IR-2 Grammar (March 2004)

CONTENTS

IR-2.1 INTRODUCTION

Chemical nomenclature may be considered to be a language. As such, it consists of words and it should obey the rules of syntax.

In the language of chemical nomenclature, the simple names of atoms are the words. As words are assembled to form a sentence, so names of atoms are assembled to form names of chemical compounds. Syntax is the set of grammatical rules for building sentences out of words. In nomenclature, syntax includes the use of symbols, such as dots, commas and hyphens, the use of numbers for appropriate reasons in given places, and the order of citation of various words, syllables and symbols.

Generally nomenclature systems require a root on which to construct the name. This root can be an element name (*e.g.* 'cobalt' or 'silicon') for use in additive nomenclature, or can be derived from an element name (*e.g.* 'sil' from 'silicon', 'plumb' from 'plumbum' for lead) and elaborated to yield a parent hydride name (*e.g.* 'silane' or 'plumbane') for use in substitutive nomenclature.

Names are constructed by joining other units to these roots. Among the most important units are affixes. These are syllables or numbers added to words or roots and can be suffixes, prefixes or infixes according to whether they are placed after, before or within a word or root.

Suffixes (endings) are of many different kinds (Table III)*, each of which conveys specific information. The following examples illustrate particular uses. They may specify the degree of unsaturation of a parent compound in substitutive nomenclature: hex*ane*, hex*ene*; and phosph*ane*, diphosph*ene*, diphosph*yne*. Other endings indicate the nature of the charge carried by the whole compound; cobalt*ate* refers to an anion. Further suffixes can indicate that a name refers to a group, as in hex*yl*.

Prefixes indicate, for example, substituents in substitutive nomenclature, as in the name *chloro*trisilane, and ligands in additive nomenclature, as in the name *aqua*cobalt. The prefixes can also be numbers to express specific information such as a point of attachment, *e.g.* 2-chlorotrisilane, or they can be multiplicative prefixes (Table IV) to indicate the number of constituents or ligands, *e.g. hexa*aquacobalt.

Prefixes may be used to describe the structural types or other structural features of species; geometrical and structural prefixes are listed in Table V. Other devices may be used to complete the description of the compound. These include the charge number to indicate the ionic charge, *e.g.* hexaaquacobalt(2+), and, alternatively, the oxidation number to indicate the oxidation state of the central atom, *e.g.* hexaaquacobalt(II).

The designation of central atom and ligands, generally straightforward in mononuclear complexes, is more difficult in polynuclear compounds where there are several central atoms in the compound to be named, *e.g.* in polynuclear coordination compounds, polyoxoanions, and chain and ring compounds. In each case, a priority order or hierarchy has to be established. A hierarchy of functional groups is an established feature of substitutive nomenclature; Table VI shows one of the priority sequences used in additive nomenclature.

The purpose of this Chapter is to guide the users of nomenclature in building the name or formula of an inorganic compound and to help them verify that the derived name or formula fully obeys the accepted principles. The various devices used in names (or formulae) are described successively below, together with their meanings and fields of application.

IR-2.2 ENCLOSING MARKS

IR-2.2.1 **General**

Chemical nomenclature employs three types of enclosing mark, namely: braces { }, square brackets [ ], and parentheses ( ).

---

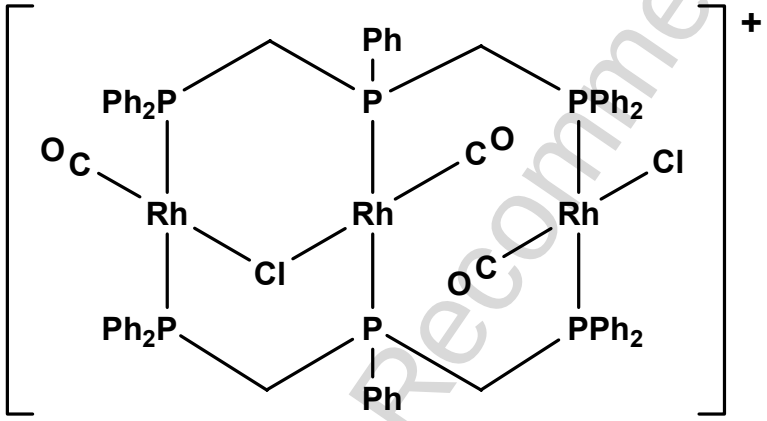
* Tables numbered with a Roman numeral are collected together at the end of this book.

In *formulae*, square brackets, parentheses and braces are used in the following nesting order: [], [( )], [{( )}], [({( )})], [{({( )})}], *etc*. Square brackets are normally used only to enclose formulae; parentheses and braces are then used alternately (see also Sections IR-4.2.3 and IR-9.2.3.2).

In *names*, the nesting order is: (), [()], {[()]}, ({[()]}), *etc.* This ordering is that used in substitutive nomenclature (see Section P-16.4.3.2 of Ref. 1). (See also, Section IR-9.2.2.3 for the use of enclosing marks with ligand names).

Example:

1. $[Rh_3Cl(\mu\text{-}Cl)(CO)_3\{\mu_3\text{-}Ph_2PCH_2P(Ph)CH_2PPh_2\}_2]^+$



tricarbonyl-1κ*C*,2κ*C*,3κ*C*-μ-chlorido-1:2κ^2*Cl*-chlorido-3κ*Cl*-bis{μ$_3$-bis[(diphenylphosphanyl)-1κ*P*':3κ*P*''-methyl]phenylphosphane-2κ*P*}trirhodium(1+)

IR-2.2.2 **Square brackets**

IR-2.2.2.1 *Use in formulae*

Square brackets are used in *formulae* in the following ways.

(a) To enclose the whole coordination entity of a neutral (formal) coordination compound.

Examples:

1. $[Fe(\eta^5\text{-}C_5H_5)_2]$

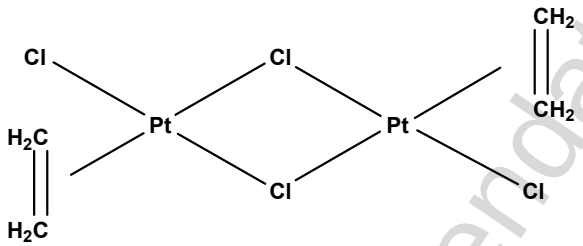
(for use of the symbol η see Sections IR-9.2.4.3 and IR-10.2.5.1)

2. $[Pt(\eta^2\text{-}C_2H_4)Cl_2(NH_3)]$
3. $[PH(O)(OH)_2]$

No numerical subscript should follow the square bracket used in this context. For example, where the molecular formula is double the empirical formula, this should be indicated inside the square bracket.

