


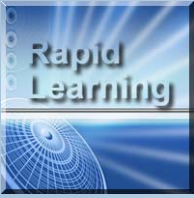
 **Rapid Learning Center**
Chemistry :: Biology :: Physics :: Math 

Rapid Learning Center Presents ...

Teach Yourself
Inorganic Chemistry in 24 Hours




1/68 <http://www.RapidLearningCenter.com> 

 **Introduction to
Coordination
Chemistry**

Inorganic Chemistry Rapid Learning Series

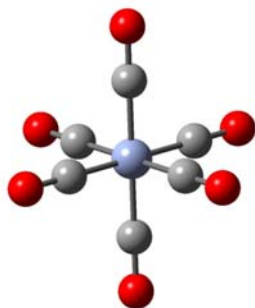
Wayne Huang, PhD
Larry Pratt, PhD
Dru DeLaet, PhD
Andrew Graham, PhD
Kelly Dempewolf, PhD

Rapid Learning Center
www.RapidLearningCenter.com/
© Rapid Learning Inc. All rights reserved. 



Learning Objectives

By completing this tutorial, you will learn about:

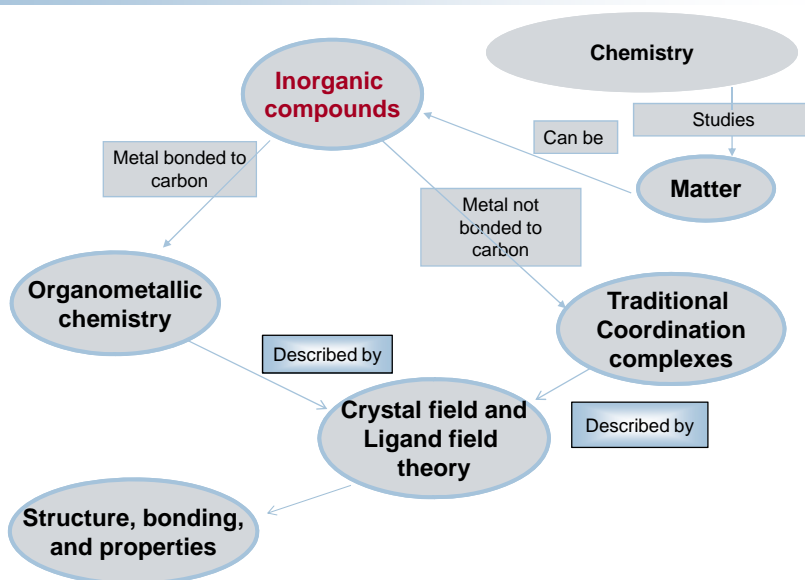


- Historical background
- Nomenclature of coordination compounds
- Constitutional isomers
- Stereoisomers
- The octet rule
- The 18 electron rule
- Crystal field and ligand field theory
- Complexes with common coordination numbers

3/68



Coordination Chemistry Concept Map



4/68





Basic Concepts and Definitions



1. Coordination compounds and nomenclature
2. Isomers
3. The octet and 18 electron rules
4. Crystal Field Theory and Ligand Field Theory
5. Complexes with common coordination numbers



What are Coordination Compounds?

A **Coordination Compound** or Coordination Complex is a compound of a metal and ligands. A ligand can be thought of as an atom, ion, or molecule that donates both electrons of the bond to the metal. However, the bonding may be more complex than this simple model suggests.

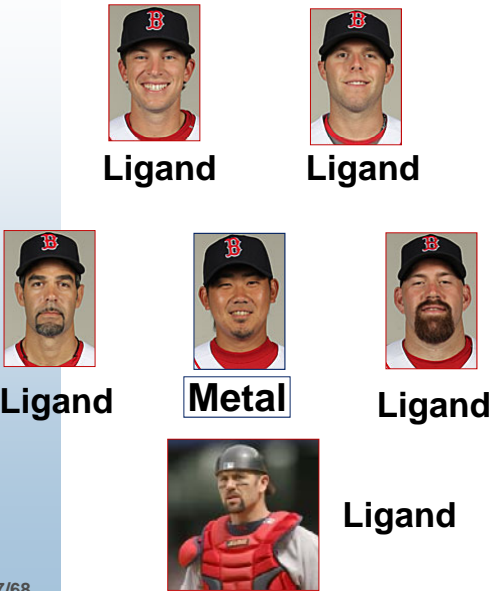


The metal-ligand bond is often polar but it usually has a substantial amount of covalent character.

6/68




➤ Analogy to Baseball



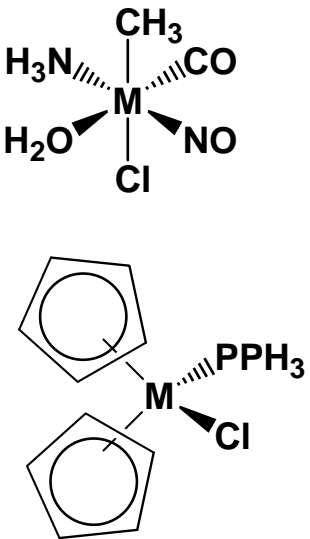
If a baseball pitcher was a metal, he would be surrounded by 5 **ligands**.

