Republic of Iraq
Ministry of Higher Education & Scientific research
Al-Mustaqbal University
Science College
Biochemistry Department

Introduction in Chemistry

For

First Year Student/course 2

Lecture 6

By

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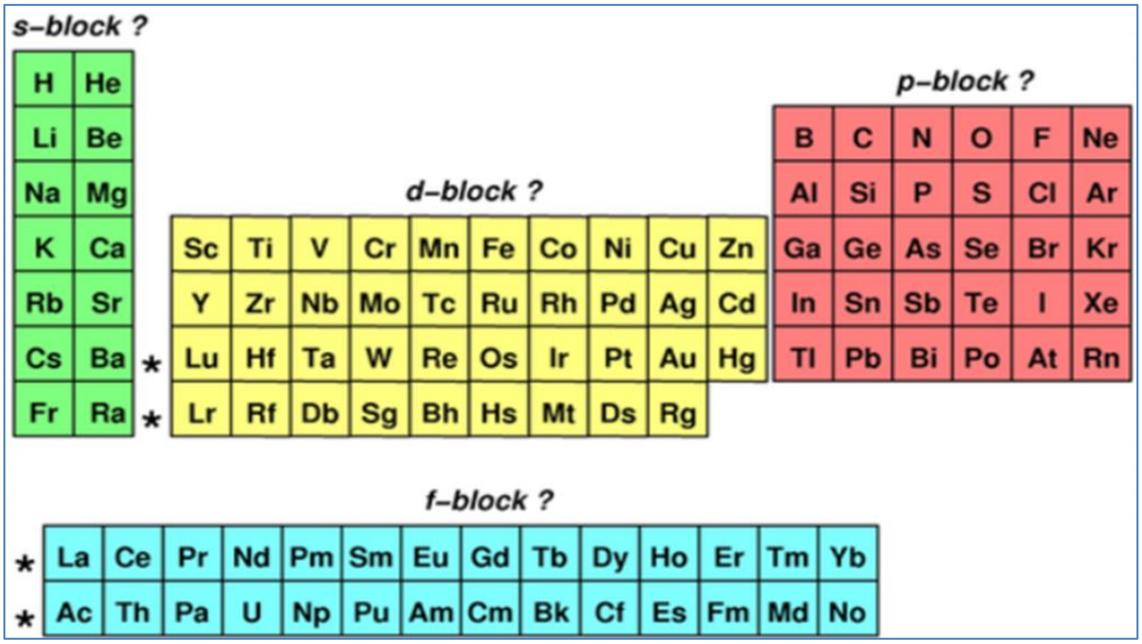
2024-2025

Introduction of Coordination Chemistry

Coordination or Complexes Compounds: Coordination chemistry is the chemistry of transition elements because coordination compounds contain a central metal ion or atom surrounded by a number of ions or molecules (ligands). The central metal ion is represented by transition metals, which are elements of the d- or f-block. These metals exhibit different magnetic and spectral properties, so we will focus in some detail on studying the properties of transition metals.

Transition Elements: The d-block elements in the periodic table include transition metals that have partially filled d-orbitals. There are three series of transition metals:

- The first series begins with scandium (Sc) and ends with zinc (Zn).
- The second series starts with yttrium (Y) and ends with cadmium (Cd).
- The third series begins with lanthanum (La) and ends with mercury (Hg), as shown in the following periodic table.



s-block ?

H	He
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	Ra

d-block ?

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
*	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	

p-block ?

B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn

f-block ?

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
*	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

The main group elements that precede the transition group do not have electrons in the **d** orbital, whereas transition elements contain electrons in the **d** orbital.

In the first transition series, all elements have a completely filled **s** orbital except for **chromium (Cr) and copper (Cu)**. Normally, the **s** orbital is filled first before the **d** orbital, as it is at a lower energy level.

However, in the case of **chromium (Cr) and copper (Cu)**, the electron configuration follows a different pattern due to stability reasons:

- **Chromium (Cr):** Instead of **$4s^2$ $3d^4$**, it adopts **$4s^1$ $3d^5$**, as a half-filled **d** orbital provides extra stability.
- **Copper (Cu):** Instead of **$4s^2$ $3d^9$**, it adopts **$4s^1$ $3d^{10}$**, as a fully filled **d** orbital is more stable.

