notes on nomenclature



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Numbers in Nomenclature

How are Multiplying Affixes Used in Nomenclature?

Chemical nomenclature makes extensive use of multiplying affixes for various purposes

(1) stoichiometric proportions
  ClO_2 *chlorine dioxide*
  S_4N_4 tetrasulfur tetranitride
(2) extent of substitution
  $SiBr_3H$ tribromosilane
  $AsO_2S_2^{3-}$ dithioarsenate ion
(3) number of identical coordinated groups
  $[Cr(NH_3)_4(NO_2)_2]^+$ tetraamminedinitritocobalt(III).

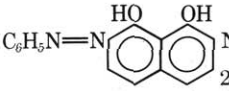
The simple multiplying affixes used for these purposes are: mono, di, tri, tetra, penta, hexa, hepta, octa, nona, deca, undeca, dodeca, etc. The forms ennea for nona and hendeca for undeca have also been used, particularly in inorganic nomenclature. For twenty both eicosa and icosa are in use; the first is favored by organic chemists and the latter by inorganic chemists. Hemi ($^1/_2$) and sesqui ($^3/_2$) are used occasionally in English and more frequently in other languages.

The above affixes have additional but somewhat different uses in designating

(4) the number of identical central atoms in condensed acids and their characteristic anions
  H_2CrO_4 (mono)chromic acid
  $H_2Cr_2O_7$ *dichromic acid*
  $H_5P_3O_{10}$ triphosphoric acid
(5) the number of atoms of the same element forming the skeleton of some molecules or ions
  Ge_3H_8 trigermane
  $B_{10}H_{16}$ decaborane(16)
  $S_4O_6^{2-}$ tetrathionate ion

The so-called multiplicative affixes (derived from the adverbial Greek forms): bis, tris, tetrakis, pentakis, etc., have caused considerable concern as to their proper use. They were originally introduced into organic nomenclature to indicate a set of identical radicals each substituted in the same way

$(ClCH_2CH_2)_2S$ bis(2-chloroethyl) sulfide



2,7-bis(phenylazo)-1,8-naphthalenediol

or to avoid ambiguity

$OC{=}CH{-}C_6H_4CH{=}CO$ *p*-phenylenebisketene
$P(C_{10}H_{21})_3$ tris(decyl)phosphine

In the first case immediately above, bis is used to avoid confusion with the trivial name diketene used to describe the dimer of ketene. In the second case, tris-(decyl) avoids any ambiguity with the organic radical tridecyl, $C_{13}H_{27}$.

These uses have been extended to inorganic nomenclature

$[Fe(CN)_2(CH_3NC)_4]$ dicyanotetrakis(methyl isocyanide)iron(II)
$Ca_5F(PO_4)_3$ pentacalcium fluoride tris(phosphate)

In the first case one wishes to avoid any doubt that the ligand is CH_3NC. In the latter case, one must distinguish a double salt with phosphate from a salt of the condensed acid, *triphosphate* $[P_3O_{10}]^{5-}$.

These affixes proved so convenient that their use has been extended, expecially by *Chemical Abstracts*, to all "complex expressions"

$\{[(CH_3)_2NCH_2]NH\}_3Bi$
tris{[(dimethylamino)methyl]amino}bismuthine

$[P(CH_2OH)_4]Cl$ tetrakis(hydroxymethyl)phosphonium chloride

Confusion arises here because many seem to mistake "complex expression" for "complex structure." It is the *name* not the composition that determines whether di, tri, etc., or bis, tris, etc., is used.

Chemists are not agreed on the use of multiplicative affixes. Some limit their use to a minimum and others follow the practice of "when in doubt use multiplicative forms." The former would restrict the use of bis, tris, etc., to expressions containing another numerical affix, e.g., bis(dimethylamino) and to cases where their absence would cause ambiguity (see above). These affixes are used more widely in this country than in the United Kingdom. The practice of *Chemical Abstracts* is a good guide.

Organic nomenclature makes considerable use of the affixes bi, ter, quater, etc., in such names as binaphthalene, terpyridine, and quaterphenyl. In inorganic chemistry, these affixes are used only in the names of a few organic molecules or radicals which combine with inorganic compounds. However, these affixes appear in such adjectives of Latin origin as bi-, ter-, . . . multidentate, although, the affixes di, tri, . . . poly

of Greek origin are used almost as frequently even with words of Latin origin. The confusing use of bi- to indicate an acid salt

$NaHSO_4$	sodium bisulfate

has largely disappeared from scientific writings.

How are Numbers Used in Names?

