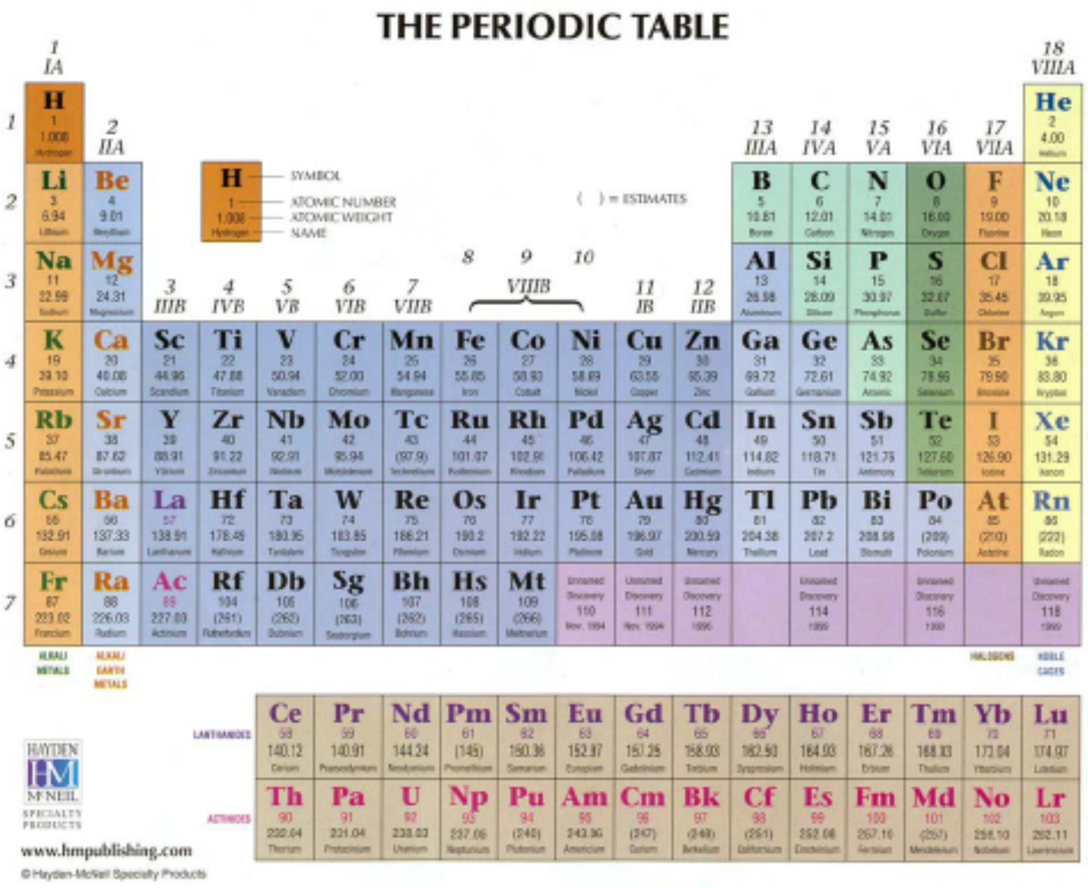
Lecture Notes:

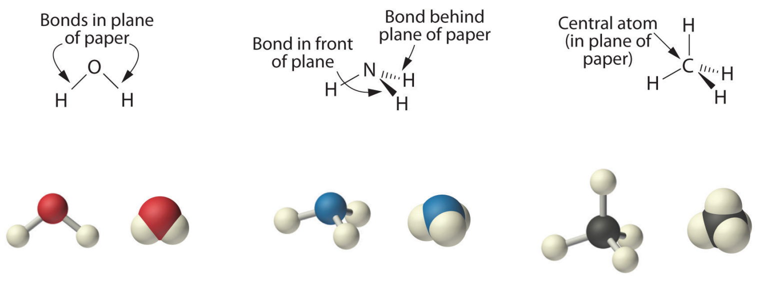
Chapter 1: Coordination Complexes: Definitions, Structure, Nomenclature, and Isomers

Important dates:
Quiz 30% of your grade scheduled on April 9th, 2025
Final exam 70 % of your grade on May 28th, is the final exam, last day of the class



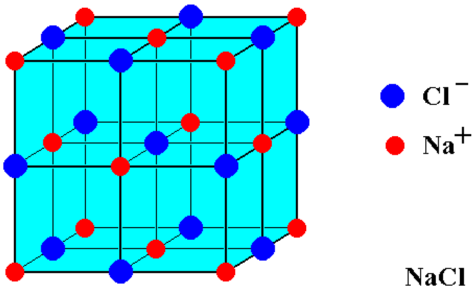
1. Coordination Bonding vs Ionic and Covalent

Covalent Bonding: In your previous courses you have likely learned about traditional covalent compounds that consist mainly of nonmetals like C, N, O, H and S. Some examples are below. These materials usually consist of elements that have minimal differences in their electronegativity and hence they share their valence electrons in orbitals a type of bonding that is referred to as covalent type bonding.