Example:

4.



[{Pt(η^2-C_2H_4)Cl(μ-Cl)}$_2$] is more informative than [$Pt_2(\eta^2$-$C_2H_4)_2Cl_4$]; the representation [Pt(η^2-C_2H_4)Cl_2]$_2$ is incorrect.

(b) To enclose the coordination entity of a charged (formal) coordination compound. In this case, the superscript showing the charge appears outside the square bracket as do any subscripts indicating the number of ions in the salt.

Examples:

5. $[BH_4]^-$
6. $[Al(OH)(OH_2)_5]^{2+}$
7. [Pt(η^2-C_2H_4)Cl_3]$^-$
8. $Ca[AgF_4]_2$
9. $[Co(NH_3)_5(N_3)]SO_4$
10. $[S_2O_5]^{2-}$
11. $[PW_{12}O_{40}]^{3-}$

(c) In a salt comprising both cationic and anionic coordination entities, each ion is separately enclosed in square brackets. (The cation is placed before the anion and no individual charges are shown). Any subscripts indicating the number of complex ions in the salt are shown outside the square brackets.

Examples:

12. $[Co(NH_3)_6][Cr(CN)_6]$

(comprising the ions $[Co(NH_3)_6]^{3+}$ and $[Cr(CN)_6]^{3-}$)

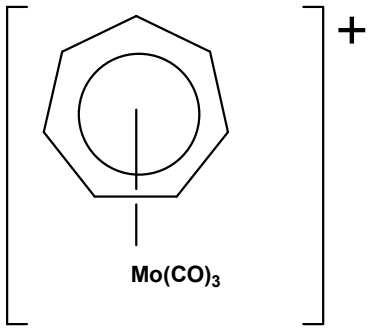
13. $[Co(NH_3)_6]_2[Pt(CN)_4]_3$

(comprising the ions $[Co(NH_3)_6]^{3+}$ and $[Pt(CN)_4]^{2-}$)

(d) To enclose structural formulae.

Example:

14.



$[Mo(\eta^7\text{-}C_7H_7)(CO)_3]^+$

(e) In solid state chemistry, to indicate an atom or a group of atoms in an octahedral site. (See Section IR-11.4.3)

Example:

15. $(Mg)[Cr_2]O_4$

(f) In specifically labelled compounds (see also Section II-2.4.2.2 of Ref. 2).

Example:

16. $H_2[^{15}N]NH_2$

Note that this distinguishes the specifically labelled compound from the isotopically substituted compound $H_2{}^{15}NNH_2$.

(g) In selectively labelled compounds (see also Section II-2.4.3.2 of Ref. 2).

Example:

17. $[^{18}O,^{32}P]H_3PO_4$

(h) To indicate repeating units in chain compounds.

Example:

18. $SiH_3[SiH_2]_8SiH_3$

IR-2.2.2.2 *Use in names*

Square brackets are used in *names* in the following ways.

(a) In specifically and selectively labelled compounds the nuclide symbol is placed in square brackets before the name of the part of the compound that is isotopically modified. (Compare with the use of parentheses for isotopically substituted compounds in Section IR-2.2.3.2, and also see Sections II-2.4.2.3 and II-2.4.3.3 of Ref. 2).

Examples:

1. $[^{15}N]H_2[^{2}H]$ $[^{2}H_1,^{15}N]$ammonia
2. $[^{13}C][Fe(CO)_5]$ $[^{13}C]$pentacarbonyliron

For more details, see Section II-2.4 of Ref. 2.

(b) When naming organic ligands and organic parts of coordination compounds the use of square brackets obeys the principles of substitutive nomenclature.[1]

(c) In chain and ring nomenclature, square brackets are used to enclose the nodal descriptor (Section IR-7.4.2 and Chapter II-5 of Ref. 2).

IR-2.2.3 **Parentheses**

IR-2.2.3.1 *Use in formulae*

Parentheses are used in *formulae* in the following ways.

(a) To enclose sets of identical groups of atoms (the entity may be an ion, substituent group, or molecule). Usually a multiplicative subscript follows the closing parenthesis. In the case of common ions such as nitrate and sulfate parentheses are recommended but not mandatory.

Examples:

1. $Ca_3(PO_4)_2$
2. $B_3H_3(NMe)_3$
3. $[Ni(CO)_4]$
4. $[NO_3]^-$ or NO_3^-
5. $[FeH(H_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$

(b) To enclose the formula of a moiety which is an atom or set of atoms forming a neutral or charged ligand in a coordination compound. The purpose is to separate the ligands from each other or from the remaining part of the molecule in order to avoid ambiguity. Parentheses may be used even if a multiplicative suffix is not needed.

Example:

7. $[Co(NH_3)_5(ONO)]SO_4$ or $[Co(NH_3)_5(ONO)][SO_4]$
8. $[Co(NH_3)_5(ONO)][PF_6]_2$

(c) To enclose the abbreviation of a ligand name in formulae. (Recommended ligand abbreviations are given in Tables VII and VIII. See also Sections IR-4.4.4 and IR-9.2.3.4).

Example:

9. $[Co(en)_3]^{3+}$

(d) To enclose the superscripted radical dot and its multiplier for polyradicals, in order to avoid ambiguity in relation to multiplying the charge symbol.

Example:

10. $NO^{(2\bullet)-}$

(e) In solid state chemistry, to enclose symbols of atoms occupying the same type of site in a random fashion. The symbols themselves are separated by a comma, with no space.

Example:

11. K(Br,Cl)

(f) In solid state chemistry, to indicate an atom or a group of atoms in a tetrahedral site.

Example:

12. $(Mg)[Cr_2]O_4$

(g) To indicate the composition of a non-stoichiometric compound.

Examples:

13. $Fe_{3x}Li_{4-x}Ti_{2(1-x)}O_6$ ($x = 0.35$)
14. $LaNi_5H_x$ ($0 < x < 6.7$)

(h) In the Kröger-Vink notation (see Section IR-11.4), to indicate a complex defect.

Example:

15. $(Cr_{Mg}V_{Mg}Cr_{Mg})^x$

(i) For crystalline substances, to indicate the type of crystal formed (see Chapter IR-11).

Examples:

16. ZnS(*c*)
17. AuCd (*CsCl* type)

(j) In optically active compounds, to enclose the signs of rotation or the symbols for absolute configuration.

Example:

18. $(+)_{589}$-$[Co(en)_3]Cl_3$
19. (2*R*,3*S*)-1,2,3-$ClSiH_2SiHClSiHClSiH_2SiH_3$

(k) To enclose configuration indices (see Section IR-9.3.3.2)

Example:

20. (*OC*-6-22)-$[Co(NH_3)_3(NO_2)_3]$

(l) For crystalline substances, to indicate the type of crystal formed (see Chapter IR-11).

