

Coordination Compounds

Historical aspects:

The coordination chemistry was pioneered by Alfred Werner. He received the Nobel price in 1913 for his coordination theory of transition metal- ammine complexes.

Definition

Coordination compound:

A neutral complex or an ionic compound in which one of the ions is a complex. A complex is a combination of a Lewis acid (central atom) with a number of Lewis bases (ligands).

- the atom in the Lewis base ligand that forms the bond to the central atom/ion is called the donor atom
- the metal atom or ion, the Lewis acid, is the acceptor atom

Nomenclature

- the cationic part is named prior to the anionic one
- the name starts with the ligands in alphabetical order, the number of ligands is indicated by the prefixes mono, di, tri, tetra...
→ if there could be a confusion because the name already includes a prefix, the alternative prefixes bis, tris, tetrakis... are used (ethylenediammine → bis(ethylenediammine))
- names of anionic ligands end with “o”: chloro, oxo, cyano, fluoro...
The cationic and neutral ones without specific ending!
- After that the name of the central atom/ion follows with the oxidation state as roman number at the end of the name in brackets
- if the complex is anionic the name ends with “ate”
Cationic and neutral ones have no specific ending!

Important ligands (s. Shriver & Atkins, “Inorganic chemistry” Chapter 7.2)

- **monodentate ligands:** donating one single electron pair to the central atom
- **ambidentate ligands:** different potential donor atoms
NCS⁻: * attach to a metal atom by N → isothiocyanato complex
 * attach to a metal atom by S → thiocyanato complex
- **Chelating ligands:** ligands forming a ring that includes the metal atom by donating more than one electron pair to the central atom.
Example: bidentate ethylenediammine which forms a five- membered ring when both N atoms attach to the same metal atom

Chelate effect

The formation constant of a chelate is more favorable because the formation constant is higher and the entropy is positive.

Coordination Polyhedra:

- CN=2: linear (for monovalent central atoms)
- CN=3: trigonal (very rare)
- CN=4: - tetragonal (small central atom, big ligands)
 - square planar: (central atom with d⁸ configuration)
- CN=5: square pyramidal or trigonal bipyramidal
- CN=6: octahedral (mostly found in coordination complexes)
- CN>6: pentagonal bipyramidal, capped octahedral or capped trigonal prismatic (4d and 5d central atoms)

Questions:

- 1) Name and draw structures of the following complexes:
a) $[\text{Ni}(\text{CO})_4]$ b) $[\text{CoCl}_4]^{2-}$ c) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- 2) Draw the structure of a typical square planar four coordinate complex, a typical trigonal prismatic six- coordinate complex and a typical complex of $\text{CN}=2$.

References:

[1] *Shriver & Atkins` Inorganic Chemistry*, 3th edition, 1999, Oxford University Press, Oxford