The ligands are, counterclockwise from the bottom, the catcher, 1st baseman, 2nd baseman, shortstop, and 3rd baseman.


Thus, the pitcher is a pentacoordinate coordination compound.

7/68 

➤ Some Common Ligands



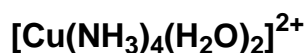
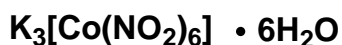
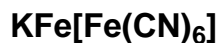
- Water, ammonia, some other solvents
- Halogens, Hydroxide
- CO
- Alkyl and aryl groups
- Polydentate alkenes and aromatics: benzene, allenyl, and cyclopentadienyl (Cp)
- Phosphines
- Amines and polyamines

8/68 

➤ Historical Background - 1

Coordination compounds have been known since ancient times but their structures remained unknown. An entrenched idea was the concept that a metal has a fixed valence. CoCl_2 and CoCl_3 were known, but not CoCl_4 , for example.

Therefore, Co was believed to have a valence of 2 or 3, and cobalt should accommodate a maximum of 3 ligands.



Colored coordination compounds known in the 1800's or earlier.

9/68

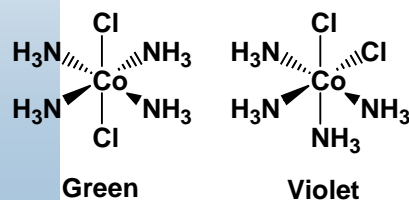


➤ Historical Background - 2



Metal complexes were known. **Alfred Werner** proposed that cobalt could be bonded to 6 ligands.

The green trans complex was known, but its structure was not.



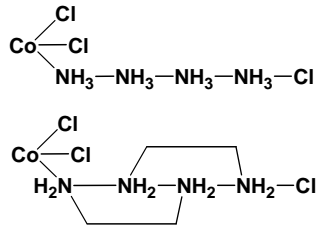
The violet cis complex had not yet been discovered. The traditional way of thinking, led by S. M. Jorgensen, believed that the ammonias formed chains.

10/68



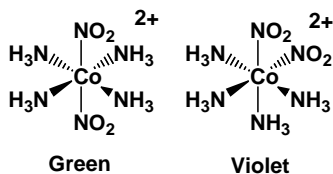


Historical Background - 3



Jorgensen argued for ligand chains, sometimes involving chain isomers.

He argued that two isomers of $\text{Co}(\text{NH}_3)_4\text{Cl}_2$ should be formed but only one isomer was known.



Werner synthesized green violet isomers of $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^{2+}$. Jorgensen argued that one isomer was Co-N bonded and the other was Co-O bonded. In 1907 Werner synthesized cis $\text{Co}(\text{NH}_3)_4\text{Cl}_2$. This proved his coordination theory.

11/68

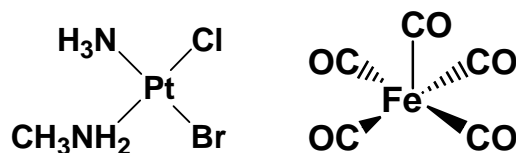


Nomenclature - 1

Simple coordination compounds are named with the ligands in alphabetical order, followed by the metal. Prefixes di-, tri-, etc. indicate the number of ligands of the same type. These prefixes do not count towards alphabetizing.

The oxidation number of the metal may be given by a Roman numeral.

Pentacarbonyliron, also known as Iron pentacarbonyl
Amminebromochloromethylamine-platinum (II).



12/68



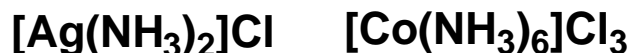


Nomenclature - 2

Complexes that consist of ions are written as the cation first, then the anion.

Inner sphere ligands, those connected directly to the metal, are placed with the metal in square brackets. The cation is named as though it were a simple complex.

Diamminesilver (I) chloride. Note that ammonia is named ammine, not amine.
Hexaamminecobalt (III) chloride.



13/68

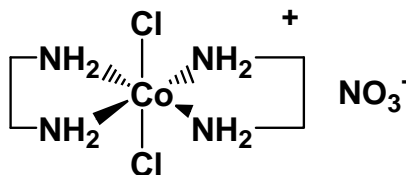


Nomenclature - 3

Prefixes to indicate the number of ligands are usually di, tri, tetra, penta, hexa, hepta, octa, ...

If the ligand name includes these prefixes, or is especially complex, an alternate set is used for naming the complex: Bis, tris, tetrakis, pentakis, hexakis, heptakis, octakis, ...

Dichlorobis(ethylenediamine)cobalt(III) nitrate.



14/68

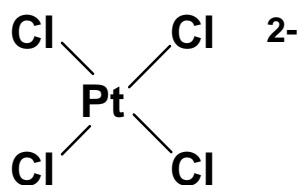




Nomenclature - 4

The **more common convention** is to indicate the metal oxidation number by a roman numeral. Alternatively, the charge of the metal-containing fragment can be indicated in parentheses after the name.

