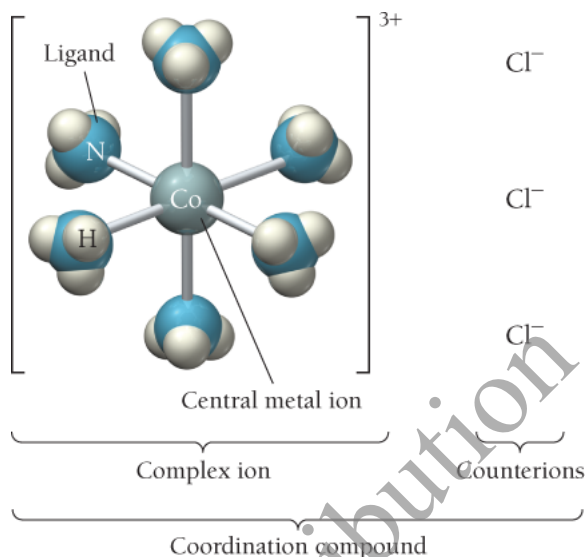


22.3: Coordination Compounds

We discussed at the end of [Chapter 17](#) that transition metals tend to form *complex ions*. A **complex ion** contains a central metal ion bound to one or more *ligands*. A **ligand** is a Lewis base (or electron donor) that forms a bond with the metal. When a complex ion combines with one or more *counterions* (ions of opposite charge that are not acting as ligands), the resulting neutral compound is a **coordination compound**.



Coordination Compound A coordination compound contains a complex ion and corresponding counterions. The complex ion contains a central metal atom coordinated to several ligands. The compound shown here is $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$.

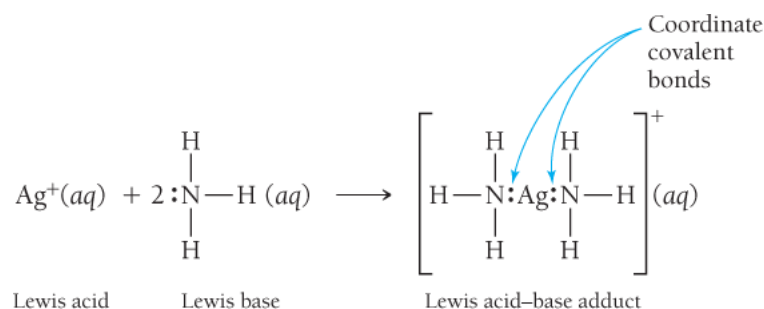
The first coordination compounds were discovered in the early eighteenth century, but their nature was not understood until nearly 200 years later. Swiss chemist Alfred Werner (1866–1919) studied coordination compounds extensively—especially a series of cobalt(III) compounds with ammonia, which had formulas that at that time were written as $\text{CoCl}_3 \cdot 6 \text{NH}_3$, $\text{CoCl}_3 \cdot 5 \text{NH}_3$, and $\text{CoCl}_3 \cdot 4 \text{NH}_3$. In 1893, he proposed that the central metal ion has two types of interactions, which he named **primary valence** and **secondary valence**. The primary valence is the oxidation state on the central metal atom, and the secondary valence is the number of molecules or ions (ligands) directly bound to the metal atom, called the **coordination number**. In $\text{CoCl}_3 \cdot 6 \text{NH}_3$ the primary valence is +3, and the ammonia molecules are directly bound to the central cobalt, giving a coordination number of 6. Today we write the formula of this compound as $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ to better represent the coordination compound as the combination of a complex ion, $\text{Co}(\text{NH}_3)_6^{3+}$, and three Cl^- counterions.

We write the formulas of the other cobalt(III) coordination compounds studied by Werner as $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}$. In these two cases, the complex ions are $\text{Co}(\text{NH}_3)_5 \text{Cl}^{2+}$ (with two Cl^- counterions) and $\text{Co}(\text{NH}_3)_4 \text{Cl}_2^+$ (with one Cl^- counterion), respectively. With this series of compounds, Werner demonstrated that the Cl^- can replace NH_3 in the secondary valence. In other words, Cl^- can act as a counterion, or it can bond directly to the metal as a ligand and, therefore, be part of the complex ion.

Ligands

The complex ion itself contains the metal ion in the center and the ligands—which can be neutral molecules or ions—arranged around it. We can think of the metal–ligand complex as a Lewis acid–base adduct (see [Section 16.11](#)) because the bond is formed when the ligand donates a pair of electrons to an empty orbital on the

10.11-), because the bond is formed when the ligand donates a pair of electrons to an empty orbital on the metal. For example, consider the reaction between the silver ion and ammonia:



A bond of this type, which we first encountered in Sections 5.5 and 6.2, is a **coordinate covalent bond**. Ligands are therefore good Lewis bases and have at least one pair of electrons to donate to, and bond with, the central metal ion. Table 22.2 contains a number of common ligands.

