INTERNATIONAL COLLEGE OF PHARMACEUTICAL INNOVATION

国际创新药学院

Fundamentals of Medicinal and Pharmaceutical Chemistry

FUNCHEM.10 Coordination Chemistry

Professor Dan Wu

DATE: 23rd October 2024

Learning outcomes

At the end of this lecture, the learner will be able to

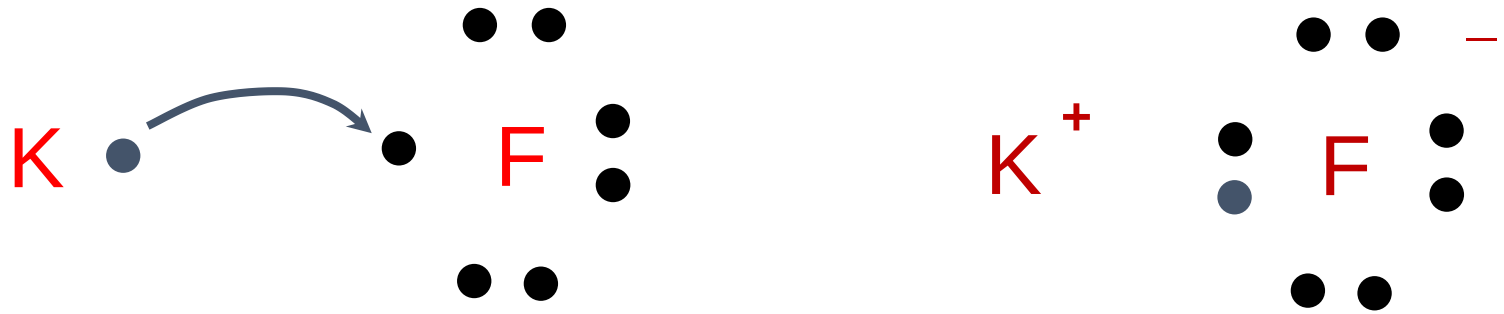
- Define ‘dative or coordinate bonds’.
- Define ‘Lewis acids and bases’, ‘Arrhenius acids and bases’, ‘Bronsted-Lowry acids and bases’.
- Define ‘coordination compounds’.
- Recall examples of Lewis acids and bases.
- Define ‘ligand’ and ‘metal complex’.
- Determine ‘coordination number’ and ‘oxidation number’ of a metal ion in a metal complex formula or structure.
- Identify or predict geometry around a metal ion in various complexes.
- Define ‘ligand denticity’.
- Recall and identify examples of monodentate and bidentate ligands.

Recommended reading

- General Chemistry - The Essential Concepts by Chang and Goldsby 7e
  - Chapter 20
  - Chapter 10, Section 10.1 on molecular geometry

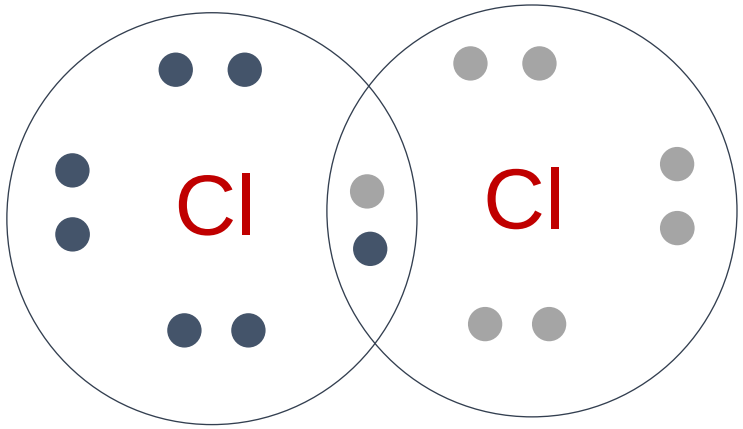
Recall: Ionic Bonding

In an **IONIC** bond, electrons are lost or gained, resulting in the formation of **IONS** in ionic compounds.



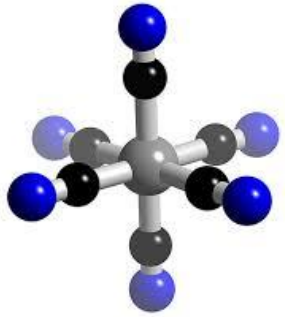
The ionic **bond** is the attraction between the positive K^+ ion and the negative F^- ion

Recall: Covalent Bonding



The octet is achieved by each atom sharing the electron pair in the middle

What is a dative or coordinate bond?

