Unit 3 – Deck 3

Inorganic Chemistry

Introduction to inorganic chemistry and chemical bonds

Lecture Topics

Introduction to Inorganic Coordination Chemistry

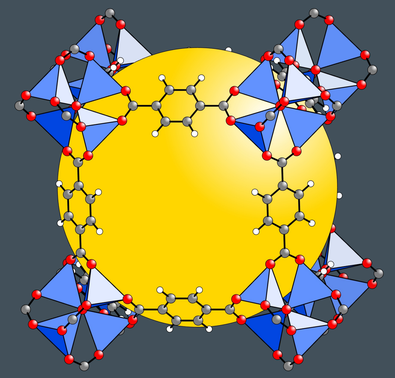
- Coordination Complexes
- Lewis Acids and Bases
- The Dative Bond
- Ions and Molecules as Ligands
- Coordination Complex Formation

Organic vs Inorganic Chemistry

Organic chemistry – study of compounds that contain a C-H bond. *A specialized field of chemistry*.

Inorganic chemistry – study of all compounds, including those with C-H bonds. A field of generalists.

Inorganic chemistry = chemistry

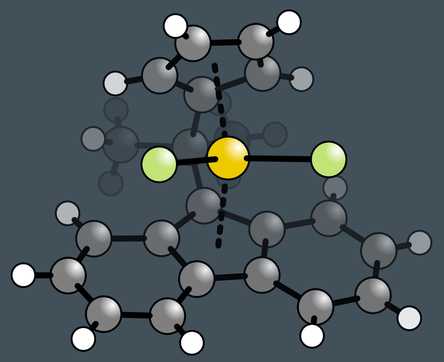


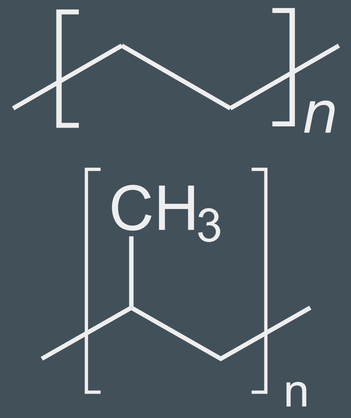
According to the American Chemical Society, inorganic chemistry is the study of the properties and behavior of inorganic compounds, which include metals, minerals, and organometallic compounds.

Inorganic Chemistry - Catalysis

Homogeneous Catalysis

Ziegler Natta

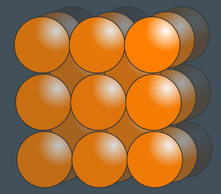




Heterogeneous Catalysis

Haber-Bosch

$$N_2 + 3H_2 \xrightarrow{Fe\ cat.} 2NH_3 \qquad \Delta H° = -92\,\frac{kJ}{mol}$$



