Transition metal ions and some main block elements form coordination compounds which typically consist of a coordinate complex and counter ions. Coordination complexes are composed of ligands surrounding a central metal atom or ion. The coordinate complex itself consists of a transition metal atom or ion and the surrounding ligands. The coordinate complex is always enclosed in square brackets, [ ]. The coordinate complex can be an ion, cation or anion, or a neutral complex. Counter ions are needed to produce a neutral coordinate compound if the complex is an ion.

Ligands possess one or more donor atoms, atoms that donate the lone pair of electrons. Donor atoms may possess more than one lone pair of electrons, but only one pair is involved in the bond. An electron pair donor is referred to as a Lewis Base. The central metal atom or ion accepts the lone pair of electrons involved in the bond. An electron pair receptor is referred to as a Lewis Acid. Bonds that are formed between the ligands and the central metal atom or ion are distinctive in that the bonds of the molecule are formed with both of the electrons involved in the bond being donated by just one of the atoms involved in the bond; this is known as a coordinate covalent bond.

Example: \([\text{Fe(OH}_2\text{)}_6]\text{Cl}_2\); Hexaaquaiiron (II), \([\text{Fe(OH}_2\text{)}_6]^+\), is a complex ion consisting of the transition metal ion Fe\(^{+2}\) and six attached neutral water, OH\(_2\), ligands. The oxygen atom of each water molecule has two lone pairs of electrons one of which the neutral ligand donates to the coordinate covalent bond. The oxygen atom is referred to as the donor atom. The donor atom is listed first in the chemical formula of the ligand in contrast with the normal pattern for the ordering of atoms in a chemical formula: cation then anion. Also, note that when bringing together the complex ion with the counter ion, the complex ion is always enclosed in brackets [ ] while names of common ligands are enclosed in parenthesis ( ). The counter ion in for this example is the chloride anion, Cl\(^-\).

Many transition metal complexes, e.g., \([\text{Cu(NH}_3\text{)}_4]\text{Cl}_2\) are neutral and do not require counter ions.

### Q3.1: Oxidation States of Transition Metals in Complexes

Determine the (1) oxidation number for each of the transition metal atoms (2) the charge of each cation, and (3) the charge of each anion in these compounds (if existing). You will have to consult Tables \(\PageIndex{1}\) and \(\PageIndex{2}\).

a. \([\text{V(OH}_2\text{)}_6]\text{(NO}_3\text{)}_3\)
b. \((\text{NH}_4\text{)}_2[\text{CoCl}_4]\)
c. \([\text{Co(py)}_4]\text{Br}_2\)
d. \(\text{K}_4[\text{Mn(CN)}_6]\)
e. \([\text{Co(P(CH}_3\text{)}_3\text{)}_4]\text{SO}_4\text{)}_3\)
Complex Ion Nomenclature

The chemical formula and the chemical name for **Complex cations** have different rules. The complex cation **chemical formula** follows traditional rules for naming ionic compounds with the cation listed first. For example \([\text{Cu(OH}_2\text{)}_6]^{2+}\), the cationic copper II ion is listed first and the neutral water ligand is listed second. Complex cation **chemical names** are assembled by alphabetically listing the number and name of the ligands attached to the central metal atom or ion followed by the name of the central atom and its oxidation number indicated by a Roman numeral in parenthesis, for example, hexaaquacopper (II).

The chemical names and formulas for **Complex anions** follow the same rules as complex cations with one additional step. The name of the central atom is changed by adding an –ate ending and then the oxidation number in parentheses. For example: \([\text{FeF}_6]^{3-}\), hexafluoroferrate (III). Note here also that the Latin name for iron is used to avoid an awkward sounding name. A list of such transition metals follows in the section on naming rules.