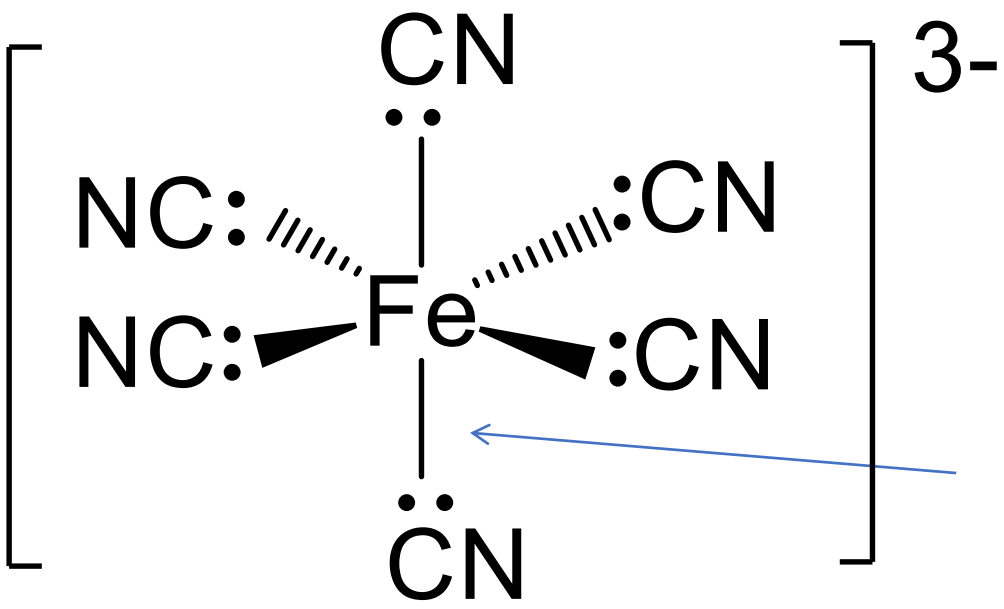


$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$

Recall the Lewis Dot Structure for CN^- (isoelectronic with CO):

This lone pair of electrons can be donated to the Fe^{3+} metal ion to generate a new complex

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$



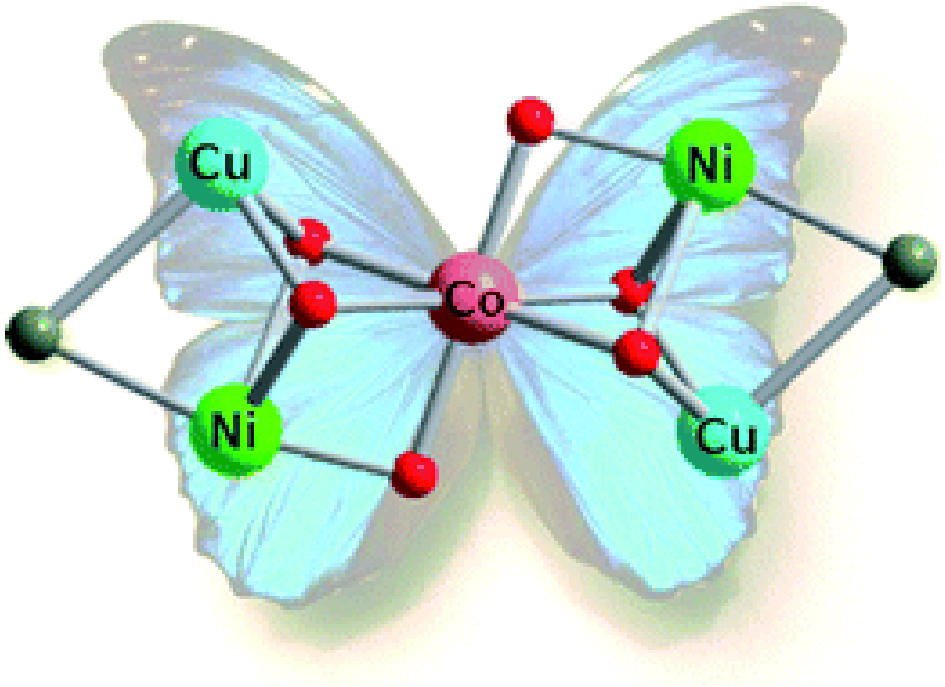
What is the oxidation state of the metal?
Its coordination number?
Its geometry?
Its magnetic properties?
Its biological activity?

Each bond is called a dative or coordinate bond

The substance above is a coordination compound or a coordination complex ion since it has a charge.

What is coordination chemistry and why study it?

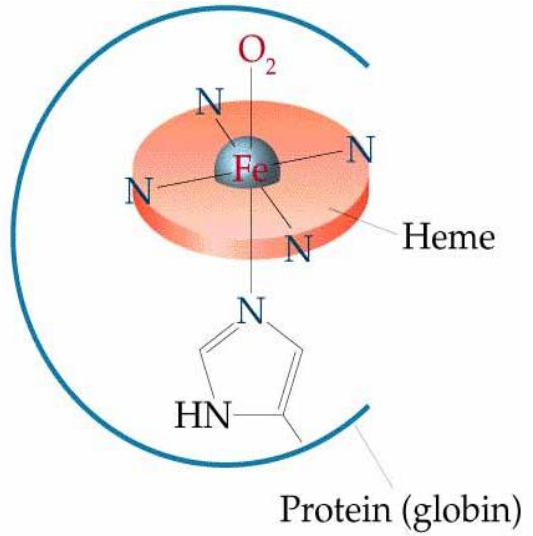
- Coordination chemistry is the study of the interactions between transition metal ions and other molecules and/or ions



A coordination compound will generally contain one or more metal ions (usually transition metals) which is surrounded by a small number of small molecules or ions called ligands.