Table 22.2 Common Ligands

Name	Lewis structure
water	$\text{H}-\ddot{\text{O}}-\text{H}$
ammonia	$\text{H}-\ddot{\text{N}}(\text{H})_2$
chloride ion	$[\text{:}\ddot{\text{Cl}}\text{:}]^-$
carbon monoxide	$\text{:C}\equiv\text{O:}$
cyanide ion	$[\text{:C}\equiv\text{N:}]^-$
thiocyanate ion	$[\text{:S}=\text{C}=\ddot{\text{N}}:]^-$
oxalate ion (ox)	$\left[\begin{array}{c} \ddot{\text{O}} \quad \ddot{\text{O}} \\ \parallel \quad \parallel \\ \text{C} - \text{C} \\ \parallel \quad \parallel \\ \ddot{\text{O}} \quad \ddot{\text{O}} \end{array} \right]^{2-}$
ethylenediamine (en)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\ddot{\text{N}}-\text{C}-\text{C}-\ddot{\text{N}}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
ethylenediaminetetraacetate (EDTA)	$\left[\begin{array}{c} \text{:O:} \quad \text{:O:} \\ \parallel \quad \parallel \\ \text{:}\ddot{\text{O}}-\text{CCH}_2-\text{NCH}_2\text{CH}_2-\text{N}-\text{CH}_2\text{C}-\ddot{\text{O}}\text{:} \\ \parallel \quad \parallel \quad \parallel \quad \parallel \\ \text{:}\ddot{\text{O}}-\text{CCH}_2-\text{NCH}_2\text{CH}_2-\text{N}-\text{CH}_2\text{C}-\ddot{\text{O}}\text{:} \\ \parallel \quad \parallel \quad \parallel \quad \parallel \\ \text{:O:} \quad \text{:O:} \end{array} \right]^{4-}$

Ligands that donate only one electron pair to the central metal are **monodentate**. Some ligands, however, have the ability to donate two pairs of electrons (from two different atoms) to the metal; these are **bidentate**.

Examples of bidentate ligands include the oxalate ion (abbreviated ox) and the ethylenediamine molecule (abbreviated en), which we show below. **Figure 22.5a** shows the ethylenediamine ligand bonded to Co^{3+} .

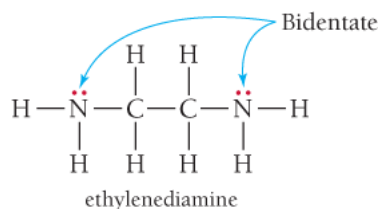
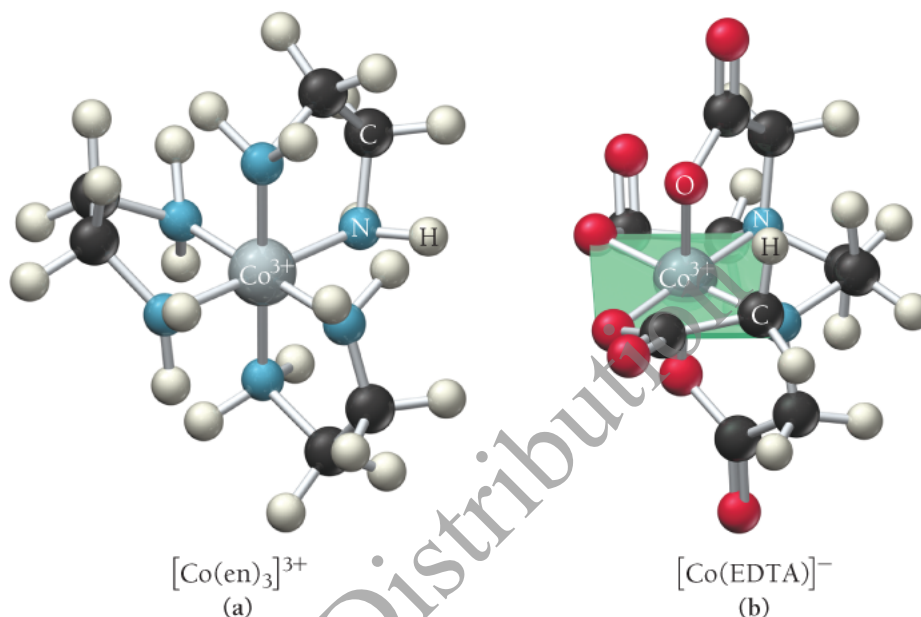