(m) In polymers, the repeating unit is enclosed in strike-through parentheses, with the dash superimposed on the parentheses representing the bond.[3]

Example:

21. (S)_n

IR-2.2.3.2 *Use in names*

Parentheses are used in *names* in the following ways.

(a) Following multiplicative prefixes such as bis and tris, unless a nesting order is to be used (see Section IR-2.2.1).

Example:

1. $[CuCl_2(NH_2Me)_2]$ dichloridobis(methylamine)copper(II)

(b) To enclose oxidation and charge numbers.

Example:

2. $Na[B(NO_3)_4]$ sodium tetranitratoborate(III), or
   sodium tetranitratoborate(1–)

(c) For radicals, to enclose the radical dot, and the charge number if appropriate.

Examples:

3. $ClOO^{\bullet}$ chloridodioxygen(•)
4. $Cl_2^{\bullet-}$ dichloride(•1–)

(d) To enclose stoichiometric ratios for addition compounds and clathrates.

Example:

5. $8H_2S{\cdot}46H_2O$ hydrogen sulfide—water (8/46)

(e) To enclose italic letters representing bonds between two (or more) metal atoms in coordination compounds.

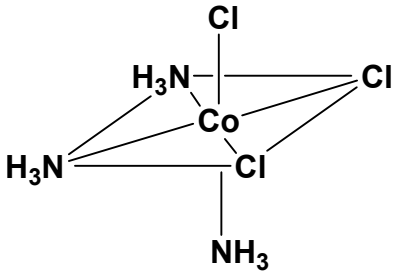
Example:

6. $[Mn_2(CO)_{10}]$ bis(pentacarbonylmanganese)(*Mn*—*Mn*)

(f) To enclose stereochemical descriptors (see Section IR-9.3.2)

Example:

7.



$[CoCl_3(NH_3)_3]$ (*OC*-6-22)-triamminetrichloridocobalt(III)

(g) To enclose inorganic ligand names, such as (triphosphato), which contain numerical prefixes.

(h) To enclose organic ligand names whether they are neutral or not, or whether they are substituted or not, *e.g.* (benzaldehyde), (benzoato), *etc*. It may be necessary to use a higher order of enclosing marks if the ligand names themselves include parentheses.

Example:

8. $[Pt(\eta^2\text{-}C_2H_4)Cl_3]^-$ trichlorido(η^2-ethene)platinate(II)

(i) In isotopically substituted compounds, the appropriate nuclide symbol(s) is placed in parentheses before the name of the part of the compound that is isotopically substituted (see Section II-2.3.3 of Ref. 2). Compare with the use of square brackets for specifically and selectively labelled compounds in Section IR-2.2.2.2(a).

Example:

9. H^3HO ($^3H_1$)water

(j) To enclose the number of hydrogen atoms in boron compounds.

Example:

10. B_6H_{10} hexaborane(10)

(k) In hydrogen names (Section IR-8.4), to enclose the part of the name following the word hydrogen.

Example:

11. $[HMo_6O_{19}]^-$ hydrogen(nonadecaoxidohexamolybdate)(1–)

IR-2.2.4 **Braces**

Braces are used in *names* and *formulae* within the hierarchical sequence outlined and exemplified in Section IR-2.2.1.

IR-2.3 HYPHENS, PLUS AND MINUS SIGNS, 'EM' DASHES AND BOND INDICATORS

IR-2.3.1 **Hyphens**

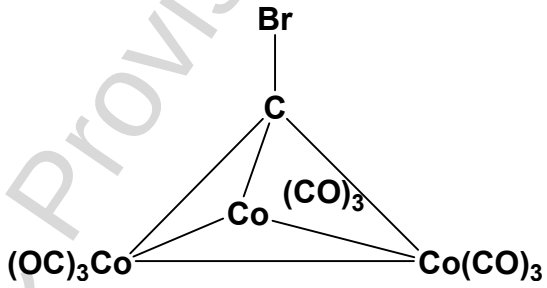
Hyphens are used in *formulae* and in *names*. Note that there is no space on either side of a hyphen.

(a) To separate symbols such as μ (mu), η (eta) and κ (kappa) from the rest of the formula or name.

(b) To separate geometrical or structural and stereochemical designators such as *cyclo, catena, triangulo, quadro, tetrahedro, octahedro, closo, nido, arachno, cis* and *trans* from the rest of the formula or name. In dealing with aggregates or clusters, locant designators are similarly separated.

Example:

1.



μ_3-(bromomethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co*—*Co*)

(c) To separate locant designators from the rest of the name.

Example:

2. $SiH_2ClSiHClSiH_2Cl$ 1,2,3-trichlorotrisilane

(d) To separate the labelling nuclide symbol from its locant in the formula of a selectively labelled compound.

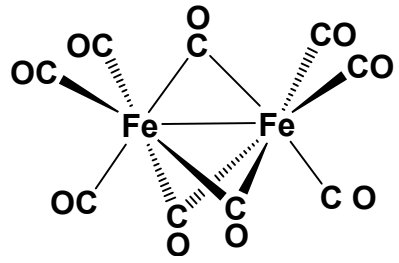
Example:

3. $[1\text{-}^{2}H_{1;2}]SiH_3OSiH_2OSiH_3$

(e) To separate the name of a bridging ligand from the rest of the name.

Example:

4.



$[Fe_2(\mu\text{-}CO)_3(CO)_6]$ tri-μ-carbonyl-bis(tricarbonyliron)

IR-2.3.2 **Plus and minus signs**

The signs + and – are used to indicate the charge on an ion in a formula or name.

Examples:

1. Cl^-
2. Fe^{3+}
3. $[SO_4]^{2-}$
4. $[Co(CO)_4]^-$ tetracarbonylcobaltate(1–)

They can also indicate the sign of optical rotation in the formula or name of an optically active compound.

Example:

5. $(+)_{589}[Co(en)_3]^{3+}$ $(+)_{589}$-tris(ethane-1,2-diamine)cobalt(3+)

IR-2.3.3 **'Em' dashes**

'Em' dashes are used in *formulae* only when the formulae are structural. (The less precise term 'long dashes' was used in Ref. 4).

In *names*, 'em' dashes are used in two ways.

(a) To indicate metal-metal bonds in polynuclear compounds. They separate the italicized symbols of the bond partners which are contained in parentheses at the end of the name.

Example:

1. $[Mn_2(CO)_{10}]$ bis(pentacarbonylmanganese)(*Mn*—*Mn*)

(b) To separate the molecular constituents in names of addition compound.