This rearrangement occurs because atoms tend to adopt the most stable electronic configuration, which in these cases is achieved by filling the **d** orbital to either five or ten electrons.

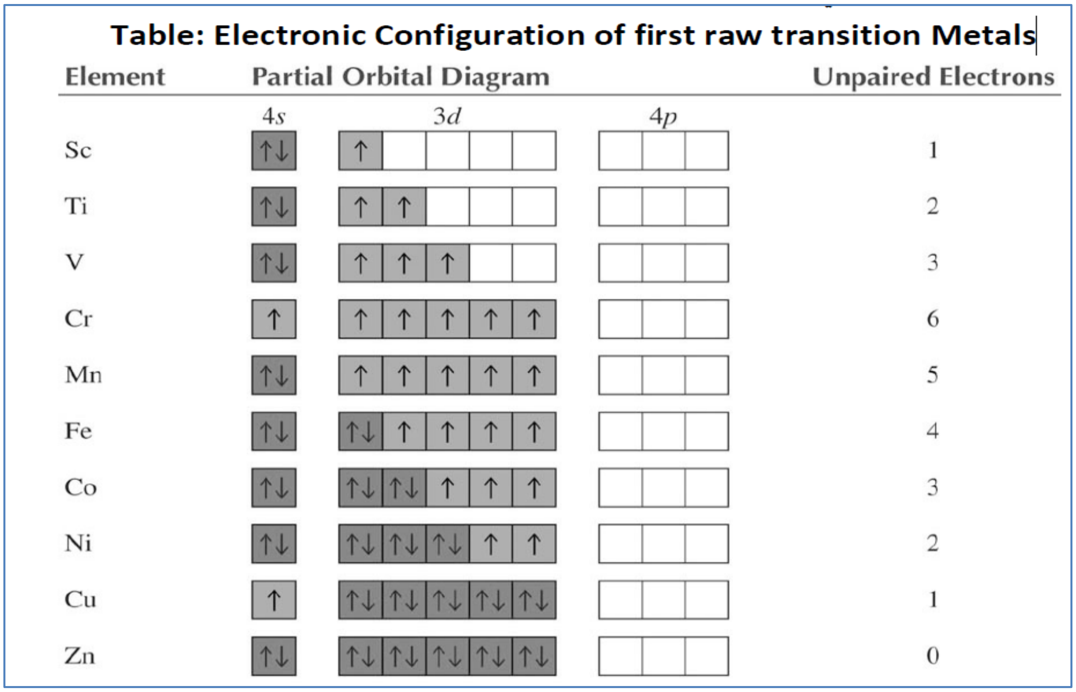


Table: Electronic Configuration of first raw transition Metals

Element	Partial Orbital Diagram									Unpaired Electrons
	4s	3d					4p			
Sc	↑↓	↑								1
Ti	↑↓	↑	↑							2
V	↑↓	↑	↑	↑						3
Cr	↑	↑	↑	↑	↑	↑				6
Mn	↑↓	↑	↑	↑	↑	↑				5
Fe	↑↓	↑↓	↑	↑	↑	↑				4
Co	↑↓	↑↓	↑↓	↑	↑	↑				3
Ni	↑↓	↑↓	↑↓	↑↓	↑	↑				2
Cu	↑	↑↓	↑↓	↑↓	↑↓	↑↓				1
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				0

Chemical Properties of Transition Elements:

Transition elements have distinct properties that set them apart from other elements, including:

- Formation of multiple oxidation states.
- Formation of colored ions and compounds.
- Exhibiting paramagnetic properties.
- Formation of complex compounds**.**

Variable Oxidation States:

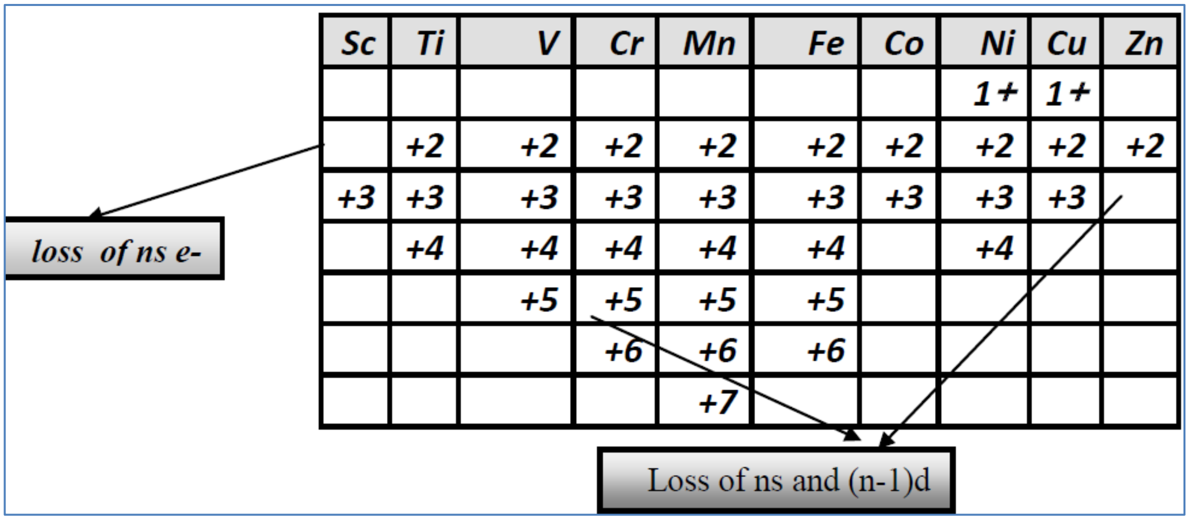
Transition elements are characterized by their ability to form **positive ions** in multiple oxidation states.

This is due to the **similar energy levels** of **(n-1)d** and **ns** orbitals, allowing these elements to participate in bonding by donating a varying number of electrons.

The stability of oxidation states depends on several factors, including:

- **Electronic configuration**
- **Type of bonding**
- **Coordination chemistry (spatial arrangement of ligands)**

The table below illustrates the different oxidation states of transition elements.



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							1+	1+	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4		+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

loss of ns e-

Loss of ns and (n-1)d

A Specific Trend Appears Across the Transition Series:

1-The oxidation number of each ion **increases** until reaching **manganese (Mn)**.

- After **Mn,** the oxidation number **starts to decrease**.
- This is due to the **increase in the effective nuclear charge**, which enhances the attraction between the nucleus and the electrons.

2-As the **oxidation state increases, the stability of transition elements decreases** across the period.

Coordination Compounds:

Coordination compounds are formed by the combination of two species:

- **Ligand:** A species that has a tendency to donate an electron pair.
- **Metal (Central Atom/Ion):** A species that provides empty orbitals (the space occupied by electrons) to accommodate the donated electron pair.

Definition of Coordination Compounds (Complexes):

A coordination compound (or complex) is formed when several ions or neutral molecules directly bond with a metal atom, exceeding its normal valence (oxidation state).

Components of a Coordination Compound:

1. **Central Metal Ion:** A positively charged metal ion acts as the central atom.
2. **Surrounding Ligands:** A set of negative ions or neutral molecules that surround the metal, exceeding its usual oxidation state.

  - Example: **Silver chloride (AgCl)** dissolves in ammonia, forming the complex ion **$[Ag(NH_3)_2]^+$**, as the number of coordinated ligands exceeds silver's oxidation state (+1). This structure is called the **coordination sphere** and is enclosed in brackets **[ ]**.

3. **Ligands:** Groups directly bonded to the central metal ion, donating electron pairs.
4. **Coordination Number:** The number of ligands attached to the central metal ion.
5. **Donor Molecules (Ligands):** Ligands possess **lone electron pairs**, which they donate to the metal center, forming a **coordinate covalent bond**.
6. **Central Metal Orbitals:** The metal must have **empty orbitals** in its valence shell to accept electron pairs from the ligands, interacting with them effectively. The **effective nuclear charge** also plays a role in bond formation.
7. **Coordination Bond:** The bond formed between a ligand and the central metal ion is called a **coordinate covalent (dative) bond**.
8. **Charge of the Coordination Sphere:** The overall charge depends on the sum of the metal ion's charge and the ligand charges. It can be **neutral, positively charged, or negatively charged**.
9. **Complex Formation in Aqueous Solutions:** In aqueous solutions, even simple metal salts form complexes, as **water itself acts as a ligand**. This means that a transition metal ion in solution is always part of a coordination complex.