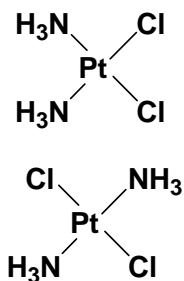
If the charge is negative, the suffix **-ate** is added. Tetrachloroplatinate (II) or tetrachloroplatinate (-2).



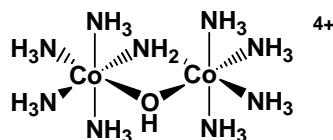
15/68



Nomenclature - 5



The **prefixes** *cis* and *trans* are used to indicate adjacent or opposite coordination sites. *Cis* (top) and *trans* (middle) diamminedichloroplatinum (II).



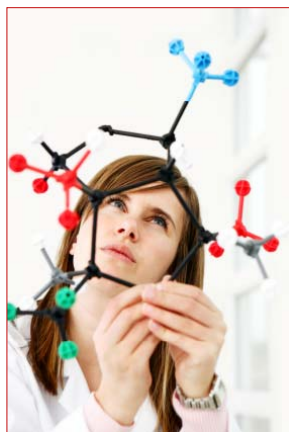
Bridging ligands between 2 metals are given the prefix μ -. μ -Amido- μ -hydroxo-bis(tetramminecobalt)(4+).

16/68





Nomenclature - 6



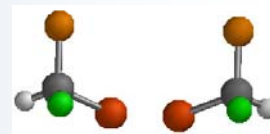
Negatively charged complexes are sometimes given alternate names: Ferrate (Fe), plumbate (Pb), stannate (Sn), aurate (Au), argentate (Ag).

Examples: Hexacyanoferrate (II), hexacyanoferrate (III), dicyanoaurate (1), tetrachlorostannate (-2).

17/68



Isomerization in Coordination Compounds



1. Isomers are different compounds with the same molecular formula.
2. We will examine different kinds of isomers that are commonly found in coordination chemistry.



➤ Isomers

1 (np. 65°) 2 (np. 60°) 3 (np. 63°)

4 (np. 60°) 5 (np. 65°)

Isomers are two different compounds with the same molecular formula. The word isomer comes from the Greek words meaning “same parts”.

Constitutional isomers have the atoms connected differently. Stereoisomers have the same connectivity but the atoms are oriented differently in space.

19/68 💡

? Question: Challenge

With respect to coordination sites, what do *cis* and *trans* stand for?

The prefixes *cis* and *trans* are used to indicate adjacent or opposite coordination sites. For example, *cis* (top) and *trans* (middle) diamminedichloroplatinum (II).

20/68 💡



Constitutional Isomers



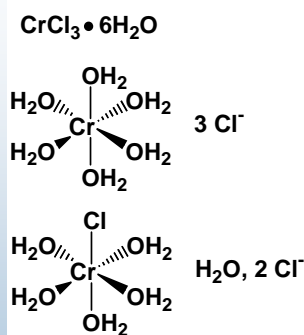
The following types of **constitutional isomers** are common in coordination chemistry:

Hydrate isomers, Ionization isomers
 Coordination isomers, Linkage isomers - Each of these will be discussed in detail.
 In addition, the ligands themselves can sometimes exist as constitutional isomers, such as butyl and isobutyl.

21/68



Hydrate Isomers



Other isomers are also possible.

Many **metal salts** exist as hydrates. Several isomers of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are possible. They differ in which atoms are directly bonded to the metal.

Two of the isomers are shown. The first binds all 6 water molecules to the metal. The 3 chloride ions are outside the inner coordination sphere.

In the second example, one Cl is attached to the metal. These isomers (and others) have different colors.

22/68





Ionization Isomers

Ionization isomers are compounds with the same molecular formula which generate different ions in solution.

One or more ions act as ligands, and one or more ions balance the overall charge.
Ionization isomers interchange those two roles.



23/68

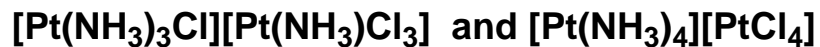


Coordination Isomers

Coordination isomers need two or more metal atoms. The ligands are arranged on the metal atoms differently in the different isomers.

Diamminedichloroplatinum, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, can exist as cis or trans isomers. Its dimer can also exist as a pair of coordination isomers, differing in which ligands are attached to each platinum atom.

The second example involves Pt(II) and Pt(IV) in the same complex.



24/68



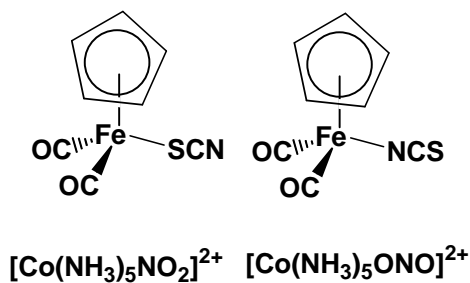


Linkage Isomers

Some ligands can bond to the metal through more than one atom.