Examples:

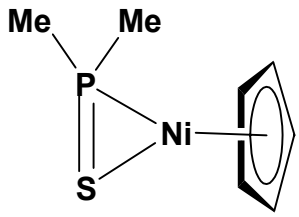
2. $3CdSO_4 \cdot 8H_2O$ cadmium sulfate—water (3/8)
3. $2CHCl_3 \cdot 4H_2S \cdot 9H_2O$ chloroform–hydrogen sulfide—water (2/4/9)

IR-2.3.4 **Special bond indicators for line formulae**

The structural symbols ⌜‾‾⌝ and ⌞__⌟ may be used in line formulae to indicate bonds between non-adjacent atom symbols.

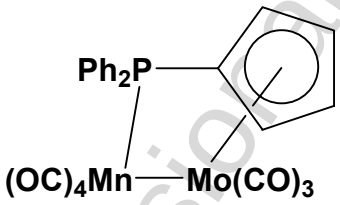
Examples:

1.



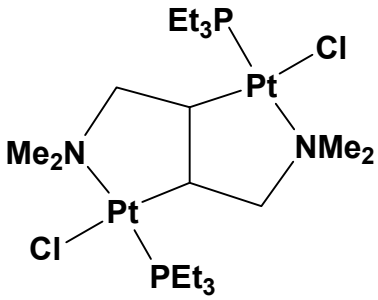
$[Ni(S{=}PMe_2)(\eta^5\text{-}C_5H_5)]$

2.



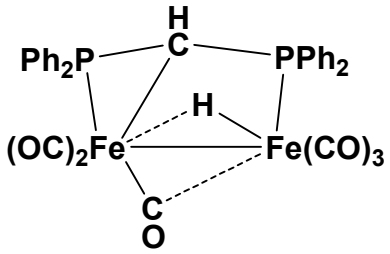
$[(CO)_4MnMo(CO)_3(\eta^5\text{-}C_5H_4PPh_2)]$

3.



$[(Et_3P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PEt_3)]$

4.



$[(OC)_3Fe(\mu\text{-}Ph_2PCHPPh_2)FeH(CO)_3]$

IR-2.4 SOLIDUS

The solidus (/) is used in names of addition compounds to separate the arabic numerals which indicate the proportions of individual constituents in the compound.

Examples:

1. $BF_3 \cdot 2H_2O$ boron trifluoride—water (1/2)
2. $BiCl_3 \cdot 3PCl_5$ bismuth trichloride—phosphorus pentachloride (1/3)

IR-2.5 DOTS, COLONS, COMMAS AND SEMICOLONS

IR-2.5.1 **Dots**

Dots are used in *formulae* in various positions.

(a) As right superscripts they indicate unpaired electrons in radicals (see Section IR-4.6.2).

Examples:

1. $HO^{\bullet}$
2. $O_2^{2\bullet}$

(b) As right superscripts in the Kröger-Vink notation of sold-state chemistry, they indicate the unit of positive effective charge (see Section IR-11.4.4).

Example:

3. $Li^{x}_{Li,1-2x}Mg^{\bullet}_{Li,x}V'_{Li,x}Cl^{x}_{Cl}$

(c) Centre dots in *formulae* of hydrates, addition compounds, double salts, and double oxides separate the individual constituents. The dot is written in the centre of the line to distinguish it from a full stop (period).

Examples:

4. $ZrCl_2O \cdot 8H_2O$

5. $NH_3 \cdot BF_3$
6. $CuCl_2 \cdot 3Cu(OH)_2$
7. $Ta_2O_5 \cdot 4WO_3$

Dots are used in *names* of radicals to indicate the presence of unpaired electrons.

Examples:

8. $ClO^{\bullet}$ oxidochlorine(•)
9. $Cl_2^{\bullet -}$ dichloride(•1−)

IR-2.5.2 **Colons**

Colons are used in *names* in the following ways.

(a) In coordination compounds, to separate the ligating atoms of a ligand which bridges central atoms.

Example:

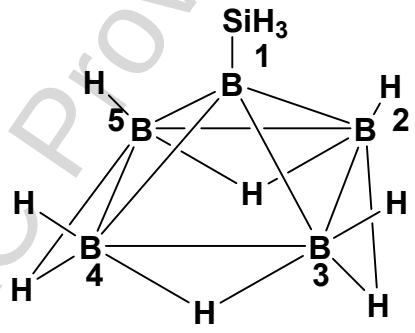
1. $[\{Co(NH_3)_3\}_2(\mu\text{-}NO_2)(\mu\text{-}OH)_2]^{3+}$
   di-μ-hydroxido-μ-nitrito-κ*N*:κ*O*-bis(triamminecobalt)(3+)

   (See Sections IR-9.2.4.2 and IR-10.2.3.3 for the use of κ, and Sections IR-9.2.5.2 and IR-10.2.3.1 for the use of μ)

(b) In boron compounds, to separate the sets of locants of boron atoms which are connected by bridging hydrogen atoms.

Example:

2.



1-silyl-2,3:2,5:3,4:4,5-tetra-μ*H*-pentaborane(9)

(c) In chains and rings nomenclature, to separate nodal descriptors of individual modules of an assembly (see Section IR-7.4.2).

IR-2.5.3 **Commas**

Commas are used in the following ways.

(a) To separate locants.

Example:

1. $SiH_2ClSiHClSiH_2Cl$ 1,2,3-trichlorotrisilane

(b) To separate the symbols of the ligating atoms of a polydentate chelating ligand.

Example:

2. *cis*-bis(glycinato-*N*,*O*)platinum

(c) In solid state chemistry, to separate symbols of atoms occupying the same type of site in a random fashion.

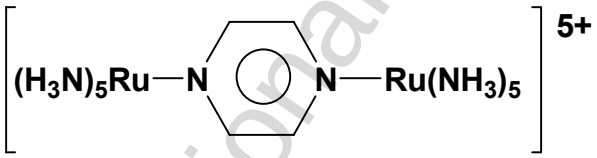
Example:

3. $(Mo,W)_nO_{3n-1}$

(d) To separate oxidation numbers in a mixed valence compound.

Example:

4.



$[(NH_3)_5Ru(\mu\text{-pyz})Ru(NH_3)_5]^{5+}$

μ-pyrazine-bis(pentaammineruthenium)(II,III)

(e) To separate symbols of labelled atoms in selectively labelled compounds.

Example:

5. $[^{18}O,^{32}P]H_3PO_4$ $[^{18}O,^{32}P]$phosphoric acid

IR-2.5.4 **Semicolons**

Semicolons are used in the following ways.