**Ligands** are ions, ionic molecules, or neutral molecules that have atoms which possess lone pairs and thus act as Lewis bases. Ligand is derived form the Latin *legare* meaning to bind. The lone electron pairs are donated to empty d orbitals of the transition metal atom or ion creating a coordinate covalent bond. When a ligand donates only a single pair of electrons to the metal center the ligand is referred to as **monodentate**. **Dentate** comes from the Latin *dens* meaning tooth. Monodentate then figuratively means single toothed. Ligands that donate two, three, four, five, or six lone pairs of electrons are collectively referred to as **polydentate**, and **bidentate, tridentate, tetradeante, pentadentate, and sexadentate** respectively. Polydentate ligands typically form five- and six-membered rings and are referred to as **chelating agents** and the complex is referred to as **chelate**. Chelate comes from the Greek *chela* meaning claw.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>aqua</td>
<td>OH₂</td>
<td>monodentate</td>
</tr>
<tr>
<td>ammine</td>
<td>NH₃</td>
<td>monodentate</td>
</tr>
<tr>
<td>benzene</td>
<td>C₆H₆</td>
<td>monodentate</td>
</tr>
<tr>
<td>carbonyl</td>
<td>CO</td>
<td>monodentate</td>
</tr>
<tr>
<td>nitrosyl</td>
<td>NO</td>
<td>monodentate</td>
</tr>
<tr>
<td>methylamine</td>
<td>CH₃NH₂</td>
<td>monodentate</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>(CH₃)₂NH₂</td>
<td>monodentate</td>
</tr>
<tr>
<td>trimethylamine</td>
<td>N(CH₃)₃</td>
<td>monodentate</td>
</tr>
<tr>
<td>ethylenediamine or en</td>
<td>H₂NCH₂CH₂NH₂</td>
<td>bidentate</td>
</tr>
<tr>
<td>diethylenetriamine or dien</td>
<td>NH(CH₂CH₂NH₂)₂</td>
<td>tridentate</td>
</tr>
<tr>
<td>Ligand</td>
<td>Formula</td>
<td>Coordination</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>triethylenetetraamine or trien</td>
<td>N(CH₂CH₂NH₂)₃</td>
<td>tetradentate</td>
</tr>
<tr>
<td>Pyridine or py</td>
<td>C₅H₅N</td>
<td>monodentate</td>
</tr>
<tr>
<td>2,2'-bipyridine or bipy</td>
<td>(C₅H₄N)₂</td>
<td>bidentate</td>
</tr>
<tr>
<td>2,2',6',2''-terpyridine or terpy</td>
<td>(C₅H₄N)₃</td>
<td>tridentate</td>
</tr>
<tr>
<td>bis(diphenylphosphine) ethylene or dppe</td>
<td>(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂</td>
<td>bidentate</td>
</tr>
<tr>
<td>bis(dimethylphosphino) ethylene or dmpe</td>
<td>(CH₃)₂P(CH₂)₂P(CH₃)₂</td>
<td>bidentate</td>
</tr>
<tr>
<td>trimethylphosphine (PMe₃)</td>
<td>P(CH₃)₃</td>
<td>monodentate</td>
</tr>
</tbody>
</table>

Many of the ligands have different protonation states when unbound, so the charge of the unbound ligands will vary depending on pH. Many of these ligands make dative bonds to the transition metal with lone pairs on nitrogens. At low pHs, these nitrogens are protonated and the ligands will not be able to bind.

Table \(\PageIndex{2}\): Anionic Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluoro</td>
<td>F⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>chloro</td>
<td>Cl⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>bromo</td>
<td>Br⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>iodo</td>
<td>I⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>carbonato</td>
<td>CO₃²⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>cyano</td>
<td>CN⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>hydrido</td>
<td>H⁺</td>
<td>monodentate</td>
</tr>
<tr>
<td>hydroxo</td>
<td>OH⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>nitro</td>
<td>NO₂⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>nitrito</td>
<td>ONO⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>nitrato</td>
<td>NO₃⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>oxalate (ox)</td>
<td>C₂O₄²⁻</td>
<td>bidentate</td>
</tr>
<tr>
<td>oxo</td>
<td>O²⁻</td>
<td>monodentate</td>
</tr>
<tr>
<td>sulfato</td>
<td>SO₄²⁻</td>
<td>monodentate</td>
</tr>
</tbody>
</table>
Coordination Number

The number of coordinate covalent bonds formed typically ranges from two to eight depending on the charge, size, and electron configuration of the transition metal atom or ion. The coordination number may also be as low as 1 and as high as 12. The number the number of coordinate covalent bonds is the coordination number (CN) with two, four and six the most common coordination numbers. This may be different than the number of ligands bound to the metal since ligands may also bond via multiple sites (polydentate).

Q3.2: Coordination Number

Identify the coordination number for each transition metal in the coordination compounds below.

a. [V(OH)$_2$]$_6$(NO$_3$)$_3$

b. (NH$_4$)$_2$[CoCl$_4$]

c. [Co(py)$_4$]Br$_2$

d. K$_4$[Mn(CN)$_6$]

e. [Co(P(CH$_3$)$_3$)$_4$]$_2$(SO$_4$)$_3$

f. Ni(NH$_3$)$_4$Cl$_2$

Simplified IUPAC Rules

1. Cations are always named before the anions.

2. Ligands are named before the metal atom or ion.

3. Ligand names are modified with an -o added to the root name of an anion. For neutral ligands the name of the molecule is used, with the exception of OH$_2$, NH$_3$, CO and NO. Names of common neutral ligands are listed in Table \(\PageIndex{1}\), and common anionic ligands are listed in Table \(\PageIndex{2}\).
4. The prefixes mono-, di-, tri-, tetra-, penta-, and hexa- are used to denote the number of simple ligands.