α-iron

50% of the nitrogen in your body came from this reaction

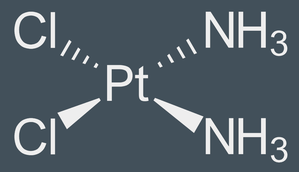
Inorganic Chemistry

Surfactants / Soaps

Sodium stearate

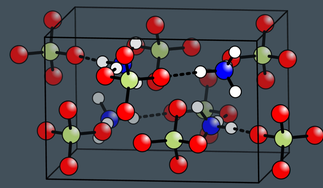
50% commercial soap

Medicines

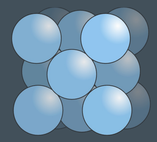


Cisplatin - chemotherapy

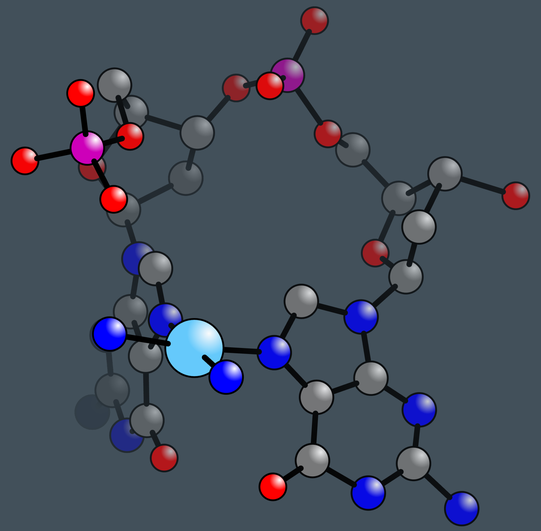
Fuels



Ammonium perchlorate



Aluminum

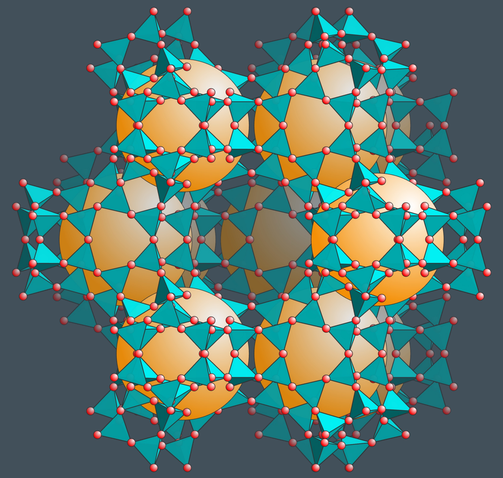


DNA Adduct

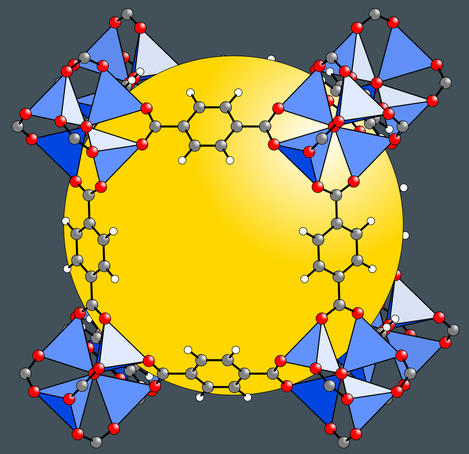
Space Shuttle Solid Rocket Boosters

Inorganic Chemistry

Chemical Separations, Storage & Catalysis

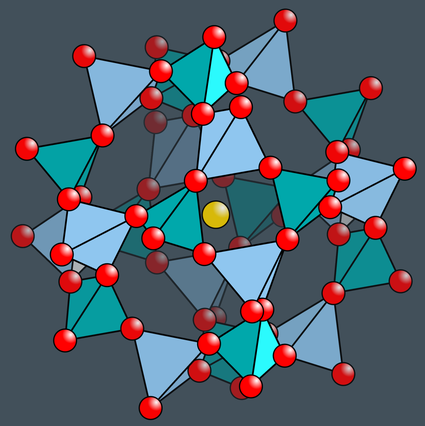


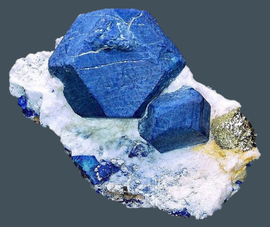
Faujasite



MOF-5

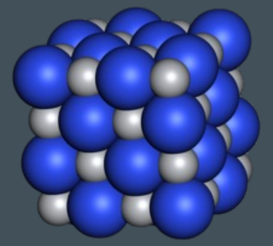
Pigments





Lazaurite (aka Lapis Lazuli)