(a) In the names of coordination compounds, to order locants separated by commas, as in the kappa convention. (See Sections IR-9.2.4.2 and IR-10.2.3.3).

Example:

(1) (2)

1. $[Cu(bpy)(H_2O)(\mu\text{-}OH)_2Cu(bpy)(SO_4)]$

aqua-1κ*O*-bis(2,2'-bipyridine)-1κ^2*N*^{1},*N*$^{1'}$;2κ^2*N*^{1},*N*$^{1'}$-di-μ-hydroxido[sulfato(2–)-2κ*O*]dicopper(II)

(b) To separate the subscripts in order to indicate the number of possible positions in selectively labelled compounds.

Example:

2. $[1\text{-}^2H_{1;2}]SiH_3OSiH_2OSiH_3$

IR-2.6 SPACES

In inorganic nomenclature, spaces are used in *names* in the following ways in English; the rules may differ in other languages. Spaces are never used in formulae.

(a) To separate the names of ions in salts.

Examples:

1. NaCl sodium chloride
2. $NaTl(NO_3)_2$ sodium thallium(I) dinitrate

(b) In binary compounds, to separate the electropositive part from the electronegative part.

Example:

3. P_4O_{10} tetraphosphorus decaoxide

(c) To separate the arabic numeral from the symbols of central atoms written in italics between parentheses at the end of the name of a polynuclear compound.

Example:

4. $[Os_3(CO)_{12}]$ *cyclo*-tris(tetracarbonylosmium)(3 *Os*—*Os*)

(d) In addition compounds, to separate constituent proportions from the remainder of the name.

Example:

5. $3CdSO_4{\cdot}8H_2O$ cadmium sulfate—water (3/8)

(e) In solid state chemistry, to separate name and structural type.

Example:

6. TiO_2(*r*) (*brookite* type)

IR-2.7 ELISIONS

In general, in compositional and additive nomenclature no elisions are made when using numerical prefixes.

Example:

1. tetraaqua and not tetraqua
2. monoooxygen and not monoxygen
3. tetraarsenic hexaoxide

However, monoxide, rather than monooxide (preferred), is an allowed exception through general use.

IR-2.8 NUMERALS

IR-2.8.1 **Arabic numerals**

Arabic numerals are crucially important in nomenclature; their place in a formula or name is especially significant.

They are used in *formulae* in many ways.

(a) As right subscripts, to indicate the number of individual constituents (atoms or groups of atoms). Unity is not indicated.

Examples:

1. $CaCl_2$
2. $[Co(NH_3)_6]Cl_3$

(b) As a right superscript, to indicate the charge number. Unity is not indicated.

Examples:

3. Cl^-

4. NO^{+}
5. Cu^{2+}
6. $[Al(H_2O)_6]^{3+}$

(c) To indicate the composition of addition or non-stoichiometric compounds. The numeral is written on the line before the molecular formula of each constituent except that unity is omitted.

Examples:

7. $Na_2CO_3 \cdot 10H_2O$
8. $8WO_3 \cdot 9Nb_2O_5$

(d) To designate the mass number and/or the atomic number of nuclides represented by their symbols. The mass number is written as a left superscript, and the atomic number as a left subscript.

Examples:

9. ${}^{18}_{8}O$
10. ${}^{3}_{1}H$

(e) As a right superscript to the symbol η, to indicate the hapticity of a ligand (see Sections IR-9.2.4.3 and IR-10.2.5.1).

Example:

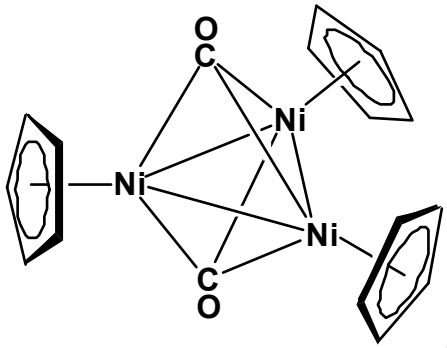
11. $[Fe(\eta^5\text{-}C_5H_5)_2]$

Arabic numerals are also used as locants in *names* (see Section IR-2.14.2), and in the following ways.

(a) To indicate the number of metal-metal bonds in polynuclear compounds.

Example:

12.



$[\{Ni(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}CO)_2]$

di-μ_3-carbonyl-*cyclo*-tris(cyclopentadienylnickel)(3 *Ni—Ni*)

(b) To indicate the charge number.

Example:

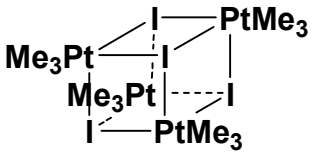
13. $[CoCl(NH_3)_5]^{2+}$ pentaamminechloridocobalt(2+)
14. $[AlCl_4]^-$ tetrachloridoaluminate(1–)

Note that the number '1' must be included in order to avoid ambiguity in relation to symbols for optical rotation [see Section IR-2.2.3.1(j)].

(c) As a right subscript to the symbol μ, to indicate bridging multiplicity.

Example:

14.



$[\{Pt(\mu_3\text{-}I)Me_3\}_4]$ tetra-μ_3-iodidotetrakis[trimethylplatinum(IV)]

(d) In the nomenclature of boron compounds (see Chapter IR-6.2.3), to indicate the number of hydrogen atoms in the parent borane molecule. The arabic numeral is enclosed in parentheses immediately following the name.

Examples:

15. B_2H_6 diborane(6)
16. $B_{10}H_{14}$ decaborane(14)

(e) As a right superscript to the symbol κ, to indicate the number of donor atoms of a particular type bound to a central atom (see Section IR-9.2.4.2).

(f) As a right superscript to the symbol η, to indicate the hapticity of a ligand. (See Sections IR-9.2.4.3 and IR-10.2.5.1).

(g) In polynuclear structures, arabic numerals are part of the CEP descriptor[6] used to identify polyhedral shapes. (See also Section IR-9.2.5.6).

(h) In addition compounds, to indicate the numbers of molecules of the constituents.

Example:

17. $8H_2S{\cdot}46H_2O$ hydrogen sulfide—water (8/46)

(i) As a right superscript, to indicate the non-standard bonding number in the λ convention. (See Section IR-6.2.1).

Example:

18. IH_5 λ^5-iodane

IR-2.8.2 **Roman numerals**

Roman numerals are used in *formulae* as right superscripts to designate the oxidation number.

Examples:

1. $[Co^{II}Co^{III}W_{12}O_{42}]^{7-}$
2. $[Mn^{VII}O_4]^-$
3. $Fe^{II}Fe^{III}{}_2O_4$

In *names* they indicate the oxidation number of an atom, and are enclosed in parentheses immediately following the name of the atom being qualified.