Stock Versus Ewens-Bassett Numbers

Chemists have long used two procedures for distinguishing between two compounds formed between the same two elements: the use of -ic and -ous or stoichiometric names

N_2O	nitrous oxide	dinitrogen monoxide
NO	nitric oxide	nitrogen monoxide

The difficulties with the first scheme is that there are often more than two compounds between the same two elements (e.g., NO_2, N_2O_4, and N_2O_5 for nitrogen-oxygen compounds), and they cannot be accommodated by only two suffixes. The difficulty with the second is that it is a bit cumbersome and in practice the specification of the number of atoms of the first element in the name has been omitted: phosphorous pentoxide for P_2O_5 instead of diphosphorous pentoxide.

Alfred Stock sought to clarify the situation by introducing Roman numerals to represent the oxidation state of the element of variable combining power

$FeCl_2$	iron (II) chloride
$FeCl_3$	iron(III) chloride

Although he intended the system to apply to ionic compounds, its extension to covalent compounds was inevitable

SO_2	sulfur(IV) oxide
Cl_2O_7	chlorine(VII) oxide

An attractive feature of the Stock proposal was its extension to coordination compounds

$[Pt(NH_3)_2Cl_2]$	diamminedichloroplatinum(II)
$[Co(NH_3)_5Br]Br_2$	pentaamminebromocobalt(III) bromide
$[Pt(NH_3)_4Cl_2]Cl_2$	tetraamminedichloroplatinum(IV) chloride

These Roman numerals, often called Stock numbers, were adopted in the 1941 IUPAC report and found ready acceptance. Since there is no symbol for zero in Roman numerals, the Arabic zero is used.

$K_4[Ni(CN)_4]$	potassium tetracyanonickelate(0)

If one's interest were the charge on the ion rather than the oxidation state, this was obtained by algebraic addition of the oxidation state and the number of unit negative charges associated with the coordinated groups. There was confusion in some instances because a few groups, especially NO, seemed to coordinate in more than one fashion yet one could not always be sure which fashion in a given instance.

In a general review of inorganic nomenclature practices, Ewens and Bassett[1] proposed to indicate by Arabic numerals the charge on an ion rather than the oxidation state

$FeCl_2$	iron(2+) chloride
$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(3+) chloride

Zero is not used with uncharged coordination entities because of its use in the Stock system. Although the IUPAC Commission did not adopt this practice in the 1957 version of the rules, the Ewens-Bassett proposal found acceptance elsewhere. It became an integral part of the nomenclature developed for ions related to boron hydrides and for designating the charge on coordinated groups.

$Na_2[B_{10}H_{10}]$	sodium decahydrodecaborate(2−)
$[Mn\{C_6H_4(O)(COO)\}_2(H_2O)_4]^-$	bis[salicylato(2−)]tetraaquamanganate(III) ion

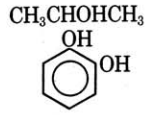
E-B numbers, as they are called, now have been accepted by the IUPAC for the two uses given above and as an alternate pattern to the Stock number indicating oxidation state.

Other Uses of Numbers in Names

In addition to the use of numbers in the Stock and Ewens-Bassett systems, Arabic numerals have other uses in nomenclature. They are sometimes used in place of numerical prefixes.

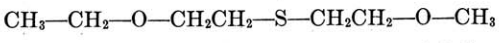
$CsCr(SO_4)_2 \cdot 12H_2O$	cesium chromium sulfate 12-water
$8H_2S \cdot 46H_2O$	hydrogen sulfide-water (8/46)
B_6H_{10}	hexaborane(10)

Arabic numbers are frequently used as locants to designate the atoms in a chain, ring or cluster of atoms at which there is substitution



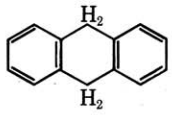
2-propanol
1,3-benzenediol (resorcinol)

replacement



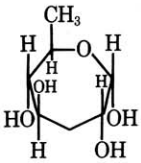
2,8-dioxa-5-thiadecane

addition



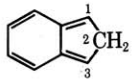
9,10-dihydroanthracene

or subtraction



6-deoxy-α-D-glucopyranose

Closely related to the above is the designation of the position of hydrogen in order to distinguish among possible isomers.



2*H*-indene

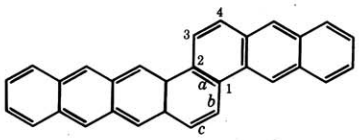
To be sure, a standard pattern for assigning locants to each skeletal arrangement of atoms is necessary. Numerous other examples will appear in discussions of

[1] Ewens, R. V. G., and Bassett, H., *Chem. Ind.*, 137 (1949).

[2] With the many uses of numbers in names, it is understandable why they are not recommended as locants for the spatial positions around the central atom in a coordination compound. Lower case letters printed in italics are used instead. See notes to appear later on coordination compounds.