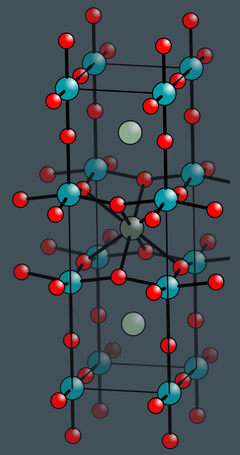
Coatings



TiN

Inorganic Chemistry

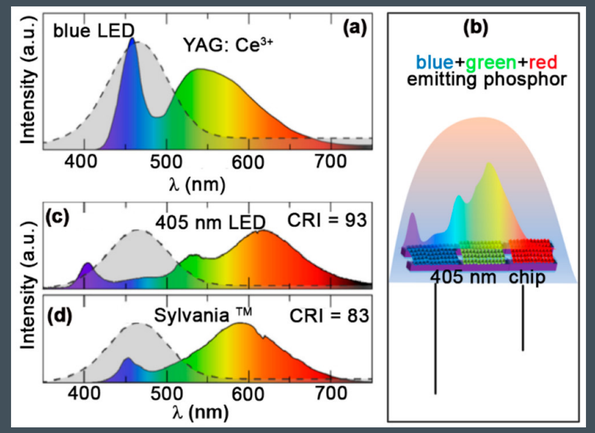
Superconductors



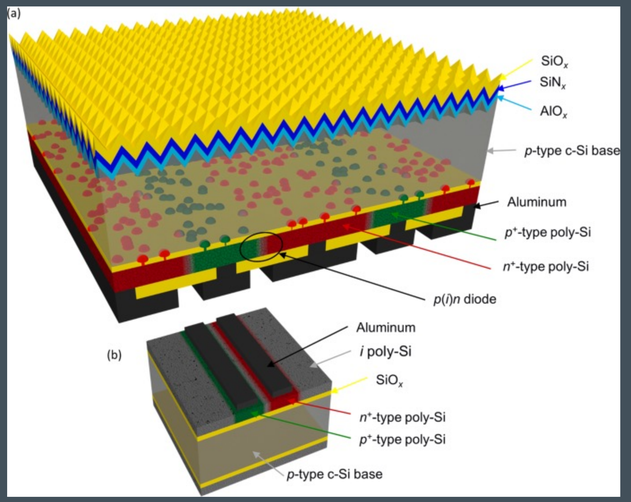
YBCO

T_c = 92 K

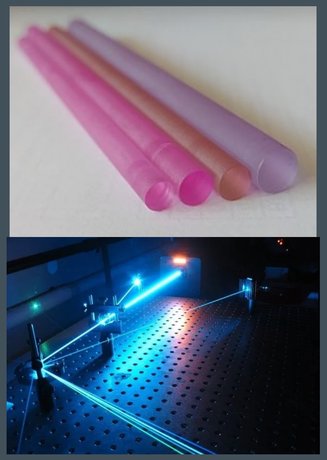
Emitters



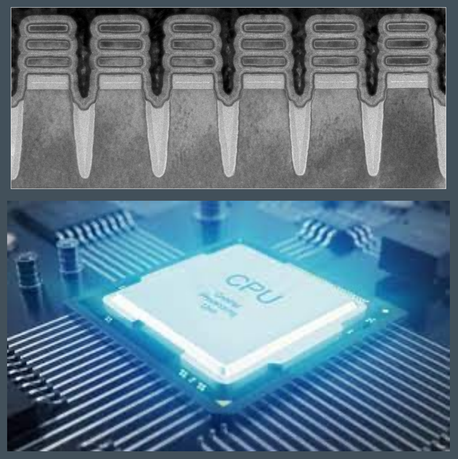
Solar Energy



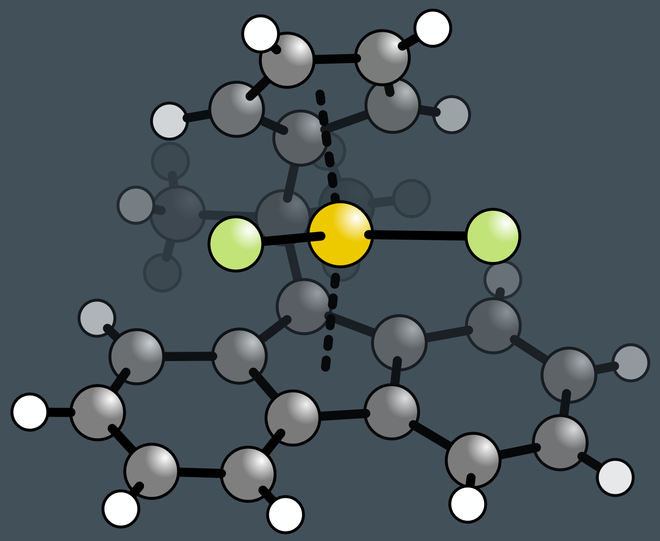
Lasers



Semiconductors



Organometallic chemistry



$Zr(CpCp')Cl_2$

- Grignard's Reagent: RCH_2-MgBr
- Alkyl lithium: RCH_2Li
- Alkyl aluminum: $(CH_3)_3Al$
- Metallocenes
- Polymerization catalysts
- Cross coupling catalysts (Shonogashira, Kumada, Negishi, Buchwald-Hartwig)

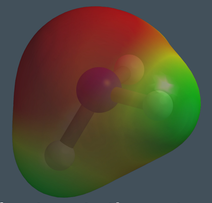
Other fields that fall under inorganic chemistry

- Energy storage
- Organometallic (metal-C bonds, usually also with C-H)
- Transuranic chemistry (heavier than uranium)
- Magnetic molecules & materials (MRI, energy transduction, information storage)
- Quantum computing
- Nuclear chemistry
- Bioinorganic “metals in biology”