Example:

4. $[Fe(H_2O)_6]^{2+}$ hexaaquairon(II)

IR-2.9 ITALIC LETTERS

Italic letters are used in *names* as follows.

(a) For geometrical and structural prefixes such as *cis, cyclo, catena, triangulo* and *nido.* (see Table V).

(b) To designate symbols of metal atoms bonded to other metal atoms in polynuclear compounds.

Example:

1. $[Mn_2(CO)_{10}]$ bis(pentacarbonylmanganese)(*Mn—Mn*)

(c) In double oxides and hydroxides when the structural type is to be indicated.

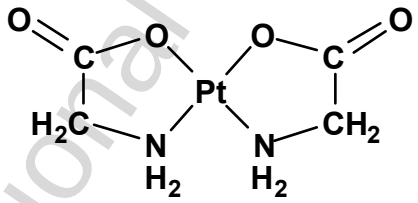
Example:

2. $MgTiO_3$ magnesium titanium trioxide (*ilmenite* type)

(d) In coordination compounds, to designate the symbols of the atom or atoms of a ligand (usually polydentate) to which the metal is bound, whether the kappa convention is used or not. (See Section IR-9.2.4.4).

Example:

3.



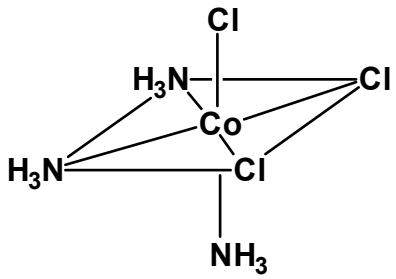
cis-bis(glycinato-*N,O*)platinum

(e) In solid state chemistry, in Pearson and crystal system symbols. (See Sections IR-3.5.3 and IR-11.5).

(f) In coordination compounds, italicized capital letters designate polyhedral symbols. (See Section IR-9.3.2.1).

Example:

4.



$[CoCl_3(NH_3)_3]$ (*OC*-6-22)-triamminetrichloridocobalt(III)

(g) Italic letters are also used to represent numbers, especially in formulae, where the numbers are undefined.

Examples:

5. $(HBO_2)_n$
6. Fe^{n+}

IR-2.10 GREEK ALPHABET

Greek letters (in Roman type) are used in inorganic nomenclature as follows:

Δ to show absolute configuration, or as a structural descriptor to designate deltahedra (see Section IR-9.3.4);

δ to denote the absolute configuration of chelate rings (see Section IR-9.3.4); in solid state chemistry to indicate small variations of composition (see Section IR-11.3.2); to designate cumulative double bonds in ring or ring systems (see Section P-25.7.2 of Ref 1);

η to designate the hapticity of a ligand (see Sections IR-9.2.4.3 and IR-10.2.5.1);

κ as a ligating atom designator in the kappa convention (see Sections IR-9.2.4.2 and IR-10.2.3.3);

Λ to show absolute configuration (see Section IR-9.3.4);

λ to indicate non-standard bonding number in the lambda convention (see Section IR-6.2.1 and Section P-14.1 of Ref.1); to denote the absolute configuration of chelate rings (see Section IR-9.3.4);

μ to designate a bridging ligand (see Sections IR-9.2.5.2 and IR-10.2.3.1).

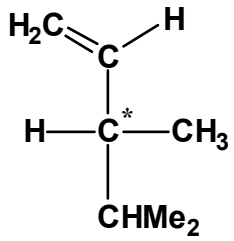
IR-2.11 ASTERISKS

The asterisk (*) is used in *formulae* as a right superscript to the symbol of an element, in the following ways:

(a) To highlight a chiral centre.

Example:

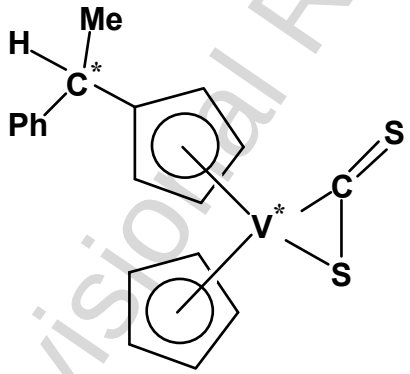
1.



This usage has been extended to label a chiral ligand or a chiral centre in coordination chemistry.

Example:

2.



(b) To designate excited molecular or nuclear states.

Example:

3. NO*

IR-2.12 PRIMES

(a) Primes ('), double primes (''), triple primes ('''), *etc.* may be used in the names and formulae of coordination compounds in the following ways:

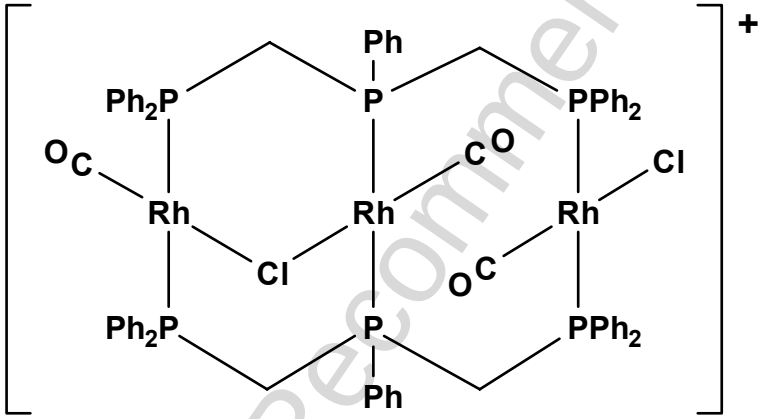
(i) within ligand names, in order to differentiate between sites of substitution;

(ii) when specifying donor atoms (IR-9.2.4.2), in order to differentiate between donor atoms;

(iii) when specifying stereochemistry using configuration indices (IR-9.3.5.3), in order to differentiate between donor atoms of the same priority, depending on whether they are located within the same ligand or portion of the ligand.

Example:

1. $[Rh_3Cl(\mu\text{-}Cl)(CO)_3\{\mu_3\text{-}Ph_2PCH_2P(Ph)CH_2PPh_2\}_2]^+$



tricarbonyl-1κ*C*,2κ*C*,3κ*C*-μ-chlorido-1:2κ^2*Cl*-chlorido-3κ*Cl*-bis{μ_3-bis[(diphenylphosphanyl)-1κ*P*':3κ*P*"-methyl]phenylphosphane-2κ*P*}trirhodium(1+)

(b) Primes, double primes, triple primes, *etc.* are also used as right superscripts in the Kröger-Vink notation (see Section IR-11.4) where they indicate a site which has one, two, three, *etc*. units of negative effective charge.