Thiocyanate ion, SCN can bind via S or N. The result is a pair of linkage isomers, sometimes called ambidentate isomers.

The nitrite ion, NO₂⁻, can also bind via N or O.



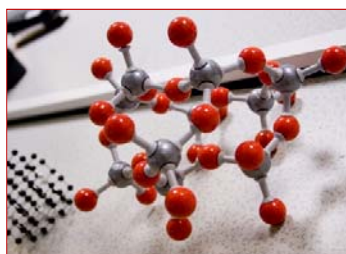
25/68



Stereoisomers

In contrast to constitutional isomers, **stereoisomers** differ only in the orientation of the atoms in space.

Enantiomers are isomers that are non-superimposable (not identical) mirror images of each other.



Stereoisomers that are not enantiomers are called diastereomers.

Cis and *trans* isomers are examples of diastereomers.

26/68





Stereoisomers of Common Coordination Numbers

The possible **stereoisomers of all coordination compounds** are too numerous to list. However, a few geometries are particularly common in coordination chemistry, and these have characteristic types of stereoisomers.



Tetrahedral, Square planar, and Octahedral.

27/68



Question: Challenge

What is an ionization isomer?

Ionization isomers are compounds with the same molecular formula which generate different ions in solution. One or more ions act as ligands, and one or more ions balance the overall charge. Ionization isomers interchange these two roles.

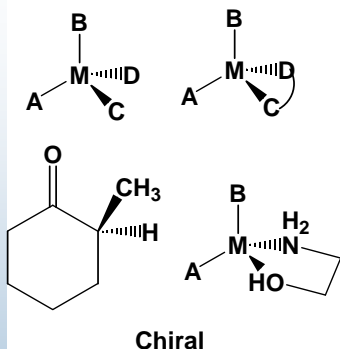


28/68



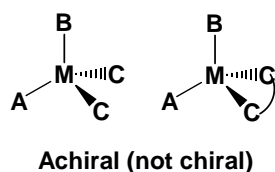


Stereoisomers of Tetrahedral Complexes



Tetrahedral complexes are analogous to the tetrahedral carbon of most organic compounds.

A carbon or metal atom is a chiral center (asymmetric center, stereogenic center) if it is attached to 4 different groups.

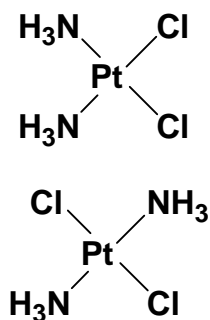


The different groups can be two sides of an unsymmetrical ring. This includes chelated complexes.

29/68



Stereoisomers of Square Planar Complexes



Cis and trans isomers are common in square planar complexes. These isomers are diastereomers.

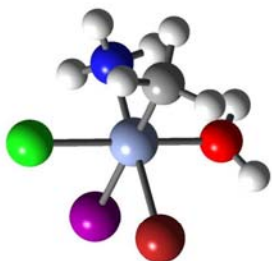
The metal of a square planar complex is not a chiral center. Most square planar complexes are achiral.

However, such a complex can be chiral if a ligand has a chiral center, or if the ligand is locked into a chiral conformation by coordination to the metal.

30/68



> Stereoisomers of Octahedral Complexes - 1



Octahedral complexes may exist as **diastereomers** and/or **enantiomers**.

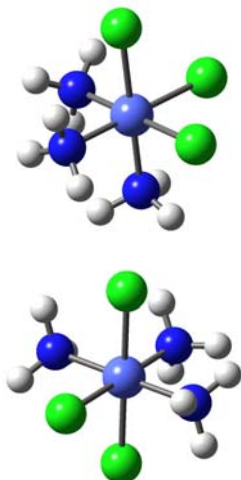
An octahedral metal complex with 6 different ligands can form up to 15 different diastereomers.

Each of those has an enantiomer, for a total of 30 stereoisomers. We will focus on a few special cases.

31/68



> Stereoisomers of Octahedral Complexes - 2



Consider a **complex of the type $ML_3L'_3$** .

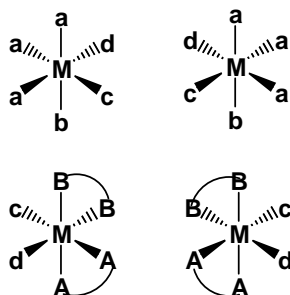
The isomer with 3 like ligands on one face of the octahedron is called facial (fac).

The other isomer is called the meridional (mer) isomer. It is a diastereomer of the fac isomer.

32/68



Stereoisomers of Octahedral Complexes - 3



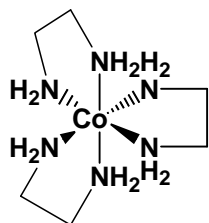
In general, **octahedral complexes** can produce many isomers. These include both enantiomers and diastereomers. Two pairs of enantiomers are shown on the left.

Chelating ligands bind the metal at more than one site. An example is $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2$, which can bind the metal through both nitrogen atoms.