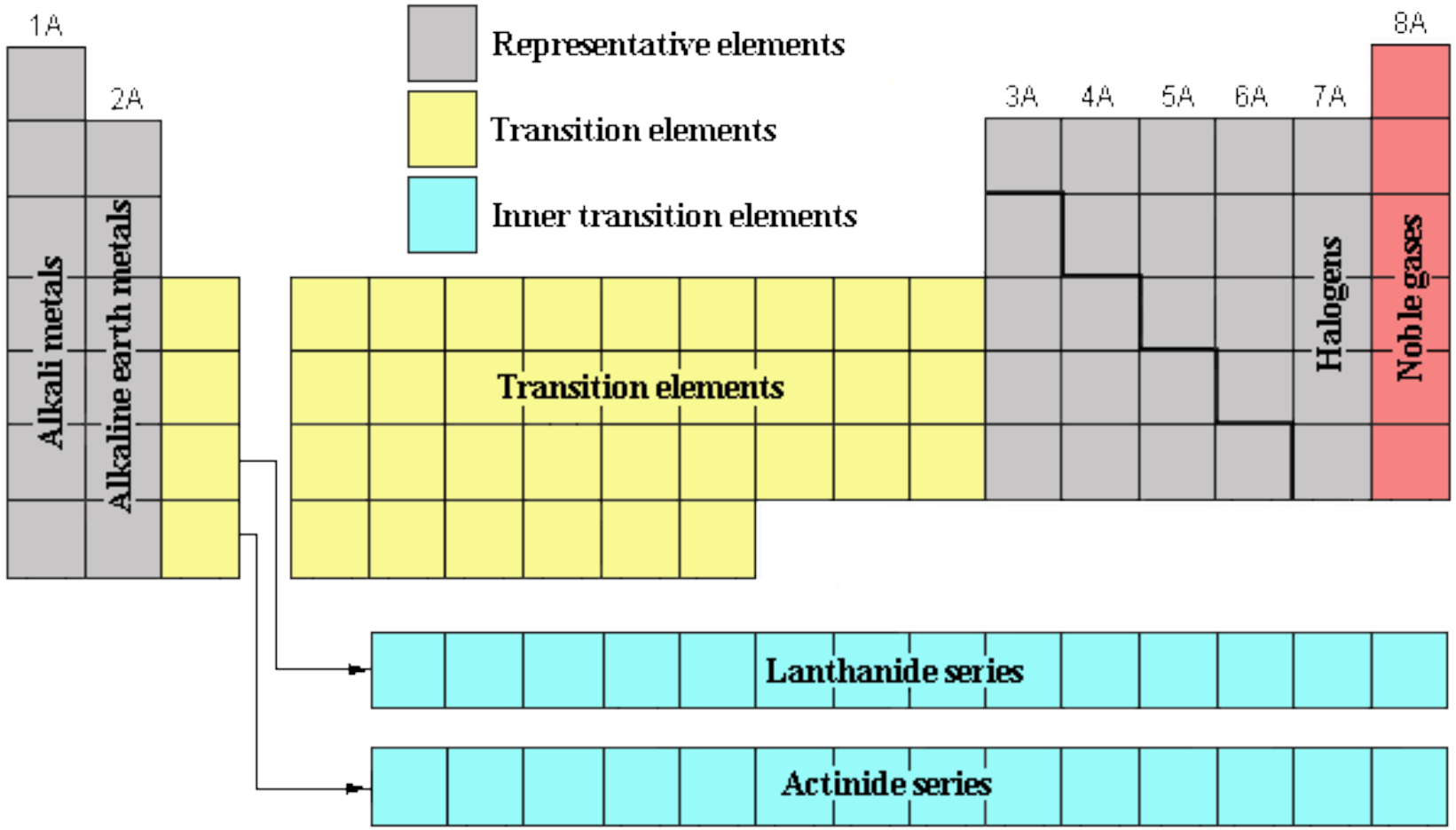
Why study coordination chemistry?

- Many biomolecules contain transition metals which play a key role in the functions of these biomolecules
  - Vitamin B12 contains Co
  - Metalloenzymes such as matrix metalloproteinases and histone deacetylases contain Zn
  - Hemoglobin, myoglobin contain Fe – responsible for O_2 transport and storage