(a) Water, H_2O (b) Ammonia, NH_3 (c) Methane, CH_4

Ionic Bonding: Such materials are largely ionic in nature, where you have alkali and alkaline earth metals and nonmetals where electrons are actually exchanged for example in the case of Na^+Cl^-, which gives rise to extended salt-like solids. These materials have arrays of spheres that are packed in a variety of different ways that are dependent on the size and charge of the ions involved.



Coordination bonding: occurs between a ligand and a metal, where the ligand donates electron density to the metal

These form **Coordination compounds**: a compound that consists of a metal or metal-ion and one or more ligands that donate electrons to the metal. Within the coordination compound there are **coordination spheres** or **complexes** that are found in square brackets $[ML_x]^n$

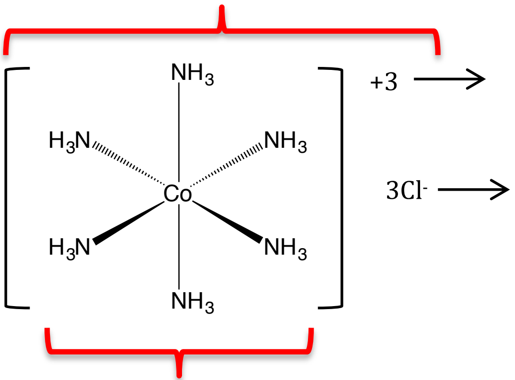
The metal can be positive, negative, or neutral.
The ligand can also be an ion or a molecule so it can be positive, negative, or neutral.
More often than not, metals are positive and ligands are either negative or neutral

Coordination complexes are alternatively called **Lewis acid/base** pairs, meaning the metals are the electron acceptors (Lewis acid) and the ligands are the donors (Lewis base). I remember this relationship by the phrase "Lewis acid accepts". The coordination compounds can be complexes or complex ions if charged.

Some examples of coordination complexes include the following:

1). $[Co(NH_3)_6]Cl_3$ This coordination complex is ionic and so it has an inner complex. This complex is known to be **homoleptic** – this means that all of the ligands are the same. **Heteroleptic** means they are different.

Coordination compound includes the ligand, metal, and counter ions.



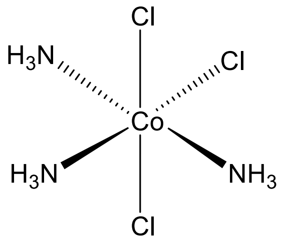
Charge of coordination sphere

Counter ions are readily exchanged without changing any coordination bonding within the inner sphere.

Coordination sphere or complex, found in brackets is the ligand attached to the metal

Coordination number is the number of ligands attached to the metal, in this case it is 6.

2). $[Co(Cl)_3(NH_3)_3]$



Lewis acid or Metal: Co

Lewis base or Ligands: NH_3, Cl^-.

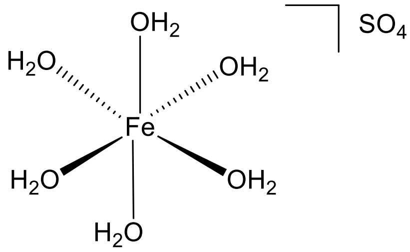
Charge of complex: 0 (neutral)

The bonds "Co-Cl", "Co-NH_3" are called **Coordination Bonds**.

In this complex, ligands (Cl^- and NH_3) donate electrons to Co by lone-pair electrons.

Coordination Number: 6

Another example.



Write the formula $[Fe(H_2O)_6]SO_4$

Lewis acid or Metal: Fe.

