

Coordination Chemistry

Complexes or **coordination compounds** are molecules that possess a metal center that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighboring counter-ions.

Introduction

Coordination chemistry emerged from the work of Alfred Werner, a Swiss chemist who examined different compounds composed of cobalt(III) chloride and ammonia. Upon the addition of hydrochloric acid, Werner observed that ammonia could not be completely removed. He then proposed that the ammonia must be bound more tightly to the central cobalt ion. However, when aqueous silver nitrate was added, one of the products formed was solid silver chloride. The amount of silver chloride formed was related to the number of ammonia molecules bound to the cobalt(III) chloride. For example, when silver nitrate was added to $\text{CoCl}_3 \cdot 6\text{NH}_3$, all three chlorides were converted to silver chloride. However, when silver nitrate was added to $\text{CoCl}_3 \cdot 5\text{NH}_3$, only 2 of the 3 chlorides formed silver chloride. When $\text{CoCl}_3 \cdot 4\text{NH}_3$ was treated with silver nitrate, one of the three chlorides precipitated as silver chloride.

The resulting observations suggested the formation of **complex** or **coordination compounds**. In the **inner coordination sphere**, which is also referred to in some texts as the **first sphere**, ligands are directly bound to the central metal. In the **outer coordination sphere**, sometimes referred to as the **second sphere**, other ions are attached to the complex ion. Werner was awarded the Nobel Prize in 1913 for his coordination theory. The following table is a summary of Werner's observations:

Initial compound	Resulting compounds upon adding AgNO_3
$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+}(\text{Cl})_3$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{Cl})_2$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+(\text{Cl})$
$\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

As the table above shows, the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ is countered by the three chloride ions. The multi-level binding of coordination complexes play an important role in determining the dissociation of these complexes in aqueous solution. For example, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{Cl})_2$ dissociates into 3 ions while $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+(\text{Cl})$ dissociates into 2 ions. It further dissociates. By applying a current through the aqueous solutions of the resulting complex compounds, Werner measured the electrical conductivity and thus the dissociation properties of the complex compounds. The results confirmed his hypothesis of the formation of complex compounds. It is important to note that the above compounds have a [coordination number](#) of 6, which is a common coordination number for many inorganic complexes. Coordination numbers for complex compounds typically range from 1 to 16.

Properties of Coordination Complexes

Some methods of verifying the presence of complex ions include studying its chemical behavior. This can be achieved by observing the compounds' color, solubility, absorption spectrum, magnetic properties, etc. The properties of complex compounds are separate from the properties of the individual atoms. By forming coordination compounds, the properties of both the metal and the ligand are altered.

Metal-ligand bonds are typically thought of Lewis acid-base interactions. The metal atom acts as an electron pair acceptor (Lewis acid), while the ligands act as electron pair donors (Lewis base). The nature of the bond between metal and ligand is stronger than [intermolecular forces](#) because they form directional bonds between the metal ion and the ligand, but are weaker than covalent bonds and ionic bonds.

Common Ligands

Monodentate ligands donate one pair of electrons to the central metal atoms. An example of these ligands are the halide ions (F⁻, Cl⁻, Br⁻, I⁻). Polydentate ligands, also called chelates or chelating agents, donate more than one pair of electrons to the metal atom forming a stronger bond and a more stable complex. A common chelating agent is ethylenediamine (en), which, as the name suggests, contains two amines or :NH₂ sites which can bind to two sites on the central metal. An example of a tridentate ligand is bis-diethylenetriamine. An example of such a coordination complex is bis-diethylenetriamine cobalt ^{III}.

Complex compound/ion	Coordination number	Oxidation State of Metal Atom
[Fe(CN) ₆] ⁴⁻	6	2+
[Co(NH ₃) ₄ SO ₄] ⁻	5	1+
[Pt(NH ₃) ₄] ²⁺	4	2+
[Ni(NH ₂ CH ₂ CH ₂ NH ₂) ₃] ²⁺	6	2+

Complex ions can form many compounds by binding with other complex ions in multiple ratios. This leads to many combinations of coordination compounds. The structures of certain coordination compounds can also have isomers, which can change their interactions with other chemical agents. The binding between metal and ligands is studied in [metals, tetrahedral, and octahedral structures](#). There are many pharmaceutical and biological applications of coordination complexes and their isomers.

Nomenclature

[Coordination complexes](#) have their own classes of [isomers](#), different [magnetic properties](#) and [colors](#), and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal Anions Neutrals]^{±Charge}, while names are written Prefix Ligands Metal(Oxidation State).

Introduction

According to the [Lewis base theory](#), ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. Coordination complexes consist of a ligand and a metal center cation. The overall charge can be positive, negative, or neutral. Coordination compounds are complex or contain complex ions, for example:

- Complex Cation: $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Complex Anion: $[\text{CoCl}_4(\text{NH}_3)_2]^-$
- Neutral Complex: $[\text{CoCl}_3(\text{NH}_3)_3]$
- Coordination Compound: $\text{K}_4[\text{Fe}(\text{CN})_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex. Ex: NH_3 , H_2O , Cl^- . The number of ligands that attach to a metal depends on whether the ligand is monodentate, bidentate, or polydentate. For more information, see [Ligands](#) and [Chelation](#).

Naming Coordination Complexes

Given Formula → Write Name

To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rules for Naming the Ligands

1. Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro).

Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Anionic Monodentate Ligands			
F ⁻	Fluoro	OH ⁻	Hydroxo
Cl ⁻	Chloro	SO ₄ ²⁻	Sulfato
Br ⁻	Bromo	S ₂ O ₃ ²⁻	Thiosulfato
I ⁻	Iodo	NO ₂ ⁻	Nitrito-N-; Nitro
O ²⁻	Oxo	ONO ⁻	Nitrito-O-; Nitrito
CN ⁻	Cyano	SCN ⁻	Thiocyanato-S-; Thiocyanato
NC ⁻	Isocyano	NCS ⁻	Thiocyanato-N-; Isothiocyanato

2. Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Neutral Monodentate Ligands	
NH ₃	Ammine
H ₂ O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH ₃ NH ₂	Methylamine
C ₅ H ₅ N	Pyridine

(Note: Ammine is spelled with two *m*'s when referring to a ligand. [Amines](#) are something else.)

Polydentate ligands follow the same rules for anions and neutral molecules.

en	Ethylenediamine
ox ²⁻	Oxalato
EDTA ⁴⁻	Ethylenediaminetetraacetato

3. The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and EDTA⁴⁻ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use bis, tris, and tetrakis.

	Normal	Polydentates
1	mono	-
2	di	bis

3	tri	tris
4	tetra	tetrakis
5	penta	-
6	hexa	-

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[\text{FeCl}(\text{CO})_2(\text{NH}_3)_3]^{2+}$ would be called triammine*chloro*dicarbonyliron(III) ion. Remember that ligands are always named first, before the metal is.

Source: http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Coordination_Chemistry