Example:

- **Copper(II) sulfate ($CuSO_4$)** in its solid form is a **simple salt**.

- When dissolved in water, it forms a **clear blue solution**, which consists of **complex ions** where water molecules coordinate around the central **Cu^{2+} ion**:

$CuSO_4 + H_2O \rightarrow [Cu(H_2O)_6]^{2+} + SO_4^{2-}$

White Blue

Double Salt:

A double salt is a stable additive compound that, when dissolved in water, gives all the ions that make it up.

$KCl \cdot MgCl_2 \cdot 6H_2O \rightarrow Cl^-, K^+, Mg^{2+}$

Coordination Compound:

A coordination compound is a stable additive compound, but it does **not give all the ions** that make it up when dissolved in water.

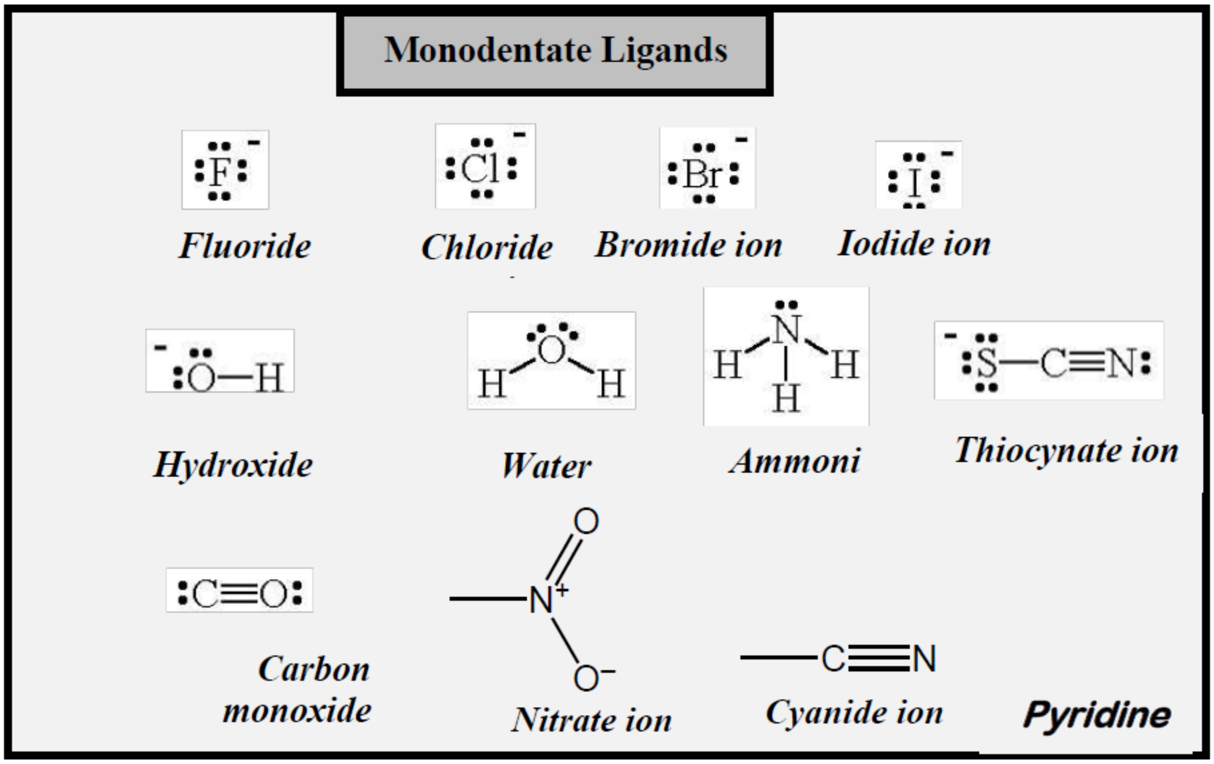
$CuSO_4 \cdot 4NH_3 \cdot 2H_2O \rightarrow [Cu(H_2O)_2(NH3)_4]^{2+}$

In the coordination compound, the copper ion is surrounded by water and ammonia molecules, and the complex retains its coordination structure without fully dissociating into all individual ions.