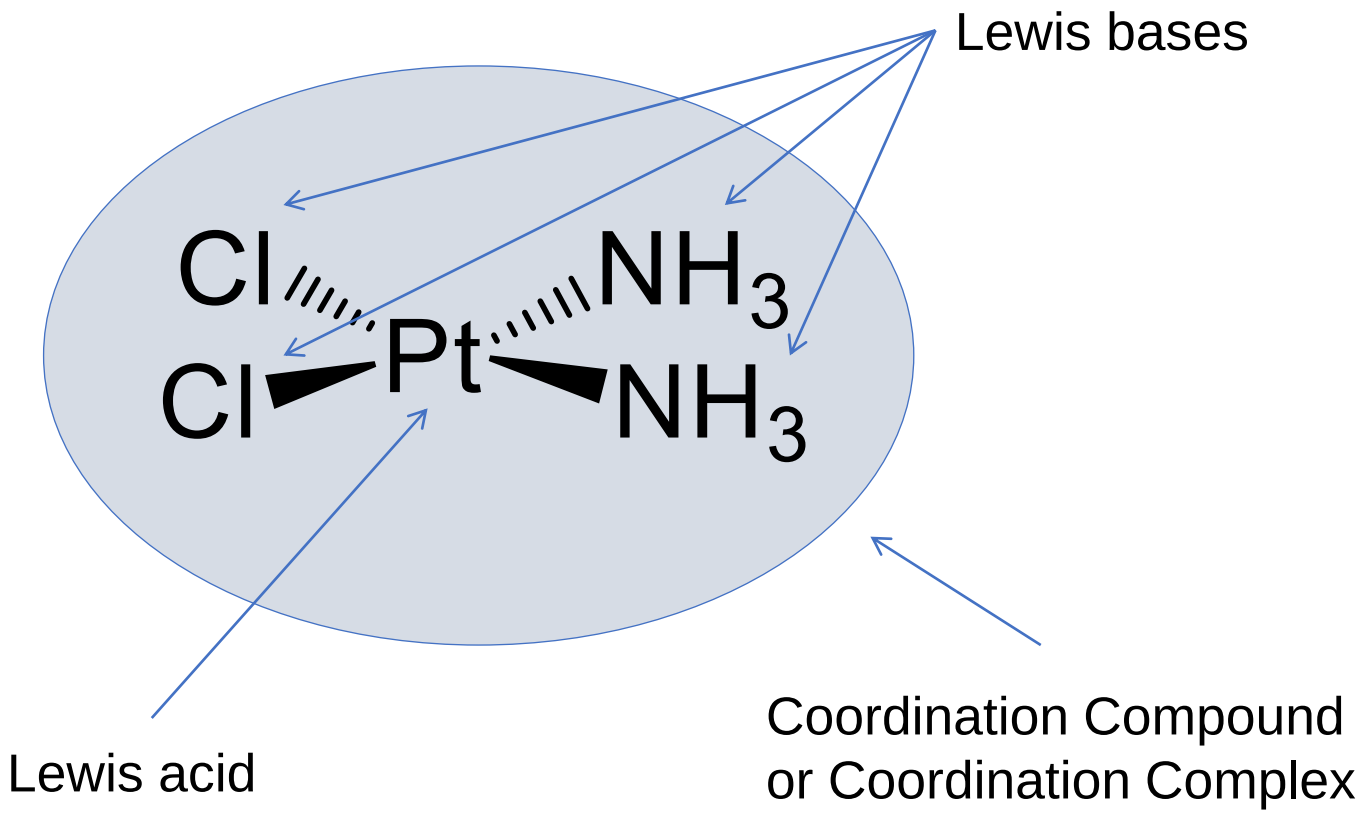


- Transition metal complexes can also be used as therapeutic agents
  - Pt complexes as anti-cancer agents; Gold complexes as anti-arthritic agents ……

What are transition metals?



Structure of Cisplatin – used to treat various types of cancers e.g. testicular, lung, ovarian



What are Lewis acids and Lewis bases?

- Lewis acid is a species that can accept a pair of electrons i.e. an electron pair acceptor

- Lewis base is a species that can donate a pair of electrons i.e. an electron pair donor

But I thought acids and bases donated H^+ and OH^- ions in solution?

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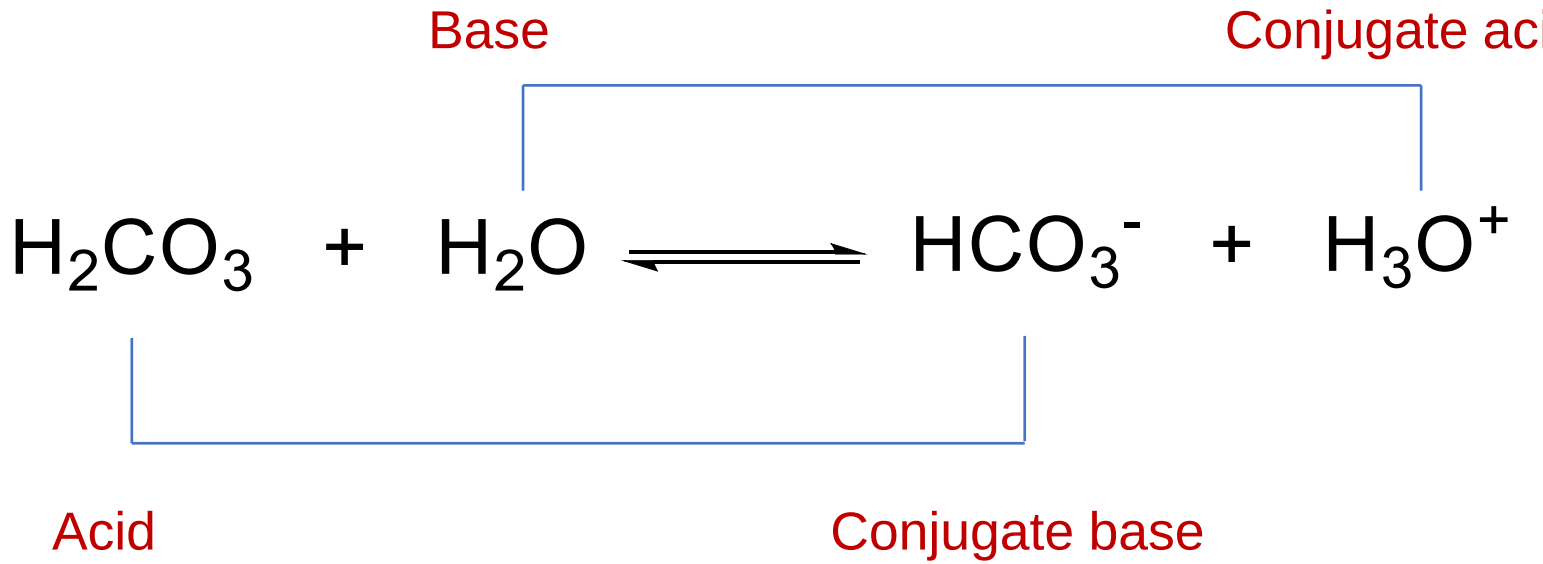
ca. 1885 - Svante Arrhenius