Example:

2. $Li^{x}_{Li,1-2x}Mg^{\bullet}_{Li,x}V'_{Li,x}Cl^{x}_{Cl}$

IR-2.13 MULTIPLICATIVE PREFIXES

The number of identical chemical entities in a name is expressed by a numerical prefix (see Table IV).

In the case of simple entities such as monoatomic ligands the multiplicative prefixes di, tri, tetra, penta, *etc*., are used.

The multiplying prefixes bis, tris, tetrakis, pentakis, *etc*. are used with organic ligands (particularly if substituted) or to avoid ambiguity (even with simple ligands, see Examples 4 and 5 below). The modified entity is placed within parentheses.

Examples:

1.	Fe_2O_3	diiron trioxide
2.	$[PtCl_4]^{2-}$	tetrachloridoplatinate(2–)
3.	$[Fe(CCPh)_2(CO)_4]$	tetracarbonylbis(phenylethynyl)iron
4.	TlI_3	thallium(III) tris(iodide)
5.	$Ca_3(PO_4)_2$	tricalcium bis(phosphate)
6.	$Pt(PPh_3)_4$	tetrakis(triphenylphosphane)platinum(0)

Composite numeral prefixes are built up by citing units first, then tens, hundreds and so on, *e.g.* 35 is written pentatriaconta (or pentatriacontakis).

IR-2.14 LOCANTS

IR-2.14.1 **Introduction**

Locants are used to indicate the position of a substituent or structural feature on or within a parent molecule. These can be arabic numerals or lower case letters.

IR-2.14.2 **Arabic numerals**

Arabic numerals are used as locants in the following ways.

(a) For numbering skeletal atoms in parent hydrides, to indicate: the placement of hydrogen atoms when there are non-standard bonding numbers; unsaturation; the positions of bridging hydrogen atoms in a borane structure.

Examples:

1. $\overset{1}{H_5}\overset{2}{S}\overset{3}{S}\overset{4}{S}H_4SH$

   1λ⁶, 3λ⁶-tetrasulfane (not 2λ⁶, 4λ⁶)

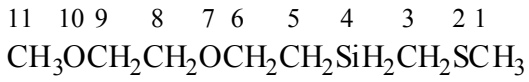
2. $\overset{1}{H_2}\overset{2}{N}\overset{3}{N}=\overset{4}{N}H\overset{5}{N}NH_2$ pentaaz-2-ene

3. 2,3:2,5:3,4:4,5-tetra-μ*H*-*nido*-pentaborane(9)

(b) In replacement nomenclature.

Example:

4.



7,10-dioxa-2-thia-4-silaundecane

(c) In additive nomenclature.

Example:

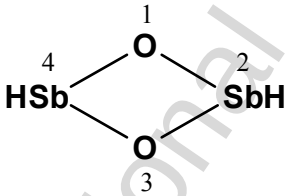
5.

1,1,1,2,2,3,3,4,4,5,5,5-dodecahydrido-2-germy-1,3,4,5-tetrasily-[5]catena

(d) In the Hantzsch-Widman nomenclature, to indicate positions of skeletal atoms.

Example:

6.

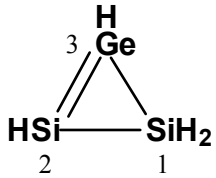


1,3,2,4-dioxadistibetane

(e) In the Hantzsch-Widman nomenclature, to denote indicated hydrogen.

Example:

7.



1*H*-1,2,3-germadisilirene

(f) In substitutive nomenclature, to specify the positions of substituent groups.

Example:

8. ^{1} ^{2} ^{3} ^{4} ^{5}
$HOSiH_2SiH_2SiH_2SiHClSiH_2Cl$
4,5-dichloropentasilane-1-ol

(g) In substitutive nomenclature, to illustrate a subtractive operation.

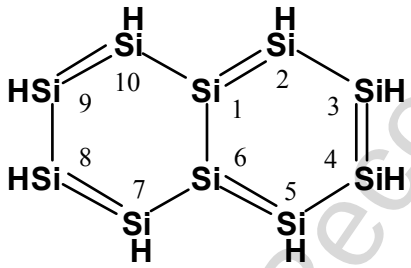
Example:

9. $^{\bullet}NHNH^{\bullet}$ and –NHNH– hydrazine-1,2-diyl

(h) In von Baeyer names to indicate the topology of a polycyclic ring system.

Example:

9.



bicyclo[4.4.0]decasila-1,3,5,7,9-pentaene

(i) In polynuclear coordination compounds, for numbering the central atoms (see Section IR-9.2.5).

Example:

10.

^{1} ^{2}
$[(OC)_5ReCo(CO)_4]$ nonacarbonyl-1κ^5*C*,2κ^4*C*-rheniumcobalt(*Re*—*Co*)

(j) To indicate stereochemistry at particular atoms in structures where arabic numerals have been used for numbering those atoms.

Example:

11. ^{1} ^{2} ^{3} ^{4} ^{5}
$ClSiH_2SiHClSiHClSiH_2SiH_3$
(2*R*,3*S*)-1,2,3-trichloropentasilane

IR-2.14.3 **Lower case letters**

Lower case letters are used in polyoxometallate nomenclature to designate the vertices of the coordination polyhedra around the central atoms. They are attached to the number of the central atom to which a particular vertex refers. A detailed treatment is given in Chapter II-1 of Ref. 2.

IR-2.15 PRIORITIES

IR-2.15.1 **Introduction**

In chemical nomenclature the terms priority, seniority and precedence convey the notion of rank or order among a number of possibilities and are ubiquitous concepts of fundamental importance. Chemical nomenclature deals with elements and their combinations among themselves, either individually or as groups (element with element; group with group). The groups of atoms can be ions, ligands in coordination compounds, or substituents in hydrides.

Whereas writing the symbol or the name of an element is straightforward, a choice of which element to write first in the *formula* and in the *name* has to be made as soon as one element is associated with a second to form, for example, a binary compound. The order of citation is based upon the methods outlined below.

IR-2.15.2 **Electronegativity criterion**

In formulae and compositional names of binary compounds of non-metallic elements, the constituent which appears earlier in the sequence below is cited first. This is an approximate electronegativity sequence, though it departs in detail from the usually accepted electronegativity sequence, for example in the relative positions of C and H (see Table VI).

Rn, Xe, Kr, Ar, Ne, He, B, Si, C, Sb, As, P, N, H, Te, Se, S, At, I, Br, Cl, O, F.

Example:

1. S_2Cl_2

IR-2.15.3 **Alphabetical order**

Alphabetical order is used in *names* as follows.