- Biomineralization
- Optoelectronic / non-linear optics
- Nanomaterials
- Colloids
- Self-assembly

Review: Lewis acid and bases

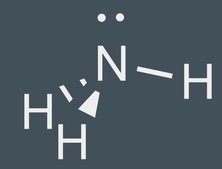
Lewis Base: donates at least one pair of electrons to a Lewis acid

Compare Lewis Base to “nucleophile”



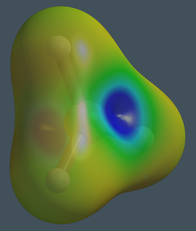
Electrostatic potential
Blue = δ^+; Red = δ^-

HOMO

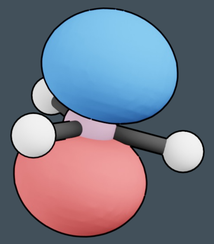


Lewis Acid: accepts at least one pair of electrons to a Lewis acid

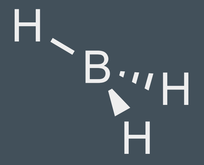
Compare Lewis Acid to “electrophile”



Electrostatic potential
Blue = δ^+; Red = δ^-



LUMO



Types of bonding in coordination chemistry

Ionic Bond: Electrostatic interaction between charged ions

Covalent Bond: Bonding electrons are shared between interacting atoms

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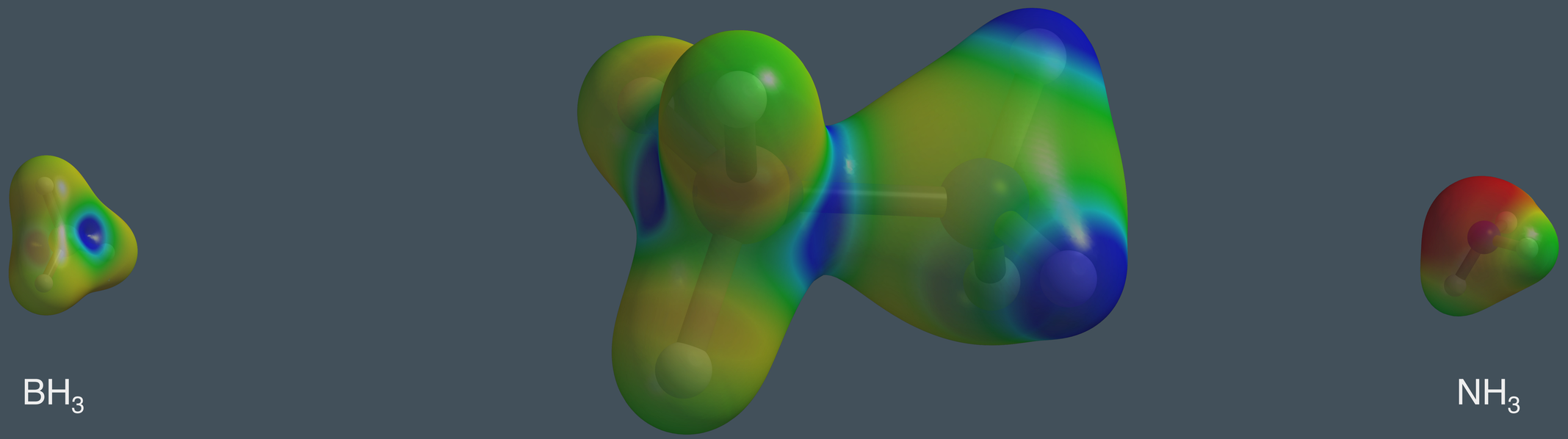
Dative Bond: The interaction between a Lewis Acid and Lewis Base. On a spectrum of ionic – covalent.