Lewis base or Ligands: H_2O

Metal oxidation state: 2+

Counter ion: SO_4^{2-} (anion)

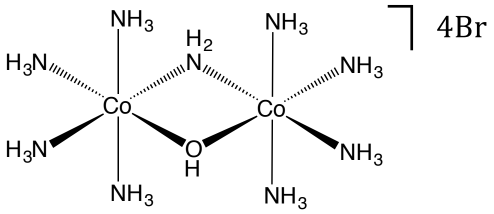
Charge of complex: 2+ (to keep the whole compound neutral)

The complex is positively charged.

Fe, six H_2O, and the six Fe-OH_2 coordination bonds constitute a **Coordination Sphere**. One can say that the coordination sphere is +2 charged.

Coordination Number :6

Exercise 1. Poll 1



(1) Is it a coordination compound? Yes

(2) What are the ligands for each Co center? Cl^-, NH_3, NH_2^-

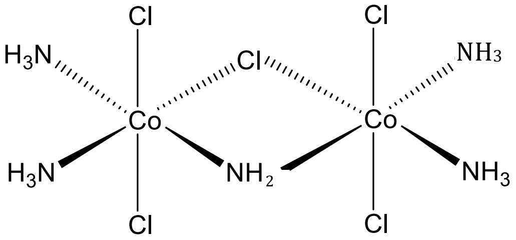
(3) What is the coordination numbers for each Co center? 6

(4) What is the charge of the coordination sphere?4+

(5) What is the chemical formula of the coordination sphere? $[Co_2(\mu\text{-}NH_2)(\mu\text{-}OH)(NH_3)_8]^{4+}$

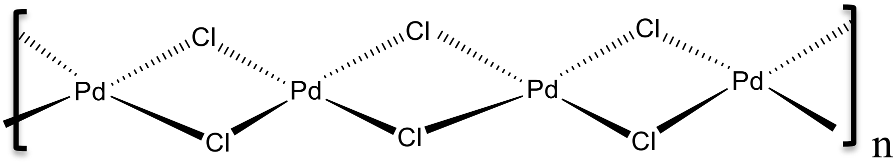
By definition, even the polymeric compound $PdCl_2$ is a coordination compound. There are infinite numbers of metal centers in $PdCl_2$ as the chain extends infinitely. Most studies in coordination chemistry however deal with complexes with finite numbers of metal centers, except in the field of "coordination polymers".

Exercise 2.



(1) Is it a coordination compound? Yes
(2) What are the ligands for each Co center? Cl^-, NH_3, NH_2^-
(3) What is the coordination numbers for each Co center? 6
(4) What is the charge of the coordination sphere? 0
(5) What is the chemical formula of the coordination sphere? $[Co_2(\mu\text{-}NH_2)(\mu\text{-}Cl)(NH_3)_4Cl_4]$

Exercise. 3 Poll 2



Is it a coordination compound? Yes
(2) What are the ligands for each Co center? Cl^-
(3) What is the coordination numbers for each Pd center? 4
(4) What is the charge of the coordination sphere? 0

*One note is that there are compounds that are expressed in a bit different terms:

If you buy cobalt chloride from Sigma Aldrich, it is expressed as $CoCl_2{\cdot}6H_2O$, and this gives you no reflection of the coordination complex as it is actually $[CoCl_2(H_2O)_4]$. This complex is neutral but it has 2 extra water molecules that crystalize in the solid that is referred to as **lattice solvent** or **solvent of crystallization.**

2. Metals, their oxidation states and d electron counting

Oxidation state is a parameter that describes the number of electrons lost or gained in the formation of a compound. It can be +, -, or zero.

For a complex $[ML_x]^n$, that is, a complex with a metal center coordinated by x number of ligands, and with an overall charge of n, the following equations are valid:

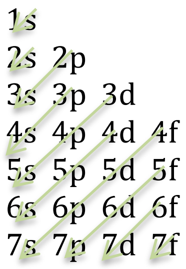
Oxidation State (O.S.) of metal + overall charge of L_x = n (1.1)

Number of **valence electrons** of metal = group number (periodic table) – O.S. (1.2)

Example.
$[Co(NH_3)_6]Cl_3$
Oxidation state = +3 – charge of ligands (which is 0); then oxidation state is 3+
Group 9 – 3 (oxidation state) = 6 valence electrons

You should know how to write out electronic configurations.