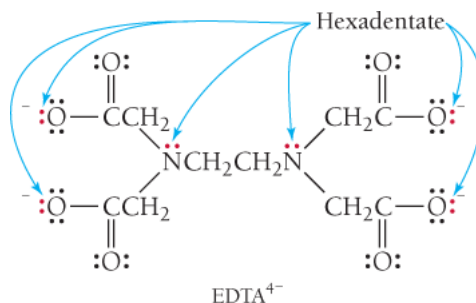
Figure 22.5 Bidentate and Polydentate Ligands Coordinated to Co(III)

(a) Ethylenediamine is a bidentate ligand; (b) EDTA is a hexadentate ligand.

Bidentate and Polydentate Ligands Coordinated to Cobalt(III)



Some ligands, called **polydentate** ligands, can donate even more than two electron pairs (from more than two atoms) to the metal. The most common polydentate ligand is the ethylenediaminetetraacetate ion (EDTA^{4-}) shown here:



The EDTA ligand wraps itself completely around the metal, donating up to six pairs of electrons (**Figure 22.5b**). A complex ion that contains either a bidentate or polydentate ligand is a **chelate** (pronounced “key-late”), and the coordinating ligand is known as a **chelating agent**.


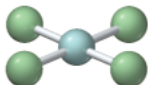
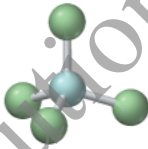
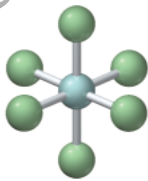
Coordination Numbers and Geometries

A survey of many coordination compounds shows that coordination numbers can vary from as low as 2 to as

high as 12. The most common coordination numbers are 6, as occurs in $[\text{Co}(\text{NH}_3)_6]^{3+}$, and 4, as occurs in $[\text{PdCl}_4]^{2-}$. Coordination numbers greater than 6 are rarely observed for the first-row transition metals. Typically, only 1+ metal ions have a coordination number as low as 2, as occurs in $[\text{Ag}(\text{NH}_3)_2]^+$. Odd coordination numbers exist, but they are rare.

The common geometries of complex ions, shown in Table 22.3, depend in part on their coordination number. A coordination number of 2 results in a linear geometry, and a coordination number of 6 results in an octahedral geometry. A coordination number of 4 can have either a tetrahedral geometry or a square planar geometry, depending on the number of d electrons in the metal ion. Metal ions with a d^8 electron configuration (such as $[\text{PdCl}_4]^{2-}$) exhibit square planar geometry, and metal ions with a d^{10} electron configuration (such as $[\text{Zn}(\text{NH}_3)_4]^{2+}$) exhibit tetrahedral geometry.

Table 22.3 Common Geometries of Complex Ions

Coordination Number	Shape	Model	Example
2	Linear		$[\text{Ag}(\text{NH}_3)_2]^+$
4	Square planar		$[\text{PdCl}_4]^{2-}$
4	Tetrahedral		$[\text{Zn}(\text{NH}_3)_4]^{2+}$
6	Octahedral		$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Naming Coordination Compounds

To name coordination compounds, we follow a series of general rules based on the system originally proposed by Werner. As with ionic compounds, the name of the cation goes before the name of the anion.

Guidelines for Naming Complex Ions	Examples
1. Name the ligands. <ul style="list-style-type: none"> Name neutral ligands as molecules with the following notable exceptions: <ul style="list-style-type: none"> H_2O (aqua) NH_3 (ammine) CO (carbonyl) Name anionic ligands with the name of the ion plus an ending modified as follows: <ul style="list-style-type: none"> -ide becomes -o -ate becomes -ato -ite becomes -ito 	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ is ethylenediamine. H_2O is aqua. Cl^- is chloro. SO_4^{2-} is sulfato. SO_3^{2-} is sulfito.
Table 22.4 lists the names of some common ligands.	
2. List the names of the ligands in alphabetical order before the name of the metal cation.	Ammine (NH_3) is listed before chloro (Cl^-), which is listed before nitrito (NO_2^-).
3. Use a prefix to indicate the number of ligands (when there is more than one of a particular type): di- (2), tri- (3), tetra- (4), penta- (5), or hexa- (6). If the name of the ligand already contains a prefix, such as ethylenediamine, place parentheses around the ligand name and use bis- (2), tris- (3), or tetrakis- (4) to indicate the number. Prefixes do not affect the order in which you list the ligands.	Trichloro indicates three Cl^- ligands. Tetraammine indicates four NH_3 ligands. Tris(ethylenediamine) indicates three ethylenediamine ligands.
4. Name the metal. <ul style="list-style-type: none"> When the complex ion is a cation, use the name of the metal followed by the oxidation state written with a Roman numeral. 	In cations: Co^{3+} is cobalt(III). Pt^{2+} is platinum(II). Cu^{+} is copper(I).