Coordination Bond: a dative bond. The Lewis acid is usually a metal. The Lewis base is called a ligand.

Types of bonding in coordination chemistry

Dative Bond: The interaction between a Lewis Acid and Lewis Base. On a spectrum of ionic – covalent.



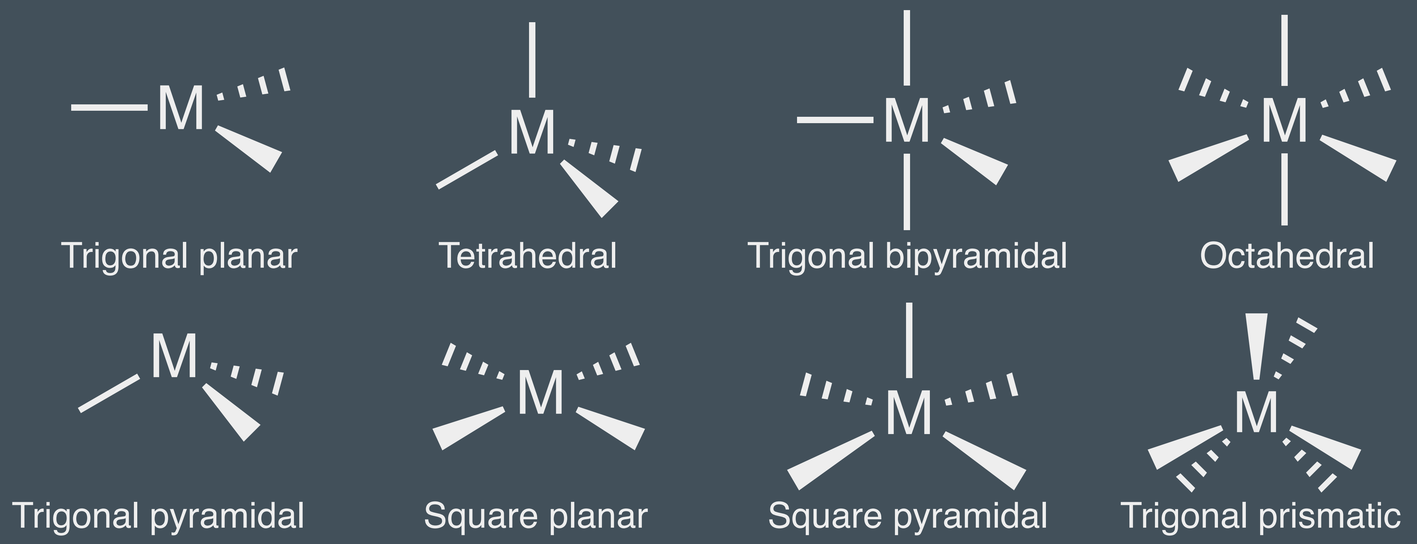
BH_3 NH_3

Coordination complex

A coordination complex is formed when a central atom or ion is coordinated by one or more ligands through a coordination bond.