33/68

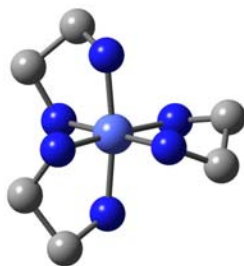


Stereoisomers of Octahedral Chelates - 1



Complexes with more than one non-coplanar chelate ring may be chiral due to ring handedness.

This is analogous to the pitch of a screw or a propeller. Most screws have right handed threads.



An example is a Co-tris(ethylenediamine) complex, shown at the left. In the bottom structure, hydrogen atoms are omitted for clarity.

34/68

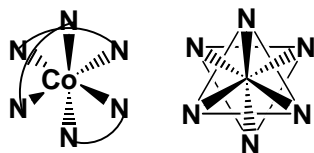




Stereoisomers of Octahedral Chelates - 2



To assign the **handedness** of the “screw”, first orient the molecule as shown, with one ring at the top and back. Now, the top and bottom sets of nitrogen atoms will form 2 intersecting triangles.

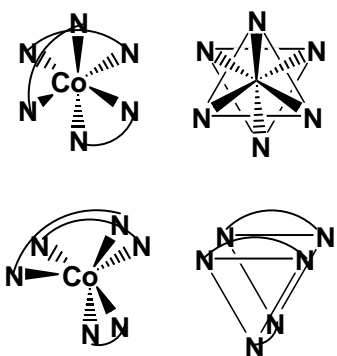


The bottom triangle contains one Co-N-N ring, and the top triangle contains a different ring. There is one additional ring that uses a nitrogen atom from both triangles.

35/68



Stereoisomers of Octahedral Chelates - 3



Now, **rotate the top triangle so its atoms are directly over the atoms of the bottom triangle**, forming a trigonal prism. The two nitrogen atoms at the bottom are connected. One belongs to each triangle.

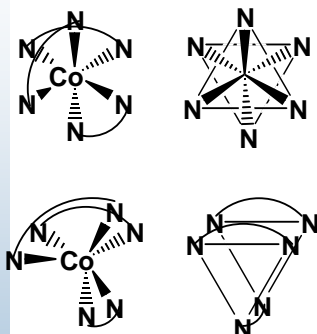
To get back to the original (top) conformation, you must rotate the top triangle either clockwise or counterclockwise. Make a note of which direction you must rotate.

36/68





Stereoisomers of Octahedral Chelates - 4



To restore the original (top) conformation from the bottom conformation, you must rotate **counterclockwise**.

Therefore, this is the Λ (lambda – left handed) isomer. If you had rotated the bottom conformation clockwise to restore the original, it would have been the Δ (delta – right handed) isomer.

The Λ isomer is analogous to a left handed screw. The Δ isomer is analogous to a right handed screw.

37/68



Stereoisomers of Octahedral Chelates - 5

For more complex ring systems, this procedure must be done for each pair of rings.

Ring chirality can be $\Lambda\Lambda\Lambda$, $\Lambda\Delta\Delta$, $\Lambda\Delta\Lambda$, etc. in those systems. The order in which the ring chirality is reported is arbitrary.

(Read those symbols carefully – lambda and delta)

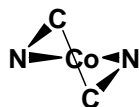
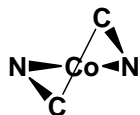


38/68





Chirality of Chelate Complexes due to Ligand Conformation - 1



Hydrogen atoms
omitted for clarity

Achiral compounds may become chiral chelated ligands due to their conformation. A procedure similar to the one used to find ring handedness has been developed. Consider one chelate ring of ethylene diamine on cobalt. This ring can exist in either of two enantiomeric conformations.

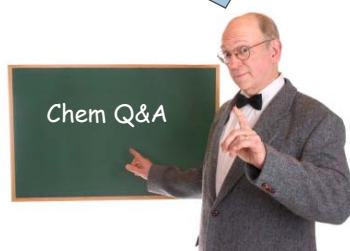
39/68



Question: Challenge

What is a left handed isomer labeled with?

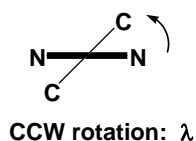
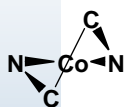
A left handed isomer is labeled with the Greek letter lambda, and is called a Λ isomer. A right handed or clockwise rotation, would be called a (Delta) Δ isomer.



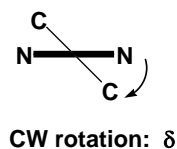
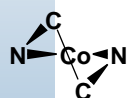
40/68



Chirality of Chelate Complexes due to Ligand Conformation - 2



Consider two lines. The first connects the point of ligand attachment to the metal, N in this case. The second line connects the two carbon atoms.



Imagine the two lines were initially parallel. Rotating the top (C-C) line counter-clockwise results in the top conformation, λ . Clockwise rotation results in the δ conformation.

41/68



Chirality of Chelate Complexes due to Ligand Conformation - 3



For complexes with more than one chelate ring, this procedure must be done for each ring.

A **chelate complex** with 3 rings might be labeled $\lambda\lambda\lambda$, $\delta\delta\delta$, $\delta\delta\lambda$, etc.