numeral.	In anions: Co ³⁺ is cobaltate(III). Pt ⁴⁺ is platinate(IV). Cu ⁺ is cuprate(I).
b. If the complex ion is an anion, drop the ending of the metal and add -ate followed by the oxidation state written with a Roman numeral. Some metals use the Latin root with the -ate ending. Table 22.5 lists the names for some common metals in anionic complexes.	
5. Write the entire name of the complex ion by listing the ligands first, followed by the metal.	[Pt(NH ₃) ₂ Cl ₄] ²⁻ is diamminetetrachloroplatinate(II). [Co(NH ₃) ₆] ³⁺ is hexaamminecobalt(III).

Table 22.4 Names and Formulas of Common Ligands

Ligand	Name in Complex Ion
Anions	
bromide, Br ⁻	bromo
chloride, Cl ⁻	chloro
hydroxide, OH ⁻	hydroxo
cyanide, CN ⁻	cyano
nitrite, NO ₂ ⁻	nitro
oxalate, C ₂ O ₄ ²⁻ (ox)	oxalato
ethylenediaminetetraacetate (EDTA ⁴⁻)	Ethylenediaminetetraacetato
Neutral molecules	
water, H ₂ O	aqua
ammonia, NH ₃	ammine
carbon monoxide, CO	carbonyl
ethylenediamine (en)	ethylenediamine

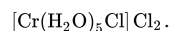
Table 22.5 Names of Common Metals When Found in Anionic Complex Ions

Metal	Name in Anionic Complex
chromium	chromate
cobalt	cobaltate
copper	cuprate
gold	aurate
iron	ferrate
lead	plumbate
manganese	manganate
molybdenum	molybdate
nickel	nickelate
platinum	platinate
silver	argentate
tin	stannate
zinc	zincate

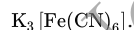
When we write the *formula* of a complex ion, we write the symbol for the metal first, followed by neutral molecules and then anions. If there is more than one anion or neutral molecule acting as a ligand, we list them in alphabetical order based on the chemical symbol.

Example 22.3 Naming Coordination Compounds

Name the compound.

**PROCEDURE** Identify the cation and anion and first name the simple ion (i.e., not the complex one).**SOLUTION** $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ is a complex cation. Cl^- is chloride.**PROCEDURE** Give each ligand a name and list them in alphabetical order.**SOLUTION** H_2O is aqua. Cl^- is chloro.**PROCEDURE** Name the metal ion.**SOLUTION** Cr^{3+} is chromium(III).**PROCEDURE** Name the complex ion by adding prefixes to indicate the number of each ligand, followed by the name of each ligand, followed by the name of the metal ion.**SOLUTION** $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ is pentaquachlorochromium(III).**PROCEDURE** Name the compound by writing the name of the cation before the anion. The only space is between ion names.**SOLUTION** $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ is pentaquachlorochromium(III) chloride.**FOR PRACTICE 22.3** Name the following compound: $[\text{Mn}(\text{CO})(\text{NH}_3)_5]\text{SO}_4$.**Example 22.4 Naming Coordination Compounds**

Name the compound.

**PROCEDURE** Identify the cation and anion and first name the simple ion (i.e., not the complex one).**SOLUTION** K^+ is potassium. $[\text{Fe}(\text{CN})_6]^{3-}$ is a complex anion.**PROCEDURE** Give each ligand a name and list them in alphabetical order.**SOLUTION** CN^- is cyano.**PROCEDURE** Name the metal ion.**SOLUTION** Fe^{3+} is ferrate(III) because the complex is anionic.**PROCEDURE** Name the complex ion by adding prefixes to indicate the number of each ligand, followed

PROCEDURE Name the complex ion by adding prefixes to indicate the number of each ligand, followed by the name of each ligand, followed by the name of the metal ion.

SOLUTION $[\text{Fe}(\text{CN})_6]^{3-}$ is hexacyanoferrate(III).

PROCEDURE Name the compound by writing the name of the cation before the anion. The only space is between ion names.

SOLUTION $\text{K}_3[\text{Fe}(\text{CN})_6]$ is potassium hexacyanoferrate(III)

FOR PRACTICE 22.4 Name the following compound: $\text{Na}_2[\text{PtCl}_4]$.

Not for Distribution

Not for Distribution