Coordination number

The coordination number is the number of bonds between the metal center and the ligands.



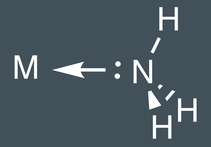
Coordination number:	3	4	5	6

Ligands

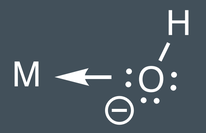
Ligands are molecules or ions that are stable as independent species (ions or molecules) **but** can be incorporated into coordination compounds by forming dative bonds.

Ligands bond with metals (Lewis acids). Ligands are almost always Lewis bases.

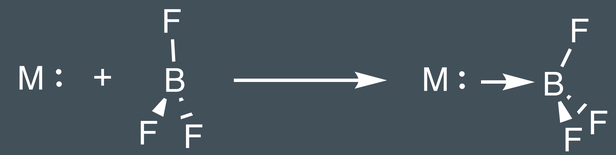
- L-type ligands donate a charge neutral lone pairs (NH_3).
- X-type ligands donate a negatively charged lone pair (^{-}OH).
- Z-type ligands are quite rare. They are Lewis acids that bond to electron rich (i.e. basic) metals.



L-type

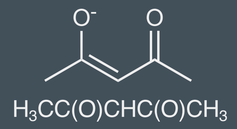
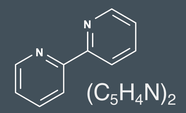
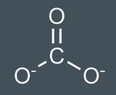


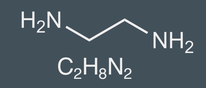
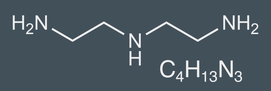
X-type



Z-type (rare)

Examples: L-type and X-type ligands

Name	Structure	Donating Lone Pairs	Charge	Donor Atoms
acetylacetonate		2	–1	O, O
ammonia	:NH_3	1	0	N
2,2-bipyridine		2	0	N,N
bromide	Br^-	1	–1	Br
carbonate		1 or 2	–2	O,O
carbonyl		1	0	C

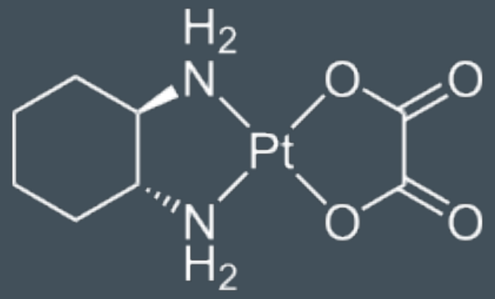
Name	Structure	Donating Lone Pairs	Charge	Donor Atoms
chloride	Cl^-	1	–1	Cl
cyanide		1	–1	C
ethylenediamine (en)		2	0	N,N
diethylenediamine (den)		3	0	N,N,N
fluoride	F^-	1	–1	F
hydride	H^-	1	–1	H
hydroxide	OH^-	1	–1	O

Denticity vs Hapticity

The denticity of a ligand is the number of donor atoms through which the ligand coordinates to a metal atom or ion.

- The denticity of a ligand is designated by the prefix ***κ***
- The hapticity of a ligand is designated by the prefix ***η***

κ A Non-contiguous set of atoms coordinate



diamine is κ^2 oxalate is κ^2

Cp is η^5

η A contiguous set of atoms coordinate

Monodentate

Ligands that are coordinated to one metal center through **one** coordination bond are called monodentate ligands

Thiocyanato-**κ***N*

Thiocyanato-**κ***S*

Kappa for can also denote which atom is coordinated to the metal

Bidentate

Ligands that are coordinated to one metal center through two coordination bonds are called bidentate ligands

1,2-ethanediamine-κ^2 N

1,3-propanediamine-κ^2 N

Chelation and the chelate ring

When polydentate ligands coordinate to an ion, a chelate ring is formed.