Chirality in octahedral complexes is much more complex than in simple organic compounds.

42/68





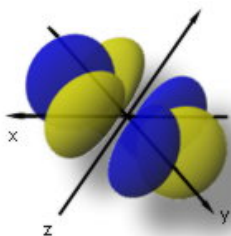
The Octet and 18 Electron Rules



1. The octet rule.
2. Exception to the octet rule.
3. Extension of the octet rule to compounds with d-orbitals: The 18 electron rule.



The Octet Rule



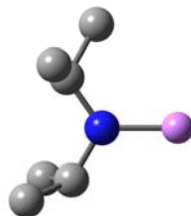
The **octet rule**, and its extension to the 18 electron rule, is based on the stability of filled orbitals. Most second and third row compounds use the *s* and *p* valence orbitals. These can hold a total of 8 electrons, 2 from the *s*, and 2 from each of the *p* orbitals.

When all 4 orbitals are filled, the compound has a total of 8 valence electrons. This is a particular stable electron configuration.





Octet Rule Examples



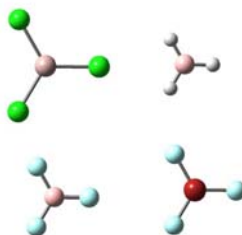
Methane, CH_4 . Each hydrogen has two shared electrons. Two is the “octet” for hydrogen. Carbon has 8 shared electrons.

Ammonia, NH_3 . Each hydrogen has 2 electrons. Nitrogen has 6 shared electrons, plus one lone pair, for a total of 8.

45/68



Exceptions to the Octet Rule



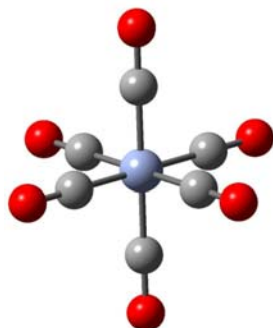
Many compounds of boron and aluminum only have 6 valence electrons. These can achieve an octet by dimerization or acting as a Lewis acid. Examples are BH_3 , BF_3 , and AlCl_3 . Compounds of P, S, Xe, and other heavy nonmetals can accommodate more than 8 electrons by using low lying d -orbitals. Examples include PF_5 and XeF_4 . Note that the noble gases are not always completely inert.

46/68





The 18 Electron Rule - 1



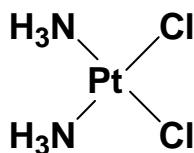
In a **transition metal complex**, we have the $3s$, $3p$, and $5d$ orbitals, for a total of 9 orbitals that can hold 18 electrons. Some of these electrons come from the metal.

The rest of the electrons come from the ligands. Only certain metal-ligand combinations give 18 valence electrons. For example, $\text{Cr}(\text{CO})_6$ has 6 e^- from Cr and 12 e^- from 6 Co, or 18 e^- .

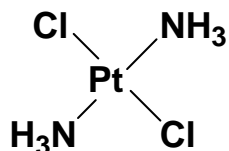
47/68



The 18 Electron Rule - 2



Just as there are exceptions to the octet rule, there are many exceptions to the **18 electron rule**. Many 16 electron compounds are stable, such as the platinum compounds shown here.



Many 17 electron radical species are known. These frequently dimerize, or are reduced to the anion. A few 19 or 20 electron species are known. These are usually unstable and readily react.

48/68



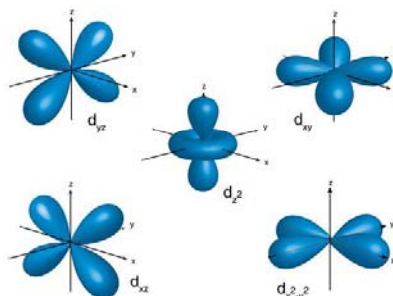


Introduction to Crystal Field and Ligand Field Theories

1. Crystal Field Theory
2. Ligand Field Theory



Crystal Field Theory - 1



In an **isolate metal atom**, the 5 *d*-orbitals are degenerate. Ligands generally contain lone pairs of electrons, and these destabilize the *d*-orbitals closest to the ligands.

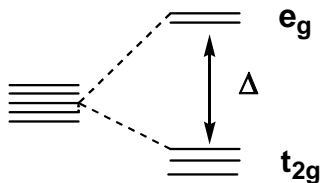
In an octahedral complex, the ligands point toward the *x*, *y*, and *z* axes. This destabilizes the $d_{x^2-y^2}$ and d_{z^2} orbitals. In a tetrahedral complex, the ligands point between the axes. This destabilizes the d_{xy} , d_{xz} , and d_{yz} orbitals.

50/68





Crystal Field Theory - 2



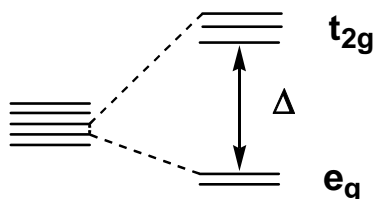
Crystal field theory gives an approximate and qualitative picture of the d -orbital energies in a coordination compound. In an octahedral complex, the $d_{x^2-y^2}$ and d_{z^2} orbitals are raised in energy. These are given the symmetry label " e_g " by group theory.