‘Arrhenius’ definitions of acids and bases:

Arrhenius acid - a substance that ionizes to produce H^+ in aqueous solution

Arrhenius base - a substance that ionizes to produce OH^- in aqueous solution

Bronsted-Lowry Acids and Bases!



Bronsted-Lowry acid is a proton (H^+) donor
Bronsted-Lowry base is a proton acceptor

How do Lewis acids and bases combine to give coordination compounds?

Let’s go back to our first example

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$

Lewis acid
- metal ion

Lewis bases –
also called ligands

Recall electronic configurations of the first row transition elements

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

where [Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$

Fe [Ar] $4s^2 3d^6$

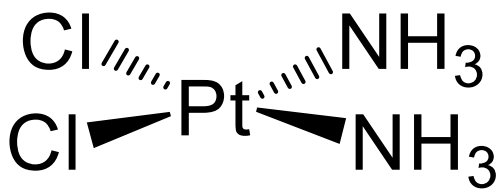
Fe^{3+} has lost 3 electrons Fe^{3+} [Ar] $3d^5$

To get a d-block metal ion (1st row) from the neutral atom you remove the 4s electrons first before removing 3d electrons

Co	→	Co^{3+} + $3e^-$
[Ar]$3d^7 4s^2$		[Ar]$3d^6$

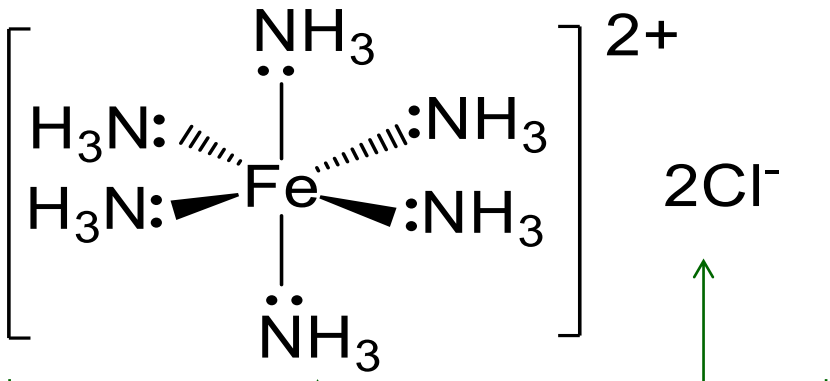
Mn	→	Mn^{4+} + $4e^-$
[Ar]$3d^5 4s^2$		[Ar]$3d^3$