5. The prefixes bis-, tris-, tetrakis-, etc., are used for more complicated ligands or ones that already contain di-, tri-, etc.

6. The oxidation state of the central metal ion is designated by a Roman numeral in parentheses.

7. When more than one type of ligand is present, they are named **alphabetically**. Prefixes do not affect the order.

8. If the complex ion has a negative charge, the suffix –ate is added to the name of the metal.

9. (Advanced and not questioned in this worksheet) In the case of complex-ion isomerism the names cis, trans, fac, or mer may precede the formula of the complex-ion name to indicate the spatial arrangement of the ligands. *Cis* means the ligands occupy adjacent coordination positions, and *trans* means opposite positions just as they do for organic compounds. The complexity of octahedral complexes allows for two additional geometric isomers that are peculiar to coordination complexes. *Fac* means facial, or that the three like ligands occupy the vertices of one face of the octahedron. *Mer* means meridional, or that the three like ligands occupy the vertices of a triangle one side of which includes the central metal atom or ion.

**Nomenclature Examples:**

- \([\text{CrCl}_2(\text{OH}_2)_4]^+\) is the tetraaquadichlorochromium (III) ion
- \([\text{CrCl}_4(\text{OH}_2)_2]^−\) is the diaquatetrachlorochromate (III) ion
- \([\text{Cr(OH)}_2(\text{NH}_3)_5]^{3+}\) is the pentaammineaquachromium (III) ion
- \([\text{Ga(OH)Cl}_3]^-\) is the trichlorohydroxogallate (III) ion
- \(\text{cis-[PtBrCl(NO}_2)_2]^{2−}\) is the *cis*-bromochlorodinitroplatinate (II) ion
- \(\text{trans-[Co(OH)Clen}_2]^+\) is the *trans*-chlorobis(ethylenediamine)hydroxo cobalt (III) ion
- \([\text{Mn(CO)}_3(\text{C}_6\text{H}_6)]^+\) is the benzenetricarbonvlmanganese (I) ion
- \([\text{Ni(CO)}_4]\) is tetracarbonylnickel (0)
- \(\text{NH}_4[\text{AuCl}_4]\) is ammonium tetrachloroaurate (III)
Q3.3

Put the following compounds together to give the formula of the compound.

- Remember to use [ ] to identify the complex ion in ionic complexes.
- Where you need a counter-ion to produce a neutral compound, use either K⁺ or Cl⁻ (If you use SO₄²⁻, you would need half amounts)
- Remember to list the cation first, followed by anion for ionic compounds.

**Metal/charge Ligands Formula**

a. V⁺³ Four H₂O and two SCN [V(OH₂)₄(SCN)₂]SO₄
b. Co⁺² Four Br
c. Ru⁺³ Three oxalates
d. Os⁺³ Three dppe
e. Ni⁺² Two Br⁻, two NH₃, and two CN
f. Fe⁺³ Six CN⁻

Q3.4

Name the following.

a. K₄[Ni(CN)₄]
b. (NH₄)₃[Fe(SCN)₆]
c. Na₂[Ni(CN)₄]
d. [Fe(ox)₃]³⁻
e. [Co(NH₃)₅Cl]Br₂
f. [Cr(OH₂)₄Cl₂]Cl
g. [Pt(NH₃)₂]Cl₂
h. Na₂[MoOCl₄]
i. [Cr(OH₂)₆](NO₃)₃
j. [Fe(NH₃)₆]SO₄
k. (NH₄)₂[CoCl₄]
l. Cr(NH₃)₄Cl₂
m. [Co(P(CH₃)₃)₄]₂(SO₄)₃
n. [Ni(OH₂)₆]Cl₂
Q3.5

Write formulas for the following.

a. potassium hexacyanoferrate(III)
b. sodium hexafluoroaluminate(III)
c. pentaaquabromomanganese(III) sulfate
d. hexaamminechromium(III) nitrate
e. sodium tetrahydroxochromate(III)
f. hexaammineruthenium(III) tetrachloronickelate(II)
g. tetraamminecopper(II) pentacyanohydroxoferrate(III)
h. potassium diaquatetrabromovanadate(III)

Q3.6

Provide the name or chemical formula for the following complex compounds or ions.

a. \([\text{Al(OH}_2\text{)}_6]\text{Br}_3\)
b. \([\text{Cr(NH}_3\text{)}_6]\text{Cl}_3\)
c. potassium hexafluoroferate (III)
d. tetrahydroxozincate (II) ion
e. \([\text{Co(OH}_2\text{)}_4\text{Cl}_2]\text{Cl}\)
f. \([\text{Cu(NH}_3\text{)}_4]\text{Cl}_2\)\(^2\)
g. potassium hexachlorostannate (IV)
h. tetraamminedichloroplatinum (IV) hexachloroplatinate (IV)