The d_{xy} , d_{xz} , and d_{yz} orbitals are lower in energy. These are given the t_{2g} symmetry label. The t_{2g} orbitals are filled with electrons first.

51/68



Crystal Field Theory - 3



In **tetrahedral complexes**, the roles of the two and 3 orbital sets are reversed. The e_g orbitals are occupied first, followed by the t_{2g} if additional electrons are present.

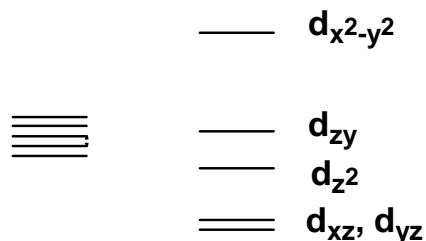
Because only 4 ligands are present instead of 6, the energy difference (Δ) between the two sets is smaller in tetrahedral compounds.

52/68





Crystal Field Theory - 4



The crystal field splitting is more complex in **square planar complexes**. The $\text{d}_{x^2-y^2}$ orbital is much higher in energy than the others, and is often vacant in square planar complexes.

Electrons can move from a filled to a vacant orbital by absorbing visible or UV light. That is why so many transition metal compounds are colored.

53/68



Question: Challenge

Define the octet rule.

The **octet rule**, and its extension to the 18 electron rule, is based on the stability of filled orbitals. Most second and third row compounds use the s and p valence orbitals. These can hold a total of 8 electrons, 2 from the s , and 2 from each of the p orbitals. When all 4 orbitals are filled, the compound has a total of 8 valence electrons. This is a particularly stable electron configuration.



54/68



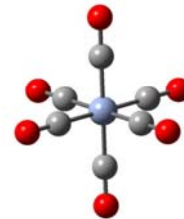


Ligand Field Theory - 1

Ligand Field Theory reaches the same conclusions via an approximate molecular orbital treatment. Ligand lone pair orbitals may be of the proper energy and symmetry to interact with the metal *s*, *p*, and *d*-orbitals.



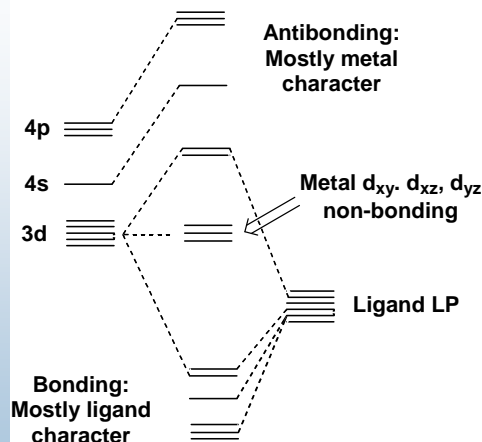
Let's consider orbital interactions in an octahedral complex.



55/68



Ligand Field Theory - 2



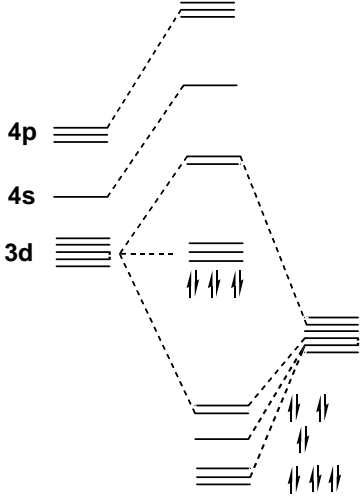
The ligands come in along the *x*, *y*, and *z* axes. They are of **proper symmetry** to match the metal *s*, *3p*, $d_{x^2-y^2}$ and d_{z^2} orbitals.

The d_{xy} , d_{xz} , and d_{yz} orbitals do not find a symmetry match with the ligands lone pair orbitals, and remain nonbonding. The bonding orbitals have mostly ligand character.

56/68




Ligand Field Theory - 3


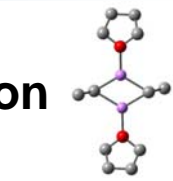


The 18 electron rule can be understood from Ligand Field Theory. 12 electrons fill the 6 bonding orbitals with mostly ligand character.


The remaining 6 electrons fill the 3 non-bonding metal *d*-orbitals. With the antibonding orbitals empty, this gives us a total of 18 electrons.

57/68 

Complexes with Common Coordination Numbers

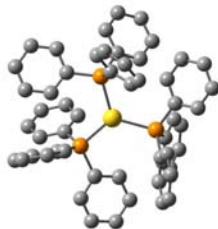



1. Coordination numbers up to 16 are known, but coordination numbers greater than 8 are relatively rare.
2. For main group elements and transition metals with filled *d*-shells, VSEPR theory can predict the geometry.
3. VSEPR theory fails for most transition metal complexes.