Coordination complex or coordination compound



Neutral

Coordination complex or coordination compound



Complex ion

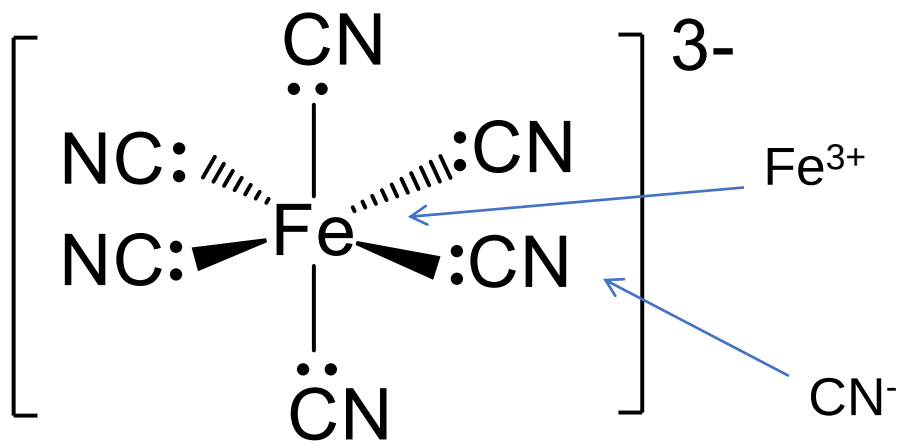
Counter ions

Neutral

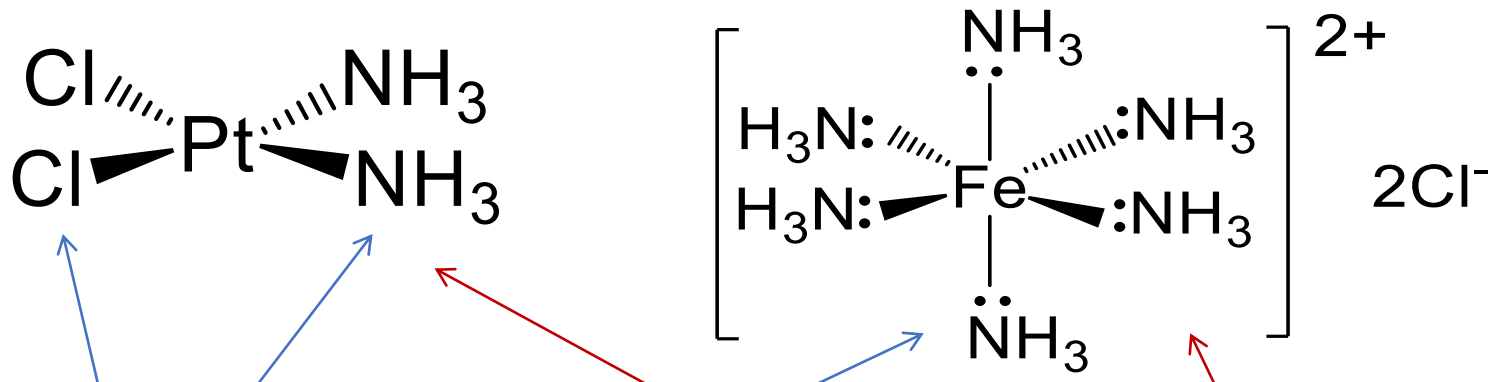
How do Lewis acids and bases combine to give coordination compounds?

Let’s go back to our first example

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$



Crystal Field Theory (explained later!)



Each ligand is classified according to the number of donor atoms – in this case, each N in NH_3 and each Cl^- donates one pair of electrons, hence they are monodentate ligands

CN = 4 and CN = 6

Coordination number is the number of donor atoms bonded to the central metal ion in the complex

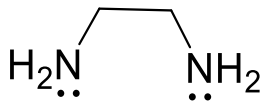
Ligand Denticity

- classified according to the number of donor atoms
- Examples
  - monodentate = 1
  - bidentate = 2
  - Tridendate = 3
  - tetradentate = 4
  - hexadentate = 6
  - polydentate = 2 or more donor atoms

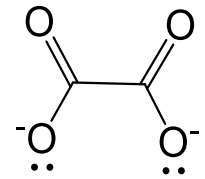
Examples of monodentate ligands

Examples of bidendate ligands

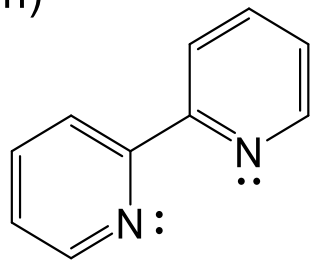
- oxalate ion (ox) = $C_2O_4^{2-}$
- ethylenediamine (en) = $NH_2CH_2CH_2NH_2$
- 2,2’-bipyridine (bpy)



ethylenediamine (en)

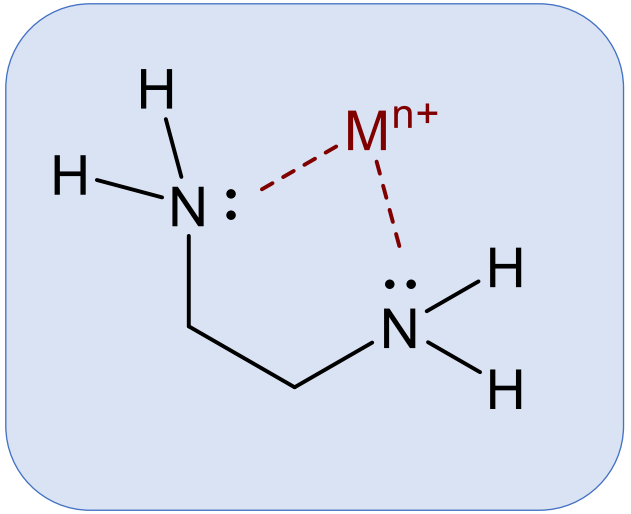


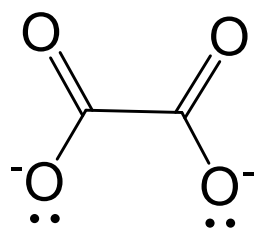
oxalate (ox)



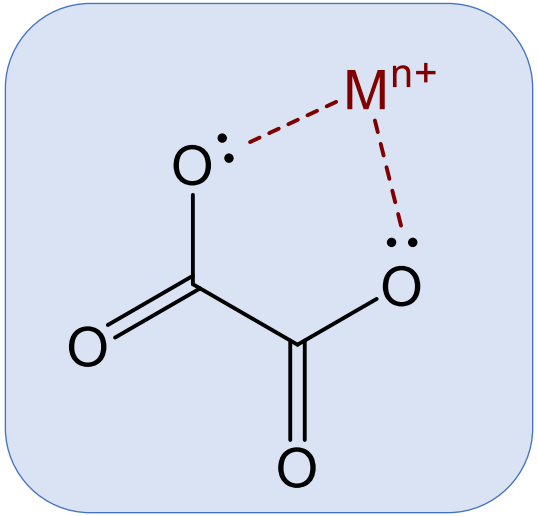
2,2'-bipyridine

The bidentate ligand 1,2-diaminoethane or ethylenediamine (en)