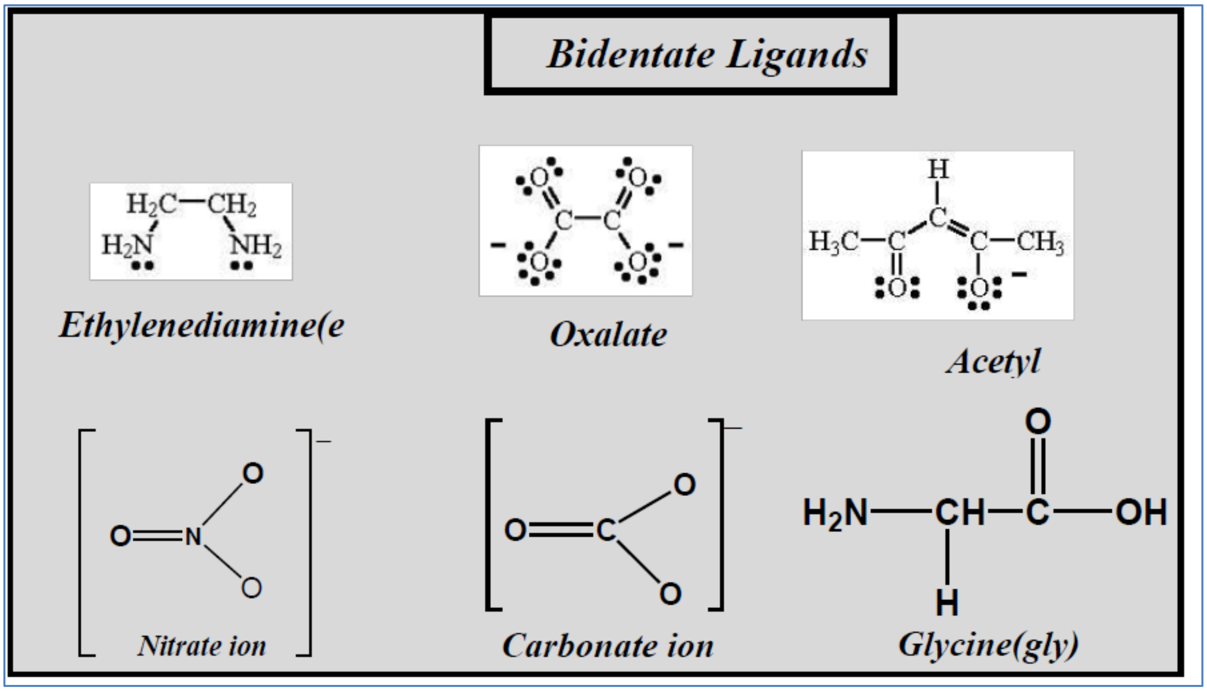
Type of Ligands

A **ligand** can be defined as any atom, ion, or molecule that is capable of donating one or more electron pairs to form one or more coordinate bonds. Most ligands provide an electron pair that can form a coordinate bond with the central atom. Some ligands, such as **C_2H_4** (ethylene) or **C_6H_6** (benzene), use **π-electrons** for bonding.

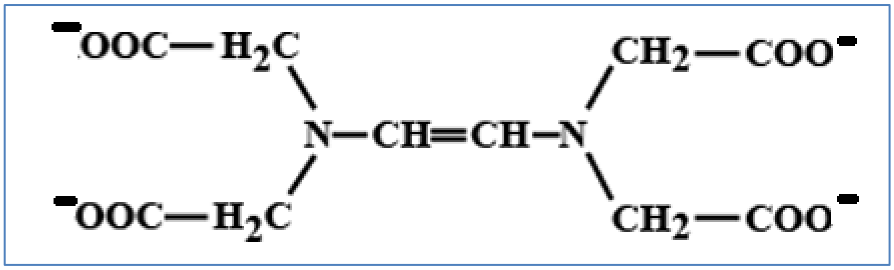
Ligands that bind to the central metal atom through a single donor atom are called **monodentate ligands**. Examples include ligands that donate only one electron pair to the central metal.

