

## Coordination substances

In chemistry, a coordination complex consists of a central atom or ion, which is usually metallic and is called the coordination center, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents. Many metal-containing compounds, especially those of transition metals, are coordination complexes. A coordination complex whose center is a metal atom is called a metal complex.

Classification of complex solutions:

- By substance class:
  - Complex acids  $\text{H[AuCl}_4\text{]}; \text{H[BiI}_4\text{]}; \text{H[B(OH)}_4\text{]}$
  - Complex bases  $[\text{Ni(NH}_3\text{)}_6\text{]OH}; [\text{Ag(NH}_3\text{)}_2\text{]OH}$
  - Complex salts  $\text{K}_3[\text{Fe(CN)}_6\text{]}; [\text{Cr(H}_2\text{O)}_6\text{]Cl}_3$
- By ligand nature
  - Ammines  $[\text{Cu(NH}_3\text{)}_4\text{]SO}_4\text{; } [\text{Pt(NH}_3\text{)}_6\text{]Cl}_2$
  - Aquacomplexes  $[\text{Co(H}_2\text{O)}_6\text{]SO}_4\text{; } [\text{Cu(H}_2\text{O)}_4\text{]SO}_4 \cdot \text{H}_2\text{O}$
  - Hydroxocomplexes  $\text{K[Al(OH)}_4\text{]}; \text{K}_2[\text{Zn(OH)}_4\text{]}$
  - Acidocomplexes  $\text{K}_2[\text{HgI}_4\text{]}; \text{K}_4[\text{Fe(CN)}_6\text{]}$
- Iodocomplexes  $\text{KI}_3 \rightarrow \text{K[I} \cdot \text{I}_2\text{]}; \text{KI}_5 \rightarrow \text{K[I}_2 \cdot \text{I} \cdot \text{I}_2\text{]}$
- Mixed complex substances  $\text{Na}_2[\text{Fe(CN)}_5\text{NO}]$
- By the number of central atoms
  - Monocore complex substances
  - Multicore complex substances
    - $\text{H}_2\text{CrO}_3(\text{CrO}_4) \rightarrow \text{H}_2\text{Cr}_2\text{O}_7$
    - $\text{H}_2\text{CrO}_2(\text{CrO}_4)_2 \rightarrow \text{H}_2\text{Cr}_3\text{O}_{10}$
- Clusters – central atoms are connected  $[\text{Co}_2(\text{CO})_{10}\text{]}; [(\text{CO})_5\text{Co} - \text{Co}(\text{CO})_5\text{]}; \text{Hg}_2\text{Cl}_2$
- Clathrates – inclusion substances (Iodine with starch (amylum))
- Chelates – formed by organic polydentate ligand.

### II. Ligands by donor atom type:

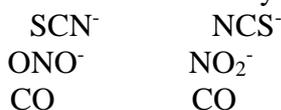
Oxygen containing	O	$\text{H}_2\text{O}, \text{OH}^-, \text{CO}, \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{ONO}^-$
Nitrogen containing	N	$\text{NH}_3, \text{NO}_2^-, \text{CN}^-, \text{NCS}^-$
Sulfur containing	S	$\text{S}^{2-}, \text{SCN}^-, \text{S}_2\text{O}_3^{2-}$
Carbon containing	C	$\text{CO}, \text{CN}^-$
Halogen containing	Hal	$\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$

By the number of donor atoms:

Monodentate (1 donor atom –  $\text{H}_2\text{O}, \text{OH}^-$ )

Polydentate (–  $\text{SO}_4^{2-}, \text{CO}_3^{2-}$ )

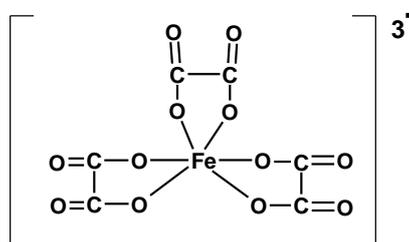
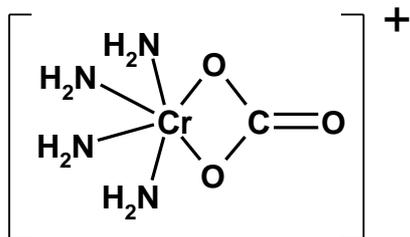
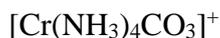
Ambidentate – 2 donor atoms, but coordination only with one atom.