Low Coordination Numbers



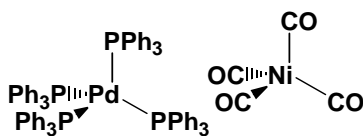
Compounds with a **coordination number (CN)** of one are rare. These usually involve a ligand that is so sterically hindered that no other ligands can approach the metal. The CN of 2 is also rare. $\text{Ag}(\text{NH}_3)_2^+$ is one example.

Coinage metal (Cu, Ag, Au) complexes with 10 *d*-electrons often have a CN of 3.

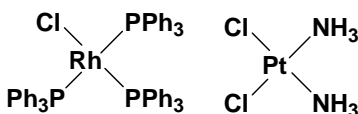
59/68



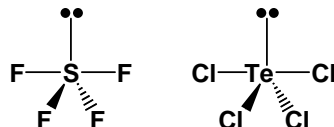
Coordination Number 4



Tetracoordinate coordination compounds are fairly common. Tetrahedral and square planar structures are known for transition metal complexes.



Square planar complexes are common for 16 electron compounds, especially of Ni, Pd, Pt, and some Cu and Rh compounds. Some main group compounds have a seesaw structure. Examples: SF_4 , TeCl_4

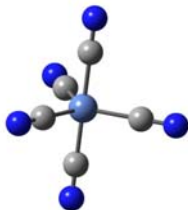


60/68





Coordination Number 5



Common geometries for CN 5 are the trigonal bipyramid and square pyramid. The energy difference between these two structures is small.

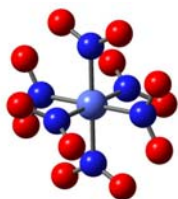


Many compounds adopt an intermediate structure or a fluxional structure between the two. Both structures are observed in the salt $[\text{Cren}_3][\text{Ni}(\text{CN})_5]$. A pentagonal planar structure is known for XeF_5^- .

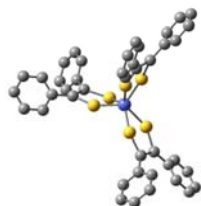
61/68



Coordination Number 6



The **octahedral geometry** is the most common in transition metal coordination compounds. Many complexes adopt distorted octahedral geometries with one dimension lengthened or compressed.



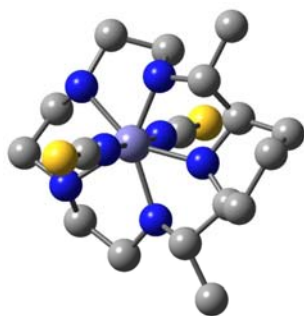
Rotation of one face of the octahedron results in a trigonal prism geometry. Several compounds with the trigonal prism geometry are known. One example is the $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ complex shown.

62/68





Coordination Number 7



While relatively uncommon, compounds with a CN of 7 can adopt 3 idealized structures:

Pentagonal bipyramidal (shown in the iron complex on the left).

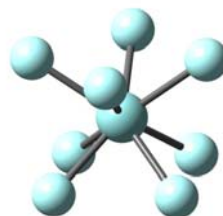
Capped octahedron: An octahedron with an extra ligand on one face.

Capped trigonal prism: A trigonal prism with an extra ligand on one face.

63/68



Coordination Number 8



Octacoordinate compounds are mostly those of heavy metals. The most common geometries are the dodecahedron and square antiprism. The square antiprism geometry is found in the ZrF_8 anions of the complex salt $\text{Na}_7\text{Zr}_6\text{F}_{31}$. Coordination numbers higher than 8 are uncommon.

64/68

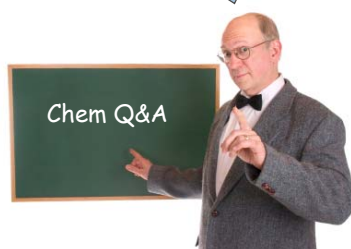




Question: Challenge

What orbitals correspond to the t_{2g} symmetry label?

Crystal field theory gives an approximate and qualitative picture of the d -orbital energies in a coordination compound. The d_{xy} , d_{xz} , and d_{yz} orbitals are lower in energy. These are given the t_{2g} symmetry label. The t_{2g} orbitals are filled with electrons first.



65/68



Learning Summary

Coordination compounds consist of a metal and its ligands.

Naming coordination compounds follows a set of simple rules.

Isomers are different molecules with the same molecular formula. They can be constitutional isomers or stereoisomers.

Many **coordination compounds** obey the **18 electron rule**. This can be understood by crystal field theory and ligand field theory.

Compounds of coordination numbers of up to 16 are known. **Coordination numbers 6 and 4 are the most common**. Many coordination compounds adopt geometries of simple or distorted polyhedra.

66/68






Congratulations

You have successfully completed
the core tutorial

**Introduction to
Coordination Chemistry**

Rapid Learning Center


67/68 

 **Rapid Learning Center** 
Chemistry :: Biology :: Physics :: Math

What's Next ...

Step 1: Concepts – Core Tutorial (Just Completed)
→ Step 2: Practice – Interactive Problem Drill
Step 3: Recap – Super Review Cheat Sheet

Go for it!

68/68 

<http://www.RapidLearningCenter.com>