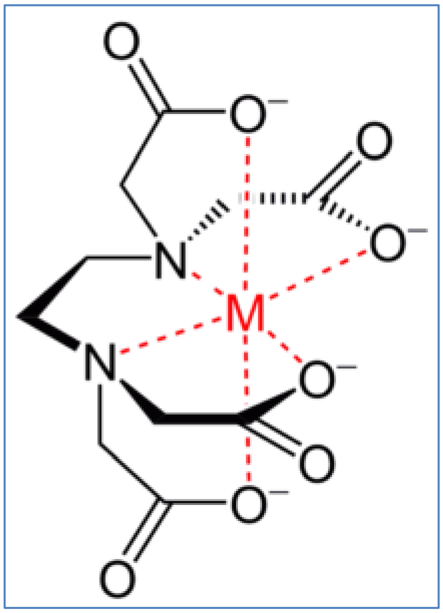


There are many ions or molecules that have the ability to bind to a metal ion through **more than one donor atom**. If a molecule or ion contains **two atoms** capable of coordinating with the central metal ion, it is called a **bidentate ligand**.



The groups that contain three, four, or sometimes more atoms capable of contributing to coordinate bonding are called **multidentate ligands**. These ligands can form multiple coordinate bonds with the central metal ion, providing even greater stability to the complex.



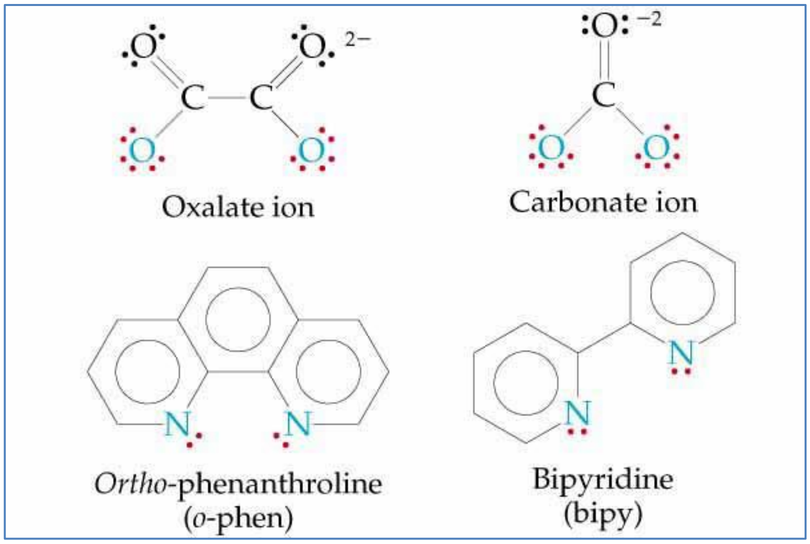


EDTA(Ethylediamine tetraacetic acid)bounded Co^{+3} by six donors in

Chelating Ligands are ligands that contain two or more functional groups capable of donating electron pairs. These ligands bind strongly to metal ions, forming one or more stable rings around the central metal ion, which increases the stability of the resulting complex.

For example, **amines (NH_2)** and functional groups such as **-COOH**, **$-SO_3H$**, and **-NHO** can form coordinate bonds at multiple positions with the same metal ion, creating one or more rings. These **bidentate ligands** are among the simplest and most well-known types of **chelating ligands**.

These chelating ligands have many important uses due to their ability to form stable complexes with metal ions.

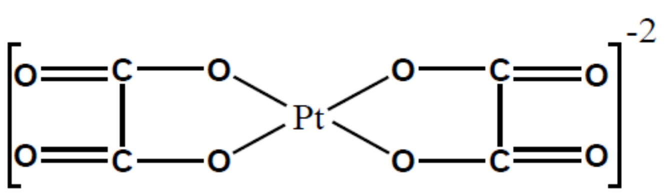


Oxalate ion

Carbonate ion

Ortho-phenanthroline (*o*-phen)

Bipyridine (bipy)



Bis(oxalato)platinate(IV)ion

It is important to mention that some ligands can occupy **coordination sites** in the same structure for **two or even three central metal atoms**. These ligands act as **bridges**, forming **polynuclear complex compounds**. Such ligands are called **bridging ligands (Bridge Ligands).**

In many cases, **monodentate bridging ligands** are commonly found, such as **halides (Cl^-, Br^-, etc.), hydroxide (OH^-),** and **amines (NH_2).**

Examples of bridging ligands include:

- **Halide ions (Cl^-, Br^-, I^-)**
- **Hydroxide (OH^-)**
- **Amino groups (NH_2)**

These ligands help connect multiple metal centers, leading to the formation of polynuclear coordination complexes.