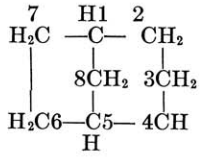
coordination compounds,[2] of boron hydrides and derivatives, and of various aspects of organic chemical nomenclature.

Among organic compounds, Arabic numbers have two other applications. They are used in brackets to indicate the positions of attachment of an attached group in fused polycyclic hydrocarbons.



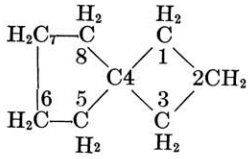
anthra[2,1-*a*]naphthacene[3]

In the naming of bridged aliphatic hydrocarbons, numbers in brackets indicate the number of carbon atoms in each bridge.



bicyclo[3.2.1]octane

The use of numbers in names for spiranes is similar



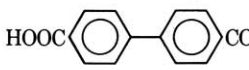
spiro[3.4]octane

Use of Primed Numbers

When two or more identical or different sets of numerical locants apply to separate parts of a structure, primes are used with one or more of the sets of numerical locants.

$HN(CH_2CH_2Cl)_2$	2,2′-dichlorodiethylamine or bis(2-chloroethyl)amine
$N(CH_2CH_2CH_3NH_2)_3$	3,3′,3″-triaminotripropylamine or tris(3-aminopropyl)amine

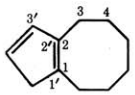
Primed numbers are also used with ring assemblies for substitution or point of attachment



4,4′-biphenyldicarboxylic acid

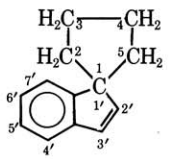
2,2′-bipyridine

with fused polycyclic hydrocarbons



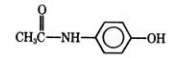
1,2-cyclopenta-1′,3′-dienocyclooctene

and with some spiro compounds

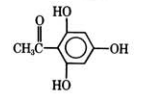


spiro[cyclopentane-1,1′-indene]

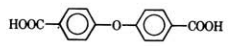
Additional examples are



4′-hydroxyacetanilide



2,′4,′6′,-trihydroxyacetanilide



4,4′-oxydibenzoic acid

Use of Numbers as Subscripts and Superscripts

Probably the most familiar use of numbers in nomenclature is as subscripts to the right of the atom symbol to represent the number of atoms or, with parentheses, the number of identical groups in the formula of a compound: C_2H_6, $Th(NO_3)_4$. A subscript to the left of the symbol of an element is used to designate the atomic number of that element: $_{13}Al$. One other use of a subscript is with the Greek letter μ to indicate the number of atoms bound by a single bridging group.

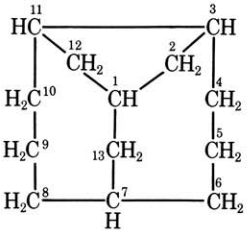
$[EuI(Et_3As)]_4$
tetra-μ_3-iodo-tetrahedro-tetrakis[(triethylarsine) copper(I)]

(This structure consists of a tetrahedron of four Cu ions to each of which one Et_3As molecule is attached; one I ion is bound to each of the three Cu ions in the four faces of the tetrahedron.)

$[Be_4O(OOCCH_3)_6]$ hexa-μ-acetato-μ_4-oxo-tetraberyllium

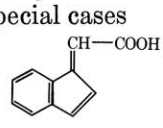
(This structure consists of a tetrahedron of beryllium ions with an oxygen in the center and one acetate ion bridging the two beryllium ions along each edge.) Subscripts have other uses as indicated in Vitamin B_{12} and methan-d_3-ol.

A number as superscript to the right of a symbol is used to designate the charge on an ion: Fe^{3+}, $Fe(CN)_6^{4-}$. A superscript to the left of a symbol indicates the mass number of a particular isotope of an element:[4] ^{29}Al. Superscript numbers are also used to designate the atoms involved in bridging for certain alicyclic hydrocarbons.

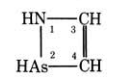


tricyclo[5.5.1.$0^{3,11}$] tridecane

Use is also made of superscripts in the nomenclature of nitrogen compounds: N^1,N^4-dimethylsulfanilamide. An older use of superscripts with the Greek letter Δ to indicate the position of a double bond is now used only in some special cases



indene-$\Delta^{1,\alpha}$-acetic acid



Δ^3-1,2-azarsetine

[3] For the significance of "*a*," see "Uses of Letters in Names" in the next part of this series.

[4] The practice in this country on this matter is by no means uniform. Many write the mass numbers to the right of a symbol. When this is done, the simultaneous designation of mass number and charge on an ion is difficult.