Chelation and the chelate ring

When polydentate ligands coordinate to an ion, a chelate ring is formed.

Empirical stability of chelate rings

3- and 4-atom chelate rings are unstable.

5-atom chelate rings are stable with larger metal ions.

(TM and octahedral metals)

6-atom chelate rings are stable with smaller metal ions.

(tetrahedral metals)

Complex stability

Almost always, atoms in *p*-block molecules follow the octet rule.

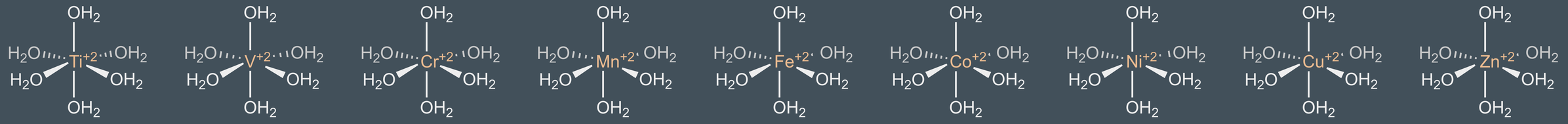
Compounds that don’t follow the octet rule can sometimes be made but are generally less stable

BH_3 vs CH_4

Complex stability

Almost always, atoms in *p*-block molecules follow the octet rule.

Metal coordination generally compounds do not follow the octet rule.



14 e⁻ 15 e⁻ 16 e⁻ 17 e⁻ 18 e⁻ 19 e⁻ 20 e⁻ 21 e⁻ 22 e⁻

Transition metals have more complicated electron counting rules

Complex stability – rules?

There are some electron counting rules for transition metal complexes, but you must think more deeply about the chemical bonding to apply them correctly.

Organometallics
(octahedral & participate in M-C π-bonding)
“18 electron rule”

Organometallics
(square planar & participate in M-C π-bonding)
“16 electron rule”

Metal clusters
Use polyhedral skeletal electron pair theory
“a set of 4n rules”

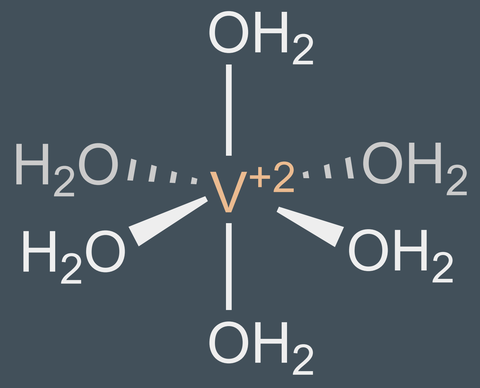
Counting Electrons

When counting electrons, we need count

(1) only the electrons that the ligand “donates” to the metal cation

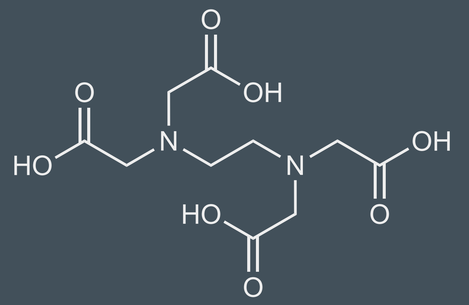
(2) the number of valence electrons remaining for the metal cation.

