

Nomenclature of coordination compounds

The first comprehensive system of nomenclature was suggested by A. Werner. Though this has been modified by the inorganic nomenclature committee of the international Union of pure and applied chemistry (IUPAC), the fundamental rules suggested by Werner essentially remain the same. Trivial names for certain coordination compounds still persist, e.g. many authors still prefer to call the ions viz. $[\text{Fe}(\text{CN})_6]^{-4}$ and $[\text{Fe}(\text{CN})_6]^{-3}$ ferrocyanide and ferricyanide instead of hexacyanoferrate (II) and hexacyanoferrate (III) ions respectively as suggested by IUPAC system.

On the basis of the nature of the cation and anion of the complexes, these are classified as :

- (I) Cation complexes, e.g. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, $[\text{Cu}(\text{NH}_3)_4]^{+2}$, $[\text{Ni}(\text{en})_2\text{Cl}_2]^{+2}$ etc.
- (II) Ionic complexes, e.g. $[\text{Cr}(\text{en})\text{I}_4]^{-1}$, $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^{-1}$, $[\text{Fe}(\text{CN})_6]^{+4}$, $[\text{Fe}(\text{CN})_6]^{+3}$ etc.
- (III) Ionic complexes. These contain simple or complex cation and simple or complex anion, e.g. $\text{K}_2[\text{PtCl}_6]^{-2}$, $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Br}_2$, $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$etc.
- (IV) Neutral complexes. These are non-ionic (non-electrolyte) or molecular complexes, e.g. $[\text{Ni}(\text{CO})_4]$, $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$,.....etc.

For naming all the types of complexes mentioned above the following rules are observed:

1-order of naming ligands: If the coordination sphere of a given complex compound contain various types of ligands. The ligands are named in alphabetical order. The prefixes di, tri....etc. are not to be considered while determining this alphabetical order. For example $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$ ion is named as tetramminechloronitrocobalt(III)ion.

2-naming of the negative ligands; In general, if the anion name ends in -ide, -ite, or -ate, the final -e is replaced by -o, giving -ido, -ito and -ato respectively, e.g. SO_3^{-2} (Sulfito), NO_3^{-1} (Nitrito), NH^{-2} (imido), NH_2^{-1} (amino or

amine), N_3 (azido), NHOH^{-1} (hydroxylamido), $\text{HON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NO}^{-1}$ (dimethyl glyoximato).

Some exceptions to this rule are: F^{-1} (fluoro), Cl^{-1} (chloro), CN^{-1} (cyano), O^{-2} (oxo), OH^{-1} (hydroxo), O_2^{-2} (peroxo), O_2H (perhydroxo).

Thus we see that the names of the negative ligands end in –O. The negative ligands are named in the order: H^{-1} , O^{-2} , OH^{-1} other simple monoatomic anionic ligands, polyatomic anionic ligands and finally organic anions in alphabetical order. Where the two ligands have the same number of atoms, the order is that of decreasing atomic number of the central metal species in the ligand, e.g. CrO_4^{-2} first and then SO_4^{-2} .

3-Naming of the neutral ligands: For neutral ligands, the names are not systematic. For less common neutral ligands (e.g. PH_3), the names of free molecules is used as such. For some of the more common neutral ligands, special names are used e.g. H_2O (aquo), NH_3 (ammine), CO (carbonyl), NO (itrosyl), CS (thiocarbonyl), NS (Thionitrosyl).

Neutral ligands are named in the following order:

First; H_2O (aquo), then NH_3 (ammine), second: other neutral coordinated ligands in the order in which the coordinated atom falls in the series: B, Si, C, Sb, As, P, N, H, Te, Se, S, At, I, Br, Cl, O, F, third: neutral organic ligands in alphabetical order.

4-Naming of the positive ligands: Positively charged ligands have suffix ium., e.g. $\text{NH}_2\text{NH}^{+3}$ (hydrazinium) and NO^+ (nitrosylium).

5-Indication of the number of ligands; The number of simple ligands such as Cl^{-1} , CH_3COO^- , $\text{C}_2\text{O}_4^{-2}$,...etc. is indicated by using before them the Greek prefixes; di, tri, tetra, penta, hexa, hepta, octa,...etc. In case of chelating ligands like ethylenediamine, trialkyl phosphine which contain the prefixes, di-, tri-, ...etc. in their ligand names, the prefixes bis (for two), tris (for three), tetrakis (for four), pentakis (for five), hexakis (for six), ...etc. are used before

their names. The ligands to which these prefixes refer are often placed in parentheses. For example;

$[\text{Co}(\text{NH}_3)_2(\text{en})_2]\text{Cl}_3$ Diammine-bis(ethylenediamine)cobalt(III)chloride.

$[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ Tris(ethylenediamine)cobalt(III)sulphate.

$[\text{Fe}(\text{CN})_2(\text{CH}_3\text{NC})_4]$ dicyano tetrakis(methylisocyanide)iron(II)

6-Naming of bridging ligands of the bridged polynuclear complexes. The complexes having two or more metal atom are called polynuclear complexes.

The greek letter μ - should be repeated before the name of each different bridging group two or more bridging groups of the same kind are indicated by $-\mu$ -di, $-\mu$ -tri,.....etc.

Example:

$[(\text{NH}_3)_4\text{Co}(\text{OH})-\text{Co}(\text{OH})(\text{NH}_3)_4](\text{SO}_4)_2$

μ -dihydroxo octammine dicobalt(III)sulphate.

7-Naming of ambidentate ligands: the ligands which can be coordinated to the central metal ion through either of the two donor atoms.

Examples:

(M- NO_2) Nitro

(M- $\text{ON}=\text{O}$) Nitrito

(M-CN) Cyano

(M-NC) Isocyano

(M-SCN) Thiocyanato

(M-NCS) Isothiocyanato

8-naming of the central metal ion and mononuclear;

(I) Anionic complexes: In naming different complexes like $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^{-1}$, $[\text{Cr}(\text{en})\text{I}_4]^{-1}$...etc. Ligands are named first and then the central metal ion. To name the central metal ion the suffix ate is attached to its name and in order to indicate the oxidation state of the metal ion this suffix is followed by roman numeral (such as I, II, III, ...etc.). In some cases the metal name is derived from the Latin name, e.g. plumate, argentite, ferrate, aurate, copperate are used for lead, silver, iron, gold and copper respectively.

Examples:

$[\text{Cr}(\text{en})\text{I}_4]^{-1}$ tetraiodo(ethylenediamine)chromate(III)ion.

$[\text{AgCl}_2]^{-1}$ dichloro argentate(I)ion.

$[\text{Ni}(\text{CN})_4]^{-4}$ tetracyano nickelate(0).

$[\text{Co}(\text{CO})_4]^{-1}$ tetra carbonyl cobaltate(-1).

(II) Ionic complexes: In ionic complexes like $\text{K}_2[\text{PtCl}_6]$ the cation named first and then anion, as we do in naming a simple salt like NaCl. The rules for naming the anionic and cation above at (I) and (II) respectively.

Examples:

$\text{K}_2[\text{PtCl}_6]$ Potassium hexachloroplatinate(IV).

$\text{NH}_4[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]$ Ammonium tetrathiocyanato diammine chromate(III).

$[\text{Pt}(\text{Py})_4][\text{PtCl}_4]$ tetrapyridine platinum(II)tetrachloroplatinate(II).

Prof.Dr. Waleed Ali Mahmoud