Easy way to determining the electronic configuration:



Examples:

What is the electronic configuration for Ti metal:
Atomic number is 22 so $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$
A short hand way of doing this is $[Ar]\ 4s^2\ 3d^2$

What is the electronic configuration for Pd^{2+}?
Atomic number is 46
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^8$ and short hand is $[Kr]\ 5s^2\ 4d^8$
but I asked for the 2+ oxidation state so the ion lost two electrons so remove two from the 5s shell and you have $[Kr]\ 5s^0\ 4d^8$

Exercise 4

Give the electronic configuration of V^{2+}
Answer: $V^{2+} = [Ar]\ 4s^0\ 3d^3$
V metal has atomic number of 23 so V^{2+} is 21
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

Give the electronic configuration of Cu^{3+}
Cu metal has atomic number of 29 so Cu^{3+} is 26
Answer: $Cu^{3+} = [Ar]\ 4s^0\ 3d^8$

Give the electron configuration of Mn in $K[MnO_4]$
Answer: Mn^{7+} So $= [Ar]\ 4s^0\ 3d^0$

Below is a table that I made you showing most of the oxidation states observed for first-row transition metals. The common oxidation states in red and less common oxidation states in grey. Further, the first row shows the electronic configuration of metals in their 0 oxidation state. As you remove electrons or **oxidize** (meaning to lose electrons) the metals you first remove electrons from the 4s shell. You should note that the ground state configuration for Cr and Cu are unique. Electrons are promoted from the 4s subshell to the 3d shell in order to obtain very stable half-filled or filled d orbitals.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$[Ar]4s^2 3d^1$	$[Ar]4s^2 3d^2$	$[Ar]4s^2 3d^3$	$[Ar]4s^1 3d^5$	$[Ar]4s^2 3d^5$	$[Ar]4s^2 3d^6$	$[Ar]4s^2 3d^7$	$[Ar]4s^2 3d^8$	$[Ar]4s^1 3d^{10}$	$[Ar]4s^2 3d^{10}$
		+1 d^3	+1 d^5	+1 d^5	+1 d^6	+1 d^7	+1 d^8	+1 d^{10}	
	+2 d^2	**+2** d^3	**+2** d^4	**+2** d^5	**+2** d^6	**+2** d^7	**+2** d^8	**+2** d^9	**+2** d^{10}
+3 d^0	+3 d^1	**+3** d^2	**+3** d^3	**+3** d^4	**+3** d^5	**+3** d^6	+3 d^7	+3 d^8	
	+4 d^0	**+4** d^1	+4 d^2	**+4** d^3	+4 d^4	+4 d^5	+4 d^6		
		+5 d^0	+5 d^1	+5 d^2	+5 d^3	+5 d^4			
			+6 d^0	**+6** d^1	+6 d^2	+6 d^3			
				+7 d^0					

There is no simple rule for oxidation states!! Familiarize yourself with the above table. ☺

For transition metal oxidation states, the following are some general ideas:

1). Unlike group 1 and 2 elements, which are typically 1+ and 2+, respectively, the d-block elements have a wide array of different oxidation states. These can lend to rich structural and physical properties.

- many different coordination environments
- rich electronic properties
- participate in catalytic reactions

- have important roles in biological processes

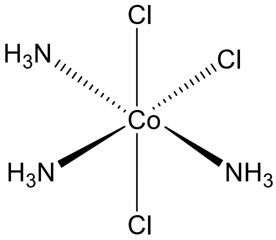
2). As a general rule 4s electrons are removed first so the d electron configuration stays the same up through the 2+ oxidation state.

3). The larger the number of unpaired d-electrons, the higher the potential oxidation state b/c unpaired electrons are unstable. Notice the left-hand side of the periodic chart from Sc to Mn (d^1 to d^5). These all can be fully oxidized.

4). +2 and +3 oxidation states are the most common

Exercise 5

1). What are the oxidation states and numbers of valence electrons of the metal centers in the following complexes? Write out the electron configuration, short hand.



Answer: It is Co^{3+}. The chloro ligand is -1 and the ammine ligand is neutral. Electronic configuration for Co^{3+} is $[Ar]4s^03d^6$
6 valence electrons

(2) $[Fe(H_2O)_6]SO_4$

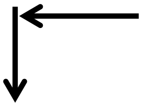
Answer: $[Ar]4s^03d^6$
Oxidation state +2
6 valence electrons

3. Geometries & coordination numbers

Of the examples, most have coordination numbers of 6. However, with transition metals the number of coordinating ligands and the geometries formed can vary quite a lot.

So the main factors that influence the coordination number include:

(1) The size of the metal atom or ion. This trend is metal or ion size increases from right to left and down the periodic chart.



(2) Steric interactions between ligands. Bulky ligands take up a lot of space around metals limiting their ability to support large coordination numbers as there is repulsive interactions that limit approachability to the metal.

(3) Electronic Interactions. Small numbers of d-electrons support large coordination numbers while large numbers of d-electrons support lower coordination numbers. Given that metals on the left side have fewer d electrons and also can be readily oxidized, these early transition metals tend to support larger coordination numbers.

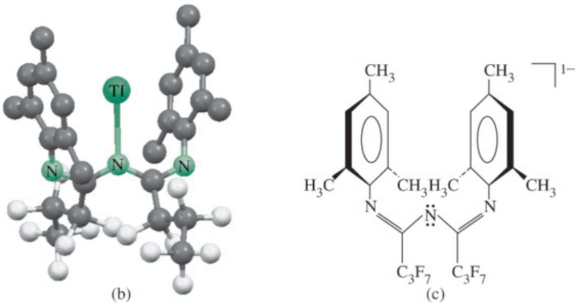
Ex). $[Mo(CN)_8]^{4-}$ and $[PtCl_4]^{2-}$
Mo4+ = 38 electrons   Pt2+ = 76 electrons
$[Kr]\ 5s^0\ 4d^2$ $[Xe]\ 6s^0\ 4f^{14}\ 5d^8$

The coordination number of a complex can range from 1 to more than 10. Among all coordination compounds, 6-coordinate complexes are the most abundant.

- Coordination number of 1

It is very rare to see a complex with a coordination number of 1. They normally have huge ligands. There are a couple of Thalium and Indium complexes reported.

Example) coordination complex with the triazapentadienyl ligand



- Coordination number of 2

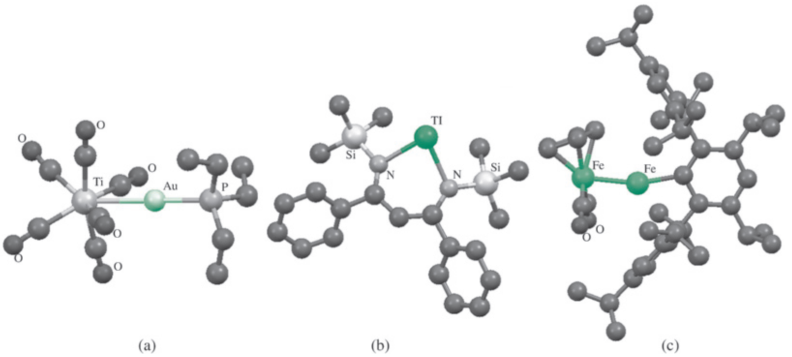
There are not many complexes with a coordination number of 2. The 2-coordinate complexes are mostly d^{10} metal complexes. The reason is they have a large number of electrons and are less likely to want to support very large coordination numbers. Also, large bulky ligands can be used to generate Coordination number =2. The geometry is **linear**.

$[H_3N-Ag-NH_3]^+$

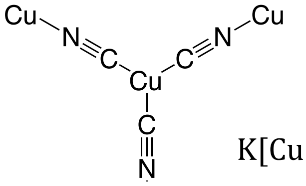
$[Cl-Cu-Cl]^-$

$NC-Hg-CN$

$[CN-Au-CN]^-$



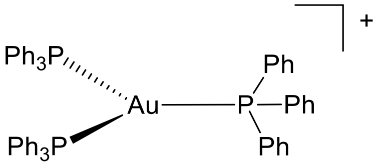
* There are a number of coordination compounds that appear to have a CN = 2 based on their chemical formulas. An example is K[Cu(CN)$_2$]. However, this is a polymeric compound with the coordination number of 3. Coordination Polymer- extends infinitely along Cu-CN bonds.

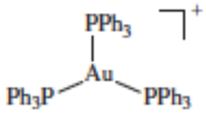


K[Cu(CN)$_2$]

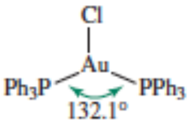
- <u>Coordination number of 3</u>

Again, this coordination number is rare and often metal halide complexes appear to be 3-coordinate based on their chemical formula, but they are actually polymeric compound as the halides bridge metal ions. The metal centers in 3-coordinate complexes often have 10 d electrons. The most common geometry is **trigonal planar**. Typical L-M-L bond angle is 120 º, however these can deviate due to bulky ligands.