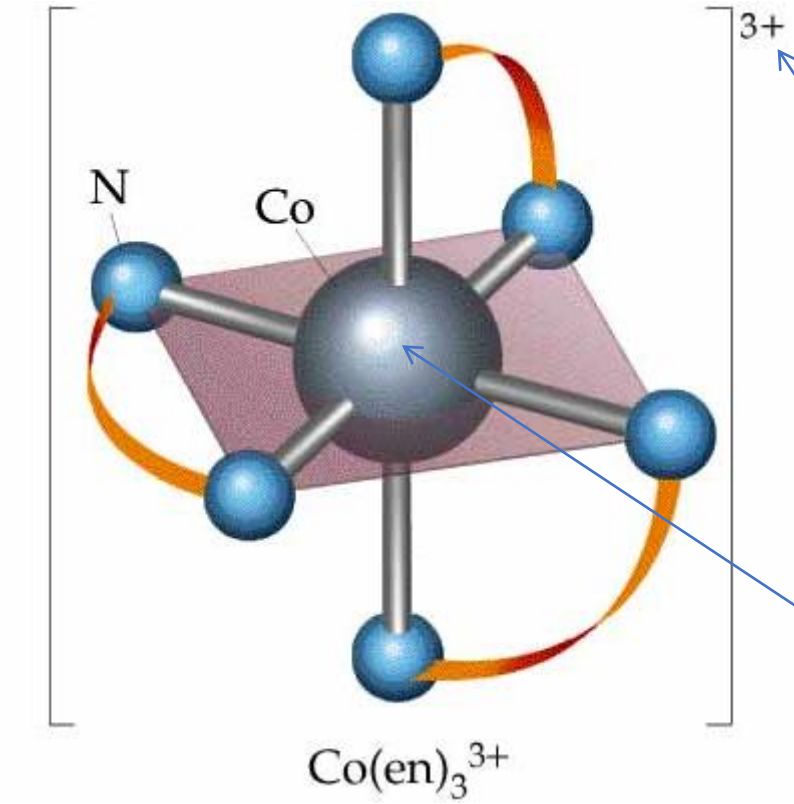




oxalate (ox)



Oxidation State of the Metal Ion



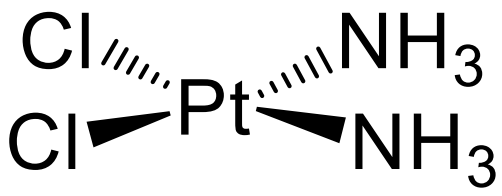
Three en ligands
Each en ligand is bidentate and neutral

Overall charge on complex ion is = 3+

Oxidation state of metal ion: +3

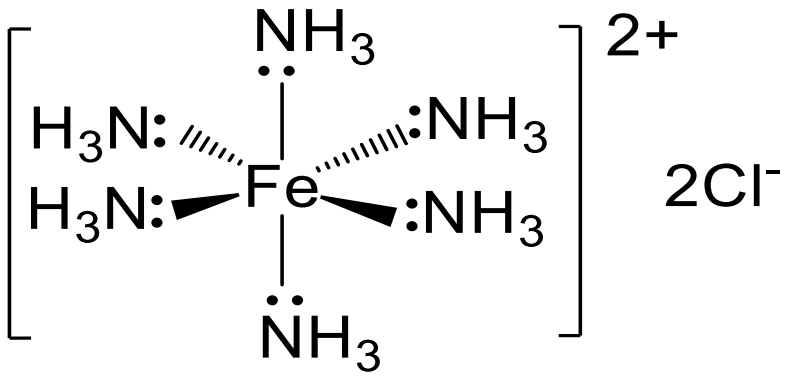
Co + 3(0) = +3

Oxidation State of the Metal Ion



Each Cl is -1 i.e. Cl^-
Each NH_3 is neutral
Complex is neutral

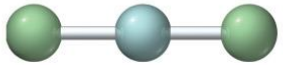
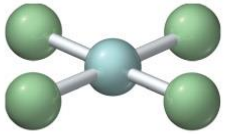
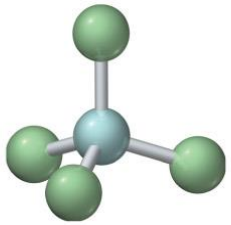
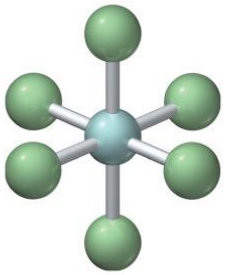
$Pt + 2\ Cl^- + 2\ NH_3 = 0$
$Pt + 2(-1) + 2(0) = 0$
$Pt = +2$



Each NH_3 is neutral
Complex ion has a charge of 2+

$Fe + 6\ NH_3 = +2$
$Fe + 6(0) = +2$
$Fe = +2$

Geometries in Complex Ions

Coordination Number	Shape	Model	Example
2	Linear		$[Ag(NH_3)_2]^+$
4	Square planar		$[PdCl_4]^{2-}$
4	Tetrahedral		$[Zn(NH_3)_4]^{2+}$
6	Octahedral		$[Fe(H_2O)_6]^{3+}$