### III. Coordination number of central atom.

- Coordination number is the number of connections of central atom with ligands.

2. If ligands are monodentate, the coordination number is equal to the number of ligands:  
 $[\text{Cr}(\text{NH}_3)_6]^{3+}$  c.n. = 6
3. If ligands are bidentate and more, than coordination number is equal to the number of bonds:



#### IV. Nomenclature of complex substances

The coordination compounds are named in the following way.

- A. To name a coordination compound, no matter whether the complex ion is the cation or the anion, always name the cation before the anion. (This is just like naming an ionic compound.)
- B. In naming the complex ion:
1. Name the ligands first, in alphabetical order, then the metal atom or ion. Note: The metal atom or ion is written before the ligands in the chemical formula.
  2. The names of some common ligands are listed in Table 1.

For anionic ligands end in "-o"; for anions that end in "-ide"(e.g. chloride), "-ate" (e.g. sulfate, nitrate), and "-ite" (e.g. nitrite), change the endings as follows: -ide -o; -ate -ato; -ite -ito

For neutral ligands, the common name of the molecule is used e.g.  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethylenediamine). Important exceptions: water is called 'aqua', ammonia is called 'ammine'.

#### Names of Some Common Ligands

Anionic Ligands	Names	Neutral Ligands	Names
$\text{Br}^-$	bromo	$\text{NH}_3$	ammine
$\text{F}^-$	fluoro	$\text{H}_2\text{O}$	aqua
$\text{O}^{2-}$	oxo	$\text{NO}$	Nitrosyl
$\text{OH}^-$	Hydroxo	$\text{CO}$	Carbonyl
$\text{CN}^-$	cyano	$\text{O}_2$	dioxygen
$\text{C}_2\text{O}_4^{2-}$	oxalato	$\text{N}_2$	dinitrogen
$\text{CO}_3^{2-}$	carbonato	$\text{C}_5\text{H}_5\text{N}$	pyridine
$\text{CH}_3\text{COO}^-$	acetato	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	ethylenediamine

3. Greek prefixes are used to designate the number of each type of ligand in the complex ion, e.g. di-, tri- and tetra-. If the ligand already contains a Greek prefix (e.g. ethylenediamine) or if it is polydentate ligands (ie. can attach at more than one binding site) the prefixes bis-, tris-, tetrakis-, pentakis-, are used instead. (See examples 3 and 4.) The numerical prefixes are listed in Table 2.

### Numerical Prefixes

Number	Prefix	Number	Prefix	Number	Prefix
1	mono	5	penta (pentakis)	9	nona (ennea)
2	di (bis)	6	hexa (hexakis)	10	deca
3	tri (tris)	7	hepta	11	undeca
4	tetra (tetrakis)	8	octa	12	dodeca

4. After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is call cobalt and Pt is called platinum. (See examples 1-4). If the complex ion is an anion, the name of the metal ends with the suffix –ate. (See examples 5 and 6.). For example, Co in a complex anion is called cobaltate and Pt is called platinate. For some metals, the Latin names are used in the complex anions e.g. Fe is called ferrate (not ironate).

### Name of Metals in Anionic Complexes

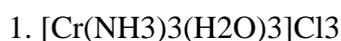
Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argenate
Gold	Aurate
Tin	Stannate

5. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

C. To name a neutral complex molecule, follow the rules of naming a complex cation. **Remember:** Name the (possibly complex) cation **BEFORE** the (possibly complex) anion. See examples 7 and 8.