(a) In coordination compounds, to define the order of citation of ligands. This order follows the alphabetical listing of the names of the ligands. The alphabetical citation of

ligands is maintained regardless of the number of each ligand, or whether the compounds are mono- or polynuclear.

Example:

1. $K[AuS(S_2)]$ potassium (*di*sulfido)*s*ulfidoaurate(1–)

The term 'coordination compound' is extended here to include compounds where two or more different atoms or groups are attached to a single central atom, regardless of whether this central atom is a metal or not.

(b) In salts, the cations and the anions are each arranged alphabetically with cations preceding anions. However, deviation is allowed when structural relationships between different compounds are being emphasized.

Examples:

2. $KMgF_3$ magnesium potassium fluoride
3. ZnI(OH) zinc hydroxide iodide
4. $NaNbO_3$ niobium sodium trioxide (*perovskite* type)

Alphabetical order is used in *formulae* as follows.

(a) In coordination compounds, ligands are cited in alphabetical order of the first symbols of the formulae or abbreviations that are used. Where possible, the donor atom should be placed nearest the central atom to which it is coordinated. Some deviation is allowed if it is desired to convey specific structural information. (See Section IR-9.2.5.1)

Example:

5. $[CrCl_2(NH_3)_2(OH_2)_2]$

(b) In salts and double salts, to establish the sequential orders in cations and anions, respectively.

Examples:

6. BiClO
7. $KNa_4Cl(SO_4)_2$

IR-2.15.4 **Element priority sequence**

This sequence is based on the Periodic Table and is shown in Table VI. The element columns (1 to 18) are connected by arrows leading in a direction starting from the less

metallic elements and moving towards the more metallic elements. This order had its origin in electronegativity considerations. It is followed in the situations cited below.

(a) In polynuclear coordination compounds:

(i) To order the central atoms in names (IR-9.2.5.1). The first central atom encountered when following the arrow is listed *last*.

(ii) To number the central atoms for use in conjunction with the kappa convention (IR-9.2.5.1). The *last* central atom reached in the direction of the arrow is given the *lowest* number. This number will represent the position of the central atom in the list of central atoms that forms part of the name.

(b) Where there is a choice of parent hydride among those listed in Table IR-6.1 (or corresponding hydrides with non-standard bonding numbers, *cf.* Section IR-6.2.2.2), the name is based on the parent hydride of the element occurring first in the sequence: N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, Al, Ga, In, Tl, O, S, Se, Te, C, F, Cl, Br, I.

IR-2.15.5 **Other priority sequences**

IR-2.15.5.1 *Organic priority orders*

In substitutive nomenclature, an order for the choice of principal functional group is defined (see Section P-41 of Ref.1). In coordination compounds, the organic ligands that would normally be named by substitutive nomenclature retain their substitutive names with the chosen principal group expressed as a suffix (modified to designate a ligand).

IR-2.15.5.2 *Priority of ligand types*

In *formulae* of coordination compounds, ligands are cited in alphabetical order. Bridging ligands are cited after terminal ligands, and in increasing order of bridging multiplicity. (See also Sections IR-9.2.3 and IR-9.2.5).

In *names* of coordination compounds, the ligands precede the metal and are cited in alphabetical order of the ligand name. For each ligand, bridging ligands are cited before terminal ligands, *e.g.* di-μ-chlorido-tetrachlorido, and in decreasing order of bridging multiplicity, *e.g.* μ_3-oxido-di-μ-trioxido.... (See also Sections IR-9.2.2 and IR-9.2.5).

Thus, for both *formulae* and *names* the terminal ligands are closer to the metal, with the multiplicity of the bridging ligands increasing further away from the metal.

IR-2.15.5.3 *Priorities in salt formulae and names*

In formulae and names of salts, double salts, and coordination compounds, cations precede anions.

IR-2.15.5.4 *Isotope labelling and modification*

In isotopically modified compounds, a priority principle governs the order of citation of nuclide symbols. (See Section II-2.2.5 of Ref. 2).

IR-2.15.5.5 *Stereochemical priorities*

In the stereochemical nomenclature of coordination compounds, the procedure for assigning priority numbers to the ligating atoms of a mononuclear coordination system is based upon the standard sequence rules developed for chiral carbon compounds (the Cahn, Ingold, Prelog or CIP rules[5], see Section IR-9.3.3.2).

IR-2.15.5.6 *Priority sequences of punctuation marks*

In the names of coordination compounds and boron compounds, the punctuation marks used to separate the symbols of atoms from the numerical locants, the locants indicating bridging atoms, and the various other sets of locants which may be present, are arranged in the following hierarchy:

comma < colon < semicolon.

The colon is only used for bridging ligands, so that the more restricted general hierarchy is simply comma < semicolon. The sequence when bridging ligands are being specified is comma < colon. (See Example 2 in Section IR-2.5.2, and Section IR-9.2.5.5).

IR-2.16 AFFIXES (Prefixes, suffixes and infixes)

Any name more complex than a simple element name has a structure, *i.e.* a root with a prefix or a suffix. The suffix is a terminal vowel or a combination of letters. Some common affixes are listed in Tables III-V.

IR-2.17 FINAL REMARKS

In this Chapter, the various uses of letters, numerals and symbols in names and formulae have been gathered under common headings to provide an easy check to ensure that the constructed name or formula is in accord with agreed practice. However, this Chapter is not sufficient to make clear all the rules needed to build a name or a formula, and the reader is therefore advised to consult other appropriate Chapters for the more detailed treatment.

IR-2.18 REFERENCES

1. **New Blue Book title needed to replace:** *Nomenclature of Organic Chemistry,* Pergamon Press, Oxford, 1979; *A Guide to IUPAC Nomenclature of Organic Compounds*, *Recommendations 1993*, Blackwell Scientific Publications, Oxford, 1993; *Pure Appl. Chem*., **71**, 1327 (1999).
2. *Nomenclature of Inorganic Chemistry II, Recommendations 2000*, Royal Society of Chemistry, 2001.
3. *Compendium of Macromolecular Nomenclature,* Blackwell Scientific Publications, Oxford, 1991.
4. *Nomenclature of Inorganic Chemistry, Recommendations 1990*, Blackwell Scientific Publications, Oxford, 1990.
5. J. B. Casey, W.J. Evans and W.H. Powell, *Inorg. Chem.*, **20**, 1333 (1981).
6. R.S. Cahn, C. Ingold and V. Prelog, *Angew. Chem., Int. Ed. Engl.,* **5**, 385 (1966); V. Prelog and G. Helmchen, *Angew. Chem., Int. Ed. Engl.,* **21**, 567 (1982).