Geometries

Coordination Number: 2

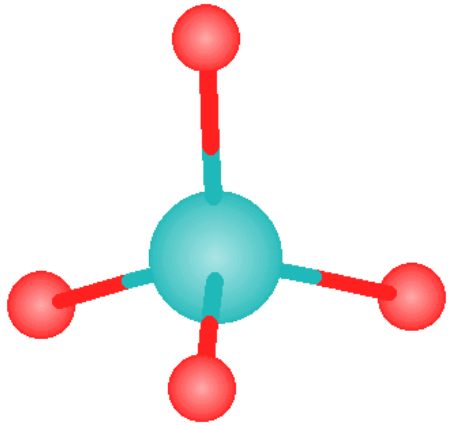
Geometry: Linear

Example: $[Ag(NH_3)_2]^+$

Common Geometries of Complexes

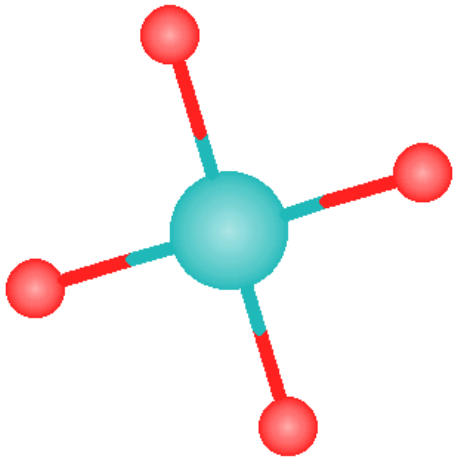
Coordination Number: 4

Geometry: Tetrahedral
(most common)



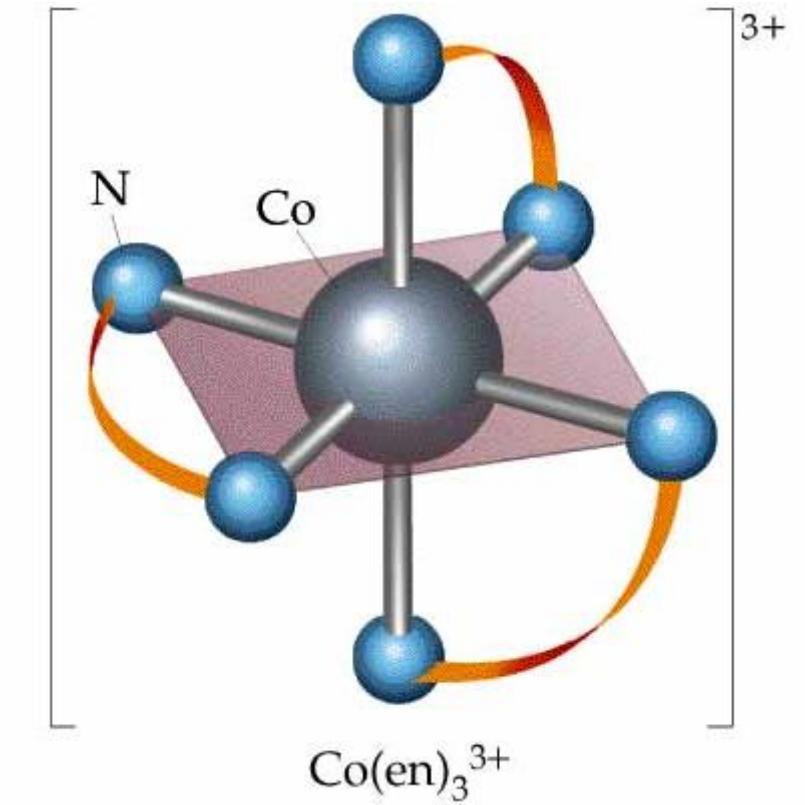
Examples: $[Zn(NH_3)_4]^{2+}$, $[FeCl_4]^-$

Geometry: Square planar (characteristic of metal ions with 8 d e^-)



Example: $[Ni(CN)_4]^{2-}$

Geometry

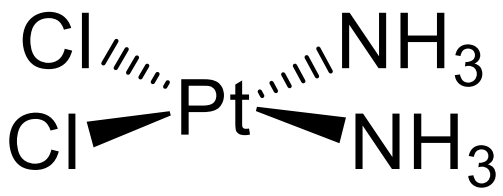


Octahedral

If the coordination no is 6 the ligand donor atoms are arranged octahedrally around the metal ion (octahedral complex)

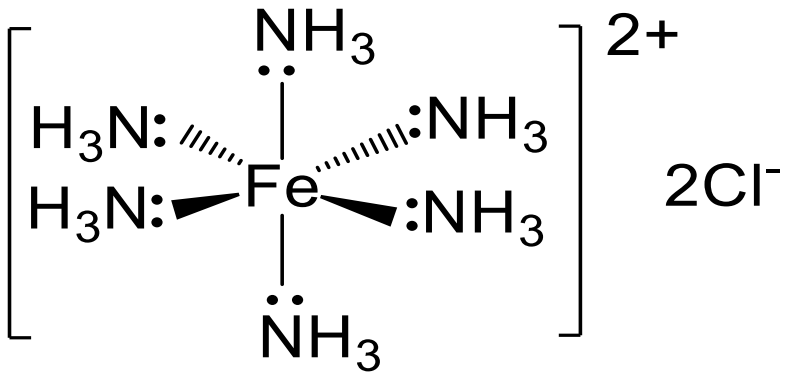
For 1st row d-block metal ions, coordination no = 6 (octahedral) is by far the most common

Geometry



Square planar

Oxidation State:
Coordination Number:



Octahedral

Oxidation State:
Coordination Number:

Learning outcomes

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Thank you

FOR MORE INFORMATION PLEASE CONTACT

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