Electron Count = # Ligand Electrons + # Metal Electrons

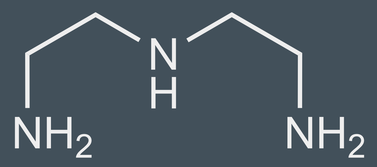


Common Ligands

en



EDTA

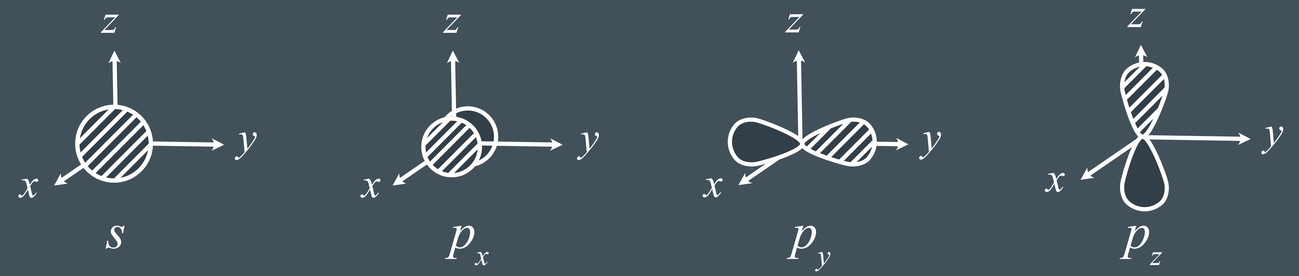


den

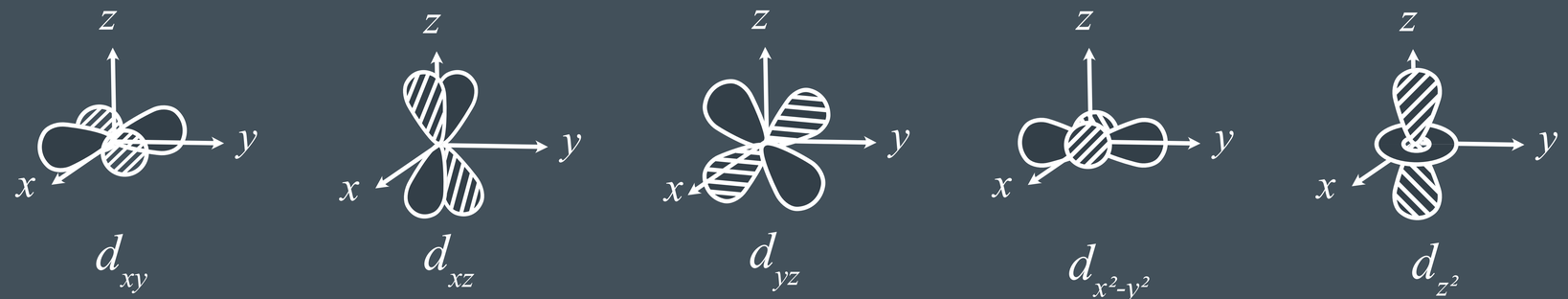
Ligand	Electron Count	Ligand Charge	Denticity
H_2O	2	0	1
F, Cl, I, Br	2	-1	1
H, CH_3, Phenyl ($–C_6H_5$)	2	-1	1
CO	2	0	1
NH_3, PPh_3	2	0	1
Ethylenediamine (en)	4	0	2
Diethylenetriamine (trien)	6	0	3
EDTA	12	-4	6

d-orbitals

Main group compounds either have a filled *d*–orbitals that are too stable (Sn) or empty *d*–orbitals that are too unstable (C) to participate in bonding.



Transition metal compounds have **partially filled *d*–orbitals** that gives the organometallic compounds their characteristic properties.



Counting metal electrons (d^n)

When counting metal electrons, you first must determine the oxidation state of the metal.

Oxidation State = Overall Charge of Complex – Total Charge of Ligands

Then you can determine the number of metal electrons.

Metal Electrons = (# *s* Electrons + # *d* Electrons) – (Oxidation State)

Total Electron Count

Finally, we can determine the number of complex electrons.

Complex Electrons = # Ligand Electrons + # Metal Electrons

Example: $FeBr_4(NH_3)_2$

Example

Determine the total electron count for the octahedral complex $[Fe(NH_3)_6]Br_2$.

Next time

- Equilibrium Constants of Coordination Complexes
- Chelate Effect
- Polydentate Ligands

- Ionic Size and Charge
- **Hard and Soft Acid Base Theory**