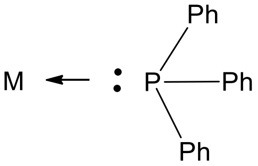


[Au(PPh$_3$)$_3$]$^+$



Au(PPh$_3$)$_2$Cl

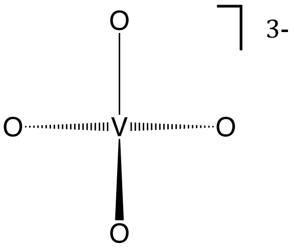
The ligand, PPh$_3$, is triphenylphosphine. PR$_3$, where R is an organic group, is called phosphine. It is a very important class of ligand. It is a neutral ligand, and it donates the lone-pair electrons on the phosphorus to the metal center. These are extremely popular in catalysis because they are readily soluble in organic solvents (unlike many N containing complexes) and they are stable with metals in many oxidation states. Most popular phosphine ligand is the triphenylphosphine because it has a long shelf life (undergoes oxidation very slowly)

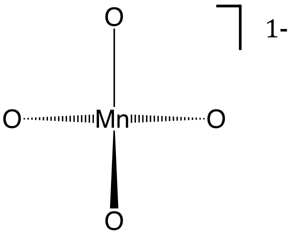


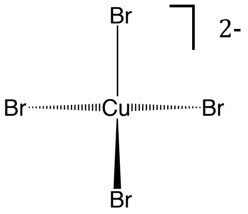
- <u>Coordination number of 4</u>

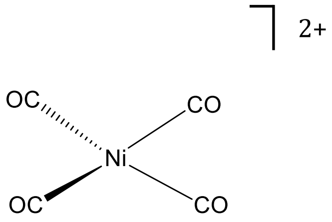
These are the second most common class of complexes. For 4-coordinate complexes, the two most common geometries are **square planar** and **tetrahedral**. Tetrahedral complex is favored if the metal is small and ligands are large. It is very common for oxoanions of transition metals, typically those on the left side of the periodic chart (known as early transition metals) and also halide complexes on the right side. O-V-O angle is 109.5 º just like 4-coordinate organic compounds like methane. The tetrahedral geometry optimizes the distance between neighboring ligands due to the larger bond angle.

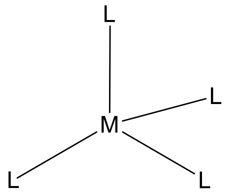
Tetrahedral: an example is $K[MnO_4]$ the metal is fully oxidized and so is isoelectronic with [Ar]. The $[MnO_4]^{1-}$ complex and others are shown below.







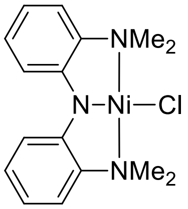




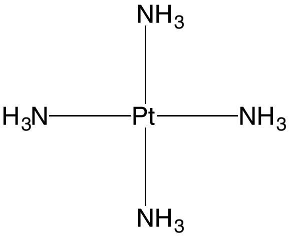
Here, CO is a carbon monoxide ligand. It is neutral, and is often called "carbonyl". It is a common ligand and very important for your Organometallic Chemistry class.

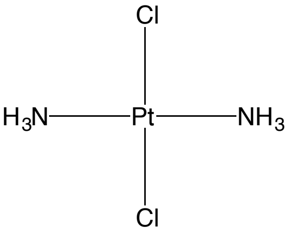
Square planar the L-M-L angles are 90º and 180º: Sq. Planar can also be forced on a metal with certain ligands that are planar and have 4 connecting points. A good example are porphyrins (shown later) and pincer ligands.

One example is below:

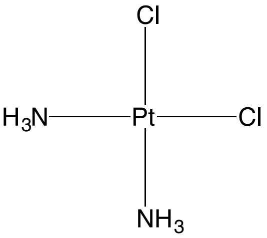


nickamine – what is known as a pincer complex, which contains a ligand that binds a metal in 3 adjacent coplanar spots, it is tridentate. The great thing about the ligand is that it is quite rigid and so it inhibits metalocyclization and hence the deactivation of the complex. These types of ligands have been studied quite extensively.





trans-platin



cis-platin

Square planar complexes are common for metals with d^8 electrons. You will understand more of why when we go Crystal field theory. These include Ni^{2+}, Rh^+, Ir^+, Pd^{2+} and Au^{3+}. 4th and 5th row transition metals with d^8 electronic configurations are almost invariably square planar.

For tetrahedral you can have only one spatial arrangement of atoms, where as for square planar materials you can have two, which is illustrated with the above *cis* and *trans* isomers.