For historic reasons, some coordination compounds are called by their common names. For example,  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  are named ferricyanide and ferrocyanide respectively, and  $\text{Fe}(\text{CO})_5$  is called iron carbonyl.

Examples:



Answer: triamminetriaquachromium(III) chloride

Solution: The complex ion is inside the parentheses, which is a cation.

The ammine ligands are named before the aqua ligands according to alphabetical order.

Since there are three chlorides binding with the complex ion, the charge on the complex ion must be +3 (since the compound is electrically neutral).

From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be same as the charge of the complex ion, +3.



Answer: pentaamminechloroplatinum(IV) bromide

Solution: The complex ion is a cation, the counter anion is the 3 bromides.

The charge of the complex ion must be +3 since it bonds with 3 bromides.

The  $\text{NH}_3$  are neutral molecules while the chloride carries - 1 charge. Therefore, the oxidation number of platinum must be +4.



Answer: dichlorobis(ethylenediamine)platinum(IV) chloride

Solution: ethylenediamine is a bidentate ligand, the bis- prefix is used instead of di-



Answer: tris(ethylenediamine)cobalt(III) sulfate

Solution: The sulfate is the counter anion in this molecule. Since it takes 3 sulfates to bond with two complex cations, the charge on each complex cation must be +3.

Since ethylenediamine is a neutral molecule, the oxidation number of cobalt in the complex ion must be +3.

Again, remember that you never have to indicate the number of cations and anions in the name of an ionic compound.



Answer: potassium hexacyanoferrate(II)

Solution: potassium is the cation and the complex ion is the anion.

Since there are 4 K<sup>+</sup> binding with a complex ion, the charge on the complex ion must be - 4.

Since each ligand carries -1 charge, the oxidation number of Fe must be +2.

The common name of this compound is potassium ferrocyanide.

6. Na<sub>2</sub>[NiCl<sub>4</sub>]

Answer: sodium tetrachloronickelate(II)

Solution: The complex ion is the anion so we have to add the suffix -ate in the name of the metal.

7. Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>

Answer: diamminetetrachloroplatinum(IV)

Solution: This is a neutral molecule because the charge on Pt<sup>+4</sup> equals the negative charges on the four chloro ligands.

If the compound is [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>, even though the number of ions and atoms in the molecule are identical to the example, it should be named: diamminedichloroplatinum(II) chloride, a big difference.

8. Fe(CO)<sub>5</sub>

Answer: pentacarbonyliron(0)

Solution: Since it is a neutral complex, it is named in the same way as a complex cation. The common name of this compound, iron carbonyl, is used more often.

9. (NH<sub>4</sub>)<sub>2</sub>[Ni(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

Answer: ammonium diaquabis(oxalato)nickelate(II)

Solution: The oxalate ion is a bidentate ligand.

10. [Ag(NH<sub>3</sub>)<sub>2</sub>][Ag(CN)<sub>2</sub>]

Answer: diamminesilver(I) dicyanoargentate(I)

## V. Stability of complex substances

Cationic and anionic complexes dissociate in water solutions as strong electrolytes – this process is called primary dissociation, i.e.  $K_2[HgI_4] \rightarrow 2K^+ + [HgI_4]^{2-}$

Complex ion undergoes secondary dissociation:  $[HgI_4]^{2-} \leftrightarrow Hg^{2+} + 4I^-$

This process is reversible and is characterized by the equilibrium constant, called the instability constant.

The less instability constant is, more stable is the complex substance.

If  $K_i < 10^{-6}$ , then complex substance is stable.

The equation for common instability constant:

$$K_{inst.} = [Hg^{2+}] \times [I^-]^4 / [[HgI_4]^{2-}] = 10^{-30}$$

When adding to complex substance some reagent, that forms low solvable precipitate with  $Hg^{2+}$  ions, SP (solubility product)  $< K_{inst.}$ , than complex substance can be destroyed, because the equilibrium is totally shifted to the precipitate.

Example:

