiomers**. If each isomer is identical to its mirror image, then they are geometric isomers. If each isomer is not identical to its mirror image, then they are enantiomers.

(a) **Diastereomers or geometric isomers** - a set of molecules that have different spatial distributions but are not mirror images of one another.

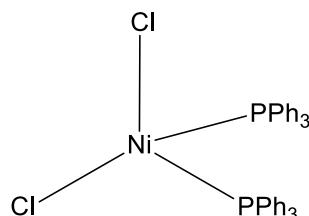
Cis/trans-isomers and facial/meridional isomers are the most common geometric isomers. Let's look at 4- and 6-coordinate compounds.

For 4-coordinate complexes, if two of the ligands are the same, then there are two situations. For square planar complexes, there are the possibilities of having *cis-trans*-isomers.



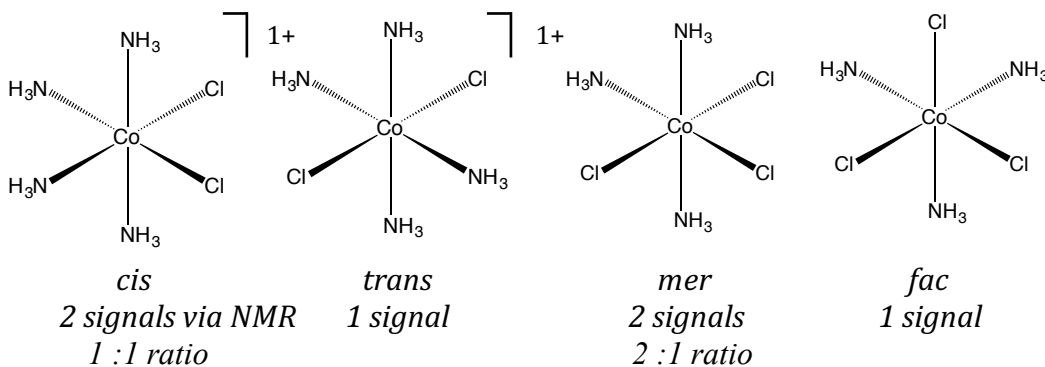
The *cis/trans* isomers can have very different properties. For example, *cis*-diamminedichloroplatinum(II) is an anti-cancer agent, while *trans*-diamminedichloroplatinum(II) has no anti-cancer activity.

For tetrahedral complexes, there is no possibility of having *cis-trans*-isomers.

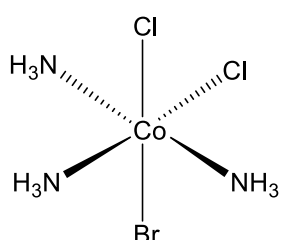


So if we consider 6-coordinate compounds there are two types of geometric isomers, the ones you considered before *cis* and *trans* and also *fac* or *mer*. [MX<sub>2</sub>Y<sub>4</sub>] and [MX<sub>3</sub>Y<sub>3</sub>] For 6-coordinate complexes, if three ligands are the same, it is possible to have facial-/meridional isomers.

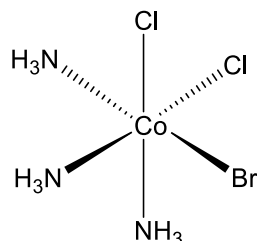
**Exercise:** Draw tetraamminedichlorocobalt(III) and triamminetrichlorocobalt(III)



For these isomers if you could probe the ligands via NMR you would see that all are equivalent with the exception of the *cis* and *mer* isomer (*mer* = meridional). For NMR for instance *mer* would have two signals for  $\text{NH}_3$ , where as *fac* (*fac* = facial) would have 1 signal because the 3 ammines are the same. For the *cis*, there are two different  $\text{NH}_3$  while for *trans* there is only 1.

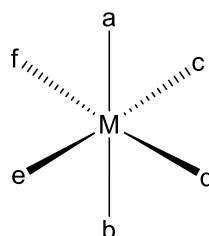
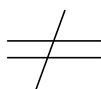
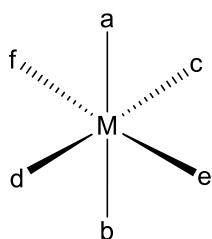


meridional isomer  
*mer*-

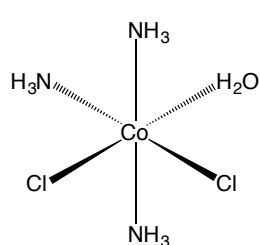


facial isomer  
*fac*-

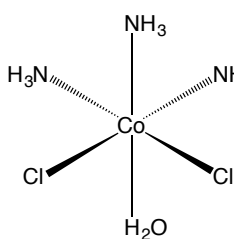
The following are also geometric isomers:



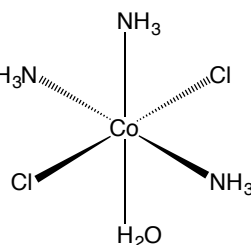
**Exercise:** Write the possible geometric isomers for  $[\text{Co}(\text{NH}_3)_3\text{Cl}_2(\text{H}_2\text{O})]$  and name them.



*mer*  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  
*cis*  $\text{Cl}$



*fac*  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  
*cis*  $\text{Cl}$



*mer*  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  
*trans*  $\text{Cl}$

*mer*-triammineaqua-*cis*-dichloro cobalt (II)

*fac*-triammineaquadichlorocobalt (II)

*mer*-triammineaqua-*trans*-dichlorocobalt (II)